

p-Block Elements - I

SOLUBILITY OF SALTS

Section - 1

[A] In Aqueous Solvent :

A solvent may be polar (having high dielectric constant such as water or mineral acids) or non-polar (having low dielectric constant such as benzene and tetrachloromethane). Ionic compounds are usually soluble in polar solvents while covalent compounds usually dissolve in covalent solvents. This rule may be stated as '*like dissolves like*'.

For a substance to dissolve in an aqueous solvent (water) the energy evolved when the ions are hydrated (hydration energy) must be larger than the energy required to break the crystal lattice (lattice enthalpy). Thus solubility in principle depends upon two major factors.

- (i) **Lattice Enthalpy** : The lattice enthalpy is inversely proportional to the distance between the cation and the anion (i.e. $r^+ + r^-$). Thus the lattice enthalpy decreases as we go down the group due to the increase in size of cation if the anion being considered is same.
- (ii) **Hydration Enthalpy** : Hydration enthalpy usually varies as the inverse of radius of cation (r^+). This is because as the size of cation increases, the polarizing power of cation decreases and thus the tendency to attract water molecules decreases. (also known as *Dehydration Capacity*). This decrease in dehydrating capacity decreases the hydration energy that is released when a molecule is hydrated.

The General Solubility Rules in Water are as follows :

1. All nitrates (NO_3^-), chlorates (ClO_3^-) are soluble. All sulphates (SO_4^{2-}) are soluble except those of $[\text{Sr}^{2+}, \text{Ba}^{2+} \text{ and } \text{Pb}^{2+}]$ which are sparingly soluble and hence are used in qualitative analysis.
2. All the carbonates (CO_3^{2-}), sulphites (SO_3^{2-}), phosphates (PO_4^{3-}) and dichromates ($\text{Cr}_2\text{O}_7^{2-}$) are insoluble except of Group I, Na^+, K^+ and NH_4^+ . Practically almost all salts of Group I, Na^+, K^+ and NH_4^+ are soluble in water.
3. All simple salts of Group I metals dissolve in water producing ions. The solubility of most salts ($\text{NO}_3^-, \text{CO}_3^{2-}, \text{HCO}_3^-$) decreases down the group. This is because the decrease in hydration energy of metal ions is much more than the decrease in the lattice energy given.

Exception : The solubility of alkali metal fluorides, hydroxides and carbonates increases rapidly down the group. The reason is L. E. is proportional to $1/(r^+ + r^-)$ and thus the lattice energy will vary most when r^- is small (as in fluorides) and least when r^+ is longer (with I^-). Thus the change in lattice enthalpy exceeds the change in hydration enthalpy in this case.

4. The solubility of most salts of *Group II* also decreases down the group. For example, $\text{BeSO}_4 > \text{MgSO}_4 \gg \text{CaSO}_4 > \text{SrSO}_4 > \text{BaSO}_4$. (As has been stated, all sulphates except these of Ca, Sr, Ba, Pb, Ag are very soluble).

Exception : The fluorides and hydroxide of Group II metals show an increase in solubility down the group. The reason is same as that for Group I salts.

5. All hydroxides are insoluble except those of alkali metals (Group I) leaving LiOH. Those of Ca^{2+} , Sr^{2+} and Ba^{2+} are moderately soluble.
6. All sulphides (S^{2-}) are insoluble except those of alkali metals, alkali earth metals and the ammonium (NH_4^+) ion.
7. All chlorides, bromides and iodides are soluble except those of Ag^+ , Hg_2^{2+} and Pb^{2+} which are used in qualitative analysis.
8. It has been noticed that compounds with large difference in radii of ions are generally soluble while the least soluble salts are those of ions with similar radii. Thus:



[Here the difference in size between the cation and anion increases down the group].

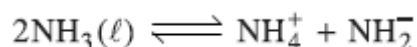
while, $\text{LiBr} > \text{NaBr} > \text{KBr} > \text{RbBr} > \text{CsBr}$.



[Here the difference in size between the cation and anion decreases down the group].

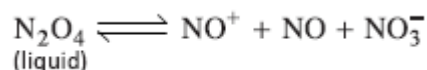
[B] In Non-aqueous Solvents :

Important non-aqueous solvents include liquid hydrofluoric acid (HF), liquid NO_2 and liquid ammonia (NH_3). Liquid ammonia is the most studied non aqueous solvent and it resembles the aqueous system quite closely.

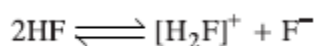


Thus substances producing NH_4^+ are acids (like NH_4Cl) in liquid ammonia and those producing NH_2^- are bases (like NaNH_2)

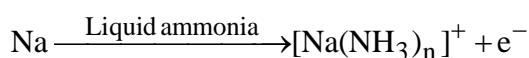
Similarly,



Thus in N_2O_4 substances containing NO^+ are acid (like NOCl) and those containing NO_3^- are bases (like NH_4NO_3).



Like in water, acid-base neutralization and precipitation reactions also occur in liquid ammonia. Liquid ammonia is an extremely good solvent for the alkali metals and the heavier Group II metals Ca, Sr and Ba. The metals are very soluble and solutions in liquid ammonia have a conductivity comparable to that of pure metals. Thus solutions are very good reducing agents because of the presence of free electrons.



GROUP 13 ELEMENTS

Section - 2

Ionisation Energy

The first ionisation energies (IE_1) of group 13 elements are lower than the corresponding elements of group 2 (alkaline earth metals). This is due to the fact that group 13 elements have ns^2, np^1 configuration in their valence shell and the electron thus has to be removed from the p -orbital. This is much easier than removing an s -electron of group 2 elements which being nearer the nucleus is more strongly attracted. Boron is considerably smaller than other elements of the group and thus has a higher ionization energy than others. The ionization energy is so high that B is always covalent.

Oxidation States

Due to ns^2, np^1 configuration of the valence shell, group 13 elements are expected to be trivalent but there is increasing tendency to form univalent compounds on descending the group. B and Al show an O. S. of +3 while Ga, In, Tl show O. S. of both +1 and +3. This is due to the **Inert Pair Effect**.

Metallic Character/Reducing Power

The order is : $\text{B} < \text{Al} < \text{Ga} < \text{In} < \text{Tl}$

The increase in metallic character from B to Al is the usual trend on descending a group associated with increasing size. However Ga, In, Tl do not continue the trend. Ga, In and Tl follow immediately after a row of ten transition elements and thus have ten d electrons which are less efficient at shielding the nuclear charge than s,p electrons. Thus outer electrons being more firmly held by the nucleus are more difficult to remove than would be expected. This leads to contraction in size as well as decreases in metallic character than would be expected. The phenomenon is known as **d-block Contraction**. Similarly Tl follows immediately after 14-f-block elements and the size and metallic character are affected even more. This contraction due to the f-block elements is called **Lanthanide Contraction**. Note that the size increases down the group as usual but is less than that expected.

Acidic Character

On moving down the group acidic character decreases and basic character increases because ionization energy increases. Thus we find that B(OH)_3 , and B_2O_3 are acidic ; Al(OH)_3 and Al_2O_3 are amphoteric ; Ga(OH)_3 and Ga_2O_3 are amphoteric ; and In(OH)_3 , TlOH are basic.

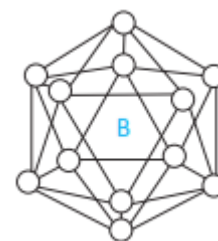
Boron & its compound :

Physical Properties and Occurrence :

Boron occurs in two allotropic form :

- (a) Crystalline – It is black, chemically inert and very hard
- (b) Amorphous – It is brown, chemically active, a non – conductor and difficult to fuse.

All allotropic form contain icosahedral unit with atoms at all 12 corners. The important minerals of boron are :

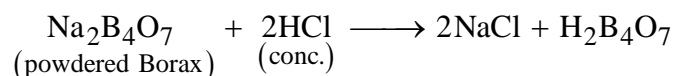


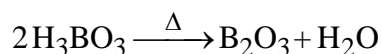
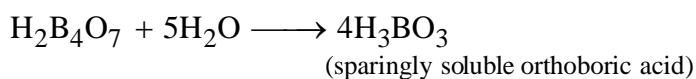
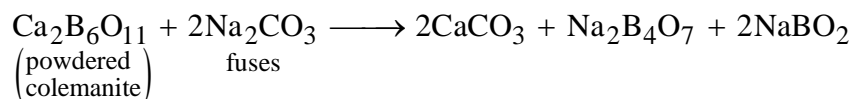
Borax (Tincal)	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	Boric acid	H_3BO_3
Kernite (Resorite)	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$	Boronatro calcite	$\text{CaB}_4\text{O}_7 \cdot \text{NaBO}_2 \cdot 8\text{H}_2\text{O}$
Colemanite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$	Boracite	$2\text{Mg}_3\text{B}_8\text{O}_{15} \cdot \text{MgCl}_2$
Pandertite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 3\text{H}_2\text{O}$		

Extraction of Boron : It includes 2 steps :

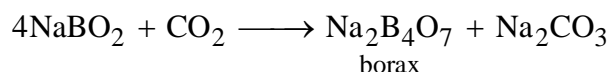
1. Preparation of Boric anhydride (B_2O_3) :

[Method I]



**[Method II]**

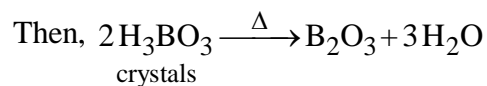
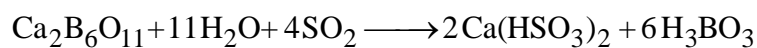
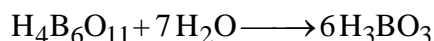
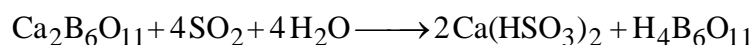
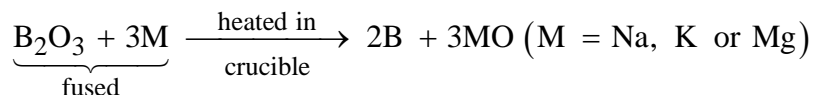
The fused mass is extracted with hot water. CaCO_3 remains insoluble and filtrate containing borax and sodium metaborate is put to crystallisation when borax crystals are obtained. The remaining solution is treated with carbon dioxide.



Then Method I is followed.

[Method III]

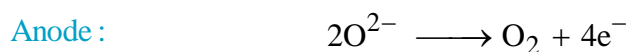
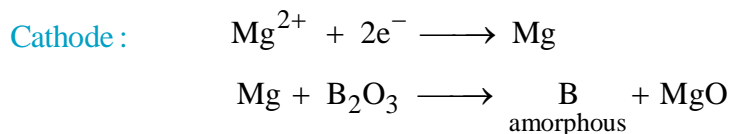
Suspension of colemanite mineral in water is formed and SO_2 gas is passed to obtain crystal of boric acid on cooling.

**2. Reduction B_2O_3 :****[Method 1]**

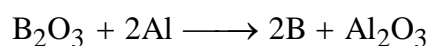
The fused mass is stirred with iron rod so as to oxidise unreacted metal M. The mass is then boiled with dil. HCl to obtain insoluble amorphous boron powder which is 95% pure.

[Method II] : Modern Method

A fused mixture containing boric anhydride, magnesium oxide and magnesium fluoride at 1100°C is electrolysed in a carbon crucible (anode). Iron rod is used as cathode.

**[Method III]**

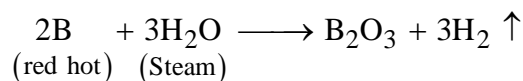
To obtain *crystalline boron* in small amounts, B_2O_3 is reduced with aluminium powder.



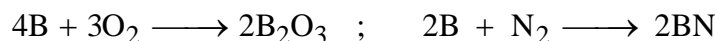
Aluminium is removed by heating the fused mass with NaOH solution.

Chemical Properties of Boron :

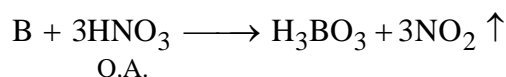
1. Boron is unaffected by water under ordinary conditions but :



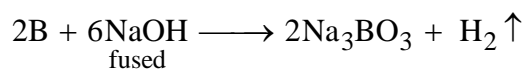
2. Amorphous boron burns in air at 700°C with a reddish flame forming oxide and nitride.



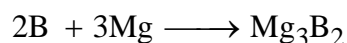
3. Boron is unaffected by reducing acids. With oxidising acids it gives boric acid.



4. Boron dissolves in fused alkalis liberating hydrogen.



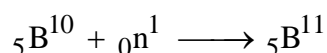
5. Boron often forms non-stoichiometric compounds with metals (not of Group 1)



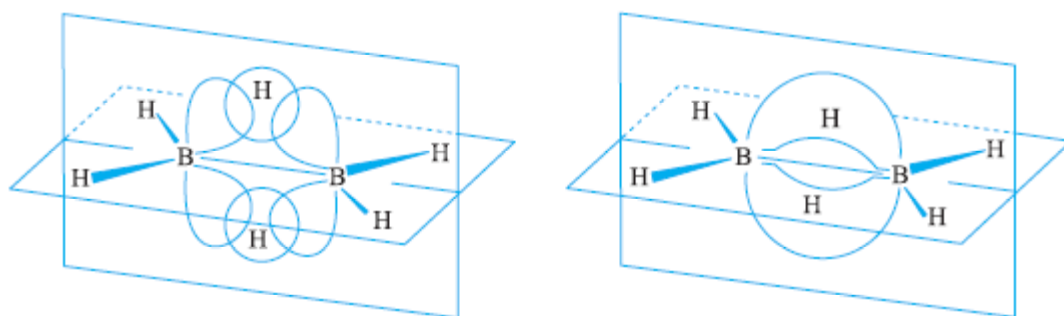
6. Action of non-metals :



Uses : Boron carbide rods are used to control nuclear reactions. Boron has a very high cross-section to capture the neutrons. Also B absorbs neutrons to make boron having an even number of neutrons.

[a] Diborane B_2H_6 :

Structure and Physical Properties :

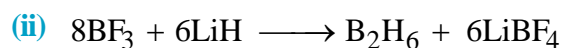
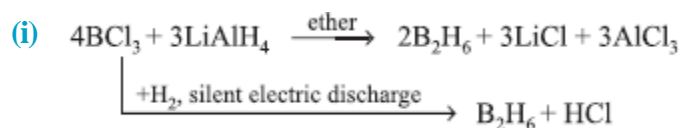


The bridge hydrogens form abnormal 3 centre 2 electron 'banana-shaped' bonds with two B atoms.

An sp^3 hybrid orbital from each boron atom overlaps with the 1s orbital of the hydrogen to give a delocalized molecular orbital covering all three nuclei.

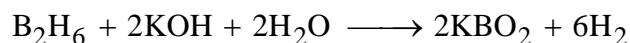
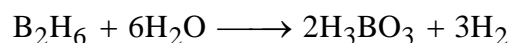
Diborane is a colorless and highly reactive gas with a disagreeable odour. It is used as a reducing agent in organic reactions and as a catalyst in polymerization reactions.

Preparation :

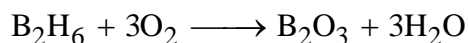


Chemical Properties :

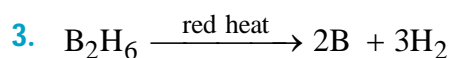
1. It is instantly hydrolysed by water or aqueous alkali.



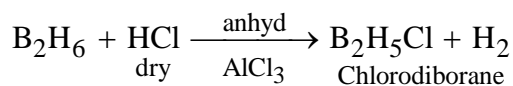
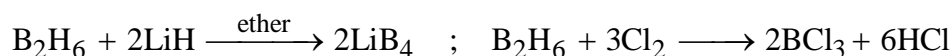
2. It catches fire spontaneously in air and explodes with dioxygen.



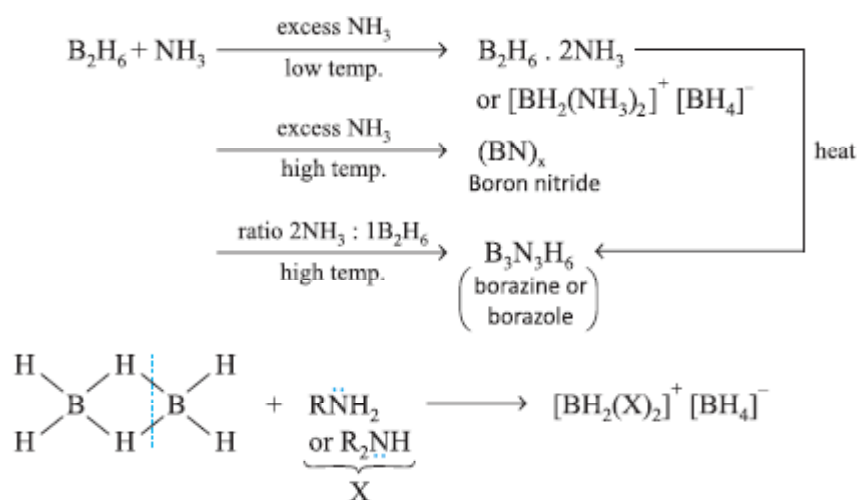
Thus in the laboratory, it is handled in a vacuum frame.



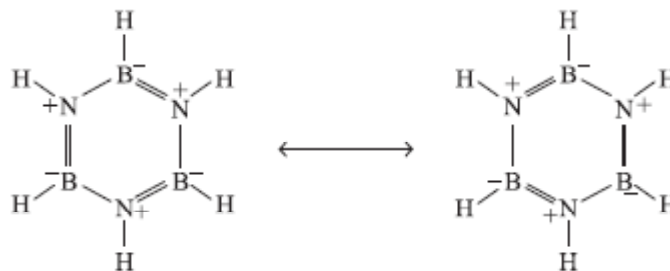
4. Other reactions :



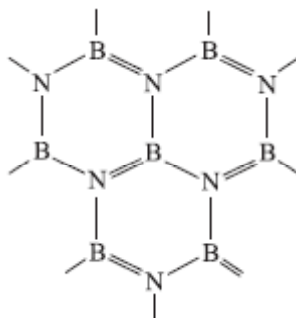
5. Reaction with ammonia and amines :



Borazole is called 'inorganic benzene' due to its similar structure and aromatic character.



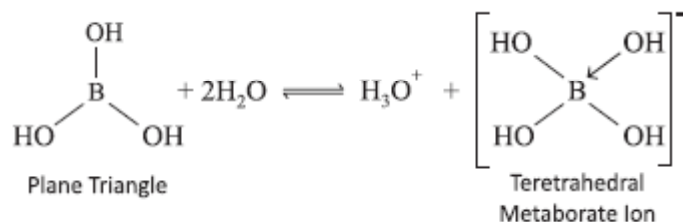
Boron nitride (BN) is a white slippery solid called 'inorganic graphite' which has a layer structure similar to graphite.



[b] Orthoboric Acid H_3BO_3 :

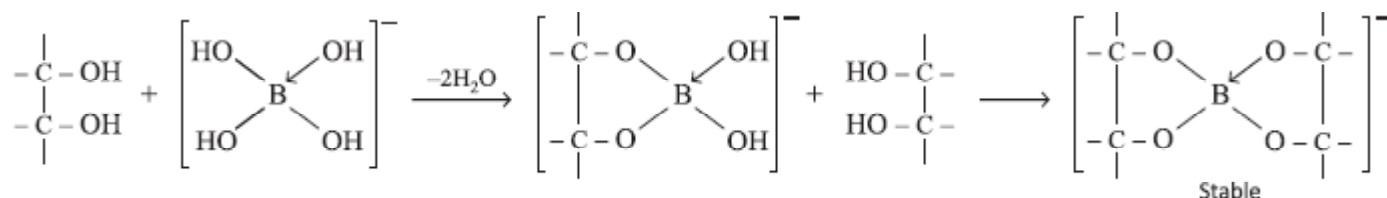
Structure and Physical Properties :

Orthoboric acid is a weak monobasic acid, sparingly soluble in water. It is a Lewis acid and better written as $\text{B}(\text{OH})_3$.



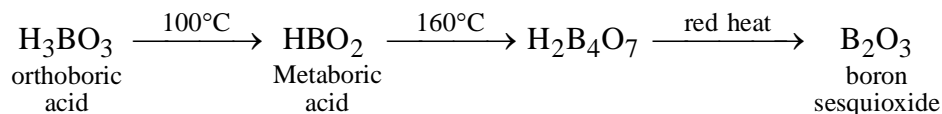
Thus $\text{B}(\text{OH})_3$ alone is not titrated with NaOH as a sharp end point is not obtained. However if a cis-diol is added then $\text{B}(\text{OH})_3$ behaves as a strong monobasic acid and can now be titrated with NaOH

using phenolphthalein as indicator Cis-diols form stable complexes with $\left[\text{B}(\text{OH})_4 \right]^-$ thus effectively removing them and carrying the reaction forward.

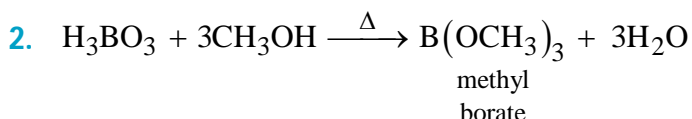


Chemical Properties :

1. Effect of heat :



Thus, B_2O_3 is also called boric anhydride as it is the anhydride of boric acid.



H_2O is removed by conc. H_2SO_4 and the mixture boruns with green flame. This is used as a test for boron compounds.

3. Boric acid dissolves in $\text{HF}(\text{aq})$ to give fluoroboric acid HBF_4 which is a strong acid. In dry HF borates give BF_3 which burns with a green colour.

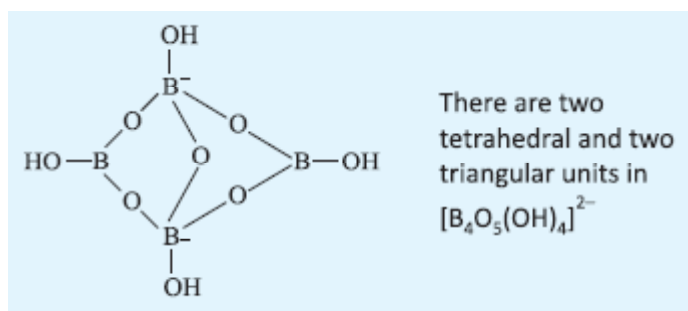
Uses :

Boric acid is used in glass industry and as an antiseptic and eyewash under the name 'Boric Lotion'.

[c] Borax :

Structure

Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) is better written as $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ having 8 water molecules and the ion $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ associated with Na^+ .

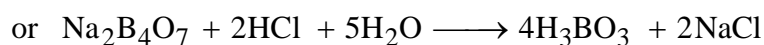
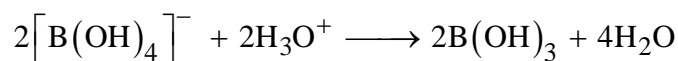


Chemical Properties :

1. When borax dissolves in water equal amounts of weak acid and its salt are formed. Thus it is used as a buffer.



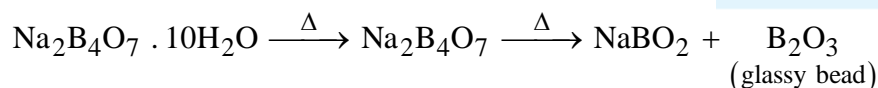
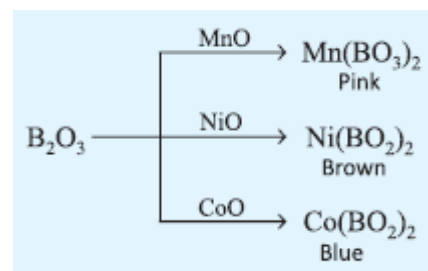
2. Borax reacts with 2 moles of acid because only $\left[\text{B}(\text{OH})_4\right]^-$ formed will react with H^+ .



The indicator used is methyl oranges as it is unaffected by the boric acid formed.

3. Borax Bead Test :

Metaborates $\left[\text{M}(\text{BO}_2)\right]$ of many transition elements have characteristic colours and this provides a means of identifying the metal through this test.



Uses :

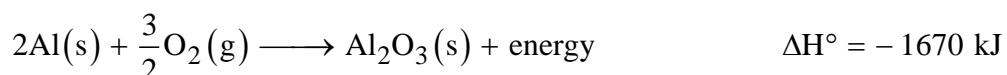
- (i) It is used as a flame retardant for wood and fabric.
- (ii) It is used as a flux in brazing and silver soldering.
- (iii) Used in glass industry.
- (iv) Used in Borax Bead Test in analytical chemistry.

Aluminium :

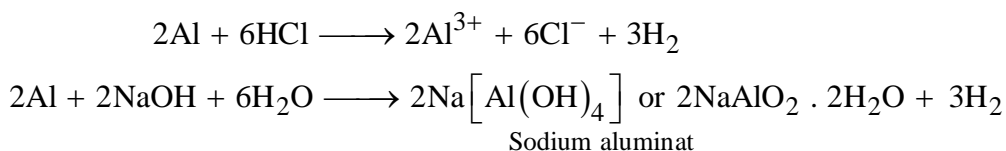
1. Aluminium metal is moderately soft but much stronger and lighter when alloyed with metals. Some alloys of Aluminium are :

Alloys	Composition	Uses
Magnalium	Al – 95%, Mg – 5%	In construction of airships, balances.
Duralumin	Al – 95%, Cu – 4%, Mg – 0.5%, Mn – 0.5%	In aeroplanes and automobile parts
Aluminium bronze	Cu – 90%, Al – 9.5%, Sn – 0.5%	For making utensils, cheap artificial jewellery.
Alnico	Steel – 77%, Al – 20%, Ni – 2%, Co – 1%	For making permanent magnet.

2. Thermodynamically Al should react with water and air but in fact it is stable in both. The reason is that a very thin oxide film of Al_2O_3 forms on the surface and protects it. Due to this resistance to corrosion and high thermal conductivity it is used in making domestic utensils.
3. Reduction of some metal oxides like Mn_3O_4 and Cr_2O_3 require temperature high enough for carbon to be used as a reducing agent. Thus Al, a highly electropositive metal which liberates a large amount of energy on oxidation to Al_2O_3 is used as the reducing agent. This is known as thermite process. The thermite reaction is :



4. Al is amphoteric and dissolves in both acid and bases.



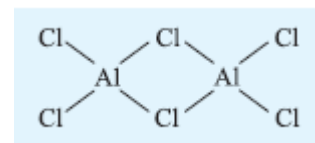
However, conc. HNO_3 renders it passive due to the formation of a protective oxide layer.

[A] Aluminium Oxide Al_2O_3 (Alumina)

Alumina is a white crystalline powder, insoluble in water. It is stable, quite unreactive and amphoteric in nature. The α -form of Al_2O_3 called *corundum* and found as a mineral in nature.

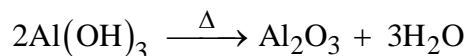
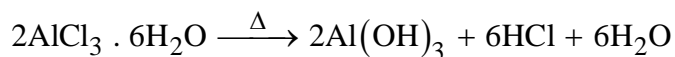
[B] Aluminium Oxide AlCl_3 :

AlCl_3 exists as a dimer, thus attaining an octet of electrons. It is largely covalent when anhydrous or in a non-polar solvent such as benzene. However, when dissolved in water, the high enthalpy of hydration is sufficient to break the covalent dimer into $\left[\text{Al}(\text{H}_2\text{O})_6\right]^{3+}$ and 3Cl^- ions.

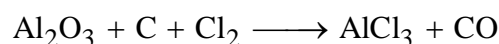
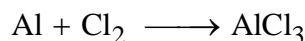


At low temperature, AlCl_3 exists as a close packed lattice of Cl^- with Al^{3+} occupying octahedral holes.

Crystalline AlCl_3 exist as $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. This on heating cannot give anhydrous salt just like $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (diagonal relationship). Instead it undergoes hydrolysis on heating :



The anhydrous compound is prepared by action of dry chlorine gas on aluminium or alumina :



IN-CHAPTER EXERCISE-A

- Give reasons for the following :
 - Phosphoric acid is preferred to sulphuric acid in the preparation of H_2O_2 from barium peroxide.
 - Red phosphorus is less volatile than white form.
 - Diborane is called an electron-deficient compound.
 - Anhydrous AlCl_3 fumes in moisture.
 - A mixture of NaOH and Al pieces is used to open the drain.
- Identify the unknown compounds in the following reactions :
 - $$\text{Na}_2\text{B}_4\text{O}_7 + \text{conc. H}_2\text{SO}_4 \longrightarrow \text{A} \xrightarrow[2. \text{Ignite}]{1. \text{C}_2\text{H}_5\text{OH}} \text{B}$$

B is identified by the characteristic colour of the flame. Identify *A* and *B*.
 - $$\text{BCl}_3 + \text{LiAlH}_4 \longrightarrow \text{A} \xrightarrow{\text{excess NH}_3} \text{B}$$

$\uparrow \quad \quad \quad \downarrow$
 $\quad \quad \quad +\text{C}$
 - $$\text{BCl}_3 + \text{NH}_4\text{Cl} \xrightarrow{140^\circ\text{C}} \text{A} \xrightarrow{\text{Na [BH}_4\text{]}} \text{B} \xrightarrow{+3 \text{ HCl}} \text{C}$$
 - $$\text{H}_3\text{BO}_3 + \text{HF (non aqueous)} \longrightarrow \text{A} \xrightarrow{\text{LiH}} \text{B} \xrightarrow{\text{excess LiH}} \text{C}$$
- AlF_3 is insoluble in anhydrous HF but when little KF is added to the compound it becomes stable. On addition of BF_3 ; AlF_3 is precipitated. Write the balanced chemical equations.
- RCN , RNO_2 and RCHO can be reduced by B_2H_6 . What are the products due to reduction ?

NOW ATTEMPT IN-CHAPTER EXERCISE-A FOR REMAINING QUESTIONS

GROUP 14 ELEMENTS

Section - 3

Oxidation States :

C and Si show oxidation state of +4 while Ge, Sn, Pb show oxidation states of both +2 and +4 due to the Inert Pair Effect.

Metallic Character :

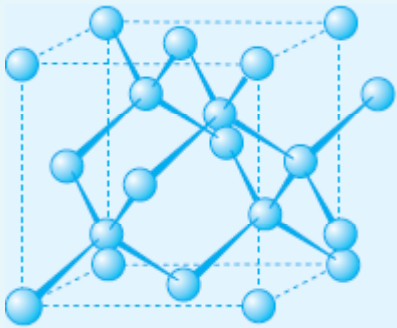
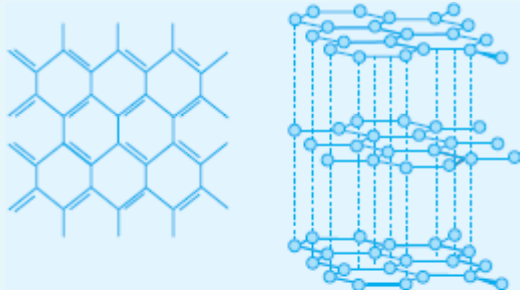
It decreases down the group. Thus, C and Si are non – metals, Ge is a metalloid and Sn and Pb are metals.

Catenation :

Due to smaller size and higher electron negativity of carbon atom it has the property of linking to other carbon atoms forming long chains. However as we move down, the tendency for catenation decreases in the order :

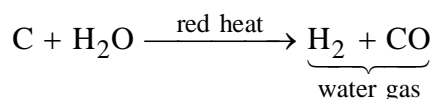
**Carbon and its compounds**

Allotropy : carbon exists in a large number of allotropic forms. Two main form are diamond and graphite

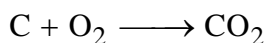
Diamond	Graphite
<ul style="list-style-type: none"> ❑ Extremely unreactive, colourless, non conductor and shows brilliance due to total internal reflection. ❑ The structure comprises of sp^3 hybrid C atoms forming σ – bonds and arranged tetrahedrally.  <p>The crystal structure of diamond.</p>	<ul style="list-style-type: none"> ❑ Quite reactive and soft. ❑ It has a layer structure with layers held together by weak van der Waals forces. Each sheet consists of hybridised carbon atoms which are covalently bonded to three carbon atoms by σ – bonds. The fourth e^- is in unhybridised 'p' orbital and forms a partial 'π' bond  <p>(a) The structure of a graphite sheet. (b) Structure of a-graphite It is used as a lubricant due to slippery layers and electricity is conducted only along sheets.</p>

Chemical Properties :

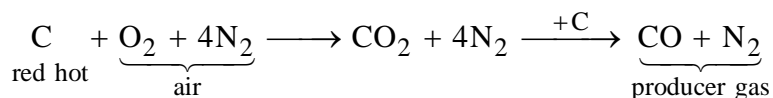
1. Water gas is made by blowing air through red or white hot coke :



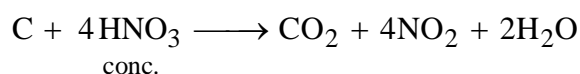
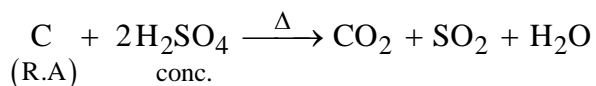
2. All allotropes burn in oxygen to form CO_2 .



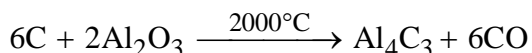
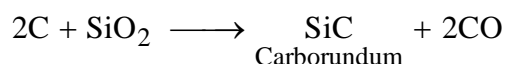
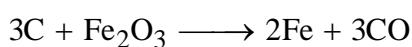
Producer gas is made by blowing air through red hot coke.



3. Carbon as reducing agent :



4. Carbon as Oxygen acceptor :

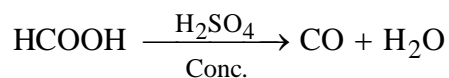


Reaction with	CO	CO ₂	H ₂ CO ₃
	Colourless odourless, poisonous, neutral, quite reactive	Colourless, odourless, acidic	Weak diacidic acid
	$\text{:}\overset{+}{\text{C}}\equiv\overset{-}{\text{O}}\text{:}$	$\text{O}=\text{C}=\text{O}$	$\left[\text{O}=\text{C}(\text{OH})_2 \right]^{2-}$ Plane Triangle
H ₂ O	Sparingly Soluble $+\text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	Dissolves and slightly hydrated to H ₂ CO ₃ , HCO ₃ ⁻ , CO ₃ ²⁻	Has never been isolated from aqueous solution.

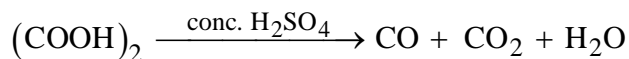
Air	$+O_2 \longrightarrow 2CO_2$ Burns with a blue flame (test for CO)		
Alkalies	$CO + NaOH \longrightarrow HCOONa$	$Ca(OH)_2 \xrightarrow{CO_2} CaCO_3 \downarrow$ Lime water White (test for CO_2) $CaCO_3 \xrightarrow[\text{excess}]{CO_2} Ca(HCO_3)_2$ Soluble	
Non Metals	$+H_2 \xrightarrow[200^\circ]{ZnO, Cu} CH_3OH$ $+Cl_2 \xrightarrow[h\nu]{ZnO, Cu} COCl_2$ (phosgene) $HCl + CO_2 \xleftarrow{H_2O} \begin{array}{c} \downarrow NH_3 \\ NH_2 \\ \diagup \\ C=O + HCl \\ \diagdown \\ NH_2 \end{array}$ Urea	$+C \xrightarrow[\text{Red hot}]{} CO$	
Metal	$+Ni \xrightarrow{28^\circ C} Ni(CO)_4$ $+Fe \xrightarrow{200^\circ C} Fe(CO)_5$	$+Zn \longrightarrow CO + ZnO$ $+Mg \longrightarrow C + MgO$	
NH_3	Soluble in ammonical cuprous chloride and forms $[Cu(CO)Cl(H_2O)_2]$	$+NH_3 \xrightarrow[\text{Pressure}]{180^\circ C} NH_4CO_2NH_2$ Ammonium carbamate $H_2O + CO(NH_2)_2 \xleftarrow{\quad}$ Urea	

Preparation of CO :

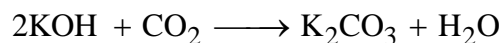
- (i) In laboratory it is prepared by dehydrating formic acid with concentrated H_2SO_4



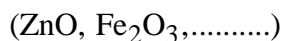
Also,

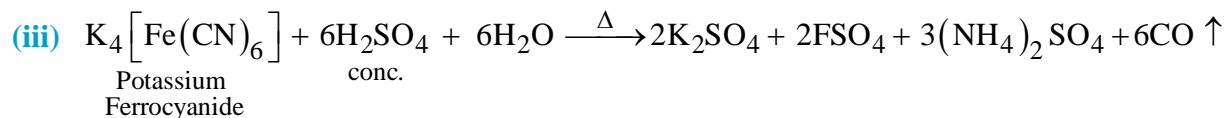


CO_2 is removed by passing through soda :



- (ii) $C + \text{oxides of heavy metal} \longrightarrow CO \uparrow + \text{metal}$

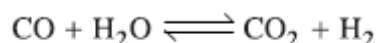




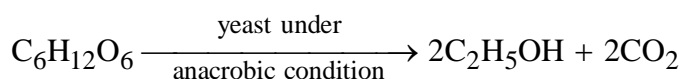
Note : Dil H_2SO_4 is not used, as it gives extremely poisonous HCN.

Preparation of CO_2 :

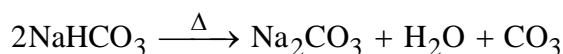
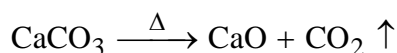
- (i) The main industrial source is as a by product from the manufacture of hydrogen for making ammonia :



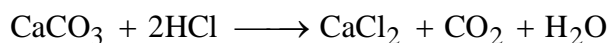
- (ii) It is recovered from alcoholic fermentation :



- (iii) It is obtained by heating carbonates :



- (iv) In laboratory it is prepared by the action of dilute acids on carbonates :



	Si	SiC (Carborundum)	SiO ₂ (Silica)
Reaction with	<ul style="list-style-type: none"> <input type="checkbox"/> 2nd most abundant element, widely present as SiO₂ <input type="checkbox"/> Crystalline, very hard, inert <input type="checkbox"/> Amorphous, brownish, powder, more reactive 	<ul style="list-style-type: none"> <input type="checkbox"/> Colourless but commercial samples are yellow, green, blue due to traces of Fe, <input type="checkbox"/> Extremely hard, inert, (structure similar to diamond) and used as abrasive. <input type="checkbox"/> Amorphous, brownish, powder, more reactive 	<ul style="list-style-type: none"> <input type="checkbox"/> Widely found as sand, quartz, flint. <input type="checkbox"/> High melting point <input type="checkbox"/> Acidic in nature.

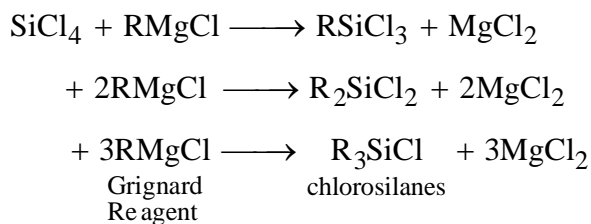
Water	<input type="checkbox"/> Unaffected in ordinary conditions <input type="checkbox"/> $+H_2O \xrightarrow{\text{Red heat}} SiO_2 + H_2\uparrow$	Unaffected	<input type="checkbox"/> $SiO_2 + H_2O \rightleftharpoons H_4SiO_4$
Air	<input type="checkbox"/> $Si + O_2 \xrightarrow{\Delta} SiO_2$ Amorphous (Burns brilliantly) <input type="checkbox"/> $Si + O_2 \xrightarrow{\Delta} \text{no effect}$ Crystalline	Unaffected	Unaffected
Acids	<input type="checkbox"/> Unaffected by dilute acids but amorphous form dissolves in $HNO_3 + HCl$ while crystalline form dissolves in $HNO_3 + HF$	Unaffected by acids (except H_3PO_4)	<input type="checkbox"/> Unaffected being acidic oxide (except in HF) <input type="checkbox"/> $HF \xrightarrow{SiO_2} SiF_4 + H_2O$ SiF_4 when comes in contact with a drop of water it forms silicic acid seen as floating white solid. [Test for silicates] <input type="checkbox"/> $SiF_4 \xrightarrow{H_2O} Si(OH)_4 + HF$
Alkalies	$+ KOH + H_2O \longrightarrow K_2SiO_3 + H_2$ (Slowly if cold and readily if hot)	$+ 2NaOH + 2O_2 \longrightarrow Na_2SiO_3 + CO_2 + H_2O$	$+ NaOH \longrightarrow \text{Silicates}$ This is the reason why gases stoppers stick in $NaOH$ bottles.
Halogen	<input type="checkbox"/> $Si + 2F_2 \longrightarrow SiF_4$ Amorphous (spontaneous reaction)	Unaffected except for : $+ SiC + 2Cl_2 \xrightarrow{100^\circ C} SiCl_4$	Unaffected except for : $SiO_2 + 2F_2 \longrightarrow SiF_4 + O_2$
Carbon			$+ SiO_2 + 2C \xrightarrow{\Delta} Si + 2CO$
Preparation	<input type="checkbox"/> $SiO_2 + 2Mg \xrightarrow{\Delta} 2MgO + Si$ Powder (Amorphous) <input type="checkbox"/> $SiO_2 + C \xrightarrow[\text{Fe}]{\text{Electric furnace}}$ (Sand powdered) \downarrow $Si + CO$ (Crystalline) [Fe is added to prevent formation of SiC]	<input type="checkbox"/> $SiO_2 + C (\text{excess})$ Sand Coke $2000 - 2500^\circ C$ \downarrow $NaCl$ + saw electric furnace (flux) + dust $SiC + CO\uparrow$ \downarrow Crushed, washed with H_2SO_4 , $NaOH$ and H_2O and then dried	

[a] Silicones

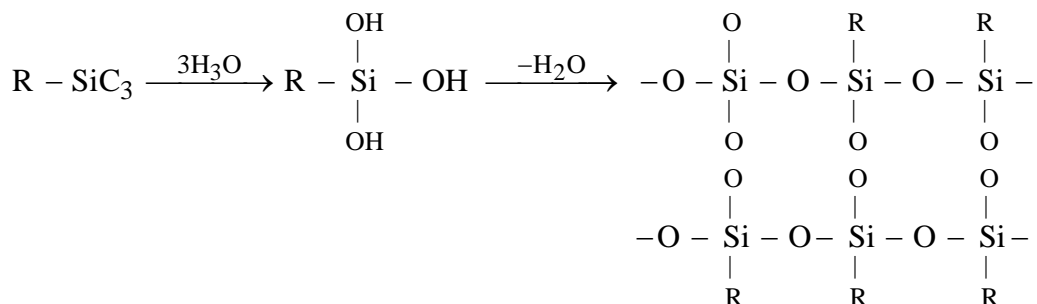
Silicones are a group of organo - silicon polymers containing Si - O - Si linkages.

Preparation :

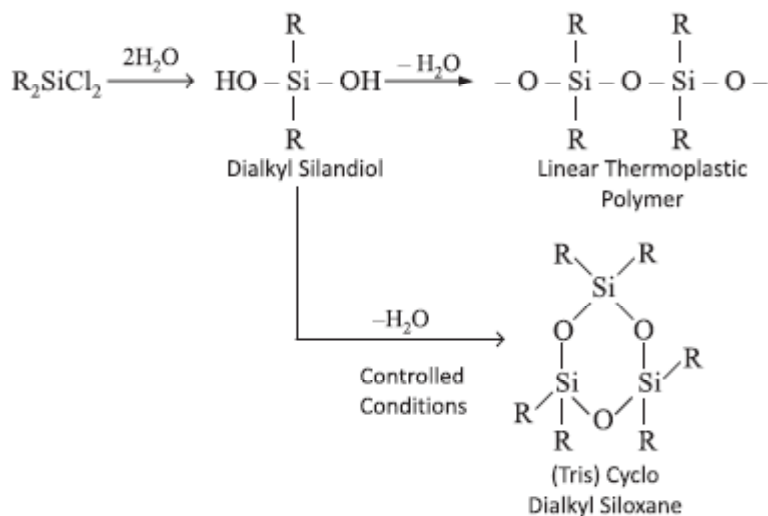
Silicones are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes (formed by reaction Grignard reagents and silicon tetrachloride) and their subsequent polymerization.



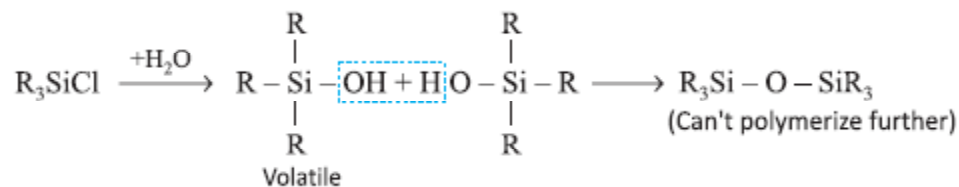
(i) Formation of cross-linked silicones :



(ii) Formation of linear polymers :



(iii) Formation of dimers :



Properties :

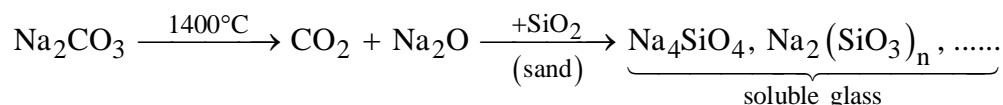
1. R_3SiCl is a chain stopping unit and reduces polymer size as it blocks the end of chain. While R_2SiCl_2 is used to produce new cross – links and increase polymerization.
2. Silicones are electrical insulators, water-repellent, strong and inert. Their b.p. and viscosity increase with increase in chain length.
3. Silicones are stable towards heat (hence used as electrical insulators). The order of stability varies with R attached in the orders: $ph > CH_3 > Et > Pr$.
4. Being water – repellent they are used for treating glass ware and fabrics.
5. They are also used as hydraulic fluids and silicone rubbers.

[b] Silicates

Silicates are derivatives of silicic and $Si(OH)_4$ or H_2SiO_4 . They have basic tetrahedral units SiO_4^{4-} and Si – O bond may be considered 50% covalent and 50% ionic (suggested by a difference of 1.7 in electronegativities).

Preparation :

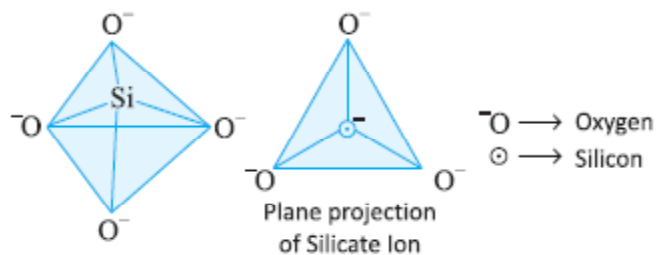
Silicates can be prepared by fusing an alkali metal carbonate with sand in an electric furnace at about $1400^\circ C$.

**Classification of Silicate Minerals :**

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

For example :	Zircon (gemstone)	$ZrSiO_4$
	Forestrite or Olivine	Mg_2SiO_4
	Phenacite	Be_2SiO_4
	Willemite	Zn_2SiO_4

Number of shared oxygen atom = 0



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

Pyrosilicate ion $\text{Si}_2\text{O}_7^{6-}$.



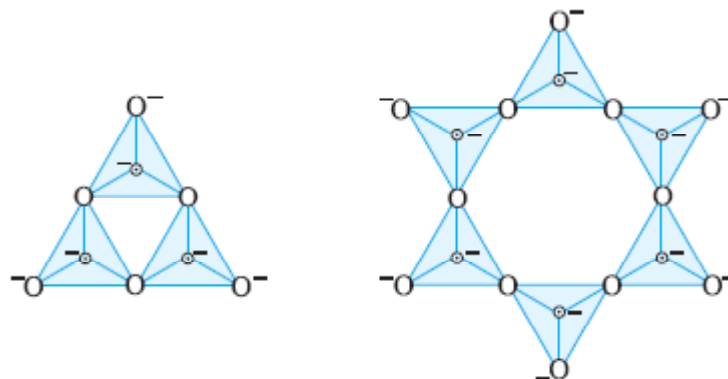
For example :

Thortveitite	$\text{Sc}_2\text{Si}_2\text{O}_7$
Hemimorphite	$\text{Zn}_3(\text{Si}_2\text{O}_7) \cdot \text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$

Number of shared oxygen atom = 1

- (iii) **Cyclic Structure** : Cyclic or ring silicates have general formula $(\text{SiO}_3)_n^{2n-}$.

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 :

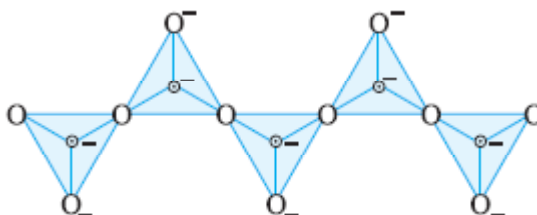
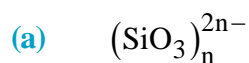


For example :

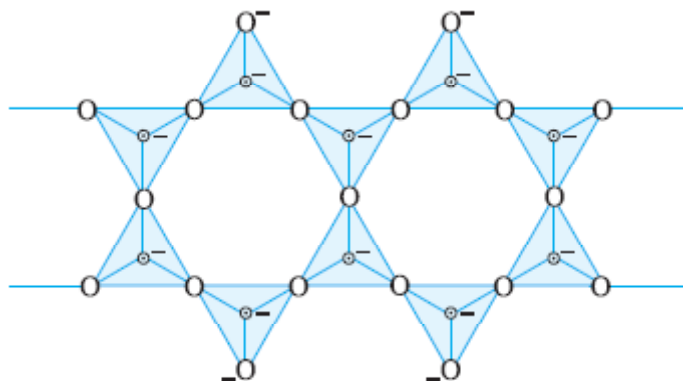
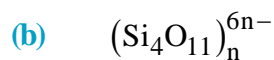
Beryl	$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$
Wollastonite	$\text{Ca}_3\text{Si}_3\text{O}_9$

Number of shared oxygen atoms = 2

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



Number of shared oxygen atom = 2

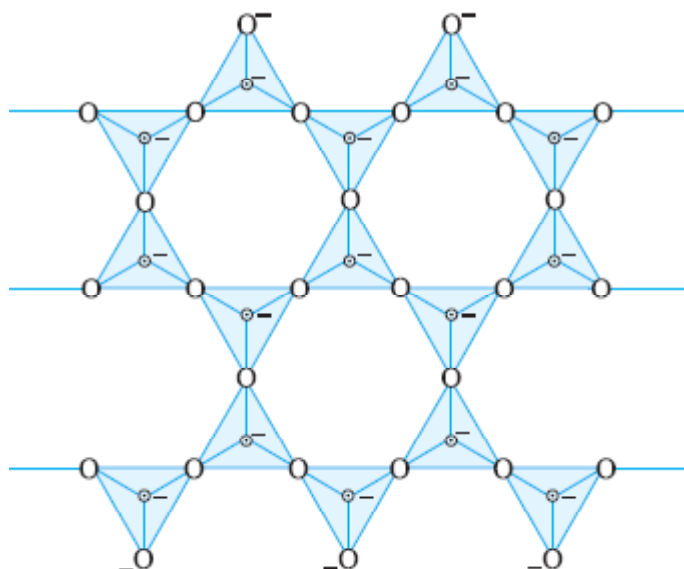


Number of shared oxygen atom = 2.5

For example :

Spodumene	$\text{LiAl}(\text{SiO}_3)_2$
Diposide	$\text{CaMg}(\text{SiO}_3)_2$
Tremolite	$\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$

- (v) **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 $(\text{Si}_2\text{O}_5)_n^{2n-}$.



For example :

Tale	$\text{Mg}(\text{Si}_2\text{O}_5)_2 \text{Mg}(\text{OH})_2$
Kaolin	$\text{Al}_2(\text{OH})_4(\text{Si}_2\text{O}_5)$

Number of shared oxygen atom = 3

- (vi) **Three Dimensional Sheet Silicates :** These silicates involve all four oxygen atoms in sharing with adjacent SiO_4^{4-} tetrahedral. For example, Quartz, Feldspars, Zeolites and Ultramarines. Here all 4 oxygen atoms are shared.

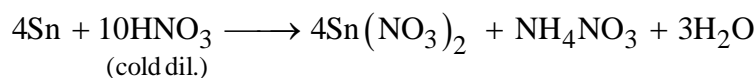
Tin and its compounds :

Tin is a white lustrous, soft, malleable metal. It produces a cracking sound called *tinny* whenever it is bent.

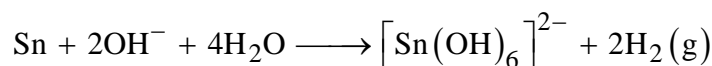
Properties :

1. Tin reacts with steam to give SnO_2 and H_2 .

2. It dissolves in dilute HNO_3 forming $\text{Sn}(\text{NO}_3)_2$



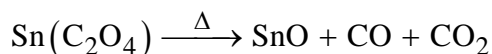
3. It is slowly attacked by cold alkalies and rapidly by hot alkalies. Thus it is amphoteric.



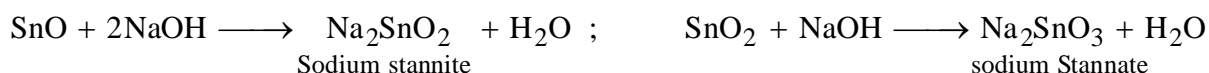
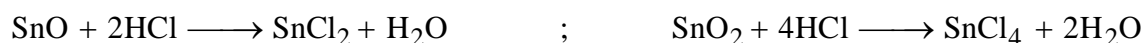
4. Sn is used in tin plating (coating iron or steel sheets with tin) and making alloys like bronze (75% Cu + 25% Sn) and solder (67% + 33% Pb).

 Sn^{2+} and Sn^{4+}

Tin ion exists in two states +II and +IV with the +IV state being more stable. SnO_2 is known as cassiterite and found as a mineral in nature. The other oxide SnO is less stable and is obtained by heating stannous oxalate.

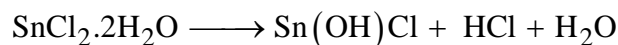


Both SnO and SnO_2 are amphoteric but SnO is slightly more basic than SnO_2 and a good reducing agent too.

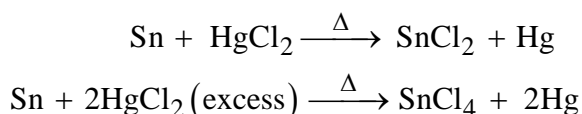


Among halides, stannous chloride (SnCl_2) and stannic chloride (SnCl_4) are the most important.

SnCl_2 exists as a di-hydrate which undergoes hydrolysis on heating



The anhydrous salt SnCl_2 is obtained by reaction of Sn with a calculated quantity of HgCl_2 . Excess of HgCl_2 result in the formation of stannic chloride.



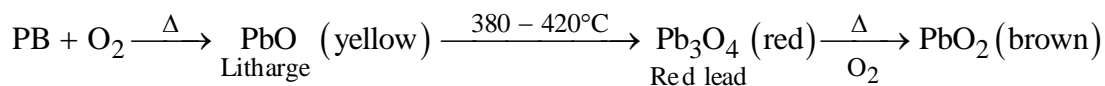
Most of the reactions of SnCl_2 are due to its reducing character. It reduces MnO_4^- to Mn^{2+} , $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+} and itself get oxidized to Sn^{4+} .

Lead and its Compounds

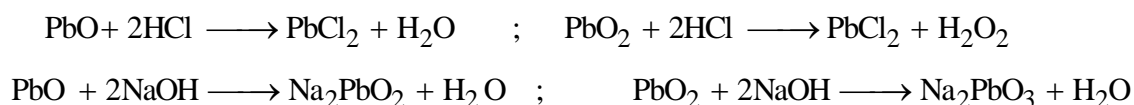
- (i) Lead is a bluish grey soft metal which can be cut with a knife and extremely poisonous.
- (ii) Pb often appears more unreactive than expected from its standard electrode potential. The unreactiveness is due to the surface coating of basic carbonate $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ which forms over lead when exposed to air and moisture. Thus lead is unaffected by water.
- (iii) Pb is amphoteric and dissolves in both acids and hot alkalies similar to Sn. In alkali it forms plumbates like $\text{Na}_2[\text{Pb}(\text{OH})_6]$ or Na_2PbO_3 . However, lead does not dissolve in concentrated HCl because a surface coating of PbCl_2 is formed.
- (iv) Lead is used in making lead chamber for H_2SO_4 plant and certain alloys like solder (Sn – Pb)

[a] Oxides

Pb exists as Pb^{+2} and Pb^{+4} with Pb^{+2} being more stable. This is due to the inert pair effect which increases the stability of +II state while going down the group. Oxide formation is shown as :



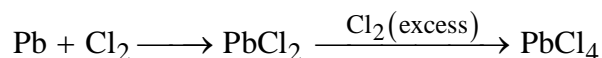
- (i) PbO and PbO_2 are both amphoteric and dissolve in both acids and bases.



- (ii) Pb_3O_4 or Red Lead may be represented as $2\text{PbO} \cdot \text{PbO}_2$ and is used in paint to prevent the rusting of iron and steel.
- (iii) PbO (Litharge) is commercially important and is used in large amounts to make lead glass. PbO_2 is used as a strong oxidising agent and produced in lead storage batteries.

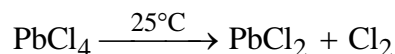
[b] Chlorides

Chlorides are prepared by passing lead through a current of chlorine gas.



Dissolving Pb^{2+} salt (PbO , PbCO_3 , $\text{Pb}(\text{NO}_3)_2$) in HCl produces PbCl_2 .

PbCl_4 is less stable and decomposes on heating at room temperature and liberates Cl_2 .

**[c] Tetraethyl Lead $(\text{CH}_3\text{CH}_2)_4\text{Pb}$:**

It is produced in large amount and used as an 'anti-knock' additive to increase the octane number of petrol. The commercial preparation uses a sodium/lead alloy.



Once it was produced in larger tonnages than any other organometallic compound but the production is declining rapidly as a result of legislation requiring that new cars must run on lead-free petrol.

IN-CHAPTER EXERCISE-B

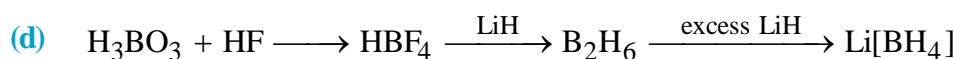
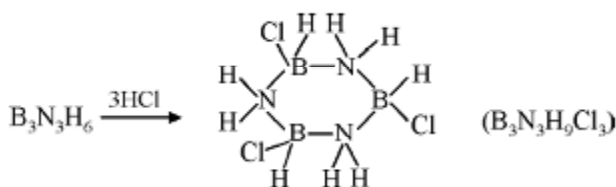
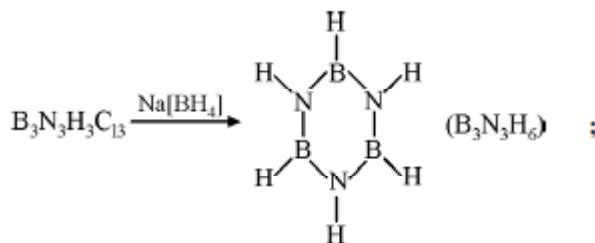
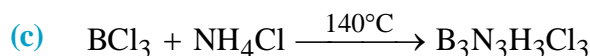
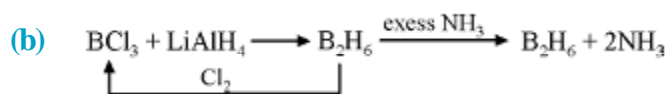
1. Identify the group 14 element that best fits each of the following description :
 - (i) Prefers the +2 oxidation state
 - (ii) Forms the strongest π bonds.
 - (iii) Is the second most abundant element in the earth's crust.
 - (iv) Forms the most acidic oxide.
2. Give reasons for the following observations/applications :
 - (i) Solid CO_2 is known as dry ice.
 - (ii) Carbon acts as an abrasive and also as a lubricant.
 - (iii) Glass stoppers stick in NaOH bottles.
 - (iv) Thermodynamically, graphite is more stable than diamond but still diamond (the less stable forms) exists.
 - (v) CCl_4 is unaffected by water whilst SiCl_4 is rapidly hydrolysed.
 - (vi) SnCl_4 fumes in moist air.

SOLUTION TO IN-CHAPTER EXERCISE - A

1. (a) In B_2H_6 (diborane), B does not have enough valency electrons to form conventional two - electron bonds between all of the adjacent pairs of atoms and so it is termed as electron - deficient.
- (b) $AlCl_3$ hydrolyses in moist air to give fumes of HCl .
- $$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl \text{ (white fumes)}$$
- (c) $NaOH$ reacts with Al and evolves hydrogen. The pressure of the evolved hydrogen opens up the clogged drain.

2. (a) $Na_2B_4O_7 + \text{conc. } H_2SO_4 \longrightarrow H_3BO_3 \xrightarrow[2. \text{ Ignite}]{1. C_2H_5OH} B(OC_2H_5)_2$
(A) (B)

The colour of flame produced is green.



4. $RCN \longrightarrow RCH_2NH_2$
 $RNO_2 \longrightarrow RNH_2$
 $RCHO \longrightarrow RCH_2OH$

SOLUTION TO IN-CHAPTER EXERCISE - B

1. (i) Pb (ii) C (iii) Si (iv) Sn
2. (i) Solid CO_2 is used as dry ice to maintain low temperatures
 (ii) Carbon in the form of diamond is used as abrasive and in the form of graphite as a lubricant. This is due to the hardness of diamond and slipperiness of graphite.
 (iii) NaOH reacts with glass (SiO_2) forming silicates which block the stopper of the bottle.
 (iv) Although thermodynamically it is favourable for diamonds to turn into graphite but this does not happen because there is a high energy of activation required for the process. If this energy is available, the change occurs.
 (v) Carbon halides cannot hydrolyse because they do not have d orbitals and cannot form a hydrolysis intermediate while silicon halides readily hydrolyse.
 (vi) SnCl_4 forms hydrates in moisture : -

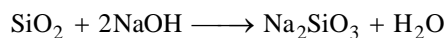
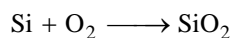
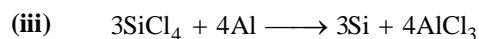
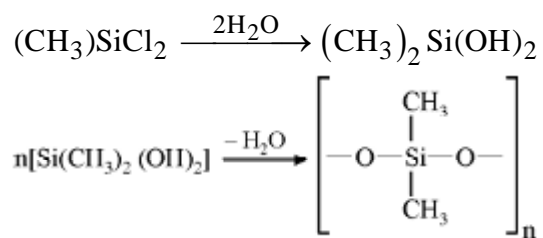
$$\text{SnCl}_4 \xrightarrow[\text{(limite)}]{\text{H}_2\text{O}} \text{SnCl}_4 \cdot 3\text{H}_2\text{O} \text{ (fumes)}$$
3. (a)
$$\begin{array}{c} \text{CO} + \text{Cl}_2 \longrightarrow \text{COCl}_2 \xrightarrow{\text{NH}_3} (\text{NH}_2)_2\text{CO} \xleftarrow{\text{NH}_3(\text{E})} \text{CO}_2 \\ \downarrow \text{H}_2\text{O} \quad \text{urea} \quad (\text{D}) \\ \text{HCl} + \text{CO}_2 \\ (\text{D}) \end{array}$$

 (b) $\text{Si} \xrightarrow{\text{HNO}_3/\text{HF}} \text{SiF}_4 \xrightarrow{\text{HF}} [\text{SiF}_6]^{2-} ; \quad \text{SiF}_4 \xrightarrow{\text{H}_2\text{O}} \text{Si}(\text{OH})_4 + \text{HF}$
 (c) $\text{Na}_2\text{CO}_3 + \text{Si}(\text{fused}) \longrightarrow \text{Na}_2\text{SiO}_3 + \text{CO}_2$
 (d) $\text{Sn}(\text{C}_2\text{O}_4) \xrightarrow{\Delta} \text{SnO} + \text{CO} \uparrow + \text{CO}_2 \uparrow$

$$\text{SnO} \xrightarrow{\text{dil. HCl}} \text{SnCl}_2$$

 (A)
 Among CO and CO_2 ; CO is measured quantitatively by I_2O_5 solution. Thus (B) is CO and (C) is CO_2 .
4. CO_2 being an acidic oxide decreases the pH of water and thus makes the soil acidic.
5. (i) $2\text{SiCl}_4 + 4\text{Al} \longrightarrow 4\text{AlCl}_3 + 3\text{Si} ; \quad \text{SiCl}_4 + 3\text{Mg} \longrightarrow \text{Si} + 2\text{MgCl}_2$
 (ii) $\text{SiCl}_4 + \text{CH}_3\text{MgCl} \longrightarrow \text{CH}_3\text{SiCl}_3 + \text{MgCl}_2 ;$

$$\text{CH}_3\text{SiCl}_3 + \text{CH}_3\text{MgCl} \longrightarrow (\text{CH}_3)_2\text{SiCl}_2 + \text{MgCl}_2$$



6. (i) CO is detected by flame test. It burns with a blue flame.
- (ii) CO₂ is detected by lime water test. It turns lime water milky.
- (iii) Silicates are detected by first dissolving them in HF to form SiF₄ which when comes in contact with a water droplet forms silicic acid (seen as floating white solid)
- (iv) PbCl₂ forms a yellow precipitate of PbCrO₄ in presence of K₂CrO₄ which dissolves in NaOH forming a yellow solution.

My Chapter Notes

