

THE P BLOCK ELEMENTS (BORON AND CARBON FAMILY)

1. INTRODUCTION :

Group 13 to 18 of the periodic table of elements constitute the p-block. The p-block contains metals, metalloids as well as non-metals.

Configuration	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
						He
	B	C	N	O	F	Ne
	Al	Si	P	S	Cl	Ar
	Ga	Ge	As	Se	Br	Kr
	In	Su	Sb	Te	I	Xe
	Tl	Pb	Bi	Po	At	Rn
Group Oxidation State	+3	+4	+5	+6	+7	+8
Other Oxidation State	+1	+2, -4	+3, -3	+4, +2, -2	+5, +3, +1, -1	+6, +4, +2

The p-block elements have general valence shell electronic configuration $ns^2 np^{1-6}$.

The first member of each group from 13–17 of the p-block elements differ in many respects from the other members of their respective groups because of small size, high electronegativity and absence of d-orbitals.

The first member of a group also has greater ability to form $p\pi-p\pi$ multiple bonds to itself (e.g. $C=C$, $C\equiv C$, $N\equiv N$) and to element of second row (e.g. $C=O$, $C=N$, $C\equiv N$, $N=O$) compared to the other members of the same group.

The highest oxidation state of p-block element is equal to the group number minus 10. Moving down the group, the oxidation state two less than the highest group oxidation state and becomes more stable in groups 13 to 16 due to inert pair effect (reluctance of s-subshell electrons to participate in chemical bonding)

- Ge liquid expands when it forms the solid. This property is unique to Ga, Ge and Bi.

Catenation :

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation. This is because C–C bonds are very strong. Down the group the size increases tendency to show catenation decreases. This can be clearly seen from bond enthalpies values. The order of catenation is $C \gg Si > Ge \approx Sn$. Lead does not show catenation. Due to the property of catenation and $p\pi-p\pi$ bonds formation, carbon is able to show allotropic forms.

(Table)

Bond	Bond enthalpy (kJ mol ⁻¹)
C—C	348
Si—Si	297
Ge—Ge	260
Sn—Sn	240

2. IMPORTANT TRENDS AND ANOMALOUS PROPERTIES OF BORON

The tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water. Species like tetrahedral $[M(OH)_4]^-$ and octahedral $[M(H_2O)_6]^{3+}$, except in boron, exist in aqueous medium. It is due to the absence of d orbitals that the maximum covalence of boron is 4. Since the d-orbitals are available with Al and other elements, the maximum covalence can be expected beyond 4.

2.1. Anomalous Behaviour of carbon:

Like first member of other groups, carbon also differs from rest of the members of its group. It is due to its smaller size, higher electronegativity, higher ionisation enthalpy and unavailability of d orbitals.

Carbon accommodate only four pairs of electrons around it and thus this would limit the maximum covalence to four whereas other members can expand their covalence due to the presence of d orbitals, Carbon also has unique ability to form $p\pi-p\pi$ multiple bonds with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are $C = C$, $C \equiv C$, $C = O$, $C = S$ and $C \equiv N$. Heavier elements do not form $p\pi-p\pi$ bonds because their atomic orbital are too large and diffuse to have effective overlapping.

3. ALLOTROPY

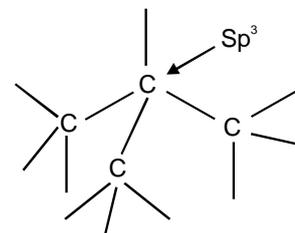
- Silicon is a very high melting-point solid with the same structure as diamond. The non-existence of an allotrope with the graphite structure clearly shows the inability of silicon atoms to multiple bond with themselves.

Allotropes of Carbon:

Allotrope	Hybridisation	C-C bond length	C=C bond length	ΔH_f (KJ/mol)	Density (g/cm ³)
Diamond	sp ³	154 pm	NA	1.9	3.51
Graphite	sp ²	141.5 pm	141.5 pm	0	2.22
Fullerenes	sp ²	143.5 pm	138.3 pm	38.1	1.65

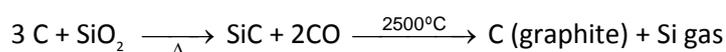
3.1. Diamond :

- Crystalline lattice
- 3-D network : each C-atoms is linked to four other C-atoms in tetrahedral manner.
- one of the hardest – next to boron nitride (only at certain conditions)
- uses : sharpening hard tools, cutter tools; as a gem.

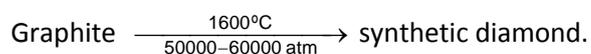


3.2. Graphite :

- Layered structure
- Interlayer force – Vanderwaal's forces
- Each carbon atom is linked to three other carbon atoms, fourth electron forms a π bond.
- Good conductor along the sheet and semi-conductor perpendicular to the sheet.
- Inter layer distance 340 pm so cleavage between layers is easy. Soft and slippery – lubricant at high temperature
- Natural graphite is found as a mixture with mica, quartz & silicates.



- Thermodynamically most stable among allotropes.



3.3. Fullerenes :

- heating of graphite in an electrical arc in the presence of inert gases such as helium or argon can result into fullerene
- Cage like molecules.
- C₆₀ – Soccer ball shape – Buckminsterfullerene
- 20- six membered rings and 12- five membered rings.
- Six membered ring is fused with six or five membered ring
- Five membered ring is fused only with six membered ring.
- C – C bond length = 143.5 pm ; C = C bond length = 138.3 pm

Solved Examples

Example 1. Thermodynamically graphite is more stable than diamond but diamond does not transform into graphite on its own. Why ?

Solution This conversion is not favoured by kinetic factors (the activation energy for this is very high).

4. ELEMENTS : PROPERTIES & TRENDS

4.1. Physical Properties & Trends :

Boron is non-metallic in nature . It is extremely hard and black coloured solid. It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point. Rest of the member are soft metals with low melting point and high electrical conductivity. Gallium with low melting point (303 K), could exist in liquid state during summer. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures. Aluminium is a good conductor of heat and electricity. It is malleable and ductile. Density of the elements increases down the group from boron to thallium.

(Table No. 1) Atomic and physical properties of Boron family :

Element		B	Al	Ga	In	Tl	
Atomic Number		5	13	31	49	81	
Atomic Mass		10.81	26.98	69.72	114.82	204.38	
Electronic configuration		[He] 2s ² 2p ¹	[Ne] 3s ² 3p ¹	[Ar] 3d ¹⁰ 4s ² 4p ¹	[Kr] 4d ¹⁰ 5s ² 5p ¹	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	
Atomic Radius / pm		85	143	135	167	170	
Ionic Radius M ³⁺ / pm		27	53.5	62	80	88.5	
Ionization enthalpy (kJ mol ⁻¹)	$\Delta_i H_1$	I	801	577	579	558	589
	$\Delta_i H_2$	II	2427	1816	1979	1820	1971
	$\Delta_i H_3$	III	3659	2744	2962	2704	2877
Electronegativity		2.0	1.5	1.6	1.7	1.8	
Density/[g cm ⁻³ (at 293 K)]		2.35	2.70	5.90	7.31	11.85	
Melting point / K		2453	933	303	430	576	
Boiling point / K		3923	2740	2676	2353	1730	

(Table No. 2) Atomic and physical properties of Carbon family

Element		C	Si	Ge	Sn	Pb	
Atomic Number		6	14	32	50	82	
Atomic Mass		12.01	28.09	72.60	118.71	207.2	
Electronic configuration		[He] 2s ² 2p ²	[Ne] 3s ² 3p ²	[Ar] 3d ¹⁰ 4s ² 4p ²	[Kr] 4d ¹⁰ 5s ² 5p ²	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	
Atomic Radius / pm		77	118	122	140	146	
Ionic Radius M ⁴⁺ / pm		–	40	53	69	78	
Ionization enthalpy (kJ mol ⁻¹)	Δ ₁ H ₁	I	1086	786	761	708	715
	Δ ₁ H ₂	II	2352	1577	1537	1411	1450
	Δ ₁ H ₃	III	4620	3228	3300	2942	3081
Electronegativity		2.5	1.8	1.8	1.8	1.9	
Melting point / K		4373	1693	1218	505	600	
Boiling point / K		–	3550	3123	2896	2024	

Properties	Boron Family	Carbon Family
Character	B - Metalloid Al - Metallic Ga - Metallic In - Metallic Tl - Metallic	C - Non metallic Si - Non metallic Ge - Metalloid Sn - Metallic Pb - Metallic
Configuration	ns ² np ¹	ns ² np ²
Atomic size	B < Al > Ga < In < Tl In Ga, poor shielding of 10 d-electrons	C < Si < Ge < Sn < Pb
Ionisation Energy	B > Al < Ga > In < Tl Poor shielding of d-orbital and f-orbital in Ga & Tl respectively	C > Si > Ge > Sn < Pb Poor shielding of f-orbital.
Electronegativity	B > Al < Ga < In < Tl Marginal increase after Al	C > Si ≈ Ge ≈ Sn ≈ Pb
Oxidation State	B Al Ga In Tl +3 +3 +3 +3 +3 +1 +1 +1	C Si Ge Sn Pb +4 +4 +4 +4 +4 +2 +2 +2
Stability of Oxidation state	+1 : Al < Ga < In < Tl +3 : Al > Ga > In > Tl	+2 : Ge < Sn < Pb +4 : Ge > Sn > Pb
Density	B < Al < Ga < In < Tl	C (diamond) > Si < Ge < Sn < Pb

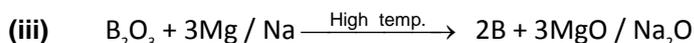
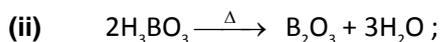
4.2. Chemical Properties :

ACTION	CARBON FAMILY	BORON FAMILY
Reactivity towards air	$4E + 3O_2 \xrightarrow{\text{heat}} 2E_2O_3$	$E + O_2 \xrightarrow{\text{heat}} EO_2$ dioxide $E + \frac{1}{2}O_2 \xrightarrow{\text{heat}} EO$ mono oxide
	B_2O_3 – acidic	CO_2 – acidic CO – neutral
	Al_2O_3 – amphoteric	SiO_2 – acidic SiO – unstable
	Ga_2O_3 – amphoteric	GeO_2 – acidic GeO – acidic
	In_2O_3 – basic	SnO_2 – amphoteric SnO – amphoteric
	Tl_2O_3 – basic	PbO_2 – amphoteric PbO – amphoteric
Reactivity towards Halogens	$2E + 3X_2 \rightarrow 2EX_3$; (X=F,Cl,Br,I)	$E + 2X_2 \rightarrow EX_4$; (X=F,Cl,Br,I)
	BX_3 – covalent; Bl_3 cannot be formed directly	All members form MX_4 ; Ge & Pb form MX_2
	AlF_3 – Ionic	PbI_4 does not exist
	GaF_3 – Ionic	stability of EX_4 decreases down the group 14
	InF_3 – Ionic	stability of EX_2 increases down the group 14
	TlI & TlI_3 – forms	stability: $GeX_4 > GeX_2$; $PbX_2 > PbX_4$
Reactivity towards water (H_2O)	B – does not react with water	$C(s) + H_2O(\text{steam}) \xrightarrow[\text{heat}]{\text{red}} CO + H_2$ (water gas)
	Al – $Al(OH)_3$ for $25^\circ C$ Al_2O_3 for $T > 480^\circ C$	$E(s) + H_2O(\text{steam}) \xrightarrow[\text{heat}]{\text{red}} EO_2 + H_2$; (E=Si,Ge, Sn)
	Ga & In – not attacked by cold & hot water unless oxygen is present	C, Si, Ge – not attacked by cold water $2Pb + H_2O + 1/2O_2 \rightarrow 2Pb(OH)_2$
	Tl – oxidises in moist air & decomposes steam at red heat	
Reactivity towards acids	Boron reacts with only oxidising acids	C, Si & Ge does not react with dilute HCl
	$2B + 3H_2SO_4(\text{hot \& conc}) \rightarrow 2H_3BO_3 + 3SO_2$ $2B + 6HNO_3(\text{hot \& conc}) \rightarrow 2H_3BO_3 + 6NO_2$	Sn dissolves in HCl (dil. & conc) but Pb in only dil. HCl
	$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$	$Pb + \text{conc. HCl} \rightarrow PbCl_2$ (coating) + H_2
	Al do not react with conc. HNO_3 , forms passive oxide layer	$C(\text{graphite}) + HNO_3 \rightarrow$ *Mellitic acid $C(\text{graphite}) + HF/HNO_3 \rightarrow$ Graphite oxide
	Ga reacts with HCl & H_2SO_4	$Si + 6HF \rightarrow H_2SiF_6 + 2H_2$
	In & Tl can react with mineral acid	$E + \text{dil. } HNO_3 \rightarrow E(NO_3)_2$; E = Sn or Pb
Reactivity towards alkali (NaOH)	$2B + 2NaOH + 2H_2O \rightarrow 2NaBO_2 + 3H_2$ $2B + 6NaOH \xrightarrow{\text{fused}} 2Na_3BO_3 + 3H_2$	C – unaffected by alkalies
	Al & Ga readily dissolves in alkalies. $2Al + 2NaOH + 6H_2O \rightarrow 2NaAlO_2 \cdot 2H_2O$ or $Na^+ [Al(OH)_4]^- + 3H_2$ $Al + 3NaOH \rightarrow Na_3AlO_3 + \frac{3}{2}H_2$	$Si + 2OH^-(\text{aq.}) + H_2O \rightarrow SiO_3^{2-}(\text{aq.}) + 2H_2(g)$ $Si + 4NaOH \xrightarrow{\Delta} Na_4[SiO_4]$
	In & Tl do not react with alkali.	$E + NaOH \xrightarrow{\Delta} Na_2[E(OH)_6]$; E = Sn or Pb
Reactivity towards Metal	$3Mg + 2B \rightarrow Mg_3B_2$ $3Ca + 2B \rightarrow Ca_3B_2$	$2Mg + Si \xrightarrow{\Delta} Mg_2Si$ (magnesium silicide)
Reducing Property	$3SiO_2 + 4B \xrightarrow{\Delta} 2B_2O_3 + 3Si$ $3CO_2 + 4B \xrightarrow{\Delta} 2B_2O_3 + 3C$ $3MnO_2 + 4Al \xrightarrow{\Delta} 2Al_2O_3 + 3Mn$ $Cr_2O_3 + 2Al \xrightarrow{\Delta} Al_2O_3 + 2Cr$	

4.3. Preparation of elements :

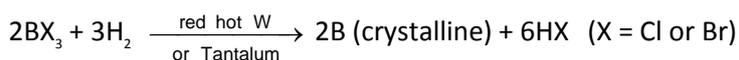
4.3.1 Boron :

(1) From Borax ($\text{Na}^+\text{B}_4\text{O}_7^{2-} \cdot 10\text{H}_2\text{O}$); low purity (95-98%) boron (black)



The product thus obtained is boiled with HCl and filtered when Na_2O or MgO dissolves leaving behind elemental boron. It is thoroughly washed to remove HCl and then dried finally.

(2) Reduction of BX_3 :



99.9 % pure

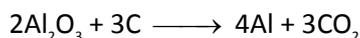
Problem in obtaining high purity boron :

- High melting point (2180°C)
- Liquid gets corroded.

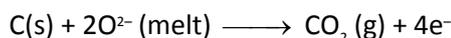
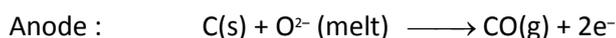
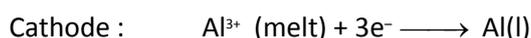
4.3.2 Aluminium :

Electrolytic reduction (Hall-Heroult process) :

The purified Al_2O_3 is mixed with Na_3AlF_6 (cryolite) or CaF_2 (fluorspar) which lowers the melting point of the mixture and brings conductivity. The fused matrix is electrolysed. Steel cathode and graphite anode are used. The graphite anode is useful here for reduction to the metal. The overall reaction may be taken as :



The electrolysis of the molten mass is carried out in an electrolytic cell using carbon electrodes. The oxygen liberated at anode reacts with the carbon of anode producing CO and CO_2 . This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away. The electrolytic reactions are :



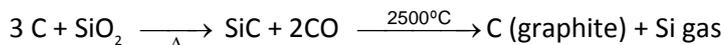
Several other extraction processes will be studied in detail in Metallurgy.



3.2.3 CARBON :

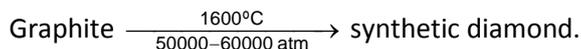
(i) Preparation of carbon black (soot) by incomplete combustion of hydrocarbon.

(ii) Graphite



(iii) Diamond :

- Natural diamond can be extracted from mines.
- Synthetic diamond

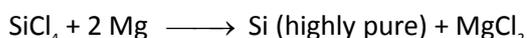


4.3.3 Silicon :

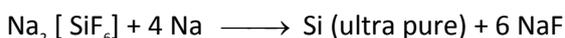
(i) Reducing SiO_2 with high purity coke in an electric furnace.



(ii) $\text{Si (pure)} + 2 \text{ Cl}_2 \longrightarrow \text{SiCl}_4$



(iii) Sodium Reduction of $\text{Na}_2[\text{SiF}_6]$



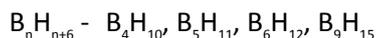
Zone refining is used to get ultra pure silicon from highly pure silicon, which can be used in semi-conductor industry.

5. COMPOUNDS

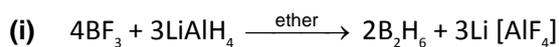
5.1. Hydrides

5.1.1 Boranes

Binary compounds of B with H are called boron hydrides or boranes. These compounds form following two types of series :



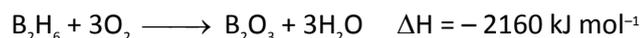
The chemistry of diborane has aroused considerable interest because of its usefulness in many synthetic reactions and also because the elucidation of its structure helped to clarify the basic concepts about the structure of electron deficient compounds.

Preparation of Diborane(B₂H₆) :

Properties :

(i) B₂H₆ is colourless gas and highly reactive (boiling point 183 K).

(ii) Controlled pyrolysis of diborane leads to most of the higher boranes.

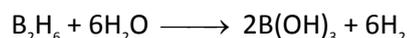
It catches fire spontaneously in air and explodes with O₂. Reaction with oxygen is extremely exothermic.



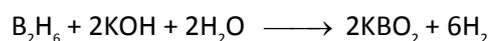
○ Mixtures of diborane with air or oxygen inflame spontaneously producing large amount of heat. Diborane has a higher heat of combustion per unit weight of fuel than most other fuels. It is therefore used as a rocket fuel.

○ At red-heat the boranes decomposes to boron and hydrogen.

(iii) Reaction with water is instantaneous.

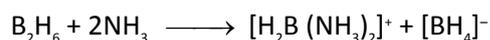


Diboroane is also hydrolysed by weaker acids (e.g. alcohols) or aqueous alkali.

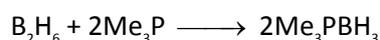
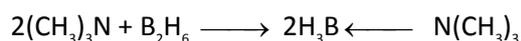


(iv) The electron deficient 3c-2e BHB bridges are sites of nucleophilic attack.

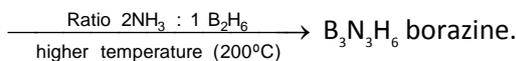
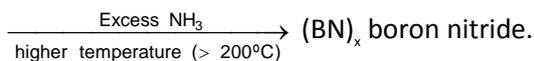
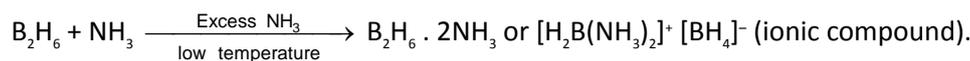
○ Small amines such as NH₃, CH₃NH₂ and (CH₃)₂NH give unsymmetrical cleavage of diborane.



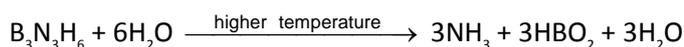
○ Large amines such as (CH₃)₃N and pyridine give symmetrical cleavage of diborane.



- The reaction with ammonia depends on conditions.

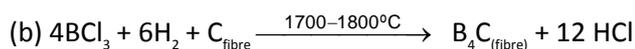
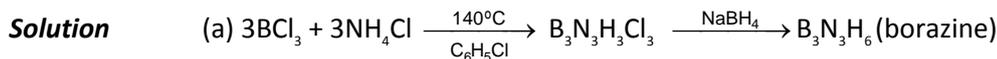
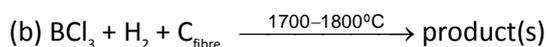
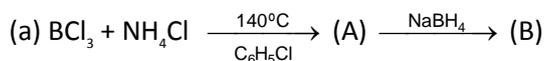


Borazine is much more reactive than benzene. Borazine readily undergoes addition reactions which do not occur with benzene. Borazine also decomposes slowly and may be hydrolysed to NH_3 and boric acid at elevated temperature. If heated with water, $\text{B}_3\text{N}_3\text{H}_6$ hydrolyses slowly.



Solved Examples

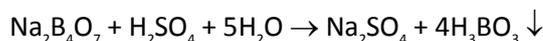
Example 1. Complete the following reactions and identify the products formed.



5.1.2 Boric acid (H_3BO_3) :

Preparation :

- (i) It is precipitated by treating a concentrated solution of borax with sulphuric acid.

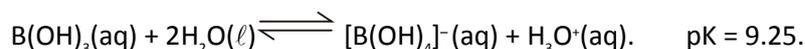


- (ii) From Colemanite: Powdered colemanite is suspended in water and excess SO_2 is passed through it. On filtering and cooling the filtrate, white crystals of H_3BO_3 are obtained.



Properties:

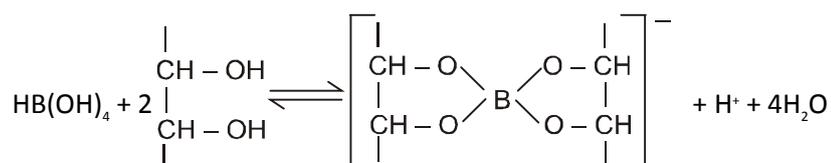
It is a weak monobasic acid soluble in water and in aqueous solution the boron atom completes its octet by accepting OH^- from water molecules:



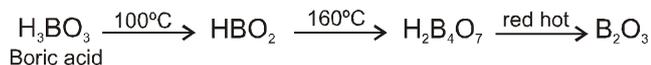
It, therefore, functions as a Lewis acid and not as a proton donor like most acids.

Since $B(OH)_3$ only partially reacts with water to form H_3O^+ and $[B(OH)_4]^-$, it behaves as a weak acid. Thus H_3BO_3 can not be titrated satisfactorily with $NaOH$ as a sharp end point is not obtained. If certain organic polyhydroxy compounds such as glycerol, mannitol or sugars are added to the titration mixture, then $B(OH)_3$ behaves as a strong monobasic acid and it can be now titrated with $NaOH$ and the end point is detected using phenolphthalein as indicator ($pH = 8.3 - 10.0$).

The added compound must be a cis-diol, to enhance the acid properties. The cis-diol forms very stable complex with the $[B(OH)_4]^-$, thus removing it from solution. The reaction is reversible and thus removal of one of the products shifts the equilibrium in the forward direction and thus all the $B(OH)_3$ reacts with $NaOH$; in effect it acts as a strong acid in the presence of the cis-diol.



When heated it first forms metaboric acid (HBO_2) and then boron trioxide.



Orthoboric acid is greasy to touch less soluble in cold water but more soluble in hot water. In the solid state, the $B(OH)_3$ units are hydrogen bonded together in to two dimensional sheets with almost hexagonal symmetry. The layered are quite a large distance apart (3.18 \AA) and thus the crystal breaks quite easily into very fine particles.

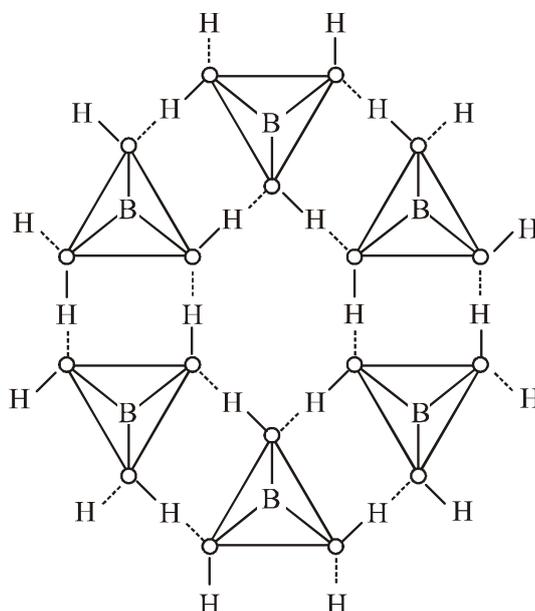
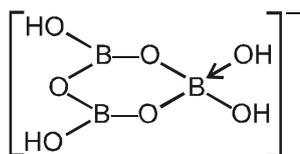
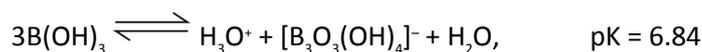


Figure : 1

- Polymeric metaborate species are formed at higher concentration, for example,



Test for Borate radical :

When boric acid is heated with ethyl alcohol, the evolved gas is burned forming a green edged flame.



ethyl borate (volatile)

Uses :

- (i) It is an antiseptic and its water solution is used as an eyewash.
- (ii) It is also used in glass, enamel and pottery industry.

Solved Examples

Example 1. It has been observed that BF_3 does not hydrolyses completely whereas BCl_3 or BBr_3 get easily hydrolysed to form $\text{B}(\text{OH})_3$ and HX ? Explain.

Solution The greater stability of B–F bond as compared to B–Cl and B–Br bonds is due to additional π -bonding in B–F bonds of BF_3 molecules. The B–Cl and B–Br bonds are relatively weak and are easily cleaved by water forming strong B–OH bonds instead of stable addition product ($\text{BF}_3 \cdot \text{OH}_2$) formed by BF_3 .

5.1.3 Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) :

Preparation :

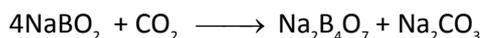
It is found in nature but can also be prepared by the following methods.

- (i) From Colemanite.

When colemanite powder is heated with Na_2CO_3 solution, the following reaction occurs with the precipitation of CaCO_3 .

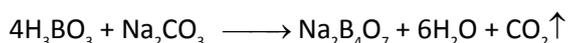


The filtrate is cooled when white crystals of borax are precipitated. The mother liquor on treatment with CO_2 converts NaBO_2 to $\text{Na}_2\text{B}_4\text{O}_7$, which precipitates out on crystallization.



(ii) From orthoboric acid.

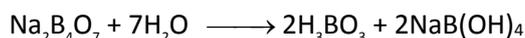
Borax is obtained by the action of Na_2CO_3 on orthoboric acid.



Properties :

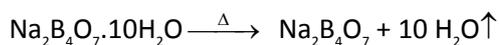
(i) Borax is a white powder, less soluble in cold water, more soluble in hot water.

(ii) Its aqueous solution is alkaline because of its hydrolysis to weak acid H_3BO_3 and strong alkali NaOH .



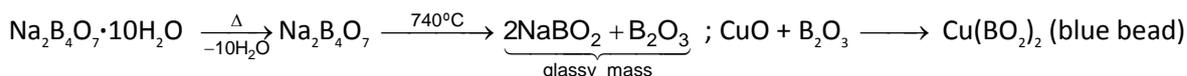
(iii) Action of heat.

When borax powder is heated, it first swells due to loss of water in the form of steam but at 740°C it becomes converted into colourless transparent borax bead.



Borax-bead test :

Borax reacts with certain metal salts such as, Ni^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Mn^{2+} etc. to form coloured metaborates. The colour of the metaborates can be used to identify the metallic ions (cations) in salts.



Uses :

(i) In borax bead test.

(ii) In purifying gold.

(iii) As flux during welding of metals.

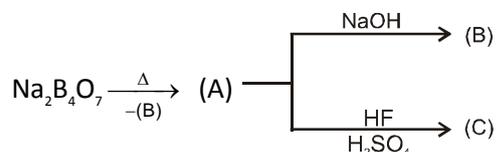
(iv) In production of glass.

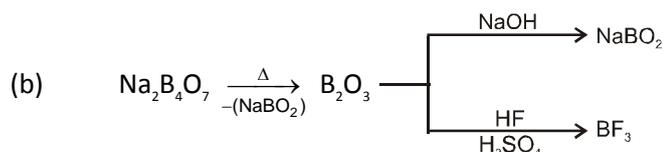
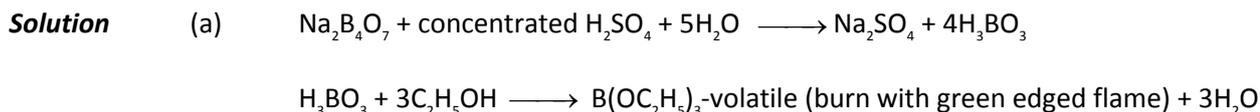
Solved Examples



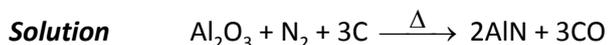
(B) is identified by the characteristic colour of the flame. Identify (A) and (B).

(b) Complete the following reaction and identify the products formed.





Example 2. What will happen if aluminium is heated with coke in an atmosphere of nitrogen ?



5.2. Halides, Alums and Other metal salts :

5.2.1 Boron Halide :

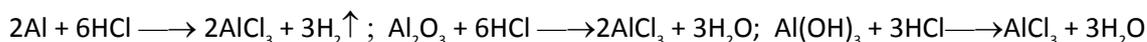
Boron trihalides are strictly monomeric, trigonal planar molecules. This difference from aluminium is attributed to back-donation from “nonbonding” electrons on halogen atoms into the “empty” p_z orbital of boron which lends some double bond character to B–X bonding (manifested by bond shortening) and stabilizes the monomer.

5.2.2 Aluminium Chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) :

It is a colourless crystalline solid, soluble in water. It is covalent. Anhydrous AlCl_3 is a deliquescent white solid.

Preparation :

(i) By dissolving aluminium, Al_2O_3 , or $\text{Al}(\text{OH})_3$ in dilute HCl :



The solution obtained is filtered and crystallized when the crystals of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ are obtained.

(ii) Anhydrous AlCl_3 is obtained by the action of Cl_2 on heated aluminium.

(iii) By heating a mixture of Al_2O_3 and coke and passing chlorine over it.

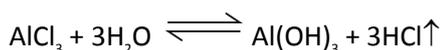


Properties :

(i) **Action of heat :** Hydrated salt when heated strongly is converted to Al_2O_3 .



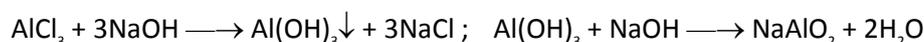
(ii) **Action of moisture on anhydrous AlCl_3 :** When exposed to air, anhydrous AlCl_3 produces white fumes of HCl.



(iii) **Action of NH_3** : Anhydrous AlCl_3 absorbs NH_3 since the former is a Lewis acid.



(iv) **Action of NaOH solution** : When NaOH solution is added dropwise to an aqueous AlCl_3 solution, a gelatinous precipitate of $\text{Al}(\text{OH})_3$ is first formed which dissolves in excess of NaOH solution to give a colourless solution of sodium meta-aluminate.



This reaction is important as a test to distinguish between an aluminium salt from salts of Mg, Ca, Sr, and Ba. (When NaOH solution is added to their salt solutions, a white precipitate of hydroxide forms which does not dissolve in excess of NaOH).

(v) $4\text{LiH} + \text{AlCl}_3 \longrightarrow \text{LiAlH}_4 + 3\text{LiCl}$

Uses :

(i) As catalyst for cracking of petroleum.

(ii) As catalyst in Friedel-Crafts reactions.

(iii) For preparing aluminium compounds.

Solved Examples

Example 1. What happens when :

(write chemical equations only)

(a) Anhydrous AlCl_3 is exposed to atmosphere.

(b) AlCl_3 dissolves in aqueous sodium hydroxide (excess)

Solution (a) $\text{AlCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{Al}(\text{OH})_3 + 3\text{HCl}$ (HCl fumes in air).

(b) $\text{AlCl}_3 + 3\text{NaOH} \longrightarrow \text{Al}(\text{OH})_3 \downarrow + 3\text{NaCl}$

$\text{Al}(\text{OH})_3 + \text{OH}^- \longrightarrow [\text{Al}(\text{OH})_4]^-$

Example 2. Anhydrous AlCl_3 cannot be prepared by heating hydrated salt. Why ?

Solution Gets hydrolysed forming Al_2O_3 .





5.2.3 Alums ; $M_2SO_4 \cdot M'_2(SO_4)_3 \cdot 24H_2O$ or $MM'(SO_4)_2 \cdot 12H_2O$

Alums are transparent crystalline solids having the above general formula where M is almost any univalent positive cation (except Li^+ because this ion is too small to meet the structural requirements of the crystal) and M' is a trivalent positive cation (Al^{3+} , Ti^{3+} , V^{3+} , Cr^{3+} , Fe^{3+} , Mn^{3+} , Co^{3+} , Ga^{3+} etc.). Alums contain the ions $[M(H_2O)_6]^+$, $[M'(H_2O)_6]^{3+}$ and SO_4^{2-} in the ratio 1 : 1 : 2. Some important alums are :

- (i) Potash alum $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ (ii) Chrome alum $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$
- (iii) Ferric alum $K_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$ (iv) Ammonium alum $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

Alums are double salts which when dissolved in water produce metal ions (or ammonium ions) and the sulphate ions.

Preparation :

A mixture containing solutions of M_2SO_4 and $M'_2(SO_4)_3$ in 1 : 1 molar ratio is fused & then the resulting mass is dissolved into water. From the solution thus obtained, alums are crystallised.

Uses :

- (i) As a mordant in dye industry. The fabric which is to be dyed is dipped in a solution of the alum and heated with steam. $Al(OH)_3$ obtained as hydrolysis product of $[Al(H_2O)_6]^{3+}$ deposits into the fibres and then the dye is absorbed on $Al(OH)_3$.
- (ii) As a germicide for water purification
- (iii) As a coagulating agent for precipitating colloidal impurities from water.

Solved Examples

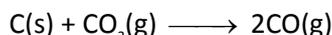
Example 1. List the cations which are capable of replacing aluminium in alums ?

Solution Cations of about the same size as that of Al^{3+} such as Ti^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} and Co^{3+} are capable of replacing aluminium in alums.

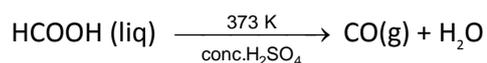
5.2.4 Carbonmonoxide (CO) :

Preparation :

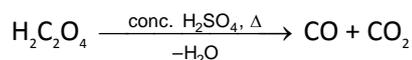
- (i) It is formed together with CO_2 , when carbon or carbonaceous matter is oxidized by air or oxygen. It is also produced when CO_2 is reduced by red-hot carbon; this reaction is of importance in metal extractions.



- (ii) In the laboratory it can be prepared by dehydrating methanoic acid with concentrated sulphuric acid



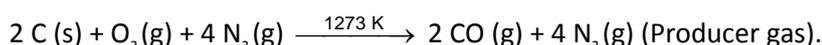
- (iii) If oxalic acid is dehydrated in the same way, CO_2 is formed as well.



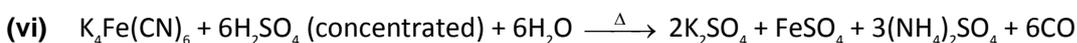
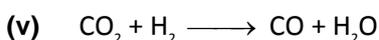
- (iv) On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and H_2 thus produced is known as water gas or synthesis gas.



When air is used instead of steam, a mixture of CO and N_2 is produced, which is called producer gas.



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



- (viii) Also obtained as by-product when carbon is used in reduction processes such as, of phosphite rock to give phosphorus.

Properties :

- I. Carbon monoxide is a colourless, odourless gas which burns in air with a blue flame, forming CO_2 . It is sparingly soluble in water and is a neutral oxide. CO is toxic, because it forms a complex with haemoglobin in the blood and this complex is more stable than oxy-haemoglobin. This prevents the haemoglobin in the red blood corpuscles from carrying oxygen round the body. This causes oxygen deficiency, leading to unconsciousness and then death.



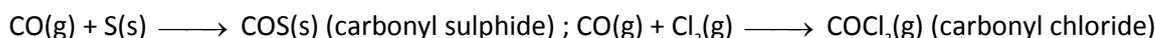
Ordinary gas masks are no protection against the gas, since it is not readily adsorbed on active charcoal. In the presence of air, a mixture of manganese (IV) oxide and copper(II) oxide catalytically oxidizes it to CO_2 , and this mixed catalyst is used in the breathing apparatus worn by rescue teams in mine disasters.

II. Carbon monoxide is a powerful reducing agent, being employed industrially in the extraction of iron and nickel . $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \longrightarrow 2\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g})$; $\text{NiO}(\text{s}) + \text{CO}(\text{g}) \longrightarrow \text{Ni}(\text{s}) + \text{CO}_2(\text{g})$

III. It reacts with many transition metals, forming volatile carbonyls; the formation of nickel carbonyl followed by its decomposition is the basis of the Mond's process for obtaining very pure nickel .



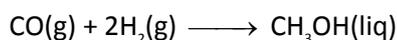
I. In addition to reacting with oxygen, carbon monoxide combines with sulphur to give carbonyl sulphide and with chlorine in the presence of light to give carbonyl chloride (phosgene), used in the production of polyurethane foam plastics. Phosgene is an exceedingly poisonous gas.



II. Although carbon monoxide is not a true acid anhydride since it does not react with water to produce an acid, it reacts under pressure with fused sodium hydroxide to give sodium methanoate :



III. With hydrogen under pressure and in the presence of zinc oxide or chromium (III) oxide catalyst it reacts to give methanol; this reaction is of industrial importance.



IV. CO is readily absorbed by an ammonical solution of copper (I) chloride to give $\text{CuCl}\cdot\text{CO}\cdot 2\text{H}_2\text{O}$. It reduces an ammonical solution of silver nitrate to silver (black) and, in the absence of other gaseous reducing agents, this serves as a test for the gas. It can be estimated by reaction with iodine pentoxide, the iodine which is produced quantitatively being titrated with standard sodium thiosulphate solution.



It reduces an aqueous PdCl_2 solution to metallic Pd.

5.2.5 Carbon dioxide (CO₂) :

Preparation :

- (i) In the laboratory it can be conveniently made by the action of dilute hydrochloric acid on marble chips :

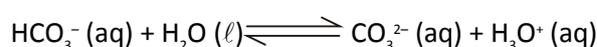


- (ii) Industrially it is produced as a by-product during the manufacture of quicklime and in fermentation processes:



Properties :

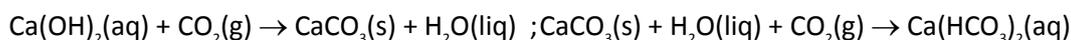
- (i) It is a colourless, odourless and heavy gas which dissolves in its own volume of water at ordinary temperature and pressure. Like all gases, it dissolves much more readily in water when the pressure is increased and this principle is used in the manufacture of soda water and fizzy drinks.
- (ii) CO₂ is easily liquefied (critical temperature = 31.1°C) and a cylinder of the gas under pressure is a convenient fire extinguisher. When the highly compressed gas is allowed to expand rapidly solid carbon dioxide ('dry ice') is formed. Solid carbon dioxide sublimates at -78°C and, since no massy liquid is produced, it is a convenient means of producing low temperatures.
- (iii) Carbon dioxide is the acid anhydride of carbonic acid, which is a weak dibasic acid and ionises in two steps as follows :



H₂CO₃ / HCO₃⁻ buffer system helps to maintain pH of blood between 7.26 to 7.42.

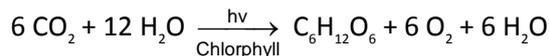
A solution of carbonic acid in water will slowly turn blue litmus red and when the solution is boiled, all the CO₂ is evolved.

- (iv) Carbon dioxide readily reacts with alkalies forming the carbonate and, if CO₂ is in excess, the hydrogen carbonate. This is the basis of the lime-water test for CO₂ gas.



The above reaction accounts for the formation of temporarily hard water.

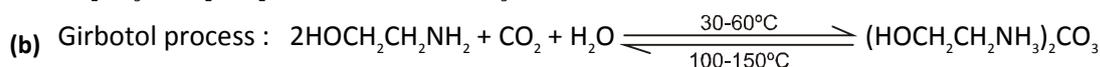
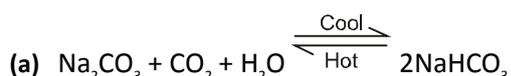
- (v) Carbon dioxide, which is normally present to the extent of ~ 0.03% by volume in the atmosphere, is removed from it by the process known as photosynthesis. It is the process by which green plants convert atmospheric CO₂ into carbohydrates such as glucose. The overall chemical change can be expressed as :



By this process plants make food for themselves as well as for animals and human beings. But the increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years seem to increase the CO_2 content of the atmosphere. This may lead to increase in green house effect and thus, raise the temperature of the atmosphere which might have serious consequences.

(vi) Gaseous CO_2 is extensively used to carbonate soft drinks. Being heavy and non-supporter of combustion it is used as fire extinguisher. A substantial amount of CO_2 is used to manufacture urea.

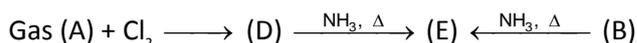
Recovery of CO_2 :



Solved Examples

Example 1. $\text{H}_2\text{C}_2\text{O}_4 \xrightarrow{\Delta} \text{gas (A)} + \text{gas (B)} + \text{liquid (C)}$
oxalic acid

Gas (A) burns with blue flame and is oxidised to gas (B). Gas (B) turns lime water milky.



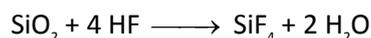
Identify (A) to (E) and explain reactions involved.

Solution $\text{H}_2\text{C}_2\text{O}_4 \xrightarrow{\Delta} \text{CO} + \text{CO}_2 + \text{H}_2\text{O}$



5.2.6 Silicon Dioxide (SiO_2) :

Silicon dioxide, commonly known as silica, occurs in several crystallographic forms. Quartz, cristobalite and tridymite are some of the crystalline forms of silica, and they are interconvertible at suitable temperature. Silicon dioxide is a covalent, three-dimensional network solid in which each silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms. Each oxygen atom in turn covalently bonded to another silicon atoms. Each corner is shared with another tetrahedron. The entire crystal may be considered as giant molecule in which eight membered rings are formed with alternates silicon and oxygen atoms. Silica in its normal form is almost non-reactive because of very high Si–O bond enthalpy. It resists the attack by halogens, dihydrogen and most of the acids and metals even at elevated temperatures. However, it is attacked by HF and NaOH.



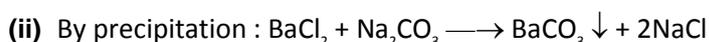
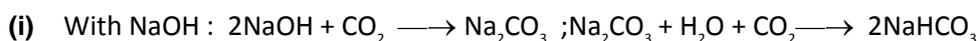
Quartz is extensively used as a piezoelectric material ; it has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications. Silica gel used as a drying agent and as a support for chromatographic materials and catalysts. Kieselghur, an amorphous form of silica is used in filtration plants.

5.2.7 Carbonates (CO_3^{2-}) and Bicarbonates (HCO_3^-)

Carbonic acid is a dibasic acids giving rise to two series of salts, carbonates (normal salts) and bicarbonates (acid salts) due to successive removal of the replaceable hydrogens from H_2CO_3 .



Preparation :

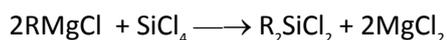
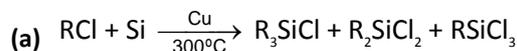


5.3. SiCl_4 , Silicones, Silicates & Zeolites :

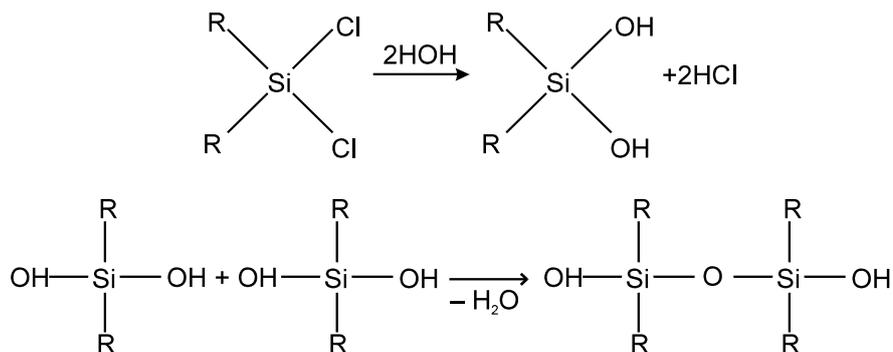
5.3.1 Silicones :

Silicones are synthetic organosilicon compounds having repeated R_2SiO units held by Si – O – Si linkages. These compounds have the general formula $(\text{R}_2\text{SiO})_n$ where R = alkyl or aryl group.

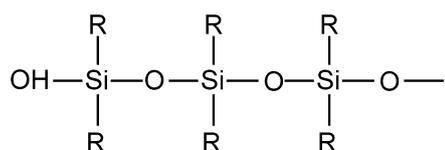
The silicones are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes and their subsequent polymerisation. The alkyl or aryl substituted chlorosilanes are prepared by the following reactions.



After fractional distillation, the silane derivatives are hydrolysed and the 'hydroxides' immediately condense by intermolecular elimination of water. The final product depends upon the number of hydroxyl groups originally bonded to the silicon atom:



In this manner several molecules may combine to form a long chain polymer whose both the ends will be occupied by –OH groups. Such compounds are generally represented from the following formula.

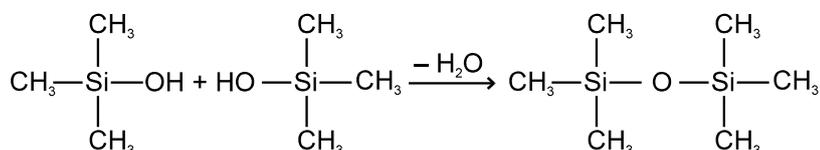
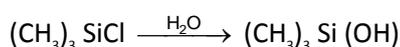


The polymer chain depicted above is terminated by incorporating a small quantity of the monochlorosilane derivative into the hydrolysis mixture.

- Silicones can be prepared from the following types of compounds only.

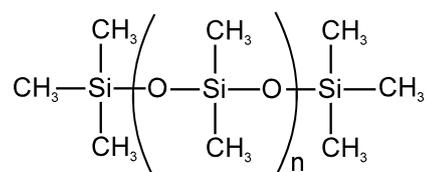


- Silicones from the hydrolysis of $(\text{CH}_3)_3\text{SiCl}$



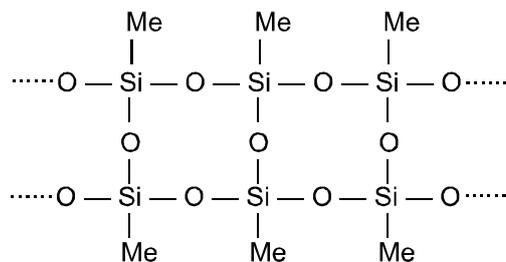
- Silicones from the hydrolysis of a mixture of $(\text{CH}_3)_3\text{SiCl}$ & $(\text{CH}_3)_2\text{SiCl}_2$

The dichloro derivative will form a long chain polymer as usual. But the growth of this polymer can be blocked at any stage by the hydrolysis product of mono-chloro derivative.



- Silicones from the hydrolysis of trichloro derivative.

When a compound like CH_3SiCl_3 undergoes hydrolysis, a complex cross-linked polymer is obtained as chain can grow in three places as

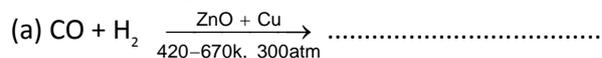


- The hydrocarbon layer along the silicon-oxygen chain makes silicones water-repellent.
- Silicones find a variety of applications because of their chemical inertness, water repelling nature, heat resistance and good electrical insulation property.

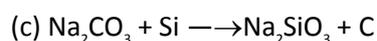
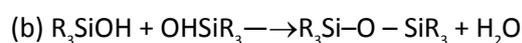
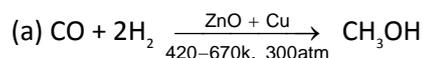
Products having the physical properties of oils, rubbers and resins can be produced using silicones. Silicone varnishes are such excellent insulators and so heat-resistance that insulating wiring with them enabled motors to work over-loads that would have set fire to the insulation formerly used. Silicone fluids are used as hydraulic systems of planes as they are thermally stable and their viscosity alters very little with temperature. Silicone rubbers are used in place of ordinary rubber as they retain their elasticity at much lower temperature than ordinary rubber.

Solved Examples

Example 1. Complete the following reactions



Solution



5.3.2 Silicates :

Binary compounds of silicon with oxygen are called silicates but they contain other metals also in their structures.

(i) Since the electronegativity difference between O & Si is about 1.7, so Si-O bond can be considered 50% ionic & 50% covalent.

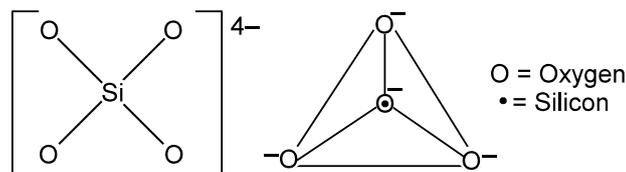
(ii) If we calculate the radius ratio then, $\frac{r_{\text{Si}^{4+}}}{r_{\text{O}^{2-}}} = 0.29$

It suggests that the coordination number of silicon must be 4 and from VBT point of view we can say that Si is sp^3 hybridized. Therefore silicate structures must be based upon SiO_4^{4-} tetrahedral units.

(iii) SiO_4^{4-} tetrahedral units may exist as discrete units or may polymerise into larger units by sharing corners.

Classification of Silicates :**(A) Orthosilicates :**

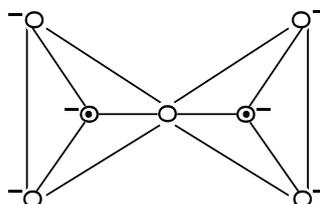
These contain discrete $[\text{SiO}_4]^{4-}$ units i.e., there is no sharing of corners with one another as shown in figure.

**Figure : 2**

e.g. Zircon (ZrSiO_4), Forsterite of Olivine (Mg_2SiO_4), Willemitte (Zn_2SiO_4)

(B) Pyrosilicate :

In these silicates two tetrahedral units are joined by sharing oxygen at one corner thereby giving $[\text{Si}_2\text{O}_7]^{6-}$ units.

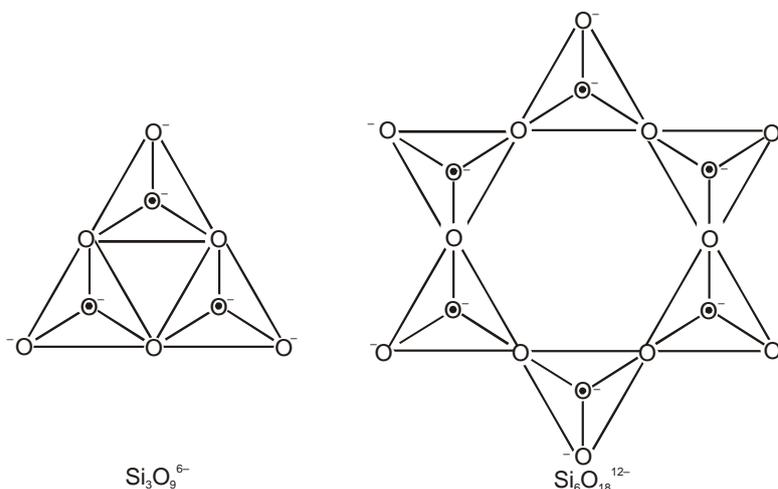
**Figure : 3**

e.g. Thortveitite ($\text{Sc}_2\text{Si}_2\text{O}_7$), Hemimorphite ($\text{Zn}_3(\text{Si}_2\text{O}_7)\text{Zn}(\text{OH})_2\text{H}_2\text{O}$)

○ (–) charge will be present on the oxygen atoms which is bonded with one Si atom.

(C) Cyclic silicates :

If two oxygen atoms per tetrahedron are shared to form closed rings such that the structure with general formula $(\text{SiO}_3^{2-})_n$ or $(\text{SiO}_3)_n^{2n-}$ is obtained, the silicates containing these anions are called cyclic silicates. $\text{Si}_3\text{O}_9^{6-}$ and $\text{Si}_6\text{O}_{18}^{12-}$ anions are the typical examples of cyclic silicates.

**Figure : 4****Figure : 5**

(D) Chain silicates :

Chain silicates may be further classified into simple chain & double chain compounds.

In case of simple chains two corners of each tetrahedron are shared & they form a long chain of tetrahedron. Their general formula is also same as the cyclic silicates i.e. $(\text{SiO}_3)_n^{2n-}$

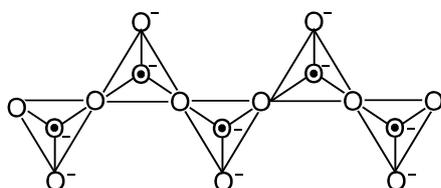


Figure : 6

Similarly, double chain silicates can be drawn in which two simple chains are joined together by shared oxygen. Such compounds are also known as amphiboles. The asbestos mineral is a well known example of double chain silicates. The anions of double chain silicates have general formula $(\text{Si}_4\text{O}_{11})_n^{6n-}$

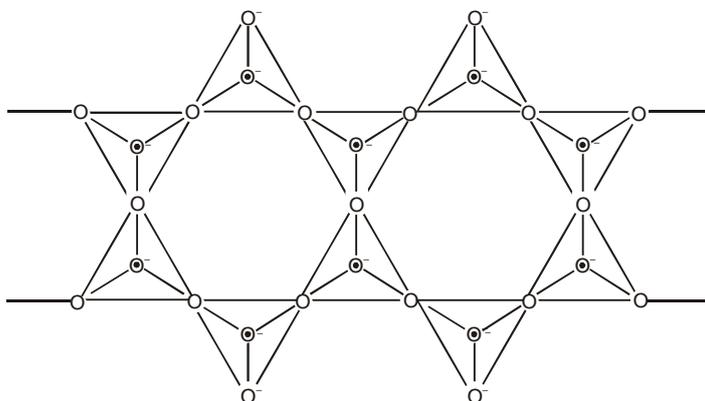


Figure : 7

e.g., Synthetic silicates (Li_2SiO_3 , Na_2SiO_3), Spondumene ($\text{LiAl}(\text{SiO}_3)_2$),

Enstatite (MgSiO_3), Diopside ($\text{CaMg}(\text{SiO}_3)_2$), Tremolite ($\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$), etc.

(E) Two dimensional sheet silicates :

In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent SiO_4^{4-} tetrahedrals. Such sharing forms two dimension sheet structure with general formula $(\text{Si}_2\text{O}_5)_n^{2n-}$

e.g. Talc ($\text{Mg}(\text{Si}_2\text{O}_5)_2$), $\text{Mg}(\text{OH})_2$, Kaolin $\text{Al}_2(\text{OH})_4(\text{Si}_2\text{O}_5)$

(F) Three dimensional silicates :

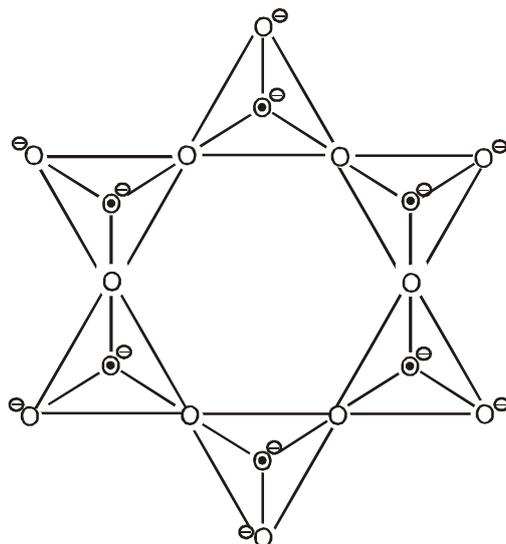
These silicates involve all four oxygen atom in sharing with adjacent SiO_4^{4-} tetrahedral units.

e.g. Quartz, Tridymite, Cristobalite, Feldspar, Zeolite and Ultramarines.

Solved Examples

Example 1. Draw the structure of cyclic silicate containing $\text{Si}_6\text{O}_{18}^{12-}$ ion.

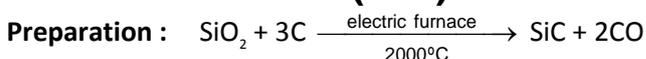
Solution



5.3.3 Zeolites :

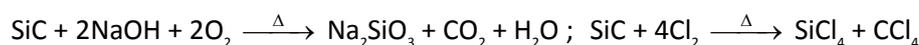
If aluminium atoms replace few silicon atoms in three-dimensional network of silicon dioxide, overall structure known as aluminosilicate, acquires a negative charge. Cations such as Na^+ , K^+ or Ca^{2+} balance the negative charge. Examples are feldspar and zeolites. Zeolites are widely used as a catalyst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

5.3.4 Carborundum (SiC) :



Properties :

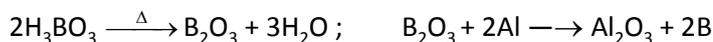
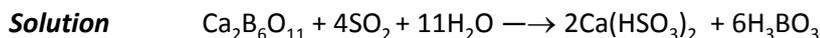
- (i) It is a very hard substance (Hardness = 9.5 Mho)
- (ii) On heating it does not melt rather decomposes into elements.
- (iii) Not attacked by acids. However, it gives the following two reactions at high temperature.



- It has a diamond like structure in which each atom is sp^3 hybridized. Therefore, each atom is tetrahedrally surrounded by 4 atoms of other type.

Solved Examples

Example 1. Write the chemical equations involved in the preparation of elemental boron from mineral colemanite.



Uses of boron :

- (i) Boron is used in the construction of high impact-resistant steel and, since it absorbs neutrons, in reactor rods for controlling atomic reactions.
- (ii) Boron carbide is used as an abrasive.

Uses of Al :

It is extensively used :

- (i) for manufacture of cooking and household utensils.
- (ii) as aluminium plating for tanks, pipes, iron bars and other steel objects to prevent corrosion.
- (iii) for manufacture of aluminium cables.
- (iv) for making precision instruments, surgical apparatus, aircraft bodies, rail coaches, motorboats, car.
- (v) Aluminates are important constituents of portland cement.

Uses of carbon

Graphite fibres embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircraft and canoes. Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis. Crucibles made from graphite are inert to dilute acids and alkalies. Being highly porous and having enormous surface area activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminants and in air conditioning system to control odour. Carbon black is used as black pigment in black ink and as filler in automobile tyres. Coke is used as a fuel and largely as a reducing agent in metallurgy. Diamond is a precious stone and used in jewellery. It is measured in carats (1 carat = 200 mg.).

Uses of silicon :

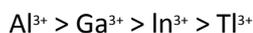
- (i) Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.
- (ii) Silicon is a very important component of ceramics, glass and cement.



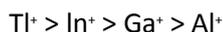
6. MISCELLANEOUS SOLVED EXAMPLES

1. Al and Ga are trivalent in their compounds but monovalent compounds are the most stable down the 13th group. Why ?

Sol. Down the group (13th), the stability of +3 state decreases and that of +1 state increases due to the prominent "inert pair" effect.



Most stable \longrightarrow least stable



2. If you have a mixture of CO and CO₂, how would you know about the relative proportions of the two gases in the given mixture ?

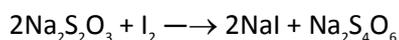
Sol. (i) Pass mixture through the Ca(OH)₂ solution; CO₂ is absorbed by Ca(OH)₂. The residual volume will be that of CO



(ii) Pass mixture through I₂O₅; CO reduces I₂O₅ to I₂.



I₂ thus liberated is determined by titration with Na₂S₂O₃.



This is the quantitative method of estimation of CO.

3. What will happen if borontrifluoride is kept in moist air ?

(A) It will strongly fume.

(B) It will partially hydrolyse.

(C) It will completely hydrolyse.

(D) None of these

Ans. (A)

Sol. In moist air it strongly fume : but it is partially hydrolysed by excess of water.



BF₃ is a colourless gas.

4. What happens when : (write only chemical reactions)

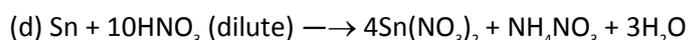
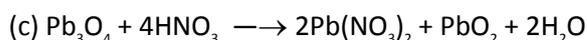
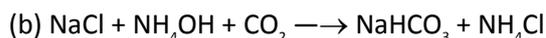
(a) iodine is treated with SnCl_2 .

(b) carbon dioxide is passed through a concentrated aqueous solution of sodium chloride saturated with ammonia.

(c) red lead is treated with nitric acid.

(d) dilute nitric acid is slowly reacted with tin.

Sol.



5. **True / False**

(a) BCl_3 in aqueous solution exists as B^{3+} and Cl^- .

(b) Pure crystalline boron is very unreactive and it is attacked only at high temperatures by strong oxidising agents such as a mixture of hot concentrated H_2SO_4 and HNO_3 .

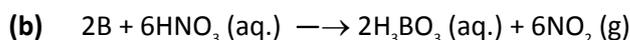
(c) AlX_3 ($\text{X} = \text{Cl}, \text{Br}$) exists as dimer and retains dimer formula in non-polar solvents like ether, benzene etc.

(d) Be_2C is called acetylide because it reacts with water yielding ethyne.

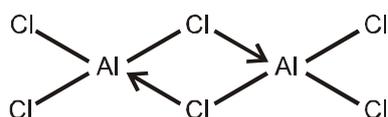
(e) Pb_3O_4 a double oxide, is obtained by heating lead (II) oxide in air.

Ans. (a) False (b) True (c) True (d) False (e) True

Sol. (a) Statement is incorrect. BCl_3 hydrolyses in aqueous solution to give boric acid. Because it has large ionisation energies and to make the enthalpy of solution of BCl_3 negative, the enthalpy of hydration of B^{3+} should be very high ($\sim 600 \text{ kJ}$) which is unlikely for the small B^{3+} cation.

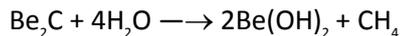


(c) Statement is correct and its dimer structure is as follows. It acquires this structure for attaining an octet of electrons. Dimer formula retains in non-polar solvent like ether, benzene





(d) Statement is incorrect as it is methanide because it gives methane on reaction with water.



(e) $3\text{PbO} + \text{O}_2 \xrightarrow{\Delta} \text{Pb}_3\text{O}_4$

6. **Statement - 1** : PbO_2 is an oxidising agent and reduced to PbO .

Statement - 2 : Stability of $\text{Pb}(\text{II}) > \text{Pb}(\text{IV})$ on account of inert pair effect.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

Ans. (A)

Sol. Both are correct statements and statement-2 is the correct explanation of statement-1.

7. Write the chemical equations to represent the following reactions.

(a) The oxidation of $\text{HCl}(\text{aq})$ to $\text{Cl}_2(\text{g})$ by PbO_2 .

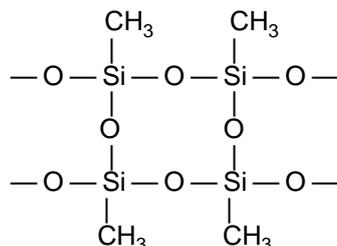
(b) The disproportionation of SnO to Sn and SnO_2 .

Sol. (a) $\text{PbO}_2 + 4\text{HCl} \longrightarrow \text{PbCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$

(b) $2\text{SnO} \longrightarrow \text{Sn} + \text{SnO}_2$

8. What will happen if we take $\text{Si}(\text{CH}_3)_3\text{Cl}_3$ as a starting material for the preparation of commercial silicon polymer ?

Sol. With $\text{Si}(\text{CH}_3)_3\text{Cl}_3$ the chain will grow in three places and we will get cross-linked silicon polymer as shown below :



9. Give three properties of diamond.

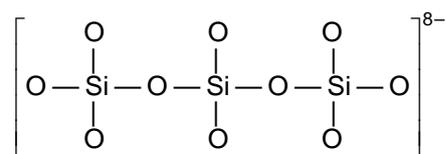
Sol. Diamond is very hard, high melting solid. It is an electrical insulator.

10. The silicate anion in the mineral kionite is a chain of three SiO_4 tetrahedra that share corners with adjacent tetrahedra. The mineral also contains Ca^{2+} ions, Cu^{2+} ions, and water molecules in a 1 : 1 : 1 ratio.

(a) Give the formula and charge of the silicate anion.

(b) Given the complete formula for the mineral.

Sol. (a) The silicate anion has three SiO_4 tetrahedra that share corners with adjacent tetrahedra thus silicate is $\text{Si}_3\text{O}_{10}^{8-}$, hence it can be represented as with charge as $= 3 \times 4n + 10 \times (-2) = -8$



(b) Ca^{2+} , Cu^{2+} and H_2O are in the ratio of 1 : 1 : 1 and to balance (-8) charge of silicate as ion, $(+8)$ charge is required thus there are two units each of Ca^{2+} , Cu^{2+} and H_2O thus, kionoite has formula $\text{Ca}_2\text{Cu}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$.

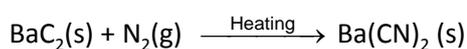
11. In what respect the reaction of N_2 with (i) CaC_2 (calcium carbide) & (ii) BaC_2 (barium carbide) differ from each other.

Sol. (i) CaC_2 reacts with N_2 to form calcium cyanamide.



Calcium cyanamide

(ii) BaC_2 reacts with N_2 to form barium cyanide



Barium cyanide



12. **Statement - 1** : The thermal stability of hydrides of carbon family is in order :



Statement - 2 : E—H bond dissociation enthalpies of the hydrides of carbon family decrease down the group with increasing atomic size.

- (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
 (C) Statement-1 is True, Statement-2 is False
 (D) Statement-1 is False, Statement-2 is True

Ans. (A)

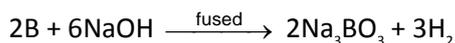
Sol. Both are correct statements and statement-2 is the correct explanation of statement-1. Down the group the size of atom increases and thus bond length increases.

13. Which one of the following element does not dissolve in fused or aqueous alkalis ?

- (A) Boron (B) Silicon (C) Aluminium (D) None of these

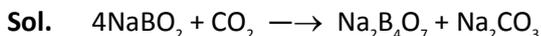
Ans. (D)

Sol. Boron dissolved in fused alkalis according to the following reaction.



Silicon and aluminium dissolved in both fused and aqueous alkalis.

14. What happens when CO_2 (g) is passed through sodium meta borate solution ?

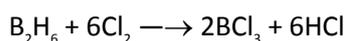


15. Which of the following statement(s) is/are correct ?

- (A) B_2O_3 and SiO_2 are acidic in nature and are important constituents of glass.
 (B) Borides and silicide are hydrolysed by water forming boranes and silanes respectively.
 (C) Diborane on reaction with chlorine (g) forms $\text{B}_2\text{H}_5\text{Cl}$.
 (D) SiO_4^{4-} gets hydrolysed by acid or water and form $\text{Si}_2\text{O}_7^{6-}$.

Ans. (A), (B) and (D)

Sol. (A), (B) and (D) are correct statements but (C) is incorrect.

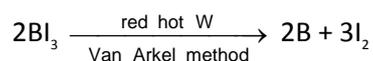


16. Match the following :

Column - I	Column - II
(A) Boron	(p) Forms acidic oxides.
(B) Carbon	(q) Pure crystalline form is obtained by Van Arkel method.
(C) Tin	(r) Exists in allotropic forms.
(D) Aluminium	(s) Hydroxide is amphoteric in nature.

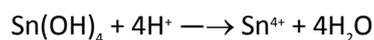
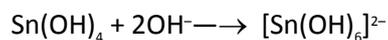
Ans. (A - p,q,r); (B - p,r) ; (C - r,s) ; (D - s)

Sol. (A) Exists in various allotropic forms and its oxide, B_2O_3 is acidic in nature.



(B) Exists in various allotropic forms like diamond, graphite etc. and its oxide CO_2 is acidic in nature.

(C) Exists in allotropic forms like grey tin (α -Sn) and white tin (β -Sn). Hydroxide is amphoteric in nature.



(D) Hydroxide is amphoteric in nature.

