p-block elements (Boron and Carbon Family)

Section (A), (B) & (C) : General facts about elements, Based on Periodic trends & Based on Chemical Bonding

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	ns²np¹	ns²np²	ns²np³	ns²np ⁴	ns²np⁵	ns²np ⁶
						He
	В	С	Ν	0	F	Ne
	Al	Si	Р	S	Cl	Ar
	Ga	Ge	As	Se	Br	Kr
	In	Su	Sb	Те	I	Xe
	TI	Pb	Bi	Ро	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 ns² np¹⁻⁶.

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=C, N=N) and to element of second row (e.g C=O, C=N, C=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 -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) **O** 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 >> Si > Ge \approx Sn. Lead does not show catenation. Due to the property of catenation and p π -p π bonds formation, carbon is able to show allotropic forms.

Bond enthalpy (kJ mol ⁻¹)
348
297
260
240

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=C, C=O, C=S and C=N. Heavier elements do not form $p\pi$ - $p\pi$ bonds because their atomic orbital are too large and diffuse to have effective overlapping.

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.

GROUP 13 : BORON FAMILY & GROUP 14 : CARBON FAMILY Occurrence :

Element	Abundance	Source	Element	Abundance	Source
B (Boron)	9 ppm (Rare element)	 Borax : Na₂[B₄O₅(OH)₄].8H₂O Colemnite : Ca₂B₆O₁₁.5H₂O Kernite : Na₂[B₄O₅(OH)₄].2H₂O Boric acid : H₃BO₃ 	C (Carbon)	180 ppm	 Coal Natural gas oil (hydrocarbon) Natural Graphite Natural diamond Carbonates: Calcite(CaCO₃) Magnesite (MgCO₃) Dolomite(MgC O₃.CaCO₃]
Al (Aluminium)	83000 ppm (Most abundant metal, 3 rd most Abundant element)	 Bauxite : Al₂O₃.H₂O-Al₂O₃.3H₂O Aluminosilicate rocks (feldspars, mica) Cryolite : Na₃AlF₆ 	Si (Silicon)	272000 ppm	 Silica (sand & quartz) SiO₂ Silicate minerals
Ga (Gallium)	19 ppm	Ores of Al, Zn, Ge	Ge (Germanium)	1.5 ppm	 Silver and Zinc ores, coal
In (Indium)	0.24 ppm	ZnS & PbS ores	Sn (Tin)	2.1 ppm	Cassiterite (SnO ₂)
TI (Thallium)	0.5 ppm	ZnS & PbS ores	Pb (Lead)	13 ppm	Galena (PbS)

Allotropy :

Elements	Allotropes	Elements	Allotropes	
	E onvotalling forma :		Crystalline Diamond,	
B	B rhombohodral	C	hexagonal diamond	
В	p-momboneurai	C	α -graphite, β -graphite	
	2 amorphous forms		fullerenes	
ΔΙ	No allotropo	Si	Amorphous - brown powder	
AI	No allotrope	5	Crystalline - greyish metallic	
		Ca	α-Germanium	
Ga	No allotrope	Ge	β-Germanium	
			γ-Germanium	
	In No allotrope		α -tin (grey tin)	
In			β-tin (white tin)	
		α -Sn(diamond structure) $\stackrel{13.2^{\circ}C}{\longleftarrow} \beta$ -Sn(metallic)		
TI	α-Thallium		α-lead (Pb-I)	
	β-Thallium	Pb	β-lead (Pb-II)	

Allotropy of carbon family

O 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.

			1
	Diamond	Graphite	Fullerene
Structure	154 pm	z	
Hybridisation	sp ³	sp ²	sp ²
Density (g/cm³)	3.51	2.22	1.65
∆H _f (KJ/mol)	1.9	0	38.1
Bond length	154 pm	141.5 pm	143.5 pm & 138.3 pm
	 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. 	 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. 3C+SiO₂ ^Δ→ SiC + 2CO ^{2500°C}→ C(graphite) + Si gas Thermodynamically most stable among allotropes. Graphite ^{1600°C}→ synthetic diamond ^{50000-60000 atm} 	 Cage like molecules. C₆₀–Soccer ball shape–Buck minsterfullerene 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. Heating of graphite in an electrical arc in the presence of inert gases such as helium or argon can result into fullerene

Allotropes of Carbon:

Solved Examples

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

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

Atomic & Physical Properties

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.

Boron family:

Property			В	AI	Ga	In	TI
Character			Metalloid	Metallic	Metallic	Metallic	Metallic
Atomic Number			5	13	31	49	81
Atomic Mass/g mol-1			10.81	26.98	69.72	114.82	204.38
Electronic configuration General electronic configuration	on=(ns² n	1)	[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
Covalent Radius / pm			85	143	135	167	170
(B < Ga < Al < In < Tl)			In Ga, poo	or shielding c	of 10 d-electrons		-
Ionic Radius X⁻ / pm (B < AI < Ga < In < TI)			27	53.5	62	80	88.5
Ionization enthalpy (kJ mol ⁻¹)	$\Delta_i H_1$	Ι	801	577	579	558	589
(B > AI < Ga > In < TI)	$\Delta_i H_2$	II	2427	1816	1979	1820	1971
	$\Delta_i H_3$	III	3659	2744	2962	2704	2877
			Poor shiel	ding of d-ork	bital and f-orbital	in Ga & TI res	spectively
Electronegativity			2.0	1.5	1.6	1.7	1.8
(B > AI < Ga < In < TI)			Marginal increase after Al				
Melting point / K			2453	933	303	430	576
Boiling point / K ($B > AI > Ga > In > TI$)		3923	2740	2676	2353	1730	
Density/[g cm ⁻³ (at 293 K) <i>(B < AI < Ga < In < TI)</i>		2.35	2.70	5.90	7.31	11.85	
			+3	+3	+3, +1	+3, +1	+3, +1
Oxidation State		+1 oxidation state arises due to inert pair effect.					
			Stability of Oxidation state: +1: Ga < In < TI				
					+3 . AI > G	a > 111 > 11	

<u>*p-Block Elements (B & C family)*</u>

Carbon failing .								
Property			С	Si	Ge	Sn	Pb	
Character			Non Metallic	Non Metallic	Metalloid	Metallic	Metallic	
Atomic Number			6	14	32	50	82	
Atomic Mass/g mol-1			12.01	28.09	72.60	118.71	207.2	
Electronic configuration General electronic configurati	ion=(ns² r	np²)	[He] 2s ² 2p ²	[Ne] 3s ² 3p ²	[Ar] 3d ¹⁰ 4s ² 4p ²	[Kr] 4d ¹⁰ 5s² 5p²	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	
Covalent Radius / pm (C < Si < Ge < Sn < Pb)			77	118	122	140	146	
Ionic Radius M ⁺⁴ / pm (Si < Ge < Sn < Pb)			_	40	53	69	78	
lonization enthalpy (kJ mol ⁻¹)	$\Delta_{i}H_{1}$	Ι	801	577	579	558	589	
(C > Si > Ge > Sn < Pb)	$\Delta_i H_2$	II	2427	1816	1979	1820	1971	
	$\Delta_i H_3$	III	3659	2744	2962	2704	2877	
			Poor shiel	lding f-orbita	ĺ			
Electronegativity ($C > Si \approx Ge \approx Sn \approx Pb$)			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	
Density/[g cm ⁻³ (at 293 K) (C (diamond) > Si < Ge < Sn < Pb)			3.51	2.34	5.32	7.26	11.34	
			+4	+4	+4, +2	+4, +2	+4, +2	
Ovidation State			+2 oxidati	on state aris	es due to inert p	air effect.		
			Stability of Oxidation state: +2: Ge < Sn < Pb					
			+4: Ge > Sn > Pb					

The Elements Preparation of elements :

BORON :		
Source	Process	Comments
From Borax (Na ⁺)2B4O7 ²⁻ .10H2O	• Na ₂ B ₄ O ₇ +2HCl+5H ₂ O \longrightarrow 4H ₃ BO ₃ +2NaCl • 2H ₃ BO ₃ $\xrightarrow{\Lambda}$ B ₂ O ₃ + 3H ₂ O • B ₂ O ₃ +3Mg/Na $\xrightarrow{\text{High temp.}}$ 2B+3MgO/Na ₂ O	 low purity (95-98%) boron (black) The product thus obtained is boiled with HCl and filtered when Na₂O or MgO dissolves leaving behind elemental boron. It is thoroughly washed to remove HCl and then dried finally.
From BX ₃	• $2BX_3+3H_2 \xrightarrow{\text{red hot W}} 2B(\text{crystalline}) + 6HX$ (X = CI or Br) 99.9% pure • $2BCI_3 + 3Zn \longrightarrow 3ZnCI_2 + 2B$ • $2BI_3 \xrightarrow{\text{red hot W}} 2B\uparrow + 3I_2\uparrow$ (Van Arkel method)	 Problem in obtaining high purity boron: High melting point (2180°C) Liquid gets corroded
From Diborane (B ₂ H ₆)	• $B_2H_6 \xrightarrow{\Delta} 2B$ (crystalline) + $3H_2\uparrow$	Thermal decomposition of diborane.

p-Block Elements (E	8 & C family)	
From potassium fluoroborate (KBF ₄)	• KBF ₄ + 3K $\xrightarrow{\Delta}$ 4KF + B	 By heating it with potassium metal. It is then treated with dilute HCl to remove KF and B is then washed and dried.

ALUMINIUM :

Method	Process	Comments
Electrolytic reduction (Hall-Heroult process)	The electrolytic reactions are: Cathode : $AI^{3+}(melt) + 3e^{-} \longrightarrow AI(I)$ Anode : $C(s) + O^{2-}(melt) \longrightarrow CO(g) + 2e^{-}$ $C(s) + 2O^{2-}(melt) \longrightarrow CO_{2}(g) + 4e^{-}$ The overall reaction may be taken as: $2AI_{2}O_{3} + 3C \longrightarrow 4AI + 3CO_{2}$ Several other extraction processes will be studied in detail in Metallurgy.	 The purified Al₂O₃ is mixed with Na₃AlF₆ (cryolite) or CaF₂ (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 electolysis 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 CO₂. This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away.

CARBON:

Preparation of	Process
Carbon black (soot)	By incomplete combustion of hydrocarbon.
Graphite	$3C + SiO_2 \xrightarrow{\Delta} SiC + 2CO \xrightarrow{2500^{\circ}C} C$ (graphite) + Si gas
Diamond	 Natural diamond can be extracted from mines. Synthetic diamond Graphite <u>1600°C</u> <u>50000-60000 atm</u> → synthetic diamond.

SILICON :

From	Process	Comments
SiO ₂	SiO ₂ (excess) + 2C \longrightarrow Si (pure) + 2CO Si (pure) + 2Cl ₂ \longrightarrow SiCl ₄ SiCl ₄ + 2Mg \longrightarrow Si (highly pure) + MgCl ₂	Reducing SiO ₂ with high purity coke in an electric furnace
Na ₂ [SiF ₆]	Sodium Reduction of Na ₂ [SiF ₆] Na ₂ [SiF ₆] + 4Na \longrightarrow Si (ultra pure) + 6NaF	Zone refining is used to get ultra pure silicon from highly pure silicon, which can be used in semi-conductor industry.

<u>p-Block Elements (B & C family)</u> Section (D) : Properties of Elements Chemical Properties :

Reaction with	Boron Family	Carbon Family		
0	$4E + 3O_2 \xrightarrow{\Delta} 2E_2O_3$	$E + O_2 \xrightarrow{\Delta} EO_2$ (dioxide) $E + \frac{1}{2}O_2 \xrightarrow{\Delta} EO$ (mono oxide)		
02	$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{ccccc} CO_2 & - & acidic & CO & - & neutral \\ SiO_2 & - & acidic & SiO & - & unstable \\ GeO_2 & - & acidic & GeO & - & acidic \\ SnO_2 & - & amphoteric & SnO & - & amphoteric \\ PbO_2 & - & amphoteric & PbO & - & amphoteric \end{array}$		
N ₂	$2E + N_2 \xrightarrow{\Delta} 2EN$ $EN + H_2O \xrightarrow{\Delta} E(OH)_3 + NH_3$ $\therefore E = B \text{ or Al}$	$2C(s)+O_2(g)+4N_2(g) \xrightarrow{1273 \text{ K}} 2CO(g)+4N_2(g)$ (Producer gas)		
X ₂ (Halogen)	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$E + 2X_2 \longrightarrow EX_4 ; (X = F, Cl, Br, I)$ • All members form MX ₄ ; Ge & Pb form MX ₂ • PbI ₄ does not exist • Stability of EX ₄ decreases down the group • Stability of EX ₂ increases down the group • Stability : GeX ₄ > GeX ₂ ; PbX ₂ > PbX ₄		
H₂O	B – does not react with water $25^{\circ}C$ → Al(OH) ₃ Al → +H ₂ O → Al ₂ O ₃ Ga → Not attacked by cold & hot water unless oxygen is present.	$\begin{array}{c} C(s) + H_2O \ (steam) \xrightarrow{\text{red}} CO(g) + H_2(g) \\ \xrightarrow{\text{(water gas)}} \\ \hline \\ E(s) + H_2O(steam) \xrightarrow{\text{red}} EO_2 + H_2; \\ (Si,Ge,Sn) & \xrightarrow{\text{heat}} EO_2 + H_2; \\ \hline \\ \bullet \ Pb \ is \ unafftected \ by \ water, \ probably \\ because \ of \ a \ protective \ oxide \ layer. \\ \bullet \ C, \ Si, \ Ge - not \ attacked \ by \ cold \ water. \end{array}$		
Acids	TI – oxidises in moist air & decomposes steam at red heat. $+H_2SO_4 \rightarrow H_3BO_3 + SO_2$ $B \rightarrow (Hot \& Conc.) \rightarrow H_3BO_3 + NO_2$ (Hot & Conc.) $H_3BO_3 + NO_2$ (Boron reacts with only oxidising acids) $+HCI \rightarrow AlCI_3 + H_2$ $Al \rightarrow (Conc.) \rightarrow Do not react$ because it forms passive oxide layer. Ga, In, T \square can also react with dilute mineral acids.	$\begin{array}{c} C \\ Si \\ Ge \\ Sn \ dissolves in HCI \ (dil. \& conc) \ but \ Pb \ in \ only \ dil. HCI. \\ \\ \hline HCI \\ HCI \\ \hline HCI \\ (conc.) \\ H_2SO_4 \\ H_2SO_4 \\ H_2SO_4 \\ H_2SO_4 \\ HOC \\ HOC \\ (coating) \\ \hline H_2SO_4 \\ HOC \\ \hline HOC \\ (coating) \\ \hline HOC \\ (coording) \\ \hline HOC \\ \hline HOC \\ (coording) \\ \hline HOC \\ \hline $		
NaOH		C – unaffected by alkalies		



Section (E) : Oxides, Hydroxides, Oxyacids, Borax

Oxides, oxy acids and hydroxide Boron trioxide (B₂O₃) :

Preparation :

 $H_3BO_3 \xrightarrow{100^{\circ}C} HBO_2 \xrightarrow{160^{\circ}C} H_3B_4O_7 \xrightarrow{\text{red hot}} B_2O_2$

Boric acid

Properties :

It is a acidic oxide and is anhydride of boric acid and it reacts with alkalies or bases to form borates.

 $3Na_2O + B_2O_3 \longrightarrow 2Na_3BO_3$ (sodium orthoborate).

It reacts with water slowly to form orthoboric acid.

 $H_2O + B_2O_3 \longrightarrow 2HBO_2; HBO_2 + H_2O \longrightarrow H_3BO_3$

When heated with transition metal salts, it forms coloured compounds.

 $3B_2O_3 + Cr_2(SO_4)_3 \xrightarrow{\Lambda} 3SO_3 \uparrow + 2Cr(BO_2)_3(green)$

 $2B_2O_3 + 2Cu(NO_3)_2 \xrightarrow{\Delta} 4NO_2 \uparrow + O_2 \uparrow + 2Cu(BO_2)_2$ (blue)

It also shows weakly basic properties according to the following reaction.

 $B_2O_3 + P_2O_5 \longrightarrow 2BPO_4$

It reacts with hydrogen fluoride in presence of H_2SO_4 forming BF₃.

 $\mathsf{B}_2\mathsf{O}_3 + \mathsf{6}\mathsf{HF} + \mathsf{3}\mathsf{H}_2\mathsf{SO}_4 \longrightarrow \mathsf{2}\mathsf{BF}_3 + \mathsf{3}\mathsf{H}_2\mathsf{SO}_4.\mathsf{H}_2\mathsf{O}.$

Boric acid (H₃BO₃) :

Preparation :

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

 $Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3 \downarrow$

(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.

 $Ca_{2}B_{6}O_{11} + 4SO_{2} + 11H_{2}O \longrightarrow 2Ca(HSO_{3})_{2} + 6H_{3}BO_{3}$

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:

 $B(OH)_3(aq) + 2H_2O(\Box) \rightleftharpoons [B(OH)_4]^-(aq) + H_3O^+(aq).$ pK = 9.25. 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 cannot 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.

$$2B(OH)_{3} + 2NaOH \longrightarrow Na[B(OH)_{4}] + NaBO_{2} + 2H_{2}O$$

$$HB(OH)_{4} + 2I \longrightarrow \begin{bmatrix} I & I \\ CH - OH \\ CH - OH \end{bmatrix} \xrightarrow{I} B \xrightarrow{O-CH} I \xrightarrow{I} H^{+} + 4H_{2}O$$

Ethanol does not form similar complex but catechol, salicylic acids, mannitol form similar complexes.



When heated it first forms metaboric acid (HBO₂) and then boron trioxide.

 $H_3BO_3 \xrightarrow{100^{\circ}C} HBO_2 \xrightarrow{160^{\circ}C} H_2B_4O_7 \xrightarrow{\text{red hot}} B_2O_3$ Boric acid

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 Å) and thus the crystal breaks quite easily into very fine particles.



O Polymeric metaborate species are formed at higher concentration, for example, $3B(OH)_3 \longrightarrow H_3O^+ + [B_3O_3(OH)_4]^- + H_2O, \quad pK = 6.84$



O Boric acid dissolves in aqueous HF forming HBF₄ (fluoroboric acid). B(OH)₃ + 4HF \longrightarrow H₃O⁺ + BF₄⁻ + 2H₂O

Test for Borate radical :

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

 $H_3BO_3 + 3C_2H_5OH \longrightarrow B(OC_2H_5)_3 + 3H_2O$ ethylborate (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 -

- *Ex-2.* It has been observed that BF₃ does not hydrolyses completely whereas BCl₃ or BBr₃ get easily hydrolysed to form B(OH)₃ and HX ? Explain.
- **Sol.** 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 BF₃ 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 (BF₃.OH₂) formed by BF₃.

Borax (Na₂B₄O₇.10H₂O) :

Preparation :

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

(i) From Colemanite.

When colemanite powder is heated with Na₂CO₃ solution, the following reaction occurs with the precipitation of CaCO₃.

 $Ca_{2}B_{6}O_{11} + 2Na_{2}CO_{3} \longrightarrow 2CaCO_{3} \downarrow + Na_{2}B_{4}O_{7} + 2NaBO_{2}$

The filtrate is cooled when white crystals of borax are precipitated. The mother liquor on treatment with CO₂ converts NaBO₂ to Na₂B₄O₇ which precipitates out on crystallization.

 $4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$

(ii) From orthoboric acid.

Borax is obtained by the action of Na₂CO₃ on orthoboric acid.

 $4H_{3}BO_{3} + Na_{2}CO_{3} \longrightarrow Na_{2}B_{4}O_{7} + 6H_{2}O + CO_{2}\uparrow$

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 H₃BO₃ and strong alkali NaOH.

 $Na_{2}B_{4}O_{7} + 7H_{2}O \longrightarrow 4H_{3}BO_{3} + 2NaOH$

(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.

Na₂B₄O₇.10H₂O $\xrightarrow{\Lambda}$ Na₂B₄O₇ + 10 H₂O[↑]

Na₂B₄O₇ $\xrightarrow{740^{\circ}C}$ 2NaBO₂ + B₂O₃ (borax bead)

(iv) Oxidation of boric acid or sodium metaborate with H₂O₂.

 $Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + 2H_2O_2 + 6H_2O \longrightarrow Na_2 [(OH)_2B (O-O)_2B(OH)_2].6H_2O$

Sodium per oxoborate is used as a brightner in washing powder. In very hot water (over 80° C) the peroxide linkages -O-O break down to give H_2O_2 .

(v) It is a useful primary standard for titrating against acids. One mole of it reacts with two moles of acid. This is because when borax is dissolved in water both $B(OH)_3$ and $[B(OH)_4]^-$ are formed, but only the $[B(OH)_4]^-$ reacts with HCI.

 $[B_4O_5(OH)_4]^{2-} + 5H_2O \implies 2B(OH)_3 \text{ (weak acid)} + 2[B(OH)_4]^- \text{ (salt)}$ $2[B(OH)_4]^{2-} + 2H_3O^+ \longrightarrow 2B(OH)_3 + 4H_2O$

On cooling, the white flakes of boric acid are obtained

Borax is also used as a buffer since its aqueous solution contain equal amounts of weak acid and its salt. (vi) Na₂[B₄O₅(OH)₄] + 12HF $\longrightarrow [Na_2O(BF_3)_4] \longrightarrow 4BF_3 + 2NaHSO_4 + H_2O$

Correct formula of borax is $Na_2[B_4O_5(OH)_4]$. $8H_2O$. It contains boron in both planar BO_3 and tetrahedral BO_4 units. It contains five B—O—B linkages.



Aluminium Oxide (Al₂O₃) :

It is also called alumina. It occurs in nature in the form of bauxite and corundum. It is also found in the form of gems. Some important aluminium oxide gems are : (A) Oriental Topaz-yellow (Fe³⁺), (B) Sapphire-blue (Fe^{2+/3+} / Ti⁴⁺), (C) Ruby-red (Cr³⁺), (D) Oriental Emerald-green (Cr³⁺ / V³⁺)

Preparation :

Pure Al₂O₃ is obtained by igniting Al₂(SO₄)₃, Al(OH)₃ or ammonium alum. Al₂(SO₄)₃ $\xrightarrow{\Delta}$ Al₂O₃ + 3SO₃[↑]; 2Al(OH)₃ $\xrightarrow{\Delta}$ Al₂O₃ + 3H₂O[↑] (NH₄)₂SO₄.Al₂(SO₄)₃.24H₂O $\xrightarrow{\Delta}$ 2NH₃[↑] + Al₂O₃ + 4SO₂[↑] + 25H₂O[↑]

Properties :

It is a white amorphous powder insoluble in water but soluble in acids (forming eg., AlCl₃) as well as alkalies (forming e.g., NaAlO₂), Thus amphoteric in nature. It is a polar covalent compound. Exists in two forms α -Al₂O₃ or corundum and γ -Al₂O₃.

Addition of Cr₂O₃ or Fe₂O₃ makes alumina coloured.

$$\gamma$$
-Al₂O₃ $\xrightarrow{1000^{\circ}C}$ α -Al₂O₃

Uses :

(i) It is used for the extraction of aluminium.

(ii) It is used for making artificial gems.

(iii) It is used for the preparation of compounds of aluminium.

(iv) α -Al₂O₃ is used in making furnace linings. It is a refractory material.

(v) It is used as a catalyst in organic reactions.

(vi) Corundum is extremely hard and is used as 'Jewellers rouge' to polish glass.

(vii) γ -Al₂O₃ dissolves in acids absorbs moisture and is used in chromatography.

Solved Examples

Ex-4 What will happen if aluminium is heated with coke in an atmosphere of nitrogen ? **Sol.** $Al_2O_3 + N_2 + 3C \xrightarrow{\Delta} 2AIN + 3CO$

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.

 $C(s) + CO_2(g) \longrightarrow 2CO(g)$

- (ii) In the laboratory it can be prepared by dehydrating methanoic acid with concentrated sulphuric acid. HCOOH (liq) $\xrightarrow{373K}_{\text{conc.H}_2SO_4}$ CO(g) + H₂O
- (iii) If oxalic acid is dehydrated in the same way, CO2 is formed as well.

 $\begin{array}{c} H_2C_2O_4 \xrightarrow[-H_2O]{conc. H_2SO_4, \Delta} & CO + CO_2 \\ \hline \end{array}$

(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.

C (s) + H₂O (g) $\xrightarrow{473-1273K}$ CO (g) + H₂(g) (water gas).

When air is used instead of steam, a mixture of CO and N₂ is produced, which is called producer gas. 2 C (s) + O₂ (g) + 4 N₂ (g) $\xrightarrow{1273K}$ 2 CO (g) + 4 N₂ (g) (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.

(v) $CO_2 + H_2 \longrightarrow CO + H_2O$

(vi) K₄Fe(CN)₆ + 6H₂SO₄ (concentrated) + 6H₂O $\xrightarrow{\Delta}$ 2K₂SO₄ + FeSO₄ + 3(NH₄)₂SO₄ + 6CO

(vii) HCN + $2H_2O \longrightarrow HCOOH + 2NH_3$ (absorbed by H_2SO_4)

HCOOH $\xrightarrow{\Lambda}$ H₂O + CO

(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 CO₂. 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.

 $Hb - O_2 + CO \longrightarrow Hb - CO + O_2$

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 CO₂, 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.

 $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 2CO_2(g)$; NiO(s) + CO(g) \longrightarrow Ni(s) + CO₂(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.

 $Ni(s) + 4CO(g) \xrightarrow{28^{\circ}C} Ni(CO)_{4}(Iiq) \xrightarrow{180^{\circ}C} Ni(s) + 4CO(g)$

(iv) 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.

 $CO(g) + S(s) \longrightarrow COS(s)$ (carbonyl sulphide) ;

 $CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$ (carbonyl chloride)

(v) 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 :

 $NaOH(Iiq) + CO(g) \longrightarrow HCOONa(s) \xrightarrow{dil. HCl} HCOOH(aq)$

(vi) 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.

 $CO(g) + 2H_2(g) \longrightarrow CH_3OH(liq)$

(vii) CO is readily absorbed by an ammonical solution of copper (I) chloride to give CuCl.CO.2H₂O. 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.

 $5CO(g) + I_2O_5(s) \longrightarrow I_2(s) + 5CO_2(g)$

(viii) It reduces an aqueous PdCl₂ solution to metallic Pd.

Carbon dioxide (CO₂) :

Preparation :

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

$$CO_3^{2-}(aq) + 2H^+(aq) \longrightarrow CO_2(g) + H_2O(\Box)$$

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

 $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$; $C_6H_{12}O_6(aq)$ {glucose} $\longrightarrow 2C_2H_5OH(aq) + 2CO_2(g)$

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 sublimes 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 :

> $H_2CO_3(aq) + H_2O(\Box) = HCO_3^-(aq) + H_3O^+(aq)$ $HCO_{3^{-}}(aq) + H_{2}O(\Box) \longrightarrow CO_{3^{2^{-}}}(aq) + H_{3}O^{+}(aq)$

 H_2CO_3/HCO_3^- 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.

 $Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(Iiq); CaCO_3(s) + H_2O(Iiq) + CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$ The above reaction accounts for the formation of temporarily hard water.

(v) Carbon dioxide, which is normally present to the extent of $\sim 0.03\%$ 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:

$$6 \text{ CO}_2 + 12 \text{ H}_2\text{O} \xrightarrow[\text{Chlorphyll}]{hv} \text{C}_6\text{H}_12\text{O}_6 + 6 \text{ O}_2 + 6 \text{ H}_2\text{O}$$

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 CO₂ 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 CO2 is extensively used to carbonate soft drinks. Being heavy and non-supporter of combustion it is used as fire extinguisher. A substantial amount of CO₂ is used to manufacture urea. **Recovery of CO₂ :**

 $Na_2CO_3 + CO_2 + H_2O \xrightarrow{Cool} 2NaHCO_3$ (a)

Girbotol process : $2HOCH_2CH_2NH_2 + CO_2 + H_2O \xrightarrow{30-60^\circC} (HOCH_2CH_2NH_3)_2CO_3$ (b)

– Solved Examples .

Ex-5.	$H_2C_2O_4 \xrightarrow{\Delta} gas(A) + gas(B) + liquid(C)$				
	oxalic acid				
	Gas (A) burns with blue flame and is oxidised to gas (B). Gas (B) turns lime water milky				
	Gas (A) + Cl ₂ \longrightarrow (D) $\xrightarrow{NH_3, \Delta}$ (E) $\xleftarrow{NH_3, \Delta}$ (B)				
	Identify (A) to (E) and explain reactions involved.				
Sol.	$H_2C_2O_4 \xrightarrow{\Delta} CO + CO_2 + H_2O$				
	$CO + Cl_2 \longrightarrow COCl_2 \xrightarrow{NH_3, \Delta} NH_2CONH_2 \xleftarrow{NH_3, \Delta} CO_2$				

Carbon suboxide (C₃O₂) :

This is an evil-smelling gas and can be made by dehydrating propanedioic acid (malonic acid), of which it is the anhydride, with phosphorus pentoxide :

 $3 \text{ CH}_2(\text{COOH})_2 + \text{P}_4\text{O}_{10} \longrightarrow 3\text{C}_3\text{O}_2 + 4\text{H}_3\text{PO}_4$

When heated to about 200°C, it decomposes into CO_2 and C:

 $C_3O_2(g) \longrightarrow CO_2(g) + 2C(s)$

The molecule is thought to have a linear structure: O=C=C=C=O.

Silicon Dioxide (SiO₂) :

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 interconvertable 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.

 $SiO_2 + 2 NaOH \longrightarrow Na_2SiO_3 + H_2O$; $SiO_2 + 4 HF \longrightarrow SiF_4 + 2 H_2O$ 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.

Stannous Oxide (SnO) :

Preparation :

By heating stannous hydroxide, $Sn(OH)_2$, in absence of air.

 $Sn(OH)_2 \longrightarrow SnO + H_2O^{\uparrow}$

Properties :

SnO is an amphoteric dark grey or black solid oxide, insoluble in water. It dissolves in acids to form stannous salts.

SnO (basic) + $2H^+ \longrightarrow Sn^{2+} + H_2O$;

SnO (acidic) + 4OH⁻ + H₂O \longrightarrow [Sn(OH)₆]⁴⁻ or SnO₂²⁻ (stannite)

Stannites are only known in aqueous solutions. Stannites absorb oxygen from air and are oxidised to stannate which are stable in nature.

 $2 \text{ Na}_2\text{SnO}_2 + \text{O}_2 \longrightarrow 2 \text{ Na}_2\text{SnO}_3$

Uses :

For the preparation of stannous chloride and stannous sulphate.

Stannic Oxide (SnO₂) :

Preparation :

By heating tin with concentrated HNO_{3.}

Sn + 4HNO₃ \longrightarrow H₂SnO₃ + 4NO₂↑ + H₂O ; H₂SnO₃ $\xrightarrow{\Delta}$ H₂O↑ + SnO₂

Properties :

(i) It is a white solid insoluble in water.

- (ii) It is amphoteric in nature.
- (iii) It dissolves in concentrated H_2SO_4 to form stannic sulphate.

 $SnO_2 + 2H^+ \longrightarrow Sn^{+4} + 2H_2O$

(iv) It also dissolves in concentrated alkalies to form alkali metal stannate solution.

 $SnO_2 + 6OH^- \longrightarrow [Sn(OH)_6]^{2-} \text{ or } SnO_3^{2-} \text{ (stannate)}$

Litharge (PbO) :

PbO is prepared by heating Pb at 180°C. It is a volatile yellow organic solid.

 $2Pb + O_2 \xrightarrow{\Delta} 2PbO$

It is an amphoteric oxide and dissolves in acids as well as in alkalies.

It is used in rubber industry and in the manufacture of flint glasses, enamels, and storage batteries.

Lead Dioxide (PbO₂) :

Preparation :

(i) PbO + NaOCI $\xrightarrow{\Lambda}$ PbO₂ (insoluble) + NaCl

(ii) $Pb_3O_4 + 4HNO_3$ (dilute) $\longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

Properties :

It is a chocolate/dark brown coloured insoluble solid.

(i) On heating at 440°C it gives the monoxide.

$$2PbO_2 \xrightarrow{440^{\circ}C} 2PbO + O_2$$

(ii) PbO_2 is an oxidising agent and reduced to PbO since stability of Pb(II) > Pb(IV) based on inert pair effect.

(a) It oxidizes HCl to Cl_2 .

 $PbO_2 + 4HCI \longrightarrow PbCl_2 + 2H_2O + Cl_2\uparrow$

(b) It oxidises Mn salt to permanganic acid.

 $2MnSO_4 + 5PbO_2 + 6HNO_3 \longrightarrow 2HMnO_4 + 2PbSO_4 + 3Pb(NO_3)_2 + 2H_2O_3$

(c) It reacts with SO₂ at red heat to form lead sulphate.

 $PbO_2 + SO_2 \xrightarrow{\Delta} PbSO_4$

(iii) It dissolves in concentrated NaOH solution.

 $PbO_2 + 2OH^- + 2H_2O \longrightarrow [Pb(OH)_6]^{2-}$ (plumbate)

(iv) It reacts with concentrated HNO_3 to evolve oxygen gas.

 $PbO_{2} + 2HNO_{3} \longrightarrow Pb(NO_{3})_{2} + 1/2O_{2} + H_{2}O$ $PbO_{2} + H_{2}SO_{4} \longrightarrow PbSO_{4} + 2H_{2}O + O_{2}$

Uses :

It is used in match industry for making ignition surface of match boxes, in the preparation of KMnO₄ and in explosives.

Red Lead (Pb₃O₄) :

Preparation :

It is prepared by heating PbO at 450°C for a long time.

 $6PbO + O_2 \xrightarrow{450^{\circ}C} 2Pb_3O_4$

Properties :

(i) It is a red powder insoluble in water but when heated with concentrated HNO₃ it gives a red precipitate of PbO₂.

 $Pb_{3}O_{4} + 4HNO_{3} \longrightarrow 2Pb(NO_{3})_{2} + PbO_{2}\downarrow + 6H_{2}O_{3}$

(ii) When heated above 550°C, it decomposes into PbO.

 $Pb_3O_4 \xrightarrow{\Delta} 6PbO + O_2\uparrow$

(iii) It oxidizes concentrated HCI to chlorine.

 $Pb_{3}O_{4} + 8HCI \longrightarrow 3PbCl_{2} + 4H_{2}O + Cl_{2}\uparrow$

(iv) When heated with concentrated H_2SO_4 it evolves oxygen.

 $2Pb_{3}O_{4} + 6H_{2}SO_{4} \longrightarrow 6PbSO_{4} + 6H_{2}O + O_{2}\uparrow$

Uses :

It is used as an oxidizing agent, for making metal protecting paints like red oxide paint, for making special lead cement and for making flint glass.

Section (F) : Hydrides

Compounds

Hydrides Boranos

Boranes

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

 $B_nH_{n+4} - B_2H_6$, B_5H_9 , B_6H_{10} , $B_{10}H_{14}$

 B_nH_{n+6} - B_4H_{10} , B_5H_{11} , B_6H_{12} , B_9H_{15} 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) :

- (i) $4BF_3 + 3LiAIH_4 \xrightarrow{\text{ether}} 2B_2H_6 + 3Li[AIF_4]$
- (ii) $2BCI_3 + 6H_2 \text{ (excess)} \xrightarrow{\text{silent electric}} B_2H_6 + 6HCI$
- (iii) $8BF_3 + 6LiH \xrightarrow{ether} B_2H_6 + 6LiBF_4$
- (iv) $2NaBH_4 + I_2 \xrightarrow{ether} B_2H_6 + 2NaI + H_2$
- (v) $3NaBH_4 + 4BF_3 \xrightarrow{ether} 3NaBF_4 + 2B_2H_6$
- (vi) It can also be prepared by treating NaBH₄ with concentrated H₂SO₄ or H₃PO₄.

 $2NaBH_4 + H_2SO_4 \longrightarrow B_2H_6 + 2H_2 + Na_2SO_4 ; 2NaBH_4 + 2H_3PO_4 \longrightarrow B_2H_6 + 2H_2 + 2NaH_2PO_4$

- (vii) $2BF_3 + 6NaH \xrightarrow{453 \text{ K}} B_2H_6 + 6NaF$ (Industrial method)
- (viii) $B_2O_3 + 3H_2 + 2AI \xrightarrow{750 \text{ atm}} B_2H_6 + Al_2O_3$
- (ix) $Mg_3B_2 + H_3PO_4 \longrightarrow mixture of boranes mainly, B_4H_{10} \xrightarrow{\Delta} B_2H_6.$

Properties :

- (i) B_2H_6 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. $B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$ $\Delta H = -2160 \text{ kJ mol}^{-1}$

- 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.
- O At red-heat the boranes decomposes to boron and hydrogen.
- (iii) Reaction with water is instantaneous.

 $B_2H_6 + 6H_2O \longrightarrow 2B(OH)_3 + 6H_2$

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

 $B_2H_6 + 6ROH \longrightarrow 2B(OR)_3 + 6H_2$

$$\mathsf{B}_2\mathsf{H}_6 + 2\mathsf{KOH} + 2\mathsf{H}_2\mathsf{O} \longrightarrow 2\mathsf{KBO}_2 + 6\mathsf{H}_2$$

- (iv) Reaction with HCI replaces a terminal H with CI.
 - $B_2H_6 + HCI \longrightarrow B_2H_5CI + H_2$
- (v) Reaction with chlorine gives the trichloride.

 $\mathsf{B_2H_6} + \mathsf{6Cl_2} {\longrightarrow} \mathsf{2BCl_3} + \mathsf{6HCl}$

- (vi) The electron deficient 3c-2e BHB bridges are sites of nucleophilic attack.
 - O Small amines such as NH₃, CH₃NH₂ and (CH₃)₂NH give unsymmetrical cleavage of diborane. B₂H₆ + 2NH₃ \longrightarrow [H₂B (NH₃)₂]⁺ + [BH₄]⁻

- Large amines such as $(CH_3)_3N$ and pyridine give symmetrical cleavage of diborane. О $2(CH_3)_3N + B_2H_6 \longrightarrow 2H_3B \longleftarrow N(CH_3)_3$
 - $B_2H_6 + 2Me_3P \longrightarrow 2Me_3PBH_3$
- $B_2H_6 + 2CO \xrightarrow{200^{\circ}C, 20 \text{ atm}} 2BH_3CO \text{ (borane carbonyl)}$ Ο
- Ο The boronium ion products [H₂BL₂]⁺, are tetrahedral and can undergo substitution by other bases

 $[H_2B(NH_3)_2]^+ + 2PR_3 \longrightarrow [H_2B(PR_3)_2]^+ + 2NH_3$

- Ο The reaction with ammonia depends on conditions.
 - Excess $NH_3 \longrightarrow B_2H_6.2NH_3$ or $[H_2B(NH_3)_2]^+$ $[BH_4]^-$ (ionic compound). $B_2H_6 + NH_3 =$
 - low temperature

higher temperature (> 200°C) (BN)_x boron nitride.

 $\xrightarrow[higher temperature (200^{\circ}C)]{Ratio 2NH_3 : 1 B_2H_6} B_3N_3H_6 \text{ borazine.}$

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 NH₃ and boric acid at elevated temperature. If heated with water, B₃N₃H₆ hydrolyses slowly.

$$B_3N_3H_6 + 9H_2O \longrightarrow 3NH_3 + 3H_3BO_3 + 3H_2O$$

Reduction of diborane can be accomplished with sodium or with sodium borohydride. (vii)

- $2B_2H_6 + 2Na \longrightarrow NaBH_4 + NaB_3H_8$
- $B_2H_6 + NaBH_4 \longrightarrow NaB_3H_8 + H_2.$
- Ο Reductions of diborane with NaBH₄ can also lead to higher borane anions. $2NaBH_4 + 5B_2H_6 \longrightarrow Na_2B_{12}H_{12}$
- $B_2H_6 + 2LiH \longrightarrow 2LiBH_4$ (viii)

Solved Examples

- Complete the following reactions and identify the products formed. Ex-6.
 - (a) $BCI_3 + NH_4CI \xrightarrow{140^{\circ}C}$ (A) $\xrightarrow{NaBH_4}$ (B) C₆H₅CI
 - (b) $BCI_3 + H_2 + C_{fibre} \xrightarrow{1700-1800^{\circ}C} product(s)$
- (a) $3BCI_3 + 3NH_4CI \xrightarrow{140^{\circ}C} B_3N_3H_3CI_3 \xrightarrow{NaBH_4} B_3N_3H_6$ (borazine) Sol.
 - C₆H₅Cl

(b) $4BCI_3 + 6H_2 + C_{fibre} \xrightarrow{1700-1800^{\circ}C} B_4C_{(fibre)} + 12 HCI$

Aluminium Hydride (AIH₃) :

Aluminium hydride is obtained by interaction of LiAIH₄ with100% H₂SO₄ in THF :

 $2\text{LiAlH}_4 + \text{H}_2\text{SO}_4 \longrightarrow 2\text{AlH}_3 + 2\text{H}_2 + \text{Li}_2\text{SO}_4$

The white hydride is thermally unstable. With donor ligands however, a range of molecular complexes AlH₃L & AlH₃L₂ are formed indicative of the lewis acidic behaviour of AlH₃.

Hydrides of carbon :

Carbon forms a vast number of chain and ring compounds including :

- The alkanes (Paraffins) C_nH_{2n+2}
- The alkynes (acetylenes) C_nH_{2n-2}
- The alkenes (olefines) C_nH_{2n} • Aromatic compounds

Silanes

SiH₄ (monosilane)

- (1) small scale preparation : SiO₂ + LiAlH₄ $\xrightarrow{160^{\circ}C}$ SiH₄
- (2) Hydrolysis of Magnesium silicide
 - $Mg_2Si + H_2O \longrightarrow mixture of silanes$
- (3) Reduction of chlorosilanes by LiAlH₄ to produce silane
- (4) Photolysis of SiH₄–H₂ mixture can make higher silanes
- (5) Among silanes only SiH₄ & Si₂H₆ are indefinitely stable at 25°C.

Section (G) : Halides

Halides, Alums and Other metal salts :

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.

Aluminium Chloride (AICl₃.6H₂O) :

It is a colourless crystalline solid, soluble in water. It is covalent. Anhydrous AICI₃ is a deliquescent white solid.

Preparation :

(i) By dissolving aluminium, Al₂O₃, or Al(OH)₃ in dilute HCI :

 $\begin{array}{l} \text{2AI} + 6\text{HCI} \longrightarrow \text{2AICI}_3 + 3\text{H}_2\uparrow; \ \text{Al}_2\text{O}_3 + 6\text{HCI} \longrightarrow \text{2AICI}_3 + 3\text{H}_2\text{O}; \ \text{AI}(\text{OH})_3 + 3\text{HCI} \longrightarrow \text{AICI}_3 + 3\text{H}_2\text{O}\\ \text{The solution obtained is filtered and crystallized when the crystals of AICI}_3.6\text{H}_2\text{O} \text{ are obtained}. \end{array}$

(ii) Anhydrous AlCl₃ is obtained by the action of Cl_2 on heated aluminium.

(iii) By heating a mixture of $\ensuremath{\mathsf{Al}_2\mathsf{O}_3}$ and coke and passing chlorine over it.

 $AI_2O_3 + 3C + 3CI_2 \longrightarrow 2AICI_3$ (anhydrous) + $3CO^{\uparrow}$

Properties :

(i) Action of heat : Hydrated salt when heated strongly is converted to Al₂O₃.

 $2AICI_{3}.6H_{2}O \xrightarrow{\Delta} AI_{2}O_{3} + 6HCI^{\uparrow} + 3H_{2}O$

(ii) Action of moisture on anhydrous AICI₃: When exposed to air, anhydrous AICI₃ produces white fumes of HCI.

AICl₃ + 3H₂O AI(OH)₃ + 3HCl↑

(iii) Action of NH₃: Anhydrous AlCl₃ absorbs NH₃ since the former is a Lewis acid.

 $AICI_3 + 6NH_3 \longrightarrow AICI_3.6NH_3$ (white solid)

(iv) Action of NaOH solution: When NaOH solution is added dropwise to an aqueous AlCl₃ solution, a gelatinous precipitate of Al(OH)₃ is first formed which dissolves in excess of NaOH solution to give a colourless solution of sodium meta-aluminate.

AICl₃ + 3NaOH \longrightarrow AI(OH)₃ \downarrow + 3NaCl; AI(OH)₃ + NaOH \longrightarrow NaAIO₂ + 2H₂O

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) Action of NH₄OH solution: When NH₄OH solution is added to a solution of AlCl₃, a white precipitate of Al(OH)₃ is formed which does not dissolve in excess of NH₄OH.

AlCl₃ + 3NH₄OH \longrightarrow Al(OH)₃ \downarrow (white gelatinous) + 3NH₄Cl

This reaction is important as a test to distinguish an AI salt from a Zn salt. (With a Zn salt a white precipitate of $Zn(OH)_2$ is formed which dissolves in excess of NH_4OH solution).

(vi) **Hydrolysis with water:** When $AlCl_3$ is dissolved in water, it undergoes hydrolysis rapidly to produce $Al(OH)_3$ which is a weak base and HCl which is a strong acid. Hence the solution is acidic to litmus.

 $[AI(H_2O)_6]^{3+} \xleftarrow{} [AI(H_2O)_5OH]^{+2} + H^+$

The complex cation has a high tendency to get dimerised.

 $2[AI(H_2O)_5OH]^{2+} \longrightarrow [(H_2O)_4AI \xrightarrow{OH}_{OH}AI(H_2O)_4]^{+4} + 2H_2O$

(vii) $4LiH + AICI_3 \longrightarrow LiAIH_4 + 3LiCI$

Uses :

(i) As catalyst for cracking of petroleum.

(ii) As catalyst in Friedel-Crafts reactions.

(iii) For preparing aluminium compounds.

Solved Examples -

- Ex-7. What happens when :
 - (write chemical equations only)
 - (a) Anhydrous AICI₃ is exposed to atmosphere.
 - (b) AICl₃ dissolves in aqueous sodium hydroxide (excess)
- Sol. (a) $AICI_3 + 3H_2O \longrightarrow AI(OH)_3 + 3HCI$ (HCI fumes in air). (b) $AICI_3 + 3NaOH \longrightarrow AI(OH)_3 \downarrow + 3NaCI$ $AI(OH)_3 + OH^- \longrightarrow [AI(OH)_4]^-$
- **Ex-8.** Anhydrous AICl₃ cannot be prepared by heating hydrated salt. Why ?
- **Sol.** Gets hydrolysed forming Al₂O₃.

 $2\text{AICI}_3.6\text{H}_2\text{O} \xrightarrow{\Delta} \text{AI}_2\text{O}_3 + 6\text{HCI}^\uparrow + 3\text{H}_2\text{O}$

Alums ; M₂SO₄. M'₂ (SO₄)₃. 24H₂O or MM' (SO₄)₂. 12H₂O

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 (Al³⁺, Ti³⁺, V³⁺, Cr³⁺, Fe³⁺, Mn³⁺, Co³⁺, Ga³⁺ 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 :

Potash alum K_2SO_4 . $Al_2(SO_4)_3$.24 H_2O (ii) Chrome alum K_2SO_4 . $Cr_2(SO_4)_3$.24 H_2O

(iii) Ferric alum K_2SO_4 .Fe₂(SO₄)₃.24H₂O (iv) Ammonium alum (NH₄)₂SO₄.Al₂(SO₄)₃.24H₂O 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)

(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. $AI(OH)_3$ obtained as hydrolysis product of $[AI(H_2O)_6]^{3+}$ deposits into the fibres and then the dye is absorbed on $AI(OH)_3$.

(ii) As a germicide for water purification

(iii) As a coagulating agent for precipitating colloidal impurities from water.

Solved Examples

Ex-9. List the cations which are capable of replacing aluminium in alums ?

Sol. Cations of about the same size as that of Al³⁺ such as Ti³⁺, Cr⁺³, Mn⁺³, Fe³⁺ and Co³⁺ are capable of replacing aluminium in alums.

Carbon Halides :

CF₄ (Carbon tetrafluoride)

• It is an extraordinarily stable compound.

- Lab preparation : SiC + $F_2 \xrightarrow{\Delta} SiF_4 + CF_4$
- No hydrolysis is possible.

CCl₄ (Carbon tetrachloride)

• Common solvent, fairly readily decomposed photo chemically.

• Although it is thermodynamically unstable with respect to hydrolysis, the observe of acceptor orbitals carbon makes the attack very difficult.

CBr₄ (Carbon tetrabromide)

- Pale yellow solid at room temperature.
- Insoluble in water, soluble in non-polar solvent.
- CI₄ (Carbon tetraiodide)
- Bright red, crystalline material.
- odor like that of iodine.

Stannous Chloride (SnCl₂-2H₂O) :

Preparation :

(i) Sn + 2HCI (concentrated) \longrightarrow SnCl₂(aq) + H₂↑

(ii) SnO + 2HCl \longrightarrow SnCl₂(aq) + H₂O

The solution on crystallization gives colourless crystals of SnCl₂·2H₂O.

Properties :

(i) It is a colourless solid soluble in water. It is soluble in alcohol and ether also.

(ii) It is a stronger reducing agent.

(a) Reaction with Hg_2Cl_2 solution: When $SnCl_2$ solution is added to an aqueous solution of mercuric chloride, a silky white precipitate of mercurous chloride, Hg_2Cl_2 is formed which turns black due to further reduction of Hg_2Cl_2 to black mercury.

 $2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 \downarrow + SnCl_4; Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg \downarrow + SnCl_4$

(b) It reduces ferric chloride, $FeCl_3$ to ferrous chloride, $FeCl_2$.

 $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$

(c) It also reduces CuCl₂ to CuCl (white).

(iii) SnCl₂ partially hydrolyses in water forming the basic chloride, Sn(OH)Cl.

 $SnCl_2 + H_2O \longrightarrow Sn(OH)CI \text{ (white)} \downarrow + HCI$

As it produces a weak base and strong acid its aqueous solution is acidic. Its hydrolysis can be prevented by adding concentrated HCI to it during the process of its preparation.

Uses :

(i) In dye industry as a reducing agent.

(ii) For the test of mercuric salt.

(iii) For the preparation of other stannous compounds.

Stannic Chloride (SnCl₄) :

Preparation :

(i) By the action of Cl_2 gas on heated Sn, $Sn + 2Cl_2 \longrightarrow SnCl_4$

(ii) By the action of Cl_2 on stannous chloride, $SnCl_2 + Cl_2 \longrightarrow SnCl_4$

Properties :

(i) It is a colourless fuming liquid ; boiling point is 114°C.

(ii) Action of moisture: It absorbs moisture and becomes converted into hydrated stannic chlorides, $SnCl_{4}\cdot 3H_{2}O$, $SnCl_{4}\cdot 5H_{2}O$, $SnCl_{4}\cdot 6H_{2}O$ and $SnCl_{4}\cdot 8H_{2}O$. $SnCl_{4}$. 5 $H_{2}O$ is known as "butter of tin" or "oxymercurate of tin".

(iii) Hydrolysis with water : It hydrolyses in dilute solution but it is incomplete and can be repressed in presence of halogen acid.

 $SnCl_4 + 4H_2O \longrightarrow Sn(OH)_4 + 4HCI;$

 $SnCl_4 + 2HCl \longrightarrow H_2SnCl_6$ (stannic acid)

 $Sn(OH)_4 + 4HCI \longrightarrow SnCl_4 + 4H_2O$;

(v) In presence of ammonium chloride, it forms ammonium salt of H₂SnCl₆ (stannic acid).

 $SnCl_4 + 2 NH_4Cl \longrightarrow (NH_4)_2SnCl_6$

Uses :

For the preparation of stannic compounds.

Lead Chloride (PbCl₂) :

Preparation:

 $Pb(OH)_2 \cdot PbCO_3$ (basic lead carbonate) + 4HCl $\longrightarrow 2PbCl_2 \downarrow + CO_2 \uparrow + 3H_2O$

Properties :

It is a white crystalline solid, insoluble in cold water but soluble in boiling water. It dissolves in concentrated HCl forming a complex ion.

2 HCl + PbCl₂ \longrightarrow H₂PbCl₄ (chloroplumbous acid)

Uses :

It is used for making pigments for paints.

Lead Tetrachloride (PbCl₄) :

Preparation :

It is prepared by the following methods:

(i) By dissolving PbO_2 in cold concentrated HCl

 $PbO_2 + 4HCI \longrightarrow PbCI_4 + 2H_2O$

PbCl₄ dissolves in excess of HCl to form a stable solution of H₂PbCl₆.

 $PbCl_4 + 2HCl \longrightarrow H_2PbCl_6$

When NH_4CI is added to a solution of chloroplumbic acid, a yellow precipitate of ammonium chloroplumbate is formed.

 $H_2PbCl_6 + 2NH_4Cl \longrightarrow (NH_4)_2PbCl_6\downarrow + 2HCl$

When crystals of ammonium chloroplumbate is added to ice cold concentrated H_2SO_4 , lead tetrachloride is formed and separates as a yellow oily liquid.

 $(NH_4)_2PbCl_6 + H_2SO_4 \longrightarrow PbCl_4 + (NH_4)_2SO_4 + 2HCl_4$

(ii) By the action of Cl₂ on a solution of PbCl₂ in concentrated HCl

 $PbCl_2 + Cl_2 \longrightarrow PbCl_4$

Properties :

(i) It is a yellow oily liquid which solidifies at -10°C and is soluble in organic solvents like ethanol and benzene.

(ii) Rapid hydrolysis with water forms PbO₂ precipitate

 $PbCl_4 + 2H_2O \longrightarrow PbO_2\downarrow + 4HCl$

Uses :

It is used for making stannic compounds.

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 .

 $H_2CO_3 + NaOH \longrightarrow NaHCO_3 + H_2O$; $NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$

Preparation :

(i) With NaOH : $2NaOH + CO_2 \longrightarrow Na_2CO_3$; $Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$ (ii) By precipitation : $BaCl_2 + Na_2CO_3 \longrightarrow BaCO_3 \downarrow + 2NaCl$

SiCl₄, Silicones, Silicates & Zeolites :

Silicones :

Silicones are synthetic organosilicon compounds having repeated R_2SiO units held by Si–O–Si linkages. These compounds have the general formula $(R_2SiO)_n$ 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.

(a) RCl + Si $\xrightarrow{Cu}_{300^{\circ}C}$ R₃SiCl + R₂SiCl₂ + RSiCl₃

(b) $RMgCl + SiCl_4 \longrightarrow RSiCl_3 + MgCl_2$ $2RMgCl + SiCl_4 \longrightarrow R_2SiCl_2 + 2MgCl_2$ $3RMgCl + SiCl_4 \longrightarrow R_3SiCl + 3MgCl_2$

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.

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

(i) R₃SiCl (ii) R₂SiCl₂ (iii) RSiCl₃ O Silicones from the hydrolysis of (CH₃)₃ SiCl



O Silicones from the hydrolysis of a mixture of (CH₃)₃ SiCl & (CH₃)₂ SiCl₂

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.



O Silicones from the hydrolysis of trichloro derivative.

When a compound like CH_3SiCI_3 undergoes hydrolysis, a complex cross-linked polymer is obtained as chain can grow in three places as



O The hydrocarbon layer along the silicon-oxygen chain makes silicones water-repellent.

O 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 placed of ordinary rubber as they retain their elasticity at much lower temperature than ordinary rubber.

Solved Examples

Ex-10. Complete the following reactions

- (a) $CO + H_2 \xrightarrow{ZnO+Cu}$
 - 420-670k, 300atm

(b) $R_3SiOH + OHSiR_3 \longrightarrow + \dots + \dots$

(c) Na₂CO₃ + Si \longrightarrow +

Sol.

- (a) CO + 2H₂ $\xrightarrow{ZnO+Cu}$ CH₃OH
- (b) $R_3SiOH + OHSiR_3 \longrightarrow R_3Si O SiR_3 + H_2O$
- (c) $Na_2CO_3 + Si \longrightarrow Na_2SiO_3 + C$

Section (H) : Miscellaneous (Silicones, Silicates, Zeolites & Alums)

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.

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

> It suggests that the coordination number of silicon must be 4 and from VBT point of view we can say that Si is sp³ hybridized. Therefore silicate structures must be based upon SiO₄⁴⁻ 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 [SiO₄]⁴⁻ units i.e., there is no sharing of corners with one another as shown is figure.



Figure : 2

e.g. Zircon (ZrSiO₄), Forsterite of Olivine (Mg₂SiO₄), Willemite (Zn₂SiO₄)

(B) **Pyrosilicate :**

In these silicates two tetrahedral units are joined by sharing oxygen at one corner thereby giving [Si₂O₇]⁶⁻ units.



Figure : 3

e.g. Thorteveitite (Sc₂Si₂O₇), Hemimorphite (Zn₃(Si₂O₇) Zn(OH)₂H₂O)

О (-) 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 $(SiO_3^{2-})_n$ or $(SiO_3)_n^{2n-}$ is obtained, the silicates containing these anions are called cyclic silicates. $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$ anions are the typical examples of cyclic silicates.



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. $(SiO_3)_n^{2n-1}$



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 $(Si_4O_{11})_n^{6n}$



e.g., Synthetic silicates (Li₂SiO₃, Na₂SiO₃), Spondumene (LiAl(SiO₃)₂), Enstatite (MgSiO₃), Diopside (CaMg(SiO₃)₂), Tremolite (Ca₂Mg₅(Si₄O₁₁)₂ (OH)₂), etc.

(E) Two dimensional sheet silicates :

In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent SiO₄^{4–} tetrahedrals. Such sharing forms two dimension sheet structure with general formula $(Si_2O_5)n^{2n-}$ e.g. Talc $(Mg(Si_2O_5)_2 Mg(OH)_2$, Kaolin Al₂(OH)₄ (Si_2O_5)

(F) Three dimensional silicates :

These silicates involve all four oxygen atom in sharing with adjacent SiO₄^{4–} tetrahedral units. e.g. Quartz, Tridymite, Crystobalite, Feldspar, Zeolite and Ultramarines.

Solved Examples -

Ex-11.

Draw the structure of cyclic silicate containing Si₆O₁₈^{12–} ion.

Si₆O₁₈¹²⁻

Sol.

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 Ca²⁺ 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.

Carborundum (SiC) :

Preparation : SiO₂ + 3C $\xrightarrow{\text{electric furnace}}$ SiC + 2CO

Properties :

(i) It is a very hard substance (Hardness = 9.5 Moh)

(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.

SiC + 2NaOH + 2O₂ $\xrightarrow{\Delta}$ Na₂SiO₃ + CO₂ + H₂O ; SiC + 4Cl₂ $\xrightarrow{\Delta}$ SiCl₄ + CCl₄

• It has a diamond like structure in which each atom is sp³ hybridized. Therefore, each atom is tetrahedrally surrounded by 4 atoms of other type.

Solved Examples

Ex-12. Write the chemical equations involved in the preparation of elemental boron from mineral colemanite.

Sol. Ca₂B₆O₁₁ + 4SO₂ + 11H₂O \longrightarrow 2Ca(HSO₃)₂ + 6H₃BO₃ 2H₃BO₃ $\xrightarrow{\Delta}$ B₂O₃ + 3H₂O : B₂O₃ + 2AI \longrightarrow Al₂O₃ + 2B

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 AI :

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 contaminators 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.

p-Block Elements (B & C family) MISCELLANEOUS SOLVED PROBLEMS (MSPS)

1. Al and Ga are trivalent in their compounds but monovalent compounds are the most stable down the 13th aroup. 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. Al³⁺ > Ga³⁺ > In³⁺ > Tl³⁺ Most stable \longrightarrow least stable $TI^{+} > In^{+} > Ga^{+} > AI^{+}$ 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. Pass mixture through the $Ca(OH)_2$ solution; CO_2 is absorbed by $Ca(OH)_2$. The residual volume (i) will be that of CO $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$ (ii) Pass mixture through I_2O_5 ; CO reduces I_2O_5 to I_2 . $5CO + I_2O_5 \longrightarrow I_2 + 5CO_2$ I₂ thus liberated is determined by titration with Na₂S₂O₃. $2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$ This is the quantitative method of estimation of CO.

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.

$$4BF_3 + 6H_2O \longrightarrow 3H_3O^+ + 3BF_4^- + B(OH)_3$$

 BF_3 is a colourless gas.

What happens when : (write only chemical reactions)(a) iodine is treated with SnCl₂.

(b) carbondioxide 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.
- $\textbf{Sol.} \hspace{0.5cm} (a) \hspace{0.1cm} 2 \hspace{-0.1cm} Sn \hspace{-0.1cm} Cl_2 + l_2 \hspace{-0.1cm} \longrightarrow \hspace{-0.1cm} 2 \hspace{-0.1cm} Sn \hspace{-0.1cm} Cl_4 + \hspace{-0.1cm} Sn \hspace{-0.1cm} l_4$
 - (b) NaCl + NH₄OH + CO₂ \longrightarrow NaHCO₃ + NH₄Cl
 - (c) $Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$
 - (d) Sn + 10HNO₃(dilute) \longrightarrow 4Sn(NO₃)₂ + NH₄NO₃ + 3H₂O

5. True / False

(a) BCl₃ 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) AIX_3 (X = CI, Br) exists as dimer and retains dimer formula in non-polar solvents like ether, benzene etc.

(d) $\mathsf{Be}_2\mathsf{C}$ 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. BCl₃ hydrolyses in aqueous solution to give boric acid. Because it has large ionisation energies and to make the enthalpy of solution of BCl₃ negative, the enthalpy of hydration of B³⁺ should be very high (~ 600 g kJ) which is unlikely for the small B³⁺ cation.

(b) $2B + 6HNO_3 (aq.) \longrightarrow 2H_3BO_3 (aq.) + 6NO_2 (g)$

(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. $Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$
- (e) $3PbO + O_2 \xrightarrow{\Delta} Pb_3O_4$
- **6. Statement-1** : PbO₂ is an oxidising agent and reduced to PbO.
 - Statement-2 : Stability of Pb(II) > Pb(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.

- 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 HCl (aq) to Cl_2 (g) by PbO₂.
 - (b) The disproportionation of SnO to Sn and SnO₂.
- **Sol.** (a) $PbO_2 + 4HCI \longrightarrow PbCl_2 + 2H_2O + Cl_2$ (b) $2SnO \longrightarrow Sn + SnO_2$
- **8.** What will happen if we take Si (CH₃) Cl₃ as a starting material for the preparation of commercial silicon polymer ?
- **Sol.** With Si(CH₃)Cl₃ 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.
- The silicate anion in the mineral kionite is a chain of three SiO₄ tetrahedra that share corners with adjacent tetrahedra. The mineral also contains Ca²⁺ ions, Cu²⁺ 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 SiO₄ tetrahedra that share corners with adjacent tetrahedra thus silicate is Si₃O₁₀, hence it can be represented as with charge as = $3 \times 4n + 10 \times (-2) = -8$

$$\begin{bmatrix} 0 & 0 & 0 \\ | & | & | \\ 0 - i - 0 - i - 0 - i - 0 \\ | & | & | \\ 0 & 0 & 0 \end{bmatrix}^{t}$$

(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, kinoite has formula $Ca_2Cu_2Si_3O_{10.}2H_2O$.

11. In what respect the reaction of N₂ with (i) CaC₂ (calcium carbide) & (ii) BaC₂ (barium carbide) differ from each other.

(i) CaC₂ reacts with N₂ to form calcium cyanamide. CaC₂(s) + N₂(g) $\xrightarrow{1373K}$ CaCN₂(s) + C(s) Calcium cyanamide

(ii) BaC₂ reacts with N₂ to form barium cyanide BaC₂(s) + N₂(g) $\xrightarrow{\text{Heating}}$ Ba(CN)₂ (s) Barium cyanide

<u>p-B</u> l	ock El	ements (B &	C fam	ily)				
12.	State	ment-1 : The t	therma	I stability of hydrides of carbon family is in order :				
	-	CH	₄ > Si⊦	$4 > \text{GeH}_4 > \text{SnH}_4 > \text{PbH}_4$				
	Statement-2 : E—H bond dissociation enthalpies of the hydrides of carbon family decrease down the							
	group with increasing atomic size.							
	(A) St (B) St	atement-1 is T	rue, c rue Sta	tement-2 is True. Statement-2 is NOT a correct explanation for	or Statement-1			
	(C) St	atement-1 is T	rue, S	tatement-2 is False.				
	(D) Statement-1 is False, Statement-2 is True.							
Ans.	(A)							
501.	BOIN a	30th are correct statements and statement-2 is the correct explanation of statement-1. Down the group						
13.	Which	n one of the fol	element does not dissolve in fused or aqueous alkalies?					
Ans	(A) Boron (B) Silicon			(C) Aluminium (D) None of these				
Sol.	איי (ש) Boron dissolved in fused alkalies according to the following reaction.							
	$2B + 6NaOH \xrightarrow{\text{fused}} 2Na_3BO_3 + 3H_2$							
	Silico	Silicon and aluminium dissolved in both fused and aqueous alkalies.						
14.	What	happens wher	n CO2	g) is passed through sodium meta borate solution ?				
Sol.	4NaB	O ₂ + CO ₂	$\rightarrow Na$	$B_4O_7 + Na_2CO_3$				
15.	Whick	n of the followi	ng stat	ement(s) is/are correct ?				
	(A) B2	$2O_3$ and SiO ₂ a	ire aci	lic in nature and are important constituents of glass.				
	(B) Borides and silicide are hydrolysed by water forming boranes and silanes respectively.							
	(C) D (D) Si	Ω_4^{4-} dets hydr	olvsec	by acid or water and form $Si_2\Omega_7^{6-}$				
Ans.	(A), (E	B) and (D)	orysec					
Sol.	(A), (E	3) and (D) are	correc	t statements but (C) is incorrect.				
		$B_2H_6 + 6Cl_2$;	2BCl ₃ + 6HCl				
16. Match the following :					1			
	(A)	Column-I Boron	(n)	Column-II Forms acidic oxides				
	(A) (B)	Carbon	(p) (a)	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	(A - p,q,r); (B - p,r); (C - r,s); (D - s)						
301.	(A) E)	(A) Exists in various allotropic forms and its oxide, B_2O_3 is acidic in nature.						
		$2DI3 \xrightarrow{\text{Constant}} 2D + 3I2$ Van Arkel method						
	(B) E>	(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 nat							
		Sn(Оп)4 - ОЦ)	$2OH \longrightarrow [SH(OH)_6]^2$				
	$Sn(OH)_4 + 4H^+ \longrightarrow Sn^{4+} + 4H_2O$							
	$Al(OH)_{2} + OH^{-} \longrightarrow [Al(OH)_{4}]^{-}$							
	$AI(OH)_3 + 3H^+ \longrightarrow AI^{3+} + 3H_2O$							
		,	,					