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	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≡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)

❍ 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 ≈ 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.

Bond	**Bond enthalpy (kJ mol^{-1})**
C—C	348
Si—Si	297
Ge—Ge	260
Sn—Sn	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 : $Na_2[B_4O_5(OH)_4].8H_2O$ • Colemnite : $Ca_2B_6O_{11}.5H_2O$ • Kernite : $Na_2[B_4O_5(OH)_4].2H_2O$ • Boric acid : H_3BO_3	C (Carbon)	180 ppm	• Coal • Natural gas • oil (hydrocarbon) • Natural Graphite • Natural diamond • Carbonates: • Calcite($CaCO_3$) • Magnesite ($MgCO_3$) • Dolomite($MgCO_3.CaCO_3$]
Al (Aluminium)	83000 ppm (Most abundant metal, 3rd most Abundant element)	• Bauxite : $Al_2O_3.H_2O–Al_2O_3.3H_2O$ • Aluminosilicate rocks (feldspars, mica) • Cryolite : Na_3AlF_6	Si (Silicon)	272000 ppm	• Silica (sand & quartz) SiO_2 • 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)
Tl (Thallium)	0.5 ppm	• ZnS & PbS ores	Pb (Lead)	13 ppm	• Galena (PbS)

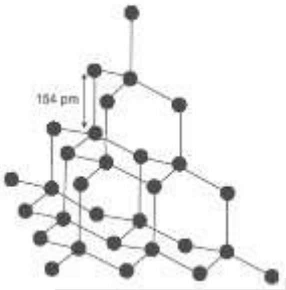
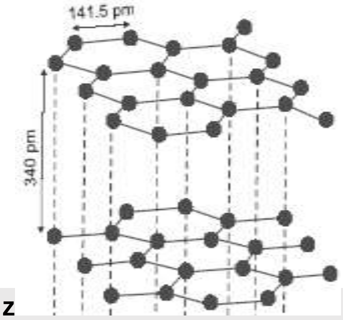
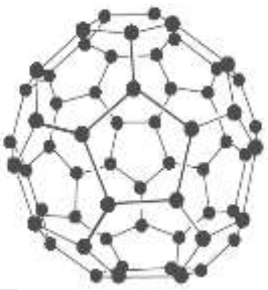
Allotropy :

Elements	Allotropes	Elements	Allotropes
B	5 crystalline forms : β-rhombohedral	C	Crystalline Diamond, hexagonal diamond
			α-graphite, β-graphite
	2 amorphous forms		fullerenes
Al	No allotrope	Si	Amorphous - brown powder
			Crystalline - greyish metallic
Ga	No allotrope	Ge	α-Germanium
			β-Germanium
			γ-Germanium
In	No allotrope	Sn	α-tin (grey tin)
			β-tin (white tin)
			$\alpha\text{-Sn(diamond structure)} \xrightleftharpoons{13.2^{o}C} \beta\text{-Sn(metallic)}$
Tl	α-Thallium	Pb	α-lead (Pb-I)
	β-Thallium		β-lead (Pb-II)

Allotropy of carbon family

❍ 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:

	Diamond	**Graphite**	**Fullerene**
Structure			
Hybridisation	sp^3	sp^2	sp^2
Density (g/cm^3)	3.51	2.22	1.65
ΔH_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. $3C+SiO_2 \xrightarrow{\Delta} SiC + 2CO \xrightarrow{2500^\circ C} C(graphite) + Si\ gas$ • Thermodynamically most stable among allotropes. $Graphite \xrightarrow[50000\text{–}60000\,atm]{1600^\circ C} synthetic\ diamond$	• Cage like molecules. • C_{60}–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

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			B	Al	Ga	In	Tl
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=($ns^2\ np^1$)*			[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 *($B < Ga < Al < In < Tl$)*			85	143	135	167	170
			In Ga, poor shielding of 10 d-electrons				
Ionic Radius X$^-$ / pm *($B < Al < Ga < In < Tl$)*			27	53.5	62	80	88.5
Ionization enthalpy (kJ mol^{-1}) *($B > Al < Ga > In < Tl$)*	Δ_iH_1	I	801	577	579	558	589
	Δ_iH_2	II	2427	1816	1979	1820	1971
	Δ_iH_3	III	3659	2744	2962	2704	2877
			Poor shielding of d-orbital and f-orbital in Ga & Tl respectively				
Electronegativity *($B > Al < Ga < In < Tl$)*			2.0	1.5	1.6	1.7	1.8
			Marginal increase after Al				
Melting point / K			2453	933	303	430	576
Boiling point / K *($B > Al > Ga > In > Tl$)*			3923	2740	2676	2353	1730
Density/[g cm^{-3} (at 293 K) *($B < Al < Ga < In < Tl$)*			2.35	2.70	5.90	7.31	11.85
Oxidation State			+3	+3	+3, +1	+3, +1	+3, +1
			+1 oxidation state arises due to inert pair effect.				
			Stability of Oxidation state: +1: Ga < In < Tl +3 : Al > Ga > In > Tl				

Carbon family :

Property	C	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 configuration=($ns^2\ np^2$)*	[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] $4f^{14}$ $5d^{10}\ 6s^2$ $6p^2$

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
Ionization enthalpy (kJ mol^{-1}) *(C > Si > Ge > Sn < Pb)*	Δ_iH_1	I	801	577	579	558	589
	Δ_iH_2	II	2427	1816	1979	1820	1971
	Δ_iH_3	III	3659	2744	2962	2704	2877
			Poor shielding f-orbital				
Electronegativity *(C > Si ≈ Ge ≈ Sn ≈ 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
Oxidation State			+4	+4	+4, +2	+4, +2	+4, +2
			+2 oxidation state arises due to inert pair effect.				
			Stability of Oxidation state: +2: Ge < Sn < Pb +4: Ge > Sn > Pb				

The Elements

Preparation of elements :

BORON :

Source	Process	Comments
From Borax $(Na^+)_2B_4O_7^{2-}.10H_2O$	• $Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCl$ • $2H_3BO_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O$ • $B_2O_3 + 3Mg/Na \xrightarrow{\text{High temp.}} 2B + 3MgO/Na_2O$	• 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.
From BX_3	• $2BX_3 + 3H_2 \xrightarrow[\text{or Tantalum}]{\text{red hot W}} 2B(\text{crystalline}) + 6HX$ (X = Cl or Br) 99.9% pure • $2BCl_3 + 3Zn \longrightarrow 3ZnCl_2 + 2B$ • $2BI_3 \xrightarrow[\text{or Tantalum}]{\text{red hot W}} 2B\uparrow + 3I_2\uparrow$ (Van Arkel method)	Problem in obtaining high purity boron: • High melting point (2180ºC) • Liquid gets corroded
From Diborane (B_2H_6)	• $B_2H_6 \xrightarrow{\Delta} 2B\ (\text{crystalline}) + 3H_2\uparrow$	• Thermal decomposition of diborane.
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 : $Al^{3+}(melt) + 3e^- \longrightarrow Al(l)$ 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: $2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$ *Several other extraction processes will be studied in detail in Metallurgy.*	• 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 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 CO_2. This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away.

CARBON :

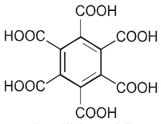
Preparation of	Process
Carbon black (soot)	By incomplete combustion of hydrocarbon.
Graphite	$3C + SiO_2 \xrightarrow{\Delta} SiC + 2CO \xrightarrow{2500^oC} C\text{ (graphite)} + Si\text{ gas}$
Diamond	• Natural diamond can be extracted from mines. • Synthetic diamond $\text{Graphite} \xrightarrow[50000-60000\text{ atm}]{1600^oC} \text{synthetic diamond.}$

SILICON :

From	Process	Comments
SiO_2	$SiO_2\text{ (excess)} + 2C \longrightarrow Si\text{ (pure)} + 2CO$ $Si\text{ (pure)} + 2Cl_2 \longrightarrow SiCl_4$ $SiCl_4 + 2Mg \longrightarrow Si\text{ (highly pure)} + MgCl_2$	Reducing SiO_2 with high purity coke in an electric furnace
$Na_2[SiF_6]$	Sodium Reduction of $Na_2[SiF_6]$ $Na_2[SiF_6] + 4Na \longrightarrow Si\text{ (ultra pure)} + 6NaF$	Zone refining is used to get ultra pure silicon from highly pure silicon, which can be used in semi-conductor industry.

Section (D) : Properties of Elements

Chemical Properties :

Reaction with	Boron Family	Carbon Family
O_2	$4E + 3O_2 \xrightarrow{\Delta} 2E_2O_3$	$E + O_2 \xrightarrow{\Delta} \underset{\text{(dioxide)}}{EO_2}$ $E + \frac{1}{2}O_2 \xrightarrow{\Delta} \underset{\text{(monoxide)}}{EO}$
	B_2O_3 – acidic Al_2O_3 – amphoteric Ga_2O_3 – amphoteric In_2O_3 – basic Tl_2O_3 – basic	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
N_2	$2E + N_2 \xrightarrow{\Delta} 2EN$ $EN + H_2O \xrightarrow{\Delta} E(OH)_3 + NH_3$ $\therefore$ E = B or Al	$2C(s)+O_2(g)+4N_2(g) \xrightarrow{1273\,K} \underset{\text{(Producer gas)}}{2CO(g)+4N_2(g)}$
X_2 (Halogen)	$2E + 3X_2 \longrightarrow 2EX_3$; (X=F, Cl, Br, I) BX_3 – covalent *(BI_3 cannot be formed directly)* AlF_3 – Ionic GaF_3 – Ionic InF_3 – Ionic TlI_3 – exist as $Tl^+I_3^-$ & TlI also forms	$E + 2X_2 \longrightarrow EX_4$; (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 : $GeX_4 > GeX_2$; $PbX_2 > PbX_4$
H_2O	B – does not react with water $Al \xrightarrow[+H_2O]{25^\circ C} Al(OH)_3$ $Al \xrightarrow[+H_2O]{>480^\circ C} Al_2O_3$ Ga, In – Not attacked by cold & hot water unless oxygen is present. Tl – oxidises in moist air & decomposes steam at red heat.	$C(s) + H_2O\ (steam) \xrightarrow[heat]{red} \underset{\text{(water gas)}}{CO(g)+H_2(g)}$ $\underset{(Si,Ge,Sn)}{E(s)} + H_2O(steam) \xrightarrow[heat]{red} EO_2+H_2$; • Pb is unafftected by water, probably because of a protective oxide layer. • C, Si, Ge – not attacked by cold water.
Acids	$B \xrightarrow[\text{(Hot \& Conc.)}]{+H_2SO_4} H_3BO_3 + SO_2$ $B \xrightarrow[\text{(Hot \& Conc.)}]{+HNO_3} H_3BO_3 + NO_2$ *(Boron reacts with only oxidising acids)* $Al \xrightarrow{+HCl} AlCl_3 + H_2$ $Al \xrightarrow[\text{(Conc.)}]{+HNO_3}$ Do not react because it forms passive oxide layer. Ga, In, $T\ell$ can also react with dilute mineral acids.	C, Si, Ge $\xrightarrow[dilute]{+HCl}$ No reaction Sn dissolves in HCl (dil. & conc) but Pb in only dil.HCl. Pb (does not dissolve in) $\xrightarrow[\text{(conc.)}]{HCl} \underset{\text{(coating)}}{PbCl_2} + H_2$ Pb (does not dissolve in) $\xrightarrow{H_2SO_4} \underset{\text{(coating)}}{PbSO_4} + H_2$ C (graphite) $\xrightarrow[\text{(Hot \& conc.)}]{+HNO_3}$  (Mellitic acid) C (graphite) $\xrightarrow[\text{(mixture)}]{+HF/HNO_3}$ Graphite oxide $Si + 6HF \rightarrow H_2SiF_6 + 2H_2$ $\underset{(Sn,Pb)}{E} + \text{dil. } HNO_3 \rightarrow E(NO_3)_2$

NaOH	$2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2$ $2B + 6NaOH \xrightarrow{\text{fused}} 2Na_3BO_3 + 3H_2$ $Al \xrightarrow{NaOH + H_2O} NaAlO_2.2H_2O + H_2$ or $Na^+[Al(OH)_4]^-$ $Al \xrightarrow{NaOH} Na_3AlO_3 + H_2$ *(Al & Ga readily dissolves in alkalies).* In & Tl do not react with alkali.	C – unaffected by alkalies $Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$ $\underset{(Sn,Pb)}{E} + NaOH \xrightarrow{\Delta} Na_2EO_3 + H_2$ or $Na_2[E(OH)_6]$
Metal	$3Mg + 2B \rightarrow Mg_3B_2$ $3Ca + 2B \rightarrow Ca_3B_2$	$2Mg + Si \xrightarrow{\Delta} Mg_2Si$ (magnesium silicide)
Reducing Property	$B \xrightarrow[\Delta]{SiO_2} B_2O_3 + Si$ $B \xrightarrow[\Delta]{CO_2} B_2O_3 + C$ $Al \xrightarrow[\Delta]{MnO_2} Al_2O_3 + Mn$ $Al \xrightarrow[\Delta]{Cr_2O_3} Al_2O_3 + Cr$	

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

Oxides, oxy acids and hydroxide

Boron trioxide (B_2O_3) :

Preparation :

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

Properties :

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

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

It reacts with water slowly to form orthoboric acid.

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

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

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

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

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

$$B_2O_3 + P_2O_5 \rightleftharpoons 2BPO_4$$

It reacts with hydrogen fluoride in presence of H_2SO_4 forming BF_3 .

$$B_2O_3 + 6HF + 3H_2SO_4 \longrightarrow 2BF_3 + 3H_2SO_4.H_2O.$$

Boric acid (H_3BO_3) :

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.

$$Ca_2B_6O_{11} + 4SO_2 + 11H_2O \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$$

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:

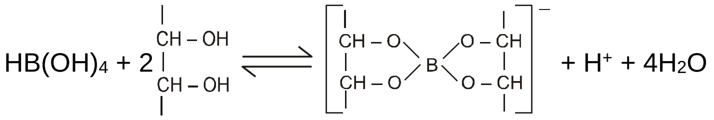
$$B(OH)_3(aq) + 2H_2O(\ell) \rightleftharpoons [B(OH)_4]^-(aq) + H_3O^+(aq). \qquad pK = 9.25.$$

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).

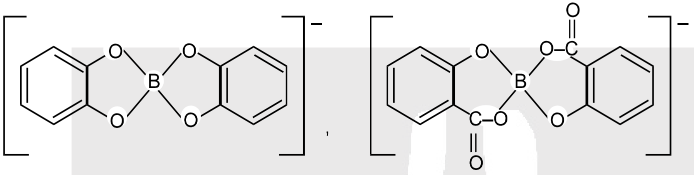
The added compound must be a cis-diol, to enhance the acid properties. The cis-diol forms very stable complex with the $[B(OH)_4]^-$, thus removing it from solution. The reaction is reversible and thus removal of one of the products shifts the equilibrium in the forward direction and thus all the $B(OH)_3$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

$$2B(OH)_3 + 2NaOH \longrightarrow Na[B(OH)_4] + NaBO_2 + 2H_2O$$



$$HB(OH)_4 + 2\,\begin{matrix} | \\ CH-OH \\ | \\ CH-OH \\ | \end{matrix} \rightleftharpoons \left[\begin{matrix} | & & | \\ CH-O & & O-CH \\ | & B & | \\ CH-O & & O-CH \\ | & & | \end{matrix}\right]^- + H^+ + 4H_2O$$

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



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

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

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.

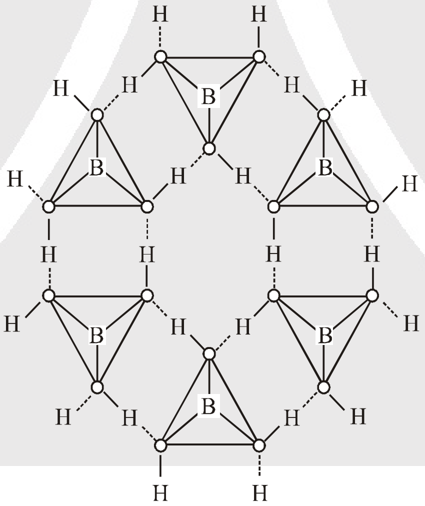
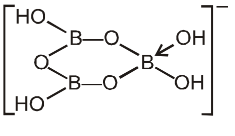


Figure : 1

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

$$3B(OH)_3 \rightleftharpoons H_3O^+ + [B_3O_3(OH)_4]^- + H_2O, \qquad pK = 6.84$$



- Boric acid dissolves in aqueous HF forming HBF_4 (fluoroboric acid).

$$B(OH)_3 + 4HF \rightleftharpoons H_3O^+ + BF_4^- + 2H_2O$$

Test for Borate radical :

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

$$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\text{ethylborate (volatile)}}{B(OC_2H_5)_3} + 3H_2O$$

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 BF_3 does not hydrolyses completely whereas BCl_3 or BBr_3 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 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 ($BF_3.OH_2$) formed by BF_3.

Borax ($Na_2B_4O_7.10H_2O$) :

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 $CaCO_3$.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3\downarrow + Na_2B_4O_7 + 2NaBO_2$$

The filtrate is cooled when white crystals of borax are precipitated. The mother liquor on treatment with CO_2 converts $NaBO_2$ to $Na_2B_4O_7$ 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 Na_2CO_3 on orthoboric acid.

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2\uparrow$$

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 H_3BO_3 and strong alkali NaOH.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 4H_3BO_3 + 2NaOH$$

(iii) Action of heat.

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

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10\ H_2O\uparrow$$

$$Na_2B_4O_7 \xrightarrow{740^oC} 2NaBO_2 + B_2O_3 \text{ (borax bead)}$$

(iv) Oxidation of boric acid or sodium metaborate with H_2O_2.

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

Sodium per oxoborate is used as a brightner in washing powder. In very hot water (over 80ºC) 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 HCl.

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

$$2[B(OH)_4]^{2-} + 2H_3O^+ \longrightarrow 2B(OH)_3 + 4H_2O$$

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) $Na_2[B_4O_5(OH)_4] + 12HF \xrightarrow{-H_2O} [Na_2O(BF_3)_4] \xrightarrow{+H_2SO_4} 4BF_3 + 2NaHSO_4 + H_2O$

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.

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.

$$Na_2B_4O_7\cdot 10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{740^oC} \underbrace{2NaBO_2 + B_2O_3}_{\text{glassy mass}} \; ; \; CuO + B_2O_3 \longrightarrow Cu(BO_2)_2 \text{ (blue bead)}$$

Uses :

(i) In borax bead test.	(ii) In purifying gold.
(iii) As flux during welding of metals.	(iv) In production of glass.

Solved Examples

Ex-.3 (a) $Na_2B_4O_7 + \text{concentrated } H_2SO_4 + H_2O \longrightarrow (A) \xrightarrow[\text{(ii) ignite}]{\text{(i) } C_2H_5OH} (B)$

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

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

$$\begin{tikzcd} Na_2B_4O_7 \arrow[r, "\Delta", "-(B)"'] & (A) \arrow[r, "NaOH"] \arrow[dr, "HF", "H_2SO_4"'] & (B) \\ & & (C) \end{tikzcd}$$

Sol. (a) $Na_2B_4O_7 + \text{concentrated } H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$

$H_3BO_3 + 3C_2H_5OH \longrightarrow B(OC_2H_5)_3$-volatile (burn with green edged flame) + $3H_2O$

(b)

$$\begin{tikzcd} Na_2B_4O_7 \arrow[r, "\Delta", "-(NaBO_2)"'] & B_2O_3 \arrow[r, "NaOH"] \arrow[dr, "HF", "H_2SO_4"'] & NaBO_2 \\ & & BF_3 \end{tikzcd}$$

Aluminium Oxide (Al_2O_3) :

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 (Fe^{3+}),	(B) Sapphire-blue ($Fe^{2+/3+}$ / Ti^{4+}),
(C) Ruby-red (Cr^{3+}),	(D) Oriental Emerald-green (Cr^{3+} / V^{3+})

Preparation :

Pure Al_2O_3 is obtained by igniting $Al_2(SO_4)_3$, $Al(OH)_3$ or ammonium alum.

$Al_2(SO_4)_3 \xrightarrow{\Delta} Al_2O_3 + 3SO_3\uparrow$; $2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O\uparrow$

$(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O \xrightarrow{\Delta} 2NH_3\uparrow + Al_2O_3 + 4SO_2\uparrow + 25H_2O\uparrow$

Properties :

It is a white amorphous powder insoluble in water but soluble in acids (forming eg., $AlCl_3$) as well as alkalies (forming e.g., $NaAlO_2$), Thus amphoteric in nature. It is a polar covalent compound. Exists in two forms α-Al_2O_3 or corundum and γ-Al_2O_3.

Addition of Cr_2O_3 or Fe_2O_3 makes alumina coloured.

$$\gamma\text{-}Al_2O_3 \xrightarrow[\Delta]{1000^oC} \alpha\text{-}Al_2O_3$$

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-Al_2O_3 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-Al_2O_3 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. $Al_2O_3 + N_2 + 3C \xrightarrow{\Delta} 2AlN + 3CO$

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.

$$HCOOH\ (liq) \xrightarrow[\text{conc.}H_2SO_4]{373K} CO(g) + H_2O$$

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

$$H_2C_2O_4 \xrightarrow[-H_2O]{\text{conc. } H_2SO_4,\Delta} CO + CO_2$$

(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.

$$C\ (s) + H_2O\ (g) \xrightarrow{473\text{–}1273K} CO\ (g) + H_2(g)\ \text{(water gas).}$$

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

$$2\ C\ (s) + O_2\ (g) + 4\ N_2\ (g) \xrightarrow{1273K} 2\ CO\ (g) + 4\ N_2\ (g)\ \text{(Producer gas).}$$

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) $K_4Fe(CN)_6 + 6H_2SO_4$ (concentrated) $+ 6H_2O \xrightarrow{\Delta} 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

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

$$HCOOH \xrightarrow{\Delta} H_2O + CO$$

(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 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.

$$Hb—O_2 + CO \longrightarrow Hb—CO + O_2$$

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 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 .

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

(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 .

$$Ni(s) + 4CO(g) \xrightarrow{28^\circ C} Ni(CO)_4(liq) \xrightarrow{180^\circ C} Ni(s) + 4CO(g)$$

(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.

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

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

(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 :

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

(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 $CuCl.CO.2H_2O$. 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 $PdCl_2$ solution to metallic Pd.

Carbon dioxide (CO_2) :

Preparation :

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

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

(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) CO_2 is easily liquefied (critical temperature = 31.1ºC) 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 –78ºC 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 :

$$H_2CO_3(aq) + H_2O(\ell) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

$$HCO_3^-(aq) + H_2O(\ell) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

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 CO_2 is evolved.

(iv) Carbon dioxide readily reacts with alkalies forming the carbonate and, if CO_2 is in excess, the hydrogen carbonate. This is the basis of the lime-water test for CO_2 gas.

$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(liq); CaCO_3(s) + H_2O(liq) + CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$

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

(v) Carbon dioxide, which is normally present to the extent of ~ 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 CO_2 into carbohydrates such as glucose. The overall chemical change can be expressed as:

$$6\,CO_2 + 12\,H_2O \xrightarrow[\text{Chlorphyll}]{hv} C_6H_{12}O_6 + 6\,O_2 + 6\,H_2O$$

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 :

(a) $Na_2CO_3 + CO_2 + H_2O \underset{\text{Hot}}{\overset{\text{Cool}}{\rightleftharpoons}} 2NaHCO_3$

(b) Girbotol process : $2HOCH_2CH_2NH_2 + CO_2 + H_2O \underset{\text{100-150°C}}{\overset{\text{30-60°C}}{\rightleftharpoons}} (HOCH_2CH_2NH_3)_2CO_3$

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 (C_3O_2) :

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 :

$$3\ CH_2(COOH)_2 + P_4O_{10} \longrightarrow 3C_3O_2 + 4H_3PO_4$$

When heated to about 200ºC, 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 (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 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.

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

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.

$$SnO\ (basic) + 2H^+ \longrightarrow Sn^{2+} + H_2O\ ;$$
$$SnO\ (acidic) + 4OH^- + H_2O \longrightarrow [Sn(OH)_6]^{4-}\ or\ SnO_2^{2-}\ (stannite)$$

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

$$2\ Na_2SnO_2 + O_2 \longrightarrow 2\ Na_2SnO_3$$

Uses :

For the preparation of stannous chloride and stannous sulphate.

Stannic Oxide (SnO_2) :

Preparation :

By heating tin with concentrated HNO_3.

$$Sn + 4HNO_3 \longrightarrow H_2SnO_3 + 4NO_2\uparrow + H_2O\ ; \quad H_2SnO_3 \xrightarrow{\Delta} H_2O\uparrow + SnO_2$$

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 180ºC. 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 (PbO_2) :

Preparation :

(i) $PbO + NaOCl \xrightarrow{\Delta} PbO_2 \text{ (insoluble)} + NaCl$

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

Properties :

It is a chocolate/dark brown coloured insoluble solid.
(i) On heating at 440ºC it gives the monoxide.

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

(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.

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

(b) It oxidises Mn salt to permanganic acid.

$$2MnSO_4 + 5PbO_2 + 6HNO_3 \longrightarrow 2HMnO_4 + 2PbSO_4 + 3Pb(NO_3)_2 + 2H_2O$$

(c) It reacts with SO_2 at red heat to form lead sulphate.

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

(iii) It dissolves in concentrated NaOH solution.

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

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

$$PbO_2 + 2HNO_3 \longrightarrow Pb(NO_3)_2 + 1/2O_2 + H_2O$$

$$PbO_2 + H_2SO_4 \longrightarrow PbSO_4 + 2H_2O + O_2$$

Uses :

It is used in match industry for making ignition surface of match boxes, in the preparation of $KMnO_4$ and in explosives.

Red Lead (Pb_3O_4) :

Preparation :

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

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

Properties :

(i) It is a red powder insoluble in water but when heated with concentrated HNO_3 it gives a red precipitate of PbO_2.

$$Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2\downarrow + 6H_2O$$

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

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

(iii) It oxidizes concentrated HCl to chlorine.

$$Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2\uparrow$$

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

$$2Pb_3O_4 + 6H_2SO_4 \longrightarrow 6PbSO_4 + 6H_2O + O_2\uparrow$$

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

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 (B_2H_6) :

(i) $4BF_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 2B_2H_6 + 3Li\,[AlF_4]$

(ii) $2BCl_3 + 6H_2 \text{ (excess)} \xrightarrow[\text{discharge}]{\text{silent electric}} B_2H_6 + 6HCl$

(iii) $8BF_3 + 6LiH \xrightarrow{\text{ether}} B_2H_6 + 6LiBF_4$

(iv) $2NaBH_4 + I_2 \xrightarrow{\text{ether}} B_2H_6 + 2NaI + H_2$

(v) $3NaBH_4 + 4BF_3 \xrightarrow[\text{450K}]{\text{ether}} 3NaBF_4 + 2B_2H_6$

(vi) It can also be prepared by treating $NaBH_4$ with concentrated H_2SO_4 or H_3PO_4.

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

(vii) $2BF_3 + 6NaH \xrightarrow{453\text{ K}} B_2H_6 + 6NaF$ (Industrial method)

(viii) $B_2O_3 + 3H_2 + 2Al \xrightarrow[150^{\circ}C]{750\text{ atm}} B_2H_6 + Al_2O_3$

(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 O_2.Reaction with oxygen is extremely exothermic.

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

- 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.
- 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.

$$B_2H_6 + 6ROH \longrightarrow 2B(OR)_3 + 6H_2$$
$$B_2H_6 + 2KOH + 2H_2O \longrightarrow 2KBO_2 + 6H_2$$

(iv) Reaction with HCl replaces a terminal H with Cl.

$$B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2$$

(v) Reaction with chlorine gives the trichloride.

$$B_2H_6 + 6Cl_2 \longrightarrow 2BCl_3 + 6HCl$$

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

- Small amines such as NH_3, CH_3NH_2 and $(CH_3)_2NH$ give unsymmetrical cleavage of diborane.

  $B_2H_6 + 2NH_3 \longrightarrow [H_2B\ (NH_3)_2]^+ + [BH_4]^-$
- Large amines such as $(CH_3)_3N$ and pyridine give symmetrical cleavage of diborane.

  $2(CH_3)_3N + B_2H_6 \longrightarrow 2H_3B \longleftarrow N(CH_3)_3$

  $B_2H_6 + 2Me_3P \longrightarrow 2Me_3PBH_3$
- $B_2H_6 + 2CO \xrightarrow{200^{\circ}C,\ 20\ atm} 2BH_3CO$ (borane carbonyl)
- The boronium ion products $[H_2BL_2]^+$, are tetrahedral and can undergo substitution by other bases

  $[H_2B(NH_3)_2]^+ + 2PR_3 \longrightarrow [H_2B(PR_3)_2]^+ + 2NH_3$
- The reaction with ammonia depends on conditions.

$$B_2H_6 + NH_3 \xrightarrow[\text{low temperature}]{\text{Excess } NH_3} B_2H_6.2NH_3 \text{ or } [H_2B(NH_3)_2]^+\ [BH_4]^- \text{ (ionic compound).}$$

$$\xrightarrow[\text{higher temperature } (> 200^{\circ}C)]{\text{Excess } NH_3} (BN)_x \text{ boron nitride.}$$

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

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 NH_3 and boric acid at elevated temperature. If heated with water, $B_3N_3H_6$ hydrolyses slowly.

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

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

$2B_2H_6 + 2Na \longrightarrow NaBH_4 + NaB_3H_8$

$B_2H_6 + NaBH_4 \longrightarrow NaB_3H_8 + H_2$.

- Reductions of diborane with $NaBH_4$ can also lead to higher borane anions.

  $2NaBH_4 + 5B_2H_6 \longrightarrow Na_2B_{12}H_{12}$

(viii) $B_2H_6 + 2LiH \longrightarrow 2LiBH_4$

Solved Examples

Ex-6. Complete the following reactions and identify the products formed.

(a) $BCl_3 + NH_4Cl \xrightarrow[C_6H_5Cl]{140^{\circ}C} (A) \xrightarrow{NaBH_4} (B)$

(b) $BCl_3 + H_2 + C_{fibre} \xrightarrow{1700\text{–}1800^{\circ}C}$ product(s)

Sol. (a) $3BCl_3 + 3NH_4Cl \xrightarrow[C_6H_5Cl]{140^{\circ}C} B_3N_3H_3Cl_3 \xrightarrow{NaBH_4} B_3N_3H_6$ (borazine)

(b) $4BCl_3 + 6H_2 + C_{fibre} \xrightarrow{1700\text{–}1800^{\circ}C} B_4C_{(fibre)} + 12\ HCl$

Aluminium Hydride (AlH_3) :

Aluminium hydride is obtained by interaction of $LiAlH_4$ with100% H_2SO_4 in THF :

$2LiAlH_4 + H_2SO_4 \longrightarrow 2AlH_3 + 2H_2 + Li_2SO_4$

The white hydride is thermally unstable. With donor ligands however, a range of molecular complexes AlH_3L & AlH_3L_2 are formed indicative of the lewis acidic behaviour of AlH_3.

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

SiH_4 (monosilane)

(1) small scale preparation : $SiO_2 + LiAlH_4 \xrightarrow{160^{\circ}C} SiH_4$

(2) Hydrolysis of Magnesium silicide

$Mg_2Si + H_2O \longrightarrow$ mixture of silanes

(3) Reduction of chlorosilanes by $LiAlH_4$ to produce silane

(4) Photolysis of SiH_4–H_2 mixture can make higher silanes

(5) Among silanes only SiH_4 & Si_2H_6 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 ($AlCl_3.6H_2O$) :

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 $Al(OH)_3$ in dilute HCl :

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2\uparrow;\ \ Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O;\ \ Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

The solution obtained is filtered and crystallized when the crystals of $AlCl_3.6H_2O$ 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.

$$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 \text{ (anhydrous)} + 3CO\uparrow$$

Properties :

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

$$2AlCl_3.6H_2O \xrightarrow{\Delta} Al_2O_3 + 6HCl\uparrow + 3H_2O$$

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

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl\uparrow$$

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

$$AlCl_3 + 6NH_3 \longrightarrow AlCl_3.6NH_3 \text{ (white solid)}$$

(iv) **Action of NaOH solution:** When NaOH solution is added dropwise to an aqueous $AlCl_3$ 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.

$$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3\downarrow + 3NaCl;\ \ Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$

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 NH_4OH solution:** When NH_4OH solution is added to a solution of $AlCl_3$, a white precipitate of $Al(OH)_3$ is formed which does not dissolve in excess of NH_4OH.

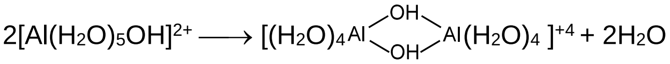
$$AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3\downarrow \text{ (white gelatinous)} + 3NH_4Cl$$

This reaction is important as a test to distinguish an Al 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.

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

The complex cation has a high tendency to get dimerised.



$$2[Al(H_2O)_5OH]^{2+} \longrightarrow [(H_2O)_4Al(\mu\text{-}OH)_2Al(H_2O)_4]^{+4} + 2H_2O$$

(vii) $4LiH + AlCl_3 \longrightarrow LiAlH_4 + 3LiCl$

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 $AlCl_3$ is exposed to atmosphere.
(b) $AlCl_3$ dissolves in aqueous sodium hydroxide (excess)

Sol. (a) $AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$ (HCl fumes in air).
(b) $AlCl_3 + 3NaOH \longrightarrow Al(OH)_3\downarrow + 3NaCl$
$Al(OH)_3 + OH^- \longrightarrow [Al(OH)_4]^-$

Ex-8. Anhydrous $AlCl_3$ cannot be prepared by heating hydrated salt. Why ?
Sol. Gets hydrolysed forming Al_2O_3.
$2AlCl_3.6H_2O \xrightarrow{\Delta} Al_2O_3 + 6HCl\uparrow + 3H_2O$

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

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 $K_2SO_4.Al_2(SO_4)_3.24H_2O$
(ii) Chrome alum $K_2SO_4.Cr_2(SO_4)_3.24H_2O$
(iii) Ferric alum $K_2SO_4.Fe_2(SO_4)_3.24H_2O$
(iv) Ammonium alum $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$

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

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

Carbon Halides :

CF_4 (Carbon tetrafluoride)

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

CCl_4 (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.

CBr_4 (Carbon tetrabromide)

- Pale yellow solid at room temperature.
- Insoluble in water, soluble in non-polar solvent.

CI_4 (Carbon tetraiodide)

- Bright red, crystalline material.
- odor like that of iodine.

Stannous Chloride ($SnCl_2{\cdot}2H_2O$) :

Preparation :

(i) Sn + 2HCl (concentrated) $\longrightarrow SnCl_2(aq) + H_2\uparrow$

(ii) SnO + 2HCl $\longrightarrow SnCl_2(aq) + H_2O$

The solution on crystallization gives colourless crystals of $SnCl_2{\cdot}2H_2O$.

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 $CuCl_2$ to CuCl (white).

(iii) $SnCl_2$ partially hydrolyses in water forming the basic chloride, Sn(OH)Cl.

$SnCl_2 + H_2O \longrightarrow$ Sn(OH)Cl (white)$\downarrow$ + HCl

As it produces a weak base and strong acid its aqueous solution is acidic. Its hydrolysis can be prevented by adding concentrated HCl 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 ($SnCl_4$) :

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 114ºC.

(ii) Action of moisture: It absorbs moisture and becomes converted into hydrated stannic chlorides, $SnCl_4{\cdot}3H_2O$, $SnCl_4{\cdot}5H_2O$, $SnCl_4{\cdot}6H_2O$ and $SnCl_4{\cdot}8H_2O$.$SnCl_4$. 5 H_2O 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.

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

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

(v) In presence of ammonium chloride, it forms ammonium salt of H_2SnCl_6 (stannic acid).

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

Uses :

For the preparation of stannic compounds.

Lead Chloride ($PbCl_2$) :

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.

$2\,HCl + PbCl_2 \rightleftharpoons H_2PbCl_4$ (chloroplumbous acid)

Uses :

It is used for making pigments for paints.

Lead Tetrachloride ($PbCl_4$) :

Preparation :

It is prepared by the following methods:

(i) By dissolving PbO_2 in cold concentrated HCl

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

$PbCl_4$ dissolves in excess of HCl to form a stable solution of H_2PbCl_6.

$$PbCl_4 + 2HCl \longrightarrow H_2PbCl_6$$

When NH_4Cl 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.

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

(ii) By the action of Cl_2 on a solution of $PbCl_2$ in concentrated HCl

$$PbCl_2 + Cl_2 \longrightarrow PbCl_4$$

Properties :

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

(ii) Rapid hydrolysis with water forms PbO_2 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.

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

Preparation :

(i) With NaOH : $2NaOH + CO_2 \longrightarrow Na_2CO_3$; $Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$

(ii) By precipitation : $BaCl_2 + Na_2CO_3 \longrightarrow BaCO_3\downarrow + 2NaCl$

$SiCl_4$, 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.

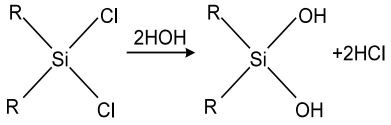
(a) $RCl + Si \xrightarrow[300^oC]{Cu} R_3SiCl + R_2SiCl_2 + RSiCl_3$

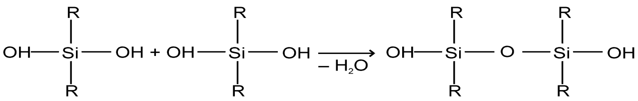
(b) $RMgCl + SiCl_4 \longrightarrow RSiCl_3 + MgCl_2$

$2RMgCl + SiCl_4 \longrightarrow R_2SiCl_2 + 2MgCl_2$

$3RMgCl + SiCl_4 \longrightarrow R_3SiCl + 3MgCl_2$

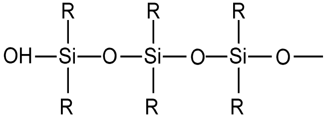
After fractional distillation, the silane derivatives are hydrolysed and the 'hydroxides' immediately condense by intermolecular elimination of water. The final product depends upon the number of hydroxyl groups originally bonded to the silicon atom:





$$HO-SiR_2-OH + HO-SiR_2-OH \xrightarrow[-H_2O]{} HO-SiR_2-O-SiR_2-OH$$

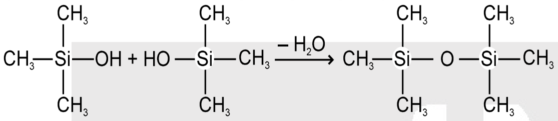
In this manner several molecules may combine to form a long chain polymer whose both the ends will be occupied by –OH groups. Such compounds are generally represented from the following formula.



$$HO-SiR_2-O-SiR_2-O-SiR_2-O-$$

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

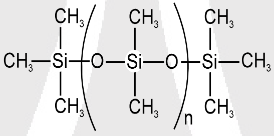
- ❍ Silicones can be prepared from the following types of compounds only.
  (i) R_3SiCl (ii) R_2SiCl_2 (iii) $RSiCl_3$
- ❍ Silicones from the hydrolysis of $(CH_3)_3$ SiCl
  $(CH_3)_3SiCl \xrightarrow{H_2O} (CH_3)_3Si(OH)$



$$CH_3-Si(CH_3)_2-OH + HO-Si(CH_3)_2-CH_3 \xrightarrow{-H_2O} CH_3-Si(CH_3)_2-O-Si(CH_3)_2-CH_3$$

- ❍ Silicones from the hydrolysis of a mixture of $(CH_3)_3$ SiCl & $(CH_3)_2$ $SiCl_2$

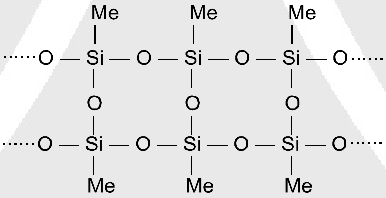
The dichloro derivative will form a long chain polymer as usual. But the growth of this polymer can be blocked at any stage by the hydrolysis product of mono-chloro derivative.



$$CH_3-Si(CH_3)_2-\left(O-Si(CH_3)_2-O\right)_n-Si(CH_3)_2-CH_3$$

- ❍ 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 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) $CO + H_2 \xrightarrow[420-670k,\ 300atm]{ZnO+Cu}$ ....

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

(c) $Na_2CO_3 + Si \longrightarrow$ .... + ...

Sol. (a) $CO + 2H_2 \xrightarrow[420-670k,\ 300atm]{ZnO+Cu} CH_3OH$

(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.

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

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 $[SiO_4]^{4-}$ units i.e., there is no sharing of corners with one another as shown is figure.

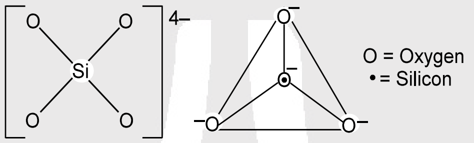


Figure : 2

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

(B) Pyrosilicate :

In these silicates two tetrahedral units are joined by sharing oxygen at one corner thereby giving $[Si_2O_7]^{6-}$ units.

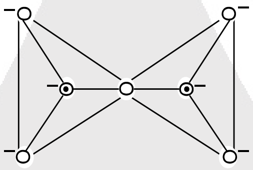


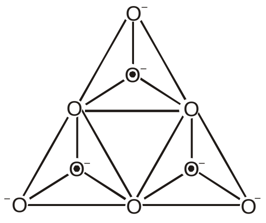
Figure : 3

e.g. Thorteveitite ($Sc_2Si_2O_7$), Hemimorphite ($Zn_3(Si_2O_7)\ Zn(OH)_2H_2O$)

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

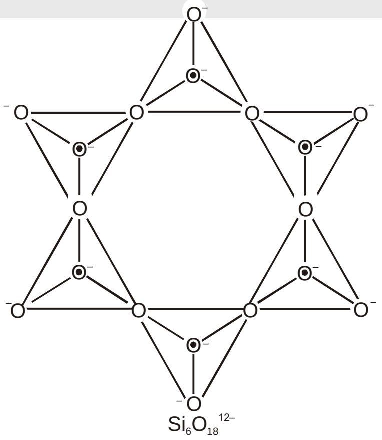
(C) Cyclic silicates :

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.



$Si_3O_9^{6-}$

Figure : 4



$Si_6O_{18}^{12-}$

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

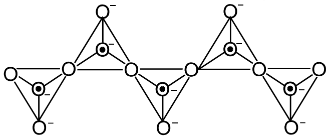


Figure : 6

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

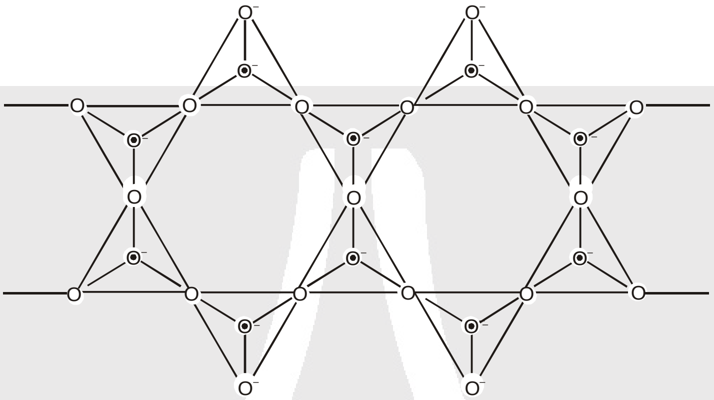


Figure : 7

e.g., Synthetic silicates (Li_2SiO_3, Na_2SiO_3), Spondumene ($LiAl(SiO_3)_2$), Enstatite ($MgSiO_3$), Diopside ($CaMg(SiO_3)_2$), Tremolite ($Ca_2Mg_5(Si_4O_{11})_2(OH)_2$), 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 $(Si_2O_5)_n^{2n-}$

e.g. Talc ($Mg(Si_2O_5)_2\ Mg(OH)_2$), Kaolin $Al_2(OH)_4(Si_2O_5)$

(F) Three dimensional silicates :

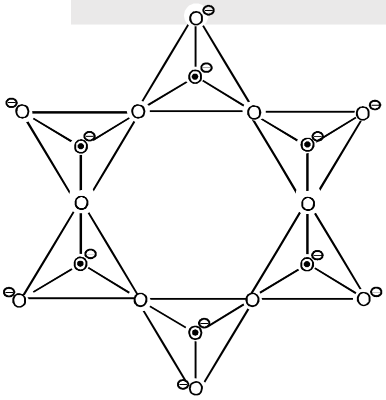
These silicates involve all four oxygen atom in sharing with adjacent SiO_4^{4-} tetrahedral units.

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

Solved Examples

Ex-11. Draw the structure of cyclic silicate containing $Si_6O_{18}^{12-}$ ion.

Sol.



$Si_6O_{18}^{12-}$

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.

Carborundum (SiC) :

Preparation : $SiO_2 + 3C \xrightarrow[2000^oC]{\text{electric furnace}} SiC + 2CO$

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.

$$SiC + 2NaOH + 2O_2 \xrightarrow{\Delta} Na_2SiO_3 + CO_2 + H_2O \; ; \qquad SiC + 4Cl_2 \xrightarrow{\Delta} SiCl_4 + CCl_4$$

- 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

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

Sol. $Ca_2B_6O_{11} + 4SO_2 + 11H_2O \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$

$2H_3BO_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O$; $B_2O_3 + 2Al \longrightarrow Al_2O_3 + 2B$

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 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 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.

MISCELLANEOUS SOLVED PROBLEMS (MSPS)

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.

$Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}$

Most stable ⟶ least stable

$Tl^{+} > In^{+} > Ga^{+} > Al^{+}$

2. If you have a mixture of CO and CO_2, 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; CO_2 is absorbed by $Ca(OH)_2$. The residual volume 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.

$$5CO + I_2O_5 \longrightarrow I_2 + 5CO_2$$

I_2 thus liberated is determined by titration with $Na_2S_2O_3$.

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$

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.

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

BF_3 is a colourless gas.

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

(a) iodine is treated with $SnCl_2$.

(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.

Sol. (a) $2SnCl_2 + I_2 \longrightarrow 2SnCl_2I_2 \longrightarrow SnCl_4 + SnI_4$

(b) $NaCl + NH_4OH + CO_2 \longrightarrow NaHCO_3 + NH_4Cl$

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

(d) $Sn + 10HNO_3(\text{dilute}) \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$

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 (X = Cl, 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.

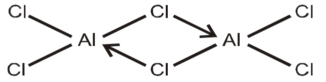
(e) Pb_3O_4 a double oxide, is obtained by heating lead (II) oxide in air.

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 (~ 600 g kJ) which is unlikely for the small B^{3+} 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 :** PbO_2 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)**

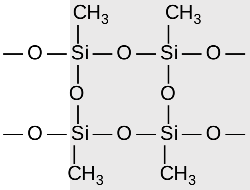
Sol. Both are correct statements and statement-2 is the correct explanation of statement-1.

7. Write the chemical equations to represent the following reactions.
(a) The oxidation of HCl (aq) to Cl_2 (g) by PbO_2.
(b) The disproportionation of SnO to Sn and SnO_2.

Sol. (a) $PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$ (b) $2SnO \longrightarrow Sn + SnO_2$

8. What will happen if we take Si (CH_3) Cl_3 as a starting material for the preparation of commercial silicon polymer ?

Sol. With $Si(CH_3)Cl_3$ the chain will grow in three places and we will get cross-linked silicon polymer as shown below :

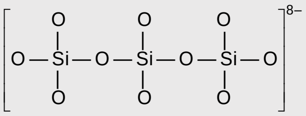


9. Give three properties of diamond.

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 Si_3O_{10}, 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, kinoite has formula $Ca_2Cu_2Si_3O_{10}.2H_2O$.

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.

$$CaC_2(s) + N_2(g) \xrightarrow{1373K} \underset{\text{Calcium cyanamide}}{CaCN_2(s)} + C(s)$$

(ii) BaC_2 reacts with N_2 to form barium cyanide

$$BaC_2(s) + N_2(g) \xrightarrow{\text{Heating}} \underset{\text{Barium cyanide}}{Ba(CN)_2\ (s)}$$

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

$CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$

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 alkalies?

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

Ans. **(D)**

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

$$2B + 6NaOH \xrightarrow{\text{fused}} 2Na_3BO_3 + 3H_2$$

Silicon and aluminium dissolved in both fused and aqueous alkalies.

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

Sol. $4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$

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 B_2H_5Cl.
(D) SiO_4^{4-} gets hydrolysed by acid or water and form $Si_2O_7^{6-}$.

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

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

$$B_2H_6 + 6Cl_2 \longrightarrow 2BCl_3 + 6HCl$$

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.

$$2BI_3 \xrightarrow[\text{Van Arkel method}]{\text{red hot W}} 2B + 3I_2$$

(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.

$$Sn(OH)_4 + 2OH^- \longrightarrow [Sn(OH)_6]^{2-}$$
$$Sn(OH)_4 + 4H^+ \longrightarrow Sn^{4+} + 4H_2O$$

(D) Hydroxide is amphoteric in nature.

$$Al(OH)_3 + OH^- \longrightarrow [Al(OH)_4]^-$$
$$Al(OH)_3 + 3H^+ \longrightarrow Al^{3+} + 3H_2O$$

Additional Problems for Self Practice (APSP)

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

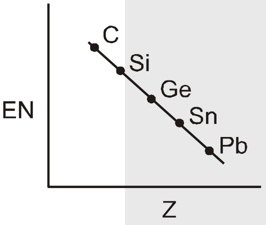
Max. Time : 1 Hr. **Max. Marks : 120**

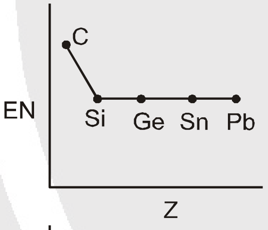
Important Instructions

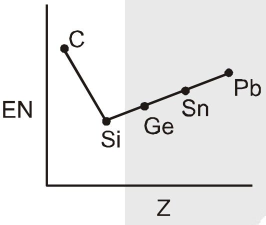
1. The test is of **1 hour** duration.
2. The Test Booklet consists of **30** questions. The maximum marks are **120.**
3. Each question is allotted **4 (four)** marks for correct response.
4. Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question. **¼ (one fourth)** marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
5. There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted accordingly as per instructions 4 above.

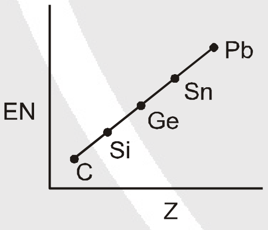
---

1. Which of the following is the correct graph for EN values of carbon family :

(1)


(2)


(3)


(4)


2.✍ Select the incorrect statement :
(1) Silicon does not form an allotrope like graphite because of its no tendency of multiple bond formation.
(2) Catenation tendency is greater in C than in Si.
(3) CO is stable in nature but SiO does not
(4) None of these

3. Which of the following statement about Si is correct.
(1) Si predominantly forms covalent componds with oxidation number as +4.
(2) Ionisation enthalpy of Si is more than that of carbon.
(3) Electron affinity of Si is less than that of carbon.
(4) Si can't show coordination number more than 4.

4.✍

$$\begin{tikzcd}
A + H_2 \arrow[r, "\text{Silent}", "\text{Electric discharge}"'] \arrow[d, "H_2O"] & B + C \arrow[d, "\text{Red heat}"] \\
H_3BO_3 + C & A + H_2
\end{tikzcd}$$

Identify correct statement.
(1) C is a weak lewis acid
(2) B is a weak lewis base
(3) C is a strong acid
(4) D reacts with NaOH to produce C

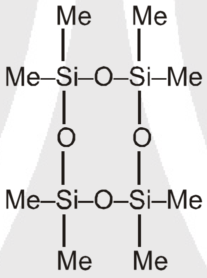
5.✍ $4BCl_3 + 3LiAlH_4 \longrightarrow A + 3AlCl_3 + 3\,LiCl$
When A reacts with NaOH it produces a colourless combustible gas and another compound 'B'. Select incorrect statement about 'B'.
(1) It aqueous solution turns red litmus blue
(2) It shows anionic hydrolysis
(3) It shows cationic hydrolysis
(4) It can also produce by reaction of boron with NaOH

6. When heating white lead then find out released gas (A) and (B)
$2PbCO_3.Pb(OH)_2 \xrightarrow{\Delta} Pb_3O_4 + (A) + (B) + H_2O$
(white lead)
(1) CO, O_2
(2) CO_2 , O_2
(3) CO_2, CH_4
(4) CO, CO_2

7. Amorphous boron is extracted from borax by following step
Borax $\xrightarrow{(A)} H_3BO_3 \xrightarrow{\text{Heat}} B_2O_3 \xrightarrow{(B)}$ Boron
Then (A) and (B) are :
(1) H_2SO_4, Al
(2) HCl, carbon
(3) H_2SO_4, Mg
(4) HCl, Fe

8. The role of addition of Me_3SiCl during the hydrolysis followed by conduction of Me_2SiCl_2 is.
(1) To catalyte the reaction.
(2) To terminate the chain and hence controlling the molecular weight.
(3) For obtaiming a proper cross linking.
(4) All of the above

9. Given type of silicones are called [P]



[P] is prepared by controlled hydrolysis of [Q]. [P] & [Q] are respectively.
(1) Linear silicone, CH_3SiCl_3
(2) branched silicone, $(CH_3)_3SiCl$
(3) Cyclic silicone, $(CH_3)_2SiCl_2$
(4) Cyclic silicone, CH_3SiCl_3

10. Which of the following is not a property of silicones ?
(1) They are combustible
(2) They are water - repellant
(3) They are polymeric liquids or solids
(4) Their viscosity does not change significaltly with rise in tamperature.

11. Tourmalene is a class of cyclosilicates with general formula.
(Ca, K, Na) (Al, Fe, Li, Mg, Mn)$_3$ (Al, Cr, Fe, V)$_6$ $(BO_3)_3$ (Si, Al, B)$_6O_{18}$ (OH, F)$_4$
Which of the following is not a correct example of tourmalene ?
(1) $CaAl_3Fe_6(BO_3)_3\ S_6O_{18}F_4$
(2) $Ca_2Li_3V_6(BO_3)_3\ Si_6O_{18}(OH)_4$
(3) $KMg_3Cr_6(BO_3)_3\ Si_6\ O_{18}\ F_4$
(4) $CaAl_9\ (BO_3)_3\ Si_6O_{18}\ (OH)_4$

12. The silicate anion in the mineral kinoite is a chain of three SiO_4 tetrahedra, that share corners with adjacent tetrahedra. The charge of the silicate anion is :
(1) –4
(2) –8
(3) –6
(4) –2

13.✍ The dehydration of malonic acid $CH_2(COOH)_2$ with P_4O_{10} gives :
(1) carbon monoxide
(2) carbon suboxide
(3) carbon dioxide
(4) all three

14.✍ Borax on heating with cobalt oxide forms a blue bead of :
(1) $Co(BO_2)_2$
(2) $CoBO_2$
(3) $Co_3(BO_3)_2$
(4) $Na_3Co(BO_3)_2$

15.✍ The dissolution of $Al(OH)_3$ by a solution of NaOH results in the formation of :
(1) $[Al(H_2O)_4(OH)]^{2+}$
(2) $[Al(H_2O)_2(OH)_4]^{-}$
(3) $[Al(H_2O)_3(OH)_3]$
(4) $[Al(H_2O)_6(OH)_3]$

16. Select the incorrect statement about the boron.
(1) Pure form of the elements are obtained by the reduction of BCl_3 with zinc at 900ºC.
(2) Crystalline boron is attacked only by hot concentrated oxidising agents.
(3) Amorphous boron and ammonia at white heat gives $(BN)_x$, a slippery white solid with a layer structure resembling that of graphite.
(4) Boron does form B^{3+} cation easily.

17. Aqueous solution containing 1 mol of borax reacts with 2 mol of acids. This is because of :
(1) formation of 2 mol of $B(OH)_3$ only
(2) formation of 2 mol of $[B(OH)_4]^-$ only
(3) formation of 1 mol each of $B(OH)_3$ and $[B(OH)_4]^-$
(4) formation of 2 mol each of $[B(OH)_4]^-$ and $B(OH)_3$, of which only $[B(OH)_4]^-$ reacts with acid

18.✍ Match List (Fuels) with List II (composition) and select the correct answer using the codes given below the lists :

List I (Fuels)	**List II (Composition)**
(1) Water gas	i. A mixture of CO and N_2
(2) Producer gas	ii. Methane
(3) Coal gas	iii. A mixture of CO and H_2
(4) Natural gas	iv. A mixture of CO, H_2, CH_4 and CO_2

	(1)	(2)	(3)	(4)		(1)	(2)	(3)	(4)
(1)	iii	i	iv	ii	(2)	iii	i	ii	iv
(3)	i	iii	iv	ii	(4)	iii	ii	iv	i

19.✍ Water transported through lead pipes becomes poisonous due to the formation of:
(1) PbO (2) PbO_2 (3) $Pb(OH)_2$ (4) Pb_3O_4

20. When steam is passed over red hot coke, the outgoing gas contains –
(1) Producer gas (2) Water gas (3) Coal gas (4) None of the above

21.✍ In BF_3, the B-F bond length is 1.30 Å, when BF_3 is allowed to be treated with Me_3N, it forms an adduct, $Me_3N \rightarrow BF_3$, The bond length of B-F in the adduct is :
(1) Greater than 1.30Å (2) Smaller than 1.30 Å
(3) Equal to 1.30 Å (4) None of these

22. Aluminium is extracted by the electrolysis of :
(1) alumina (2) bauxite
(3) molten cryolite. (4) alumina mixed with molten cryolite

23. A compound of boron X reacts at 200ºC temperature with NH_3 to give another compound Y which is called as inorganic benzene. The compound Y is a colourless liquid and is highly light sensitive. Its melting point is –57ºC. The compound X with excess of NH_3 and at a still higher temperature gives boron nitride $(BN)_n$. The compounds X and Y are respectively :
(1) BH_3 and B_2H_6 (2) $NaBH_4$ and C_6H_6 (3) B_2H_6 and $B_3N_3H_6$ (4) B_4C_3 and C_6H_6

24. For given processes, choose the correct order of purity of silicon obtained.

I. $SiO_2 + 2C \longrightarrow Si + 2CO$

II. $Si(pure) + 2Cl_2 \longrightarrow SiCl_4$

$SiCl_4 + 2Mg \longrightarrow Si + MgCl_2$

III. $Na_2[SiF_6] + 4Na \longrightarrow 6NaF + Si$ Zone refined Si
(1) I > II > III (2) III > II > I (3) I = II = III (4) II > I > III

25.✍ E represents an element belonging to boron family.

$$2E + 3X_2 \longrightarrow 2EX_3 \quad (X = F, Cl, Br, I)$$

(1) Oxidation state of E in all EX_3 is +3
(2) All EX_3 are predominantly ionic
(3) Tl does not form TlX_3 as Tl^{+1} is more stable than Tl^{+3}
(4) There exists some EX_3 for which E shows +1 oxidation state.

26.✍ E represents an element belonging to carbon family.

$$E + 2X_2 \longrightarrow EX_4 \qquad (X = F, Cl, Br, I)$$

(1) Stability of EX_4 decreases down the 14th group
(2) PbI_4 does not exist
(3) Ge & Pb forms EX_2 as well.
(4) All are correct

27. When Al is added to KOH solution
(1) No action takes place
(2) Oxygen is evolved
(3) Water is produced
(4) Hydrogen is evolved

28. Which of the following reactions lead to chemical inertness :
(1) Lead with dilute H_2SO_4
(2) Lead with conc. HCl
(3) Aluminium with oxygen
(4) All of above reactions

29. Which of the following statements regarding ortho boric acid (H_3BO_3) is false ?
(1) It acts as a weak monobasic acid
(2) It is soluble in hot water
(3) It has a planar structure
(4) It acts as a tribasic acid

30. Which of the following is a correct match :
I : Potash alum – $K_2SO_4.Al_2(SO_4)_3.24H_2O$
II : Chrome alum – $K_2SO_4.Cr_2(SO_4)_3.24H_2O$
III : Potash alum $K_2SO_4.Fe_2(SO_4)_3.24H_2O$
IV : Ammonium alum – $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$
(1) I, II, II & IV
(2) I, II & III
(3) I, II & IV
(4) Only II & IV

Practice Test-1 (IIT-JEE (Main Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Ans.										
Que.	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Ans.										
Que.	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
Ans.										

PART - II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

1. Carborundum is the commercial name of : **[NSEC-2000]**
(A) H_3PO_4
(B) $Ca(H_2PO_4)_2$
(C) Al_2O_3
(D) SiC

2. Which of the following is used in making printer's ink, black varnish and shoe polish ? **[NSEC-2000]**
(A) gas black
(B) carbon black
(C) bone black
(D) lamp black

3. Graphite is used in nuclear reactor : **[NSEC-2000]**
(A) for reducing the speed of neutrons
(B) as a fuel
(C) as a lubricant
(D) for lining the inner surface of the reactor which will work as an insulator.

4. Which Group IIIA element is expected to have physical and chemical properties least similar to other members of that group ? **[NSEC-2000]**
(A) Ga
(B) Al
(C) B
(D) Ln

5. Select the group of oxides that cannot be reduced by carbon to give the respective metals. **[NSEC-2000]**
(A) CaO, K_2O
(B) Fe_2O_3, ZnO
(C) Cu_2O, K_2O
(D) PbO, Fe_2O_3

6. $SnCl_2$ acts as a reducing agent because **[NSEC-2003]**
(A) $SnCl_2$ can accept electrons readily
(B) Sn^{3+} is more stable than Sn^{2+}
(C) Sn^{4+} is more stable than Sn^{2+}
(D) Sn^{2+} can be readily converted to metallic tin.

7. The acidic hydroxide is **[NSEC-2003]**
(A) $Ca(OH)_2$ (B) $Al(OH)_3$ (C) $B(OH)_3$ (D) TlOH.

8. Carbon dioxide is gaseous, while SiO_2 is solid because **[NSEC-2003]**
(A) CO_2 is a linear molecule, while SiO_2 is an angular one
(B) the van der Waal`s forces are very strong in SiO_2
(C) CO_2 is covalent, while SiO_2 is ionic
(D) unlike C, Si cannot form stable bonds with O, hence Si has to form a 3D lattice.

9. The metal that can be extracted from its oxide by reduction with carbon is **[NSEC-2003]**
(A) sodium (B) calcium (C) iron (D) aluminium.

10. Aluminium oxide exists in nature as gems with different colours. The reason for the difference in colour is that **[NSEC-2003]**
(A) the oxidation states of aluminium in these gems are different
(B) the extent of crystallinity in these gems is different
(C) the Al–O bonding is different in these gem structures
(D) there are different transition metal ions present as impurities in these gems.

11. White lead is **[NSEC-2004]**
(A) $PbCO_3$ (B) $PbCO_3$. PbO (C) $2PbCO_3.Pb(OH)_2$ (D) $2PbSO_4$.PbO.

12. Boron nitride is isoelectronic with **[NSEC-2004]**
(A) LiF (B) CO (C) $(CN)^-$ (D) AlN.

13. Which of the following carbides on treatment with water evolves methane? **[NSEC-2005]**
(A) CaC_2 (B) Al_4C_3 (C) B_4C (D) SiC.

14. In borax bead test, the borax used is $Na_2B_4O_7.10H_2O$. However, the species that is responsible for the test is **[NSEC-2006]**
(A) Na_3BO_3 (B) B_2O_3 (C) $Na[B(OH)_4]$ (D) $Na[BO)_4$.

15. Thallium forms stable chloride, TlCl, unlike Aluminum which forms chloride $AlCl_3$. This is because:
(A) inert pair effect makes Tl^+ more stable than Tl^{3+} **[NSEC-2007]**
(B) Tl is not a group 13 element.
(C) Tl-X bond is covalent while Al-Cl bond is ionic.
(D) Tl-X bond is ionic while Al-Cl bond is covalent.

16. Silicones are water repelling in nature because- **[NSEC-2007]**
(A) they have highly covalent Si–O–Si linkages.
(B) they have organic groups forming hydrophobic exterior.
(C) they are polymeric in nature.
(D) they have Si-H bonds as in hydrocarbons.

17. The correct balanced chemical equation for the reaction between Al and S is : **[NSEC-2009]**
(A) $16Al + 3S_8 \longrightarrow 8Al_2S_3$
(B) $12Al + S_8 \longrightarrow 4Al_3S_2$
(C) $8Al + S_8 \longrightarrow 8AlS$
(D) $4Al + S_8 \longrightarrow 4AlS_2$

18. The silicates formed from $[SiO_4]^{4-}$ tetrahedral units by sharing three oxygen atoms are : **[NSEC-2009]**
(A) Sheet silicates
(B) Pyrosilicates
(C) Linear Chain silicates
(D) Three dimensional silicates

19. The change in hybridization of aluminium when Al_2Cl_6 decomposes in the gas phase is : **[NSEC-2010]**
(A) $sp^2 \rightarrow sp^3$ (B) $sp \rightarrow sp^2$ (C) $sp \rightarrow sp^3$ (D) $sp^3 \rightarrow sp^2$

20. Pure germanium is an example of- **[NSEC-2010]**
(A) an intrinsic semiconductor
(B) a n-type semiconductor
(C) a p-type semiconductor
(D) a n-p type semiconductor

21. Lead dissolves most readily in dilute **[NSEC-2011]**
(A) acetic acid (B) sulphuric acid
(C) phosphoric acid (D) sodium hydroxide

22. The most abundant element in the earth's crust is : **[NSEC-2011]**
(A) aluminium (B) oxygen (C) silicon (D) iron

23. In chlorides, the common oxidation states of aluminium and thallium are +3 and +1 respectively because. **[NSEC-2017]**
(A) Tl–Cl bond is ionic and Al–Cl bond is covalent
(B) 6s electrons of Tl are bound more strongly than the 3s electron of Al
(C) Tl–Cl bond is stronger than Al–Cl bond
(D) 3s electrons of Al are bond strongly than the 6s electrons of Tl

24. Sn^{2+} compounds like SnO and $SnCl_2$ are well known reducing agents, while PbO_2 acts as an oxidizing agent. Which of the following statements support these reactivities? **[NSEC-2017]**
I. SnO is more stable than SnO_2 II. Sn^{4+} is more stable than Sn^{2+}
III. Pb^{4+} is more stable than Pb^{2+} IV. Pb^{2+} is more stable than Pb^{4+}
(A) I and III (B) I, III and IV (C) II and IV (D) I, II and IV

25. The gaseous product obtained on reaction of BF_3 with LiH is **[NSEC-2018]**
(A) HF (B) H_2 (C) B_2H_6 (D) F_2

26. Which one of the following is *not* used as a monomer for the synthesis of a high molecular weight silicone polymer ? **[NSEC-2018]**
(A) $MeSiCl_3$ (B) Me_2SiCl_2 (C) Me_3SiCl (D) $PbSiCl_3$

27. Which of the following is a strong oxidizing agent ? **[NSEC-2018]**
(A) $AlCl_3$ (B) $TlCl_3$ (C) NF_3 (D) PCl_3

28. During World War II, soldiers posted at high altitudes experienced crumbling of the tin buttons of their uniforms into a grey powder. This can be attributed to **[NSEC-2018]**
(A) oxidation of tin (B) interaction with nitrogen in the air at low pressure
(C) change in the crystal structure of tin (D) reaction of tin with water vapour in the air

PART - III : HIGH LEVEL PROBLEMS (HLP)

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Boron can be obtained by :
(A) reduction of B_2O_3 by C.
(B) reduction of BCl_3 with H_2 at 1270 K.
(C) thermal decomposition of boron halides at 1173 K.
(D) electrolytic reduction of KBF_4 in KF at 1073 K.

2. Aluminium can be prepared by :
(A) Electrolytic reduction of alumina in presence of Cryolite & fluorspar.
(B) Reduction of $AlCl_3$(s) by potassium amalgam.
(C) Reduction of aqueous solution of $Al_2(SO_4)_3$ (aq) by zinc metal.
(D) Thermal decomposition of aluminium oxide.

3. Which of the following can produce silicon.
(A) Reduction of SiO_2 by carbon (B) Reduction of SiO_2 by Silicon carbide
(C) Thermal decomposition of SiH_4 (D) Thermal decomposition of SiC

4.✍ Which of the following facts regarding boron and silicon is/are true ?
(A) Boron is used to make boron steel or boron carbide control rods for nuclear reactor.
(B) Boron and silicon form halides which are not hydrolysed.
(C) Boron and silicon react with magnesium to form magnesium boride and magnesium silicide which are decomposed by acids to give volatile borane and silane, respectively.
(D) Both boron and silicon react with alkali to form borates and silicates containing BO_3^{3-} and SiO_4^{4-} tetrahedral units, respectively.

5.✍ Which of the following statements are true.
(A) Red lead (Pb_3O_4) is diamagnetic and contains both Pb^{+2} and Pb^{+4} ions.
(B) Both PbO and PbO_2 are amphoteric in nature.
(C) Stannate and plumbate ions results in SnO_2 and PbO_2 with acidic solution.
(D) Concentrated Nitric acid oxidises red lead into lead dioxide.

6.✍ Which is/are incorrect about permutit or zeolite :
(A) By it both temporary and permanent hardness of water can not be removed.
(B) It formula is $Na_2Al_2Si_3O_8.xH_2O$
(C) It softens hard water by exchanging its Na^+ ions with Ca^{2+} and Mg^{2+} present in hard water.
(D) Exhausted zeolite can be regenerated by passing conc. solution of NaCl through it.

PART - IV : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr. **Max. Marks : 69**

Important Instructions

A. General :

1. The test is of 1 hour duration.
2. The Test Booklet consists of 23 questions. The maximum marks are 69.

B. Question Paper Format

3. Each part consists of five sections.
4. Section 1 contains 8 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
5. Section 2 contains 5 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
6. Section 3 contains 6 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
7. Section 4 contains 1 paragraphs each describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a partcular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
8. Section 5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

C. Marking Scheme

9. For each question in Section 1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (– 1) mark will be awarded.
10. For each question in Section 2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
11. For each question in Section 3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

SECTION-1 : (Only One option correct Type)

This section contains 8 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

1.✍ Which of the following statements is false.
(A) PbO, PbO_2 are amphoteric, CO is neutral and CO_2, SiO_2 are acidic.
(B) Carbon shows oxidation number from –4 to +4 in its various compounds.
(C) B_2O_3 is acidic, SnO is amphoteric and Ga_2O_3, GeO_2 are acidic.
(D) Boron is non metal, Ge, Ga are metalloids and Pb, Sn, In are metals.

2. Which of the following are correct matches :

Miniral	**Element present**
(i) Kernite	Boron
(ii) Carbonandum	Aluminium
(iii) Colemanite	Calcium
(iv) Mica	Silicon
(v) Carnalite	Boron

(A) (ii) ,(i) (B) (i) ,(ii) (iv) (C) (i) ,(iii), (iv) (D) none of these

3.
$$\begin{tikzcd} Si \arrow[r, "HNO_3/HF"', "\text{Conc, } \Delta"'] & (A) \arrow[r, "HF"] \arrow[d, "H_2O"] & (B) \\ & (B) + (C) & \end{tikzcd}$$

Select the correct option :

(A) (A) is SiF_4 (B) (B) is H_2SiF_6 (C) (C) is H_4SiO_4 (D) All of these

4. $NaBH_4 + I_2 \longrightarrow X\uparrow + Y\uparrow + 2NaI$

$X + C_2H_5OH \longrightarrow Y\uparrow + D$

$X + HCl \longrightarrow Y\uparrow + E$

D gives following colour with flame

(A) Red (B) Green (C) Blue (D) No colour

5. $B_2H_6 + NH_3 \xrightarrow[\text{Heating}]{\text{Slowly}} X \xrightarrow{\Delta} Y$

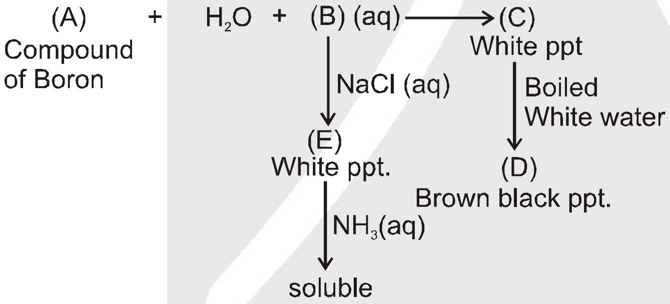
Which of the following around X is correct.

(A) X is ionic in nature, Hybridisation state of B in both cationic and anionic part is same.

(B) X is ionic in nature, hybridisation state of B in cationic and anionic part are differernt.

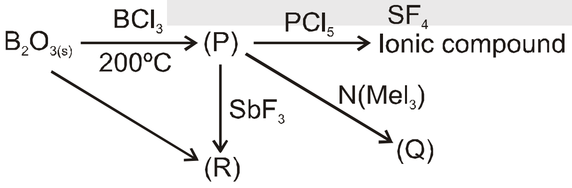
(C) Y is covalent and hybridisation state of all B is not same.

(D) Y is ionic and hybridisation state of all B are same.

6.


(C) & (D) are respectively.

(A) $Mn(BO_2)_2$, MnO_2 (B) $AgNO_2$, Ag_2O (C) $Cu(BO_2)_2$, CuO (D) none of these

7.


Select the correct option ?

	(P)	(Q)	(R)
(A)	B_2Cl_4	B_2F_2	$B_2Cl_4\ (NMe_3)_2$
(B)	B_4Cl_4	B_2F_4	$B_2Cl_4\ (MMe_3)_4$
(C)	B_2Cl_4	B_2F_4	$B_2Cl_4\ (NMe_3)_2$
(D)	B_4Cl_4	B_2F_6	$B_2Cl_2\ (NMe_3)_2$

8. Thortretite, $Sc_2Si_2O_7$ is :

(A) a orthosilicate (B) a pyrosilicate (C) a sheet silicate (D) a cyclic silicate

Section-2 : (One or More than one options correct Type)

This section contains 5 multipole choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

9. Which of the following are the ores of Boron
(A) Tincal (B) Kernite (C) Colemanite (D) Bauxite

10. When an inorganic compound X having electron dificient bonding (banana bonding) react with ammonia gas at certain temperature gives a compound (Y), isostructural with benzene. Compound (X) with ammonia at a high temperature produces a substance (Z).
(A) X is B_2H_6
(B) Y is $B_3N_3H_6$
(C) Z is hard substance
(D) compound X contain 3C-2e and 2C-2e bond.

11. Which of the following statement is/are correct ?
(A) All III A group elements forms trihalide
(B) Only Al react dirrelly with N_2 at high temperature and form AlN
(C) Al Passivated by concentrated HNO_3
(D) All IV A (14th) group elements forms trihalide

12.✍ Which of the following is/are true about silicones.
(A) Silicones contain repeated R_2SiO units
(B) $RSiCl_3$ gives a complex cross linked silicones
(C) $(CH_3)_2\ SiCl_2$ gives a chain silicone.
(D) When silicone undergo combustion, it form solid white powder as one of the products.

13. Cation exchanger zeolite $Na_{12}Al_{12}Si_{17}O_{58}.27H_2O$ can exchange cation with which of the following in aqueous solution ?
(A) $Mg(HCO_3)_2$ (B) K_2SO_4 (C) $CaCl_2$ (D) NH_4NO_3

Section-3 : (One Integer Value Correct Type.)

This section contains 6 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)

14.✍ How many of the following parameters/properties are greater for diamond as compared to graphite?
Denisty, Electrical resistivity, Thermal conductivity, Stability, % s-character for hybridised orbitals, Hardness, Bond angle, C–C (bond length), Standard enthalpy of formation.

15.✍ $Na_2B_4O_7 \xrightarrow{\Delta} NaBO_2 + B_2O_3$
$NaBO_2 + H_2O_2 + H_2O \longrightarrow$ compound A(aq)
The compound A the sum of oxidation states of all the oxygen atoms is X. Then the value of |X| is

16.✍ A Boron mineral have pentaborate anion whose molecular formula is $[B_5O_6(OH)_4]^-$. The number of B–O–B linkage present are.......

17.✍ Consider the following sequence of reactions :
$B_2O_3 + CaF_2 + H_2SO_4 \longrightarrow (A) + (B) + H_2O$
$(A) + LiAlH_4 \longrightarrow (C)(g) + (D) + LiF$
$(C) + H_2O \xrightarrow{\Delta} (D) + H_2\uparrow$
$(D) + Na_2CO_3 \longrightarrow (E) + NaBO_2 + CO_2\uparrow$
$(E) + NH_4Cl \longrightarrow (F) + B_2O_3 + NaCl + H_2O$
What is the empirical formula mass of compound (F) ?

18. How many of the following statatment are correct ?
(1) CF_4 can be prepared by reaction between SiC and F_2.
(2) In SiF_4 Si–F observed bond length is shorter than actual Si–F bond length
(3) $(C_2F_4)_n$ is known as PTFE.
(4) CCl_4 react with Anyelrony HF, gives Chloro Flouro carbon ($CCl_2\ F_2$)
(5) CCl_4 can hydrolysis under super heating conditious.
(6) Hydrolysis of SiF_4 is not complete of SiF_4 is partially hydrolysis.

19.✍ How many of the following may react with $SiCl_4$ to produce a non-polar product ?
NaH, CH_3MgCl, H_2O, $LiAlH_4$, $H_2SO_4(l)$, NH_3, Be

SECTION-4 : Comprehension Type (Only One options correct)

This section contains 1 paragraphs, each describing theory, experiments, data etc. 3 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

Paragraph For Questions 20 to 22

(i) P + C(carbon) + $Cl_2 \longrightarrow$ Q + CO↑ (ii) Q + $H_2O \longrightarrow$ R + HCl
(iii) BN + $H_2O \longrightarrow$ R + NH_3↑ (iv) Q + $LiAlH_4 \longrightarrow$ S + LiCl + $AlCl_3$
(v) S + $H_2 \longrightarrow$ R + H_2↑ (vi) S + NaH $\longrightarrow$ T
(P, Q, R, S and T do not represent their chemical symbols)

20. Compound Q has :
(I) zero dipole moment (II) a planar trigonal structure
(III) an electron deficient compound (IV) a Lewis base
Choose the correct code
(A) I, IV (B) I, II, IV (C) I, II, III (D) I, II, III, IV

21. Compound T is used as a/an :
(A) oxidising agent (B) complexing agent (C) bleaching agent (D) reducing agent

22. Compound S is :
(I) an odd-e^- compound (II) ($2C - 3e^-$)
(III) an electron deficient compound (IV) a sp^2 hybridized compound
Choose the correct code :
(A) III (B) I, III (C) II, III, IV (D) I, II, IV

SECTION-5 : Matching List Type (Only One options correct)

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

---

23. Choose the correct match :

	Silicates		**Number of oxygen atoms shared per tetrahedron**
(a)	Ortho silicate	**(p)**	4
(b)	Pyro silicate	**(q)**	1
(c)	Cyclic silicate	**(r)**	0
(d)	3-D silicate	**(s)**	2

(A) a – p , b – q, c – r, d – s (B) a – r , b – q, c – s, d – p
(C) a – s , b – r, c – q, d – p (D) a – r , b – s, c – q, d – p

Practice Test-2 ((IIT-JEE (ADVANCED Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Ans.										
Que.	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Ans.										
Que.	**21**	**22**	**23**							
Ans.										

APSP Answers

PART - I

1.	(2)	**2.**	(4)	**3.**	(1)	**4.**	(3)	**5.**	(3)
6.	(4)	**7.**	(3)	**8.**	(2)	**9.**	(3)	**10.**	(1)
11.	(1)	**12.**	(2)	**13.**	(2)	**14.**	(1)	**15.**	(2)
16.	(4)	**17.**	(4)	**18.**	(1)	**19.**	(3)	**20.**	(2)
21.	(1)	**22.**	(4)	**23.**	(3)	**24.**	(2)	**25.**	(4)
26.	(4)	**27.**	(4)	**28.**	(4)	**29.**	(4)	**30.**	(3)

PART - II

1.	(D)	**2.**	(B)	**3.**	(A)	**4.**	(C)	**5.**	(A)
6.	(C)	**7.**	(C)	**8.**	(D)	**9.**	(C)	**10.**	(D)
11.	(C)	**12.**	(A)	**13.**	(B)	**14.**	(D)	**15.**	(A)
16.	(B)	**17.**	(A)	**18.**	(A)	**19.**	(D)	**20.**	(A)
21.	(A)	**22.**	(B)	**23.**	(B)	**24.**	(C)	**25.**	(C)
26.	(C)	**27.**	(B)	**28.**	(C)				

PART - III

1.	(BCD)	**2.**	(AB)	**3.**	(ABC)	**4.**	(ACD)	**5.**	(ABC)
6.	(AB)								

PART - IV

1.	(C)	**2.**	(C)	**3.**	(D)	**4.**	(B)	**5.**	(A)
6.	(B)	**7.**	(C)	**8.**	(B)	**9.**	(ABC)	**10.**	(ABCD)
11.	(ABC)	**12.**	(ABCD)	**13.**	(AC)	**14.**	6	**15.**	24
16.	6	**17.**	25	**18.**	6	**19.**	4	**20.**	(C)
21.	(D)	**22.**	(A)	**23.**	(B)				

APSP Solutions

PART - I

1. The EN values of Carbon family are :

Element	C	Si	Ge	Sn	Pb
EN	2.5	1.8	1.8	1.8	1.9

4.

$$\begin{tikzcd} \underset{(A)}{BCl_3} + H_2 \arrow[r] \arrow[d, "H_2O"] & \underset{(B)}{B_2H_6} + \underset{(C)}{HCl} \arrow[d, "\text{Red heat}"] \\ H_3BO_3 + \underset{(C)}{HCl} & \underset{(D)}{B} + H_2 \end{tikzcd}$$

5. A is B_2H_6

$B_2H_6 + 6\,NaOH \longrightarrow 2\,Na_3BO_3 + 6\,H_2$

B is Na_3BO_3 a salt of SBWA.

6. $2PbCO_3.Pb(OH)_2 \xrightarrow{\Delta} Pb_3O_4 + CO + CO_2 + H_2O$

7. $Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$

$2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$

$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$

8. Being contaning one halogen atom it is ultilized for terminating the chain.

9. $4(CH_3)_2 + 8H_2O \rightarrow [P] + 8HCl + 4H_2O$

10. It is a fact.

11. You are not expected to have a prior knowledge of tournaline. It is simply a common-sense based question based on adding all the charges.

(1) $+2 + 3 \times 3 + x \times 6 - 3 \times 3 + 4 \times 6 - 2 \times 18 - 1 \times 4 = 6 \times -14 \neq 0$ for $x = +2$ or $+3$ (possible on Fe)

(2) $+2 \times 2 + 1 \times 3 + 3 \times 6 - 3 \times 3 + 6 \times 4 - 18 \times 2 - 1 \times 4 = 0$

It fits, so it is possible

(3) $+1 \times 1 + 2 \times 3 + 3 \times 6 - 3 \times 3 + 4 \times 6 - 2 \times 18 - 1 \times 4 = 0$

(4) $+2 \times 1 + 9 \times 3 - 3 \times 3 + 6 \times 4 - 2 \times 18 - 1 \times 4 = 0$

14. $CoO + B_2O_3 \longrightarrow Co(BO_2)_2$ (blue bead)

15. As $Al(OH)_3$ is amphoteric in nature and thus form $[Al(H_2O)_2(OH)_4]^-$.

16. Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form +3 ions.

17. $[B_4O_5(OH)_4]^{2-} + 5H_2O \rightleftharpoons 2B(OH)_3$ (weak acid) $+ 2[B(OH_4)]^-$ (salt)

22. Alumina is mixed with cryolite, in molten state which make alumina good conductor and lowers the fusion temperature also.

23. The reactions involved are

$\underset{(X)}{3B_2H_6} + 6NH_3 \longrightarrow \underset{(Y)}{2B_3N_3H_6} + 12H_2$; $B_2H_6 + NH_3(\text{excess}) \xrightarrow{\text{at higher temperature}} (BN)_n + H_2$

Y is borazole which is isosteric with benzene.

28. (1) $Pb + H_2SO_4 \longrightarrow PbSO_4$ (layer) $+ H_2\uparrow$
(2) Pb + Conc. $HCl \longrightarrow PbCl_2$(Coating) $+ H_2\uparrow$
(3) $2Al + 3/2\ O_2 \longrightarrow Al_2O_3(s)$

29. $B(OH)_3 + 2HOH \rightleftharpoons [B(OH)_4]^- + H_3O^+$.
In aqueous solution the boron completes its octet by accepting OH^- from water molecules. It therefore function as a weak monobasic lewis acid.

PART - III

1. (B) $2BCl_3 + 3H_2 \xrightarrow{1270\ K} 2B + 6HCl$

(C) $2BCl_3 \xrightarrow{1173\ K} B + 3Cl_2$

(D) $K^+ [BF_4]^- \overset{1073\ K}{\rightleftharpoons} K^+ + [BF_4]^-$

$[BF_4]^- + e^- \longrightarrow B + 2F_2$ (At anode)

$K^+ + e^- \longrightarrow K$ (At cathode)

3. $SiO_2 + 2\ C \xrightarrow[\Delta]{} Si + 2\ CO\uparrow$

$SiO_2 + SiC \xrightarrow[\Delta]{} Si + 2\ CO\uparrow$

$SiH_4 \xrightarrow[\Delta]{} Si + 2\ H_2\uparrow$

4. (B) $BCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} H_3BO_3 + 3HCl$; $SiCl_4 + 3H_2O \xrightarrow{\text{Hydrolysis}} H_2SiO_3 + 4HCl$

(C) $B + Mg \longrightarrow Mg_3B_2 + H_3PO_4 \longrightarrow$ Mix of borones $\xrightarrow{\Delta} B_2H_6$

(D) $2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2$; $Si + 4NaOH \longrightarrow Na_4SiO_4 + 2H_2$

6. (A) Both hardness can be removed by it.
(B) Zeolite : $Na_2Al_2Si_2O_8.xH_2O$

PART - IV

1. Statements (A), (B), (D) are true.
Statement (C) SnO_2 is amphoteric, Ga_2O_3 is amphoteric.

3.
$$\begin{tikzcd}
Si \arrow[r, "HNO_3/HF", "\text{Conc}, \Delta"'] & SiF_4 \arrow[r, "HF"] \arrow[d, "H_2O"] & H_2SiF_6 \\
& H_2SiF_6 + H_4SiO_4 &
\end{tikzcd}$$

4. X : B_2H_6 Y : H_2
$NaBH_4 + I_2 \longrightarrow B_2H_6\uparrow + H_2\uparrow + 2NaI$
$B_2H_6 + C_2H_5OH \longrightarrow H_2\uparrow + B(OC_2H_5)_3$
$B_2H_6 + HCl \longrightarrow H_2\uparrow + B_2H_5Cl$

5.
$$B_2X_6 + 2NH_3 \longrightarrow \underbrace{[H_3N \longrightarrow \overset{+}{B}H_2 \longleftarrow NH_3]\ [BH_4]^-}_{x}$$
$$\downarrow \Delta$$
$$\underset{y}{B_3N_3H_6}$$

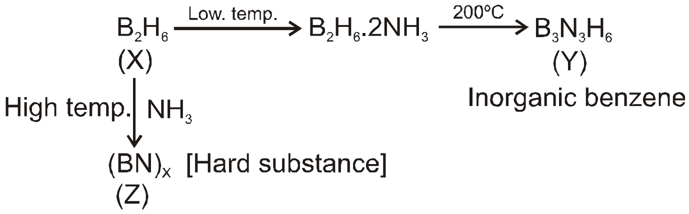
In X hybridisation state of both B is sp^3.

6. $Na_2B_4O_7 + AgNO_3(aq) + H_2O \longrightarrow AgBO_2\downarrow + NaNO_3 + H_3BO_3 \xrightarrow{\text{Boiled with water}} Ag_2O\downarrow + H_3BO_3$

8. $Sc_2Si_2O_7$ contains $Si_2O_7^{-6}$ units

9. Borax or Tincol : $Na_2B_4O_7.10H_2O$ Kernite : $Na_2B_4O_7.4H_2O$
Colemanite : $Ca_2B_6O_{11}$ Bauxite : $Al_2O_3.2H_2O$

10.



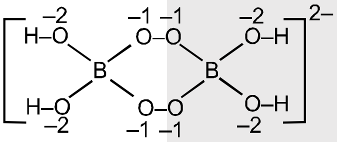
11. (A) All 13th group elements forms trihalide even Tl^+ as TlI_3 BX_3 $AlCl_3$, $GaCl_3$ $InCl_3$ Tl^+ $(I_3)^-$ tri iodide ion.
(B) At high temparature only Al react direelly with N_2 and gives AlN
(C) Conc. HNO_3 is oxidising agent, It forms an oxide layers on Al surface, this makes al passive towards conc. HNO_3.
(D) Except Pb, all 14th group element forms MX_4 tetrahalides.

12. Combustion of silicone produces solid silica.

13. Zeolites can exchange cation to release more soluble cation in aqueous solution.

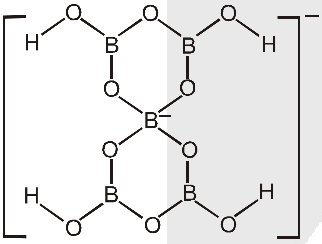
14. Density, Electrical resistivity, Thermal conductivity, Hardness, C – C (bond length), ΔH_f^o.

15. $2NaBO_2 + 2H_2O_2 + 6H_2O \longrightarrow Na_2[(OH)_2B(O–O)_2B(OH)_2]$ sodium peroxoborate



$X = [(–2) \times 4 + (–1) \times 4] = –12$ Hence $|X| = 12$

16.



No. of B–O–B linkages = 6

17. $B_2O_3 + CaF_2 + H_2SO_4 \longrightarrow \underset{(A)}{2BF_3\uparrow} + \underset{(B)}{3CaSO_4} + 3H_2O$

$4BF_3 + 3LiAlH_4 \longrightarrow \underset{(C)}{2B_2H_6\uparrow} + \underset{(D)}{3AlF_3} + 3LiF$

$\underset{(C)}{B_2H_6} + H_2O \xrightarrow{\Delta} \underset{(D)}{H_3BO_3} + H_2\uparrow$

$H_3BO_3 + Na_2CO_3 \longrightarrow \underset{(E)}{Na_2B_4O_7} + NaBO_2 + CO_2$

$\underset{(E)}{Na_2B_4O_7} + 2NH_4Cl \longrightarrow \underset{(F)}{2(BN)_x} + B_2O_3 + 2NaCl + 4H_2O$

Empirical formula mass of BN = 10.8 + 14 = 24.8 ≈ 25

18. (1) $SiC + F_2 \rightarrow SiF_4 + CF_4$ (2) Because of dπ–pπ back bonding in SiF_4.
(3) PTFE = Poly tetra flouro ethane (4) $CCl_4 + HF \rightarrow CCl_2F_2 + HCl$
(5) $CCl_4 \xrightarrow[\text{Super heating(steam)}]{+H_2O} COCl_2 + HCl$
(6) $SiF_4 + F^- \rightarrow [SiF_6]^{-2}$ (F^- form in Ist stape hydrolysis of Si F_4)

19. $4NaH + SiCl_4 \longrightarrow 4NaCl + SiH_4\uparrow$ (non-polar)
$CH_3MgCl + SiCl_4 \longrightarrow MgCl_2 + Si(CH_3)_4$ (non-polar)
$3H_2O + SiCl_4 \longrightarrow H_2SiO_3 + 4HCl$
$LiAlH_4 + SiCl_4 \longrightarrow LiCl + AlCl_3 + SiH_4$ (non-polar)
$H_2SO_4(\ell) + SiCl_4 \longrightarrow$ no reaction
$NH_3 + SiCl_4 \longrightarrow$ Polymeric substance
$2Be + SiCl_4 \longrightarrow 2BeCl_2 + Si$ (non-polar)

(20 to 22)
(i) B_2O_3 (P) + $3C + 3Cl_2 \longrightarrow 2BCl_3$ (Q) + $3CO\uparrow$
(ii) BCl_3 (Q) + $3H_2O \longrightarrow H_3BO_3$ (R) + $3HCl$
(iii) $BN + 3H_2O \longrightarrow H_3BO_3$ (R) + NH_3
(iv) $4BCl_3$ (Q) + $3LiAlH_4 \longrightarrow 2B_2H_6$ (S) + $3LiCl + 3AlCl_3$
(v) $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3$ (R) + $6H_2\uparrow$
(v) B_2H_6 (S) + $2NaH \longrightarrow 2NaBH_4$ (T)

Exercise-1

✍ **Marked questions are recommended for Revision.**

PART - I : SUBJECTIVE QUESTIONS

Section (A) : General facts about elements

A-1. Give the main ores of 3rd most abundant element?

A-2.✍ **(i)** How amorphous boron of low purity is obtained from borax ?
(ii) How ultrapure boron can be prepared from BI_3 or BCl_3 ?

A-3. Graphite is used as a lubricant. Explain?

Section (B) : Based on Periodic trends

B-1. Why does not boron form B^{3+} ions ?

B-2.✍ What do you understand by (a) inert pair effect. (b) catenation ?

Section (C) : Based on Chemical Bonding

C-1. Draw the Lewis dot structure of following :
(i) BF_3 (ii) $[B(OH)_4]^-$ (iii) CO_2 (iv) CO

C-2. Draw the Lewis dot structure of following :
(i) B_2H_6 (ii) Borax (iii) Al_2Cl_6 (iv) C_3O_2

C-3. Give the order of the bond length and bond strength of C–O bond in CO, CO_2, CO_3^{2-}.

C-4. Why B–F bond distance in BF_3 is shorter than theoratically expected value ?

C-5.✍ Identify the nature of following oxides :
CO, CO_2, B_2O_3, SiO_2, Al_2O_3, PbO

Section (D) : Properties of Elements

D-1. Which of the group-13 element exists in liquid state in nature?

D-2.✍ Write the reactions of B, Al, C and Si with air.

D-3. Give the reactions of group 13 & 14 elements with water ?

D-4.✍ Complete the following reaction :
(a) B + dil. $HNO_3 \longrightarrow$ (b) C + dil. $HNO_3 \longrightarrow$ (c) Si + dil. $HNO_3 \longrightarrow$

D-5.✍ Write balanced equation for the following :
Reaction of aluminium with aqueous sodium hydroxide. **[JEE 1997, 1]**

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

E-1.✍ A certain salt X, gives the following results.
(i) Its aqueous solution is alkaline to litmus.
(ii) It swells up to a glassy material Y on strong heating.
(iii) When concentrated H_2SO_4 is added to a hot solution of X, white crystal of an acid Z separates out.
Write equations for all the above reactions and identify X, Y and Z.

E-2.✍ (i) A white precipitate (B) is formed when a mineral (A) is boiled with Na_2CO_3 solution.
(ii) The precipitate is filtered and filtrate contains two compounds (C) and (D). The compound (C) is removed by crystallisation and when CO_2 is passed through the mother liquor left (D) changes to (C).
(iii) The compound (C) on strong heating gives two compounds (D) and (E).
(iv) (E) on heating with cobalt oxide produces blue coloured substances (F).
Identify (A) to (F) and gives chemical equations for the reactions at steps (i) to (iv).

E-3.✍ Which of the following can dissolve in HCl (hot or cold) ?
B_2O_3, CO_2, SiO_2, SnO_2, PbO_2

E-4.✍ A student of Resonance dissolves the oxides of all the group-13 & 14 elements in both HCl and NaOH one by one in chemistry lab. Oxides of which of the elements will dissolve in both?

E-5.✍ In steel industries, haematite ore (Fe_2O_3) is made to react with carbon monoxide (CO). Write the reaction involved.

Section (F) : Hydrides

F-1.✍ Arrange the following in increasing order of their thermal stability.
CH_4, SiH_4, GeH_4, SnH_4, PbH_4

F-2.✍ Give three reagents with which BF_3 reacts to give B_2H_6. Also write the reactions involved.

F-3.✍ What is inorganic benzene (borazole) and why is it so called ? How will you prepare Borazole from sodium borohydride (in three steps only)

F-4. When diborane is hydrolysed by water, a weak monobasic acid is produced which in the presence of sugar or glycerol becomes a strong monobasic acid. Give the reaction?

F-5.✍ (a) Diborane reacts with ethyl alcohol to release a gas X. What is X? Also write the reaction involved.
(b) Complete the following reaction : $B_2H_6 + CH_3COOH \longrightarrow$?

Section (G) : Halides

G-1.✍ Which of the following halide is a good oxidising agent?
$SnCl_2$, $PbCl_4$, $PbCl_2$

G-2. Complete the following reaction and identify compounds (A) and (B).

$$B(OH)_3 \xrightarrow[\text{Fusion}]{NH_4HF_2} (A) \xrightarrow[\Delta]{B_2O_3} (B)$$

G-3.✍ In a chemistry Lab of university of Berkeley it was observed that Aluminium, Alumina and $Al(OH)_3$ dissolved in dilute HCl in three separate tests to give a Lewis acid which absorbs water, truns moist blue litmus red, sublimes on heating and is predominantly covalent. Write all the reactions involved.

G-4. When BCl_3 is treated with water, it hydrolyses and forms $[B[OH]_4]^-$ only whereas $AlCl_3$ in acidified aqueous solution forms $[Al(H_2O)_6]^{3+}$ ion. Expain what is the hybridisation of boron and aluminium in these species ?

G-5.✍ Complete the following reactions :
(a) $BCl_3 + 3H–OH \longrightarrow$ (b) $4BF_3 + 3H–OH \longrightarrow$ (c) $COCl_2 + 2H–OH \longrightarrow$
(d) $COF_2 + H–OH \longrightarrow$ (e) $SiF_4 + 2H–OH \longrightarrow$ (f) $CF_4 + H–OH \longrightarrow$

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

H-1.✍ If the starting material for the manufacture of silicones is $RSiCl_3$, write the structure of the product formed.

H-2.✍ What are silicates ? How are they classified ?

H-3.✍ Write down hydrolysis of :
(i) alkyl substituted chlorosilane (ii) trialkyl chlorosilane

H-4.✍ Define alums and give their general formula. What are some of its important uses ?

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : General facts about elements

A-1. Which one of the following is most abundant in the earth's crust?
(A) B (B) Al (C) Ga (D) In

A-2. Which is not the property of diamond ?
(A) It is insoluble in all solvents
(B) It is oxidised with a mixture of $K_2Cr_2O_7$ and H_2SO_4 at 200ºC
(C) Being hardest, it is used as an abrasive for sharpening hard tools.
(D) $\Delta_f H^{\ominus}$ value of diamond is 1.90 kJ mol^{-1}.

A-3.✍ Relatively most inert form of carbon is :
(A) diamond (B) graphite (C) coal (D) charcoal

Section (B) : Based on Periodic trends

B-1. The decrease in stability of higher oxidation state in p–block with increasing atomic number is due to :
(A) increase in bond energy as going down the group.
(B) the reluctance of s-sub shell electrons to participate in the chemical bonding.
(C) both are correct.
(D) Noble gas configuration achieved by lower oxidation state.

B-2. Carbon and silicon belong to (IV) group. The maximum coordination number of carbon in commonly occurring compounds is 4, whereas that of silicon is 6. This is due to :
(A) Large size of silicon (B) More electropositive nature of silicon
(C) Availability of low lying d-orbitals in silicon (D) Both (A) and (B)

Section (C) : Based on Chemical Bonding

C-1. Sum of the lone pair of electron on central atom of following species is:
BF_3, CF_4, SiF_4
(A) 0 (B) 1 (C) 2 (D) 3

C-2.✍ In diborane the two H—B—H angles are nearly :
(A) 60º, 120º (B) 97º, 120º (C) 95º, 150º (D) 120º, 180º

C-3.✍ Choose the correct option regarding bond enthalpy of following :

	Column-A [bond]		**Column-B [bond enthalpy (KJ/mol)]**
(a)	C – C	(p)	240
(b)	Si – Si	(q)	260
(c)	Ge – Ge	(r)	297
(d)	Sn – Sn	(s)	348

(A) (a – p) ; (b – q) ; (c – r) ; (d – s) (B) (a – s) ; (b – r) ; (c – q) ; (d – p)
(C) (a – p) ; (b – r) ; (c – q) ; (d – s) (D) (a – r) ; (b – s) ; (c – q) ; (d – p)

C-4. Select the correct option regarding the bond strength of $C^{14}O^{16}$, $C^{12}O^{16}$, $C^{14}O^{18}$.
(A) $C^{14}O^{18} > C^{14}O^{16} > C^{12}O^{16}$ (B) $C^{14}O^{18} < C^{14}O^{16} < C^{12}O^{16}$
(C) $C^{14}O^{18} > C^{14}O^{16} < C^{12}O^{16}$ (D) $C^{14}O^{18} < C^{14}O^{16} > C^{12}O^{16}$

C-5.✍ The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence :
(A) $PbX_2 < SnX_2 < GeX_2 < SiX_2$ (B) $GeX_2 < SiX_2 < SnX_2 < PbX_2$
(C) $SiX_2 < GeX_2 < PbX_2 < SnX_2$ (D) $SiX_2 < GeX_2 < SnX_2 < PbX_2$

C-6. When borax is dissolved in water :
(A) $B(OH)_3$ is formed only (B) $[B(OH)_4]^-$ is formed only
(C) both $B(OH)_3$ and $[B(OH)_4]^-$ are formed (D) $[B_3O_3(OH)_4]^-$ is formed only

C-7.✍ Which of the following is acidic in nature?
(A) $Be(OH)_2$ (B) $Mg(OH)_2$ (C) $Al(OH)_3$ (D) $B(OH)_3$

C-8. Boric acid is polymeric due to :
(A) its acidic nature (B) the presence of hydrogen bonds
(C) its monobasic nature (D) its geometry

Section (D) : Properties of Elements

D-1. Thermodynamically the most stable form of carbon is :
(A) diamond (B) graphite (C) fullerenes (D) coal

D-2. Amorphous boron on burning in air forms :
(A) $B(OH)_3$ (B) Mixture of B_2O_3 and BN
(C) Only B_2O_3 (D) Only BN

D-3. Aluminium is more reactive than iron. But aluminium is less easily corroded than iron because:
(A) aluminium is a noble metal
(B) oxygen forms a protective oxide layer on aluminium surface
(C) iron unergoes reaction easily with water
(D) iron forms both mono and divalent ions

D-4.✍ Hot concentrated HNO_3 converts graphite into :
(A) graphite oxide (B) benzene hexacarboxylic acid
(C) both (A) and (B) (D) none of the above

D-5. Silicon reacts with hot solution of NaOH forming :
(A) $Si(OH)_4$ (B) $Si(OH)_2$ (C) SiO_2 (D) Na_2SiO_3

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

E-1.✍ Borax is prepared by treating colemanite with :
(A) $NaNO_3$ (B) NaCl (C) Na_2CO_3 (D) $NaHCO_3$

E-2. In the following reaction, $B(OH)_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+$
(A) $B(OH)_3$ is a tribasic acid. (B) $B(OH)_3$ is a monoacidic Lewis base.
(C) $B(OH)_3$ is a monobasic Lewis acid. (D) $B(OH)_3$ is amphoteric.

E-3. On the addition of mineral acid to an aqueous solution of borax, the compound formed is :
(A) borodihydride (B) orthoboric acid (C) metaboric acid (D) pyroboric acid

E-4.✍ Which of the following oxides will dissolve in H_2SO_4 ?
(A) B_2O_3 (B) Al_2O_3 (C) CO_2 (D) SiO_2

E-5.✍ Borax on heating with cobalt oxide forms a blue bead of :
(A) $Co(BO_2)_2$ (B) $CoBO_2$ (C) $Co_3(BO_3)_2$ (D) $Na_3Co(BO_3)_2$

E-6.✍ $B(OH)_3 + NaOH \rightleftharpoons Na[B(OH)_4]$
How can this reaction be made to proceed in forwared direction ?
(A) Addition of cis - 1,2-diol (B) Addition of boron
(C) Addition of trans-1,2-diol (D) Addition of Na_2HPO_4

E-7. Silica reacts with magnesium to form a magnesium compound (X). (X) reacts with dilute HCl and form (Y), (Y) is :
(A) MgO (B) $MgCl_2$ (C) MgSiO (D) $SiCl_4$

E-8.✍ Consider the following conversions :
$S_1 : H_3BO_3 \xrightarrow{100^\circ C} HBO_2 \xrightarrow{\text{Red heat}} B_2O_3$
$S_2 : \text{Borax} + 2HCl \longrightarrow 4H_3BO_3 + 2NaCl + 5H_2O$
$S_3 : \text{Colamanite} + 2Na_2CO_3 \longrightarrow 2CaCO_3 \downarrow + \text{Boarx} + 2NaBO_2$
$S_4 : \text{Borax} + H_2O \rightleftharpoons 2NaOH + 4H_3BO_3 + 3H_2O$
and arrange in the order of True/False :
(A) T T F F (B) T F T F (C) F T T F (D) T T T F

Section (F) : Hydrides

F-1.✍ Which one is not a borane ?
(A) B_5H_9 (B) B_5H_{10} (C) B_5H_{11} (D) B_6H_{10}

F-2.✍ In reaction, $BF_3 + 3LiBH_4 \rightarrow 3LiF + X$; X is :
(A) B_4H_{10} (B) B_2H_6 (C) BH_3 (D) B_3H_8

F-3. $B(s) \xrightarrow{(Z)} X \xrightarrow{LiH} Y + LiBF_4$
Which of the statements is true for the above sequence of reactions ?
(A) Z is hydrogen (B) Y is $LiBH_4$
(C) Z and Y are F_2 and B_2H_6 respectively (D) Z is potassium hydroxide

F-4.✍ The product obtained in the reaction of diborane with excess of ammonia at low temperature is :
(A) $B_2H_6 . NH_3$ (B) $B_2H_6 . 2NH_3$ (C) $(BN)_x$ (D) Borazine

F-5.✍ Which of the following will give symmetric cleavage of diborane :
(A) NH_3 (B) $N(CH_3)_3$ (C) $CH_3–NH_2$ (D) $(CH_2)_2NH$

F-6.✍ Diborane reacts with water to form :
(A) HBO_2 (B) H_3BO_3 (C) $H_3BO_3 + H_2$ (D) H_2

Section (G) : Halides

G-1.✍ Which one of the following compound is a gas (at 0°C) :
(A) BF_3 (B) BCl_3 (C) BBr_3 (D) BI_3

G-2. Al_2O_3 can be converted to anhydrous $AlCl_3$ by heating :
(A) hydrated Al_2O_3 with Cl_2 gas (B) Al_2O_3 with aqueous HCl
(C) Al_2O_3 with NaCl in solid state (D) a mixture of Al_2O_3 and carbon in dry Cl_2 gas

G-3.✍ Consider the following statements :
S_1 : Silicon halides can be prepared by heating wither Si or SiC with the appropriate halogen.
S_2 : Carbon halides are not hydrolysed under normal conditions because they have no d-orbitals.
S_3 : Silicon halides are readily hydrolysed by water to give silicic acid $[Si(OH)_4]$.
(A) T F T (B) F F T (C) T F F (D) T T T

G-4. Aqueous solution of potash alum is:
(A) alkaline (B) acidic (C) neutral (D) soapy

G-5. CCl_4 is inert towards hydrolysis but $SiCl_4$ is readily hydrolysed because
(A) carbon cannot expand its octet but silicon can expand its octet
(B) ionisation potential of carbon is higher than silicon
(C) carbon forms double and triple bonds
(D) electronegativity of carbon is higher than that of silicon

G-6. PbF_4, $PbCl_4$ exists but $PbBr_4$ and PbI_4 do not exist because of :
(A) Large size of $Bi^–$ and $I^–$ (B) Strong oxidising character of Pb^{+4}
(C) Shpong reducing character of Pb^{+4} (D) Low electro negativity of $Br^–$ and $I^–$

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

H-1.✍ Which silicon compound is used in machinery (with moving parts) in a manner similar to the use of an allotrope of carbon (crystalline) which possesses properties of both a covalent network solid and a molecular solid ?
(A) Silica gel (B) Zeolite (C) Silicone (D) Silane

H-2.✍ Silicone resins are made by :
(A) dissolving a mixture of $PhSiCl_3$ and $(Ph)_2SiCl_2$ in toluene and then hydrolysis with water.
(B) hydrolysing a mixture of $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$.
(C) hydrolysis of $(CH_3)_2SiCl_2$
(D) none

H-3.✍ Me_2SiCl_2 on hydrolysis will produce :
(A) $Me_2Si(OH)_2$ (B) $Me_2Si{=}O$ (C) $-\!\![O-(Me)_2Si-]_n$ (D) $Me_2SiClOH$

H-4. Which of the following anions is present in the simple single chain structure of silicate?
(A) $SiO_4^{4–}$ (B) $Si_2O_7^{6–}$ (C) $(Si_2O_5^{2–})_n$ (D) $(SiO_3^{2–})_n$

H-5.✍ The structural unit present in pyrosillicates is :
(A) $Si_3O_9^{6-}$ (B) SiO_4^{4-} (C) $Si_2O_7^{6-}$ (D) $(Si_2O_5^{2-})_n$

H-6. Select the incorrect statement.
(A) Silicones are hydrophobic in nature.
(B) Si–O–Si linkages are moisture sensitive.
(C) SnI_4 is an orange solid on account of high polarization of I^-.
(D) Silicones are resistant to most chemicals due to high strength of the Si–C bond and stable silica like structure of Si–O–Si–O–Si.

H-7. Select incorrect statement :
(A) Red lead is Pb_3O_4
(B) $(Me)_2SiCl_2$ on hydrolysis and then on subsequent intermolecular condensation gives cross linked silicones.
(C) SiO_4^{4-} on hydrolysis with water or acid produces $Si_2O_7^{6-}$
(D) None

PART - III : MATCH THE COLUMN

1.✍ Match the reactions listed in column-I with characteristic(s) / type of reactions listed in column-II.

	Column-I		**Column-II**
(A)	$BBr_3 + H_2 \longrightarrow B$	(p)	Borax bead test
(B)	$Na_2B_4O_7.10\ H_2O + CuSO_4 \longrightarrow Cu(BO_2)_2$	(q)	Reduction
(C)	$AlCl_3 + H_2O \longrightarrow HCl$	(r)	White fumes
(D)	$Cr_2O_3 + Al \longrightarrow Cr$	(s)	Hydrolysis

2. Match the reactions listed in column-I with characteristic(s) / type of reactions listed in column-II.

	Column-I		**Column-II**
(A)	$Al_2(C_2)_3 + H_2O \longrightarrow$	(p)	One of the products contains both σ and π bonds
(B)	$CH_2(COOH)_2 + P_4O_{10} \longrightarrow$	(q)	Hydrolysis
(C)	$CH_3SiCl_3 + H_2O \longrightarrow$	(r)	Dehydration
(D)	$SnCl_2.2H_2O \xrightarrow{\text{on standing}}$	(s)	complex crosslinked polymer

Exercise-2

✍ **Marked questions are recommended for Revision.**

PART - I : ONLY ONE OPTION CORRECT TYPE

1. Bauxite ($Al_2O_3.2H_2O$) and Aluminosilicate both are ores of aluminium. Bauxite is found on earth but not on Mars whereas Aluminosilicate is found on earth as well as Mars. Possible reason is :
(A) No human colony on Mars. (B) No tropical rain forests on Mars.
(C) No need of bauxite on Mars (D) Closeness of earth to sun.

2. Isolation of boron in very high purity is extremely difficult because of :
(A) Strong tendency of boron to acquire electron rich atoms such as C, N or O
(B) High melting point of boron (2180ºC)
(C) Tremendous affinity of liquid Boron towards oxygen.
(D) All of these

3.

$$\begin{tikzcd}
SiO_2 + C \arrow[r] & Si + CO \arrow[d, "Cl_2"] & \\
& SiCl_4 \arrow[r, "Mg"] & Si + MgCl_2
\end{tikzcd}$$

Identify true statement :

(A) Excess of SiO_2 should not be used in above process
(B) Produced Si is highly pure
(C) Cl_2 & Mg are oxidising agents.
(D) All of these

4. Reaction I : 3C (natural graphite) + $SiO_2 \xrightarrow{\text{heat}} \underset{+2CO}{SiC} \xrightarrow{2500^\circ C}$ C(graphite) + Si

Reaction II : $SiO_2 + 2C \longrightarrow Si + 2CO$

Reaction I is used in production of synthetic graphite, whereas Reaction II is used in extraction of silicon.
(A) Reaction I – SiO_2 in excess ; Reaction II – SiO_2 in excess
(B) Reaction I – C in excess ; Reaction II – SiO_2 in excess
(C) Reaction I – SiO_2 in excess ; Reaction II – C in excess
(D) It does not matter.

5.✍ Catenation tendency in group 14 is :
(A) C >> Si > Ge ≈ Pb due to bond energies C–H > Si–H > Ge–H > Sn–H
(B) C >> Si > Ge ≈ Sn > Pb due to bond energies C–C > Si–C > Ge–C > Sn–C
(C) C ≈ Si ≈ Ge ≈ Sn ≈ Pb due to bond energies C–H > Si–H > Ge–H > Sn–H
(D) C >> Si > Ge ≈ Sn > Pb due to bond energies C–C > Si–Si > Ge–Ge > Sn–Sn

6.✍ Given the order of density : Diamond > Graphite > Fullerene C_{60} ; choose the correct order for C–C bond length
(Consider larger bond length if there are two different bond lengths)
(A) Diamond < graphite < fullerene (C_{60})   (B) Diamond > graphite > fullerene (C_{60})
(C) Diamond > fullerene (C_{60}) > graphite   (D) Diamond < fullerene (C_{60}) < graphite

7. An element E = {B, C, Si, Ge}, predict E on the basic of given conditions :
I : Powdered E reacts with O_2 to form an oxide.
II : Oxide formed in I reacts with NaOH
III : E reacts with steam on red heat forming two gaseous products, which can be used as a fuel.
E can be :
(A) B   (B) C   (C) Si   (D) Ge

8.✍ In limited supply of oxygen C & Si are allowed to react at sufficiently high temperatures in separate vessels, favourable products are :
(A) CO_2 & SiO_2 (B) CO, CO_2, SiO & SiO_2
(C) CO, CO_2 & SiO_2 (D) CO & SiO_2

9.✍ $2E + N_2 \longrightarrow 2EN$ (very hard substance)
$EN + H_2O \longrightarrow$ Acid + pungent smelling gas
Acid is :
(A) HNO_3 (B) H_3BO_3 (C) HNO_2 (D) can be A & B

10.✍ Aluminium vessels should not be washed with materials containing washing soda because :
(A) washing soda is expensive
(B) washing soda is easily decomposed
(C) washing soda reacts with aluminium to form soluble aluminate
(D) washing soda reacts with aluminium to form insoluble aluminium oxide

11.✍ Aqueous ammonia is used as a precipitating reagent for Al^{3+} ions as $Al(OH)_3$ rather than aqueous NaOH, because :
(A) NH_4^+ is a weak base   (B) NaOH is a very strong base
(C) NaOH forms soluble $[Al(OH)_4]^-$ ions   (D) NaOH forms $[Al(OH)_2]^+$ ions

12.✍ Borax is used as a buffer since :
(A) Its aqueous solution contains both the weak acid and its salt
(B) Its aqueous solution contains H_3BO_3, which is a weak acid
(C) Its aqueous solution contains equal amount of strong acid and its salt
(D) statement that borax is a buffer, is wrong

13. Which of the following compound is obtained on heating potassium ferrocyanide with concentrated H_2SO_4?

(A) CO_2 (B) CO (C) C_2H_2 (D) $(CN)_2$

14. $B(OH)_3 + NaOH \longrightarrow Na[B(OH)_4]$ (aq).

Then addition of which of the following shifts the reaction in the backward direction.

(A) Glycerol (B) Mannitol (C) Catechol (D) Ethanol

15.✍ $H_3BO_3(s) + \text{aq. } NaOH \xrightarrow{\Delta} (X)$

$H_3BO_3(s) + \text{molten } NaOH \xrightarrow{\Delta} (Y)$

Compound (X) & (Y) are respectively,

(A) Na_3BO_3 , Na_3B (B) Na_3BO_3 , $NaBO_2$

(C) $Na[B(OH)_4]$, Na_3BO_3 (D) Na_3BO_3 , $Na[B(OH)_4]$

16. When a solution of sodium hydroxide is added in excess to the solution of potash alum, we obtain :

(A) a white precipitate (B) bluish white precipitate

(C) a clear solution (D) a crystalline mass

17.✍

$$\begin{tikzcd}
\text{Boron} \arrow[r, "z"] & x \arrow[r, "LiH"] & y(g) + LiBF_4 \arrow[ll, bend left, "w"]
\end{tikzcd}$$

true statement is :

(A) z is least reactive non-metal (B) w is cooling

(C) y is electron deficient (D) All of these

18. $B_2H_6 + NH_3 \longrightarrow \text{Addition compound } (X) \xrightarrow{450\ K} Y + Z\ (g)$

In the above sequence Y and Z are respectively :

(A) borazine, H_2 (B) boron, H_2 (C) boron nitride, H_2 (D) borazine and hydrogen

19.✍ Borazine and benzene show striking similarities in their properties. This led to a labeling of borazine as 'inorganic benzene'. However, in contrast to benzene, borazine readily undergoes addition reactions. The appropriate reason for this difference is :

(A) Alternate arrangement of B and N atoms in the hexagonal ring.

(B) Due to the difference in electronegativity between boron and nitrogen, the cloud (electron density) is more localised on the nitrogen atoms.

(C) Aromatic π-clouds of electron density are delocalised over all of the ring atoms.

(D) Net dipole moment of borazine molecule is non-zero.

20. ($SnCl_4$) stannic chloride hydrolyses in dilute solution as per given reaction

$SnCl_4 + 4H_2O \longrightarrow [Sn(OH)_4] + 4HCl$

Hydrolysis can be repressed by adding compound "A".

$SnCl_4 + A \longrightarrow B$

B can be :

(A) $Sn(OH)_4$ (B) $SnCl_2$ (C) H_2SnCl_6 (D) $Sn(OH)Cl$

21.✍ Amphoteric oxide (X) + 3C + $Cl_2 \longrightarrow$ Poisonous gas + anhydrous chloride (Y)

Hydrated chloride $\xrightarrow{\Delta}$ Z

Element forming 'Y' other than 'Cl' reacts with concentrated HCl but leads to passivation with conc. HNO_3. Select the correct option.

(A) X = Z and Y on reacting with LiH forms strong oxidising agent

(B) X = Z and Y on reacting with LiH forms strong reducing agent

(C) X $\neq$ Z and Y is used as a catalyst in Friedel crafts reaction

(D) X $\neq$ Z and Y on reacting with LiH forms strong oxidising agent

22.✍ BF_3 on hydrolysis forms :

(A) H_3BO_3 (B) HBF_4 (C) both (A) and (B) (D) none of these

23.✍ Preparation of organosilicones from $SiCl_4$ involves substitution in first step:
$SiCl_4 + xRMgCl \longrightarrow (R)_x\,SiCl_{4-x} + xMgCl_2$
Values of 'x' to obtain chain terminating & chain multiplication parts of chain silicone produced are respectively:
(A) 1 & 2 (B) 2 & 1 (C) 2 & 3 (D) 3 & 2

24.✍ To get the silicone $R_3Si–(OSiR_2)_n–SiR_3$ having 4Si–O–Si linkage, the unit taken is
(A) 4 unit of R_2SiCl_2 and 2 unit of R_3SiCl (B) 2 unit of R_2SiCl_2 and 2 unit of R_3SiCl
(C) 3 unit of R_2SiCl_2 and 2 unit of R_3SiCl (D) 3 unit of R_3SiCl and 2 unit R_2SiCl_2

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. How many of the following statements are correct regarding allotropes of carbon :
(a) Graphite is not a good conductor of electricity in perpendicular direction of layers at ordinary temperatures.
(b) Coke is the impure form of carbon.
(c) Anthracite is the purest form of Carbon.
(d) Buckminister fullerene contains 12 five membered rings and 20 six-membered rings.
(e) Diamond is a good conductor of Heat.
(f) Graphite is diamagnetic in nature.
(g) Graphite is thermodynamically more stable than diamond

2. For Boron family (B, $A\ell$, Ga, In and $T\ell$)
x : Number of elements which are solid at 40ºC.
y : Period number of element which has greater ionization energy than element just above and below it in periodic table.
z : Period number of most abundant element of group 13.
Report your answer x + 2y + 3z

3.✍ Consider a prototypical fullerene, C_{60}.
Let, a = Number of 5-membered rings
b = Number of 6-membered rings
c = Number of π-bonds in C_{60}
Find the value of (3a – 2b + c)

4. Central atom may exhibit sp^3 hybridisation in how many of the following species :
(a) CO_2 (b) Graphite (c) Diamond (d) CO
(e) H_3BO_3 (aq) (f) Zeolites (Si-central) (g) Silicones (Si) (h) Chlorosilane (Si)
(i) Borax (Boron) (j) Al_2Cl_6 (k) B_2H_6 (l) SiO_2 (solid)
(m) H_2CO_3 (n) $COCl_2$ (o) CH_4 (p) CCl_4

5.✍ The number of oxygen atoms in borax which do not form $p\pi$-$p\pi$ back bond is :

6. $B + \underset{\text{conc.}}{HNO_3} \longrightarrow \underset{\text{white solid}}{(A)} + \underset{\text{brown gas}}{(B)}$
How many of the following statements are correct regarding products (A) & (B) ?
(1) (A) can be prepared by reacting borax with dilute acids.
(2) (A) is a weak monobasic lewis acid.
(3) (A) behaves like a strong electrolyte when dissolved in water.
(4) (A) can be prepared by reacting colemanite ,SO_2 & H_2O.
(5) (B) is paramagnetic in nature.
(6) (B) is a mixed anhydride.
(7) (B) does not forms a dimer
(8) (B) reacts with NaOH(aq) undergoing disproportionation.
(9) Bond angle about central atom is greater in (A) than in (B). (Assume atom forming maximum number of bonds as central atom)

7.✍ Which of the following salts are amphoteric in nature.
(a) PbO (b) PbO_2 (c) SnO (d) SnO_2 (e) Al_2O_3
(f) ZnO (g) BeO (h) Ga_2O_3 (i) B_2O_3

8.✍ How many compounds show amphoteric nature amongst following
(a) B_2O_3 (b) Tl_2O_3 (c) $Al(OH)_3$ (d) $Ga(OH)_3$ (e) Al_2O_3 (f) Ga_2O_3
(g) $NaAlO_2$ (h) $Sr(OH)_2$ (i) Cr_2O_3

9.✍ How many compounds form acidic solution when dissolved in water
(a) H_3PO_4 (b) H_3BO_3 (c) $Na_2B_4O_7.10H_2O$ (d) $H_3P_3O_9$
(e) $Ba(OH)_2$ $Ca(OH)_2$ (f) PbO, CO

10.✍ $Mg + B \longrightarrow Mg_xB_y \xrightarrow{HCl} \text{Diborane}$
Report your answer as (x + y).

11. No of compounds producing gas on hydrolysis (with H_2O) is ....
(a) Al_4C_3 (b) BaC_2 (c) Mg_2C_3 (d) SiC (e) B_2H_6 (f) Fe_3C

12.✍ How many of the given statements are true for potash Alum.
(1) It is a white crystalline solid
(2) It swells up on heating
(3) It imparts a golden yellow colour to the bunsen flame
(4) An aqueous solution of the above gives a white precipitate with $BaCl_2$ solution soluble only in concentrated sulphuric acid.

13. What is the number of oxygen atoms which are shared between tetrahedrons in $Si_3O_9^{6-}$.

14. In benitonite ($BaTiSi_3O_9$) number of O atoms shared persilicate tetrahedron is.......

15.✍ The overall charge present on the cyclic silicate anion $[Si_6O_{18}]^{-n}$ is "–n". Report n.

16. The silicate anion in the mineral kinoite is a chain of three SiO_4 tetrahedron that share corners with adjaent tetrathedra. The mineral also contains Ca^{2+} and Cu^{2+} and As^{2+} ion & water molecule in a 1 : 1 : 1 ratio. The formula of mineral is $Ca_2Cu_2Si_3O_n$. $2H_2O$. Give value of 'n"

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1.✍ Select the correct statement(s).
(A) The graphite is diamagnetic and diamond is paramagnetic in nature.
(B) Graphite acts as a metallic conductor along the layers of carbon atoms
(C) Graphite is less denser than diamond
(D) C_{60} is called as Buckminster fullerene

2.✍ One of the most fascinating developments in Modern chemistry has been the synthesis of Buckminister fullerene, C_{60}. Identify the correct options about C_{60}.
(A) It consists of fused 5 and 6 membered carbon rings.
(B) All atoms are not-equivalent.
(C) All bonds are not-equivalent
(D) C–C bond lengths at the fusion of two 6-membered rings are shorter with the C–C bond length at the fusion of 5 and 6-membered rings.

3. Graphite and diamond will behave differently in which of the following reactions ?
(A) Burning in sufficient air (B) Reaction with hot conc. HNO_3
(C) Reaction with F_2 (D) Reaction with NaOH (aq.)

4.✍ Which statement(s) is/are correct ?
(A) Al acts as a reducing agent
(B) Al does not significantly react with steam even at high temperatures.
(C) Al forms a number of alloys with other metals
(D) Al is ionic in all its compounds

5. What products are expected from the reaction between colemanite powder and sodium carbonate solution, when they are heated ?
(A) $CaCO_3$ (B) $Na_2B_4O_7$ (C) $NaBO_2$ (D) CaO

6. Which of the following forms tetrahydridoborates
(A) (Li) (B) Na (C) NH_4^+ (D) Ag^+

7.✍ Borax bead test is given by :
(A) An aluminium salt (B) A cobalt salt (C) A copper (II) salt (D) A nickel salt

8.✍ Carbon monoxide is prepared by :
(A) heating formic acid with conc. H_2SO_4
(B) heating potassium ferrocyanide with conc H_2SO_4
(C) heating malonic acid with P_4O_{10}
(D) hydrolysis of Mg_2C_3

9.✍ The hydroxide of which metal ion is soluble in excess of sodium hydroxide solution :
(A) Fe^{3+} (B) Cr^{3+} (C) Sn^{2+} (D) Cu^{2+}

10. Which of the following statements is true ?
(A) Small amines such as NH_3, CH_3NH_2 and $(CH_3)_2NH$ give unsymmetrical cleavage of diborane.
(B) Boron hydrides can't be used as high energy fuels.
(C) Boron hydrides are readily hydrolysed.
(D) Borazine hydrolyses to NH_3 and boric acid at elevated temperature, if heated with water.

11.✍ Diborane undergoes unsymmetrical cleavage reactions with :
(A) dimethylamine
(B) ammonia at low temperature
(C) methylamine
(D) carbon dioxide

12. Select correct statements :
(A) B_2H_6 is stronger lewis acid than BF_3
(B) BF_3 is weaker lewis acid than BCl_3
(C) B_2H_6 is not a lewis acid
(D) In B_2H_6 all 'H' atoms are not in the same plane

13.✍ Which of the following statement(s) is/are correct ?
(A) The oxide, B_2O_3 and $B(OH)_3$ are acidic
(B) The halides of B (except BF_3) and Si are hydrolysed.
(C) The hydrides of B and Si are volatile, spontaneously flammable and readily hydrolysed.
(D) Aluminium hydride is a polymer, $(AlH_3)_n$.

14. Which of the following species exists :
(A) $[BF_6]^{3-}$ (B) $[AlF_6]^{3-}$ (C) $[GaF_6]^{3-}$ (D) $[InF_6]^{3-}$

15.✍ Which is/are true in case of BF_3 ?
(A) It is volatile liquid even at room temperature
(B) It is Lewis acid
(C) It has planar geometry
(D) It forms adduct with NH_3

16. Which of the following statements about anhydrous aluminium chloride is/are incorrect ?
(A) It exists as $AlCl_3$ molecule in gaseous phase
(B) It is a strong Lewis base
(C) It sublimes at 100°C under vacuum
(D) It is not easily hydrolysed

17.✍ Which of following are correct.
(A) B_2H_6 is non-planar.
(B) B_2H_6 undergo symmetrical cleavage with PF_3 , CO and $(C_2H_5)_3N$
(C) B_2H_6 undergo unsymmetrical cleavage with NH_3, CH_3NH_2, $(CH_3)_2NH$.
(D) $B_2H_6(s)$, Ga_2Me_6 , Al_2Me_6 have two type of bonds (2C–2e bond as well as 3C–2e bond)

18.✍ A complex cross-linked polymer (silicone) is formed by
(A) hydrolysis of $(CH_3)_3SiCl$.
(B) hydrolysis of a mixture of $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$
(C) hydrolysis of CH_3SiCl_3
(D) hydrolysis of $SiCl_4$.

19.✍ Select the correct statement (s)
(A) CH_3 $SiCl_3$ undergoes hydrolysis followed by inter molecular elimination of water to form a complex cross - linked polymer (i.e silicone)
(B) Silicone fluids are thermally stable.
(C) In sheet silicate, three oxygen atoms of each tetrahedral are shared with adjacent SiO_4^{4-} tetrahedrals.
(D) Silica is attacked by HF and NaOH.

PART - IV : COMPREHENSION

Read the following comprehension carefully and answer the questions

Comprehension # 1

Compound (A) on reaction with iodine in the solvent diglyme gives a hydride (B) and hydrogen gas. The product (B) is instantly hydrolysed by water or aqueous alkali forming compound (C) and liberating hydrogen gas. The compound (C) in aqueous solution behaves as a weak mono basic acid. But in presence of certain organic polyhydroxy compound behaves as a strong monobasic acid. The hydride (B) in air catches fire spontaneously forming oxide which gives coloured beads with transition metal compounds.

1. Which of the following statement is correct for the product (C) ?
(A) It is an odd electron molecule. (B) It in water acts as proton donor.
(C) It in solid state have hydrogen bonding. (D) It is a useful primary standard for titrating against acids.

2. Aqueous solution of product (C) can be titrated against sodium hydroxide using phenolphthalein indicator only in presence of :
(A) cis-1, 2 diol (B) trans-1, 2 diol (C) borax (D) Na_2HPO_4

3. Which of the following statement is correct for hydride (B) ?
(A) One mole of it react with two moles of HCl.
(B) It reacts with excess of ammonia at low temperature to form an ionic compound.
(C) One mole of it reacts with one mole of trimethylamine.
(D) It reacts with methyl alcohol to form a trimethyl compound liberating oxygen gas.

Comprehension # 2

All the boron trihalides except BI_3 may be prepared by direct reaction between the elements. Boron trihalides consist of trigonal - planar BX_3 molecules. Unlike the halides of the other elements in the group they are monomeric in the gas, liquid and solid states, BF_3 and BCl_3 are gases, BBr_3 is a volatile liquid and BI_3 is a solid. Boron trihalides are Lewis acids because they form simple Lewis complexes with suitable bases, as in the reaction :

$$BF_3(g) + :NH_3(g) \longrightarrow F_3B\text{–}NH_3(s)$$

However, boron chlorides, bromides and iodides are susceptible (sensitive) to protolysis by mild proton sources such as water, alcohols and even amines; for example BCl_3 undergoes rapid hydrolysis:

$$BCl_3(g) + 3H_2O(\ell) \longrightarrow B(OH)_3(aq) + 3HCl(aq)$$

It is supposed that the first step in the above reaction is the formation of the complex $Cl_3B \longleftarrow OH_2$ which then eliminates HCl and reacts further with water.

4. Which of the following is the best order of Lewis acid strength of BF_3, BCl_3 and BBr_3 ?
(A) $BF_3 > BCl_3 > BBr_3$ (B) $BF_3 = BCl_3 = BBr_3$ (C) $BF_3 < BCl_3 < BBr_3$ (D) $BBr_3 > BF_3 > BCl_3$

5. Which of the following is the correct prediction about observed B–X bond length, in BX_3 molecules ?
(A) B–F bond length in BF_3 is found to be less than theoretical value because the electronegativity values of B(2.04) and F(4.0) suggest the bond to be ionic and hence the attraction between oppositely charged ions must decrease the bond length
(B) BF_3 and $[BF_4]^-$ have equal B–F bond length
(C) The decrease in the B–F bond length in BF_3 is due to delocalised p_π–p_π bonding between vacant '2p' orbital of B and filled '2p' orbital of F.
(D) The correct B–X bond length order is B–F > B–Cl > B–Br > B–I

6. Which is correct about the hydrolysis of BX_3 ?
(A) All BX_3 undergo hydrolysis to produce $B(OH)_3$ (aq) and HX(aq).
(B) BF_3 does not undergo complete hydrolysis due to formation of HBF_4.
(C) BBr_3 does not undergo hydrolysis at all because it cannot form H–bonds with water.
(D) All the above are correct

7. Which of the following reactions is incorrect ?
(A) $BF_3(g) + F^-(aq) \longrightarrow [BF_4]^-(aq)$
(B) $BCl_3(g) + 3EtOH(\ell) \longrightarrow B(OEt)_3(\ell) + 3HCl(g)$
(C) $BBr_3(\ell) + F_3BN(CH_3)_3(s) \longrightarrow BF_3(g) + Br_3BN(CH_3)_3(s)$
(D) $BCl_3(g) + 2\,C_5H_5N(\ell) \longrightarrow Cl_3B(C_5H_5N)_2(s)$
(excess)

Comprehension # 3

The small size and high charge of Al^{3+} ion gives it a high charge density which is responsible for its tendency to show (a) covalency in its compounds in the gaseous state (b) high hydration energy which stabilizes its compounds in solution, and (c) high lattice energy of its compounds in the solid state. Thus aluminium can forms both covalent and ionic bond.

Like halides of boron, halides of aluminium do not show back bonding because of increase in size of aluminium. Actually aluminium atoms complete their octets by forming dimers. Thus chloride and bromide of aluminium exist as dimers, both in the vapour state and in polar-solvents like benzene while the corresponding boron halides exists as monomer. In boron trihalides the extent of back bonding decreases with increase in size of halogens and thus lewis acid character increases. All BX_3 are hydrolysed by water but BF_3 shows a different behaviour.

8. The dimeric structure of aluminium chloride disappears when :
(A) it dissolves in water
(B) it reacts with donor molecules like R_3N
(C) it dissolves in benzene
(D) (A) & (B) both

9. Which one of the following statements is correct ?
(A) All boron trihalides are hydrolysed to boric acid.
(B) Anhydrous aluminium chloride is an ionic compound
(C) Aluminium halides make up the electron deficiency by bridging with halide or alkyl groups
(D) None of these

10. Which of the following statements about anhydrous aluminium chloride is correct?
(A) It is an ionic compound.
(B) It is not easily hydrolysed.
(C) It sublimes at 100°C under vaccum.
(D) It is a strong lewis base.

11. Which of the following reaction is incorrect ?
(A) $BF_3(g) + F^-(aq) \longrightarrow BF_4^-$
(B) $BF_3(g) + 2H_2O \longrightarrow [BF_3OH]^- + H_3O^+$
(C) $BCl_3(g) + 3EtOH(\ell) \longrightarrow B(Oet)_3(\ell) + 3HCl$
(D) $BCl_3(g) + 2C_5H_5N(\ell) \longrightarrow Cl_3B(C_5H_5N)_2(s)$

Comprehension # 4

Answer Q.12, Q.13 and Q.14 by appropriately matching the information given in the three columns of the following table.

Silicates are metal derivatives of silicic acid H_4SiO_4 or $Si(OH)_4$. Silicates are formed by heating metal oxide or carbonate with silica. A silicate in general has Si–O bond & possesses a complex network solid having silicate ion $[SiO_4]^{-4}$ as the basic structural unit. In silicates each silicon atom is bounded with four oxide ions tetrahedrally. There are following types of silicates
(1) Orthosilicates (2) Pyrosilicates (3) Cyclic silicates (4) Chain silicates
(5) 2-D Sheet silicates (6) 3-D sheet silicates

Column-1 (General formula of basic unit)		**Column-2 (No. of oxygen atom shared per, SiO_4^{-4} unit)**		**Column-3 Examples**	
(I)	SiO_4^{-4}	(i)	1	(P)	Kaolin $Al_2(OH)_4(Si_2O_5)$
(II)	$(SiO_3^{2-})_n$	(ii)	None	(Q)	Benitonite $BaTiSi_3O_9$
(III)	$Si_2O_7^{-6}$	(iii)	3	(R)	Phenacite Be_2SiO_4
(IV)	$(Si_2O_5)_n^{2n-}$	(iv)	2	(S)	Thortveitite $Sc_2Si_2O_7$

12. For the orthosilicates only correct combination is -
(A) (I) (ii) (R) (B) (II) (iii) (S) (C) (III) (iv) (R) (D) (IV) (i) (P)

13. For the cyclic or ring silicates only correct combination is-
(A) (III) (iii) (R) (B) (II) (iv) (Q) (C) (IV) (i) (S) (D) (II) (i) (P)

14. For the two dimensional sheet silicates only correct combination is :
(A) (III) (iii) (Q) (B) (IV) (ii) (R) (C) (IV) (iii) (P) (D) (II), (i) (S)

Exercise-3

*** Marked Questions may have more than one correct option.**

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

Section (A) : Group 13th

1. Write the chemical reactions associated with the 'borax bead test' of cobalt (II) oxide. **[JEE 2000 (M), 3/100]**

2. Compound (X) on reduction with $LiAlH_4$ gives a hydride (Y) containing 21.72% hydrogen along with other products. The compound (Y) reacts with air explosively resulting in boron trioxide. Identify (X) and (Y). Give balanced reactions involved in the formation of (Y) and its reaction with air. Draw structure of (Y). **[JEE 2001 (M), 5/100]**

3. Write balanced equations for the reactions of the following compounds with water: **[JEE 2002 (M), 5/60]**
(i) Al_4C_3 (ii) CaNCN (iii) BF_3 (iv) NCl_3 (v) XeF_4

4. How is boron obtained from borax ? Give chemical equations with reaction conditions. Write the structure of B_2H_6 and its reaction with HCl. **[JEE 2002 (M), 5/60]**

5. H_3BO_3 is : **[JEE 2003 (S), 3/84]**
(A) monobasic and weak Lewis acid (B) monobasic and weak Bronsted acid
(C) monobasic and strong Lewis acid (D) tribasic and weak Bronsted acid

6. $B(OH)_3 + NaOH \longrightarrow Na[B(OH)_4]$ (aq).
Then addition of which of the following proceeds the reaction in the forward direction? **[JEE 2006, 3/184]**
(A) Cis-1, 2 diol (B) Trans 1, 2 diol (C) Borax (D) Na_2HPO_4

7. Match the reactions in Column-I with nature of the reactions in column-II. **[JEE 2006, 6/184]**

	Column-I		**Column-II**
(A)	$Bi^{3+} \rightarrow (BiO)^{+}$	(p)	Heat
(B)	$[AlO_2]^{-} \rightarrow Al(OH)_3$	(q)	Hydrolysis
(C)	$SiO_4^{4-} \rightarrow Si_2O_7^{-6}$	(r)	Acidification
(D)	$(B_4O_7^{2-}) \rightarrow [B(OH)_3]$	(s)	Dilution by water

8. **Statement-1 :** In water, orthoboric acid behaves as a weak monobasic acid, **because**
Statement-2 : In water, orthoboric acid acts as a proton donor. **[JEE 2007, 3/162]**
(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

9. The coordination number of Al in the crystalline state of $AlCl_3$ is : **[JEE 2009, 4/160]**

10.* The correct statement(s) for orthoboric acid is/are **[JEE(Advanced) 2014, 3/120]**
(A) It behaves as a weak acid in water due to self ionization.
(B) Acidity of its aqueous solution increases upon addition of ethylene glycol.
(C) It has a three dimensional structure due to hydrogen bonding.
(D) It is weak electrolyte in water.

11. The increasing order of atomic radii of the following Group 13 elements is:
[JEE(Advanced) 2016, 3/124]
(A) Al < Ga < In < Tl (B) Ga < Al < In < Tl (C) Al < In < Ga < Tl (D) Al < Ga < Tl < In

12.* The crystalline form of borax has **[JEE(Advanced) 2016, 4/124]**
(A) tetranuclear $[B_4O_5(OH)_4]^{2-}$ unit
(B) all boron atoms in the same plane
(C) equal number of sp^2 and sp^3 hybridized boron atoms
(D) one terminal hydroxide per boron atom

13.* Among the following, the correct statement(s) is(are) **[JEE(Advanced) 2017, 4/122]**
(A) $Al(CH_3)_3$ has the three-centre two-electron bonds in its dimeric structure.
(B) The Lewis acidity of BCl_3 is greater than that of $AlCl_3$
(C) $AlCl_3$ has the three-centre two-electron bonds in its dimeric structure.
(D) BH_3 has the three-centre two-electron bonds in its dimeric structure.

Section (B) : Group 14th

14. Starting from $SiCl_4$, prepare the following in steps not exceeding the number given in parenthesis (give reactions only) : **[JEE 2001 (M), 5/100]**
(i) Silicon (1) (ii) Linear silicone containing methyl groups (4) (iii) Na_2SiO_3 (3)

15. $(Me)_2\,SiCl_2$ on hydrolysis will produce : **[JEE 2003 (S), 3/84]**
(A) $(Me)_2\,Si(OH)_2$ (B) $(Me)_2\,Si = O$
(C) $-[-O-(Me)_2\,Si-O-]_n-$ (D) $Me_2SiCl(OH)$

16. Which of the following silicate is formed when three oxygen atoms of $[SiO_4]^{4-}$ tetrahedral units are shared ? **[JEE 2005 (S), 3/84]**
(A) Sheet silicate (B) Pyrosilicate
(C) Three dimensional silicate (D) linear chain silicate

17. **Statement-1 :** Pb^{+4} compounds are stronger oxidizing agents than Sn^{4+} compounds
Statement-2 : The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to 'inert pair effect'. **[JEE 2008, 3/162]**
(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

18.* In the reaction, $2\mathbf{X} + B_2H_6 \longrightarrow [BH_2(\mathbf{X})_2]^+ [BH_4]^-$
the amine(s) **X** is(are) : **[JEE 2009, 4/160]**
(A) NH_3 (B) CH_3NH_2 (C) $(CH_3)_2NH$ (D) $(CH_3)_3N$

19. The value of n in the molecular formula $Be_nAl_2Si_6O_{18}$ is : **[JEE 2010, 3/163]**

20. Three moles of B_2H_6 are completely reacted with methanol. The number of moles of boron containing product formed is : **[JEE-Advance 2015, 4/168]**

21. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are : **[JEE-Advance 2015, 4/168]**
(A) CH_3SiCl_3 and $Si(CH_3)_4$ (B) $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$
(C) $(CH_3)SiCl_2$ and CH_3SiCl_3 (D) $SiCl_4$ and $(CH_3)_3SiCl$

22.* Among the following, the correct statement(s) is(are) **[JEE-Advance 2017, 4/122]**
(A) $Al(CH_3)_3$ has the three-centre two-electron bonds in its dimeric structure.
(B) The Lewis acidity of BCl_3 is greater than that of $AlCl_3$
(C) $AlCl_3$ has the three-centre two-electron bonds in its dimeric structure.
(D) BH_3 has the three-centre two-electron bonds in its dimeric structure.

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

JEE(MAIN) OFFLINE PROBLEMS

1. Aluminium is extracted by the electrolysis of : **[AIEEE 2002, 3/225]**
(1) alumina (2) bauxite
(3) molten cryolite. (4) alumina mixed with molten cryolite

2. Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behaviour is that graphite : **[AIEEE 2003, 3/225]**
(1) is a non-crystalline substance.
(2) is an allotropic form of diamond.
(3) has molecules of variable molecular masses like polymers.
(4) has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interplate bonds.

3. The soldiers of Napolean army while at Alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White metallic tin buttons got converted to grey powder. This transformation is related to : **[AIEEE 2004, 3/225]**
(1) a change in the crystalline structure of tin.
(2) an interaction with nitrogen of the air at very low temperature.
(3) a change in the partial pressure of oxygen in the air.
(4) an interaction with water vapour contained in the humid air.

4. Aluminium chloride exists as dimer, Al_2Cl_6 in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives : **[AIEEE 2004, 3/225]**
(1) $[Al(OH)_6]^{3-} + 3HCl$ (2) $[Al(H_2O)_6]^{3+} + 3Cl^-$ (3) $Al^{3+} + 3Cl^-$ (4) $Al_2O_3 + 6HCl$

5. In silicon dioxide : **[AIEEE 2005, 3/225]**
(1) there are double bonds between silicon and oxygen atoms.
(2) silicon atom is bonded to two oxygen atoms.
(3) each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms.
(4) each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms.

6. Heating an aqueous solution of aluminium chloride to dryness will give : **[AIEEE 2005, 3/225]**

(1) $Al(OH)Cl_2$ (2) Al_2O_3 (3) Al_2Cl_6 (4) $AlCl_3$

7. The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence : **[AIEEE 2007, 3/120]**

(1) $GeX_2 < SiX_2 < SnX_2 < PbX_2$
(2) $SiX_2 < GeX_2 < PbX_2 < SnX_2$
(3) $SiX_2 < GeX_2 < SnX_2 < PbX_2$
(4) $PbX_2 < SnX_2 < GeX_2 < SiX_2$

8. In context with the industrial preparation of hydrogen from water gas ($CO + H_2$), which of the following is the correct statement ? **[AIEEE 2008, 3/105]**

(1) CO is removed by absorption in aqueous Cu_2Cl_2 Solution.
(2) H_2 is removed through occlusion with Pd.
(3) CO is oxidized to CO_2 with steam in the presence of a catalyst, followed by absorption of CO_2 in alkali.
(4) CO and H_2 are fractionally separated using differences in their densities.

9. Among the following substituted silanes, the one which will give rise to cross linked silicone polymer on hydrolysis is : **[AIEEE 2008, 3/105]**

(1) $RSiCl_3$ (2) R_2SiCl_2 (3) R_3SiCl_2 (4) R_4Si

10. Which one of the following is the correct statement ? **[AIEEE 2008, 3/105]**

(1) Beryllium exhibits coordination number of six.
(2) Chlorides of both beryllium and aluminium have bridged structures in vapour phase.
(3) $B_2H_6.2NH_3$ is known as 'inorganic benzene'.
(4) Boric acid is a protonic acid.

11. Boron cannot form which one of the following anions? **[AIEEE 2011, 4/120]**

(1) BF_6^{3-} (2) BH_4^- (3) $B(OH)_4^-$ (4) BO_2^-

JEE(MAIN) ONLINE PROBLEMS

---

1. The gas evolved on heating CaF_2 and SiO_2 with concentrated H2SO4, on hydrolysis gives a white gelatinous precipitate. The precipitate is : **[JEE(Main) 2014 Online (09-04-14), 4/120]**

(1) hydrofluosilicic acid
(2) silica gel
(3) silicic acid
(4) calciumfluorosilicate

2. In the following sets of reactants which two sets best exhibit the amphoteric character of $Al_2O_3.xH_2O$? **[JEE(Main) 2014 Online (09-04-14), 4/120]**

Set 1 : $Al_2O_3.\ xH_2O$ (s) and OH^- (aq)
Set 2 : $Al_2O_3.\ xH_2O$ (s) and H_2O (ℓ)
Set 3 : $Al_2O_3.\ xH_2O$ (s) and H^+ (aq)
Set 4 : $Al_2O_3.\ xH_2O$ (s) and NH_3 (aq)

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

3. Example of a three-dimensional silicate is not : **[JEE(Main) 2014 Online (19-04-14), 4/120]**

(1) Zeolites (2) Ultramarines (3) Feldspars (4) Beryls

4. Match the items in Column I with its main use listed in Column II: **[JEE(Main) 2016 Online (09-04-16), 4/120]**

	Column I		**Column II**
(A)	Silica gel	(i)	Transistor
(B)	Silicon	(ii)	Ion-exchanger
(C)	Silicone	(iii)	Drying agent
(D)	Silicate	(iv)	Sealant

(1) (A)-(iii), (B)-(i), (C)-(iv), (D)-(ii)
(2) (A)-(ii), (B)-(i), (C)-(iv), (D)-(iii)
(3) (A)-(iv), (B)-(i), (C)-(ii), (D)-(iii)
(4) (A)-(ii), (B)-(iv), (C)-(i), (D)-(iii)

5. Identify the incorrect statement regarding heavy water : **[JEE(Main) 2016 Online (09-04-16), 4/120]**

(1) It reacts with CaC_2 to produue C_2D_2 and $Ca(OD)_2$
(2) It is used as a coolant in nuclear reactors.
(3) It reacts with Al_4C_3 to produce CD_4 and $Al(OD)_3$
(4) It reacts with SO_3 to form deuterated sulphuric acid (D_2SO_4).

6. Identify the reaction which does not liberate hydrogen : **[JEE(Main) 2016 Online (10-04-16), 4/120]**

(1) Allowing a solution of sodium in liquid ammonia to stand.
(2) Reaction of zinc with aqueous alkali.
(3) Reaction of lithium hydride with B_2H_6.
(4) Electrolysis of acidified water using Pt electrodes.

7. Lithium aluminum hydride reacts with silicon tetrachloride to form :

[JEE(Main) 2018 Online (15-04-18), 4/120]

(1) LiCl, AlH_3 and SiH_4
(2) LiCl, $AlCl_3$ and SiH_4
(3) LiH, $AlCl_3$ and $SiCl_2$
(4) LiH, AlH_3 and SiH_4

8. A group 13 element 'X' reacts with chlorine gas to produce a compound XCl_3. XCl_3 is electron deficient and easily reacts with NH_3 to form $Cl_3X \leftarrow NH_3$ adduct; however, XCl_3 does not dimerize. X is :

[JEE(Main) 2018 Online (16-04-18), 4/120]

(1) B (2) Al (3) In (4) Ga

9. Correct statements amongst a to d regarding silicones are :
(a) They are polymers with hydrophobic character.
(b) They are biocompatible.
(c) In general, they have high thermal stability and low dielectric strength.
(d) Usually, they are resistant to oxidation and used as greases.

[JEE(Main) 2019 Online (09-01-19), 4/120]

(1) (a), (b) and (c) only
(2) (a) and (b) Only
(3) (a), (b) and (d) only
(4) (a), (b), (c) and (d)

10. The chloride that CANNOT get hydrolysed is : **[JEE(Main) 2019 Online (11-01-19), 4/120]**

(1) $PbCl_4$ (2) $SiCl_4$ (3) CCl_4 (4) $SnCl_4$

11. The relative stability of +1 oxidation state of group 13 elements follows the order :

[JEE(Main) 2019 Online (11-01-19), 4/120]

(1) $Tl < In < Ga < Al$ (2) $Ga < Al < In < Tl$ (3) $Al < Ga < Tl < In$ (4) $Al < Ga < In < Tl$

12. The element that does NOT show catenation is: **[JEE(Main) 2019 Online (12-01-19), 4/120]**

(1) Sn (2) Si (3) Ge (4) Pb

Answers

EXERCISE – 1

PART – I

A-1. 3rd most abundant element is Aluminium. The main ores of Al are :
(i) Bauxite ($Al_2O_3.H_2O$ – $Al_2O_3.3H_2O$).
(ii) Alumiosiliciate rocks (Feldspars, Mica).
(iii) Cryolite (Na_3AlF_6).

A-2. (i) $Na_2[B_4O_5(OH)_4].8H_2O \xrightarrow{\text{acid}} H_3BO_3 \xrightarrow{\text{heat}} B_2O_3 \xrightarrow{\text{Mg or Na}} 2B + 3MgO$
(ii) $2BCl_3 + 3H_2 \xrightarrow[\text{or Tafilament}]{\text{red hot W}} 2B + 6HCl$

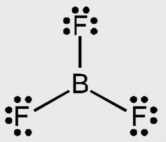
Pyrolysis of BI_3 (Van Arkel Method)
$2BCl_3 \xrightarrow[\text{Van Arkel Method}]{\text{red hot W or Tafilament}} 2B + 3I_2$

A-3. It has layered structure which can be slipped over one another, as the layers are held together by weak van der Waal's forces.

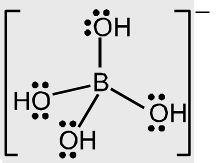
B-1. Boron has three electrons in the valence shell. Because of its small and high sum of the first three ionization enthalpies (i.e., $\Delta_iH_1 + \Delta_iH_2 + \Delta_iH_3$), boron does not lose all its valence electrons to form B^{3+} ions.

B-2. (a) Reluctance of outermost s-orbital electrons to participate in chemical bonding (more pronounced in heavier elements of p-block).
(b) Atoms of elements have the tendency to link with one another through covalent bonds to form chains and rings.

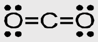
C-1. (i) BF_3



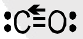
(ii) $[B(OH)_4]^-$



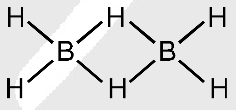
(iii) CO_2



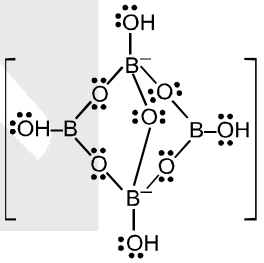
(iv) CO



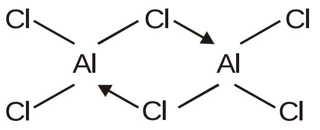
C-2. (i) B_2H_6



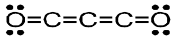
(ii) Borax



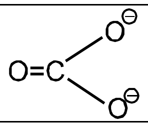
(iii) Al_2Cl_6



(iv) C_3O_2



C-3.

CO	CO_2	CO_3^{2-}
$:C \equiv O:$	O=C=O	
Bond order = 3	Bond order = 2	Bond order = 4/3

Bond length : $CO < CO_2 < CO_3^{2-}$
Bond strength : $CO > CO_2 > CO_3^{2-}$

C-4. Due to pπ-pπ back bonding.

C-5.

CO- Neutral	SiO_2 - Acidic
CO_2 - Acidic	Al_2O_3 - Amphoteric
B_2O_3 - Acidic	PbO - Amphoteric

D-1. Gallium.

D-2.

S.No.	Element	Element + O_2	Element + N_2
1	B (crystalline)	No reaction	No reaction
	B (amorphous)	B_2O_3	BN
2	Al	Al_2O_3 (at high temp.)	AlN (only at high temp.)
3	C	CO	No reaction
4	Si	SiO_2 (at high temp.)	No reaction

D-3. No reaction of group 13 & 14 elements takes place with H_2O. With Al, the reaction is usually prevented by the deposition of protective layer of Al_2O_3.

D-4. (a) B + dil. $HNO_3 \longrightarrow$ Poor or No reaction.
(b) C + dil. $HNO_3 \longrightarrow$ Poor or No reaction.
(c) Si + dil. $HNO_3 \longrightarrow$ Poor or No reaction.

D-5. $2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$

E-1. X = $Na_2B_4O_7$ Y = Z = H_3BO_3

E-2. (A) $Ca_2B_6O_{11}.5H_2O$; (B) $CaCO_3$; (C) $Na_2B_4O_7$; (D) $NaBO_2$; (E) B_2O_3; (F) $Co(BO_2)_2$

E-3. SnO_2, PbO_2. Because oxides are amphoteric.

E-4. Al, Ga, Sn, Pb.

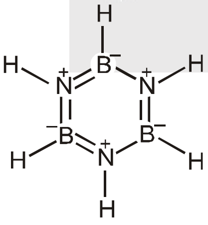
E-5. $Fe_2O_3 (s) + 3CO(g) \xrightarrow{\Delta} 2Fe(s) + 3CO_2 (g)$
CO is a powerful reducing agent which is used in the extraction of many metals from their oxide ores.

F-1. $CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$

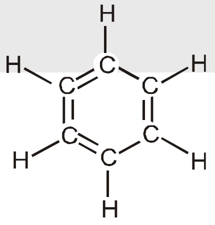
F-2. (i) $BF_3 + LiAlH_4 \longrightarrow B_2H_6 + \underbrace{LiF + AlF_3}_{Li[AlF_4]}$

(ii) $BF_3 + NaH \longrightarrow B_2H_6 + NaF$
(iii) $BF_3 + Na[BH_4] \longrightarrow B_2H_6 + Na[BF_4]$

F-3. Borazine or borazole ($B_3N_3H_6$) is known as inorganic benzene.
It is so called because the structure of borazine is similar to that of benzene.
It is also isoelectronic as well as isosteric with benzene.



Borazine



Benzene

Like carbon in benzene, both N and B in borazine are sp^2-hybridized. Each N has a p-orbital which is perpendicular to the σ-bonding orbitals and contains a lone pair of electrons. In contrast, each B has an empty p-orbital which is also perpendicular to the plane of the ring. Thus, the π-bonding in borazine is dative and it arises from the sideways overlap of fully filled orbitals of N and empty p-orbitals of B.

$3NaBH_4 + 4BF_3 \xrightarrow[450\ K]{ether} 3NaBF_4 + 2B_2H_6$; $B_2H_6 + 2NH_3 \xrightarrow{100^oC} B_2H_6.2NH_3$

$B_2H_6.2NH_3 \xrightarrow{200^oC} B_3N_3H_6 + H_2\uparrow$

F-4. $B_2H_6 + H_2O \longrightarrow H_3BO_3 + H_2\uparrow$

F-5. B_2H_6 reacts with all the species containing acidic hydrogen and releases H_2.
(a) $B_2H_6 + 6CH_3CH_2OH \longrightarrow 2(CH_3CH_2O)_3B + 6H_2\uparrow$ (X)
(b) $B_2H_6 + 6CH_3COOH \longrightarrow 2(CH_3COO)_3B + 6H_2\uparrow$

G-1. $PbCl_4$ is a good oxidising agent whereas $SnCl_2$ is a good reducing agent and $PbCl_2$ is neither.

G-2. $B(OH)_3 \xrightarrow[\text{Fusion}]{NH_4HF_2} NH_4BF_4 \xrightarrow[\Delta]{B_2O_3} BF_3$

G-3. (i) $Al + HCl \longrightarrow AlCl_3 + H_2$ (ii) $AlCl_3 + HCl \longrightarrow AlCl_3 + H_2O$
(iii) $Al(OH)_3 + HCl \longrightarrow AlCl_3 + H_2O$

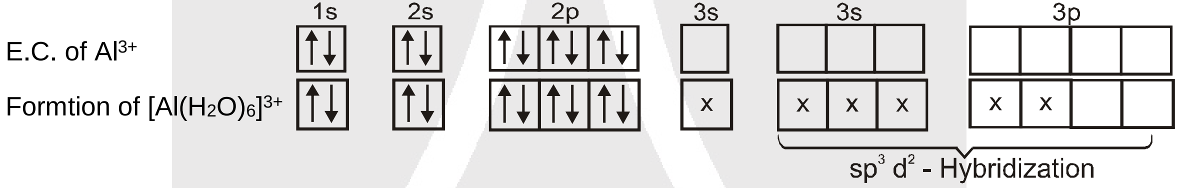
G-4. When BCl_3 reacts with water, it first undergoes hydrolysis to form boric acid, $B(OH)_3$. Due to small size and high electronegativity of B, $B(OH)_3$ polarizes H_2O molecule accepting an OH^- ion to form $[B(OH)_4]^-$ speicies and releasing a proton:

$BCl_3 + 3\,H_2O \longrightarrow B(OH)_3 + 3\,HCl$
$B(OH)_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+$

Since B lies in the 2nd period, it has only one s- and three p- orbitals but no d- orbitals. In other words, at the maximum, it can have four pairs of electrones in the valence shell. i.e., its maximum coordination number is 4. That is why, it accepts one OH^- ion forming $[B(OH)_4]^-$ in which boron is sp^3–hybridized.
In contrast, $AlCl_3$ undergoes hydrolysis in acidified aqueous solution to form $[Al(H_2O)_6]^{3+}$.

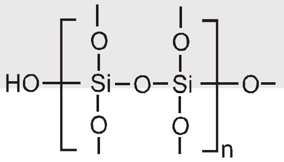
$AlCl_3 + \text{water} \xrightarrow{HCl} [Al(H_2O)_6]^{3+} + Cl^-$ (aq)

This may be explained as follows:
(i) In acidic medium, the conc. of OH^- ions is much lower than that of H^+ ions, therefor, Al^{3+} ions coordinate with H_2O molecules and not with OH^- ions.
(ii) Due to the presence of vacant d-orbitals in Al^{3+} ions, it can expand its coordination number from 4 to 6 and hence forms $[Al(H_2O)_6]^{3+}$ in which hybridization of Al is sp^3d^2.



G-5. (a) $BCl_3 + 3H–OH \longrightarrow 3HCl + H_3BO_3$
(b) $4BF_3 + 3H–OH \longrightarrow 3HBF_4 + H_3BO_3$
(c) $COCl_2 + 2H–OH \longrightarrow 2HCl + H_2CO_3$
($H_2CO_3 \rightleftharpoons H_2O + CO_2^-$)
(d) $COF_2 + H–OH \longrightarrow$ No reaction (due to strong C–F bond)
(e) $SiF_4 + 2H–OH \longrightarrow H_2SiF_6 + H_2SiO_3$
(f) $CF_4 + H–OH \longrightarrow$ No reaction.

H-1. Three dimensional silicone will be formed.



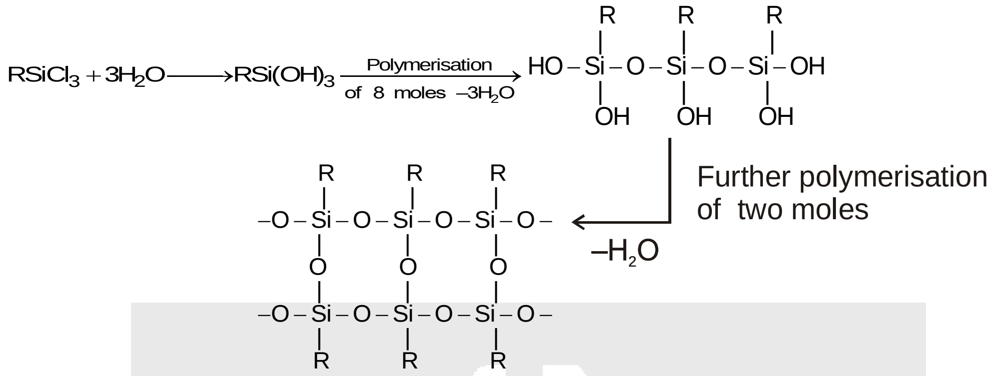
H-2. Binary compounds of silicon with oxygen are called silicates but they contain other metals also in their structures.
(i) Orthosilicates : These contain discrete $[SiO_4]^{4-}$ units i.e., there is no sharing of corners with one another.
(ii) Pyrosilicate : In these silicates two tetrahedral units are joined by sharing oxygen at one corner thereby giving $[Si_2O_7]^{6-}$ units.
(iii) 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.
(iv) 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. $(SiO_3)_n^{2n-}$

(v) 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 $(Si_2O_5)_n^{2n-}$

(vi) Three dimensional silicates : These silicates involve all four oxygen atom in sharing with adjacent SiO_4^{4-} tetrahedral units.

H-3. (i)



Cross linked silicon

(ii) $R_3SiCl \xrightarrow{H_2O} R_3SiOH \xrightarrow{\text{Dimerisation}} R_3Si-O-SiR_3$

H-4. Alums are transparent crystalline solids having the general formula $M_2SO_4.M'_2(SO_4)_3.24H_2O$ or $MM'(SO_4)_2.12H_2O$ 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 $K_2SO_4.Al_2(SO_4)_3.24H_2O$
(ii) Chrome alum $K_2SO_4.Cr_2(SO_4)_3.24H_2O$
(iii) Ferric alum $K_2SO_4.Fe_2(SO_4)_3.24H_2O$
(iv) Ammonium alum $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$

It is used :

1. 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 $Al(OH)_3$.
2. as a germicide for water purification.
3. as a coagulating agent for precipitating colloidal impurities from water.

PART – II

A-1.	(B)	**A-2.**	(B)	**A-3.**	(A)	**B-1.**	(B)	**B-2.**	(C)
C-1.	(A)	**C-2.**	(B)	**C-3.**	(B)	**C-4.**	(A)	**C-5.**	(D)
C-6.	(C)	**C-7.**	(D)	**C-8.**	(B)	**D-1.**	(B)	**D-2.**	(B)
D-3.	(B)	**D-4.**	(B)	**D-5.**	(D)	**E-1.**	(C)	**E-2.**	(C)
E-3.	(B)	**E-4.**	(B)	**E-5.**	(A)	**E-6.**	(A)	**E-7.**	(B)
E-8.	(D)	**F-1.**	(B)	**F-2.**	(B)	**F-3.**	(C)	**F-4.**	(B)
F-5.	(B)	**F-6.**	(C)	**G-1.**	(A)	**G-2.**	(D)	**G-3.**	(D)
G-4.	(B)	**G-5.**	(A)	**G-6.**	(B)	**H-1.**	(C)	**H-2.**	(A)
H-3.	(C)	**H-4.**	(D)	**H-5.**	(C)	**H-6.**	(B)	**H-7.**	(B)

PART – III

1. (A – q) ; (B – p) ; (C – r, s) ; (D – q).

2. (A – p, q) ; (B– p, r) ; (C – q, s) ; (D – q, r)

EXERCISE – 2

PART – I

1.	(B)	**2.**	(D)	**3.**	(B)	**4.**	(B)	**5.**	(D)
6.	(C)	**7.**	(B)	**8.**	(D)	**9.**	(B)	**10.**	(C)
11.	(C)	**12.**	(A)	**13.**	(B)	**14.**	(D)	**15.**	(C)
16.	(C)	**17.**	(C)	**18.**	(D)	**19.**	(B)	**20.**	(C)
21.	(B)	**22.**	(C)	**23.**	(D)	**24.**	(C)		

PART – II

1.	6 (Except (c))			**2.**	21 (x = 4, y = 4, z = 3)				
3.	26 (a = 12, b = 20, c = 30)			**4.**	11 (Except a, b, d, m, n)	**5.**	3		
6.	7 (Except 3 and 7)			**7.**	8 (Except (i))				
8.	5 (Except (a, b, g, h))			**9.**	3 (a, b, d)	**10.**	5	**11.**	4 (a, b, c, e)
12.	(1, 2, 4)	**13.**	3	**14.**	2	**15.**	12	**16.**	10

PART – III

1.	(BCD)	**2.**	(ACD)	**3.**	(BC)	**4.**	(ABC)	**5.**	(ABC)
6.	(AB)	**7.**	(BCD)	**8.**	(AB)	**9.**	(BC)	**10.**	(ACD)
11.	(ABC)	**12.**	(BD)	**13.**	(ABCD)	**14.**	(BCD)	**15.**	(BCD)
16.	(ABD)	**17.**	(ABCD)	**18.**	(C)	**19.**	(ABCD)		

PART – IV

1.	(C)	**2.**	(A)	**3.**	(B)	**4.**	(C)	**5.**	(C)
6.	(B)	**7.**	(D)	**8.**	(D)	**9.**	(C)	**10.**	(C)
11.	(D)	**12.**	(A)	**13.**	(B)	**14.**	(C)		

EXERCISE - 3

PART – I

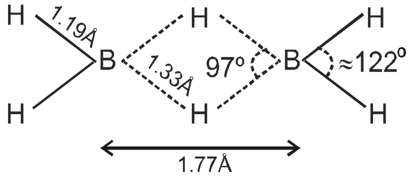
1. $Na_2B_4O_7.10H_2O \xrightarrow[-10\,H_2O]{\Delta} B_2O_3 + 2Na^+ + BO_2^-$; $B_2O_3 + CoO \longrightarrow Co(BO_2)_2$

Blue bead

2. X = BF_3 or BCl_3 ; Y = B_2H_6

$4BF_3\ (X) + 3LiAlH_4 \xrightarrow{\text{Ether}} 2B_2H_6\ (Y) + 3\ LiAlF_4$; $B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$ + Heat.

Structure of Y =



3. (i) $Al_4C_3 + H_2O \longrightarrow 4\ Al(OH)_3 + 3CH_4\uparrow$ (ii) $CaNCN + 3H_2O \longrightarrow CaCO_3\downarrow + 2NH_3\uparrow$

(iii) $4BF_3 + 6H_2O \longrightarrow H_3BO_3 + 3\ [BF_4]^- + 3H_3O^+$ (iv) $NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl$

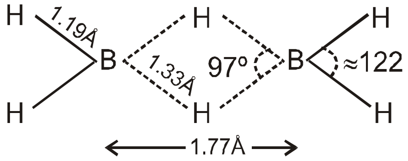
(v) $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$.

4. $Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7$ (aq) ; $Na_2B_4O_7 + 2HCl \longrightarrow 2NaCl + H_2B_4O_7$ (tetra boric acid)

$H_2B_4O_7 + 5H_2O \longrightarrow \underset{\text{Boric acid}}{4H_3BO_3}$; $2H_3BO_3 \xrightarrow{\text{red hot}} \underset{\text{Boric anhydride}}{B_2O_3} + 3H_2O$

$B_2O_3 + 3Mg/Na/Al \xrightarrow{\text{Fusion}} 2B + 3MgO$; Reaction with HCl : $B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2$

Structure of B_2H_6 :



B................ H .... B is hydrogen bridge i.e, 3 centre-2 electron bond.

5. (A) **6.** (A) **7.** (A – q, s) ; (B – q, r, s) ; (C – p, q, r, s) ; (D – q,r, s).

8. (C) **9.** 6 **10.** (BD) **11.** (B) **12.** (ACD)

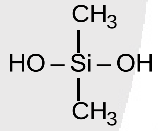
13. (ABD)

14. (i) $3SiCl_4\text{(vapour)} + 4Al\text{(molten)} \longrightarrow 4AlCl_3 + 3Si$

(ii) (a) $3SiCl_4 + 4Al \longrightarrow 4AlCl_3 + 3Si$

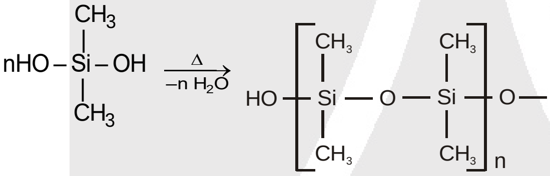
(b) $Si + 2CH_3Cl \xrightarrow[570^oC]{\text{Cu powder}} (CH_3)_2SiCl_2$

(c) $(CH_3)_2SiCl_2 \xrightarrow[-2HCl]{2H_2O}$



$HO-\underset{CH_3}{\overset{CH_3}{Si}}-OH$

(d)



$nHO-\underset{CH_3}{\overset{CH_3}{Si}}-OH \xrightarrow[-n\,H_2O]{\Delta} HO-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}\right]_n-O-$

linear silicone
(thermoplastic polymer)

(iii) (a) $SiCl_4 + 4H_2O \longrightarrow H_4SiO_4$ or $Si(OH)_4$ (ortho silicic acid) + $4HCl$

(b) $H_4SiO_4 \xrightarrow{\Delta} SiO_2 + 2H_2O$

(c) $SiO_2 + Na_2CO_3 \xrightarrow{1400^oC} Na_2SiO_3 + CO_2$

15. (C) **16.** (A) **17.** (C) **18.*** (ABC) **19.** 3

20. 6 **21.** (B) **22.*** (ABD)

PART – II

JEE(MAIN) OFFLINE PROBLEMS

1. (4) **2.** (4) **3.** (1) **4.** (2) **5.** (4)

6. (2) **7.** (3) **8.** (3) **9.** (1) **10.** (2)

11. (1)

JEE(MAIN) ONLINE PROBLEMS

1. (3) **2.** (2) **3.** (4) **4.** (1) **5.** (2)

6. (3) **7.** (2) **8.** (1) **9.** (3) **10.** (3)

11. (4) **12.** (4)