(BORON & CARBON FAMILY)

(13th & 14th group)

Contents

Syllabus

BORON & CARBON FAMILY

(group 13th to 14th)

Boron: diborane, boric acid and borax; Aluminium: alumina, aluminium chloride and alums; Carbon: oxides and oxyacid (carbonic acid); Silicon: silicones, silicates and silicon carbide;

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Boron & Carbon Family (13th & 14th group)

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.

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

The first member of each group from 13–17 of the p–block elements differ in many respects from the other members of their respective groups because of small size, high electronegativity and absence of d–orbitals. The first member of a group also has greater ability to form $p\pi$–$p\pi$ multiple bonds to itself (e.g. $C = C$, $C \equiv C$, $N \equiv N$) and to element of second row (e.g $C = O$, $C = N$, $C \equiv N$, $N = O$) compared to the other members of the same group.

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

GROUP 13 ELEMENTS : THE BORON FAMILY

Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron, and gallium, indium and thallium are almost exclusively metallic in character,

Electronic Configuration :

The valence shell electronic configuration of these elements is $ns^2\ np^1$.

Atomic Radii :

On moving down the group, for each successive member one extra shell of electrons is added and therefore, atomic radius is expected to increase. Atomic radius of Ga is less than that of Al. The presence of additional 10 d-electrons offer only poor screening effect for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

Ionization Enthalpy :

The ionisation enthalpy values do not decrease smoothly down the group. The decreases from B to Al is associated with increases in size. The observed discontinuity in the ionisation enthalpy values between Al and Ga and between In and Tl are due to the non-availability of d- and f-electrons, which have low screening effect, to compensate the increase in nuclear charge. The sum of the first three ionisation enthalpies for each of the elements is very high .

Electronegativity :

Down the group, electronegativity first decreases from B to Al and then increases marginally. This is because of the discrepancies in atomic size of the elements.

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. Density of the elements increases down the group from boron to thallium.

Atomic and physical properties :

Element			B	Al	Ga	In	Tl
Atomic Number			5	13	31	49	81
Atomic Mass			10.81	26.98	69.72	114.82	204.38
Electronic configuration			[He] $2s^2\ 2p^1$	[Ne] $3s^2\ 3p^1$	[Ar] $3d^{10}\ 4s^2 4p^1$	[Kr] $4d^{10}\ 5s^2\ 5p^1$	[Xe] $4f^{14}\ 5d^{10}\ 6s^2 6p^1$
Atomic Radius / pm			85	143	135	167	170
Ionic Radius M^{3+} / pm			27	53.5	62	80	88.5
Ionization enthalpy (kJ mol^{-1})	N_iH_1	N	801	577	579	558	589
	N_iH_2	N	2427	1816	1979	1820	1971
	N_iH_3	N7	3659	2744	2962	2704	2877
Electronegativity			2.0	1.5	1.6	1.7	1.8
Density/[g cm^{-3} (at 293 K)]			2.35	2.70	5.90	7.31	11.85
Melting point / K			2453	933	303	430	576
Boiling point / K			3923	2740	2676	2353	1730

Chemical Properties :

Oxidation state and trends in chemical reactivity

Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form + 3 ions and compel it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases, and is therefore able to form Al^{3+} ions. However, down the group, due to poor shielding, effective nuclear charge holds ns electrons tightly (responsible for inert pair effect) and thereby, restricting their participation in bonding. As a result of this only p-orbital electron may be involved in bonding. In fact in Ga, In and Tl, both + 1 and + 3 oxidations states are observed. The relative stability of + 1 oxidation state progressively increases for heavier elements: Al < Ga < In < Tl. In thallium +1 oxidation state is predominant and + 3 oxidation state highly oxidising in character. The compound in +1 oxidation state, as expected from energy considerations, are more ionic than those in + 3 oxidations state.

In trivalent state, the number of electrons around the central atom in a molecule of the compounds of these elements (e.g., boron in BF_3) will be only six. Such **electron deficient** molecules have tendency to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids. The tendency to behave as Lewis acid decreases with the increases in the size down the group. BCl_3 easily accepts a lone pair of electrons from ammonia to form $BCl_3 . NH_3$. In trivalent state most of the compounds being covalent are hydrolysed in water. The trichloride on hydrolysis in water form tetrahedral $[M(OH)_4]^-$ species; Aluminium chloride in acidified aqueous solution form octahedral $[Al(H_2O)_6]^{3+}$ ion. AlX_3 (X = Cl, Br) exists as dimer in vapour state (at lower temperature) and in non-polar solvent like benzene. However, when the halides dissolved in water, the high enthalpy of hydration is sufficient to break the covalent dimer into $[M.6H_2O]^{3+}$ and $3X^-$ ions.

(i) Reactivity towards air :

Boron is unreactive in crystalline form. Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack. Amorphous boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at high temperature they form nitrides.

$$2E(s) + 3\,O_2\,(g) \xrightarrow{\Delta} 2\,E_2O_3(s)\ ;\ 2E(s) + N_2(g) \xrightarrow{\Delta} 2\,EN\,(s).$$

The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in their properties.

(ii) Reactivity towards acids and alkalies :

Boron does not react with acids and alkalies even at moderate temperature; but aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character.

Aluminium dissolved in dilute HCl and liberates dihydrogen. However, concentrated nitric acid renders aluminium passive by forming protective oxide layer on the surface . Aluminium also reacts with aqueous alkali and liberates dihydrogen .

$$2\,Al(s) + 6\,HCl(aq) \longrightarrow 2\,Al^{3+}\,(aq) + 6\,Cl^-(aq) + 3\,H_2(g)$$

$$2Al(s) + 2NaOH\,(aq) + 6H_2O\,(\ell) \longrightarrow 2Na^+\,[Al(OH)_4]^-\,(aq) + 3H_2(g)$$

Sodium tetrahydroxoaluminate (III)

- ➢ $Al(OH)_3$ is amphoteric and reacts principally as a base. However, $Al(OH)_3$ shows some acidic properties when it dissolves in NaOH forming aluminate. The $Al(OH)_3$ is reprecipitated by the addition of CO_2, showing that the acidic properties are very weak.

  $$CO_2 + H_2O \rightarrow H_2CO_3 \rightleftharpoons CO_3^{2-} + 2H^+\ ;\ 2Al^{3+} + 3CO_3^{2-} + 3H_2O \rightarrow 2Al(OH)_3 + 3CO_2$$

  In concentrated solutions above 1.5 M and pH greater than 13, it exists as dimer $[(OH)_3Al—O—Al(OH)_3]^{2-}$.

- ➢ Aluminates are important constituents of portland cement.

- ➢ Ga_2O_3 and $Ga(OH)_3$ are both amphoteric compounds. Tl_2O_3 and In_2O_3 are completely basic and form neither hydrates nor hydroxides.

(iii) Reactivity towards halogens :

These elements react with halogen to form trihalides (except $Tl\,I_3$).

$$2E(s) + 3X_2\,(g) \rightarrow 2EX_3\,(s) \qquad (X = F, Cl\ Br, I)$$

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.

BORON (B) :

Occurrence :

Boron occurs in nature in the form of the following minerals:

(i) Borax $(Na^+)_2B_4O_7^{2-}.10H_2O$. (boron is part of an anionic complex), (ii) Boric acid H_3BO_3,

(iii) Kernite $Na_2B_4O_7.4H_2O$ & (iv) Colemanite $Ca_2B_6O_{11}.5H_2O$

Properties :

(i) It exists in five forms, four of which are crystalline and one is amorphous. All crystalline forms are very hard made up of clusters of B_{12} units. All crystalline forms are black in appearance and chemically inert. However, it is attacked at high temperature by strong oxidising agents such as a mixture of hot concentrated H_2SO_4 and HNO_3 or Na_2O_2. But amorphous form is brown and chemically active.

(ii) Reaction with air : Burns in air or oxygen forming B_2O_3.

$$4B + 3O_2 \longrightarrow 2B_2O_3$$

Also burns in nitrogen at white heat.

$$2B + N_2 \longrightarrow 2BN \; ; \quad BN + 3H_2O \xrightarrow{\text{High temperature, pressure}} H_3BO_3 + NH_3$$

(iii) Action of alkalies and acids :

$$2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2$$

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

$$2B + 3H_2SO_4 \text{ (hot \& concentrated)} \longrightarrow 2H_3BO_3 + 3SO_2$$

$$2B + 6HNO_3 \text{ (hot \& concentrated)} \longrightarrow 2H_3BO_3 + 6NO_2$$

(iv) Reaction with Mg and Ca :

$$3Mg + 2B \longrightarrow Mg_3B_2 \; ; \qquad 3Ca + 2B \longrightarrow Ca_3B_2$$

Mg_3B_2 on consequent hydrolysis gives diborane.

$$Mg_3B_2 + 6HCl \xrightarrow{\text{hydrolysis}} 3MgCl_2 + B_2H_6 \; ; \qquad B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

COMPOUNDS OF BORON :

BORON TRIOXIDE (B_2O_3) :

Preparation :

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

Properties :

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

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

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.

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

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

ORTHOBORIC ACID (H_3BO_3) :

Preparation :

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

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

(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:

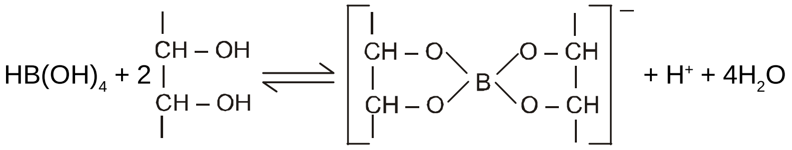
$$B(OH)_3(aq) + 2H_2O(\ell) \rightleftharpoons [B(OH)_4]^-(aq) + H_3O^+(aq). \qquad pK = 9.25.$$

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

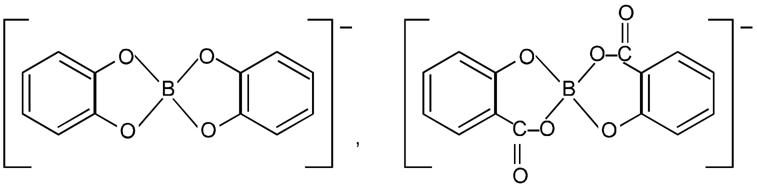
Since $B(OH)_3$ only partially reacts with water to form H_3O^+ and $[B(OH)_4]^-$, it behaves as a weak acid. Thus H_3BO_3 can not be titrated satisfactorily with NaOH as a sharp end point is not obtained. If certain organic polyhydroxy compounds such as glycerol, mannitol or sugars are added to the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

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

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



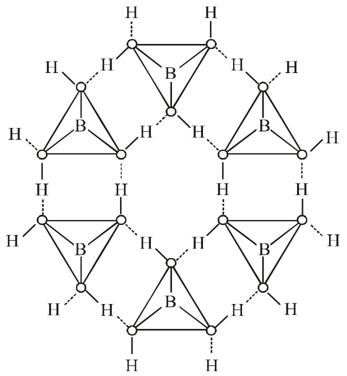
Ethanol does not form similar complex but catechol, salicylic acids, mannitol form similar complexes.



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.



Test for Borate radical :

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

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

Uses :

1. It is an antiseptic and its water solution is used as an eyewash.
2. It is also used in glass, enamel and pottery industry.

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 740°C it becomes converted into colourless transparent borax bead.

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

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

(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 80°C) the peroxide linkages —O—O— break down to give H_2O_2.

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

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.

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

Uses : It is used

1. in borax bead test, 2. in purifying gold, 3. as flux during welding of metals and 4. in production of glass.

DIBORANE (B_2H_6) :

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 :

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

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

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

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

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.

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

- 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.

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

$$B_2H_6 + 2Me_3P \longrightarrow 2Me_3PBH_3$$

- $B_2H_6 + 2CO \xrightarrow{200°C,\ 20\text{ atm}} 2BH_3CO$ (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.

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

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

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

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.

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

ALUMINIUM (Al) :

(i) It is a silvery metal with a density of 2.7 g/cc, having a melting point of 660°C, and is a good conductor of heat and electricity. It is malleable and ductile.

(ii) Action of air: Dry air has no action on aluminium. But moist air forms a thin layer of Al_2O_3 on its surface and it loses its luster. At very high temperatures it burns to form Al_2O_3 and AlN.

(iii) Reaction with halogens : When gaseous halogens are passed over aluminium, its halide are formed in an anhydrous form. $2Al + 3Cl_2 \longrightarrow 2AlCl_3$

(iv) Action of alkalies: When warmed with concentrated NaOH, it liberates H_2 gas and a colourless solution of sodium meta-aluminate is formed.

$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2\uparrow$$

(v) Action of acids: Aluminium reacts with dilute H_2SO_4 and dilute HCl but concentrated HNO_3 does not react with aluminium because aluminium becomes passive by the action of concentrated HNO_3 forming a protective oxide layer on the surface.

$$2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2\uparrow\ ;\quad 2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2\uparrow$$

(vi) Reaction with N_2 : When N_2 gas is passed over heated aluminium, aluminium nitride is formed. Hot aluminium thus acts as an absorbing agent for N_2.

$$2Al + N_2 \longrightarrow 2AlN$$

AlN reacts with hot water to form $Al(OH)_3$ and NH_3

Uses :

It is extensively used :
1. for manufacture of cooking and household utensils.
2. as aluminium plating for tanks, pipes, iron bars and other steel objects to prevent corrosion.
3. for manufacture of aluminium cables.
4. for making precision instruments, surgical apparatus, aircraft bodies, rail coaches, motorboats, car.

COMPOUNDS OF ALUMINIUM :
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.

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

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.

$$\gamma\text{-}Al_2O_3 \xrightarrow[\Delta]{1000°C} \alpha\text{-}Al_2O_3$$

Uses :

1. It is used for the extraction of aluminium.
2. It is used for making artificial gems.
3. α-Al_2O_3 is used in making furnace linings. It is a refractory material.
4. Corundum is extremely hard and is used as 'Jewellers rouge' to polish glass.

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.

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

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.

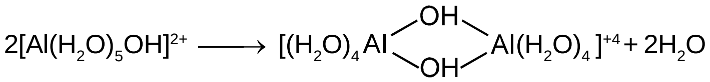
$$AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3\downarrow (\text{white gelatinous}) + 3NH_4Cl$$

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.



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

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

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 : 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.

GROUP 14 ELEMENTS : THE CARBON FAMILY

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14. Naturally occurring carbon contains two stable isotopes: ^{12}C and ^{13}C. In addition to these third isotopes, ^{14}C is also presents , it is a radioactive isotope with half-life 5770 years and used for radiocarbon dating. Silicon is a very important component of ceramics, glass and cement. Germanium exists only in traces. Tin occurs mainly as cassiterite, SnO_2 and lead as galena, PbS. Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.

Electronic Configuration

The valence shell electronic configuration of these elements is $ns^2 np^2$.

Covalent Radius

There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed. This is due to the presence of completely filled d and f orbitals in heavier members.

Ionization Enthalpy

The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electron is visible here also. In general the ionisation enthalpy decreases down the group. Small decreases in $\Delta_i H$ from Si to Ge to Sn and slight increase in $\Delta_i H$ from Sn to Pb is the consequence of poor shielding effects of intervening d and f–orbitals and increase in size of the atom.

Electronegativity

Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity value for elements from Si to Pb are almost the same. Carbon has higher electronegativity as compared to other elements of the group. As a result it can accept electrons and can form negative ions of type C_2^{2-} in acetylides and C^{4-} in methanides.

Physical Properties

All group 14 members are solids. Carbon and silicon are non-metals, germanium is metalloid whereas tin and lead are soft metals with low melting points. Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13 due to stronger metallic bonding.

Atomic and physical properties

Element			C	Si	Ge	Sn	Pb
Atomic Number			6	14	32	50	82
Atomic Mass			12.01	28.09	72.60	118.71	207.2
Electronic configuration			$[He]\ 2s^2\ 2p^2$	$[Ne]\ 3s^2\ 3p^2$	$[Ar]\ 3d^{10}\ 4s^2\ 4p^2$	$[Kr]\ 4d^{10}\ 5s^2\ 5p^2$	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$
Atomic Radius / pm			77	118	122	140	146
Ionic Radius M^{+4} / pm			–	40	53	69	78
Ionization enthalpy (kJ mol^{-1})	$\Delta_i H_1$	I	1086	786	761	708	715
	$\Delta_i H_2$	II	2352	1577	1537	1411	1450
	$\Delta_i H_3$	III	4620	3228	3300	2942	3081
Electronegativity			2.5	1.8	1.8	1.8	1.9
Melting point / K			4373	1693	1218	505	600
Boiling point / K			–	3550	3123	2896	2024

Chemical Properties :

Oxidation states and trends in chemical reactivity

The group 14 elements have four electrons in outermost shell. The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states. Since the sum of the first four ionization enthalpies is very high, compound in +4 oxidation state are generally covalent in nature. In heavier members the tendency to show +2 oxidation state increases in the sequence Ge < Sn < Pb. It is due to the inability of ns^2 electrons of valence shell to participate in bonding (inert pair effect). The relative stabilities of these two oxidation states vary down the group. Carbon cannot exceed its covalence more than 4. Other elements of the group can do so. It is because of the presence of d orbital in them. Due to this, their halides undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species. For example, the species like SiF_6^{2-}. $[GeCl_6]^{2-}$, $[Sn(OH)_6]^{2-}$ and $[Pb(OH)_6]^{2-}$ exist in solutions as covalently bonded complex ions.

(i) Reactivity towards oxygen :

All members when heated in oxygen form oxides. There are mainly two types of oxides, i.e. monoxide and dioxide of formula MO and MO_2 respectively. SiO only exists at high temperature. Oxides in higher oxidation states of elements are generally more acidic than those in lower oxidation state. The dioxides – CO_2, SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric .

(ii) Reactivity towards water :

Carbon , silicon and germanium are not affected by water . Tin decomposes steam to form dioxide and dihydrogen gas. Lead is unaffected by water, probably because of a protective oxide film formation.

(iii) Reactivity towards halogen :

These elements can form halides of formula MX_2 and MX_4 (where X = F, Cl Br, I). Except carbon all other members react directly with halogen under suitable condition to make halides. Most of the MX_4 are covalent in nature. Exceptions are SnF_4 and PbF_4, which are ionic in nature . PbI_4 does not exist because Pb–I bond initially formed during the reaction does not release enough energy to unpair $6s^2$ electrons and excite one of them to higher orbital to have four unpaired electrons around lead atom. Heavier members Ge to Pb are able to make halides of formula MX_2. Stability of dihalides increases down the group. Except CCl_4 other tetrachlorides are easily hydrolysed by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecules in d orbital.

ANOMALOUS BEHAVIOUR OF CARBON :

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

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

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**

Allotropes of Carbon

Carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985 third form of carbon known as **fullerenes** was discovered by H.W. Kroto, E Smalley and R.F.Curl.

Diamond :

It has a crystalline lattice. In diamond each carbon atom undergoes sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral manner. The C–C bond length is 154 pm. The structure extends in space and produces a rigid three dimensional network of carbon atoms. In this structure directional covalent bonds are present throughout the lattice.

It is very difficult to break extended covalent bonding and therefore, diamond is a hardest substance on the earth. It is used as an abrasive for sharpening hard tools in making dies (die casting) and in the manufacture of tungsten filament for electric light bulbs.

Graphite :

Graphite has layered structure. Layers are held by van der Waal's forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C – C bond length within the layer is 141.5 pm. Each carbon atom in hexagonal ring undergoes sp^2 hybridisation and make three sigma bonds with three neighboring carbon atoms. Fourth electron forms a π bond. The electrons are delocalised over the whole sheet. Electrons are mobile and , therefore graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

- Natural graphite is found as a mixture with mica, quartz and silicates which contains 10-60% carbon. It is purified by heating with HCl and HF in a vacuum to remove the last traces of silicon compound as SiF_4.

$$3C + SiO_2 \xrightarrow{\Delta} SiC + 2CO \xrightarrow{2500^{\circ}C} C(\text{graphite}) + Si(\text{gas})$$

Fullerenes :

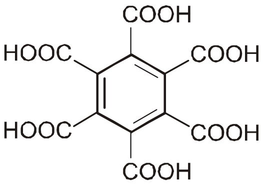
Fullerenes are made by the heating of graphite in an electrical arc in the presence of inert gases such as helium or argon. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerene are cage like molecules. C_{60} molecule has a shape like soccer ball and called **Buckminsterfullerene.**

It contains twenty six -membered rings and twelve five membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo sp^2 hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon atom is delocalised in molecular orbitals, which in turn give aromatic character to molecule. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C – C distance of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are called bucky balls in short. Carbon black is obtained by burning hydrocarbons in a limited supply of air.

- Graphite is thermodynamically most stable allotrope of carbon and, therefore, $\Delta_f H$ values of diamond and fullerene, C_{60} are 1.90 and 38.1 kJ mol^{-1}, respectively.
- Diamond is unaffected by halogens but graphite reacts with F_2 at 500ºC forming intercalation compounds or graphite fluoride $(CF)_n$.

$$\text{Graphite} \xrightarrow[50000-60000 \text{ atms.}]{1600^{\circ}C} \text{synthetic diamond.}$$

- Diamond is unaffected by concentrated acids but graphite changes to Mellitic acid also called benzene hexa-carboxylic acid with hot concentrated HNO_3 and to graphite oxide with a hot concentrated HF/HNO_3.



(Mellitic acid)

- Si, Ge and Sn also have a diamond type of structure. Ge liquid expands when it forms the solid. This property is unique to Ga, Ge and Bi.
- $\alpha\text{-Sn} \underset{}{\overset{32^{\circ}C}{\rightleftharpoons}} \beta\text{-Sn}$

grey tin	white tin
(Diamond structure)	(Metallic)

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.).

OXIDES OF CARBON :

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

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.

$$Hb\text{—}O_2 + CO \longrightarrow Hb\text{—}CO + O_2$$

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) 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.

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

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:

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

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 = 31.1°C) and a cylinder of the gas under pressure is a convenient fire extinguisher. When the highly compressed gas is allowed to expand rapidly solid carbon dioxide ('dry ice') is formed. Solid carbon dioxide sublimes at –78°C and, since no massy liquid is produced, it is a convenient means of producing low temperatures.

(iii) Carbon dioxide is the acid anhydride of carbonic acid, which is a weak dibasic acid and ionises in two steps as follows :

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

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

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, 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 :

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

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.

(v) 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.

CARBIDES :

The binary compounds of carbon with other elements (less electronegative or of similar electronegativity) are called carbides. They are classified into following 3 categories :

(i) Ionic (ii) Covalent (iii) Interstitial (or metallic)

(i) **Ionic carbides (or salt like carbides) :** Generally formed by the most electropositive elements such as alkali and alkaline earth metals and aluminium (Boron is exception). Based on the product obtained on hydrolysis, they are further sub-classified into three types.

(a) **Methanides :** These give CH_4 on reaction with H_2O.

$$Al_4C_3 + 12H_2O \longrightarrow 4Al\,(OH)_3 + 3CH_4 \; ; \quad Be_2C + 4H_2O \longrightarrow 2Be\,(OH)_2 + CH_4$$

These carbides contain C^{4-} ions in their constitution.

(b) **Acetylides :** These give C_2H_2 on reaction with H_2O.

$$CaC_2 + 2H_2O \longrightarrow Ca\,(OH)_2 + C_2H_2 \; ; \quad Al_2\,(C_2)_3 + 6H_2O \longrightarrow 2Al\,(OH)_3 + 3C_2H_2$$

$$SrC_2 + 2H_2O \longrightarrow Sr\,(OH)_2 + C_2H_2$$

Such compounds contain C_2^{2-} $[:C \equiv C:]^{2-}$ ions.

(c) **Allylides :** These give 1-propyne on reaction with H_2O.

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg\,(OH)_2 + CH_3\!-\!C \equiv CH$$

Such compounds contain C_3^{4-} $[:\ddot{\underset{\cdot\cdot}{C}} - C \equiv C:]^{4-}$ ions.

(ii) Covalent carbides

Compounds like CH_4, CO_2, CS_2 can be considered to be covalent carbides. Besides these, some giant molecules like SiC and B_4C are also examples of covalent carbides.

(iii) Interstitial or metallic carbides

Such carbides are formed by transition metals and some of the lanthanides and actinides. Interstitial carbides retain many of the properties of metals. They conduct electricity by metallic conduction and have properties of metals (a lusture like a metal). In these compounds carbon atoms occupy octahedral holes in the closed packed metal lattice. These are generally very hard and have very high melting point (e.g. WC). Carbides of Cr, Mn, Fe, Co and Ni are hydrolysed by water or dilute acids.

SILICON :

Silicon is the second most abundant element occurring in the earth's crust (about 28 per cent by weight) as the oxide, silica, in a variety of forms, e.g., sand, quartz and flint, and as silicates in rocks and clays.

Preparation :

(i) The element is obtained from silica by reduction with carbon in an electric furnace.

$$SiO_2(s) + 2C(s) \longrightarrow Si(s) + 2CO(g)$$

Extremely pure silicon is obtained from 'chemically' pure silicon by the method of zone refining.

(ii) $SiO_2 + 2Mg \xrightarrow{\Delta} 2MgO + Si$

Properties :

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. In the massive form, silicon is chemically rather unreactive but powdered silicon is attacked by the halogens and alkalies.It is not attacked by acids except hydrofluoric acid, with which it forms hexafluorosilicic acid:

$Si(s) + 6HF(g) \longrightarrow H_2SiF_6(aq) + 2H_2(g)$

$Si(powdered) + 2Cl_2(g) \longrightarrow SiCl_4(liq.)$

$Si(powdered) + 2OH^-(aq) + H_2O(liq) \longrightarrow SiO_3^{2-}(aq) + 2H_2(g)$

COMPOUNDS OF SILICON:

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.

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.

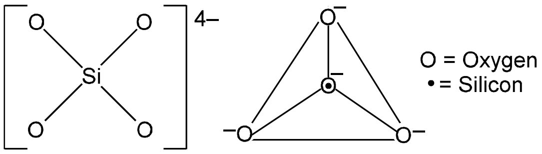
(ii) If we calculate the radius ratio then, $\dfrac{r_{Si^{4+}}}{r_{O^{2-}}} = 0.29$

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 :**



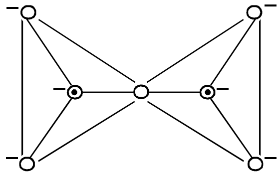
These contain discrete $[SiO_4]^{4-}$ units i.e., there is no sharing of corners with one another as shown is figure.

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.

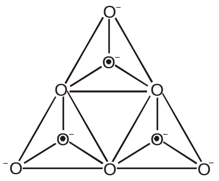
e.g. Thorteveitite ($Sc_2Si_2O_7$), Hemimorphite ($Zn_3(Si_2O_7)\ Zn(OH)_2H_2O$)



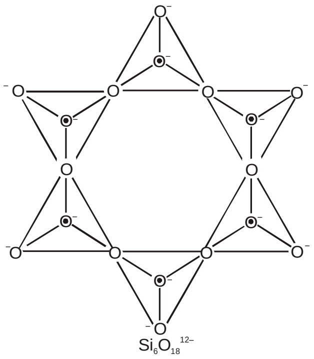
➢ (–) charge will be present on the oxygen atoms which is bonded with one Si atom.

(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.



$Si_3O_9^{6-}$

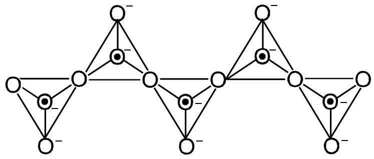


$Si_6O_{18}^{12-}$

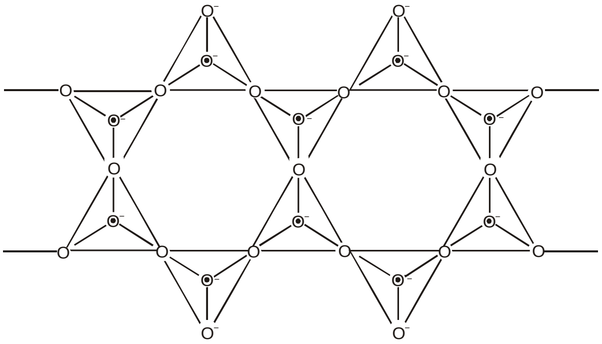
(D) **Chain silicates :**

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



Similarly, double chain silicates can be drawn in which two simple chains are joined together by shared oxygen. Such compounds are also known as amphiboles. The asbestos mineral is a well known example of double chain silicates. The anions of double chain silicates have general formula $(Si_4O_{11})_n^{6n}$



e.g., Synthetic silicates (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 sheet 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.

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.

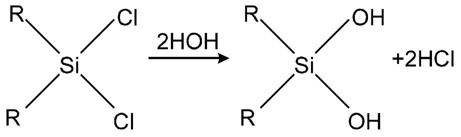
(a) $RCl + Si \xrightarrow[300^\circ C]{Cu} R_3SiCl + R_2SiCl_2 + RSiCl_3$

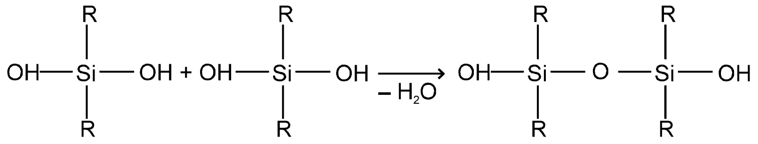
(b) $RMgCl + SiCl_4 \longrightarrow RSiCl_3 + MgCl_2$

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

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

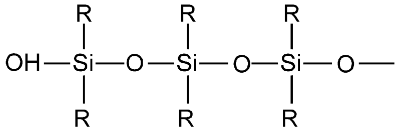
After fractional distillation, the silane derivatives are hydrolysed and the 'hydroxides' immediately condense by intermolecular elimination of water. The final product depends upon the number of hydroxyl groups originally bonded to the silicon atom:





$$OH-\overset{R}{\underset{R}{Si}}-OH + OH-\overset{R}{\underset{R}{Si}}-OH \xrightarrow[-H_2O]{} OH-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-OH$$

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.



$$OH-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-$$

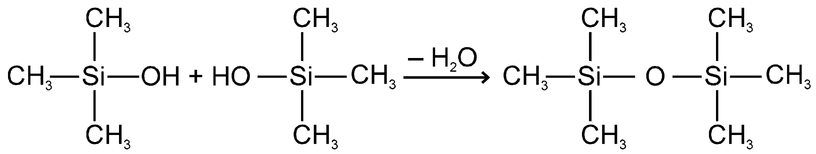
The polymer chain depicted above is terminated by incorporating a small quantity of the monochlorosilane derivative into the hydrolysis mixture.

- ➢ 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 $(CH_3)_3\ SiCl$

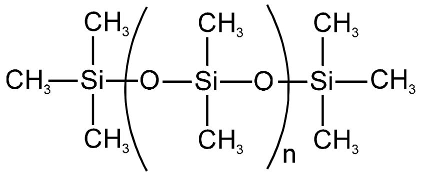
  $(CH_3)_3\ SiCl \xrightarrow{H_2O} (CH_3)_3\ Si\ (OH)$



$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-OH + HO-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3 \xrightarrow{-H_2O} CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

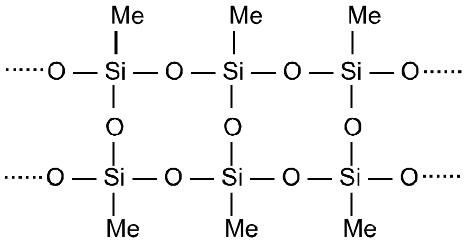
- ➢ Silicones from the hydrolysis of a mixture of $(CH_3)_3\ SiCl$ & $(CH_3)_2\ SiCl_2$

  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.



$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}\left(-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\right)_n\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

- 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.

COMPOUNDS OF TIN :

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.

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

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

Stannites are only known in aqueous solutions.

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) **Reducing agent :** It is a stronger reducing agent.

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

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

(b) It also reduces $CuCl_2$ to CuCl (white).

(iii) $SnCl_2$ partly 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.

COMPOUNDS OF LEAD :

LITHARGE (PbO) :

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

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

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

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

LEAD DIOXIDE (PbO_2) :

Preparation :

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

Properties :

It is a chocolate / dark brown coloured insoluble solid.

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

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

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

(a) It oxidizes HCl to Cl_2.

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

(b) It oxidises Mn salt to permanganic acid.

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

(iii) 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 450°C for a long time.

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

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 550°C, it decomposes into PbO.

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

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.

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.

EXERCISE # 1

PART - I : OBJECTIVE QUESTIONS

*** Marked Questions are having more than one correct option.**

Group 13th

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) none is correct.

2.* Which of the following facts regarding boron and silicon is 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.

3. B^{3+} ion cannot exist in aqueous solution because of its :
(A) strong reducing ability. (B) strong oxidizing ability.
(C) small size and large charge. (D) large size and small charge.

4. From the B_2H_6 all the following can be prepared except :
(A) H_3BO_3 (B) $[BH_2(NH_3)_2]^+ [BH_4]^-$ (C) $B_2(CH_3)_6$ (D) $NaBH_4$

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

6. The number of possible isomers for disubstituted borazine, $B_3N_3H_4X_2$ is :
(A) 3 (B) 4 (C) 6 (D) 2

7. In the following reaction : $B(OH)_3 + H_2O \rightarrow [B(OH)_4]^- + H^+$:
(A) $B(OH)_3$ is a Lewis acid. (B) $B(OH)_3$ is a Lewis base.
(C) $B(OH)_3$ is amphoteric. (D) none is correct.

8. When orthoboric acid (H_3BO_3) is heated the residue left is :
(A) boron (B) metaboric acid (C) boric anhydride (D) borax

9. Borax is:
(A) $Na_2B_4O_7$ (B) $Na_2B_4O_7.4H_2O$ (C) $Na_2B_4O_7.7H_2O$ (D) $Na_2B_4O_7.10H_2O$

10. 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

11. The borax bead is chemically :
(A) B_2O_3 (B) $Na_2B_4O_7$ (C) Na_3BO_3 (D) $B_2O_3 + NaBO_2$

12. Borax bead test is responded by :
(A) divalent metals (B) heavy metals
(C) light metals (D) metal which forms coloured metaborates

13. 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

14. An aqueous solution of borax is :
(A) neutral (B) amphoteric (C) basic (D) acidic

15. 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) $Na_3Co(BO_3)_2$

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

17. 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

18. Diborane reacts with water to form :
(A) HBO_2 (B) H_3BO_3 (C) $H_3BO_3 + H_2$ (D) H_2

19. H_2S gas can be obtained by the action of water on:
(A) CuS (B) FeS (C) Flower of sulphur (D) Al_2S_3

20. Which of the following compound is a gas (at 0°C) :
(A) BF_3 (B) BCl_3 (C) BBr_3 (D) BI_3

21. 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

22. Aluminium does not react with:
(A) NaOH (B) conc. HCl (C) N_2 (D) conc. HNO_3

23. When Al is added to sodium hydroxide solution:
(A) no reaction takes place (B) oxygen is evolved
(C) water is produced (D) hydrogen is evolved

24. Alum is found to contain hydrated monovalent cation $[M(H_2O)_6]^+$, trivalent cation $[M'(H_2O)_6]^{3+}$ and SO_4^{2-} in the ratio of :
(A) 1 : 1 : 1 (B) 1 : 2 : 3 (C) 1 : 3 : 2 (D) 1 : 1 : 2

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

26. The dissolution of $Al(OH)_3$ by a solution of NaOH results in the formation of :
(A) $[Al(H_2O)_4(OH)]^{2+}$ (B) $[Al(H_2O)_2(OH)_4]^-$ (C) $[Al(H_2O)_3(OH)_3]$ (D) $[Al(H_2O)_6(OH)_3]$

27. Which mixed sulphate is not an alum:
(A) $K_2SO_4.Al_2(SO_4)_3.24H_2O$ (B) $K_2SO_4.Cr_2(SO_4)_3.24H_2O$
(C) $Na_2SO_4.Fe_2(SO_4)_3.24H_2O$ (D) $CuSO_4.Al_2(SO_4)_3.24H_2O$

28. 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

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

Then addition of which of the following proceeds the reaction in the forward direction.

(A) Glecerol (B) Mannitol (C) Catachol (D) Ethanol

30. Reaction of diborane with chlorine produces :

(A) B_2H_5Cl (B) H_2 (C) BCl_3 (D) (B) and (C) both

31. Which of the following statement is correct for diborane ?

(A) Small amines like NH_3, CH_3NH_2 give unsymmetrical cleavage of diborane.
(B) Large amines such as $(CH_3)_3N$ and pyridine gives symmetrical cleavage of diborane.
(C) Small as well as large amines both gives symmetrical cleavage of diborane.
(D) (A) and (B) both

32. An aqueous solution of BCl_3 is :

(A) weak acid (B) weak base (C) neutral (D) strong base

33. BF_3 on hydrolysis forms :

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

34. Which of the following statements about anhydrous aluminium chloride is correct ?

(A) It exists as $AlCl_3$ molecule (B) It is not easily hydrolysed
(C) It sublimes at 100°C under vacuum (D) It is a strong Lewis base

35. 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 $[Al(OH)_4]^-$ ions (D) NaOH forms $[Al(OH)_2]^+$ ions

36. Which reaction cannot give anhydrous $AlCl_3$?

(A) Heating of $AlCl_3.6H_2O$
(B) Passing dry HCl over heated aluminium powder
(C) Passing dry Cl_2 over heated aluminium powder
(D) Heating a mixture of alumina and coke in a current of dry Cl_2

37. 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

Group 14th

38. Diamond and graphite are :

(A) isomers (B) isotopes (C) allotropes (D) none of the above

39. Which of the following is a good conductor of electricity ?

(A) Diamond (B) Graphite (C) Coal (D) None

40. Inert form of carbon is :

(A) diamond (B) graphite (C) coal (D) charcoal

41. Thermodynamically the most stable form of carbon is :

(A) diamond (B) graphite (C) fullerenes (D) coal

42. CO forms a volatile compound with :

(A) nickel (B) copper (C) sodium (D) aluminium

43. CO is absorbed by :

(A) $CHCl_3$ (B) pyrogallol

(C) CCl_4 (D) ammoniacal solution of copper (I) chloride

44. Elements of group 14 :

(A) exhibit oxidation state of +4 only (B) exhibit oxidation state of +2 and +4

(C) form M^{-2} and M^{4+} ions (D) form M^{2+} and M^{4+} ions

45. CO_2 in water behaves as :

(A) weak dibasic acid H_2CO_3 (B) weak monobasic acid $HO-CO_2H$

(C) weak diacid base $CO(OH)_2$ (D) weak monoacid base $HO-CO_2H$

46.* The carbide which does/do not give propyne on hydrolysis is/are :

(A) Al_4C_3 (B) CaC_2 (C) Fe_3C (D) Mg_2C_3

47. Allylides are ionic carbides. They contains :

(A) C^{4-} ions (B) C_2^{2-} ions (C) C_3^{3-} ions (D) C_3^{4-} ions

48. Methanides are :

(A) Mg_2C_3 , Be_2C, Al_4C_3 and CaC_2 (B) Mg_2C_3 , Be_2C and Al_4C_3

(C) Be_2C, Al_4C_3 and CaC_2 (D) Be_2C and Al_4C_3

49. A bottle of fire extinguishers contain H_2SO_4 and :

(A) $CaCO_3$ (B) $MgCO_3$ (C) $NaHCO_3$ (D) any carbonate

50. The oxide which is not a reducing agent is :

(A) CO_2 (B) NO_2 (C) SO_2 (D) ClO_2

51. 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

52. A colourless gas which burns with blue flame and reduces CuO to Cu is :

(A) N_2 (B) CO (C) CO_2 (D) NO_2

53. When steam is passed through red hot coke :

(A) CO_2 and H_2 are obtained (B) CO and N_2 are formed

(C) CO and H_2 are obtained (D) petrol gas is obtained

54. 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) $(CN)_2$

55.* Which of the following reactions are is correct ?

(A) $CF_4 + 2F^- \rightarrow [CF_6]^{2-}$ (B) $SiF_4 + 2F^- \rightarrow [SiF_6]^{2-}$

(C) $GeCl_4 + 2Cl^- \rightarrow [GeCl_6]^{2-}$ (D) $SnCl_4 + 2Cl^- \rightarrow [SnCl_6]^{2-}$

56. Glass is soluble in :

(A) HF (B) H_2SO_4 (C) $HClO_4$ (D) aqua-regia

57. Silicon reacts with hot solution of NaOH forming :

(A) $Si(OH)_4$ (B) $Si(OH)_2$ (C) SiO_2 (D) Na_4SiO_4

58. The structural unit present in pyrosillicates is :

(A) $Si_3O_9^{6-}$ (B) SiO_4^{4-} (C) $Si_2O_7^{6-}$ (D) $(Si_2O_5^{2-})_n$

59. Red lead is :

(A) PbO (B) PbO_2 (C) Pb_3O_4 (D) Pb_2O_3

60. 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+}

61. Unlike $PbCl_4$, PI_4 and PBr_4 are not found because :

(A) bromine and iodine are more electronegative than chlorine.
(B) iodine and bromine are smaller in size.
(C) larger iodine and bromine are able to reduce Pb^{4+} to Pb^{2+} or Pb.
(D) the statement is incorrect.

62. Water transported through lead pipes becomes poisonous due to the formation of :

(A) $Pb(OH)_2$ (B) PbO (C) PbO_2 (D) Pb_3O_4

63. Which of the following halides is least stable and has doubtful existence? **[JEE 1996, 1]**

(A) CI_4 (B) GeI_4 (C) SnI_4 (D) PbI_4

64. $Me_2SiCl_2 \xrightarrow{H_2O} (A) \xrightarrow{\text{condensation}} (B)$.

The nature of product (B) may be

(A) only linear polymers (B) cyclic products
(C) (A) and (B) both (D) none of these

65. 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

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

67. Tin reacts with concentrated HNO_3 and gives :

(A) stannic nitrate (B) stannous nitrate (C) metastannic acid (D) none of sigma bond

68. 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) Asbestos

PART - II : MISCELLANEOUS QUESTIONS

FILL IN THE BLANKS.

Group 13th

1. The number of hydrogen atoms bridging the boron atoms in diborane is ....

2. Boron resembles more with .... than its own family members.

3. Among the metals Na, Mg and Al, the metal with highest melting point is ....

4. Hydrogen gas is liberated by the action of aluminium with concentrated solution of ....

5. In the thermite process .... is used as a reducing agent.

6. The hydrides of boron are called ....

7. The stable oxidation state of thallium is ....

8. ✍ The chemical name of inorganic benzene is ....

9. ✍ AlF_3 is an ionic compound while $AlCl_3$ behaves as .... compound.

10. The reaction between aluminium and oxygen is an .... reaction.

11. Aluminium is a .... conductor of electricity.

12. BCl_3 is .... Lewis acid than BF_3.

13. Silver paint is made by dissolving .... powder in linseed oil.

14. An alloy of copper which has beautiful golden yellow colour is called ....

Group 14th

15. Carbon exhibits the unique property of forming chains of identical atoms, called ___________.

16. Diamond is a ______________ conductor of electricity and heat.

17. ✍ A mixture of ___________ and CO_2 is obtained when oxalic acid is heated with conc. H_2SO_4 .

18. ✍ Glass is attacked by ___________ acid.

19. SnS is solubl in _________ ammonium sulphide.

20. Carbon monoxide is poisonous because it combines with _____ and the product becomes incapable of absorbing _________.

21. Solid form of carbon dioxide is known as __________.

22. Carbon monoxide forms a volatile coordination compound with nickel, it is ___________.

23. ✍ The hydrolysis of alkyl substituted chlorosilanes gives ____________.

24. The hydrolysis of trialkyl chloro silane, R_3SiCl yields ___________.

25. One recently discovered allotrope, C_{60}, is commonly known as _____________.

26. Graphite is a better lubricant on the ___________ than on the earth.

27. The formula of litharge is __________ and that of red lead is __________ both are used as _________ in paints.

28. In drinking soda ___________ gas is present under high pressure in water.

29. ✍ The C–C bond length in diamond is __________ while the C–C bond length in graphite is ___________.

30. Carbon monoxide is absorbed in a solution of _______ under pressure while carbon dioxide is absorbed in a solution of ————.

31. Carbon dioxide has no dipole moment as it has __________ molecule.

32. ✍ Carbon monoxide combines with chlorine in the presence of sunlight to produce ___________.

TRUE OR FALSE

Group 13th

33. All the Al – Cl bonds in Al_2Cl_6 are equivalent.

34. An aqueous solution of potash alum is acidic.

35. $AlCl_3$ is a Lewis base.

36. $AlCl_3$ exists as Al_2Cl_6 in vapour state.

37. $B(OH)_3$ is acidic in nature

38. Borax forms orthoboric acid when warmed with conc. sulphuric acid.

39. Duralumin is an alloy of aluminium.

40. Boron dissolves in hydrochloric acid.

41. Boron compounds are covalent while aluminium compounds are electrovalent or covalent.

42. BCl_3 is better Lewis acid than $AlCl_3$.

43. TIOH is a strong base.

Group 14th

44. Silicon forms lesser number of hydrides than carbon.

45. CO_2 can be prepared by dehydration of formic acid.

46. Silanes act as reducing agents

47. Lead nitrate on heating gives a mixture of NO_2 and O_2.

48. Anhydrous tin (II) chlorine can be obtained by passing dry chlorine gas over heated tin.

49. Producer gas is a mixture of CO and H_2.

50. Carbon atom undergoes sp^2 hybridization in diamond structure.

51. Carborundum has structure similar to diamond.

52. Silica has the structrure O=Si=O.

53. Dry ice is the solid carbon dioxide.

54. White lead has high covering power when it is used as a paint.

55. Tin exists in three allotropic forms, white tin, grey tin and brittle tin.

56. Lead tetra ethyl is used as an additive to petrol.

57. Stannous chloride is a linear molecule.

ASSERTION AND REASONING

Group 13th

DIRECTIONS :

The following questions consist of two statements one labelled ASSERTION (A) and the another labelled REASON (R). Select the correct answers to these questions from the codes given below :

(A) Both Assertion and Reason are true and Reason is the correct explanation of Assertion.

(B) Both Assertion and Reason are true but Reason is not correct explanation of Assertion

(C) Assertion is true but Reason is false

(D) Assertion is false but Reason is true

58. **Assertion :** $Al(OH)_3$ is insoluble in NH_4OH but soluble in NaOH
Reason : NaOH is a stronger base alkali.

59. **Assertion :** Boron is metalloid
Reason : Boron shows metallic character

60. ✎ **Assertion :** Benzene is reactive while inorganic benzene is unreactive compound
Reason : Inorganic benzene is borazine, $B_3N_3H_6$

61. ✎ **Assertion :** Al forms $[AlF_6]^{3-}$ but B does not form $[BF_6]^{3-}$
Reason : BF_3 on hydrolysis gives HBF_4 .

62. **Assertion :** Aluminium(III) does not respond to borax bead test.
Reason : Aluminum(III) metaborate is a colourless compound .

63. **Assertion :** $AlCl_3$ forms dimer Al_2Cl_6 but it dissolves in H_2O forming $[Al(H_2O)_6]^{3+}$ and Cl^- ions.
Reason : Aqueous solution of $AlCl_3$ is acidic due to hydrolysis.

Group 14th

64. ✎ **Assertion :** Si–Si bonds are much weaker then Si–O bonds.
Reason : Silicon forms double bonds with itself.

65. ✎ **Assertion :** Pb^{+4} can be reduced easily to Pb^{2+}
Reason : Pb^{+2} is paramagnetic

66. **Assertion :** SiF_6^{2-} is known but $SiCl_6^{2-}$ is not.
Reason : Size of fluorine is small and its lone pair of electrons interacts with d-orbitals of Si strongly.

MATCH THE FOLLOWING

Group 13th

67.

(a) Anhydrous $AlCl_3$	(i) Antiseptic
(b) Alum	(ii) Alloy
(c) Ultramarine	(iii) Friedel-Craft's reaction
(d) Borax	(iv) Complex blue coloured silicate
(e) Magnelium	(v) Tincal

68.

(a) Colemanite	(i) Na_3AlF_6
(b) Cryolite	(ii) $KAl(SO_4)_2.12H_2O$
(c) Bauxite	(iii) $Ca_2B_6O_{11}.5H_2O$
(d) Borax	(iv) $Na_2B_4O_7.10H_2O$
(e) Potash alum	(v) $Al_2O_3.2H_2O$

69.

(a) Inorganic benzene	(i) $Na_2B_4O_7.10H_2O$
(b) Jeweller's borax	(ii) B_2H_6
(c) Borax	(iii) $Na_2B_4O_7.5H_2O$
(d) Diborane	(iv) Mordant
(e) Alum	(v) $B_3N_3H_6$

70.

Column - I	Column- II
(A) $BBr_3 + H_2 \longrightarrow$	(p) Borax bead test
(B) $Na_2B_4O_7.\ 10\ H_2O + CuSO_4 \rightarrow$	(q) Heat
(C) $AlCl_3 + H_2O \longrightarrow$	(r) Reduction
(D) $Cr_2O_3 + Al \longrightarrow$	(s) White fumes
	(t) Hydrolysis

Group 14th

71.

Column I		**Column II**
(a)	Asbestos	(i) Oxygen
(b)	Silicones	(ii) Allylides
(c)	Red lead $\xrightarrow{\Delta}$	(iii) $PbCl_4$
(d)	Carborundum	(iv) Carbon monoxide
(e)	Propyne	(v) Soccer ball shaped
(f)	Carbon suboxide	(vi) Double chain silicate
(g)	Yellow oily liquid	(vii) Oxidising agent
(h)	Mond's process	(viii) $(R_2SiO)_n$
(i)	Buckminster fullerene	(ix) $CH_2(COOH)_2 + P_4O_{10} \xrightarrow{\Delta}$
(j)	Red lead	(x) Hard, diamond like structure
		(xi) Linear structure

72.

Column - I	Column- II
(A) $Al_2\ (C_2)_3 + H_2O \longrightarrow$	(p) σ and π bonds
(B) $CH_2\ (COOH)_2\ + P_4O_{10} \rightarrow$	(q) Hydrolysis
(C) $CH_3\ SiCl_3 + H_2O \longrightarrow$	(r) Dehydration
(D) $SnCl_2.2H_2O \xrightarrow[\text{standing}]{\text{on}}$	(s) complex crosslinked polymer

EXERCISE # 2

PART - I : MIXED OBJECTIVE

Single choice type

Group 13th

1. Which of the following facts regarding boron and silicon is not true :

(A) Boron and silicon are semiconductors.

(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_4 and SiO_4 tetrahedral units, respectively.

2. B^{3+} cannot exist in aqueous solution becuase of its :

(A) Strong reducing ability. (B) Strong oxidizing ability.

(C) Small size and large charge. (D) Large size and small charge.

3. Borax is used as a buffer since :

(A) Its aqueous solution contains equal amount of weak acid and its salt

(B) It is easily available

(C) Its aqueous solution contains equal amount of strong acid and its salt

(D) Statement that borax is a buffer, is wrong

4. The product obtained in the reaction of diborane with excess of ammonia is :

(A) $B_2H_6 . NH_3$ (B) $B_2H_6 . 2NH_3$ (C) $(BN)_x$ (D) Borazine

5. Water softener is :

(A) Borax (B) Zeolite (C) Both (A) and (B) (D) None of these

6. BF_3 on hydrolysis forms :

(A) H_3BO_3 (B) HBF_4 (C) Both (A) and (B) (D) None of these

7. The bonds present in borazole are :

(A) $12\sigma, 3\pi$ (B) $9\sigma, 6\pi$ (C) $6\sigma, 6\pi$ (D) $9\sigma, 9\pi$

8. Reactivity of borazole is greater than that of benzene because:

(A) Borazole is non-polar compound (B) Borazole is polar compound

(C) Borazole has electrons in it (D) Of localized electrons in it

Group 14th

9. $Me_2SiCl_2 \xrightarrow{H_2O} (A) \xrightarrow{\text{condensation}} (B)$.

The nature of product (B) may be

(A) only linear polymers (B) cyclic products

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

10. When steam is passed through red hot coke :

(A) CO_2 and H_2 are obtained (B) CO and N_2 are formed

(C) CO and H_2 are obtained (D) petrol gas is obtained

11. Glass is soluble in

(A) HF (B) H_2SO_4 (C) $HClO_4$ (D) aqua-regia

12. 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

13. Carborundum is the commercial name of

(A) Al_2O_3 (B) SiC (C) $CaCN_2$ (D) CaC_2

14. CO is absorbed by

(A) $CHCl_3$ (B) pyrogallol
(C) CCl_4 (D) ammonical solution of copper (I) chloride

15. Select incorrect statemen (s) :

(A) Interstitial carbides are formed by metalloids like Si and B
(B) Covalent carbides are formed by metalloids
(C) CO and CN^- both are fatal due to complex formation with Fe(III) present in blood
(D) SiC is called carborundum

16. The oxide which is not a reducing agent is

(A) CO_2 (B) NO_2 (C) SO_2 (D) ClO_2

More than one choice type

Group 13th

17. Which of the following form dimeric halides ?

(A) Al (B) Mg (C) In (D) Ga

18. Which species exist:

(A) $[BF_6]^{3-}$ (B) $[AlF_6]^{3-}$ (C) $[GaF_6]^{3-}$ (D) $[InF_6]^{3-}$

19. Borax bead test is given by:

(A) An aluminium salt (B) A cobalt salt (C) A copper salt (D) A nickel salt

20. Identify the statement that is/are correct as far as structure of diborane is concerned:

(A) There are two bridging hydrogen atoms in diborane
(B) Each boron atom forms four bonds in diborane
(C) The hydrogen atoms are not in the same plane in diborane
(D) All B-H bonds in diborane are similar

21. Which is/are correct ?

(A) Al acts as a reducing agent
(B) Al does not react with steam even at higher temperature
(C) Al forms a number of alloys with other metals
(D) Al is ionic in all its compounds

22. Aluminium is/are used :

(A) In thermite welding (B) As oxidiser in metallurgy
(C) For making utensils (D) In silvery paints

23. Boric acid is used :

(A) As an antiseptic (B) As a flux in soldering
(C) In making optical glasses (D) In making enamels and pottery glazes

24. 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

25. Which of the following is/are correct in case of boron nitride :

(A) It is also called borazine

(B) It is chemically unreactive

(C) It is hard because it has diamond like structure

(D) It has magnetic properties

10. Which of the following statements about anhydrous aluminium chloride is/are incorrect:

(A) It exists as $AlCl_3$ molecule

(B) It is a strong Lewis base

(C) It sublims at 100^{o}C under vacuum

(D) It is not easily hydrolysed

Group 14th

11. 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 and as semi-conductor perpendicular to the layers of the carbon atoms.

(C) Graphite is less denser than diamond

(D) C_{60} is called as Buckminster fullerence

12. 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

13. Select the incorrect statement(s)

(A) Carborundum on strong heating does not melt but dissociates to give volatile silicon and graphite.

(B) Graphite crystallised in presence of alkali metals is found to be much more conducting.

(C) Carbon monoxide burns with blue flame.

(D) The oxidation state of central carbon atom in carbon sub-oxide is two.

14. Which of the following give(s) ethyne on reaction with water?

(A) $Al_2(C_2)_3$

(B) Al_4C_3

(C) SrC_2

(D) Mg_2C_3

15. Which of the following statement(s) is/are false for soluble bicarbonates?

(A) They give pink colour with phenolphthalein

(B) They do not liberate carbondioxide with phenol.

(C) They give white precipitate with magnesium sulphate in cold.

(D) They liberate carbondioxide on reaction with dil. H_2SO_4

16. 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 $SiCl_4$.

17. Select the correct statement(s)

(A) Double chain silicates are known as amphiboles.

(B) In cyclic silicates two oxygen atoms per tetrahedron are shared.

(C) Orthosilicates contain discrete $(SiO_4)^{4-}$ units.

(D) Asbestos mineral is a double chain silicate and mica is a sheet silicate.

PART - II : SUBJECTIVE QUESTIONS

Group 13th

1. Explain why aluminium, though an electropositive metal, finds extensive use as a structural material

2. Discuss the pattern of variation in oxidation states of the following :
(i) Al to Tl (ii) Si to Pb (iii) P to Bi

3. How is $LiAlH_4$ prepared ? What is its important uses ?

4. What happens when NaOH (aq) is added drop wise to a solution of $GaCl_3$ in water ?

5. Give formula of the following :
(i) Felspar (ii) Cryolite (iii) Jeweller's borax (iv) Corundum (v) Colemanite

6. Answer the following :
(i) What is the outer electronic configuration of group IIA elements ?
(ii) Name the first two elements of group IIIA.
(iii) What is Tincal ?
(iv) What is thermite mixture ?
(v) What is inorganic benzene ?
(vi) Name the two metals present in common alum.
(vii) Name the aluminium compound used in Friedel Craft's reaction.

7. What happens when :
(i) Borax is heated strongly
(ii) Aluminium is heated with caustic soda solution.
(iii) A mixture of borax and cobalt oxide is heated in a flame.
(iv) Water is added to aluminium nitride.
(v) Aluminium reacts with HNO_3.

8. Explain the following with relevent reason.
(i) Aluminium metal is frequently used as reducing agent for the extraction of metals such as Cr, Mn, Fe, etc.
(ii) $AlCl_3$ forms a dimer but BCl_3 does not form dimer.
(iii) The B —— X distance is shorter than what is expected theoretically in BX_3 molecule (X = Cl, F, Br, I) ?
(iv) Why boron does not form B^{3+} ion ?
(v) Although the ionisation potential of boron (8.30 eV) is less than gold (9.22 eV), yet former is a non-metal while the latter is a metal.
(vi) Borazine is more reactive than benzene.
(vii) First ionisation potential of Al is lower than that of Mg.

9. How will you obtain.
(A) sodium peroxo borate from borax (in two steps only)
(B) Borazole from sodiumboro hydride (in three steps only)
(C) Borax from Boron (in two steps)

10. Bring out points of similarity and dissimilarity between boron and aluminium ?

11. Why borax can be used as a buffer ?

Ans. Borax solution in water produces weak acid H_3BO_3 and its salt $Na[B(OH)_4]$ in equimolar quantity.
$Na_2B_4O_7 + 7H_2O \longrightarrow 2Na\,[B(OH)_4] + 2H_3BO_3$

12. ✍ Why it is difficult to produce crystalline boron ?

13. ✍ Explain why boric acid behaves as a weak monobasic acid ?

14. Which indicator can be used to detect the end point of borax-acid titration ?

15. ✍ Under what conditions boric acid can be titrated against sodium hydroxide using phenolphthalein as indicator.

16. An aqueous solution of borax acts alkaline. Explain ?

17. ✍ Borazine or borazole is more reactive than benzene. Explain ?

18. What will be the nature of reagent attacking the borazine molecule ?

19. Pure BBr_3 and BI_3 are colourless, but they become coloured on exposure to light, why ?

20. ✍ Complete the following reaction and write the structure of the product formed.

$$B_2H_6 \xrightarrow[\text{High temp.}]{\text{Excess } NH_3}$$

21. Complete the following reaction and identity compound (A) and (B).

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

22. What are different kind of borates ?

23. ✍ How pure boron can be prepared from BI_3 or BCl_3 ?

24. ✍ Why does $AlCl_3$ fumes in air ?

25. ✍ Define an alum. What are some of their important uses ?

26. Starting from boric acid how would you prepare ?
(A) BCl_3 (B) Boron Hydorxide (C) Meta and tetra boric acid

27. Discuss the change in coordination number when crystalline $AlCl_3$ is heated ?

28. Consider the compounds, BCl_3 and CCl_4, How will they behave with water ? Justify.

29. Is boric acid a protic acid ? Explain.

30. Explain what happens when boric acid is heated above 370 K ?

31. What do you understans by (a) inert pair effect. (b) allotropy and (c) catention ?

32. 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 conc. H_2SO_4 is added to a hot solution of X, white crystal of an acid Z searates out.
Write equations for all the above reactions and identify X, Y, and Z.

33. Write balanced equation for
(i) $BF_3 + LiH \rightarrow$
(ii) $B_2H_6 + H_2O \rightarrow$
(iii) $NaH + B_2H_6 \rightarrow$
(iv) $Al + NaOH \rightarrow$
(v) $B_2H_6 + NH_3 \rightarrow$ (Low tempt and 200ºC in 1 : 2 ratio)

Group 14th

34. What is the importance of ultra pure elemental silicon ? How is it obtained ?

35. Write balanced equations for the following reactions :
(A) SnO is treated with dil. HNO_3
(B) Tin is treated with an excess of chlorine gas.
(C) Lead sulphide is heated in air.

36. What are silicates ? How are they classified ?

37. What are silicones ? How are they manufactured ?

38. How far do you agree with the phenomenon concept of inert pair effect ? Justify your answer.

39. Why alkali metals should not be used for drying CCl_4 and other chlorocarbons?

40. Why in reactions of HCl & SO_2 , PbO_2 shows oxidising nature? Explain.

41. Dilute HCl is preferred over dilute H_2SO_4 for the preparation of CO_2 from lime stone. Explain.

42. $PbCl_4$ is less stable than $SnCl_4$. Explain.

43. Why does not silicon form an analogue of graphite?

44. Like CO why its analogue of SiO is not stable.

45. Why CO_2 is a gas and SiO_2 is solid ?

46. What happens when,
(a) Mixture of R_2-$SiCl_2$ and R_3 - SiCl is subjected to hydrolysis.
(b) Malonic acid is heated in presence of P_4O_{10} .
(c) Tin (IV) Chloride is exposed to moist air.

47. Explain the term "plumbosolvency".

48. $CaO + C \xrightarrow{\Delta} (A) + (B)$

$(A) + N_2 \xrightarrow{\Delta} (C) + \text{carbon}$

$(C) + H_2O \longrightarrow (D) + NH_3$

Identify (A), (B), (C) and (D)

49. How carbonates and bicarbonates can be differentiated from one another ?

50. Name two elements known for their semiconducting nature.

51. Which crystalline allotropic form of carbon has the lowest energy ?

52. Give reactions to show that CO_2 is an acidic oxide and SnO_2 is an amphoteric oxide.

53. Diamond and graphite both are allotropic forms of carbon, still only graphite is used as lubricant. Why ?

54. Complete the following reactions :

(i) $K_4[Fe(CN)_6] + H_2SO_4 + H_2O \longrightarrow$
(ii) $CS_2 + NO \longrightarrow$
(iii) $Pb_3O_4 + HNO_3 \longrightarrow$
(iv) $CaF_2 + SiO_2 + H_2SO_4 \longrightarrow$
(v) $Pb^{+2} + H_2S + 2Cl^-$ (from saturated salt. of KCl) $\longrightarrow$

55. ✎ Write the chemical reactions involved in the hydrolysis of Alkyl trichlorosilane.

56. ✎ Write at least three uses of silicones.

57. SiO_4^{4-} ion exists while CO_4^{4-} does not, why ?

58. Why PbO, a base, is not completely dissolved in HCl and H_2SO_4 but dissolves in HNO_3.

59. Which among the following oxides of lead is strong oxidising agent ?

PbO, PbO_2, Pb_3O_4

60. ✎ To which category do the following carbides belong ?

(i) SiC (ii) VC (iii) WC (iv) Al_4C_3

61. What is the formula and the colour of Buckminster fullerene in toluene ?

62. What happens when Ag_2C_2 is allowed to react with dil. HCl ?

63. ✎ During reduction of SiO_2 into Si, SiO_2 is taken in excess, why ?

64. Rationalise the given statements and give chemical reactions :

(i) Lead (II) chloride reacts with Cl_2 to give $PbCl_4$
(ii) Lead (IV) chloride is highly unstable towards heat.
(iii) lead is knwon not to form an iodide, PbI_4

65. Suggest a reason as to why CO is poisonous.

66. How is exessive contents of CO_2 responsible for global warming ?

67. Give reasons

(i) Graphite is used an lubricant.
(ii) Diamond is used as an abrasive.

68. Classify following oxides as netural, acidic, basic or amphoteric :

CO, B_2O_3, SiO_2, CO_2, Al_2O_3, PbO_2, Tl_2O_3

69. If the starting material for the manufacture of silicones is $RSiCl_3$, write the structure of the product formed.

EXERCISE # 3

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

*** Marked Questions are having more than one correct option.**

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) $Bi^{3+} \to (BiO)^+$	(p) Heat
(B) $[AlO_2]^- \to Al(OH)_3$	(q) Hydrolysis
(C) $SiO_4^{4-} \to Si_2O_7^{-6}$	(r) Acidification
(D) $(B_4O_7^{2-}) \to [B(OH)_3]$	(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, (P-I) 3/81]**

(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, (P-II) 4/80]**

10.* 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, (P-II) 4/80]**

(A) NH_3 (B) CH_3NH_2 (C) $(CH_3)_2NH$ (D) $(CH_3)_3N$

Group 14th

11. 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)

12. $(Me)_2\ SiCl_2$ on hydrolysis will produce : **[JEE 2003, (S) 3/84]**
(A) $(Me)_2Si(OH)_2$ (B) $(Me)_2\ Si = O$
(C) $-[-O-(Me)_2\ Si-O-]_n-$ (D) $Me_2SiCl(OH)$

13. 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

14. **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, (P-I) 3/82]**
(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

15. The value of n in the molecular formula $Be_nAl_2Si_6O_{18}$ is : **[JEE 2010, (P-I) 3/84]**

16.* With respect to graphite and diamond, which of the statement (s) given below is (are) correct ?
(A) Graphite is harder than diamond.
(B) Graphite has higher electrical conductivity than diamond
(C) Graphite has higher thermal conductivity than diamond.
(D) Graphite has higher C-C bond order than diamond. **[JEE 2012, 4/198]**

17. Concentrated nitric acid, upon long standing, turns yellow-brown due to the formation of: **[JEE Advanced 2013, P-I]**
(A) NO (B) NO_2 (C) N_2O (D) N_2O_4

PART - II : AIEEE PROBLEMS (PREVIOUS YEARS)

Marked Questions are having more than one correct option.

1. Aluminium is extracted by the electrolysis of **[AIEEE 2002]**
(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]**
(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. 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]**
(1) $[Al(OH)_6]^{3-} + 3HCl$ (2) $[Al(H_2O)_6]^{3+} + 3Cl^-$
(3) $Al^{3+} + 3Cl^-$ (4) $Al_2O_3 + 6HCl$

4. In silicon dioxide : **[AIEEE 2005]**

(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

5. Heating an aqueous solution of aluminium chloride to dryness will give : **[AIEEE 2005]**

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

6. 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) $PbX_2 < SnX_2 < GeX_2 < SiX_2$

7. 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.

8. 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

9. 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.

10. Select the incorrect statement. **[AIEEE 2009]**

(1) Silicones are hydrophobic in nature.

(2) Si–O–Si linkages are moisture sensitive.

(3) SnI_4 is an orange solid on account of charge transfer.

(4) 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.

11. Select incorrect statement : **[AIEEE 2009]**

(1) Red lead is Pb_3O_4

(2) $(Me)_2SiCl_2$ on hydrolysis and then on subsequent intermolecular condensation gives cross linked silicones.

(3) SiO_4^{4-} on hydrolysis with water or acid produces $Si_2O_7^{6-}$

(4) None

EXERCISE # 4

NCERT QUESTIONS

1. Discuss the pattern of variation in the oxidation states of
(i) B to Tl and (ii) C to Pb.

2. How can you explain higher stability of BCl_3 as compared to $TlCl_3$?

3. Why does boron triflouride behave as a Lewis acid ?

4. Consider the compounds, BCl_3 and CCl_4. How will they behave with water ? Justify.

5. Is boric acid a protic acid ? Explain.

6. Explain what happens when boric acid is heated.

7. Describe the shapes of BF_3 and BH_4^-. Assign the hybridisation of boron in these species.

8. Write reactions to justify amphoteric nature of aluminium.

9. What are electron deficient compounds ? Are BCl_3 and $SiCl_4$ electron deficient species ? Explain.

10. Write the resonance structures of CO_3^{2-} and HCO_3^-.

11. What is the state of hybridisation of carbon in
(a) CO_3^{2-} (b) diamond (c) graphite?

12. Explain the difference in properties of diamond and graphite on the basis of their structures.
संरचना के आधार पर हीरा तथा ग्रेफाइट के गुणों में निहित भिन्नता को समझाइए।

13. Rationalise the given statements and give chemical reactions :
- Lead(II) chloride reacts with Cl_2 to give $PbCl_4$.
- Lead(IV) chloride is highly unstable towards heat.
- Lead is known not to form an iodide, PbI_4.

14. Suggest reasons why the B–F bond lengths in BF_3 (130 pm) and BF_4^- (143 pm) differ.

15. If B–Cl bond has a dipole moment, explain why BCl_3 molecule has zero dipole moment.

16. Aluminium trifluoride is insoluble in anhydrous HF but dissolves on addition of NaF. Aluminium trifluoride precipitates out of the resulting solution when gaseous BF_3 is bubbled through. Give reasons.

17. Suggest a reason as to why CO is poisonous.

18. How is excessive content of CO_2 responsible for global warming ?

19. Explain structures of diborane and boric acid.

20. What happens when
(a) Borax is heated strongly,
(b) Boric acid is added to water,
(c) Aluminium is treated with dilute NaOH,
(d) BF_3 is reacted with ammonia ?

21. Explain the following reactions
(a) Silicon is heated with methyl chloride at high temperature in the presence of copper;
(b) Silicon dioxide is treated with hydrogen fluoride;
(c) CO is heated with ZnO;
(d) Hydrated alumina is treated with aqueous NaOH solution.

22. Give reasons :
(i) Conc. HNO_3 can be transported in aluminium container.
(ii) A mixture of dilute NaOH and aluminium pieces is used to open drain.
(iii) Graphite is used as lubricant.
(iv) Diamond is used as an abrasive.
(v) Aluminium alloys are used to make aircraft body.
(vi) Aluminium utensils should not be kept in water overnight.
(vii) Aluminium wire is used to make transmission cables.

23. Explain why is there a phenomenal decrease in ionization enthalpy from carbon to silicon ?

24. How would you explain the lower atomic radius of Ga as compared to Al ?

25. What are allotropes? Sketch the structure of two allotropes of carbon namely diamond and graphite. What is the impact of structure on physical properties of two allotropes?

26. (a) Classify following oxides as neutral, acidic, basic or amphoteric :
CO, B_2O_3, SiO_2, CO_2, Al_2O_3, PbO_2, Tl_2O_3
(b) Write suitable chemical equations to show their nature.

27. In some of the reactions thallium resembles aluminium, whereas in others it resembles with group I metals. Support this statement by giving some evidences.

28. When metal X is treated with sodium hydroxide, a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound (A) is soluble in dilute HCl to form compound (C). The compound (A) when heated strongly gives (D), which is used to extract metal. Identify (X), (A), (B), (C) and (D). Write suitable equations to support their identities.

29. What do you understand by
(a) inert pair effect (b) allotropy and (c) catenation?

30. 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 conc. 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.

31. Write balanced equations for :
(i) $BF_3 + LiH \rightarrow$ (ii) $B_2H_6 + H_2O \rightarrow$
(iii) $NaH + B_2H_6 \rightarrow$ (iv) $H_3BO_3 \xrightarrow{\Delta}$
(v) $Al + NaOH \rightarrow$ (vi) $B_2H_6 + NH_3 \rightarrow$

32. Give one method for industrial preparation and one for laboratory preparation of CO and CO_2 each.

33. An aqueous solution of borax is
(a) neutral (b) amphoteric (c) basic (d) acidic

34. Boric acid is polymeric due to
(a) its acidic nature (b) the presence of hydrogen bonds
(c) its monobasic nature (d) its geometry

35. The type of hybridisation of boron in diborane is :
(a) sp (b) sp^2 (c) sp^3 (d) dsp^2

36. Thermodynamically the most stable form of carbon is
(a) diamond (b) graphite (c) fullerenes (d) coal

37. Elements of group 14
(a) exhibit oxidation state of +4 only
(b) exhibit oxidation state of +2 and +4
(c) form M^{2-} and M^{4+} ions
(d) form M^{2+} and M^{4+} ions

38. If the starting material for the manufacture of silicones is $RSiCl_3$, write the structure of the product formed.

ANSWERS

EXERCISE # 1

PART - I

Group 13th

1. (B) **2.*** (ACD) **3.** (C) **4.** (C) **5.** (B) **6.** (B) **7.** (A)
8. (C) **9.** (D) **10.** (C) **11.** (D) **12.** (D) **13.** (B) **14.** (C)
15. (A) **16.** (C) **17.** (B) **18.** (C) **19.** (D) **20.** (A) **21.** (B)
22. (D) **23.** (D) **24.** (D) **25.** (B) **26.** (B) **27.** (D) **28.** (D)
29.* (ABC) **30.** (C) **31.** (D) **32.** (A) **33.** (C) **34.** (C) **35.** (C)
36. (A) **37.** (C)

Group 14th

38. (C) **39.** (B) **40.** (A) **41.** (B) **42.** (A) **43.** (D) **44.** (B)
45. (A) **46.*** (ABC) **47.** (D) **48.** (D) **49.** (C) **50.** (A) **51.** (A)
52. (B) **53.** (C) **54.** (B) **55.*** (BCD) **56.** (A) **57.** (D) **58.** (C)
59. (C) **60.** (C) **61.** (C) **62.** (A) **63.** (D) **64.** (A) **65.** (A)
66. (D) **67.** (C) **68.** (C)

PART - II

FILL IN THE BLANKS.

Group 13th

1. two **2.** silicon **3.** Al **4.** NaOH or KOH **5.** aluminium
6. boranes **7.** +1 **8.** ✍ borazole **9.** ✍ a covalent **10.** exothermic
11. good **12.** stronger **13.** aluminium **14.** aluminium bronze

Group 14th

15. catenation **16.** bad **17.** ✍ carbon monoxide **18.** ✍ hydrofluoric
19. yellow **20.** haemoglobin, oxygen **21.** dry ice **22.** nickel carbonyl, $Ni(CO)_4$
23. ✍ silanols, silicones **24.** $R_3Si - O - SiR_3$ **25.** Buckminsterfullerene.
26. moon **27.** PbO, Pb_3O_4, pigments **28.** CO_2 **29.** ✍ 1.54 Å, 1.42 Å
30. ammonical copper (I) chloride, KOH or NaOH **31.** Linear **32.** ✍ carbonyl chloride (phosgene)

TRUE OR FALSE

Group 13th

33. False **34.** True **35.** False **36.** ✍ False **37.** True **38.** True **39.** True
40. ✍ False **41.** True **42.** ✍ True **43.** True

Group 14th

44. T **45.** F **46.** ✍ T **47.** ✍ T **48.** T **49.** F **50.** F
51. ✍ T **52.** F **53.** T **54.** ✍ T **55.** T **56.** T **57.** F

ASSERTION AND REASONING

Group 13th **58.** **(B)** **59.** **(C)** **60.** ✍ **(D)** **61.** ✍ **(B)** **62.** **(A)** **63.** **(B)**
Group 14th **64.** ✍ (C) **65.** ✍ (C) **66.** (A)

MATCH THE COLUMN

Group 13th

67. (a–iii); (b–i); (c–iv); (d–v); (e–ii) **68.** (a–iii); (b–i); (c–v); (d–iv); (e–ii)
69. ✍ (a–v); (b–iii); (c–i); (d–ii); (e–iv) **70.** (A) – (q) (r) ; (B) – (p) (q) ; (C) – (s) (t) ; (D) – (q) (r)

Group 14th

71. ✍ (a – vi), (b – viii), (c – i, vii), (d – x) (e – ii, xi) (f – ix, xi) (g – iii), (h – iv) (i – v), (j – vii)
72. (A) – (p) (q) ; (B) – (p) (r) ; (C) – (q) (s) ; (D) – (q)

EXERCISE # 2

PART - I

Single choice type

Group 13th

1.	(B)	**2.**	(C)	**3.**	(A)	**4.**	(C)	**5.**	(C)	**6.**	(C)	**7.**	(A)
8.	(B)												

Group 14th

9.	(A)	**10.**	(C)	**11.**	(A)	**12.**	(A)	**13.**	(B)	**14.**	(D)	**15.**	(B)
16.	(A)												

More than one choice type

Group 13th

17.	(ACD)	**18.**	(BCD)	**19.**	(BCD)	**20.**	(ABC)	**21.**	(ABC)	**22.**	(ACD)	**23.**	(ACD)
24.	(BCD)	**25.**	(BC)	**10.**	(ABD)								

Group 14th

11.	(BCD)	**12.**	(AB)	**13.**	(D)	**14.**	(AC)	**15.**	(AC)	**16.**	(C)	**17.**	(ABCD)

PART - II

1. (a) being electropositive reacts with air or oxygen to form protective layer of Al_2O_3 on its surface which protects it form further action.

(b) Cheap and light metal and forms alloys with other metal which are not easily corrode.

2. (i) Al has no d-or f-electrons. Therefore, it does not exhibit inert pair effect and consequenty, it shows an oxidation state of +3 only due to the presence of two electrons in the s-and one electron in the p-orbital of the valence shell. As we move down the group from Ga to Tl, the stability of +1 oxidation state increases while that of =3 oxidation decreases due to inert pair effect. For (ii) and (iii) refer text.

3. $4LiH + AlCl_3 \xrightarrow{\text{Dry ether}} Li^+ [AlH_4]^- + 3LiCl.$

Reducing agent in organic chemistry.

4. $GaCl_3 + 3NaOH \longrightarrow Ga(OH)_3 \downarrow + 3NaCl$

$Ga(OH)_3 + NaOH \longrightarrow NaGaO_2 + 2H_2O$

5. (i) $KAlSi_3O_8$ (ii) Na_3AlF_6 (iii) $Na_2B_4O_7.5H_2O$ (iv) Al_2O_3 (v) $Ca_2B_6O_{11}.5H_2O$

6. (i) $ns^2\ np^1$

(ii) Boron and aluminium

(iii) It is a mineral of boron. Its composition is $Na_2B_4O_7.10H_2O$

(iv) Mixture containing 1 part Al powder and 3 parts Fe_2O_3 or Cr_2O_3

(v) Borazole or borazine, $B_3N_3H_6$ is known as inorganic benzene

(vi) Common alum is the double sulphate of potassium and aluminium. Its composition is, $K_2SO_4.Al_2(SO_4)_3.24H_2O$

(vii) Anhydrous aluminium chloride, $AlCl_3$.

7. (i) $Na_2B_4O_7.10H_2O \xrightarrow{-10H_2O} Na_2B_4O_7 \longrightarrow 2NaBO_2 + B_2O_3$

(ii) $2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$

(iii) $Na_2B_4O_7.10H_2O \xrightarrow{-10H_2O} Na_2B_4O_7 \longrightarrow 2NaBO_2 + B_2O_3$

$B_2O_3 + CoO \longrightarrow Co(BO_2)_2$

(iv) $AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$

(v) Nitric acid whether dilute or concentrated hardly affects aluminium at all. Aluminium is rendered passive. A thin film of Al_2O_3 is formed on the surface of the metal.

8. Refer text and chemical bonding sheet.

9. (A) Refer text.
(B) borazol from sodium borohydride in three steps.

$$3NaBH_4 + 4BF_3 \xrightarrow{\text{ether}} 3NaBF_4 + 2B_2H_6$$

$$B_2H_6 + 2NH_3 \xrightarrow[\text{tempt.}]{100} B_2H_6.2NH_3$$

$$B_2H_6.2NH_3 \xrightarrow{200^\circ C} B_3N_3H_6 + H_2$$

(C) Borax from Boron (in two steps)

$$2B + 6HNO_3 \text{ (or } H_2SO_4) \longrightarrow 2H_3BO_3 + 6NO_2$$

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

10. Both forms covalent compounds, e.g, BCl_3 and $AlCl_3$. Their chlorides are volatile and hygroscopic. They are hydrolysed by water.

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

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

Oxides and hydroxides of boron are acidic in nature. On the other hand oxides and hydroxide of Al are amphoteric in nature

$$B_2O_3 + H_2O \longrightarrow H_3BO_3$$

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O,\ Al_2O_3 + 2NaOH \longrightarrow NaAlO_2 + H_2O$$

11. Borax solution in water produces weak acid H_3BO_3 and its salt $Na[B(OH)_4]$ in equimolar quantity.
$Na_2B_4O_7 + 7H_2O \longrightarrow 2Na[B(OH)_4] + 2H_3BO_3$

12. Because its melting point is very high and liquid obtained is corrosive.

13. $B(OH)_3 + HOH \longrightarrow [B(OH)_4]^- + H^+$
As it accepts OH^- ion rather than donating H^+ ions.

14. At the end point, the pH is about 4 and thus methyl orange is used as indicator.

15. The end point in this titration is not sharp due to excessive hydrolysis of $NaBO_2$ obtained as under.

$$H_3BO_3 + NaOH \rightleftharpoons NaBO_2 + 2H_2O$$

Boric acid is complexed with a polyhydroxy compound such as glycerol or glycol. This helps in the release of H^+ as H_3O^+ and a sharp end point is possible.

16. $Na_2B_4O_7 + 3H_2O \longrightarrow NaBO_2 + 3H_3BO_3$
$NaBO_2 + 2H_2O \longrightarrow NaOH\text{(strong alkali)} + H_3BO_3$

17. In borazine B = N bonds are polar while in benzene C = C and C – C bonds are non-polar and, therefore, reactivity of borazine is more than benzene.

18. More negative group attack boron atom.

19. Due to liberation of free halogens by photolysis.

20. refer text.

21. $B(OH)_3 \xrightarrow[\text{संगलन}]{NH_4HF_2} NH_4BF_3 \xrightarrow[\Delta]{B_2O_3} BF_3$

22. (i) Metaborates (ii) Orthoborates (iii) Pyroborates (iv) Perborates (v) Complex borates

23. $2BCl_3 + 3H_2 \xrightarrow{\text{red hot W}} 2B + 6HCl$

$2BI_3 + 3H_2 \xrightarrow{\text{red hot W}} 2B + 6HI$

24. $AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl\uparrow$

25. refer text.

26. (A) $2H_3BO_3 \xrightarrow{\text{Red heat}} B_2O_3 + 3H_2O$

$B_2O_3 + 3C + 3Cl_2 \longrightarrow 2BCl_3 + 3CO$

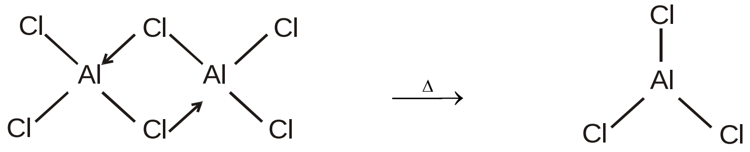
(B) $H_3BO_3 \xrightarrow{\text{Red heat}} B_2O_3 \xrightarrow[\Delta]{Mg} Mg_3B_2 \xrightarrow{\text{dil. HCl}}$ mixture of hydrides

(C) $H_3BO_3 \xrightarrow{100°C} HBO_2 + H_2O$

$4H_3BO_3 \xrightarrow{160°C} H_2B_4O_7 + 5H_2O$

$4HBO_2 \longrightarrow H_2B_4O_7 + H_2O$

27.



C.N = 4

C.N = 3

28. No reaction with CCl_4 - as it does not have empty d - orbital whereas BCl_3 will hydrolysed forming H_3BO_3.

29. No, it is weak monobasic Lewis acid according to the following reaction.
$B(OH)_3\,(aq) + 2H_2O\,(\ell) \rightarrow [B(OH)_4]^-(aq) + H_3O^+(aq)$

30. $H_3BO_3 \xrightarrow{\Delta} HBO_2 \xrightarrow{\Delta} B_2O_3$

31. (a) Reluctance of s-orbital electrons to participate in chemical bonding (more pronounced in heavier elements of p-block).
(b) Phenomenon of existence of different forms of elements having different physical properrties.
(c) Elements (i.e. carbon) have the tendency to link with one another through covalent bonds to form chains and rings.

32. (i) $Na_2B_4O_7 + 2H_2O \longrightarrow 4H_3BO_3 + 2NaOH$ (due to NaOH)

(ii) $Na_2B_4O_7 \xrightarrow{740°C} 2NaBO_2 + B_2O_3$

(iii) $Na_2\,B_4O_7 + 5H_2O + H_2SO_4 \rightarrow Na_2\,SO_4 + 4NH_3BO_3$

33. (i) $BF_3 + LiH \xrightarrow{450\,K} B_2\,H_6 + 6\,LiF$ glassy mass

(ii) $B_2H_6 + 6H_2O \rightarrow 2B(OH)_3(aq) + 6H_2(g)$
(iii) $2NaH + B_2H_6 \rightarrow 2NaBH_4$
(iv) $Al + NaOH \rightarrow NaAlO_2$ (soluble) $+ 2H_2O$

(v) $3B_2H_6 + 6NH_3 \rightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\Delta} 2B_3N_3H_6 + 12\,H_2$

Group 14th

34. Ultra pure elemental silicon is used for making semiconductors.

$$SiCl_4\,(pure) + 2H_2(g) \xrightarrow{\Delta} Si(s) + 4HCl(g)$$

$$SiHCl_3(s) + H_2(g) \xrightarrow{\Delta} Si(s) + 3HCl(g)$$

$$SiH_4(g) \xrightarrow[\text{Pyrolysis}]{675\ K} Si(s) + 2H_2(g)$$

35. (A) $SnO + 2HNO_3 \longrightarrow Sn(NO_3)_2 + H_2O$

(B) $Sn + 2Cl_2 \xrightarrow{\Delta} SnCl_4$

(C) $2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$; $PbS + 2O_2 \longrightarrow PbSO_4$

36. Refer text.

37. Refer text.

38. Inert pair effect is due to the ineffectively shielding of the s-electrons of the valence shell by the d-and f-electrons of the inner shells.

39. They violently react with alkali metals according to following reactions.

$$CCl_4(\ell) + 4Na(s) \longrightarrow 4NaCl(s) + C(s)$$

40. $\overset{IV}{P}bO_2 + 4HCl \longrightarrow \overset{II}{P}bCl_2 + Cl_2$

$\overset{IV}{P}bO_2 + SO_2 \longrightarrow \overset{II}{P}bSO_4$

41. $CaSO_4$ formed with H_2SO_4 forms a protective layer over lime stone and then reaction slowly ceases and stop. But $CaCl_2$ is soluble.

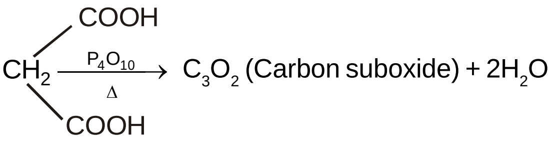
42. $PbCl_4$ is less stable than $SnCl_4$ due to more effective inert pair effect in lead. Pb–Cl bond length is more then that of Sn–Cl.

43. Due to bigger atomic size of silicon, its reluctance for pp – pp bond does not allow to form graphite like structure.

44. Low electronegativity and bigger size, Si does not have tendency to form pπ-pπ bonds like carbon.

45. Refer text.

46. (a) Refer text.

(b) 

$$CH_2(COOH)_2 \xrightarrow[\Delta]{P_4O_{10}} C_3O_2\ (\text{Carbon suboxide}) + 2H_2O$$

(c) Refer text.

47. Lead dissolves in water containing dissolved air due to the formation of lead hydroxide (a poisonous substance). This solvent action of water is called plumbo solvency. It increases if water contains nitrates, ammonium salts and organic acids, and decreases if water contains phosphates, sulphates, bicarbonates and carbonates.

48. (A) CaC_2 (B) CO (C) $CaCN_2$ (D) $CaCO_3$.

49. Carbonates evolve CO_2 with phenol but bicarbonate do not.
Soluble carbonates give pink colour with phenolphthalein but soluble bicarbonates do not.

50. Silicon and Germanium. **51.** Graphite.

52. $2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$
$SnO_2 + 2H_2SO_4$ (conc.) $\longrightarrow Sn(SO_4)_2 + 2H_2O$
$SnO_2 + 2KOH \longrightarrow k_2SnO_3 + H_2O$

53. refer text.

54. (i) $K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$
(ii) $2CS_2 + 10\,NO \longrightarrow 2CO + 4SO_2 + 5N_2$
(iii) $Pb_3O_4 + 4HNO_3 \longrightarrow PbO_2 + 2Pb(NO_3)_2 + 2H_2O$
(iv) $2CaF_2 + SiO_2 + 2H_2SO_4 \longrightarrow 2CaSO_4 + SiF_4 + 2H_2O$
(v) $2Pb^{2+} + H_2S + 2Cl^- \longrightarrow Pb_2SCl_2 \downarrow$ (red) $+ 2H^+$

55. Refer text.

56. (i) water proofing textiles (ii) as lubricants (iii) as anti-foaming agents.

57. Due to small size of carbon atom.

58. $PbO + 2HCl \longrightarrow PbCl_2 \downarrow H_2O$
$PbO + H_2SO_4 \longrightarrow PbSO_4 \downarrow + H_2O$
$PbO + 2HNO_3 \longrightarrow Pb(NO_3)_2$ (soluble) $+ H_2O$

59. PbO_2

60. (i) covalent (ii), (iii) interstitial (iv) salt like (i.e. ionic)

61. C_{60}, Purple

62. $Ag_2C_2 + 2HCl \longrightarrow CH \equiv CH + 2\,AgCl$

63. $SiO_2 + Fe + 2C \longrightarrow Fe - Si + 2CO$
If SiO_2 not taken in excess, SiC will be formed.

64. (i) $PbCl_4 + Cl_2 \longrightarrow PbCl_4$ (Pb^{+2} to being oxidised by oxidising agent Cl_2)

(ii) $PbCl_4\,(s) \xrightarrow{\Delta} PbCl_2\,(s) + Cl_2(g)$ (inert pair effect)

(iii) I^- strong reducing agent. reduces Pb^{+4} (strong oxidising agent) to PbI_2 and I_2 is liberated.

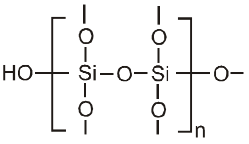
65. Forms carboxy haemoglobin which reduces the ability of haemoglobin to obsorb the oxygen.

66. Increase in CO_2 percentage will increase the temperature of the earth.

67. (i) layered structure which can be slipped over one another as the layers are held together by weak Vander Waal's forces.
(ii) Hard substance (formed by the three dimensional network of covalent bonds)

68. CO → Neutral ; B_2O_3, PbO_2 and Al_2O_3 → amphoteric ; SiO_2 – acidic and Ti_2O_3 – basic.

69. Three dimensional silicone will be formed.



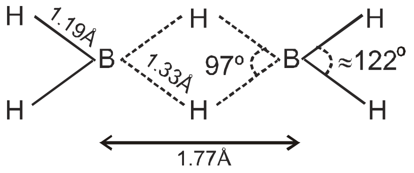
EXERCISE # 3

PART - I

Group 13th

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

2. $X = BF_3$ or BCl_3 ; $Y = B_2H_6$ 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) $NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl$

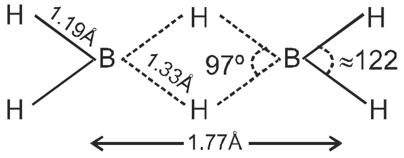
(v) $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$.

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)

$\underset{\text{Boric acid}}{H_2B_4O_7 + 5H_2O \longrightarrow 4H_3BO_3}$; $2H_3BO_3 \xrightarrow{\text{red hot}} \underset{\text{Boric anhydride}}{B_2O_3} + 3H_2O$

$B_2O_3 + 3Mg \xrightarrow{\text{Fusion}} 2B + 3MgO$; Reaction with HCl : $B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2$

Structure of B_2H_6 :



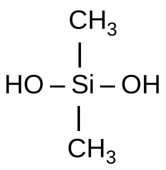
H................ B .... H is hydrogen bridge i.e, 3 centre two electron bond.

5. (A) **6.** (A) **7.** (A – q, s) ; (B – r) ; (C – q, r, s) ; (D – q,r). **8.** (C)
9. 6 **10.*** (ABC)

Group 14th

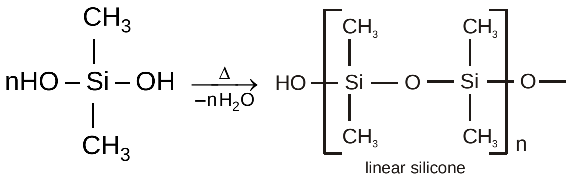
11. (i) $3SiCl_4(vapour) + 4Al(molten) \longrightarrow 4AlCl_3 + 3Si$
(ii) (a) $3SiCl_4 + 4Al \longrightarrow 4AlCl_3 + 3Si$

(b) $Si + 2CH_3Cl \xrightarrow[570°C]{\text{Cu powder}} (CH_3)_2\,SiCl_2$ (c) $(CH_3)_2\,SiCl_2 \xrightarrow[-2HCl]{2H_2O}$



$$HO-\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{Si}}-OH$$

(d)



$$nHO-\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{Si}}-OH \xrightarrow[-nH_2O]{\Delta} HO-\left[\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{Si}}-O-\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{Si}}\right]_n-O-$$

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) $SiO_2 + Na_2CO_3 \xrightarrow{1400°C} Na_2SiO_3 + CO_2$

12. (C) **13.** (A) **14.** (C) **15.** 3 **16.*** (BD) **17.** (B)

PART - II

1. (4) **2.** (4) **3.** (2) **4.** (4) **5.** (2) **6.** (3) **7.** (3)
8. (1) **9.** (2) **10.** (2) **11.** (2)