Chapter 14

p-BLOCK (GROUP 13 AND 14)

1. INTRODUCTION

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 gorup also has greater ability to form pπ–pπ 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 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 becomes more stable in groups 13 to 16 due to inert pair effect.

Group 13 Elements : The Boron Family

Boron is a typical non-metal, aluminium is a metal and gallium, indium and thallium are almost exclusively metallic in character,

1.1 Electronic Configuration

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

1.2 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 increases. Atomic radius of Ga is less than 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 redius of gallium (135 pm) is less than that of aluminium (143 pm).

1.3 Ionization Enthalpy

The ionisation enthalpy values as expected from the general trends 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 inability of d- and f electrons.

1.4 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.

1.5 Melting and Boiling Points

M.P. $B > Al > Tl > In > Ga$

B.P. $B > Al > Ga > In > Tl$

2. 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. Gallium with low melting point (303 K), could exist in liquid state during summer.

Atomic & 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	$[He]2s^22p^1$	$[Ne]3s^23p^1$	$[Ar]3d^{10}4s^24p^1$	$[Kr]4d^{10}5s^25p^1$	$[Xe]4f^{14}5d^{10}6s^26p^1$
Atomic Radius/pm	85	143	135	167	170
Ionic Radius M^{3+}/pm	–	53.5	62	80	88.5
Ionization enthalpy I	800	577	578	558	590
/(kJ mol^{-1}) II	2427	1816	1979	1820	1971
III	3659	2744	2962	2704	2877
Electronegativity	2.0	1.5	1.6	1.7	1.8
Density/[g cm^{-3} (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

3. CHEMICAL PROPERTIES

3.1 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.

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

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

Boron trioxide is acidic and reacts with base. Aluminium and gallium oxides are amphoteric and indium and thallium are basic.

3.2 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.

Aluminimum 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 .

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

$$2Al(s) + 2NaOH\,(aq) + 6H_2O\,(1) \rightarrow 2Na^{+}\,[Al(OH)_4]^{-}\,(aq) + 3H_2(g)$$

Sodium tetrahydroxoaluminate (III)

3.3 Reactivity Towards Halogens

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

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

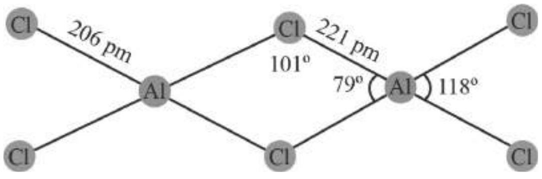
The tri-chlordes, bromides and iodies of all these elements being covalent in nature are hydrolysed in water. Species like tetrahedral $[M(OH)_4]^-$ and octahedral $[M(H_2O)_6]^{3+}$ (except in boron) exist in aqueous medium.

The monomeric trihalides, being electron deficient, are strong Lewis acids.

4. ANOMALOUS PROPERTY OF BORON

It is due to the absence of d orbitals that the maximum covalency of B is 4. Since the d orbitals are available with Al and other elements, the maximum covalence can be expected beyond 4.

Thus, boron hallides do not dimerise like other elements which can form halogen bridged molecules. (Dimer of $AlCl_3$ has 3 centre - 4 electrons bond)



Dimer of $AlCl_3$

5. COMPOUNS OF BORON

5.1 Orthoboric Acid (H_3BO_3)

5.1.1 Preparation

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

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

5.1.2 Properties

It is a weak monobasic acid and in aqueous solution. The boron atom completes its octet by removing OH^- from water molecules:

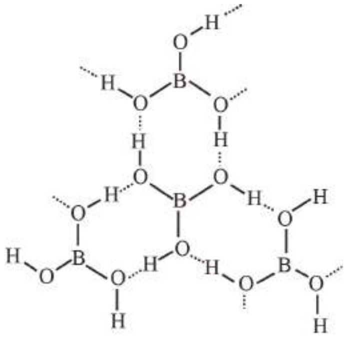
$$B(OH)_3(aq) + 2H_2O(\ell) \rightarrow B(OH)_4^{-}\,(aq) + H_3O^{+}(aq).$$

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

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

$$H_3BO_3 \xrightarrow{\Delta} \underset{\text{Metaboric acid}}{HBO_2} \xrightarrow{\Delta} \underset{\text{Boron trioxide}}{B_2O_3}$$

Orthoboric acid is greasy to touch less soluble in cold water but more soluble in hot water. It has a layered structure in which planar BO_3 units are joined by hydrogen bonds.



Structure of Boric Acid
(Dotted line represent hydrogen bonds)

5.1.3 Uses

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

5.2 Borax ($Na_2B_4O_7.10H_2O$)

5.2.1 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 $CaCO_3$.

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

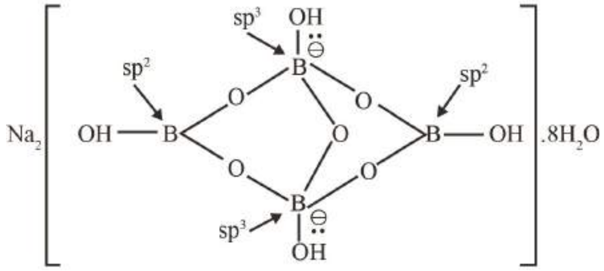
The filterate is cooled when white crystals of borax are precipitated. The mother liquor on treatment with CO_2 converts $NaBO_2$ to $Na_2B_4O_7$ which precipitates out on crystallization.

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

(ii) From orthoboric acid.

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

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



5.2.2 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) Action of acids :

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4H_3BO_3 \text{ (boric acid)}$$

Correct formula of borax is $Na_2[B_4O_5(OH)_4] . 8H_2O$

Borax-bead test: Boric anhydride 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.

$$Na_2B_4O_7.\ 10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{740°C} 2NaBO_2 + \underset{\text{Borax bead}}{B_2O_3}$$

$$CuO + B_2O_3 \longrightarrow Cu(BO_2)_2 \text{ (blue bead)}$$

5.2.3 Uses

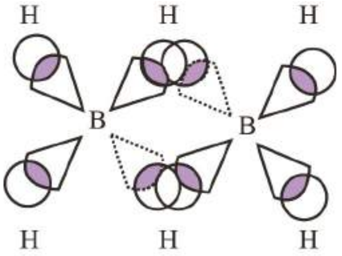
(i) In borax bead test

(ii) In purifying gold

(iii) As flux during welding of metals.

5.3 Diborane (B_2H_6)

Binary compounds of B with H are called boron hydrides or boranes.



5.3.1 Preparation

(i) $4BF_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 2B_2H_6 + 3LiF + 3AlF_3$

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

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

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

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

5.3.2 Properties

(i) Diborane is a colourless gas.

(ii) It is rapidly decomposed by water with the formation of H_3BO_3 & H_2

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

(iii) Mixtures of diborane with air or oxygen catches fire 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.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O \quad \Delta H = -\,1976 \text{ kJ mol}^{-1}$$

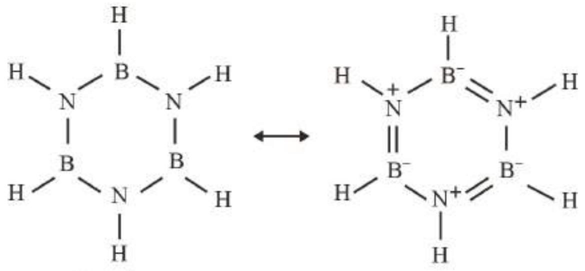
(iv) Cleavage reactions

(a) $B_2H_6 + 2Me_3N \longrightarrow 2Me_3N \rightarrow BH_3$

(b) $B_2H_6 + 2CO \xrightarrow{200^{o}C,\ 20\,atm} 2BH_3CO$

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

In above reaction $B_3N_3H_6$ is formed it is known borazine (inorganic benzene)



Borazine

(vi) $\underset{\text{Diboane}}{nB_2H_6} \xrightarrow[\text{High temperature}]{\text{Excess } NH_3} \underset{\text{Boron nitride}}{(BN)_n}$

Born nitride is known as inorganic graphite.

6. COMPOUNS OF ALUMINIUM (Al)

6.1 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.

6.1.1 Preparation

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

$$Al_2(SO_4)_3 \xrightarrow{\Delta} Al_2O_3 + 3SO_3\uparrow$$

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

6.1.2 Properties

It is a white amorphous powder insoluble in water but soluble in acids (forming eg., $AlCl_3$) as well as alkalies (forming $NaAlO_2$), Thus amphoteric in nature. It is a polar covalent compound.

$$\underset{\text{Aluminium oxide}}{Al_2O_3(s)} + \underset{\text{Hydrochloric acid}}{6HCl(aq)} \rightarrow \underset{\text{Aluminium chloride}}{2AlCl_3(aq)} + 3H_2O(l)$$

$$\underset{\text{Aluminium oxide}}{Al_2O_3} + \underset{\text{Sodium hydroxide}}{2NaOH(aq)} \rightarrow \underset{\text{Sodium aluminate}}{2NaAlO_2(aq)} + H_2O(l)$$

6.1.3 Uses

(i) For the extraction of aluminium.

(ii) For making artificial gems.

(iii) For the preparation of compounds of aluminium.

(iv) In making furnace linings. It is a refractory material.

(v) As a catalyst in organic reactions.

7. INTRODUCTION: GROUP 14 ELEMENTS

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 ceramices, 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.

7.1 Electronic Configuration

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

7.2 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 completey filled d and f orbitals in heavier members.

7.3 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 Δ_iH from Si to Ge to Sn and slight increase in Δ_iH from Sn to Pb is the consequence of poor shielding effects of intervening d and f–orbitals and increases in size of the atom.

7.4 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.

8. 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.

Atomic & 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	$[He]2s^22p^2$	$[Ne]3s^23p^2$	$[Ar]3d^{10}4s^24p^2$	$[Kr]4d^{10}5s^25p^2$	$[Xe]4f^{14}5d^{10}6s^26p^2$
Atomic Radius/pm	77	118	122	140	146
Ionic Radius M^{+4}/pm	–	40	53	69	78
Ionization enthalpy I	1086	786	761	708	715
/(kJ mol^{-1}) II	2352	1577	1537	11411	1450
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

9. CHEMICAL PROPERTIES

Oxidation State

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. (due to inert pair effects)

9.1 Reactivity Towards Oxygen

All members when heated in oxygen form oxides. There are mainly two types of oxides.

Monoxides (MO)	Dioxides (MO_2)
SiO only exists at high temperature.	CO_2, SiO_2, and GeO_2 are acidic
CO is neutral	SnO_2 and PbO_2 are amphoteric
GeO is distinctly acidic	
SnO and PbO are amphoteric	

Oxides in higher oxidation states of elements are generally more acidic than those in lower oxidation states.

9.2 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 becauses of a protective oxide film formation.

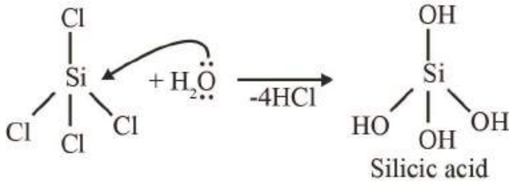
$$Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_2$$

9.3 Reactivity Towards Halogen

Except carbon, all other members react directly with halogen under suitable condition to make halides.

Dihalides (MX_2)	Tetrahalides (MX_4)
Heavier members Ge to Pb are able to make halides of formula MX_2.	All elements can form tetrahalides. However, Pb doesn't form PbI_4 because Pb-I bond initially formed during the reaction does not release enough energy to unpair and excite $6s^2$ electrons.
Stability of dihalides increases down the group. **$PbX_2 > PbX_4$**	Stability decreases down the group. **$GeX_2 < GeX_4$**
MX_2 is more ionic than MX_4	Most of the MX_4 are covalent in nature **except SnF_4 and PbF_4.**

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 molecule in d orbital.



10. IMPORTANT TRENDS AND ANOMALOUS BEHAVIOUR OF CARBON

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 atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation. This is becauses C–C bonds are very strong. Down the group the size increases tendency to show catenation decreases. The order of catenation is C > > Si > Ge ≈ Sn. Lead does not show catenation.

Bond Enthalpy Value

Bond	Bond enthalpy / kJ mol^{-1}
C — C	348
Si — Si	297
Ge — Ge	260
Sn — Sn	240

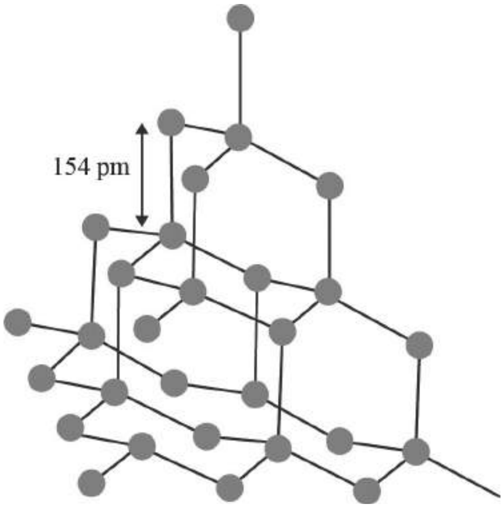
11. ALLOTROPES OF CARBON

Carbon exhibits many allotropic forms; both crystallic as well as amorphous.

11.1 Diamond

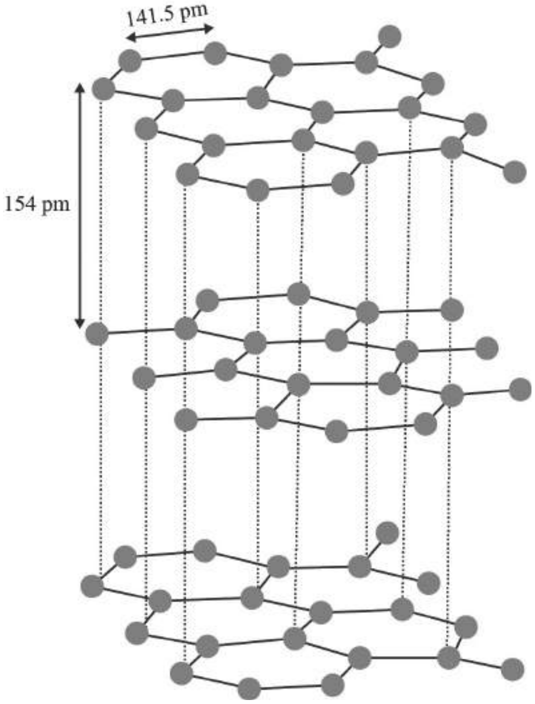
It has a crystalline lattice. In diamond each carbon atom undergoes sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. The C-C bond length is 154 pm. The structure extends in space and produces a rigid three dimensional network of carbon atoms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

It is very difficult to break extended covalent bonding and therefore, diamond is a hardest substance on the earth.



11.2 Graphite

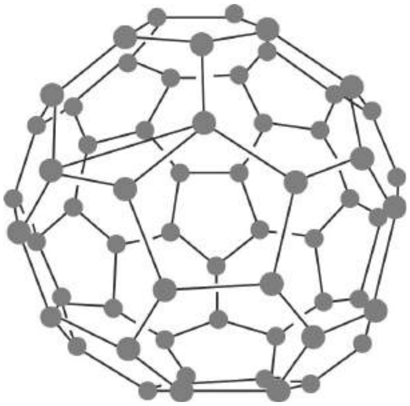
Graphite has layered structure. Layers are held by van der Waal's forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C – C bond length within the layer is 141.5 pm Each carbon atom in hexagonal ring undergoes sp^2 hybridisation and make three sigma bonds with three neighbouring 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.



11.3 Fullerenes

Fullerenes are made by the heating of graphite in an electrical arc in the presence of inert gases such as helium or argon. Fullerences are the only pure form of carbon becauses they have smooth structure without having 'dangling' bonds. Fulleren 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 also called bucky balls in short. It is very important to know that graphite is thermodynamically most stable allotrope of carbon.



Uses of Carbon

(i) Graphite fibres embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircrafts and canoes.

(ii) Graphite is used for electrodes in batteries and industrial electrolysis.

(iii) Crucibles made from graphite are inert to dilute acids and alkalies.

(iv) Carbon black is used as black pigment in black ink and as filler in automobile tyres.

(v) Coke is used as a fuel and largely as a reducing agent in metallurgy.

12. COMPOUNDS OF CARBON

12.1 Carbon dioxide (CO_2)

12.1.1 Preparation

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

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

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

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

12.1.2 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)

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

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

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

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

(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:

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

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

(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.

(vi) Carbonic acid, which is a weak dibasic acid and ionises in to steps as follows:

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

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

H_2CO_3/HCO_3^- buffer system helps to maintain pH of blood between 7.26 to 7.42

12.2 Carbon Monoxide (CO)

12.2.1 Preparation

(i) It forms 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.

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

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) $Zn + CO_2 \longrightarrow ZnO + CO$

12.2.2 Properties

(i) Carbon monoxide is a colourless, odourless gas which burns in air with a blue flame, forming CO_2. The highly poisonous nature of CO arises because of its ability to form a complex with haemoglobin, which is about 300 times more stable than the oxygen-haemoglobin complex. This prevents haemoglobin in the red blood corpuscles from carrying oxygen round the body and ultimately resulting in death

(ii) Carbon monoxide is a powerful reducing agent, being employed industrially in the extraction of iron and nickel:

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

$$NiO(s) + CO(g) \longrightarrow Ni(s) + CO_2(g)$$

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

$$Ni(s) + 4CO(g) \xrightarrow{90^\circ C} Ni(CO)_4(liq)$$

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

12.3 Carbon Suboxide (C_3O_2)

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

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

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

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

The molecule is thought to have a linear structure:

$O=C=C=C=O$

$-2\ +2\quad 0\ +2\ -2$ (Oxidation state of each atom)

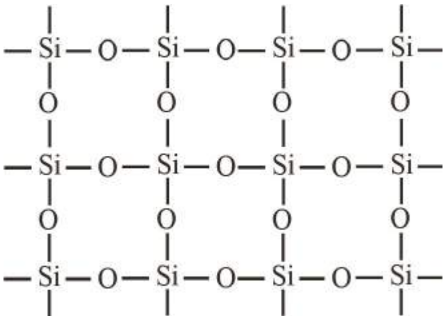
13. COMPOUNDS OF SILICON

13.1 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. Howevers it is attacked by HF and NaOH.

$$SiO_2 + 2\,NaOH \longrightarrow Na_2SiO_3 + H_2O$$

$$SiO_2 + 4\,HF \longrightarrow SiF_4 + 2\,H_2O$$



Quartz is extensively used as a piezoelectric material ; it has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications. Silica gel used as a drying agent and as a support for chromatographic materials.

13.2 Silicates

A large number of silicates minerals exist in nature. Some of the examples are - Feldspar, Zeolites and Mica

The basic structural unit of silicates is SiO_4^{4-} in which silicon atom is bonded to four oxygen atoms in tetrahedral fashion.

In silicates either the discrete unit is present or a number of such units are joined together via corners by sharing 1, 2, 3 or 4 oxygen atoms per silicate units.

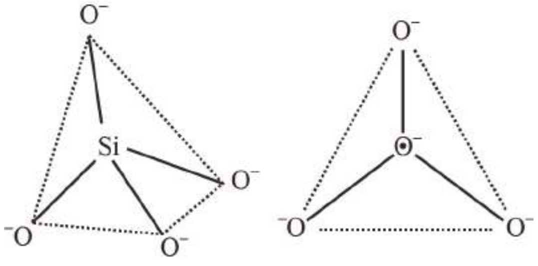
When silicate units are linked together, they form chain, ring, sheet or three-dimensional structures.

Negative charge on silicate structure is neutralised by positively charged metal ions.

13.2.1 Classification of Silicates

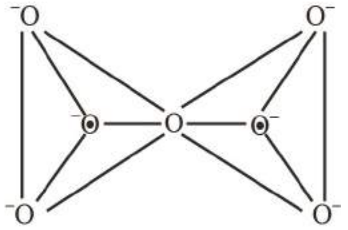
(i) Orthosilicates

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



(ii) Pyrosilicate

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

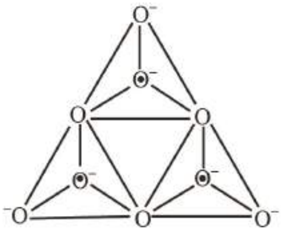


(–) charge will be present on the oxygen atoms which is bonded with one Si atom.

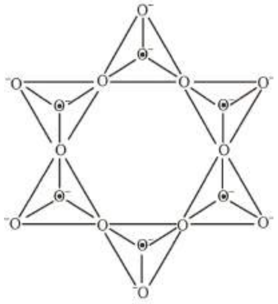
(iii) Cyclic Silicates

If two oxygen atoms per tetrahedron are shared to form closed rings such that the structure with general formula $(SiO_3^{2-})_n$ or $(SiO_3)_n^{2n-}$ is obtained, the silicates containing these anions are called cyclic silicates.

$Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$ anions are the typical examples of cyclic silicates.



$Si_3O_9^{6-}$

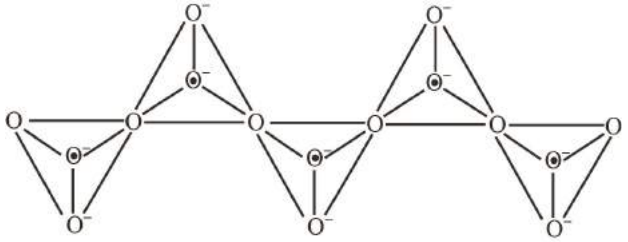


$Si_6O_{18}^{12-}$

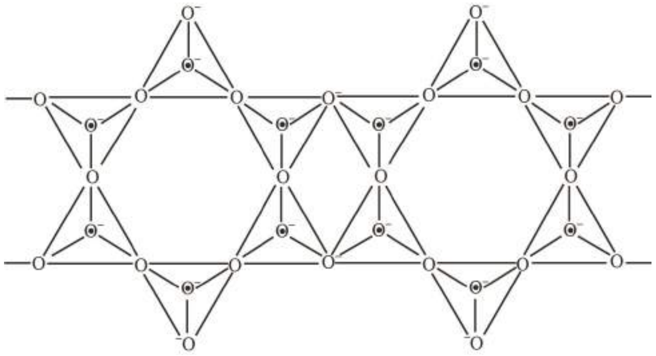
(iv) Chain silicates

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

In case of simple chains two corners of each tetrahedron are shared & they form a long chain of tetrahedron. Their general formula is also same as the cyclic silicates i.e. $(SiO_3)_n^{2n-}$

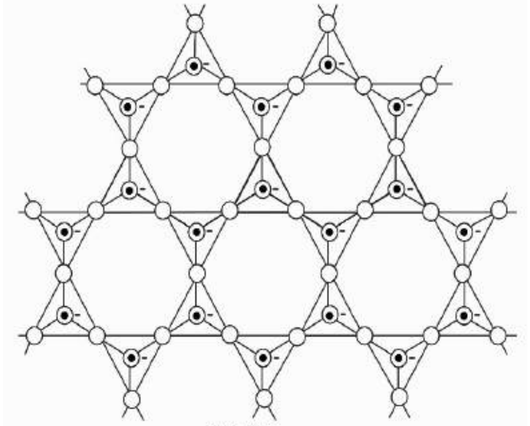


Similarly, double chain silicates can be drawn in which two simple chains are joined together by shared oxygen. Such compounds are also known as amphiboles.



(v) Sheet Silicates

When SiO_4 unit share 3 corners the structure formed is an infinite two dimension sheet structure with general formula $(Si_2O_5)_n^{2n-}$



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

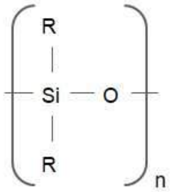
(vi) Three dimenstional sheet silicates :

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

13.3 Silicones

These are a group of organosilicon polymers, which have (R_2SiO) as a repeating unit.

The starting materials for the manufacture of silicones are alkyl or aryl substituted silicon chlorides, $R_nSiCl_{(4-n)}$, where R is 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.

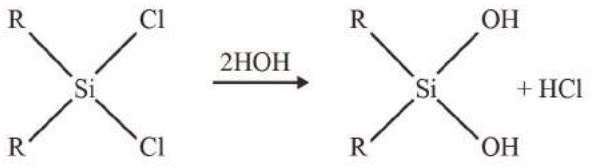
(a) $RCl + Si \xrightarrow[300°C]{Cu} R_3SiCl + R_2SiCl_2 + RSiCl_3 + R_4Si$

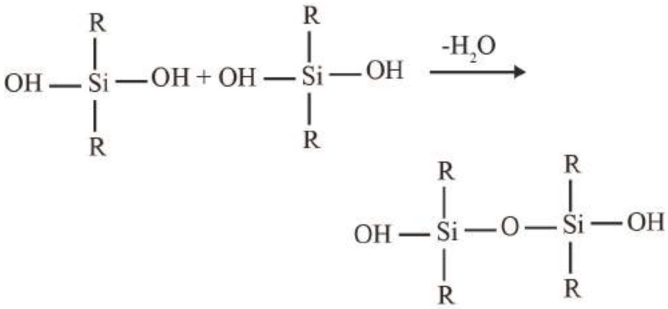
(b) $RMgCl + SiCl_4 \longrightarrow RSiCl_3 + MgCl_2$

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

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

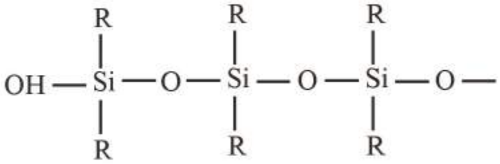
After fractional distillation, the silane derivatives are hydrolysed and the 'hydroxides' immediately condense by intermolecular elimination of water. The final product depends upon the number of hydroxyl groups originally bonded to the silicon atom:





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

In this manner several molcules 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.



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

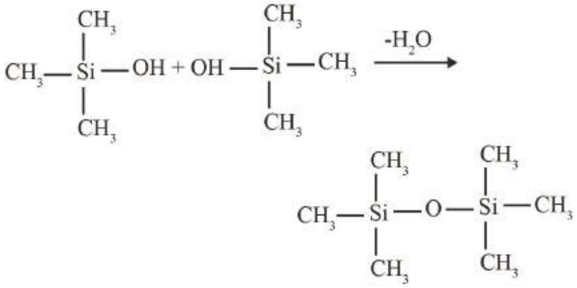
The polymer chain depicted above is terminated by incorporating a small quantity of the monochlorosilane derivative into the hydrolysis mixture.

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

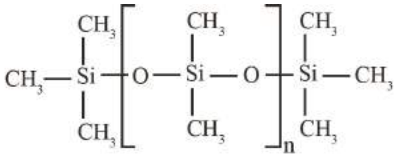
$(CH_3)_3SiCl \xrightarrow{H_2O} (CH_3)_3Si(OH)$



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

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.



$$\mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-\left[O-\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_n-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3}$$

Silicones being surrounded by non-polar alkyl groups are water repelling in nature. They have in general high thermal stability, high dielectric strength and resistance to oxidation and chemicals. They have wide applications. They are used as sealant, greases, electrical insulators and for water proofing of fabrics. Being biocompatible they are also used in surgical and cosmetic plants.

13.4 Zeolites

If aluminium atoms replace few silicon atoms in three-dimensional network of silicon dioxide, overall structure known as aluminosilicate, acquires a negative charge. Cations such as Na^+, K^+ or Ca^{2+} balance the negative charge. Examples are feldspar and zeolites.

Zeolites are widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation, e.g., ZSM-5 (A type of zeolite) used to convert alcohols directly into gasoline. Hydrated zeolites are used as ion exchangers in softening of "hard" water.

SUMMARY

Physical Properties of Group 13 and 14 Elements

Property	Group 13	Group 14
Atomic Radii	B < Al > Ga < In < Tl	C < Si < Ge < Sn < Pb
Ionisation Energy	B > Tl > Ga > Al > In	C > Si > Ge > Sn < Pb
Electronegativity	B > Tl > In > Ga > Al	C > Si = Ge = Sn < Pb
Oxidation state	General oxidation states: +1, +3	General oxidation states: +2, +4
Metallic character	Increases down the group	Increases down the group
Melting point	Decreases upto Gallium then increases	Decreases upto tin then increases
Boiling point	Decreases down the group	Decreases down the group
Density	Increases down the group	Increases down the group

Chemical Properties of Group 13 and 14 Elements

Property	Group 13	Group 14
Reactivity with air	Reacts with air to form oxide (at moderate temp.) and nitride (at high temp.) Crystalline boron unreactive, amorphous boron reacts. Aluminium forms oxide layer and does not react further.	Reacts with air to form monoxide and dioxides
Reactivity with water	In general, group 13 elements are not very reactive with water	Only Sn reacts with steam. Rest all do not react with water in any form
Reactivity with halogens	Reacts with halogens to form trihalides (except tri-iodide of Thallium)	Reacts with halogens to form dihalides and tetrahalides
Nature of oxides	Boron trioxide is acidic, Al and Ga oxides are amphoteric, In and Tl oxides are Basic	CO_2, SiO_2, GeO_2 are acidic, SnO_2 and PbO_2 are amphoteric CO is neutral, GeO is acidic and SnO, PbO are amphoteric
Reactivity with acids and alkalis	Boron does not react. Aluminium reacts with both acids and alkalis to liberate hydrogen gas. Aluminium reacts passive with conc. nitric acid.	–

SOLVED EXAMPLES

Example - 1

Amorphous boron is extracted from borax by following steps:

$$\text{Borax} \xrightarrow{(A)} H_3BO_3 \xrightarrow{\text{Heat}} B_2O_3 \xrightarrow{(B)} \text{Boron.}$$

(A) and (B) are:

(a) H_2SO_4, Al
(b) HCl, carbon
(c) H_2SO_4, Mg
(d) HCl, Fe

Ans. (c)

Sol. H_2SO_4,Mg

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{H_2SO_4} H_3BO_3 \xrightarrow{\Delta}$$

$$B_2O_3 \xrightarrow{Mg} 2B$$

Example - 2

When metal ‘M’ is treated with NaOH, a white gelatinous precipitate ‘X’ is obtained, which is soluble in excess of NaOH. Compound ‘X’ when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal ‘M’ is:

(a) Fe
(b) Zn
(c) Ca
(d) Al

Ans. (d)

Sol. When metal ‘M’ is treated with NaOH, a white gelatinous precipitate ‘X’ is obtained, in this case, the metal “M” is Aluminium. And the “x” is aluminium hydroxide.

The reaction is as follows,

$$2Al + 6H_2O \xrightarrow{(NaOH)} 2Al(OH)_3 \downarrow + 3H_2 \uparrow$$

which is soluble in the excess of NaOH. In this case, due to the formation of sodium aluminate and the gelatinous ppt get soluble in the solution. The reaction is,

$$Al(OH)_3 + NaOH \rightarrow Na[Al(OH)_4]$$

(Sodium Aluminate)

When compound ‘X’ is heated strongly, it gives an oxide. The reaction is,

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

This oxide is used in chromatography as an adsorbent. therefore, the metal is aluminium.

Example - 3

Boron does not form B^{3+} cation easily. It is due to:

(a) energy required to form B^{3+} ion is very high which will not be compensated by lattice energies or hydration energies of such ion
(b) boron is non-metal
(c) boron is semi-metal
(d) none of the above

Ans. (a)

Sol. The electronic configuration of Boron is $1s^2 2s^2 2p^1$.

Boron atom is small in size. So, the electrons are completely attracted to the nuclear charge. Therefore, a large amount of energy is needed to remove 3 electrons from the boron atom. So Boron does not form B^{3+} ion. It mainly forms covalent bond.

Example - 4

Boron cannot form which one of the following anions ?

(a) BF_6^{3-}
(b) BH_4^-
(c) $B(OH)_4^-$
(d) BO_2^-

Ans. (a)

Sol. Boron is an element of group 13 and 2nd period. The last shell of boron is 2 shells. In this shell, the total number of the orbital is 4. Therefore it can form maximum 4 bonds. In the given compounds, all compounds have 4 bonds except option (a). In the option (a) the total bonds of boron are 6, which is impossible.

Example - 5

Alumina is not used as:

(a) refractory material
(b) a medium in chromatography
(c) abrasive
(d) a white pigment

Ans. (d)

Sol. Due to its high thermal stability, it can be used as refractory products. It is widely used in spark plugs, tap washers, cutting tools etc. It is slightly basic and good for the purification of amines for chromatography purpose. It is used as abrasive. Aluminium sulphate can be used as white pigment in paint.

Example - 6

Match the column I with column II and mark the appropriate choice.

Column - I	Column - II
(A) Borax	(i) Na_3AlF_6
(B) Inorganic benzene	(ii) $Na_2B_4O_7.10H_2O$
(C) Cryolite	(iii) $Al_2O_3.2H_2O$
(D) Bauxite	(iv) $B_3N_3H_6$

(a) (A) $\rightarrow$ (ii), (B) $\rightarrow$ (iv), (C) $\rightarrow$ (i), ((D)) $\rightarrow$ (iii)

(b) (A) $\rightarrow$ (i), (B) $\rightarrow$ (ii), (C) $\rightarrow$ (iii), (D) $\rightarrow$ (iv)

(c) (A) $\rightarrow$ (ii), (B) $\rightarrow$ (iii), (C) $\rightarrow$ (i), (D) $\rightarrow$ (iv)

(d) (A) $\rightarrow$ (iii), (B) $\rightarrow$ (i), (C) $\rightarrow$ (ii), (D) $\rightarrow$ (iv)

Ans. (a)

Sol. Borax $\rightarrow Na_2B_4O_7.10H_2O$

Inorganic benzene $\rightarrow B_3H_6N_3$

Cryolite $\rightarrow Na_3AlF_6$

Bauxite $\rightarrow Al_2O_3.2H_2O$

Example - 7

The hardest substance among the following is

(a) Be_2C

(b) graphite

(c) titanium

(d) B_4C

Ans. (d)

Sol. The hardest substance among the following compounds is boron carbide i.e. B_4C . It has a hardness of 9-10 on Mohs scale. It's hardness is only exceeded by Boron Nitride and diamond.

Hence, the correct option is (d).

Example - 8

Which of the following does not exist in free state ?

(a) BF_3

(b) BCl_3

(c) BBr_3

(d) BH_3

Ans. (d)

Sol. Molecules having the whole number for a degree of unsaturation can exist in the free state as stable compounds.

Degree of unsaturation = $\frac{\sum n(v-2)}{2}+1$

n = number of atoms of a particular type

v = valency of an atom

Thus for BH_3 degree of unsaturation is not a whole number.

Hence, the correct option is (d).

Example - 9

Hydride of boron occurs as B_2H_6 but B_2Cl_6 does not exist. This is because :

(a) pπ-dπ back bonding is possible in B_2H_6 but not in B_2Cl_6

(b) boron and hydrogen have almost equal values of electronegativity

(c) boron and chlorine have almost equal atomic sizes

(d) small hydrogen atoms can easily fit in between boron atoms but large chlorine atoms do not

Ans. (d)

Sol. Small size of hydrogen atom.

Example - 10

The bond dissociation energy of B-F in BF_3 is 646 kJ mol^{-1} whereas that of C – F in CF_4 is 515 kJ mol^{-1}. The correct reason for higher B – F bond dissociation energy as compared to that of C – F is

(a) smaller size of B-atom as compared to that of C-atom

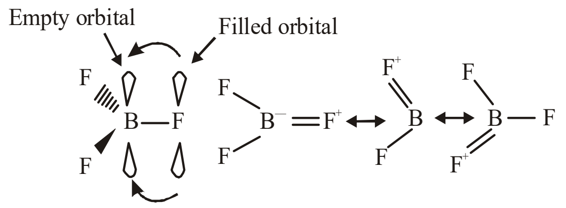
(b) Stronger σ bond between B and F in BF_3 as compared to that between C and F in CF_4

(c) significant pπ-pπ interaction between B and F in BF_3 whereas there is no possibility of such interaction between C and F in CF_4.

(d) lower degree of pπ-pπ interaction between B and F in BF_3 than that between C and F in CF_4.

Ans. (c)

Sol. The bond dissociation energy of B – F in BF_3 is 646 kJ mol^{-1}, whereas the bond dissociation energy of C – F in CF_4 is 515 kJ mol^{-1}. The correct reason for higher B-F bond dissociation energy than C – F is, due to the presence of vacant p orbital in boron the nonbonding electrons of fluorine forms $p\pi - p\pi$ bond with boron. As a result, in the molecule , the B-F bond becomes partially double bond in nature. But there is no such bond is possible for CF_4 . So, the C-F bond is purely single.



Example - 11

Aqueous solution of borax acts as a buffer because:

(a) it contains weak acid and its salt with strong base

(b) it contains tribasic acid and strong base

(c) it contains number of neutral water molecules

(d) none of the above

Ans. (a)

Sol. Borax dissolves in water to give an alkaline solution. Therefore, it is used as cleansing agent.

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

This solution contains equal amount of weak boric acid and its salt. Therefore, it can act as buffer.

Example - 12

What happens when diborane reacts with Lewis bases ?

(a) It forms boron trihydride (BH_3) due to cleavage.

(b) It undergoes cleavage to give borane adduct BH_3L (where, L = Lewis base).

(c) It oxidises to give B_2O_3.

(d) It does not react with Lewis bases.

Ans. (b)

Sol. $B_2H_6 + 2NH_3 \rightarrow 2\underset{\text{adduct}}{[NH_3 \rightarrow BH_3]}$

Example - 13

A compound X, of boron reacts with NH_3 on heating to give another compound Y which is called inorganic benzene. The compound X can be prepared by treating BF_3 with lithium aluminium hydride. The compounds X and Y are represented by the formulas

(a) B_2H_6, $B_3N_3H_6$ (b) B_2O_3, $B_3N_3H_6$

(c) BF_3, $B_3N_3H_6$ (d) $B_3N_3H_6$, B_2H_6

Ans. (a)

Sol. $\underset{X}{3B_2H_6} + 6NH_3 \xrightarrow{\Delta} \underset{Y}{2B_3N_3H_6} + 12H_2$

$$4BF_3 + 3LiAlH_4 \rightarrow \underset{X}{2B_2H_6} + 3LiF + 3AlF_3$$

Example - 14

Which of the following is not a protonic acid ?

(a) $B(OH)_3$ (b) $PO(OH)_3$

(c) $SO(OH)_2$ (d) $SO_2(OH)_2$

Ans. (a)

Sol. Protonic acid is defined as a acid which in its aqueous solution gives positive hydrogen ions. But boric acid is not a protonic acid because it is a lewis acid. According to lewis acid base theory, lewis acid means tendency to accept a pair of electron and lewis base means tendency to donate a pair of electrons. Boric acid acts as a lewis acid by accepting a lone pair of electrons.

Hence, the correct option is (a).

Example - 15

$$B(OH)_3 + NaOH \rightleftharpoons Na[B(OH)_4]$$

How can this reaction be made to proceed in forward direction?

(a) Addition of *cis*-1,2-diol

(b) Addition of borax

(c) Addition of *trans*-1, 2-diol

(d) Addition of Na_2HPO_4

Ans. (a)

Sol. Boric acid on reaction with NaOH gives sodium metaborate as product. Because of aqueous conditions, this reaction is reversible in nature. Sodium metaborate gets hydrolysed back to give boric acid and NaOH. In order to prevent the reversibility of reaction add some polyhydroxy compound such as glycerol, mannitol or 1, 2 cis- diols. These polyhydroxy compounds can form chelate complex with sodium metaborate and prevent it to get hydrolysed.

Example - 16

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

How can this reaction is made to proceed in forward direction?

(a) Addition of cis 1, 2 diol

(b) Addition of borax

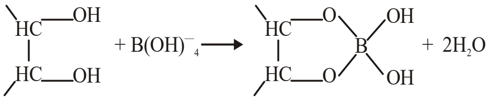
(c) Addition of trans 1, 2 diol

(d) Addition of Na_2HPO_4

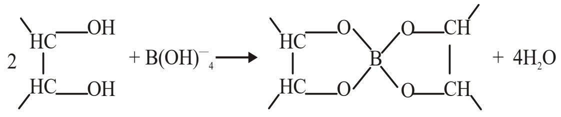
Ans. (a)

Sol. $B(OH)_3 + NaOH \rightarrow NaBO_2 + Na\left[B\left(OH\right)_4\right] + H_2O$

in this reaction, if you added cis 1,2-diol, then the product $Na\left[B\left(OH\right)_4\right]$ reacts with cis 1,2 -diol and produces a cyclic product and free water molecules. Due to the formation of cyclic products and four water molecules the entropy of the reaction increases, so the reaction becomes more feasible. Therefore, this reaction is made to proceed in the forward direction by the addition of cis 1, 2 diols. The reaction is shown below,



1 : 1 polyol-boron complex



2 : 1 polyol-boron complex

Example - 17

Which of the following minerals does not contain aluminium?

(a) Cryolite	(b) Mica
(c) Feldspar	(d) Fluorspar

Ans. (d)

Sol. Cryolite, mica, feldspar are ores of aluminium with chemical formula given below:

Mica – $KAl_2\left[AlSi_3O_{10}\right](OH)_2$

Cryolite – Na_3AlF_6

Fluorspar – CaF_2

Feldspars are the aluminosilicates with general formula AT_4O_8.

Example - 18

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

(a) $[Al(OH)_6]^{3-} + 3HCl$	(b) $[Al(H_2O)_6]^{3+} + 3Cl^-$
(c) $Al^{3+} + 3Cl^-$	(d) $Al_2O_3 + 6HCl$

Ans. (b)

Sol. Aluminium chloride can form a dimer like Al_2Cl_6. In solid-state as well as in the solution of non-polar solvents such as benzene aluminum chloride exists as a dimer. When it dissolves in water, it gives aluminium hexa hydroxide anion with hydrochloric acid, as follows.

$$Al_2Cl_6 + 12H_2O \rightarrow 2[Al(H_2O)_6]^{+3} + 6Cl^-$$

Example - 19

Which of the following hydrides is least stable to hydrolysis?

(a) CH_4	(b) SiH_4
(c) SnH_4	(d) PbH_4

Ans. (d)

Sol. PbH_4 is the least stable due to inert pair effect.

Example - 20

Which of the following is not a use of graphite ?

(a) For electrodes in batteries.

(b) Crucibles made from graphite are used for its inertness to dilute acids and alkalies.

(c) For adsorbing poisonous gases.

(d) Lubricant at high temperature.

Ans. (c)

Sol. Graphite is not used for absorbing poisonous gas.

Example - 21

Which property of CO_2 makes it of biological and geochemical importance ?

(a) Its acidic nature.

(b) Its colourless and odourless nature.

(c) Its low solubility in water.

(d) Its high compressibility.

Ans. (c)

Sol. CO_2 have low solubility in water.

Example - 22

$$SiCl_4 \xrightarrow{H_2O} X \xrightarrow{Heat} Y \xrightarrow{NaOH} Z$$

X, Y and Z in the above reaction are

	X	**Y**	**Z**
(a)	SiO_2	Si	NaSi
(b)	$Si(OH)_4$	SiO_2	Na_2SiO_3
(c)	$Si(OH)_4$	Si	SiO_2
(d)	SiO_2	$SiCl_4$	Na_2SiO_3

Ans. (b)

Sol. Silicon tetrachloride on reaction with water gives *o*-silicilic acid and HCl. This acid on heating gives silica which is acidic in nature. Therefore, silica on reaction with base like NaOH gives sodium salt of silicate and water as shown in the reactions:

$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4\,(X) + 4HCl$$

$$Si(OH)_4 \xrightarrow{\Delta} SiO_2\,(Y) + H_2O$$

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3\,(Z) + H_2O$$

Example - 23

An oxide X in its normal form is almost non-reactive due to very high X – O bond enthalpy. It resists the attack by halogens, hydrogen and most of acids and metals even at elevated temperatures. It is only attacked by HF and NaOH. The oxide X is

(a) SiO_2
(b) CO_2
(c) SnO_2
(d) PbO_2

Ans. (a)

Sol. SiO_2 have giant covalent structure and is not attacked by halogen, metal at high temp. But react with HF and NaOH.

Example - 24

Silicon has a strong tendency to form polymers like silicones. The chain length of silicone polymer can be controlled by adding

(a) $MeSiCl_3$
(b) Me_2SiCl_2
(c) Me_3SiCl
(d) Me_4Si

Ans. (c)

Sol. Chain length of silicones polymer can be controlled by adding Me_3SiCl act as inhibitor of reaction.

Example - 25

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

Sol. Electron deficient species are those species in which the octet of the central metal atom is not complete.

(i) BCl_3

Boron trichloride behave as a Lewis acid. It is electron deficient species. boron tri-chloride have three covalent bonds hence, require two electrons to complete octet.

(ii) $SiCl_4$

Silicon is belonging to group 14. The electronic configuration of this group are $ns^2\,np^2$. Most common oxidation state should be +4. The elements of group 14 show tetra valency by sharing four of its valence electrons. it forms four covalent bonds with four chlorine atoms. Therefore, $SiCl_4$ is not an electron-deficient compound.

EXERCISE - 1 : BASIC OBJECTIVE QUESTIONS

Physical Properties of Group 13 Elements

1. Which of the following is most abundant in the earth crust?

(a) Boron
(b) Aluminium
(c) Gallium
(d) Thallium

2. The element which exists in liquid state for a wide range of temperature and can be used for measuring high temperature is:

(a) B
(b) Al
(c) In
(d) Ga

3. Alumina is:

(a) acidic
(b) basic
(c) neutral
(d) amphoteric

4. The reason behind the lower atomic radius of Ga as compared to Al is

(a) poor screening effect of d-electrons for the outer electrons from increased nuclear charge
(b) increased force of attraction of increased nuclear charge on electrons
(c) increased ionisation enthalpy of Ga as compared to Al
(d) anomalous behaviour of Ga.

5. Ionisation enthalpy $(\Delta_i H_1 \text{ kJ mol}^{-1})$ for the elements of Group 13 follows the order

(a) $B > Al > Ga > In > Tl$
(b) $B < Al < Ga < In < Tl$
(c) $B < Al > Ga > In > Tl$
(d) $B > Al < Ga > In < Tl$

6. Electropositive charcter for the elements of group 13 follows the order

(a) $B > Al > Ga > In > Tl$
(b) $B < Al < Ga < In < Tl$
(c) $B < Al > Ga < In > Tl$
(d) $B < Al > Ga > In > Tl$

7. Which one of the statements is incorrect for aluminium metal?

(a) It is a good conductor of heat and electricity
(b) It is malleable and ductile
(c) It can be welded and cast but difficult to solder
(d) Its alloys are heavy

Chemical Properties of Group 13 Elements

8. Boron cannot form which one of the following anions?

(a) BF_6^-
(b) BH_4^-
(c) $[B(OH)_4]^-$
(d) BO_2^-

9. Which of the following does not show similarity between boron and aluminium ?

(a) Both form oxides of type M_2O_3 when heated with oxygen at high temperature.
(b) Both dissolve in alkalies and evolve hydrogen.
(c) Hydroxides of both the elements are basic in nature.
(d) Both form nitrides of MN type when heated with N_2.

10. Boron is unable to form BF_6^{3-} ions due to

(a) non-availability of d-orbitals
(b) small size of boron atom
(c) non-metallic nature
(d) it is a strong Lewis acid.

11. The main factor responsible for weak acidic nature of B—F bonds in BF_3 is:

(a) high electronegativity of F
(b) three centred two electron bonds in BF_3
(c) $p\pi$—$d\pi$ back bonding
(d) $p\pi$—$p\pi$ back bonding

12. Which one of the following statements regarding BF_3 is not correct?

(a) It is a Lewis acid
(b) It is an ionic compound
(c) It is an electron deficient compound
(d) It forms adducts

13. The power of halides of boron to act as Lewis acids decreases in the order:

(a) $BF_3 > BCl_3 > BBr_3$
(b) $BBr_3 > BCl_3 > BF_3$
(c) $BCl_3 > BF_3 > BBr_3$
(d) $BCl_3 > BBr_3 > BF_3$

14. BF_3 is used as catalyst in several industrial processes due to its:

(a) strong reducing nature
(b) weak reducing action
(c) strong Lewis acid nature
(d) weak Lewis acid character

15. Specify the coordination geometry around and hybridization of N and B atoms in 1:1 complex of BF_3 and NH_3:

(a) N: tetrahedral, sp^3 ; B:tetrahedral, sp^3

(b) N: pyramidal, sp^3 ; B:pyramidal , sp^3

(c) N:pyramidal, sp^3 ; B:planar, sp^3

(d) N:pyramidal, sp^3 ; B:tetrahedral, sp^3

16. The main factor responsible for weak acidic nature of B—F bonds in BF_3 is:

(a) high electronegativity of F

(b) three centred two electron bonds in BF_3

(c) $p\pi$—$d\pi$ back bonding

(d) $p\pi$—$p\pi$ back bonding

17. Which of the following is not true regarding the nature of halides of boron ?

(a) Boron trihalides are covalent.

(b) Boron trihalides are planar triangular with sp^2 hybridisation

(c) Boron trihalides act as Lewis acids.

(d) Boron trihalides cannot be hydrolysed easily.

18. The geometry of a complex species can be understood from the knowledge of type of hybridisation of orbitals of central atom. The hybridisation of orbitals of central atom in $[B(OH)_4]^-$ and the geometry of the complex are respectively

(a) sp^3, tetrahedral
(b) sp^3, square planar

(c) sp^3d^2, octahedral
(d) dsp^2, square planar.

19. Which of the following hydroxides is most acidic ?

(a) $Al(OH)_3$
(b) $Ga(OH)_3$

(c) $Tl(OH)_3$
(d) $B(OH)_3$

20. Which of the following oxides is acidic in nature ?

(a) B_2O_3
(b) Al_2O_3

(c) Ga_2O_3
(d) In_2O_3

21. Aluminium is more reactive than iron. But aluminium is less easily corroded than iron because:

(a) oxygen forms a protective oxide layer on aluminium

(b) aluminium is a noble metal

(c) iron undergoes reaction easily with water

(d) iron forms mono and divalent ions

22. When aluminium is heated with conc. H_2SO_4

(a) aluminium becomes passive

(b) hydrogen is liberated

(c) oxygen is liberated

(d) sulphur dioxide is liberated

23. A metal M reacts with sodium hydroxide to give a white precipitate X which is soluble in excess of NaOH to give Y. Compound X is soluble in HCl to form a compound Z. Identify M, X, Y and Z.

	M	X	Y	Z
(a)	Si	SiO_2	Na_2SiO_3	$SiCl_4$
(b)	Al	$Al(OH)_3$	$NaAlO_2$	$AlCl_3$
(c)	Mg	$Mg(OH)_3$	$NaMgO_3$	$MgCl_2$
(d)	Ca	$Ca(OH)_2$	Na_2CO_3	$NaHCO_3$

Inert Pair Effect

24. Aluminium exhibits +3 oxidation state. As we move down the group, +1 oxidation state gets more stable. This is a consequence of

(a) increasing size of the atom

(b) inert pair effect

(c) electron deficient nature

(d) $p\pi$ - $p\pi$ bonding.

25. The stability of +1 oxidation state increases in the sequence:

(a) $Tl < In < Ga < Al$
(b) $In < Tl < Ga < Al$

(c) $Ga < In < Al < Tl$
(d) $Al < Ga < In < Tl$

26. Group 13 elements show +1 and +3 oxidation states. Relative stability of +3 oxidation state may be given as

(a) $Tl^{3+} > In^{3+} > Ga^{3+} > Al^{3+} > B^{3+}$

(b) $B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}$

(c) $Al^{3+} > Ga^{3+} > Tl^{3+} > In^{3+} > B^{3+}$

(d) $Al^{3+} > B^{3+} > Ga^{3+} > Tl^{3+} > In^{3+}$

27. The tendency of group 14 elements to show +2 oxidation state increases in the order of

(a) $C < Si < Sn < Pb < Ge$
(b) $C < Si < Ge < Sn < Pb$

(c) $Ge < Sn < Pb < C < Si$
(d) $Pb < Sn < Ge < C < Si$

Boron and Its Compounds

28. The number of OH units directly linked to boron atoms in $Na_2B_4O_7.10H_2O$ is:

(a) 2
(b) 3

(c) 4
(d) 10

29. H_3BO_3 is:

(a) monobasic and weak Lewis acid

(b) monobasic and weak Bronsted acid

(c) monobasic acid and strong Lewis acid

(d) tribasic acid and weak Bronsted acid

30. Which is not the use of orthoboric acid ?

(a) As an antiseptic and eye wash

(b) In glass industry

(c) In glazes for pottery

(d) In borax - bead test

31. Borax bead test is responded by:

(a) divalent metals

(b) heavy metals

(c) light metals

(d) metals which form coloured metaborates

32. $Na_2B_4O_7.10H_2O \xrightarrow{\Delta} X \xrightarrow{\Delta} Y + Z$

X, Y and Z in the reaction are

(a) $X = Na_2B_4O_7, Y = NaBO_2, Z = B_2O_3$

(b) $X = Na_2B_4O_7, Y = B_2O_3, Z = H_3BO_3$

(c) $X = B_2O_3, Y = NaBO_2, Z = B(OH)_3$

(d) $X = NaBO_2, Y = B_2O_3, Z = B(OH)_3$

33. When strongly heated, orthoboric acid leaves a residue of:

(a) metaboric acid (b) tetraboric acid

(c) boric anhydride (d) boron

34. From B_2H_6, all the following can be prepared except:

(a) B_2O_3 (b) H_3BO_3

(c) $B_2(CH_3)_6$ (d) $NaBH_4$

35. On hydroloysis, diborane produces

(a) $H_3BO_2 + H_2O_2$ (b) $H_3BO_3 + H_2$

(c) $B_2O_3 + O_2$ (d) $H_3BO_3 + H_2O_2$

36. Reactivity of borazole is higher than that of benzene because:

(a) borazole is a polar compound

(b) borazole is a non-polar compound

(c) borazole is electron deficient compound

(d) of localised electrons in it

37. On the addition of mineral acid to an aqueous solution of borax, the following compound is formed:

(a) boron hydride (b) orthoboric acid

(c) metaboric acid (d) pyroboric acid

38. Which of the following compounds is formed when boron trichloride is treated with water?

(a) $H_3BO_3 + HCl$ (b) $B_2H_6 + HCl$

(c) $B_2O_3 + HCl$ (d) None of these

39. Boric acid is prepared from borax by the action of :

(a) Hydrochloric acid

(b) sodium hydroxide

(c) carbon dioxide

(d) sodium carbonate

40. $Na_2B_4O_7 + X \rightarrow H_3BO_3$. What is X in the reaction ?

(a) Aqueous solution of NaOH

(b) Dilute nitric acid

(c) Conc. H_2SO_4 or HCl

(d) Water

41. Diborane reacts with ammonia under different conditions to give a variety of products. Which one among the following is not fomed in these conditions?

(a) $B_2H_6.2NH_3$ (b) $B_{12}H_{12}$

(c) $B_3N_3H_6$ (d) $(BN)_n$

42. BCl_3 does not exist as a dimer but BH_3 exists as B_2H_6 because

(a) Cl_2 is more electronegative than hydrogen

(b) large size of chlorine atom does not fit between small sized boron atoms, while small-sized hydrogen atoms occupy the space between boron atoms

(c) There is $p\pi$-$d\pi$ back bonding in BCl_3

(d) Both (b) and (c)

43. Borazole, $B_3N_3H_6$ is related to benzene as:

(a) isoelectronic (b) isostructural

(c) both (a) and (b) (d) none of these

44. The bonds present in borazole are:

(a) $9\sigma, 9\pi$ (b) $6\sigma, 6\pi$

(c) $9\sigma, 6\pi$ (d) $12\sigma, 3\pi$

45. Which of the following compounds is known as inorganic benzene?

(a) B_6H_6 (b) C_5H_5B

(c) $C_3N_3H_3$ (d) $B_3N_3H_6$

46. Boric acid has a polymeric layer structure in which planar BO_3 units are joined by

(a) covalent bonds

(b) two centre - two electron bonds

(c) coordinate bonds

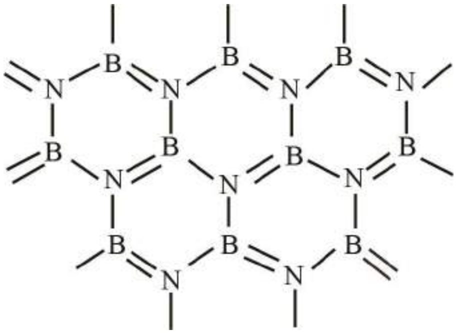
(d) hydrogen bonds.

47. The hardest compound of boron is:

(a) boric acid (b) boron nitride

(c) boron carbide (d) boron hydride

48. Boron nitride can be represented by the given structure.



The structure of BN is similar to

(a) graphite (b) diamond

(c) benzene (d) pyridine.

49. Which is the hardest compound of boron ?

(a) B_2O_3 (b) BN

(c) B_4C (d) B_2H_6

50. In the structure of diborane

(a) all hydrogen atoms lie in one plane and boron atoms lie in a plane perpendicular to this plane

(b) 2 boron atoms and 4 terminal hydrogen atoms lie in the same plane and 2 bridging hydrogen atoms lie in the perpendicular plane

(c) 4 bridging hydrogen atoms and boron atoms lie in one plane and two terminal hydrogen atoms lie in a plane perpendicular to this plane

(d) all the atoms are in the same plane.

51. Borax is not used

(a) as a styptic to stop bleeding

(b) in making enamel and pottergy glazes

(c) as a flux in soldering

(d) in making optical glasses.

52. An aqueous solution of boric acid is found to be weakly acidic in nature. This acidic character arises due to the following reasons.

(a) It is a protic acid which donates protons in aqueous solution.

(b) It is a Lewis acid which abstracts OH^- from water and leaves H^+ to make the solution acidic.

(c) It gives metaboric acid when dissolved in water.

(d) It is prepared by reaction of borax with sulphuric acid hence it behaves as an acid.

53. $NaBH_4 + I_2 \rightarrow X + Y + Z$

$BF_3 + NaH \xrightarrow{450\text{ K}} X + P$

$BF_3 + LiAlH_4 \rightarrow X + Q + R$

X, Y, Z, P, Q and R in the reactions are

	X	Y	Z	P	Q	R
(a)	$Na_4B_4O_7$	NaI	HI	HF	LiF	AlF_3
(b)	B_2H_6	NaI	H_2	NaF	LiF	AlF_3
(c)	B_2H_6	BH_3	NaI	$B_3N_3H_6$	Al_2F_6	AlF_3
(d)	BH_3	B_2H_6	H_2	$B_3N_3H_6$	LiF	AlF_3

54. A mixture of boron trichloride and hydrogen is subjected to silent electric discharge to form 'A' and HCl. 'A' is mixed with NH_3 and heated to 200°C to form 'B'. The formula of 'B' is:

(a) H_3BO_3 (b) B_2O_3

(c) B_2H_6 (d) $B_3N_3H_6$

55. Boric acid H_3BO_3 and BF_3 have the same number of electrons. The former is a solid and the latter is a gas. The reason is:

(a) BF_3 is a Lewis acid while $B(OH)_3$ is not

(b) they have different geometrics

(c) In BF_3, F^- is smaller in size than OH^- in $B(OH)_3$

(d) No molecular association is possible in BF_3 while it is possible in $B(OH)_3$ due to hydrogen bonding

Aluminium and Its Compounds

56. Al_2O_3 formation from aluminium and oxygen involves evolution of a large quantity of heat, which makes aluminium used in:

(a) deoxidiser (b) confectionary

(c) indoor photography (d) thermite welding

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

(a) It exists as $AlCl_3$ molecule

(b) It is a strong Lewis base

(c) It sublimes at 100°C under vaccum

(d) It is not easily hydrolysed

58. $AlCl_3$ on hydrolysis gives:

(a) $Al_2O_3 . H_2O$ (b) $Al(OH)_3$

(c) Al_2O_3 (d) $AlCl_3.6H_2O$

59. When aluminium hydroxide dissolves in NaOH solution, the product is:

(a) $[Al(H_2O)_3(OH)_3]$ (b) $[Al(H_2O)_4(OH)_2]^+$

(c) $[Al(H_2O)_2(OH)_4]^-$ (d) $[Al(H_2O)_5(OH)]^{2+}$

60. Alumina may be converted into anhydrous aluminium chloride by:

(a) heating it with conc. HCl

(b) heating in a current of dry chlorine

(c) heating it with rock salt

(d) mixing it with carbon and heating the mixture in a current of dry chlorine

61. When alumina is heated with carbon in nitrogen atmosphere, the products are:

(a) $Al + CO$ (b) $Al + CO_2$

(c) $Al + CO + CO_2$ (d) $AlN + CO$

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

(a) a white precipitate (b) bluish white precipitate

(c) a clear solution (d) a crystalline mass

63. When excess of NaOH solution is added in potash alum, the product is:

(a) a bluish white precipitate

(b) clear solution

(c) a white precipitate

(d) a greenish precipitate

Physical and Chemical Properties of Group 14 Elements

64. Maximum ability of catenation is shown by

(a) silicon (b) lead

(c) germanium (d) carbon

65. Which of the following oxides can act as a reducing agent?

(a) CO (b) CO_2

(c) SnO_2 (d) PbO_2

66. The most commonly used reducing agent is

(a) $AlCl_3$ (b) $PbCl_2$

(c) $SnCl_4$ (d) $SnCl_2$

67. The members of group 14 form tetrahalides of the type MX_4. Which of the following halides cannot be readily hydrolysed by water ?

(a) CX_4 (b) SiX_4

(c) GeX_4 (d) SnX_4

68. Identify the wrong example from the following for the group 14 elements.

(a) Element which forms most acidic dioxide-Carbon

(b) Element which is affected by water - Lead

(c) Commonly found in +2 oxidation state - Lead

(d) Element used as semiconductor - Silicon

69. Identify X in the reaction :

$$X + \underset{(\text{steam})}{2H_2O} \xrightarrow{\Delta} XO_2 + 2H_2$$

(a) C (b) Si

(c) Ge (d) Sn

70. All members of group 14 when heated in oxygen form oxides. Which of the following is the correct trend of oxides ?

(a) Dioxides CO_2, SiO_2 and GeO_2 are acidic while SnO_2 and PbO_2 are amphoteric.

(b) CO, GeO, SnO and PbO are amphoteric.

(c) Monoxides react with haemoglobin to form toxic compounds.

(d) All oxides burn with blue flame.

71. An oxide X in its normal form is almost non-reactive due to very high X – O bond enthalpy. It resists the attack by halogens, hydrogen and most of acids and metals even at elevated temperatures. It is only attacked by HF and NaOH. The oxide X is

(a) SiO_2 (b) CO_2

(c) SnO_2 (d) PbO_2

Carbon and Its Compounds

72. Buckminsterfullerence is

(a) graphite (b) diamond

(c) C-60 (d) quartz

73. In graphite, C atom is in .... state.

(a) sp^3 (b) sp

(c) sp^2 (d) None of these

74. In graphite, the layers of carbon atoms are held by

(a) covalent bonds (b) coordinate bonds

(c) van der Waals forces (d) ionic bonds.

75. Which of the following is not a use of graphite ?

(a) For electrodes in batteries.

(b) Crucibles made from graphite are used for its inertness to dilute acids and alkalies.

(c) For adsorbing poisonous gases.

(d) Lubricant at high temperature.

76. Dry ice is

(a) solid NH_3 (b) solid SO_2

(c) solid CO_2 (d) solid N_2

77. Which of the following does not depict properties of fullerenes ?

(a) Fullerenes are made by heating graphite.

(b) Fullerenes are pure forms of carbon.

(c) Fullerenes have open cage structure like ice.

(d) C_{60} is called Buckminsterfullerene.

78. Which of the following is not true about structure of diamond and graphite ?

(a) In diamond, each carbon in sp^3 hybridised while in graphite each carbon is sp^2 hybridised.

(b) In diamond, carbon atoms are closely packed in crystal lattice while graphite has layer structure.

(c) Diamond is a hard substance while graphite is a soft substance.

(d) Graphite is thermodynamically very less stable as compared to diamond and is amorphous form of carbon.

79. Identify the incorrect statement.

(a) Graphite is thermodynamically most stable allotrope of carbon.

(b) Other forms of elemental carbon like coke, carbon black, charcoal are impure forms of graphite.

(c) All allotropes of carbon have thermodynamically same stability.

(d) Charcoal and coke are obtained by heating wood in absence of air.

80. An element of group 14 forms two oxides one of which is highly poisonous and neutral. Other oxide can be easily liquefied and compressed to give a solid which is used as a refrigerant under the name of drikold. The element and the oxides are

(a) Si, SiO, SiO_2 (b) Pb, PbO, PbO_2

(c) C, CO, CO_2 (d) Sn, SnO, SnO_2

81. When excesss of carbon dioxide is passed through lime water, the milkiness first formed disappears due to

(a) the reversible reaction taking place

(b) formation of water soluble calcium bicarbonate

(c) huge amount of heat evolved during the reaction

(d) formation of water soluble complex of calcium.

82. CO_2 is not a poisonous gas but there is increase in concentration of CO_2 in the atmosphere due to burning of fossil fuels and decompostion of limestone. The increase in concentration of CO_2 may lead to

(a) increase in photosynthesis in plants

(b) higher concentration of CO_2 in water

(c) increase in greenhouse effect, thus raising the temperature

(d) increase in formation of metal carbonates.

83. Which is not a method of preparing carbon monoxide on a commercial scale ?

(a) $C_{(s)} + H_2O_{(g)} \xrightarrow{473-1273\text{ K}} CO_{(g)} + H_{2(g)}$

(b) $2C_{(s)} + O_{2(g)} + 4N_{2(g)} \xrightarrow{1273\text{ K}} 2CO_{(g)} + 4N_{2(g)}$

(c) $2C_{(s)} + O_{2(g)} \xrightarrow{\Delta} 2CO_{(g)}$

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

84. Carbon monoxide acts as a donor and reacts with certain metals to give metal carbonyls. This is due to

(a) presence of one sigma and two pi bonds between C and $(:C \equiv O:)$

(b) presence of a lone pair on carbon atom in CO molecule

(c) presence of lone pair on oxygen atom in CO molecule

(d) poisonous nature of CO.

85. Mark the example which is not correct.

(a) Non-combustible heavy liquid used as fire extinguisher - CCl_4

(b) Blocks used to shield radioactive materials - Lead

(c) Element which has property of leaving mark on paper-Graphite

(d) A gas in solid form used as a refrigerant - Carbon monoxide.

86. Which one of the following is not the characteristic property of carbon ?

(a) It exhibits catenation.

(b) It forms compounds with multiple bonds.

(c) Its melting point and boiling point are exceptionally high.

(d) It shows semi-metallic character.

87. Which of the following is not true about structure of carbon dioxide ?

(a) In CO_2, carbon is sp - hybridised.

(b) C forms two sigma bonds one with each oxygen atom and two $p\pi - p\pi$ bonds.

(c) CO_2 is a linear covalent compound

(d) It is a polar molecule.

88. The most stable form of carbon at high temperature is X. The C – C bond length in diamond is Y while C – C bond length in graphite is Z.

What are X, Y and Z respectively ?

(a) Graphite, 1.42 Å, 1.54 Å

(b) Coke, 1.54 Å, 1.84 Å

(c) Diamond, 1.54 Å, 1.42 Å

(d) Fullerene, 1.54 Å, 1.54 Å

Silicon and Its Compounds

89. Silicon is an important constituent of

(a) sand

(b) atmosphere

(c) plants

(d) water bodies

90. What happens when silicon is heated with methyl chloride in presence of copper as a catalyst at 573 K ?

(a) Methyl substituted chlorosilanes are formed.

(b) Only Me_4Si is formed.

(c) Polymerised chains of $(CH_3)_3SiCl$ are formed.

(d) Silicones are formed.

91. Silicon has a strong tendency to form polymers like silicones. The chain length of silicone polymer can be controlled by adding

(a) $MeSiCl_3$

(b) Me_2SiCl_2

(c) Me_3SiCl

(d) Me_4Si

92. Glass and cement are two important examples of

(a) man-made silicates

(b) silicones

(c) zeolites

(d) organic polymers.

93. Which of the following acids cannot be stored in glass ?

(a) HF

(b) HCl

(c) H_2SO_4

(d) HI

94. In SiO_4^{4-}, the tetrahedral molecule, two oxygen atoms are shared in

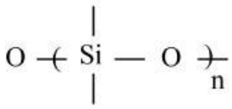
(a) sheet silicates

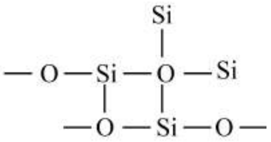
(b) double-chain silicates

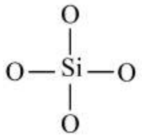
(c) chain silicates

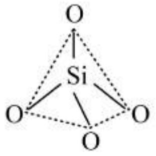
(d) three-dimensional silicates.

95. Which of the following bonds is shown in silicones ?

(a) 

(b) 

(c) 

(d) 

96. Cement, the important building material is a mixture of oxides of several elements. Besides calcium, iron and sulphur, oxides of elements of which of the group(s) are present in the mixture ?

(a) Group 2

(b) Groups 2, 13 and 14

(c) Groups 2 and 13

(d) Groups 2 and 14

97. A type of zeolite used to convert alcohols directly into gasoline is

(a) zeolite A

(b) zeolite L

(c) zeolite Beta

(d) ZSM-5

98. Complete the following reactions :

(i) $SiO_2 + 2NaOH \rightarrow X + H_2O$

(ii) $SiO_2 + 4HF \rightarrow Y + 2H_2O$

(iii) $Si + 2CH_3Cl \xrightarrow[570\,K]{Cu\,powder} Z$

	X	Y	Z
(a)	Na_2SiO_3	SiF_4	$(CH_3)_2SiCl_2$
(b)	H_2SiO_3	SiF_2	CH_3SiCl_3
(c)	Na_2SiO_3	H_2SiO_3	$(CH_3)_3SiCl$
(d)	Na_2SiO_3	H_2SiF_4	$(CH_3)_2SiCl_2$

Match the Following

Each question has two columns. Four options are given representing matching of elements from Column-I and Column-II. Only one of these four options corresponds to a correct matching. For each question, choose the option corresponding to the correct matching.

99. Match the column I with column II and mark the appropriate choice.

Column - I	**Column - II**
(A) Borax	(p) Na_3AlF_6
(B) Inorganic benzene	(q) $Na_2B_4O_7.10H_2O$
(C) Cryolite	(r) $Al_2O_3.2H_2O$
(D) Bauxite	(s) $B_3N_3H_6$

(a) (A) → (q), (B) → (s), (C) → (p), (D) → (r)

(b) (A) → (p), (B) → (q), (C) → (r), (D) → (s)

(c) (A) → (q), (B) → (r), (C) → (p), (D) → (s)

(d) (A) → (r), (B) → (p), (C) → (q), (D) → (s)

100. Match the column I with column II and mark the appropriate choice.

Column - I	**Column - II**
(A) Coal gas	(p) $CO + H_2$
(B) Synthesis gas	(q) CH_4
(C) Producer gas	(r) $H_2 + CH_4 + CO$
(D) Natural gas	(s) $CO + N_2$

(a) (A) → (p), (B) → (q), (C) → (r), (D) → (s)

(b) (A) → (r), (B) → (p), (C) → (s), (D) → (q)

(c) (A) → (s), (B) → (r), (C) → (q), (D) → (p)

(d) (A) → (p), (B) → (r), (C) → (q), (D) → (s)

EXERCISE - 2 : PREVIOUS YEAR JEE MAINS QUESTIONS

1. Identify the reaction which does not liberate hydrogen: **(2016)**

(a) Reaction of lithium hydride with B_2H_6.

(b) Electrolysis of acidified water using Pt electrodes

(c) Reaction of zinc with aqueous alkali

(d) Allowing a solution of sodium in liquid ammonia to stand

2. When metal 'M' is treated with NaOH, a white gelatinous precipitate 'X' is obtained, which is soluble in excess of NaOH. Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal 'M' is: **(2018)**

(a) Zn
(b) Ca
(c) Al
(d) Fe

3. A group 13 element 'X' reacts with chlorine gas to produce a compound XCl_3. XCl_3 is electron deficient and easily reacts with NH_3 to form $Cl_3X \leftarrow NH_3$ adduct, however, XCl_3 does not dimerize X is: **(2018)**

(a) B
(b) Al
(c) In
(d) Ga

4. Which of the following are Lewis acids? **(2018)**

(a) PH_3 and BCl_3
(b) $AlCl_3$ and $SiCl_4$
(c) PH_3 and $SiCl_4$
(d) BCl_3 and $AlCl_3$

5. In graphite and diamond, the percentage of p-characters of the hybrid orbitals in hybridisation are respectively: **(2018)**

(a) 33 and 25
(b) 67 and 75
(c) 50and 75
(d) 33 and 75

6. The correct statements among I to III regarding group 13 element oxides are,

(I) Boron trioxide is acidic

(II) Oxides of aluminum and gallium are amphoteric.

(III) Oxides of indium and thallium are basic. **(2019)**

(a) (I) and (II) only
(b) (I), (II) and (III)
(c) (I) and (III) only
(d) (II) and (III) only

7. Diborane (B_2H_6) reacts independently with O_2 and H_2O to produce, respectively; **(2019)**

(a) B_2O_3 and H_3BO_3
(b) B_2O_3 and $[BH_4]^-$
(c) H_3BO_3 and B_2O_3
(d) HBO_2 and H_3BO_3

8. The hydride that is **NOT** electron deficient is: **(2019)**

(a) SiH_4
(b) B_2H_6
(c) GaH_3
(d) AlH_3

9. The relative stability of +1 oxidation state of group 13 elements follows the order: **(2019)**

(a) $Al < Ga < Tl < In$
(b) $Tl < In < Ga < Al$
(c) $Ga < Al < In < Tl$
(d) $Al < Ga < In < Tl$

10. The electronegativity of aluminium is similar to: **(2019)**

(a) Carbon
(b) Beryllium
(c) Boron
(d) Lithium

11. The number of 2-centre-2-electron and 3-centre-2-electron bonds in B_2H_6, respectively, are: **(2019)**

(a) 2 and 1
(b) 4 and 2
(c) 2 and 2
(d) 2 and 4

12. Aluminium is usually found in +3 oxidation state. In contrast, Thallium exists in +1 and +3 oxidation states. This is due to: **(2019)**

(a) inert pair effect
(b) diagonal relationship
(c) lattice effect
(d) lanthanoid contraction

13. C_{60}, an allotrope of carbon contains: **(2019)**

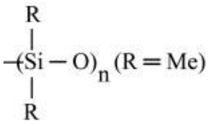
(a) 12 hexagons and 20 pentagons.

(b) 18 hexagons and 14 pentagons.

(c) 16 hexagons and 16 pentagons.

(d) 20 hexagons and 12 pentagons.

14. The basic structural unit of feldspar, zeolites, mica, and asbestos is : **(2019)**

(a) $(SiO_3)^{2-}$
(b) SiO_2
(c) $(SiO_4)^{4-}$
(d) 

$-(\underset{R}{\overset{R}{|}}\!\!\!\!\!\!\underset{|}{\overset{|}{Si}}-O)_n\ (R=Me)$

15. The correct statement among the following is: **(2019)**

(a) $(SiH_3)_3N$ is planar and less basic than $(CH_3)_3N$.

(b) $(SiH_3)_3N$ is pyramidal and more basic than $(CH_3)_3N$.

(c) $(SiH_3)_3N$ is pyramidal and less basic than $(CH_3)_3N$.

(d) $(SiH_3)_3N$ is planar and more basic than $(CH_3)_3N$.

16. The C – C bond length is maximum in: **(2019)**

(a) graphite
(b) C_{70}
(c) C_{60}
(d) diamond

17. The correct order of catenation is: **(2019)**

(a) C > Sn > Si ≈ Ge
(b) C > Si > Ge ≈ Si
(c) Si > Sn > C ≈ Ge
(d) Ge > Sn > Si ≈ C

18. The amorphous form of silica is: **(2019)**

(a) Tridymite
(b) Kieselguhr
(c) Cristobalite
(d) Quartz

19. The element that does NOT slow catenation is: **(2019)**

(a) Ge
(b) Si
(c) Sn
(d) Pb

20. The element that shows greater ability to form $p\pi - p\pi$ multiple bonds, is: **(2019)**

(a) Sn
(b) C
(c) Ge
(d) Si

21. The chloride that cannot get hydrolysed is: **(2019)**

(a) $PbCl_4$
(b) CCl_4
(c) $SnCl_4$
(d) $SiCl_4$

22. Correct statement among 'A' to 'D' regarding silicones are:

(A) They are polymers with hydrophobic character.

(B) They are biocompatible.

(C) In general, they have high thermal stability and low dielectric strength.

(D) Usually, they are resistant to oxidation and used as greases. **(2019)**

(a) (A), (B), (C) and (D)
(b) (A), (B) and (C) only
(c) (A) and (B) only
(d) (A), (B) and (D) only

23. The reaction of $H_3N_3BiCl_3$(A) with $LiBH_4$ in tetrahydrofuran gives inorganic benzene (B). Further, the reaction of (A) with (C) leads to $H_3N_3B_3(Me)_3$. Compounds (B) and (C) respectively, are: **(2020)**

(a) Borazine and MeBr
(b) Diborane and MeMgBr
(c) Boron nitride and MeBr
(d) Borazine and MeMgBr

24. The correct statement about B_2H_6 is **(2021-02-25 Shift-1)**

(a) All B – H – B angles are of 120
(b) Its fragment, BH_3, behaves as a Lewis base
(c) The two B – H – B bonds are not of same length
(d) Terminal B – H bonds have less p-character when compared to bridging bonds

25. Which one of the following gases is reported to retard photosynthesis? **(2021-07-20 Shift-2)**

(a) CO
(b) CFCs
(c) CO_2
(d) NO_2

26. Given below are the statements about diborane-

(A) Diborane is prepared by the oxidation of $NaBH_4$ with I_2

(B) Each boron atom is in sp^2 hybridized state

(C) Diborane has one bridged 3 centre-2-electron bond

(D) Diborane is a planar molecule **(2021-07-22 Shift-2)**

The option with correct statement(s) is

(a) (C) and (D) only
(b) (A) only
(c) (C) only
(d) (A) and (B) only

27. Which one of the following compounds of Group-14 elements is not known? **(2021-07-25 Shift-1)**

(a) $\left[GeCl_6\right]^{2-}$
(b) $\left[Sn(OH)_6\right]^{2-}$
(c) $\left[SiCl_6\right]^{2-}$
(d) $\left[SiF_6\right]^{2-}$

28. The INCORRECT statement regarding the structure of C_{60} is : **(2021-03-16 Shift-2)**

(a) The six-membered rings are fused to both six and five-membered rings.
(b) The five-membered rings are fused only to six-membered rings.
(c) It contains 12 six-membered rings and 24 five-membered rings.
(d) Each carbon atom forms three sigma bonds

Assertion Reason

29. **Assertion (A) :** Among the carbon allotropes, diamond is an insulator, whereas graphite is a good conductor of electricity.

Reason (R) : Hybridization of carbon in diamond and graphite are sp^3 and sp^2, respectively. (2016)

(a) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion

(b) Both assertion and reason are correct, and the reason is the correct explanation for the assertion

(c) Both assertion and reason arc incorrect

(d) Assertion is incorrect statement, but the reason is correct.

Match the Following

Each question has two columns. Four options are given representing matching of elements from Column-I and Column-II. Only one of these four options corresponds to a correct matching. For the question, choose the option corresponding to the correct matching.

30. Match the items in Column I with its main use listed in Column II: (2016)

Column - I	**Column - II**
(A) Silica gel	(p) Transistor
(B) Silicon	(q) Ion-exchanger
(C) Silicone	(r) Drying agent
(D) Silicate	(s) Sealant

(a) (A)-(r), (B)-(p), (C)-(s), (D)-(q)

(b) (A)-(s), (B)-(p), (C)-(q), (D)-(r)

(c) (A)-(q), (B)-(p), (C)-(s), (D)-(r)

(d) (A)-(q), (B)-(s), (C)-(p), (D)-(r)

EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

Objective Questions I [Only one correct option]

1. Alumina is:

(a) acidic (b) basic

(c) neutral (d) amphoteric

2. Which of the following compounds is formed in borax bead test?

(a) Metaborate (b) tetraborate

(c) Double oxide (d) Orthoborate

3. Borax is used as a cleansing agent because on dissolving in water, it gives:

(a) alkaline solution (b) acidic solution

(c) bleaching solution (d) neutral solution

4. Aqueous solution of borax acts as a buffer because:

(a) it contains weak acid and its salt with strong base

(b) it contains tribasic acid and strong base

(c) it contains number of neutral water molecules

(d) none of the above

5. Orthoboric acid behaves as a weak monobasic acid giving H_3O^+ and

(a) $[B(OH)_4]^+$ (b) $H_2BO_2^+$

(c) $[B(OH)_4]^-$ (d) $H_2BO_2^-$

6. Boron does not form B^{3+} cation easily. It is due to:

(a) energy required to form B^{3+} ion is very high which will not be compensated by lattice energies or hydration energies of such ion

(b) boron is non-metal

(c) boron is semi-metal

(d) none of the above

7. A gas other than HCl is obtained in :

(a) $BCl_3 + H_2 \xrightarrow[\text{discharge}]{\text{Silent electric}}$

(b) $LiAlH_4 + BF_3 \rightarrow$

(c) Both

(d) None of these

8. Hydride of boron occurs as B_2H_6 but B_2Cl_6 does not exist. This is because :

(a) $p\pi$-$d\pi$ back bonding is possible in B_2H_6 but not in B_2Cl_6

(b) boron and hydrogen have almost equal values of electronegativity

(c) boron and chlorine have almost equal atomic sizes

(d) small hydrogen atoms can easily fit in between boron atoms but large chlorine atoms do not

9. $Na_2B_4O_7.10H_2O$ is correctly represented as:

(a) $2NaBO_2.Na_2B_2O_3.10H_2O$

(b) $Na_2[B_4O_5(OH)_4].8H_2O$

(c) $Na_2[B_4(H_2O)_4O_7].6H_2O$

(d) all of these

10. The structure of diborane (B_2H_6) contains :

(a) four 2C-2e bonds and two 3C-2e bonds

(b) two 2C-2e bonds and four 3C-2e bonds

(c) two 2C-2e bonds and two 3C-3e bonds

(d) four 2C-2e bonds and four 3C-2e bonds

11. Al_2O_3 can be converted to anhydrous $AlCl_3$ by heating:

(a) a mixture of Al_2O_3 and carbon in dry Cl_2 gas

(b) Al_2O_3 with Cl_2 gas

(c) Al_2O_3 with HCl gas

(d) Al_2O_3 with NaCl in solid state

12. $H_3BO_3 \xrightarrow{100^\circ C} X \xrightarrow{160^\circ C} Y \xrightarrow{\text{Red hot}} B_2O_3$;

X and Y respectively are:

(a) X = Metaboric acid ; Y = Tetraboric acid

(b) X = Borax; Y = Metaboric acid

(c) X = Tetraboric acid ; Y = Metaboric acid

(d) X = Tetraboric acid ; Y = Borax

13. In which of the following, a salt of the type KMO_2 is obtained?

(a) $B_2H_6 + KOH(aq.) \rightarrow$

(b) $Al + KOH(aq.) \rightarrow$

(c) Both

(d) None of these

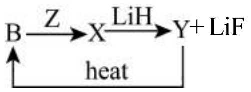
14. Amorphous boron is extracted from borax by following steps:

$$\text{Borax} \xrightarrow{(A)} H_3BO_3 \xrightarrow{\text{Heat}} B_2O_3 \xrightarrow{(B)} \text{Boron.}$$

(A) and (B) are:

(a) H_2SO_4, Al (b) HCl, carbon

(c) H_2SO_4, Mg (d) HCl, Fe

15. 

Which of the statement is true for the above sequence of reactions?

(a) Z is hydrogen

(b) X is B_2H_6

(c) Z and Y are F_2 and B_2H_6 respectively

(d) Z is potassium hydroxide

16. When an inorganic compound (X) having 3C—2e as well as 2C-2e bonds reacts with ammonia gas at a certain temperature, gives a compound (Y), isostructural with benzene. Compound (X) with ammonia at a high temperature produces a substance (Z). Which of the following is not correct?

(a) (X) is B_2H_6

(b) (Z) is known as inorganic graphite

(c) (Y) is $B_3N_3H_6$

(d) (Z) is soft like graphite

17. Which of the following is correct?

(a) The members of B_nH_{n+6} are less stable than B_nH_{n+4} series

(b) Diborane is coloured and unstable at room tempera ture

(c) The reaction of diborane with oxygen is endothermic

(d) All of the above

18. Boric acid is used in carrom boards for smooth gliding of pawns because:

(a) H_3BO_3 molecules are loosely chemically bonded and hence soft

(b) its low density makes it fluffy

(c) it is chemically inert with the plywood

(d) H-bonding in H_3BO_3 gives it a layered structure

Objective Questions II

[One or more than one correct option]

19. Orthoboric acid (H_3BO_3) and metaboric acid (HBO_2) differ in respect of:

(a) basicity (b) structure

(c) melting point (d) oxidation

20. Which of the following statements are true for H_3BO_3?

(a) It is mainly monobasic acid and a Lewis acid

(b) It does not act as a proton donor but acts as an acid by accepting hydroxyl ions

(c) It has a layer structure in which BO_3^{-3} units are joined by hydrogen bonds

(d) It is obtained by treating borax with conc. H_2SO_4

21. Select the correct statements about diborane

(a) B_2H_6 has three centred bond

(b) Each boron atom lies in sp^3 hybrid state

(c) H_b......B........H_b bond angle is 122°

(d) All hydrogens in B_2H_6 lie in the same plane

22. In Al_2Cl_6 which statement(s) is (are) incorrect?

(a) Four Al—Cl bonds are of the same length and two of different length

(b) Six Al—Cl bonds are of same length

(c) The angle Cl—Al—Cl is 118° and 79°

(d) The angle Al—Cl—Al is 101°

23. In the reaction

$$2X + B_2H_6 \rightarrow [BH_2X_2]^+[BH_4]^-$$

the amine(s) X is (are) :

(a) NH_3 (b) CH_3NH_2

(c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

Numerical Value Type Questions

24. Find the value of x in the termolite abestos:

$Ca_2Mg_x(Si_4O_{11})_2(OH)_2$

25. When B_2H_6 is allowed to react with following lewis bases, then how many given lewis bases form adduct through symmetrical cleavage of B_2H_6?

NH_3, $MeNH_2$, Pyridine, CO, T.H.F, PH_3, PF_3, Me_3N, Me_2NH

26. Consider the structure of Al_2Me_6 compound and find the vale of $\frac{x-y}{z}$.

Where x = Maximum number of atoms that can lie in plane having terminal (Al-Me) bonds.

y = Total number of 3c-2e⁻ bonds.

z = Total number of atoms that are sp^3 hybridized.

27. Consider $Al_2(OH)_6$ compound and calculate the value of $(X + Y) \div Z$

Where X = Total number of (2c—2e⁻) bond.

Y = Total number of (3c—2e⁻) bond.

Z = Total number of (3c—4e⁻) bond.

Assertion Reason

(A) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

(B) If both Assertion and Reason are true but Reason is not the correct explanation of Assertion.

(C) If Assertion is true but Reason is false.

(D) If Assertion is false but Reason is true.

28. **Assertion (A) :** Borax bead test is not suitable for Al (III)

Reason (R) : Al_2O_3 is insoluble in water.

(a) A (b) B

(c) C (d) D

29. **Assertion (A) :** In water, orthoboric acid behaves as a weak monobasic acid.

Reason (R) : In water, orthoboric acid acts as a proton donor.

(a) A (b) B

(c) C (d) D

30. **Assertion (A) :** Boron always forms covalent bond.

Reason (R) : The small size of B^{3+} favours formation of covalent bond.

(a) A (b) B

(c) C (d) D

31. **Assertion (A) :** BF_3 is a weaker Lewis acid than BCl_3.

Reason (R) : BF_3 molecule is stabilized to a greater extent than BCl_3 by B—F $P\pi$-$P\pi$ back bonding

(a) A (b) B

(c) C (d) D

32. **Assertion (A) :** AlF_3 is soluble in KF but addition of BF_3 brings its precipitation.

Reason (R) : BF_3 is more acidic than AlF_3.

(a) A (b) B

(c) C (d) D

Paragraph Type Questions

Use the following passage, to solve Q. 33 to Q. 38

Passage

Aluminium is stable in air and water in spite of the fact that it is reactive metal. The reason is that a thin film of its oxide is formed on its surface which it passive for further attack. The layer is so useful that in industry, it is purposely deposited by an electrolytic process called anodising

Reaction of aluminium with oxygen is highly exothermic and is called thermite reaction.

$$2Al(s) + \frac{3}{2}O_2(g) \rightarrow Al_2O_3(s); \quad \Delta H = -1670\,kJ$$

Thermite reaction finds applications in the metallurgical extraction of many metals from their oxides and for welding of metals. The drawback is that to start the reaction, high temperature is required for which an ignition mixture is used.

33. Anodising can be done by electrolysing dilute H_2SO_4 with aluminium as anode. This results in :

(a) the formation of $Al_2(SO_4)_3$ on the surface of aluminium anode

(b) the formation of oxide film (Al_2O_3) on the surface of aluminium anode

(c) the formation of polymeric aluminium hydride film on the surface of aluminium anode

(d) none of the above

34. The reaction which is not involved in thermite process:

(a) $3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3$

(b) $Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$

(c) $2Fe + Al_2O_3 \longrightarrow Fe_2O_3 + 2Al$

(d) $B_2O_3 + 2Al \longrightarrow 2B + Al_2O_3$

35. Thermite a mixture used for welding is:

(a) Fe and Al (b) BaO and Mg powder

(c) Cu and Al (d) Fe_2O_3 and Al powder

36. Anodised aluminium is :

(a) Al obtained at anode

(b) Al prepared electrolytically

(c) alloy of Al containing 95% Al

(d) Al electrolytically coated with aluminium oxide

37. Which one of the following metals cannot be extracted by using Al as a reducing agent?

(a) Na from Na_2O (b) Cr from Cr_2O_3

(c) W from WO_3 (d) Mn from Mn_3O_4

38. Aluminium becomes passive in:

(a) conc. HNO_3 (b) H_2CrO_4

(c) $HClO_4$ (d) all of these

Use the following passage, to solve Q. 39 to Q. 41

Passage

(i) $P + C(\text{carbon}) + Cl_2 \rightarrow Q + CO\uparrow$

(ii) $Q + H_2O \rightarrow R + HCl$

(iii) $BN + H_2O \rightarrow R + NH_3\uparrow$

(iv) $Q + LiAlH_4 \rightarrow S + LiCl + AlCl_3$

(v) $S + NaH \rightarrow T$

(P, Q, R, S and T do not represent their chemical symbols)

39. Compound Q has:

(I) Zero dipole moment

(II) a planar trigonal structure

(III) an electron deficient compound

(IV) a Lewis base

Choose the correct code:

(a) I, IV
(b) I, II, IV
(c) I, II, III
(d) I, II, III, IV

40. Compound T is used as a/an :

(a) oxidising agent
(b) complexing agent
(c) bleaching agent
(d) reducing agent

41. Compound S is:

(I) an odd-e$^-$ compound

(II) (2c-3e$^-$) compound

(III) electron deficient compound

(IV) a sp^2 hybridized compound

Choose the correct code:

(a) III
(b) I, III
(c) II, III
(d) I, II, IV

Use the following passage, to solve Q. 42 to Q. 46

Passage

$$Ca_2B_6O_{11} + Na_2CO_3 \xrightarrow{\text{Fused}} (A) + (B) + CaCO_3$$

$$\underset{\text{Solution}}{(A)} + CO_2 \longrightarrow (B) + Na_2CO_3$$

$$(B) + \text{Conc. } HCl \longrightarrow NaCl + \text{Acid} \xrightarrow{H_2O} \text{Acid }(C)$$

$$(C) \xrightarrow[\text{heated}]{\text{Strongly}} (D)$$

$$(D) + CuSO_4 \xrightarrow[\text{inflame}]{\text{Heated}} \text{Blue coloured }(E)\text{ compound}$$

42. Compound (A) is:

(a) $NaBO_2$
(b) $Na_2B_4O_7$
(c) Na_3BO_3
(d) NaOH

43. Compound (B) is:

(a) $NaBO_2$
(b) $Na_2B_4O_7$
(c) Na_3BO_3
(d) NaOH

44. Compound (C) is:

(a) $H_2B_4O_7$
(b) HBO_2
(c) H_3BO_3
(d) HB_3O_5

45. Compound (D) is:

(a) H_3BO_3
(b) B_2O_3
(c) B
(d) none of these

46. Compound (E) is:

(a) Cu_2O
(b) CuS
(c) $CuSO_3$
(d) $Cu(BO_2)_2$

Use the following passage, to solve Q. 47 to Q. 50

Passage

(i) $\text{Boron} + O_2 \xrightarrow{700^\circ C} (X)$

(ii) $(X) + C(\text{carbon}) + Cl_2 \rightarrow (Y) + CO$

(iii) $(Y) + LiAlH_4 \rightarrow (Z) + LiCl + AlCl_3$

(iv) $(Z) + NH_3 \rightarrow (A) \xrightarrow{\text{Heat}} (B)$

(v) $(Z) + NaH \rightarrow (D)$

47. Compound (Z) is:

(a) an ionic compound

(b) an electron deficient compound

(c) $2C - 3e$ compound

(d) having ethane like structure

48. Compounds (X) and (Y) are:

(a) $(X) = BO_2, (Y) = BCl_2$
(b) $(X) = BO_3, (Y) = BCl_4$
(c) $(X) = B_2O_3, (Y) = BCl_3$
(d) $(X) = BO_3, (Y) = B_4C$

49. Compound (B) is:

(a) Borazole
(b) Organic benzene
(c) Borazon
(d) Boron nitride

50. Compound (D) is used as a/an :

(a) Oxidising agent
(b) Complexing agent
(c) Buffer agent
(d) Reducing agent

EXERCISE - 4 : PREVIOUS YEAR JEE ADVANCED QUESTIONS

Objective Questions I [Only one correct option]

1. Identify the correct order of acidic strength of CO_2, CuO, CaO, H_2O. **(2002)**

(a) $CaO < CuO < H_2O < CO_2$

(b) $H_2O < CuO < CaO < CO_2$

(c) $CaO < H_2O < CuO < CO_2$

(d) $H_2O < CO_2 < CaO < CuO$

2. H_3BO_3 is **(2003)**

(a) monobasic acid and weak Lewis acid

(b) monobasic and weak Bronsted acid

(c) monobasic and strong Lewis acid

(d) tribasic and weak Bronsted acid

3. $(Me)_2\,SiCl_2$ on hydrolysis will produce **(2003)**

(a) $(Me)_2\,Si(OH)_2$

(b) $(Me)_2\,Si=O$

(c) $[—O—(Me)_2\,Si—O—]_n$

(d) $Me_2SiCl(OH)$

4. Name the structure of silicates in which three oxygen atoms of $[SiO_4]^{4-}$ are shared is **(2005)**

(a) pyrosilicate (b) sheet silicate

(c) linear chain silicate (d) three dimensional silicate

5. $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 + Na[B(OH)_4] + H_2O$

How can this reaction is made to proceed in forward direction ? **(2006)**

(a) Addition of cis 1, 2 diol

(b) Addition of borax

(c) Addition of trans 1, 2 diol

(d) Addition of Na_2HPO_4

6. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are **(2015)**

(a) CH_3SiCl_3 and $Si(CH_3)_4$

(b) $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$

(c) $(CH_3)_2SiCl_2$ and CH_3SiCl_3

(d) $SiCl_4$ and $(CH_3)_3SiCl$

7. The increasing order of atomic radii of the following Group 13 elements is **(2016)**

(a) Al <Ga<In<Tl (b) Ga<Al<In<Tl

(c) Al<In< Ga<Tl (d) Al <Ga<Tl<In

Objective Questions II [One or more than one correct option]

8. In the reaction,

$$2X + B_2H_6 \rightarrow [BH_2(X)_2]^+\,[BH_4]^-$$

the amine(s) X is (are) **(2009)**

(a) NH_3 (b) CH_3NH_2

(c) $(CH_3)_2\,NH$ (d) $(CH_3)_3\,N$

9. With respect to graphite and diamond, which of the statement(s) given below is (are) correct ? **(2012)**

(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.

10. The crystalline form of borax has **(2016)**

(a) tetranuclear $[B_4O_5\,(OH)_4]^{2-}$ unit

(b) all boron atoms in the same plane

(c) equal number of sp^2 and sp^3 hybridized boron atoms

(d) one terminal hydroxide per boron atom

11. The correct statement(s) for orthoboric acid is/are **(2017)**

(a) It behaves as a weak acid in water due to self ionization.

(b) Acidity of its aqueous solution increases upon addition of ethylene glycol.

(c) It has a three dimensional structure due to hydrogen bonding.

(d) It is a weak electrolyte in water

12. Choose the correct statement(s) among the following **(2020)**

(a) $SnCl_2.2H_2O$ is a reducing agent.

(b) SnO_2 reacts with KOH to form $K_2[Sn(OH)_6]$.

(c) A solution of $PbCl_2$ in limited HCl contains Pb^{2+} and Cl^- ions

(d) The reaction of Pb_3O_4 with hot nitric acid to give PbO_2 is a redox reaction

Numerical Value Type Questions

13. The coordination number of Al in the crystalline state of $AlCl_3$ is **(2009)**

14. The value of n in the molecular formula $Be_nAl_2Si_6O_{18}$ is **(2010)**

15. Three moles of B_2H_6 are completely reacted with methanol. The number of moles of boron containing product formed is **(2015)**

Assertion Reason

(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.

16. **Statement-1 :** $Al(OH)_3$ is amphoteric in nature

Statement-2 : Al–O and O–H bonds can be broken with equal ease in $Al(OH)_3$. **(1998)**

(a) A (b) B

(c) C (d) D

17. **Statement-1:** Between $SiCl_4$ and CCl_4 only $SiCl_4$ reacts with water.

Statement-2: $SiCl_4$ is ionic and CCl_4 is covalent. **(2001)**

(a) A (b) B

(c) C (d) D

18. **Statement-1 :** In water, orthoboric acid behaves as a weak monobasic acid because

Statement-2 : In water, orthoboric acid acts as a proton donor. **(2007)**

(a) A (b) B

(c) C (d) D

19. **Statement-1 :** Boron always forms covalent bond. because

Statement-2 : The small size of B^{3+} favours formation of covalent bond. **(2007)**

(a) A (b) B

(c) C (d) D

20. **Statement-1 :** Pb^{4+} compounds are stronger oxidising agents than Sn^{2+} 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'. **(2008)**

(a) A (b) B

(c) C (d) D

Subjective Type Questions

21. $PbS \xrightarrow[\text{air}]{\text{heat in}} A + PbS \xrightarrow{B} Pb + SO_2$;

Identify A and B. **(1991)**

22. Compound X on reduction with $LiAlH_4$ gives a hydride Y containing 21.72% hydrogen alongwith 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 the structure of Y. **(2001)**

23. Starting from $SiCl_4$, prepare the following in steps not exceeding the number given in parenthesis (give reactions only)

(i) Silicon (1)

(ii) Linear silicon containing methyl group only (4)

(iii) Na_2SiO_3 (3) **(2001)**

24. (i) How is boron obtained from borax ? Give chemical equations with reaction conditions.

(ii) Write the structure of B_2H_6 and its reaction with HCl.

(2002)

25. AlF_3 is insoluble in anhydrous HF but when little KF is added to the compound it becomes soluble. On addition of BF_3, AlF_3 is precipitated. Write the balanced chemical equations. **(2004)**

ANSWER KEY

CHAPTER -14| p-BLOCK GROUP (13 AND 14)

EXERCISE - 1 :
BASIC OBJECTIVE QUESTIONS

1.	(b)	**2.**	(d)	**3.**	(d)	**4.**	(a)	**5.**	(d)
6.	(d)	**7.**	(d)	**8.**	(a)	**9.**	(c)	**10.**	(a)
11.	(d)	**12.**	(b)	**13.**	(b)	**14.**	(c)	**15.**	(a)
16.	(d)	**17.**	(d)	**18.**	(a)	**19.**	(d)	**20.**	(a)
21.	(a)	**22.**	(d)	**23.**	(b)	**24.**	(b)	**25.**	(d)
26.	(b)	**27.**	(b)	**28.**	(c)	**29.**	(a)	**30.**	(d)
31.	(d)	**32.**	(a)	**33.**	(c)	**34.**	(c)	**35.**	(b)
36.	(d)	**37.**	(b)	**38.**	(a)	**39.**	(a)	**40.**	(c)
41.	(b)	**42.**	(b)	**43.**	(b)	**44.**	(d)	**45.**	(d)
46.	(d)	**47.**	(b)	**48.**	(a)	**49.**	(b)	**50.**	(b)
51.	(a)	**52.**	(b)	**53.**	(b)	**54.**	(d)	**55.**	(d)
56.	(d)	**57.**	(c)	**58.**	(b)	**59.**	(c)	**60.**	(d)
61.	(d)	**62.**	(c)	**63.**	(b)	**64.**	(d)	**65.**	(a)
66.	(d)	**67.**	(a)	**68.**	(b)	**69.**	(d)	**70.**	(a)
71.	(a)	**72.**	(c)	**73.**	(c)	**74.**	(c)	**75.**	(c)
76.	(b)	**77.**	(c)	**78.**	(d)	**79.**	(d)	**80.**	(c)
81.	(b)	**82.**	(c)	**83.**	(d)	**84.**	(b)	**85.**	(d)
86.	(d)	**87.**	(d)	**88.**	(c)	**89.**	(a)	**90.**	(a)
91.	(c)	**92.**	(a)	**93.**	(a)	**94.**	(c)	**95.**	(a)
96.	(b)	**97.**	(d)	**98.**	(a)	**99.**	(a)	**100.**	(b)

EXERCISE - 2 :
PREVIOUS YEAR JEE MAINS QUESTIONS

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

CHAPTER -14 | p-BLOCK GROUP (13 AND 14)

EXERCISE - 3 :
ADVANCED OBJECTIVE QUESTIONS

1. (d) **2.** (a) **3.** (a) **4.** (a) **5.** (c)
6. (a) **7.** (c) **8.** (d) **9.** (b) **10.** (a)
11. (a) **12.** (a) **13.** (c) **14.** (c) **15.** (c)
16. (d) **17.** (a) **18.** (d)
19. (a,b,c) **20.** (a,b,c,d)
21. (a,b,c) **22.** (a,c,d)
23. (a,b,c) **24.** (5.00)
25. (6.00) **26.** (1.00)
27. (5.00) **28.** (b) **29.** (c) **30.** (a) **31.** (a)
32. (a) **33.** (b) **34.** (c) **35.** (d) **36.** (d)
37. (a) **38.** (d) **39.** (c) **40.** (d) **41.** (c)
42. (a) **43.** (b) **44.** (c) **45.** (b) **46.** (d)
47. (b) **48.** (c) **49.** (a) **50.** (d)

EXERCISE - 4 :
PREVIOUS YEAR JEE ADVANCED QUESTIONS

1. (a) **2.** (a) **3.** (c) **4.** (b) **5.** (a)
6. (b) **7.** (b)
8. (a,b,c) **9.** (b,d)
10. (a,c,d) **11.** (b,d)
12. (a,b,c) **13.** (6.00)
14. (3.00) **15.** (6.00)
16. (a) **17.** (c) **18.** (c) **19.** (a) **20.** (c)