DAY THIRTEEN

p-Block Elements
(Group 13 and 14)

Learning & Revision for the Day

- Variation in Properties of *p*-Block Elements
- Group-13 Elements (Boron Family)
- Some Important Compounds of Group-13 Elements
- Group-14 Elements (Carbon Family)
- Crystalline Forms of Carbon
- Some Important Compounds of Group-14 Elements

In *p*-block elements, the last electron enters in the outermost *p*-orbital. There are six groups of *p*-block elements in the periodic table, numbering from 13 to 18.

Their valence shell electronic configuration is ns^2np^{1-6} (except for He). Effective nuclear charge from first to third period decreases and from fourth period and onwards increases, due to poor shielding effect. Therefore, ns^2 electrons bound closely to the nucleus.

As the result, another oxidation state with 2 units less than the group oxidation state become professively (on moving down the group) more stable in each group. This is also known as **inert pair effect.**

Variation in Properties of *p*-Block Elements

(i) **Metallic and Non-metallic Character** Non-metals and metalloids exist only in the *p*-block of the periodic table. On moving down the group metallic character increases and non-metallic character decreases.

(ii) **Multiple Bonding** ($p\pi - p\pi$) Second period elements have a tendency to form $p\pi - p\pi$ multiple bond (double or triple bond) due to their smaller atomic size and high bond energy, e.g. $C \equiv C, C = C, N \equiv N, O = O, O = C = O$ etc.

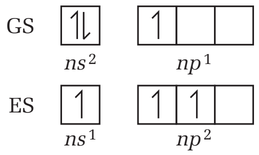
(iii) **Covalency** Second period elements do not expand their covalency due to non-availability of *d*-orbitals. Therefore, halides of such elements do not hydrolysed easily, e.g. BCl_3, CCl_4 (halides) etc. While elements of third period and onwards only form single bond and can expand their covalency due to presence of vacant *d*-orbitals, e.g. P_4, S_8, $[AlF_6]^{3-}$ ion etc.

(iv) **Nature of Oxides** Non-metal oxides of *p*- block are acidic or neutral and metal oxides are basic in nature. Generally metalloid oxides are amphoteric. In a period, from left to right acidic character increases and down a group, basic character increases. Generally, oxides with higher oxidation state are more acidic in nature.

Group 13 Elements (Boron Family)

Boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl) are the members of group 13. Boron is non-metal while rest of the members are metals.

Electronic configuration of group-13 elements is ns^2, np^1.



Occurrence of Group-13 Elements

- Boron (B) is a typical non-metal, mainly occurs as orthobasic acid (H_3BO_3), borax ($Na_2B_4O_7 \cdot 10H_2O$) and kernite ($Na_2B_4O_7 \cdot 4H_2O$).
- Aluminium (Al) is the most abundant metal and is the third most abundant element in earth crust. It is mostly present in the form of bauxite ($Al_2O_3 \cdot 2H_2O$) and cryolite (Na_3AlF_6).
- Gallium (Ga), indium, (In) and thallium (Tl) are present in traces.

Variation in Properties of Group-13 Elements

(i) **Oxidation state** of group-13 elements are +3, + 1. Stability of +3 oxidation state decreases down the group and that of +1 oxidation state increases down the group due to inert pair effect. Fourth period and onwards effective nuclear charge increases due to poor shielding effect, therefore the radius of gallium (135 pm) is less than that of aluminium (143 pm) and down the group, inert pair effect increases.

(ii) **Atomic radius** of group-13 elements increases down the group (except of Ga, which is less than of Al.)

(iii) **Ionisation enthalpy** of group-13 elements decreases down the group (except of Ga, which is slightly more than of Al), due to increase in size.

(iv) **Electronegativity** of elements of group-13 also decreases as we move down the group.

(v) **Hydrides** of boron and aluminium are of great importance. Boron hydrides exist in dimeric or polymeric form. The simplest boron hydride is diborane, B_2H_6. Aluminium forms only one colourless, solid polymeric hydride $(AlH_3)_n$, known as alane. B, Al and Ga form complex anionic hydrides, e.g. $NaBH_4$, $LiAlH_4$ and $LiGaH_4$. All are strong reducing agents.

$$LiAlH_4 > NaBH_4 \text{ (reducing power)}$$

(vi) **Halides** of group-13 have incomplete octet, therefore, have a high tendency to accept electrons and behave as Lewis acid. $BI_3 > BBr_3 > BCl_3 > BF_3$ (acidic character)

Due to back bonding and resonance, the B–F bond of BF_3 gets a bond order of 1.33.

(vii) **Oxides** of group-13 show a regular change down the group, their basic character increases. e.g. B_2O_3 is weakly acidic, Al_2O_3 is amphoteric and other oxides are basic in nature.

Anomalous Behaviour of Boron

Anomalous properties of first element of the group member, i.e. boron, are due to its extremely small size, high electron density, high electronegativity and non-availability of *d*-electrons. Boron exhibits following anomalous properties :

- Boron is a typical non-metal, while other members of the group are metals.
- Its melting and boiling points are higher than the other members of the group.
- It forms only covalent compounds while other members can form covalent as well as ionic compounds. The maximum covalency of B is four while that of Al is six.
- Only boron exhibits the property of allotropy and exists in crystalline as well as amorphous forms.
- Its oxides and hydroxides have acidic nature while that of other members have amphoteric and basic nature.
- Its hydrides are quite stable while that of other members are not so stable.
- Like non-metals, it combines with metals to form metal borides (e.g. Mg_3B_2) while other members form alloy with metals.
- Boron does not decompose steam while other members do so.
- Amorphous boron of low purity is called **Moissan boron**. It is black in colour.

Physical and Chemical Properties of Boron

- Boron exists in two allotropic forms, i.e. amorphous and crystalline. Crystalline boron is chemically inert while amorphous boron is chemically active. It is a bad conductor of heat and electricity.
- Amorphous boron on heating with air at 700°C forms a mixture of oxide and nitride.

$$4B + 3O_2 \longrightarrow 2B_2O_3\ ,$$
$$2B + N_2 \longrightarrow 2BN$$

- Boron is attacked by oxidising acids like conc. H_2SO_4 and HNO_3.

$$B + 3HNO_3 \xrightarrow{H_2SO_4} H_3BO_3 + 3NO_2$$

- It dissolves in fused alkalies and liberates hydrogen. It reacts with strong electropositive metals at high temperature and forms borides such as Mg_3B_2.
- It is a powerful reducing agent.

$$3CO_2 + 4B \longrightarrow 2B_2O_3 + 3C$$
$$3SiO_2 + 4B \longrightarrow 2B_2O_3 + 3Si$$

- Boron can be used as control rods in atomic reactors and as a deoxidiser.

Some Important Compounds of Group-13 Elements

Some important compounds of group–13 elements or boron family are given below :

1. Borax ($Na_2B_4O_7 \cdot 10H_2O$)

[Sodium Tetra Borate Decahydrate]

Borax ($Na_2B_4O_7 \cdot 10H_2O$) is one of the important compound of boron.

- It is the most important compound of boron. It is white crystalline solid.
- Borax dissolves in water to give an alkaline solution.

$$Na_2B_4O_7 + 7H_2O \longrightarrow \underbrace{2NaOH + \underset{\substack{\text{Orthoboric acid}\\\text{(weak acid)}}}{4H_3BO_3}}_{\text{Glassy mass}}$$

- On heating, it loses their water of crystallisation and swells up to form a mass of a bead.

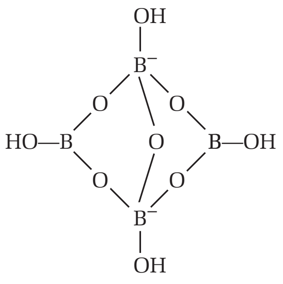
$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow[-10H_2O]{\Delta} \underset{\substack{\text{Swell up}\\\text{(Sodium metaborate)}}}{Na_2B_4O_7}$$

$$\xrightarrow{\Delta} \underbrace{\underset{\text{Sod. } meta \text{ borate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}}_{\text{Glassy mass}}$$

- With acids, it gives orthoboric acid, a weak acid.

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4B(OH)_3 \text{ or } \underset{\text{Orthoboric acid}}{H_3BO_3}$$

- **Structure of borax** contains the tetrahedral units, i.e. $[B_4O_5(OH)_4]^{2-}$

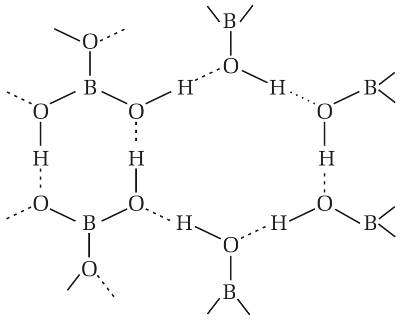


$[B_4O_5(OH)_4]^{2-}$

2. Boric Acid (H_3BO_3)

Boric Acid (H_3BO_3) is the next important compound of boron.

- Boric acid is soft white crystalline solid, soapy to touch and less soluble in cold water.
- Boric acid is a weak monobasic acid. It is not a protonic acid but acts as a **Lewis acid**.
- $H_3BO_3 \xrightarrow{\text{Heat}} \underset{\substack{\text{Metaboric}\\\text{acid}}}{HBO_2} \xrightarrow{\text{Heat}} \underset{\substack{\text{Boric}\\\text{anhydride}}}{B_2O_3}$
- **Structure of boric acid** shows that it has a layer structure in which planar BO_3 units are joined by H-bonds.



- Boric acid can be used as an antiseptic, eye wash, as food preservative, in glass industry and in pottery.

3. Hydrides of Boron, i.e. Diborane (B_2H_6)

- Diborane is a colourless, highly toxic gas with a boiling point of 180 K. Diborane catches fire spontaneously upon exposure to air.

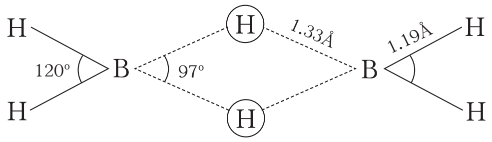
$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$$

With ammonia, diborane gives borazine.

$$3B_2H_6 + 6NH_3 \longrightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\text{Heat}} \underset{\text{Borazine}}{2B_3N_3H_6} + 12H_2$$

Borazine ($B_3N_3H_6$) is known as **"inorganic benzene"** in view of its ring structure with alternatdese BH and NH groups. However, at high temperature, inorganic graphite $(BN)_x$ is obtained instead of borazine.

- **Structure of diborane** is as follows



- Terminal hydrogens (H_a) are bonded by $2c-2e$ (two centred two electrons) bonding and bridge hydrogens (H_b) are bonded by $3c-2e$ (three centred held by two electrons) bonding. This type of bonding is also known as **banana bonding.**
- Due to banana bonding, B_2H_6 complete its electron deficiency and obtain ethane-like structure and hybridisation of B_2H_6 becomes sp^3.

$$2MH + B_2H_6 \longrightarrow 2M^+[BH_4]^- (M = \text{Li or Na})$$

It is used as a catalyst in polymerisation process, for welding torch, as reducing agent in organic reactions etc.

Aluminium

Preparation, properties and uses of the second member of the group, i.e. aluminium are as follows:

- Preparation of aluminium in India is mainly done by bauxite. Bauxite contains SiO_2, iron oxides and titanium oxide (TiO_2) as impurities. Leaching of bauxite ore is carried out with conc. NaOH solution.
- **Hall-Heroult Process** is used to obtained aluminium from Al_2O_3. Aluminium is obtained by the electrolysis of Al_2O_3 mixed with Na_3AlF_6 or CaF_2. Overall reaction is as follows $2Al_2O_3 \longrightarrow 2Al + 3O_2$

Physical and Chemical Properties of Aluminium

(i) It is bluish-white lustrous metal and loses its lustre due to the formation of protective oxide film Al_2O_3. It is light, malleable, ductile, good conductor of electricity and heat.

(ii) **With Alkalies** Al readily dissolves in alkalies evolving H_2 and forming the corresponding aluminates.

$$2Al + 2H_2O + 2NaOH \xrightarrow{\Delta} \underset{\text{Sodium meta aluminate}}{2NaAlO_2} + 3H_2$$

and also dissolve in hot conc. solution of Na_2CO_3 as

$$2Al + Na_2CO_3 + 3H_2O \xrightarrow{\Delta} 2NaAlO_2 + CO_2 + 3H_2$$

(iii) **With Acids** The metal dissolves in dil. HCl and dil. H_2SO_4 solutions evolving H_2. Conc. HNO_3 has no reaction, the metal rendered passive due to surface oxidation.

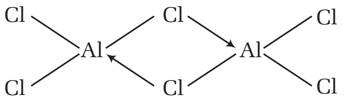
Uses of Aluminium

It is used for making house hold utensils, frames, bodies of aircraft automobiles etc. It is used in making paints, as a mordant in dyeing and calico printing. **Ammonal** (mixture of Al powder and ammonium nitrate) is used as explosive. Magnalium, duralumin and alnico are important alloys of aluminium.

Aluminium Chloride ($AlCl_3$)

Aluminium chloride is one of the most important compound of aluminium.

- Anhydrous aluminium chloride is a white deliquescent solid which fumes in air. Its vapour density corresponds to the formula Al_2Cl_6.
- It is covalent and soluble in organic solvents.



Structure of $AlCl_3$

- Due to the formation of HCl, anhydrous aluminium chloride produces fumes in moist air.

$$\underset{\text{Anhy.}}{Al_2Cl_6} + 6H_2O \longrightarrow 2Al(OH)_3 + 6HCl$$

$$Al_2Cl_6 + 12H_2O \longrightarrow \underset{\text{Hydrated aluminium chloride (ionic)}}{2AlCl_3 \cdot 6H_2O}$$

- With ammonia, it gives addition product.

$$\underset{\text{Anhy.}}{Al_2Cl_6} + 12NH_3 \longrightarrow \underset{\text{Addition product}}{2[AlCl_3 \cdot 6NH_3]}$$

- With NaOH, sodium meta aluminate is obtained.

$$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3 \downarrow + 3NaCl$$

$$Al(OH)_3 + NaOH \longrightarrow \underset{\text{Sodium meta aluminate}}{NaAlO_2} + 2H_2O$$

Uses of Aluminium Chloride

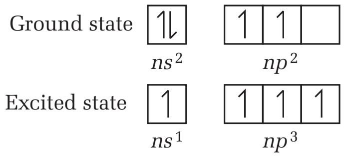
Anhyd. $AlCl_3$ is used as a reagent in Friedel-Crafts reaction, in manufacture of drugs, dyes, perfumes, in cracking of high boiling fractions of petroleum to form gasoline.

Group-14 Elements (Carbon Family)

Group-14 elements are also called **carbon family**. Carbon (C), silicon (Si), germanium (Ge), tin (Sn), and lead (Pb) are the members of group–14. Carbon is the seventeenth most abundant element by mass in the earth's crust. C is non-metal, Si, Ge are metalloids and Sn, Pb are metals.

Properties

Electronic configuration of group–14 elements is ns^2np^2.



Occurrence of Group-14 Elements

Occurrence of elements of group–14 can be summarised as follows:

- All the members of this family are well known. Silicon is the second and carbon is the seventeenth most abundant element (by mass) in the earth's crust. The percentage abundance of these elements in the earth's crust is shown below :

Element	C	Si	Ge	Sn	Pb
Abundance (mass%)	0.02	27.2	1.5×10^{-4}	2.1×10^{-4}	13×10^{-4}

- Carbon can exist in free as well as in combined state. In elemental state, it exists in the form of coal, diamond, graphite and fullerene and in combined form, it exists in the form of carbonates, hydrogen carbonates and carbon dioxide gas (which is only 0.03% in the air).

- However, C^{14} being radioactive (with half-life 5770 yr) exists only in trace amounts and is used for radiocarbon dating. Silicon generally exists in the form of silica and silicates. It is an important constituent of ceramics, glass and cement. Germanium (Ge), tin (Sn) and lead (Pb) are present in trace amounts. Sn mainly exists in the form of cassiterite, SnO_2 and Pb mainly exists as galena, PbS. Its other forms are anglesite ($PbSO_4$) and cerrussite ($PbCO_3$).

Variation in Properties of Group-14 Elements

- **Oxidation states** of group–14 mainly are +4 and +2. Carbon also exhibits negative oxidation states, i.e. –4. Down the group, stability of +4 oxidation state decreases and of +2 oxidation state increases due to inert pair effect.
- **Covalent radius** of group–14 elements increases down the group.
- **Ionisation enthalpy** of group–14 elements decreases down the group as size of elements increases.
- **Electronegativity** of group–14 element also decreases as we move down the group.
- **Oxides** CO_2, SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature.
  - (i) Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.
  - (ii) Monomeric form of CO_2 is stable due to non availability of *d*-orbitals. Carbon has tendency to form a multiple bond ($O{=}C{=}O$) but SiO_2 exists in three dimensional polymeric form and has high melting point and is solid at room temperature.
- **Reaction with Water** Carbon, silicon and germanium are not affected by water. Tin decomposes with steam to form dioxide and dihydrogen gas.

$$Sn + 2H_2O \xrightarrow{\text{Heat}} SnO_2 + 2H_2$$

Lead remains unaffected by water, probably because of a protective oxide film formation.

Group–14 elements can form MX_2 and MX_4 type halides (where M = F, Cl, Br, I). Except carbon all other members react directly with halogens under suitable conditions. Stability of dihalides (MX_2) increases down the group due to inert pair effect. Except CCl_4, all other tetrahalides are easily hydrolysed by water.

Anomalous Behaviour of Carbon

Anomalous behaviour of first element of group-14, i.e. carbon, is observed because The size of carbon is smallest among the group but it has high electronegativity and ionisation enthalpy. Moreover, *d*-orbitals are also not present in it. Due to these reasons, its properties are quite different from other members of the group.

Some such properties are :

- **Covalency** of carbon in general is four, Due to the absence of *d*-orbitals, it cannot expand its valence shell and thus, its maximum covalency is four. Other members, however, have vacant *d*-orbital and thus, can expand their covalency beyond four.
- Due to absence of d-orbitals, carbon can only form $p\pi$-$p\pi$ bonds with it self or with elements like O, N and S, etc.
- Tendency for catenation is maximum in carbon and it decreases as M-M (M = elements of group -14) bond - length increases.

Allotropy

- All the members of group 14 elements (except Pb) show allotropy.
- Carbon exhibits many allotropic forms both crystalline as well as amorphous. Diamond, graphite and fullerene are crystalline forms while coal, charcoal and lamp black are amorphous forms.

Crystalline forms of Carbon

1. Diamond

It is the purest, hardest form of carbon with high refractive index and density. In it each carbon atom (sp^3 hybridised) is tetrahedrally surrounded by four other carbon atoms. It does not conduct electricity as it has no free electrons. It is used in cutting, grinding and drilling instruments and in making jewellery.

2. Graphite

It has two dimensional structure. sp^2 hybridised carbon atom forms three covalent bonds with three other carbon atoms in the same plane and the 4th electron of each carbon remains free and is responsible for electrical conductivity of graphite. The planar hexagonal rings get fused together to form sheets of one atom thickness. These sheets are held together by weak van der Waals' forces. These layers can slide over each other and gives softness, greasiness and lubricating property to graphite. It is used in making electrodes, lead pencils and as dry lubricant.

3. Fullerenes

These are the only pure form of carbon. C_{60} molecule contains 12 five membered rings and 20 six membered rings. The five membered rings are connected to six membered rings while six membered rings are connected to both five and six membered rings. These are used in microscopic ball bearings, light weight batteries, in synthesis of new plastics and new drugs.

Some Important Compounds of Group-14 Elements

Some of the important compounds of group 14 elements or carbon family elements are given below:

1. Oxides of Carbon

Two important oxides of carbon are carbon monoxide and carbon dioxide CO_2. Carbon monoxide can be prepared by the following reactions:

$$C(s) + H_2O(g) \xrightarrow{473\text{ K-}1273\text{ K}} \underbrace{CO(g) + H_2(g)}_{\text{Water gas}}$$

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

Water gas and producer gas are very important industrial fuels.

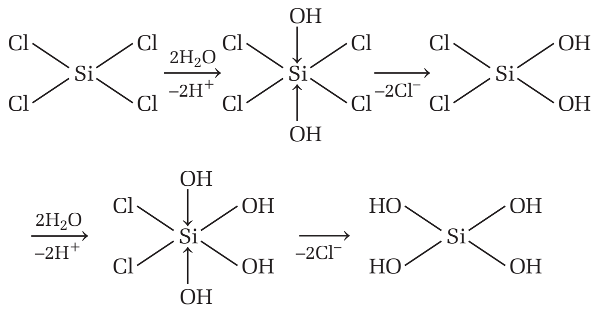
- Carbon dioxide can be prepared by complete combustion of carbon and carbon containing fuels in excess of air.
- **Carbon dioxide** can be obtained as a solid in the form of dry ice by allowing the liquified CO_2 to expand rapidly. Dry ice is used as a refrigerant for ice-cream and frozen food.

2. Silicon Tetrachloride ($SiCl_4$)

- It is tetrahedral and essentially covalent. It is readily hydrolysed by water. It fumes in moist air liberating hydrogen chloride.

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

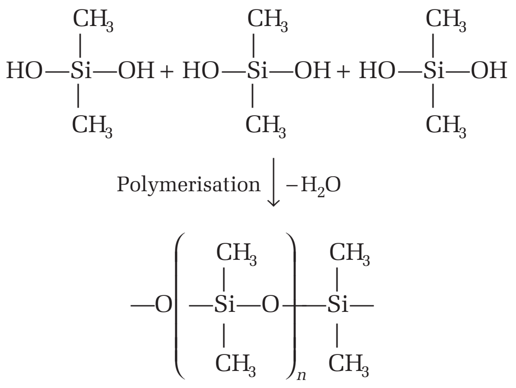
- The hydrolysis of $SiCl_4$ occurs due to coordination of OH with empty $3d$-orbitals in Si-atom of $SiCl_4$ molecule.



3. Silicones

- These are synthetic organosilicon compounds which has repeated unit of R_2SiO.
- These are prepared from alkyl halides.

$$2CH_3Cl + Si \xrightarrow[570\text{ K}]{\text{Cu powder}} (CH_3)_2SiCl_2 \xrightarrow[-2HCl]{+2H_2O} (CH_3)_2Si(OH)_2$$



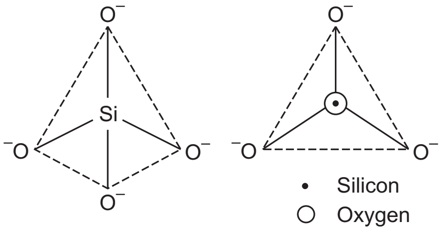
Silicone

Highly cross-linked silicone polymer is obtained by the hydrolysis of $RSiCl_3$.

- 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.

4. Silicates

- A large number of silicate minerals exist in nature. Some of the examples are feldspar, zeolites, mica and asbestos. The basic structural unit of silicates is SiO_4^{4-}.



- The SiO_4^{4-} unit is neutralised by positively charged metal ions, if all the four corners are shared with other tetrahedral units.
- Generally, the silicates have complex structures but they mainly differ in
  - (a) Number of oxygen atoms shared between SiO_4^{4-} tetrahedra.
  - (b) Geometric arrangement of tetrahedra.
  - (c) The number, type and arrangement of metallic cations.

Following are the type of silicates:

(i) **Orthosilicates** Simple silicates containing SiO_4^{4-} tetrahedra.

(ii) **Pyrosilicate** Two tetrahedral units share one O-atom to obtain $Si_2O_7^{6-}$ anion.

(iii) **Cyclic silicates** Two tetrahedral units share two oxygen atoms and form $(SiO_3^{2-})_n$ or $(SiO_3)_n^{2n-}$ anion.

(iv) **Chain silicates** Share two oxygen atoms, $(SiO_3^{2-})_n$ or $(SiO_3)_n^{2n-}$ are obtained.

(v) **Sheet silicates** Involve sharing of three O-atoms per tetrahedron to form $(Si_2O_5^{2-})_n$.

(vi) **Three dimensional silicates** All the four corners (O-atoms) of SiO_4^{4-} tetrahedra are shared with other.

(iv) Two important man-made silicates are glass and cement.

5. Zeolites

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

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 The correct order of atomic radii in group 13 elements is **→ NEET 2018**

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

2 The stability of +1 oxidation state among Al, Ga, In and Tl increases in the sequence **→ CBSE-AIPMT 2015**

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

3 The species, having bond angles of 120° is **→ NEET 2017**

(a) PH_3 (b) ClF_3 (c) NCl_3 (d) BCl_3

4 The tendency of BF_3, BCl_3 and BBr_3 behave as Lewis acid decreases in the sequence

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

5 Among the following the electron deficient compound is

(a) BCl_3 (b) CCl_4 (c) PCl_5 (d) $BeCl_2$

6 Which of the following is the electron deficient molecule?

(a) B_2H_6 (b) C_2H_6 (c) PH_3 (d) SiH_4

7 Which of the following compound has a 3-centred bond?

(a) Diborane (b) CO_2
(c) Boron trifluoride (d) Ammonia

8 Which one of the following molecular hydrides acts as a Lewis acid? **→ CBSE-AIPMT 2010**

(a) NH_3 (b) H_2O (c) B_2H_6 (d) CH_4

9 Boric acid is an acid because its molecule **→ NEET 2016, Phase II**

(a) contains replaceable H^+ ion
(b) gives up a proton
(c) accepts OH^- from water releasing proton
(d) combines with proton from water molecule

10 Which of the following statements about H_3BO_3 is not correct?

(a) It is a strong tribasic acid
(b) It is prepared by acidifying an aqueous solution of borax
(c) It has a layer structure in which planar BO_3 units are joined by hydrogen bonds
(d) It does not act as proton donor but acts as a Lewis acid by accepting hydroxyl ion

11 Which one of the following elements is unable to form MF_6^{3-} ion? **→ NEET 2018**

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

12 In borax bead test which compound is formed?

(a) *Ortho* borate (b) *Meta* borate
(c) Double oxide (d) Tetra borate

13 Al_2O_3 can be converted into anhydrous $AlCl_3$ by heating

(a) Al_2O_3 with HCl gas
(b) Al_2O_3 with NaCl in solid state
(c) a mixture of Al_2O_3 and carbon in dry Cl_2 gas
(d) Al_2O_3 with Cl_2 gas

14 Aluminium oxide is not reduced by chemical reactions since

(a) reducing agent contaminate
(b) the process pollute the environment
(c) aluminium oxide is highly stable
(d) aluminium oxide is reactive

15 It is because of inability of ns^2 electrons of the valence shell to participate in bonding that **→ NEET 2017**

(a) Sn^{2+} is reducing while Pb^{4+} is oxidising
(b) Sn^{2+} is oxidising while Pb^{4+} is reducing
(c) Sn^{2+} and Pb^{2+} are both oxidising and reducing
(d) Sn^{4+} is reducing while Pb^{4+} is oxidising

16 Formation of innumerable compounds of carbon is due to its

(a) high reactivity (b) catenation tendency
(c) covalent and ionic tendency
(d) different valency

17 Which of the following oxidation states are the most characteristics for lead and tin respectively?

(a) +4, +2 (b) +2, +4 (c) +4, +4 (d) +2, +2

18 Mark the oxide which is amphoteric in nature.

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

19 Diamond is hard because

(a) all the four valence electrons are bonded to each carbon atom by covalent bonds
(b) it is a giant molecule
(c) it is made up of carbon atoms
(d) it cannot be burnt

20 Which of the following does not show electrical conduction?

(a) Potassium (b) Graphite (c) Diamond (d) Sodium

21 Which of the following types of forces bind together the carbon atoms in diamond?

(a) Ionic (b) Covalent
(c) Dipolar (d) van der Waals'

22 In graphite, electrons are

(a) localised on each C-atom
(b) localised on every third C-atom
(c) spread out between the structure
(d) Both (b) and (c)

23 Which of the following structure is similar to graphite? → **NEET 2013**

(a) BN (b) B (c) B_4C (d) B_2H_6

24 Carbon suboxide C_3O_2 has

(a) linear structure
(b) bent structure
(c) trigonal planar structure
(d) distorted tetrahedral structure

25 The substance used as a smoke screen in warfare is

(a) $SiCl_4$ (b) PH_3 (c) PCl_5 (d) acetylene

26 When silicon is heated with CH_3Cl at higher temperature in the presence of Cu

(a) $CH_3SiCl_3 + (CH_3)_2SiCl_2$ obtained
(b) $(CH_3)_3SiCl$ is obtained
(c) $(CH_3)_4Si$ is obtained
(d) a mixture of all of the above is obtained

27 The basic structural unit of silicates is → **NEET 2013**

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

28 Name the type of the structure of silicate in which one oxygen atom of $[SiO_4]^{4-}$ is shared? → **CBSE-AIPMT 2011**

(a) Sheet silicate (b) Pyrosilicate
(c) Three dimensional silicate (d) Linear chain silicate

29 Which one of the following anions is present in the chain structure silicates?

(a) $Si_2O_7^{6-}$ (b) $(Si_2O_5^{2-})_n$ (c) $(SiO_3^{2-})_n$ (d) SiO_4^{4-}

30 Which glass will not crack when temperature changes?

(a) Pyrex (b) Boro silicate
(c) Calcium silicate (d) Flint

31 The structure and hybridisation of $Si(CH_3)_4$ is

(a) octahedral, sp^3d (b) tetrahedral, sp^3
(c) bent, sp (d) trigonal, sp^2

32 Percentage of lead in lead pencil is

(a) zero (b) 20 (c) 80 (d) 70

33 An example of a double salt is

(a) bleaching powder (b) $K_4[Fe(CN)_6]$
(c) hypo (d) potash alum

34 Which one of the following statements about the zeolites is false?

(a) They are used as cation exchangers
(b) They have open structure which enable them to take up small molecules
(c) Zeolites are aluminosilicates having three dimensional network
(d) Some of the SiO_4^{4-} units are replaced by AlO_4^{5-} and AlO_6^{9-} ions in zeolites

35 Match the types of glass (in Column I) with their characteristics (in Column II).

	Column I		Column II
A.	Alumino silicate glass	1.	Cheap laboratory glass wares
B.	Calcium-alkali silicate glass	2.	Optical glass
C.	Lead glass	3.	Domestic glass for window
D.	Soda glass	4.	Low coefficient of expansion

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	3	4	(b)	4	3	2	1
(c)	2	1	4	3	(d)	3	4	1	2

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 In BF_3

(a) all the B—F bonds are single covalents in nature
(b) boron-fluorine bond has some double bond character and this bond is delocalised
(c) bond energy and bond length of B—F bond indicate its single bond character
(d) All the bonds are ionic

2 Stabilities of adducts formed with boron-halides is in order

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

3 In B_2H_6

(a) there is direct boron-boron bond
(b) the B— H bonds are ionic
(c) it is isostructural to C_2H_6
(d) boron atoms are linked through hydrogen bridges

4 Boric acid is a weak acid. Thus, it behaves as

(a) proton donor as in $H_3BO_3 + H_2O \rightleftharpoons H_3O^+ + H_2BO_3^-$
(b) an hydroxyl acceptor as in

$$B(OH)_3 + H_2O \rightleftharpoons [B(OH)_4]^- + H^+$$

(c) proton acceptor as in

$$H_3BO_3 + H_2O \rightleftharpoons H_4BO_3^+ + OH^-$$

(d) an electron donor as in $H_3BO_3 \rightleftharpoons H_3BO_3^+ + e^-$

5 Orthoboric acid, H_3BO_3 behaves as weak monobasic acid giving H_3O^+ and

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

6 While testing BO_3^{3-}, there is green-edged flame on heating the salt with conc. H_2SO_4 and CH_3OH. Green colour is of

(a) $(CH_3)_3B$ (b) $(CH_3O)_3B$
(c) B_2O_3 (d) H_3BO_3

7 Element $M + N_2 \xrightarrow{\Delta} \xrightarrow{H_2O} NH_3$

Element *M* belonging to group 13 can be

(a) B or Al (b) Ga or Al
(c) Mg or Al or B (d) Mg or B

8 In diamond crystal each carbon atom is linked with carbon atoms. The number of carbon atoms linked is/are

(a) 2 (b) 4 (c) 3 (d) 1

9 In which of the following the angle between the two covalent bonds is maximum?

(a) H_2O (b) CO_2 (c) CH_4 (d) NH_3

10 Hot conc. HNO_3 converts graphite into

(a) graphite oxide
(b) CO_2 and water
(c) Both (a) and (b)
(d) None of the above

11 Select the correct statement about stability of cations.

(a) $Ge^{4+} > Sn^{4+} > Pb^{4+}$
(b) $Ge^{2+} < Sn^{2+} < Pb^{2+}$
(c) $Pb^{2+} > Pb^{4+} > Sn^{4+} > Sn^{2+}$
(d) All the above are correct statements

12 Which of the following halides is least stable and doubtful existence?

(a) Cl_4 (b) SnI_4 (c) GeI_4 (d) PbI_4

13 Lead is soluble in

(a) CH_3COOH (b) H_2SO_4
(c) HCl (d) HNO_3

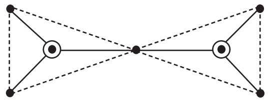
14 Pb_3O_4 reacts with HNO_3 forming nitrate and oxide which are

(a) $Pb(NO_3)_4$ from PbO_2, and PbO remains unreacted
(b) $Pb(NO_3)_2$ from PbO, and PbO_2 remains unreacted
(c) $Pb(NO_3)_2$ and $Pb(NO_3)_4$, and PbO remains unreacted
(d) Pb_3O_4 remains insoluble in HNO_3

15 Silicon reacts with hot solution of NaOH forming

(a) $Si(OH)_4$ (b) $Si(OH)_2$
(c) SiO_2 (d) Na_4SiO_4

16 Formula of the following silicate anion is



(a) SiO_4^{4-} (b) $Si_2O_7^{6-}$
(c) $Si_2O_8^{6-}$ (d) $Si_3O_9^{6-}$

17 $(Me_2)_2SiCl_2$ on hydrolysis will produce

(a) $(Me)_2Si(OH)_2$
(b) $(Me)_2Si = O$
(c) $[—O—(Me)_2Si—O—]_n$
(d) $Me_2SiCl(OH)$

ANSWERS

SESSION 1	**1** (d)	**2** (b)	**3** (d)	**4** (b)	**5** (a)	**6** (a)	**7** (a)	**8** (c)	**9** (c)	**10** (a)
	11 (a)	**12** (b)	**13** (c)	**14** (c)	**15** (d)	**16** (b)	**17** (b)	**18** (d)	**19** (a)	**20** (c)
	21 (b)	**22** (d)	**23** (a)	**24** (a)	**25** (a)	**26** (d)	**27** (b)	**28** (b)	**29** (c)	**30** (a)
	31 (b)	**32** (a)	**33** (d)	**34** (d)	**35** (b)					
SESSION 2	**1** (b)	**2** (b)	**3** (d)	**4** (b)	**5** (c)	**6** (b)	**7** (a)	**8** (b)	**9** (b)	**10** (b)
	11 (d)	**12** (d)	**13** (d)	**14** (b)	**15** (d)	**16** (b)	**17** (b)			

Hints and Explanations

1 The atomic radii as well as ionic radii increases on moving down the group 13 elements because of the successive addition of one extra shell of electrons.

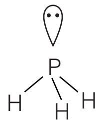
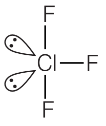
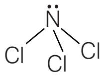
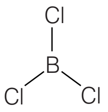
However, there is an anomaly at gallium in case of atomic radii. Atomic radii of Ga is lesser as compared to Al. Gallium (Ga) with electronic configuration, $[Ar]_{18}\, 3d^{10}\, 4s^2\, 4p^1$ has a extra d-electrons which do not screen the nucleus effectively. Consequently, electrons of Ga are more attracted by nucleus.

Thus, the increasing order of atomic radii of the group 13 elements is B (85 pm) < Ga (135 pm) < Al (143 pm) < In (167 pm) < Tl (170 pm).

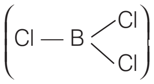
2 Al < Ga < In < Tl

This is due to inert pair effect or tendency of ns^2 electrons do not participate in bond formation (due to poor shielding effect). Thus, tendency of (+) 3 state decreases on moving down the group.

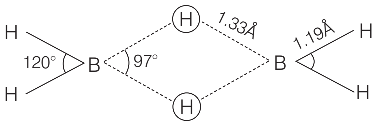
3 The species having bond angles of 120° is BCl_3. It is sp^2-hybridised and central atom does not have any lone pair of electrons.

Chemical formula	Species	Bond angle
PH_3	 (Pyramidal)	93.5°
ClF_3	 (T-shaped)	90°
NCl_3	 (Pyramidal)	107.8°
BCl_3	 (Trigonal planar)	120°

4 As the size of halogen atom increases, the acidic strength of boron halides increases. Thus, BF_3 is the weakest Lewis acid. This is because of the $p\pi - p\pi$ back bonding between the fully-filled unutilised $2p$-orbitals of F and vacant $2p$-orbitals of boron which makes BF_3 less electron deficient. Such back donation is not possible in case of BCl_3 or BBr_3 due to larger energy difference between their orbitals. Thus, these are more electron deficient. Since on moving down the group the energy difference increases, the Lewis acid character also increases. Thus, the tendency to behave as Lewis acid follows the order $BBr_3 > BCl_3 > BF_3$

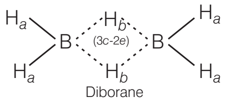
5 In BCl_3  boron contains six electrons in its valence shell so, it is capable to accommodate one pair of electrons. Hence, it acts as Lewis acid or electron deficient (incomplete octate) compound. As we know that Lewis acids are the substances having a tendency to accept a pair of electron.

6 B_2H_6 is electron deficient molecule because boron atom has three half-filled orbitals in excited state. The structure of B_2H_6 is represented as follows:



In it two electrons of a B — H bond are involved in formation of three centre bonds, these bonds are represented as dotted lines.

7 In diborane 3 centred 2 electron bond is present.



Diborane
3c -2e bond present

8 Electron deficient molecules behave as Lewis acid. Among the given molecules, only diborane is electron deficient, i.e. does not have complete octet. Thus, it acts as a Lewis acid. NH_3 and H_2O being electron rich molecules behave as Lewis base.

9 Boric acid can be considered as an acid because its molecule accepts OH^- from water, releasing proton.

$$\underset{\text{Acid}}{H_3BO_3} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Conjugate base}}{B(OH)_4^-} + \underset{\text{Conjugate acid}}{H^+}$$

In the given options, (a), (b) and (c) are correct as all of these substances have more or less similar meaning but here (c) option is the most appropriate one as it gives complete explanation of the fact that how boric acid can be combined with an acid.

10 Boric acid (H_3BO_3) is a weak monobasic acid with $K_a = 1.0 \times 10^{-9}$. It may be noted that boric acid does not act as a protonic acid (i.e. proton donor) but behaves as a Lewis acid by accepting a pair of electrons from OH^- ion.

$$B(OH)_3 + 2H—O—H \longrightarrow [B(OH)_4]^- + H_3O^+$$

11 Boron belongs to 2nd period of the periodic table with electronic configuration $1s^2, 2s^2 2p^1$. It does not have vacant d-orbitals, thus cannot increase its covalency above four.

Therefore, boron (B) cannot form MF_6^{3-} ion. In contrast, aluminium (Al), gallium (Ga), indium (In) have the vacant $3d$-orbitals, thus can increase their covalence above four and form MF_6^{3-} ion.

12 In borax bead test the coloured *meta* borates are formed by transition metal salts.

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$$

$$B_2O_3 + CuO \longrightarrow \underset{\substack{\text{Cupric metaborate}\\\text{(Blue bead)}}}{Cu(BO_2)_2}$$

13 Al_2O_3 may be converted into anhyd. $AlCl_3$ by heating a mixture of Al_2O_3 and carbon in dry chlorine.

$$Al_2O_3 + 3C + \underset{\text{Hot and dry}}{3Cl_2} \longrightarrow \underset{\text{Anhy } AlCl_3}{Al_2Cl_6}$$

14 Aluminium oxide is highly stable therefore, it is not oxidised by chemical reactions.

15 The inability of ns^2 electrons of the valence shell to participate in bonding is called as inert pair effect. Due to this effect, the lower oxidation state becomes more stable on descending the group. Thus, Sn^{2+} is a reducing agent while Pb^{4+} act as an oxidising agent.

16 Generally IVth group element shows catenation tendency and carbon has more catenation power.

17 The tendency to form +2 ionic state increase on moving down the group due to inert pair effect. Most characteristic oxidation state for lead and tin are +2, +4 respectively.

18 SnO_2 is amphoteric in nature. It dissolves in acids as well as in alkalies, e.g.

$$SnO_2 + 2H_2SO_4 \longrightarrow Sn(SO_4)_2 + 2H_2O$$
$$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$$

19 In diamond, each carbon atom is linked to four other carbon atoms by sigma bonds. Each σC—C bond is formed by the overlapping of sp^3 hybrid orbitals of carbon atom. Each carbon atom is present at the apex of a regular tetrahedron. Each carbon atom is surrounded by four other carbon atoms present at the corners of a regular tetrahedron. Structure of diamond is a rigid three dimensional network. This explain high density and hardness of diamond.

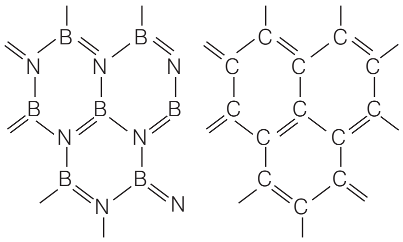
20 Diamond does not show electrical conductivity due to the absence of free electrons. Sodium and potassium are metallic conductors while graphite is a non-metallic conductor.

21 In diamond, each carbon atom undergoes sp^3 hybridisation and is covalently bonded to three other carbon atoms by single bonds.

22 Structure of graphite consists of a two dimensional sheet-like network joined together in hexagonal rings. These layers are held together by weak van der Waals' forces. In graphite each carbon atom is bonded to three others, forming sp^2 hybrid bonds. The fourth electron forms a π-bond.

Graphite is a conductor of electricity which is due to the fact that all the carbon bonds being not satisfied. Thus, some of the electrons are free to move through the crystal.

23 Boron nitride $(BN)_x$ resembles with graphite in structure as shown below



Boron nitride Graphite

24 Carbon suboxide (C_3O_2) is anhydride of malonic acid. It has linear structure. C—C bond length is 130 Å and C — O bond length is 120 Å.

$$O{=}C{=}C{=}C{=}O \longleftrightarrow \overset{\ominus}{O}{-}C{\equiv}C{-}C{\equiv}\overset{\oplus}{O}$$

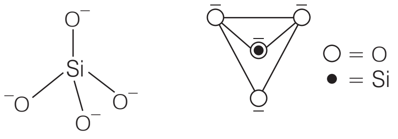
25 Silicon chloride is easily hydrolysed to give white fumes. So it is used as a smoke screen in warfare.

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

26 When Si is heated with CH_3Cl at high temperature in the presence of CO as a catalyst, a mixture of mono, di and tri methyl chlorosilanes alongwith a small amount of tetramethylsilane is formed.

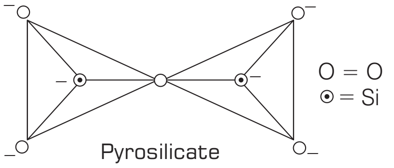
$$\underset{\text{Methyl chloride}}{CH_3Cl} + Si \xrightarrow[570\text{ K}]{\text{CO powder}} CH_3SiCl_3$$
$$+ (CH_3)_2SiCl_2 + (CH_3)_3SiCl + (CH_3)_4Si$$

27 The basic building unit of all silicates is the tetrahedral SiO_4^{4-}. It is represented as



Structure of SiO_4^{4-} unit

28 In pyrosilicate, only one oxygen atom is shared.



Pyrosilicate

29 $[SiO_3^{2-}]_n$ and $[Si_4O_{11}]^{6-}$ have chain structure of silicates.

30 **Pyrex glass** It is a mixture of sodium aluminium borosilicates. Its coefficient of expansion is very low, therefore, it does not crack with sudden temperature change.

31 In tetramethyl silicane, i.e. $Si(CH_3)_4$, Si is sp^3-hybridised. Hence it has tetrahedral structure.

32 In lead pencil graphite and clay is present, so the percentage of lead is zero.

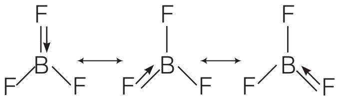
33 Double salts are additon of molecular compounds which are formed by two apparently saturated compounds but they lose their identity when dissolved in water. The most common example of double salt is potash alum $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.

34 Zeolites are aluminosilicates having three dimensional open structure in which four or six membered rings predominates. Thus, due to open chain structure, they have cavities and can take up water and other small molecules.

35

S.No.	Glass	Characteristics
A.	Alumino silicate glass	Low coefficient of expansion
B.	Calcium alkali silicate glass	Domestic glass for windows
C.	Lead glass	Optical glass
D.	Soda glass	Cheap laboratory glasswares

SESSION 2

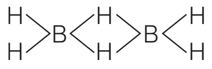
1 

2 Due to small size of fluorine (F), adducts formed by the boron-halides, BF_3 form most stable adduct.

(∵ Has shortest bond length)

Thus, order is $BCl_3 < BBr_3 < BF_3$.

3 The structure of B_2H_6 is as follows :



In this structure the boron atoms are linked with the hydrogen bridges.

4 Boric acid is a weak acid, as it accepts the hydroxide ion (OH^-) from the water and release proton :

$$B(OH)_3 + H_2O \rightleftharpoons [B(OH)_4]^- + H^+$$

5 $B(OH)_3 + 2H_2O \longrightarrow [B(OH)_4]^- + H_3O^+$

6 (i) $BO_3^{3-} + H_2SO_4 \longrightarrow H_3BO_3$

(ii) $H_3BO_3 + 3CH_3OH \longrightarrow \underset{\text{(Green)}}{(CH_3O)_3B} + H_2O$

7 $B + N_2 \longrightarrow BN \xrightarrow{H_2O} NH_3$

$Al + N_2 \longrightarrow AlN \xrightarrow{H_2O} NH_3$

8 Due to tetravalent nature of carbon.

9 CO_2 : 180°, SO_2 : 119°

CH_4 : 109°28′, NH_3 : 107.0°

10 $HNO_3 + C\text{ (Graphite)} \rightarrow CO_2 + 2H_2O + 4N_2O$

11 Due to inert-pair effect stability of +2 oxidation state increases and that of +4 oxidation state decreases along a group 14.

12 $Pb^{4+} < Pb^{2+}$ (stability). Thus, PbI_4 is not formed.

13 $PbCl_2, PbSO_4$ — Insoluble

CH_3COOH does not react

$Pb(NO_3)_2$ — Soluble

14 Pb_3O_4 is a double oxide $PbO_2 \cdot 2PbO$

PbO_2 is not affected by HNO_3

PbO changes to $Pb(NO_3)_2$

15 $4NaOH + Si \longrightarrow \underset{\text{Charge}}{Na_4SiO_4} + 2H_2$

16 Two Si^{4+} +8

Seven O^{2-} –14

Hence, formula of given eilicete anion will be $Si_2O_7^{6-}$.

17