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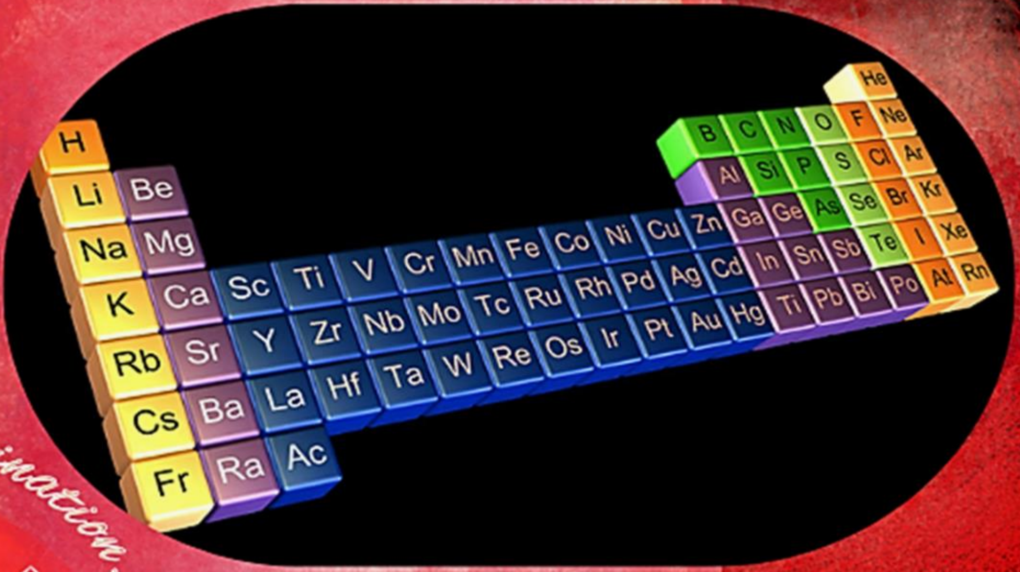

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P BLOCK ELEMENTS

p-Block Elements

IN THIS CHAPTER ....

- Elements of Group 13 (or IIIA) and their Compounds
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- Chemistry of Boron
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Elements belonging to group IIIA, IVA, VA, VIA, VIIA and zero, are collectively known as *p*-block elements. In these elements, *p*-orbitals are being progressively filled. *p*-block elements contains, metals, non-metals and metalloids. They are also called typical elements to distinguish them from the transition and inner transition series.

Here, we will study only group IIIA and IVA. Remaining groups will be discussed in "*p*-block elements-II."

Elements of Group 13 (or IIIA) and their Compounds

The group 13th is long form of the periodic table contains 5 elements namely **boron** (B), **aluminium** (Al), **gallium** (Ga), **indium** (In) and **thallium** (Tl). Thallium is also known as Duck-billed platypus because of its similarities with many other elements.

Occurrence

Boron occurs in two isotopic forms, *viz.*, ${}_5B^{10}$ (18%) and ${}_5B^{11}$ (82%). It is found mainly in the form of borax. Aluminium is the third most abundant element or the most abundant metal in the earth's crust. The other members of this family are, however, less common.

General and Physical Properties

The trends of various general and physical properties of elements of group 13 are discussed below one by one.

1. Electronic Configuration

General electronic configuration of the elements of boron family is $ns^2 np^1$ (where, $n = 2, 3, 4, \ldots$). These elements have three electrons in their valence shell and exist as M^{3+} ion in its ionic form (where, $M = 13$ group elements).

2. Atomic and Ionic Radii

Their atomic and ionic radii are smaller as compared to that of the elements of II group. This is due to increase in effective nuclear charge (Z_{eff}).

On moving down the group, the ionic radii increases with an exception of Ga. Its atomic radii is smaller as compared to Al. This is because of ten d-electrons present in Ga atom do not screen the nucleus effectively. Consequently, electrons of Ga are more attracted by nucleus.

3. Density

Density increases on moving down the group with Al lying in between having exceptionally low density. The exceptional low density of Al is attributed to its unexpected large molar volume.

4. Melting and Boiling Points

- Melting point and boiling point of elements of this group are higher as compared to that of the elements of group II elements.
- Melting point decreases considerably on moving down the group up to Ga. After that it is again increases from In to Tl. Ga because of its unusual structure exists as Ga_2 molecules and thus, has low melting point. Due to its property, to remain in liquid state even at 2000°C, Ga is used in high temperature thermometer.
- Boiling points follow a more regular trend. It decreases regularly on moving down the group. This is an indication of the fact that atoms of the elements are held less and less closely as we move down the group.

5. Ionisation Energy (IE)

- The first ionisation energy of 13th group elements is rather low as compared to the corresponding ionisation energies of s-block elements. The second and third ionisation energies are considerably higher.
- It is clear from the table that the ionisation energies change in oscillating manner. It first decreases from B to Al, then increases from Al to Ga, again decreases from Ga to Tl, i.e. $B < Al > Ga < In > Tl$ and again increases from In to Tl.
- It is sharply decreases from B to Al, due to appreciable increase in atomic size and the shielding effect of s and p-electrons of the penultimate energy shell. In case of Ga, there are 10 d-electrons in the penultimate energy shell which shield the nuclear charge less effectively, so that the outer electron is held firmly by the nucleus. As a result, the ionisation energy remains nearly the same as that of aluminium (inspite of the fact that atomic size increases).
- In case of In, the number of d electrons and their shielding effect remains the same as in gallium. The ionisation energy, decreases in indium due to increase in atomic size from Ga to In.
- The increase in ionisation energy from In to Tl is due to poor shielding effect of 14 f-electrons are present in the inner energy shell.
- Since, the total of first three successive ionisation energies is very high, these elements have very little tendency to form trivalent ion, i.e. ions of the type M^{3+}.
- The ionisation energy of boron is highest in the group since its atomic size is smallest and the shielding effect is lowest.
- *IE of Boron*–Due to its very small size, B does not form M^{3+} ion. The sum of first three ionisation energies is so large in the case of B that the small atom of B is not able to accommodate that energy even if given artificially from outside.
- In other words, we can say that if such a quantity of energy is given from outside to B atom, the repulsion between subatomic particles become so large that these cannot be remain together in the form of an atom.

6. Oxidation States

- Boron and aluminium show consistently +3 oxidation state in its compounds, while rest of the elements show +1 as well as +3 oxidation states. As compared to +3 oxidation state, +1 oxidation state becomes more and more stable as we move down the group. This is due to **inert pair effect**.
- Stability order of +3 oxidation state is $B > Al > Ga > In > Tl$. Stability of lower oxidation state (+1) increases from $Ga < In < Tl$.
- The term "**inert pair effect**" is defined as the tendency of s-electrons to remain together or the reluctance of s-electrons to participate in a reaction. However, this term is some what misleading.
- In a nut shell, we can say that because of decreases in bond energy with increase in size, the energy required to unpair the ns^2 electrons is not compensated by energy released in forming two additional bonds. Thus, two s-electrons have develop more and more tendency to remain together as we move down the group.
- Tl (III) compounds behave as strong oxidising agents, whereas Ga (I) compounds behave as strong reducing agents.
- Ga, the third element of the group 13th appears to be bivalent in some of its compounds, e.g. $GaCl_2$ but infact it is believed to contain univalent and trivalent ions as Ga^+ and $[GaCl_4]^-$ respectively.

7. Electropositive or Metallic Character

The electropositive (or metallic) character increases from B to Al. B, in fact, is regarded as a **semi-metal** and its properties more closer to non-metals than to metals. Aluminium is most electropositive metal.

The increases in electropositive character from boron to aluminium is due to increased size of aluminium. The remaining three elements are weakly metallic in nature and their electropositive nature is less than aluminium and decreases from gallium to thallium. The extra d^{10} electrons in gallium and indium while d^{10} and f^{14} electrons in thallium do not shield the nuclear charge very effectively and therefore, these metals are less electropositive.

8. Nature of Compounds

Boron have a tendency to form covalent compounds as B^{3+} ion is unstable, while other members of the group form electrovalent compounds as well.

Note There is no evidence for the existence of B^{3+} ions and the value of ionic radius is an estimate.

The physical properties of the III A group elements are summarised in the following table

Physical Properties of IIIA Group Elements

Property	Boron	Aluminium	Gallium	Indium	Thallium
Electronic configuration	$[He]2s^2 2p^1$	$[Ne]3s^2, 2p^1$	$[Ar]\,3d^{10}\,4s^2, 4p^1$	$[Kr]4d^{10}, 5s^2, 5p^1$	$[Xe]4f^{14}, 5d^{10}, 6s^2 6p^1$
Atomic number	5	13	31	49	81
Molar mass (g mol^{-1})	10.81	26.96	69.72	114.82	204.37
Density (g cm^{-3})	2.35	2.70	5.91	7.31	11.90
Melting point (°C)	2030	659	29.8	156.4	303
Boiling point (°C)	2550	2450	2237	2000	1457
Atomic radius (Å)	0.82	1.26	1.24	1.50	1.55
Molar volume (cm^{-3} mol^{-1})	4.62	10.0	11.8	15.1	17.2
Radius of trivalent ion (Å)	0.20	0.50	0.62	0.80	0.95
Ionisation energy (kJ mol^{-1})					
I	800	577	579	558	589
II	2427	1816	1979	1820	1971
III	3659	2744	2962	2704	2877
Electronegativity	2.0	1.5	1.6	1.7	1.8
Oxidation states	+3	+3	+1, +3	+1, +3	+1, +3
Heat of sublimation (kJ mol^{-1})	564.8	324.3	273.2	241.4	179.1

Chemical Properties

The chemical properties of element of group 13 are discussed below

1. Reaction with Air, Water and Acid

- Pure **boron is unreactive to air** at ordinary temperature. It reacts with air only when heated. It does not react with water. It is attacked only by hot concentrated acids like H_2SO_4, etc.

$$2B + 3H_2O \longrightarrow B_2O_3 + 3H_2\uparrow$$

- **Al reacts readily with air,** even at ordinary temperature forming a protective layer of oxide. (The oxide film protects it from further reaction).
  Al decomposes cold water.

$$2Al + 3H_2O \longrightarrow Al_2O_3 + 3H_2\uparrow$$

- Ga and In are attacked neither by cold water nor by hot water unless oxygen is present. Tl is a little more reactive than Ga and forms an oxide larger on its surface.

$$4Tl + 2H_2O + O_2 \longrightarrow 4TlOH$$

Note Thallium is preserved under oil or by smearing with vaseline.

2. Reaction towards Halogen

The elements of group 13 react with halogen (X) at high temperature forming trihalides of the general formula, MX_3.

$$2M + 3X_2 \xrightarrow{\Delta} 2MX_3 \qquad (X = F, Cl, Br, I)$$

Compounds of Group 13 Elements

The compounds group 13 elements are discussed below.

1. Hydrides

- Elements of group 13 do not react directly with hydrogen, however a large number of hydrides (13 group elements) are commonly found.
- Boron forms a number of covalent hydrides with general formulae B_nH_{n+4} and B_nH_{n+6}. These are called **boranes.** The representative compounds of two series include B_2H_6 and B_4H_{10} respectively.

- Al forms a polymeric hydride of formula $(AlH_3)_n$, which is commonly known as **alane.** It decomposes on heating above 200°C into its elements.
- GaH_3 is even less stable, while InH_3 and TlH_3 are extremely unstable.
- B, Al and Ga have the tendency to form complex anionic hydrides like $Li[AlH_4]$, $Li[BH_4]$, $Li[GaH_4]$ etc. The formation of these complexes is due to the presence of a vacant *p*-orbital in their outermost shells due to which these are readily accepts electron pair from the hydride ion (H^-) as

$$AH_3 + H^- \longrightarrow [AH_4]^- \quad [\text{Here, } A = \text{Al, Ga and B}]$$

LAH (lithium aluminium hydride) is the most important hydrides and is prepared by reacting LiH with $AlCl_3$ as,

$$4LiH + \underset{\text{(Anhydrous)}}{AlCl_3} \xrightarrow{\text{Ether}} Li^+[AlH_4]^- + 3LiCl$$

These complex hydrides are infact good reducing agents.

2. Oxides and Hydroxides

- **Oxides** All the elements of this group form oxides of M_2O_3 and M_2O type in which elements are present in +3 and +1 oxidation state respectively, e.g. $B_2O_3, Al_2O_3, Ga_2O_3, In_2O_3$ Tl_2O_3 TI_2O etc. The basic character of these oxides increases or acidic character decreases down the groups as

$$\underbrace{B_2O_3}_{\text{Acidic}} \quad \underbrace{Al_2O_3, Ga_2O_3}_{\text{Amphoteric}} \quad \underbrace{In_2O_3, Tl_2O_3 \text{ and } Tl_2D}_{\text{Basic}}$$

The oxide of B is feebly acidic while that of Al and Ga are amphoteric, In and Tl oxides have strong basic character. Thus, we can say that

$$\underset{\text{Basic oxide}}{CuO} + \underset{\text{Acidic oxide}}{B_2O_3} \longrightarrow Cu(BO_2)_2$$

$$\underset{\text{Basic oxide}}{Al_2O_3} + \underset{\text{Acid}}{6HCl} \longrightarrow 2AlCl_3 + 3H_2O$$

$$\underset{\text{Acidic oxide}}{Al_2O_3} + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

$$\underset{\text{Basic oxide}}{Tl_2O_3} + \underset{\text{Acid}}{3H_2SO_4} \longrightarrow Tl_2(SO_4)_3 + 3H_2O$$

- **Hydroxides** The hydroxides of 13th group elements are $M(OH)_3$ type. Tl also give hydroxide of type TiOH which is a very strong base, comparable to hydroxides of alkali metals. $M(OH)_3$ type hydroxides follow the same trend of basicity as shown by oxides.

$$\underbrace{B(OH)_3}_{\text{Acidic}} \quad \underbrace{Al(OH)_3, Ga(OH)_3}_{\text{Amphoteric}} \quad \underbrace{In(OH)_3, Tl(OH)_3}_{\text{Basic}}$$

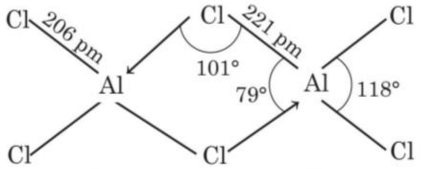
This is because, as the size of the ion increases, the tendency to rupture the O—H bond decreases and hence, acidic nature decreases, i.e. basic nature increases.

3. Halides

Group 13 elements form trihalides of MX_3 type (where, M is the metal and X is halogen). All the halides of group 13 elements are known except Tl(III) iodide, as it form TlX type of halide. In gaseous state, IIIA group element form monohalides of (MX) type which are unstable. They are covalent in nature.

4. Trihalides

- The halides of boron (BX_3) are covalent compounds with sp^2 hybridisation and trigonal planar structure. All the four halides of boron namely boron trifluoride (BF_3), boron trichloride (BCl_3) boron tribromide (BBr_3) and boron triiodide (BI_3) are known. All of them are volatile, monomeric and highly reactive.
- BF_3 and BCl_3 are gases at room temperature, BBr_3 is a volatile liquid while BI_3 is a solid. They do not conduct electricity in the liquid state. Their boiling points are also very low as compared to the halides of elements of Ist and IInd group.
- The fluorides of Al, Ga, In and Tl are ionic and have high melting points while other halides of these elements are covalent when anhydrous, e.g. anhydrous $AlCl_3$ is covalent but in water it gets hydrolysed to give Al^{3+} (aq) ions. This change mainly due to high hydration energy of Al^{3+} ions which easily compensate its ionisation energy. B does not show this characteristic just because of its small size and inability to accommodate energy given. All other halides of elements of this group also have sp^2-hybridisation and trigonal planar structure.
- **Complex Formation** These halides have an ability to complex formation. The boron trihalides have the tendency to form BX_3L type of complexes, where, L is a neutral or anionic donor (i.e. ligand) e.g. BF_4^-. These complexes are tetrahedral in shape.
- Tendency to form this type of complexes decreases down the group. The trihalides of other elements of this group have more tendency to form complexes like $[AlF_6]^{3-}$, $[GaCl_6]^{3-}$ and $[InCl_6]^-$, etc., due to the availability of vacant *d*-orbital in central atoms.
- **Dimerisation** The trihalides of Al exist as discrete molecules (monomeric) while the trihalides of other elements exist as dimers both in vapour state and in non-polar solvent, e.g.



Dimeric structure of $AlCl_3$

- Dimer structure disappears, when the halides are dissolved in water. This is due to high hydration energy when $[M(H_2O)_6]^{3+}$ and $3X^-$ ions are formed making the solution as good conductor of electricity.
- The solution becomes acidic owing to hydrolysis.

$$AlCl_3 + 9H_2O \longrightarrow [Al(H_2O)_6](OH)_3 + 3H^+ + 3Cl^-$$

However, B atom owing to its small size, cannot coordinate with four larger halide ions and hence, it cannot form the dimeric molecules. That is why boron trihalides always exist in monomeric forms.

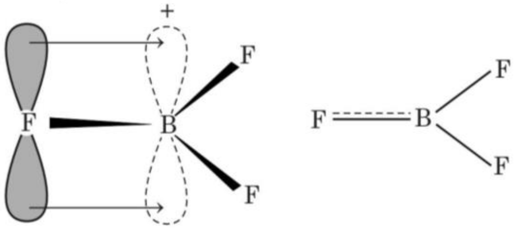
- **Electron deficient** or **Lewis acid character**
  The trihalides of all the elements of this group act as Lewis acids, i.e. they are electron deficient and have the tendency to accept the electron pair. The electron accepting tendency of trihalides follow the order

  $$B > Al > Ga > In$$

  But, the actual order of relative strengths of trihalides of B as Lewis acids have been determined by measuring their heats of formation as well as by studying their infrared spectra. The result of these studies is

  $$BF_3 < BCl_3 < BBr_3$$

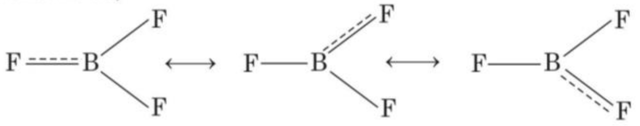
  This order is just the reverse of what should be expected normally from the electronegativities of halogens. This anomalous behaviour can be explained on the basis of tendency of halogen atom to back donate of its electron to the boron atom, which can be shown as,



Phenomenon of back bonding in BF_3 molecule

Infact in BF_3 molecule, where the $2p$-orbitals of each F atom are fully-filled, one of the $2p$-orbitals of B is vacant. Therefore, an additional $p\pi$- $p\pi$ bond is established between these $2p$-orbitals of same energy due to partial transference of electronic character from fully-filled orbital to vacant orbital as shown in the figure above. Thus, the B—F bond acquires some double bond character. This type of bond formation is called **back bonding.**

Similar structure for other two B—F bonds are equally probable as,



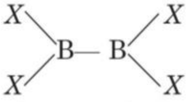
Various resonating structures of BF_3 molecules involving $p\pi$-$p\pi$ back bonding

As the result of back donation of electrons from F to B, the electron deficiency of B atom get compensated resulting in decrease in Lewis acid character.

This tendency to form back bonds is maximum in case of BF_3 and falls rapidly as we move to BCl_3 and BBr_3 due to the fact that the energy difference between fully-filled orbital of halogen (Cl-3*p*; Br-4*p*) and vacant orbital of B (2*p*) increases.

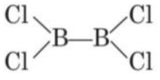
Monohalides, Dihalides and Tetrahalides

- In addition to trihalides, these elements form diholides as well as monohalides. Boron forms dimer of its dihalides, B_2X_4.

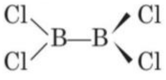


Structure of B_2X_4

- In solid state, B_2X_4 has planar structure but in liquid and vapour state, it has non-eclipsed structure.



Planar molecule



Non-eclipsed structure

- Gallium and indium also form dihalides. Gallium dihalide is more properly represented as $Ga^+[GaCl_4]^-$ showing gallium in +1 and +3 oxidation states.
- Tetrahalides can be synthesised by heating trihalides with mercury at low pressure.

$$2BCl_3 + 2Hg \xrightarrow[\text{low pressure}]{\text{Electric discharge}} B_2Cl_4 + Hg_2Cl_2$$

5. Oxyacids

Among 13th group elements, only boron forms several oxyacids, all of which are obtained by adding one or more H_2O molecules to one or more B_2O_3 molecules as,

$$B_2O_3 + 3H_2O \longrightarrow \underset{\text{Orthoboric acid}}{2H_3BO_3} \quad \text{or} \quad 2B(OH)_3$$

$$B_2O_3 + H_2O \longrightarrow \underset{\text{Metaboric acid}}{2HBO_2}$$

$$2B_2O_3 + 3H_2O \longrightarrow \underset{\text{Pyroboric acid}}{H_6B_4O_9}$$

$$3B_2O_3 + 2H_2O \longrightarrow \underset{\text{Hexaboric acid}}{H_4B_6O_{11}}$$

$$4B_2O_3 + 3H_2O \longrightarrow \underset{\text{Octaboric acid}}{H_6B_8O_{15}}$$

Example 1. *The correct statements among* I *to* III *regarding group 13 element oxides are* ***(JEE Main 2019)***

I. *Boron trioxide is acidic.*
II. *Oxides of aluminium and gallium are amphoteric.*
III. *Oxides of indium and thallium are basic.*

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

Sol. (a) All the given statements are correct.

For group 13 elements, the acidic nature of oxides decreases and the basic nature of oxides increases on moving down from B to Tl. This is because as we move down the group, the atomic size of elements goes on increasing, whereas the ionisation energy decreases, due to which the strength of metal oxide (*M*O) bond goes on decreasing.

Thus, boron trioxide or boron oxide is acidic and reacts with basic oxides to give metal borates. Aluminium and gallium oxides are amphoteric while oxides of indium and thallium are basic in nature.

Unique Behaviour of Boron

Owing 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 exhibit 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.
- It does not decompose steam while other members do so.
- It is a bad conductor of electricity while other are good conductor.

Similarities with Silicon

Boron due to its small size and similar *e/m* ratio, shows resemblance with silicon, present diagonally opposite.

It shows following similarities

- Like Si, it is also a typical non-metal with high melting and boiling points and low atomic volumes.
- It is a bad conductor of electricity and exhibits allotropy like Si.
- Chlorides of both B and Si fumes in moist air and readily hydrolysed by water.

$$BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3HCl$$
$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

- Carbides of B and Si both are very hard and used as a abrasive.

Chemistry of Boron

It occurs in two isotopic forms, i.e. ^{10}B (19%) and ^{11}B (81%). Its abundance in the earth crust is less than 0.001% by mass. B occurs mainly as the salts of boric acid.

Extraction of Boron

The important ores of boron are given below.

Borax	:	$Na_2B_4O_7 \cdot 10H_2O$;
Colemanite	:	$Ca_2B_6O_{11} \cdot 5H_2O$;
Boric acid	:	H_3BO_3;
Boronatro calcite	:	$CaB_4O_7 \cdot NaBO_2 \cdot 8H_2O$;
Boracite	:	$2Mg_3B_8O_{15} \cdot MgCl_2$;
Kernite (Rasorite)	:	$Na_2B_4O_7 \cdot 4H_2O$

Extraction Procedure

A. Boron is extracted from borax and colemanite minerals using following two steps given below.

***Step* I** Preparation of B_2O_3 from the mineral

(i) **From borax**, B_2O_3 is obtained by heating it with concentrated acids.

$$\underset{\text{Borax}}{Na_2B_4O_7} + 2HCl \longrightarrow 2NaCl + \underset{\text{Tetraboric acid}}{H_2B_4O_7}$$

$$\text{or, } Na_2B_4O_7 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2B_4O_7$$
$$H_2B_4O_7 + 5H_2O \longrightarrow \underset{\text{Orthoboric acid}}{4H_3BO_3}$$
$$2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$$

(ii) **From colemanite mineral,** first borax is obtained which on heating with concentrated acids gives B_2O_3 as,

$$\underset{\text{Colemanite}}{Ca_2B_6O_{11}} + 2Na_2CO_3 \longrightarrow 2CaCO_3 + \underset{\text{Borax}}{Na_2B_4O_7} + 2NaBO_2$$

$$4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$$
$$\Delta \Big\downarrow \text{acid}$$
$$B_2O_3$$

Colemanite also gives B_2O_3 when SO_2 gas is passed in its suspension and the obtained H_3BO_3 is heated.

$$Ca_2B_6O_{11} + 11H_2O + 4SO_2 \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$$
$$2H_3BO_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O$$

***Step* II Reduction of B_2O_3** B_2O_3 can be reduced by an electropositive metal. e.g.

$$B_2O_3(s) + 6Na(s) \longrightarrow 2B(s) + 3Na_2O(s)$$
$$B_2O_3(s) + 6K(s) \longrightarrow 2B(s) + 3K_2O(s)$$
$$B_2O_3(s) + 3Mg(s) \longrightarrow 2B(s) + 3MgO(s)`$$

The fused mass is stirred with iron rod to oxidise the unreacted sodium or potassium. The mass is then boiled with dil. HCl when insoluble boron powder is obtained. It is washed with water and made dry. **This is the amorphous variety of boron.**

B. Boron can also be obtained by the following methods given below.

- Electrolytic reduction of fused borates or tetrafluoroborates (KBF_4) in molten KCl/KF at 1073 K.
- By reduction (hydrogenation) of a volatile boron compound with H_2 at high temperature on a heated tantalum filament as,

$$2BCl_3(g) + 3H_2(g) \xrightarrow{1270\text{ K}} 2B(s) + 6HCl(g)$$

Boron obtained by this method is of high purity (almost 99.9%).

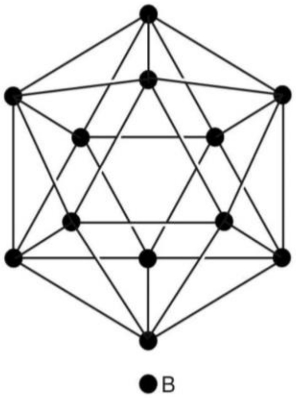
- By thermal decomposition of boranes and boron halides at temperatures above than 900°C.

Physical Properties

- Boron is a non-metallic element. It is poor conductor of electricity and is non-fusible under ordinary pressure. Its ionisation energy is highest among the group. It is an extremely hard refractory solid.

  The phenomenon of existence of an element in different forms (which generally differ is number of atoms and physical properties) is called **allotropy.** Boron exists in two allotropic forms, called **amorphous and crystalline forms**. These are defined as

- **Amorphous boron** is a brown powder of specific gravity 2.34. It melts at 2030°C and volatiles appreciably even at 1600°C.
- **Crystalline boron** exists in several different modifications. Atleast four allotrops of B may be obtained under different conditions. However, the transition between different forms is an extremely slow process. All crystalline **allotropes** have structure built up of 12 B atoms octahedral units as shown in the figure.



Icosahedron arrangement of 12 B atoms in a crystalline variety

Chemical Properties

Boron reacts differently with different reagents. Some of its characteristics reactions are as,

(i) **Action of air** When heated in air at 700°C, boron forms boric anhydride with O_2 of air and boron nitride with N_2 of air as,

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

Since, the compounds formed, form a protective layer over boron surface, these reactions do not proceed to completion.

(ii) **Action of acids** B is not attacked by HCl but is oxidised by nitric acid and sulphuric acid as,

$$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$$
$$2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2$$

(iii) **Reaction with alkalies** With fused alkali metal hydroxides, it forms borates and H_2 gas is evolved as,

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2\uparrow$$

(iv) **Reaction with metals** B combines with many metals on heating to give the corresponding borides as,

$$3Mg + 2B \longrightarrow Mg_3B_2$$

(v) **Reaction with non-metals**

- When heated with S, it forms boron sulphide, B_2S_3.
- On heating with C in an electric furnace, an extremely hard substance, called **boron carbide** (B_4C) is formed.
- Boron carbide is one of the hardest materials known ranking third behind diamond and cubic boron nitride.
- It also combines with halogens at high temperature to form covalent boron trihalides like BF_3, BCl_3 etc.

(vi) **Reaction with water** : B does not react with water, but reacts with steam at red heat liberating H_2 as,

$$2B + \underset{\text{(Steam)}}{3H_2O} \xrightarrow{\text{(Red heat)}} B_2O_3 + 3H_2\uparrow$$

(vii) **As a reducing agent** B is a powerful reducing agent, since it can replace C from CO_2, silicon from SiO_2 and N_2 from NO as

$$4B + 3CO_2 \longrightarrow 2B_2O_3 + 3C$$
$$4B + 3SiO_2 \longrightarrow 2B_2O_3 + 3Si$$
$$4B + 6NO \longrightarrow 2B_2O_3 + 3N_2$$

Uses

Boron is used

- for making bullet-proof vests and light composite material for aircrafts.
- in nuclear industry as protective shields and control rods.
- in steel industry to increase the hardness of steel.
- as a semiconductor for making electronic devices.
- in preparation of many important compounds like borax, boric acid etc.
- as a deoxidiser in casting of iron.

Chemistry of Aluminium

Next to silica and oxygen, **Al is the third widely distributed element.** It is present to the extent of 7.3% in the earth crust.

Extraction of Aluminium

Its important ores are bauxite ($Al_2O_3 \cdot H_2O$); cryolite (Na_3AlF_6); corundum (Al_2O_3).

1. Concentration of Ore

Bauxite is the principle ore of aluminium. Usually impurities like ferric oxide, silica and titanium (IV) oxide are associated with it. These are removed by one of the following methods such as,

(i) **When bauxite contains Fe_2O_3 in excess, Baeyer's process is used** In this process, the ore is powdered and digested with a concentrated solution of sodium hydroxide in an autoclave under pressure at 130°C. By this, alumina present in the ore dissolves as sodium meta aluminate ($NaAlO_2$), whereas impurities being insoluble in NaOH, settle down.

Similarly, silica of the ore reacts with NaOH to form sodium silicate which is also present in the solution along with sodium meta aluminate. Solution is filtered leaving insoluble impurities behind.

Now, the filtrate containing sodium meta-aluminate and sodium silicate is diluted and seeded with freshly prepared $Al(OH)_3$ solution which induces the precipitation of $Al(OH)_3$ leaving behind sodium silicate in solution.

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$
$$NaAlO_2 + 2H_2O \longrightarrow Al(OH)_3 + NaOH$$

The precipitate is filtered, washed and ignited to obtain pure alumina.

(ii) **If SiO_2 is in excess, Serpeck's process is used** In this method, the ore is mixed with coke and heated at 1800°C in a current of nitrogen.

By this, alumina converts into AlN and SiO_2 is reduced into Si. Si being volatile, passes off as vapours. AlN on dilution induces the precipitation of aluminium hydroxide.

$$Al_2O_3 + \underset{\text{(Coke)}}{3C} + N_2 \xrightarrow{\Delta} 2AlN + 3CO$$
$$SiO_2 + 2C \xrightarrow{\Delta} Si + 2CO$$
$$AlN + 3H_2O \xrightarrow{\Delta} Al(OH)_3 + NH_3$$
$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

Alumina is obtained by filtering, washing and igniting the precipitate.

(iii) **In Hall's process** The bauxite ore is fused with sodium carbonate. The alumina present in the ore dissolves as sodium meta aluminate leaving behind Fe_2O_3 and SiO_2. The fused mass after extraction with water and filtration, is warmed to 58°C and CO_2 is passed through it, $Al(OH)_3$ precipitates out.

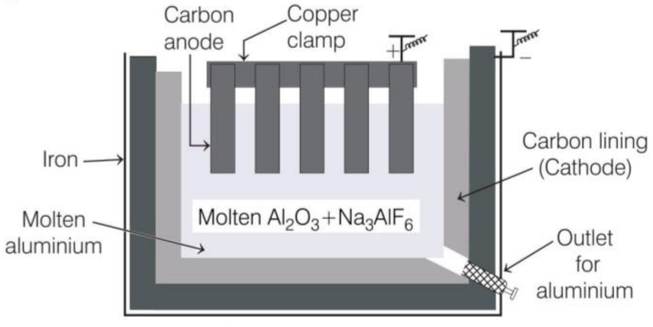
$$Na_2CO_3 + Al_2O_3 \cdot 2H_2O \longrightarrow 2NaAlO_2 + CO_2 + 2H_2O$$
$$2NaAlO_2 + CO_2 + 3H_2O \longrightarrow 2Al(OH)_3 + Na_2CO_3$$

This precipitate, when filtered, washed and ignited gives pure alumina.

2. Reduction of Alumina to Al Metal

Aluminium is obtained from alumina by electrolysis, called **Hall-Heroult process.** In this process, cathode and anode both are made up of carbon.

The electrolyte used contains Na_3AlF_6 (80-85%), CaF_2 (5-7%), AlF_3 (5-7%), Al_2O_3 (2-8%), of which Al_2O_3 is recharged intermittently. When electricity is passed, Al is deposited at cathode while O_2 is liberated at anode which reacts with C electrode to produce CO and then CO_2.



Electrolysis of alumina

Difficulties face in this process There are two main difficulties that are as follows: : (i) Pure alumina is a bad conductor of electricity, (ii) The fusion temperature of pure alumina is about 2000°C and at this temperature when the electrolysis is carried of fused mass, the metal formed vaporises as the boiling point of aluminium is 1800°C.

The above difficulties are overcome by using a mixture of alumina, cryolite (Na_3AlF_6) and fluorspar (CaF_2) in the ratio of $20:24:20$. The fusion temperature of this mixture is 900°C and it is a good conductor of electricity.

The exact mechanism of the electrolysis is not yet known. Two concepts have been proposed such as

(i) **First concept** AlF_3 from cryolite ionises as,

$$AlF_3 \rightleftharpoons Al^{3+} + 3F^-$$

Al^{3+} ions are discharged at cathode and F^- ions at anode.

At cathode, $Al^{3+} + 3e^- \longrightarrow Al$

At anode, $2F^- \longrightarrow F_2 + 2e^-$

The liberated fluorine reacts with alumina to form AlF_3 and O_2. The oxygen attacks the carbon anodes to form CO and CO_2.

$$Al_2O_3 + 3F_2 \longrightarrow 2AlF_3 + \frac{3}{2}O_2\uparrow$$
$$2C + O_2 \longrightarrow 2CO$$
$$C + O_2 \longrightarrow CO_2\uparrow$$

Anodes are replaced frequently.

(ii) **Second concept :** Alumina (Al_2O_3) ionises as,

$$Al_2O_3 \rightleftharpoons \underset{\text{Cathode}}{Al^{3+}} + \underset{\text{Anode}}{AlO_3^{3-}}$$

At cathode, $Al^{3+} + 3e^- \longrightarrow Al$

At anode, $4AlO_3^{3-} \longrightarrow 2Al_2O_3 + 3O_2\uparrow + 12e^-$

Thus, the overall chemical reaction taking place during electrolysis is

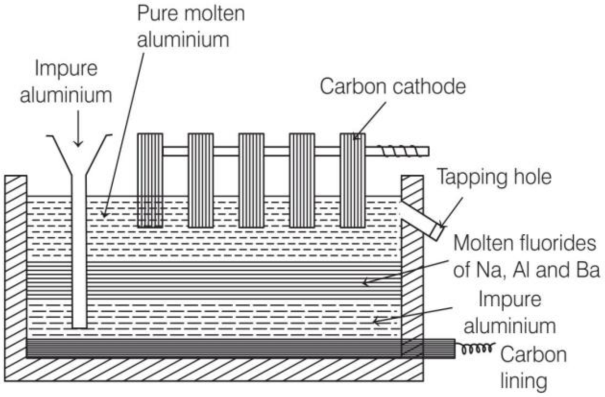
$$2Al_2O_3 \longrightarrow 4Al + 3O_2\uparrow$$

Refining of Aluminium

The aluminium obtained by reduction process is about 98% pure. In order to purify it, *Hoope's electrolytic* method is used.

Construction of cell The cell used for the refining contains three layers that differ in specific gravities. The upper most layer contains pure aluminium which acts as cathode, the middle layer contains a mixture of fluorides of Al, Na and Ba and acts as electrolyte while the lower layer contains impure aluminium which acts as anode.

Refining Process On electrolysis, pure Al is deposited at cathode from the middle layer and an equivalent quantity of Al is deposited to the lower layer. The aluminium obtained by this process is 99.98% pure.



Electrolytic refining of aluminium

Modern Method of Extraction of Al

When vapour of aluminium chloride is passed over fused oxide at 1000°C, aluminium monochloride is formed which on cooling disproportionates to give Al.

$$2Al_2O_3 + 2AlCl_3 \longrightarrow 6AlCl + 3O_2$$
$$3AlCl \longrightarrow AlCl_3 + 2Al$$

The $AlCl_3$ obtained is reused.

Physical Properties

Al is a bluish-white metal with a brilliant lusture which get destroyed due to the formation of oxide layer over it.

It is malleable and ductile in nature and can be rolled into sheets, foils and wires. Al is a very light metal (specific gravity 2.7), good conductor of heat and electricity, melts at 659°C and boils at 2450°C. On a weight to weight basis, the electrical conductivity of Al is twice that of copper.

Chemical Properties

Aluminium is a very reactive metal but formation of oxide layer over its surface reduces its reactivity.
Al shows following reactions are given as,

(i) **With air** Al is not affected by pure dry air but with moist air, a film of oxide is formed at the surface which protects the metal from further corrosion. It burns readily in oxygen giving out energy. The heat evolved in the oxidation of Al is used in **thermite process** for the reduction of oxides of Cr, Fe, Mn etc.

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3 + \text{heat}$$
$$Fe_2O_3 + 2Al \longrightarrow 2Fe + Al_2O_3 + \text{heat}$$
$$3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3 + \text{heat}$$

Al also reduces oxides of non-metals as,

$$3CO_2 + 4Al \longrightarrow 2Al_2O_3 + 3C$$
$$3SiO_2 + 4Al \longrightarrow 2Al_2O_3 + 3Si$$

(ii) **With water** Pure water does not affect pure Al. However, impure form is readily corroded by water containing salts. It decomposes boiling water evolving hydrogen.

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

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

The metal also dissolves in hot conc. solution of Na_2CO_3 as,

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

(iv) **With acids** The metal dissolves in dil. HCl and dil. H_2SO_4 solutions evolving H_2. With hot conc. H_2SO_4, SO_2 is given out. With conc. HNO_3 it does not shows, any reaction.

(v) **With halogen and nitrogen** The metal gives halides and nitrides respectively on heating.

(vi) **Displacement reactions** Al displaces Cu, Zn and Pb from the solutions of their salts as,

$$3ZnSO_4 + 2Al \longrightarrow Al_2(SO_4)_3 + 3Zn$$
$$3CuSO_4 + 2Al \longrightarrow Al_2(SO_4)_3 + 3Cu$$

Uses

Aluminium is used

- in manufacturing of household utensils, aeroplane parts, precision and surgical instruments etc.
- in HNO_3 transportation and in construction of tank for chemical plants where HNO_3 is manufactured. (Since, it rendered passive to HNO_3).
- as aluminium foil, in packing of different objects.
- for the formation of alums which is used as mordants in dyeing and paints.
- as a reducing agent.
- as building material, refractory bricks and ultra-marine.
- for sizing the paper.
- in thermite welding processes.
- in making alloys.

Some of its important alloys are tabulated below

Important Alloys of Aluminium

Alloy	Approx. composition	Uses
Magnalium	Al = 94.5%, Mg = 5.5%	Scientific apparatus, machined articles.
Duralumin	Al = 95%, Cu = 4% Mg = 0.5%, Mn = 0.5%	Aircraft parts, railroad cars, bos machinery.
Nickel alloy or Nickeloy	Al = 95%, Cu = 4%, Ni = 1%	Aircraft parts
γ-alloy	Al = 93%, Cu = 4%, Ni = 2%, Mg = 1%	Pistons and machinery parts.
Alnico	Steel = 77%, Ni = 2%, Al = 20%, Co = 1%	For making permanent magnets.
Artificial gold	Al = 10%, Cu = 90%	For making artificial ornaments, pots, paints.

Important Compounds of Boron

Some of the important compounds of elements of this group are discussed below

1. Borax, Sodium Tetraborate or Tincal

Chemical formula : $Na_2B_4O_7 \cdot 10H_2O$ or $Na_2[B_4O_5(OH)_4]$

Methods of Preparation

- It is prepared by boiling the finely powered colemanite mineral with calculated quantity of sodium carbonate solution.

$$2Ca_2B_6O_{11} + 3Na_2CO_3 + H_2O \longrightarrow 3Na_2B_4O_7 + 3CaCO_3\downarrow + Ca(OH)_2$$

- It is obtained by neutralising a solution of the boric acid by soda ash.

$$\underset{\text{Soda ash}}{Na_2CO_3} + \underset{\text{Boric acid}}{4H_3BO_3} \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2\uparrow$$

Physical Properties

Borax is a crystalline solid which exists in three forms as,

- **Prismatic borax** ($Na_2B_4O_7 \cdot 10H_2O$) is an ordinary form of borax and is obtained when a solution of the salt is crystallised at ordinary temperature.
- **Octahedral borax** ($Na_2B_4O_7 \cdot 5H_2O$) is obtained when a solution of the salt is crystallised above 60°C. This is **jeweller's borax.**
- **Borax glass** ($Na_2B_4O_7$) is anhydrous sodium tetraborate and is obtained by heating ordinary form of borax above its melting point until all the water of crystallisation is removed.

$$\underset{\text{(Colourless glassy substance)}}{\text{Borax glass}} \xrightarrow{\text{Moisture}} \text{Prismatic borax}$$

Chemical Properties

- It is sparingly soluble in **cold water** but is readily soluble in hot water. Its aqueous solution is alkaline due to hydrolysis.

$$Na_2B_4O_7 + 7H_2O \rightleftharpoons \underset{\text{Strong base}}{2NaOH} + \underset{\text{Weak acid}}{4H_3BO_3}$$

- It reacts **with conc. acid** like HCl, H_2SO_4 to form sparingly soluble boric acid as.

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$$

- When heated with NH_4Cl, it forms boron nitride.

$$Na_2B_4O_7 + 2NH_4Cl \longrightarrow 2NaCl + \underset{\text{Boron nitride}}{2BN} + B_2O_3 + 4H_2O$$

- On heating above its melting point, it loses its water of crystallisation and swells up to form a mass.
- On further heating, it melts into a liquid and then solidifies to form transparent glassy mass like bead, called the **borax bead**. This bead is employed in qualitative analysis for the detection of certain coloured radicals such as $Ni^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}$, etc.

Borax Bead Test

When a salt, containing any of these ions, is heated with borax bead on a Pt wire, the salt decomposes to corresponding oxide which combines with B_2O_3 of glassy bead and form coloured **meta borate**. This test is called **borax bead test**.

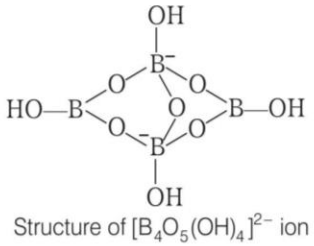
$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{-10H_2O} Na_2B_4O_7 \xrightarrow{\Delta} \underbrace{\underset{\text{Sodium metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}}_{\text{Glassy mass}}$$

$$CoO + B_2O_3 \xrightarrow{\Delta} \underset{\text{Blue}}{Co(BO_2)_2}$$

$$Cr_2O_3 + 3B_2O_3 \xrightarrow{\Delta} \underset{\text{Green}}{2Cr(BO_2)_3}$$

Structure

Borax contains the tetrahedral units, i.e. $[B_4O_5(OH)_4]^{2-}$ and its structure can be shown as,



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

Uses

Borax is used

- in leather and match industries.
- in making optical glass and heat resistant boro-silicate glassware.
- as a preservative for food.

- in borax bead test, for the detection of basic radicals.
- as a flux in metallurgy.
- as an antiseptic in the manufacture of medicinal soaps.

2. Orthoboric Acid or Boric Acid

Chemically, it is H_3BO_3 or $B(OH)_3$. Its methods of preparations physical and chemical properties are as follows

Methods of Preparation

- It can be prepared from **borax** ($Na_2B_4O_7$) or **colemanite** ore ($Ca_2B_6O_{11}$) through extraction directly.
- Besides, it can also be prepared by the action of superheated water on boron nitride (BN) and boron sulphide (B_2S_3) as,

$$BN + 3H_2O \longrightarrow H_3BO_3 + NH_3 \uparrow$$
$$B_2S_3 + 6H_2O \longrightarrow 2H_3BO_3 + 3H_2S$$

- The acid can also be obtained by the hydrolysis of BCl_3 as,

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$

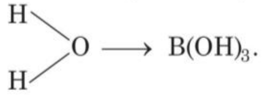
Physical Properties

It is seen as pearly white, needle like crystals with greasy feel. It is moderately soluble in water. The dissolution is accompanied by absorption of heat, i.e. its solubility increases with increase in temperature.

Chemical Properties

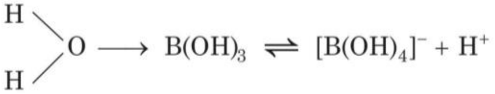
Orthoboric acid exhibits the following chemical properties as,

- **Acidic character** Boric acid is a weak acid and behaves as a monobasic Lewis acid. This is because in aqueous solution, it coordinates with a molecule of water to form a hydrated species as,



$$H_2O \longrightarrow B(OH)_3.$$

B^{3+} ion pulls the σ-electron charge of the coordinated O-atom towards itself. The coordinated oxygen, in turn, pulls the σ-electron charge of the O—H bond of the attached water molecule towards itself. This facilitates the removal of H^+ ion from the O—H bond. Thus, the aqueous solution acts as a weak acid.



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

- **Reaction with alkali solution** H_3BO_3 reacts with the aqueous solution of an alkali (e.g. NaOH, KOH) and gives various types of polymeric metaborates like $NaBO_2 \cdot 2H_2O, NaB_3O_5 \cdot 2H_2O, Na_2B_4O_7 \cdot 10H_2O, KB_5O_8 \cdot 4H_2O$ etc.

$$B(OH)_3 + NaOH(\text{dil.}) \longrightarrow \underset{\text{Sodium metaborate}}{NaBO_2 \cdot 2H_2O}$$
$$\text{or } Na^+[B(OH)_4]^-$$

$$5B(OH)_3 + KOH \longrightarrow KB_5O_8 \cdot 4H_2O + 4H_2O$$

The titration between $B(OH)_3$ and a strong alkali solution (e.g. NaOH) is not possible, because the product formed is sodium metaborate which hydrolysed to regenerate $B(OH)_3$ and NaOH.

$$Na^+[B(OH)_4]^- \longrightarrow B(OH)_3 + NaOH$$

- **Effect on heating** When heated to 100°C, H_3BO_3 loses H_2O to give metaboric acid (HBO_2) which on being heated to 160°C, gives tetraboric acid ($H_2B_4O_7$).

When $H_2B_4O_7$ is heated to redness, boron trioxide (B_2O_3) is obtained.

$$4H_3BO_3 \xrightarrow[-4H_2O]{100°C} 4HBO_2 \xrightarrow[-H_2O]{160°C} H_2B_4O_7 \xrightarrow[-H_2O]{\text{Red heat}} 2B_2O_3$$

On **heating at below 100°C,** it gives pyroboric acid which on dilution further gives H_3BO_3 as,

$$4H_3BO_3 \longrightarrow \underset{\text{Pyroboric acid}}{H_6B_4O_9} + 3H_2O$$

$$H_6B_4O_9 + 3H_2O \longrightarrow 4H_3BO_3$$

- Reaction with other important reactants are
  (i) When H_3BO_3 is treated **with sodium hydroperoxide** (NaOOH), dihydrated sodium peroxyborate, $Na_2B_2O_6 \cdot 2H_2O$ is formed.

$$2B(OH)_3 + 2NaOOH \longrightarrow Na_2B_2O_6 \cdot 2H_2O + 2H_2O$$

  (ii) When H_3BO_3 or any borate is heated **with alcohol** (C_2H_5OH), in the presence of conc. H_2SO_4, volatile triethylborate, $(C_2H_5)_3BO_3$ (ester) is formed.

$$H_3BO_3 + 3C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} (C_2H_5)_3BO_3 + 3H_2O$$

This ester burns with a green-edged flame. This property of the ester has been utilised for the identification of BO_3^{3-} radical.

  (iii) When H_3BO_3 is heated with **CaF_2 and conc. H_2SO_4**, BF_3 (volatile) is obtained. If BF_3, produced as above, is brought near the Bunsen flame, a green flame is produced.

  (iv) When H_3BO_3 is neutralised by **soda ash (Na_2CO_3)**, borax ($Na_2B_4O_7$) is obtained.

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

  (v) When H_3BO_3 is dissolved in HF, fluoroboric acid, $H^+[BF_4]^-$ (also called hydrofluoroboric acid) is obtained.

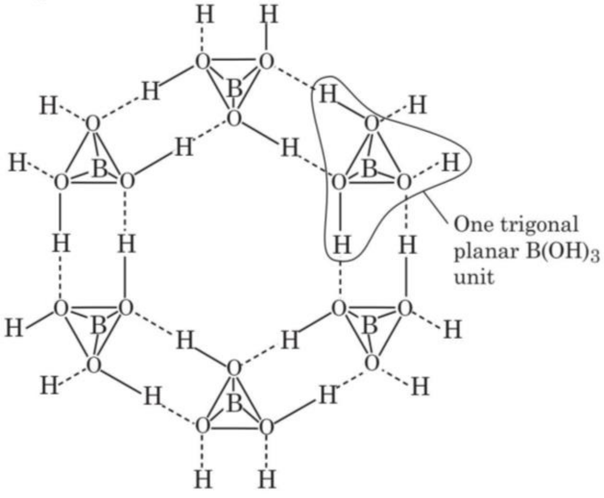
$$H_3BO_3 + 4HF \longrightarrow H^+[BF_4]^- + 3H_2O$$

  (vi) When treated with acetic anhydride $(CH_3CO)_2O$, H_3BO_3 gives boron acetate.

Structure

In solid state, boric acid has layer structure, which are linked together by van der Waals' forces and are at a distance of 318 pm from each other. Each layer is composed of various trigonal planar $B(OH)_3$ units. B atom, in each $B(OH)_3$ unit is linked with three OH groups, which are arranged at the corner of an equilateral triangle.

The structure of one layer is shown in figure below from which it may be seen that H-atom acts as a bridge between the two O-atoms, belonging to two different $B(OH)_3$ units.



Structure of boric acid

The dotted lines between O-atom of one $B(OH)_3$ unit and H-atom of the other $B(OH)_3$ unit indicates hydrogen bonds. It is due to the layer structure of boric acid which in the solid state, that are slippery to touch.

Uses

Boric acid is used

- as a preservative for milk and food stuffs.
- as a mild antiseptic in aqueous solution, for washing eyes.
- for preparing heat resistant borosilicate glass.
- for the preparation of glazes in pottery.

3. Diborane

Its formula is B_2H_6. It is the first member of B_nH_{n+4} series of boron hydrides. It is a dimer of BH_3. Its methods of preparations physical and chemical properties are as follows

Methods of Preparation

Some following methods are used for the preparation of diborane ore.

- $4BF_3 + 3LiAlH_4 \xrightarrow{\text{Diethyl ether}} 2B_2H_6 + 3LiF + 3AlF_3$
- $2NaBH_4 + I_2 \xrightarrow{\text{DIGLYME}} B_2H_6 + 2NaI + H_2$ (Lab method)
- $2BF_3 + 6NaH \xrightarrow{450\text{ K}} B_2H_6 + 6NaF$ (Industrial method)
- $2BCl_3 + 6H_2 \xrightarrow{\text{Silent electric discharge}} B_2H_6 + 6HCl$

Physical Properties

Diborane is a colourless, highly toxic gas with a boiling point of 180 K. It catches fire spontaneously on exposure to air and burns in oxygen releasing an enormous amount of energy as,

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O + 1976\text{ kJ / mol}$$

Most of the higher boranes are also spontaneously flammable in air.

Chemical Properties

Diborane shows the following chemical properties

- It gets **hydrolysed** readily as,

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

- It dissolves in strong alkali solutions giving metaborates and H_2 as,

$$B_2H_6 + 2KOH + 2H_2O \longrightarrow 2KBO_2 + 6H_2\uparrow$$

- It reacts slowly with active metals (Na, K, Ca and their amalgams). However, the reaction is faster in the presence of ether as,

$$2B_2H_6 + \underset{\text{(Alkali metals and their amalgams)}}{2M} \xrightarrow{\text{Ether}} NaBH_4 + \underset{\text{Sodium Polyborane}}{NaB_3H_8}$$

- It reacts **with CO** at 100°C and 20 atm pressure to form the carbonyl H_3BCO as,

$$B_2H_6 + 2CO \xrightarrow[20\text{ atm}]{100^\circ C} 2H_3BCO$$

- It reacts **with halogens** under different conditions to form halo diboranes as,

$$B_2H_6 + Cl_2 \xrightarrow[\text{explosive}]{25^\circ C} \underset{\text{Chloro diborane}}{B_2H_5Cl} + HCl$$

$$B_2H_6 + Br_2 \xrightarrow[\text{rapid}]{100^\circ C} \underset{\text{Bromo diborane}}{B_2H_5Br} + HBr$$

- It reacts **with halogen acids** as,

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

- It combines **with hydrides of alkali metals** to form complex hydrides as,

$$B_2H_6 + 2NaH \longrightarrow 2Na^+[BH_4]^-$$

- It adds to **alkanes** and **alkynes** in the presence of a Lewis base like THF (tetrahydro furan) or DIGLYME (diethylene glycol methyl ether) as,

$$3RCH{=}CH_2 + BH_3 \xrightarrow[\text{DIGLYME}]{\text{THF or}} \underset{\text{Trialkyl borane}}{(RCH_2CH_2)_3B}$$

$$3RC{\equiv}CH + BH_3 \xrightarrow[\text{DIGLYME}]{\text{THF or}} \underset{\text{Trialkenyl borane}}{(R{-}CH{=}CH)_3B}$$

This reaction is called **hydroboration reaction** and has been of great synthetic utility in organic chemistry.

- Diborane reacts **with NH_3** and the products formed depend upon the conditions of reaction as,

(i) At low temperature,

$$B_2H_6 + 2NH_3 \xrightarrow{\text{Low temperature}} \underset{\substack{\text{Diammoniate}\\\text{of diborane}}}{B_2H_6 \cdot 2NH_3}$$

The compound $B_2H_6 \cdot 2NH_3$ is ionic and exists as

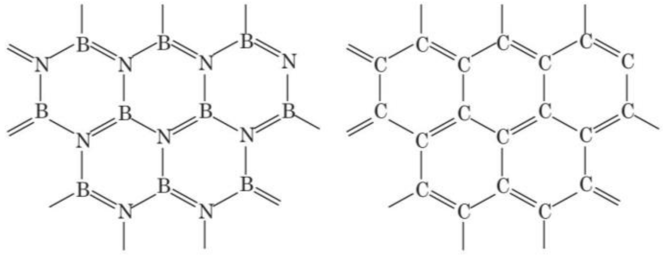
$$[H_3N \longrightarrow BH_2 \longleftarrow NH_3]^+ [BH_4]^-.$$

It forms borazine on heating.

(ii) At high temperature

$$nB_2H_6 \xrightarrow[\text{at high temperature}]{\text{Excess } NH_3} \underset{\text{Boron nitride}}{(BN)_n}$$

Boron nitride is a white crystalline solid and resembles graphite in structure as shown below

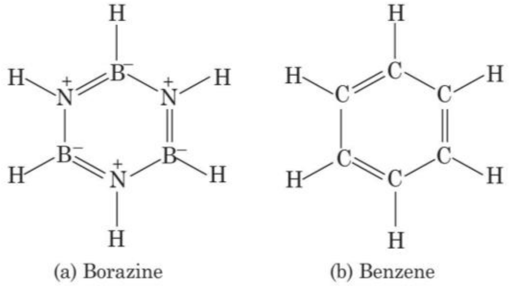


(a) Boron nitride (b) Graphite

Similarity in the structure of boron nitride and graphite

(iii) $3B_2H_6 + 6NH_3 \xrightarrow{200°C} \underset{\substack{\text{Borazine}\\\text{or borazole}}}{2B_3N_3H_6} + 12H_2$

Borazine or borazole or inorganic benzene.



(a) Borazine (b) Benzene

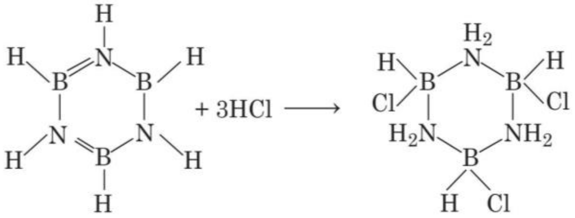
Similarity in the structure of borazine and benzene

Because of its similarities with benzene in structure, and some physical and chemical properties borazine is also called **inorganic benzene.**

Preparation It can also be prepared by heating BCl_3 and NH_4Cl together or by treating $NaBH_4$ with NH_4Cl. Its structure is similar to that of benzene as shown below.

$$2Cl_3B_3H_3N_3 + 6NaBH_4 \longrightarrow 2B_3N_3H_6 + 3B_2H_6 + 6HCl$$

Properties In benzene, the C=C bonds are non-polar and the nucleus is very resistant to addition reactions, whereas borazole nucleus is fairly reactive on account of its polarities. Thus, it readily adds three molecules of H_2O ; CH_3OH, CH_3I, HCl and more negative group generally attaches to boron atoms.



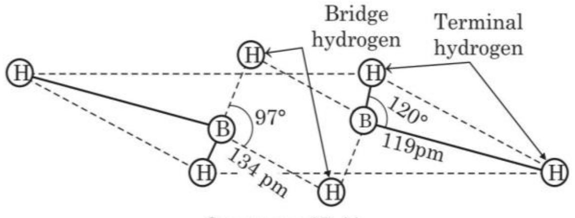
Borazole decomposes slowly on standing and undergoes hydrolysis at high temperatures.

$$B_3N_3H_6 + 9H_2O \xrightarrow{\text{High temperature}} 3B(OH)_3 + 3NH_3 + 3H_2$$

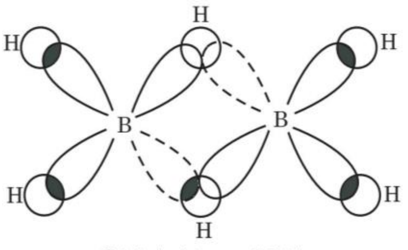
Structure of Diborane

Boranes provide interesting examples of **electron deficient compounds.** The structure of diborane shows that the four terminal hydrogens along with two boron atoms lie in one plane.

Two bridging hydrogens are seen to present above and below this plane. The four terminal B—H bonds are regular two centred two electron ($2c$-$2e^-$) bonds while two bridge bonds (B—H—B) are different and can be described in terms of three centred two electron ($3c$-$2e^-$) bonds as shown in the figure below.



Structure of B_2H_6



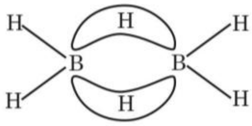
Orbital picture of B_2H_6

According to molecular orbital theory, each B-atom uses sp^3 hybrid orbitals for bonding.

Out of four sp^3 hybrid orbitals one orbital is empty, i.e. without any electron, and is shown with broken lines in the figure above.

So, the involvement of one half-filled orbital of one B-atom with one empty orbital of other B-atom and half-filled orbital of hydrogen atom results in three centred (B — H — B) two electron (one contributed by one of the B atoms and other by hydrogen atom) electron deficient bridge bond.

These type of bond is also called **banana bond** due to its banana like shape as shown in the figure below.



Banana bonds in B_2H_6

Uses

Diborane is used

- as a reducing agent in organic reaction.
- for the synthesis of a number of borohydrides like $LiBH_4$, $NaBH_4$ etc.
- as a fuel for supersonic rockets.

4. Boron Trifluoride

It is an **electron deficient compound** of formula BF_3. It is generally used as a **Lewis acid** and catalyses many organic reactions. Its methods of preparation and properties are as follows

Methods of Preparation

BF_3 is obtained by

- heating B_2O_3 or borax with calcium fluoride and conc. H_2SO_4 as,

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 \xrightarrow{\Delta} 3CaSO_4 + 3H_2O + 2BF_3$$

$$Na_2B_4O_7 + 6CaF_2 + 8H_2SO_4 \xrightarrow{\Delta} 2NaHSO_4 + 6CaSO_4 + 4BF_3 + 7H_2O$$

BF_3 is collected over Hg.

- heating together B_2O_3, ammonium fluoroborate and concentrated sulphuric acid, as

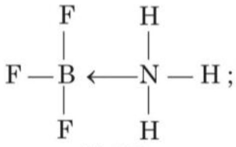
$$B_2O_3 + \underset{\text{Ammonium fluoroborate}}{6NH_4BF_4} + 6H_2SO_4 \xrightarrow{\Delta} 8BF_3 + 6NH_4HSO_4 + 3H_2O$$

- the thermal decomposition of diazonium tetrafluoroborate as,

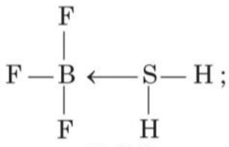
$$\underset{\substack{\text{Diazonium}\\ \text{tetrafluoroborate}}}{C_6H_5N_2BF_4} \xrightarrow{\Delta} C_6H_5F + N_2 + \underset{\text{Pure}}{BF_3}$$

Physical and Chemical Properties

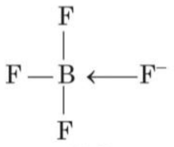
- BF_3 is a colourless pungent gas (m.p. –127.1°C and b.p. –99.9°C) which strongly fumes in moist air. It is exceedingly soluble in water that's why it is collected over Hg.
- BF_3, being an electron deficient compound, can accept a lone pair of electrons, thus it is used as a catalyst in a number of organic reactions behaves as Lewis acid, it can form complexes like



with NH_3



with H_2S



with F^-

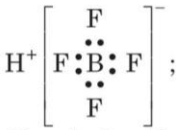
- BF_3 combines with water forming two hydrates, i.e. $BF_3 \cdot H_2O$ (mp.10.18°C) and $BF_3 \cdot 2H_2O$ (m.p. 6.36°C). It gets hydrolysed in aqueous solutions yielding boric acid and hydrofluoroboric acid as,

$$BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HF$$

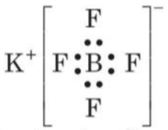
If we take BF_3 in excess, it is dissolved in HF to give hydrofluoroboric acid $H[BF_4]$ as,

$$BF_3 + HF \longrightarrow H^+[BF_4]^-$$

Fluoroboric acid forms definite salts, known as fluoroborates or borofluorides, e.g. KBF_4, in which boron is tetracovalent (as in the acid also).



Fluoroboric acid ;



Potassium borofluoride

On strong heating, these salts decompose into BF_3 and metal fluoride.

$$KBF_4 \xrightarrow{\Delta} KF + BF_3$$

Important Compound of Aluminium

Some of the important compounds of elements of this group are discussed below.

1. Aluminium Chloride ($AlCl_3$)

It is also called as aluminium trichloride. Its methods of preparation and properties are as follows

Methods of Preparation

(i) **Hydrated aluminium chloride** $AlCl_3$ is prepared by dissolving Al in excess of HCl. It is deposited as the crystals of $Al_2Cl_6 \cdot 12H_2O$. This hydrate on heating decomposes to give alumina as,

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2\uparrow$$

$$Al_2Cl_6 \cdot 12H_2O \xrightarrow{\Delta} Al_2O_3 + 6HCl + 9H_2O$$

(ii) **Anhydrous $AlCl_3$** For preparing anhydrous $AlCl_3$, Al is heated in a steam of dry chlorine or hydrogen chloride gas as, $2Al + 3Cl_2 \xrightarrow{\Delta} 2AlCl_3$

This reaction is extremely exothermic.

(iii) **Other important methods**

- A mixture of Al_2O_3 and C is strongly heated in dry chlorine gas as,

$$Al_2O_3 + 3Cl_2 + 3C \xrightarrow{\Delta} 2AlCl_3 + 3CO$$

- A mixture of CO and Cl_2 is passed over heated Al_2O_3 as,

$$\underset{\text{Heated}}{Al_2O_3} + 3CO + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO_2$$

- When AlI_3 reacts with CCl_4, also gives $AlCl_3$.

$$4AlI_3 + 3CCl_4 \longrightarrow 4AlCl_3 + 3CI_4$$

Properties

- $AlCl_3$ is white in its pure form and sublimes at 183°C. It is extremely hygroscopic and fumes strongly in moist air due to the formation of HCl as,

$$2AlCl_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 6HCl$$

- When dissolved in water, it changes into hydrated aluminium chloride which is ionic in nature.

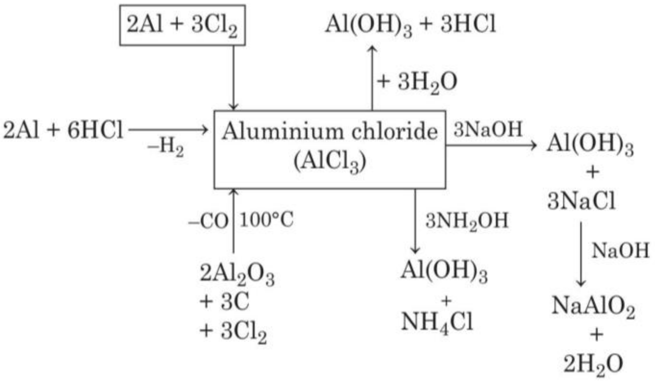
$$Al_2Cl_6 + 12H_2O \longrightarrow 2AlCl_3 \cdot 6H_2O$$

- Aluminium chloride forms addition compounds with the molecules capable of donating lone pair of electrons e.g. NH_3, phosphine, $COCl_2$ etc.

$$Al_2Cl_6 + 12NH_3 \longrightarrow 2(AlCl_3 \cdot 6NH_3)$$

- When sodium hydroxide is added to the solution of aluminium chloride drop by drop, a white gelatinous precipitate appears which dissolves in excess of sodium hydroxide forming sodium meta-aluminate.

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

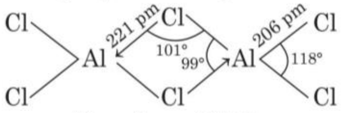


Flow chart of preparation and properties of $AlCl_3$

Structure

It exists as a monomer above 800°C with sp^2 hybridisation, trigonal planar structure and three pure covalent bond. However, below 400°C, it exists as a dimer with sp^3 hybridisation (three pure covalent and one coordinate bond). In solid state also, $AlCl_3$ exists as a dimer and is non-conducting.

The structure of Al_2Cl_6 can be represented as,



Dimer form of Al_2Cl_6

The dimeric formula exists in non-polar solvents such as benzene but due to higher heat of hydration, it changes into $[Al(H_2O)_6]^{3+}$ and $3Cl^-$ ions in aqueous solution.

Uses

- $AlCl_3$ is a strong Lewis acid and readily forms adducts with Lewis base.
- It is use as a catalyst in 'organic chemistry' and also used in the manufacture of dyes, drugs and pharmaceuticals.

2. Alums

The name *alum*, is given to all double salts with the formula, $(M')_2SO_4 \cdot (M'')_2(SO_4)_3 \cdot 24H_2O$.

where, M' = univalent basic radicals like Na^+, K^+, NH_4^+, Ag^+ etc.

M''' = trivalent metal like Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+} etc.

Some common examples include $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, potash alum or common alum;
$Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, sodium alum,
$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, ammonium alum,
$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$, chrome alum.

Methods of Preparation

Common alum is potash alum, $[KAl(SO_4)_2 \cdot 12H_2O]$ and is prepared by following methods

(i) **From alunite or alum stone** Alunite is boiled with dilute sulphuric acid and filtered. The filtrate is mixed with a requisite amount of potassium sulphate and crystallised.

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3 + 6H_2SO_4 \longrightarrow K_2SO_4 + 3Al_2(SO_4)_3 + 12H_2O$$
$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow 2[KAl(SO_4)_2 \cdot 12H_2O]$$

(ii) **From bauxite** Bauxite is dissolved in sulphuric acid, treated with calculated amount of potassium sulphate and crystallised.

(iii) **From pyrites shale with $Al_2O_3 \cdot xSiO_2$ and FeS_2** It is also known as alum shale which is aluminium silicate mixed with iron sulphide. It is roasted in excess of air when ferrous sulphide gives ferrous sulphate and sulphuric acid and the latter then reacts with alumina to form aluminium sulphate.

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2FeSO_4 + 2H_2SO_4$$
$$Al_2O_3 \cdot xSiO_2 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + xSiO_2 + 3H_2O$$

Ferrous sulphate is removed by **fractional crystallisation** and potassium sulphate is added to the mother liquor when potash alum crystallises out. Being an ionic compound, it does not contain discrete molecules and is usually represented as, $[KAl(SO_4)_2 \cdot 12H_2O]$.

Properties

All the alums are **isomorphous,** form mixed crystals in all proportions.

- Each alum has different melting point. These are usually much more soluble in hot water than in cold water.
- On heating, alum loses its water of crystallisation and swells up leaving behind a porous mass, called the **burnt alum.**

Uses

- It is used in purification of water, water proofing of textiles and in dyeing and paper industry.
- It is also employed as a styptic to arrest bleeding.

3. Pseudoalums

These are the double sulphate of divalent ions and trivalent ions. These have general formula,

$$MSO_4 \cdot (M'')_2(SO_4)_3 \cdot 24H_2O$$

Here, M = bivalent metal, M'' = trivalent metal.

Some examples are $MnSO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

$$FeSO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$$

Pseudoalums are not isomorphous with alums.

Example 2. *In the following reaction sequence Z is*

$$Z + 3LiAlH_4 \longrightarrow X + 3LiF + 3AlF_3$$
$$X + 6H_2O \longrightarrow Y + 6H_2$$
$$X + 3O_2 \xrightarrow{\Delta} B_2O_3 + 3H_2O$$

(NCERT Exemplar)

(a) boron trifluoride
(b) boron trichloride
(c) diborane
(d) Both (a) and (b)

Sol. (a) $\underset{(Z)}{4BF_3} + 3LiAlH_4 \longrightarrow \underset{\substack{\text{Diborane}\\(X)}}{2B_2H_6} + 3LiF + 3AlF_3$

$$\underset{(X)}{B_2H_6} + 6H_2O \longrightarrow \underset{\text{Orthoboric acid}}{2H_3BO_3} + 6H_2\uparrow$$

$$\underset{(X)}{B_2H_6} + 3O_2 \xrightarrow{\Delta} B_2O_3 + 3H_2O$$

Thus, the compound (Z) is boron trifluoride (BF_3).

Elements of Group 14 (or IVA) and their Compounds

The group 14 (IVA) contains 5 elements namely **carbon** (C), **silicon** (Si), **germanium** (Ge), **tin** (Sn) and **lead** (Pb). Carbon is an essential constituent of all organic matter while silicon is an important constituent of inorganic matter.

Occurrence

Carbon is the 17th most abundant element and is found both in native and combined state. Silicon occurs most abundantly, next only to oxygen, up to 26% in earth crust as silica and silicates. Ge occurs rather sparsely. Sn occurs chiefly as SnO_2 while lead occurs mainly as PbS.

General and Physical Properties

The trends of various general and physical properties of elements of group 13 are discussed below.

1. **Electronic configuration** General electronic configuration of elements of this group is ns^2np^2 (where, $n = 2, 3, 4, \ldots$)

   Although, they have same number of valence electron, yet these are known to exhibit a variation in properties. This is because, they differ in configuration of penultimate shell.

2. **Molar volumes and atomic radius** Molar volumes and atomic radius increase on moving down the group. But there is less increase in atomic radii from silicon onward. This is due to the fact that shielding effect of d^{10} electrons in Ge and Sn and $f^{14}d^{10}$ electrons in Pb is less.
   Their atomic radii are smaller than the corresponding elements of group 13 due to increase in effective nuclear charge (Z_{eff}).

3. **Melting and boiling points** The melting and boiling points of carbon are extreme high. The values decrease as we move from carbon to lead. The melting point of Sn and Pb are relatively low because the M—M bonds are weaker. They do not use all the four outer electrons for metallic bonding.

4. **Ionisation energy** Ionisation energy of C is very high and decreases sharply as we move from carbon to silicon. It is because there is an appreciable increase in the size of Si atom.

   After Si, the decrement is regular but not so much from Si to Sn due to the appearance of d-electrons and from Sn to Pb due to the appearance of f-electrons there is a marginal increase in atomic radius which increases the ionisation energy marginally.

   The d-electrons and f-electrons show very less or almost no screening due to very less electrons density in them.

5. **Metallic or electropositive character** The metallic or electropositive character increases as down the group.

   $$\underbrace{\text{C} \quad \text{Si}}_{\text{Non-metals}} \quad \underbrace{\text{Ge}}_{\text{Metalloid}} \quad \underbrace{\text{Sn} \quad \text{Pb}}_{\text{Metals}}$$

   This change is due to less effective nuclear charge and increased number of available orbitals with increase in the size of the atom.

6. **Electronegativity** C is the most electronegative element of this group. While on moving down the group electronegativity decreases upto Si and then remains constant.

   Such a different trend in electronegativity is due to the fact that d-orbitals are filled up in the case of Ge and Sn while in the case of Pb f-orbitals are filled up.

7. **Covalency** Carbon, due to the absence of d-orbitals, 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.
   They form pentacoordinated and hexacoordinated complex.
   e.g. SiF_4 can combine with $2F^-$ ions.

   $$SiF_4 + 2F^- \longrightarrow [SiF_6]^{2-}$$

   But, $[CF_6]^{2-}$ does not exist.

Physical Properties of Elements of Group 14

Property	Carbon	Silicon	Germanium	Tin	Lead
Electronic configuration	$[\text{He}]2s^22p^2$	$[\text{Ne}]3s^23p^2$	$[\text{Ar}]3d^{10},4s^24p^2$	$[\text{Kr}]4d^{10},5s^25p^2$	$[\text{Xe}]4f^{14},5d^{10},6s^26p^2$
Atomic number	6	14	32	50	82
Molar mass (g mol^{-1})	12.00	28.086	72.59	118.89	207.19
Density (g cm^{-3})	3.52	2.49	5.35	7.30	11.34
Atomic radius (Å)	0.77	1.17	1.22	1.41	1.44
Molar volume ($\text{cm}^{-3}\ \text{mol}^{-1}$)	3.4	11.4	13.6	16.3	18.27
Melting point (°C)	4100	1410	937.5	231.8	327.4
Boiling point (°C)	4833	2680	2830	2270	1725
Electronegativity Ionisation enthalpy (kJ mol^{-1})	2.5	1.8	1.8	1.8	1.8
$\Delta_i H_1$	1086	786	761	708	715
$\Delta_i H_2$	2352	1577	1537	1411	1450
$\Delta_i H_3$	4620	3228	3300	2942	3081
$\Delta_i H_4$	6220	4354	4409	3929	4082
Oxidation states (stable)	+4	+4	+2, +4	+2, +4	+2, +4

8. **Catenation** The ability of like atoms to link together, through covalent bond is called **catenation**. Carbon exhibits the remarkable property of catenation. The tendency of catenation depends upon the strength of element-element bond which is described in terms of bond energy.

   The bond energy values for different elements of this group are given as,

Bond Energies of Elements of Carbon Family

Bond	**Bond energy** (kJ/mol)
C—C	354
Si—Si	222
Ge—Ge	167
Sn—Sn	155

The abvoe table shows that the bond energy is maximum in case of carbon and minimum in case of Sn. Thus, we can say the tendency of catenation decreases down the group as,

$$\text{C} > \text{Si} > \text{Ge} > \text{Sn} > \text{Pb}$$

The reason for greater tendency of carbon for catenation than other elements may further be explained by the fact that C—C bonds energy is approximately of the same value as the energies of bonds between carbon and other elements. On the other hand, Si—Si bond is weaker than the bonds between silicon and other elements.

Bond	Bond energy (kcal/mol)	Bond	Bond energy (kcal/mol)
C—C	83 kcal/mol	Si—Si	54 kcal/mol
C—O	86 kcal/mol	Si—O	88 kcal/mol
C—Cl	81 kcal/mol	Si—C	186 kcal/mol

Carbon forms a number of compounds in which large number of carbon atoms are linked together in the form of straight chains, branched chains or closed rings.

The property of catenation is responsible for a very large number of compounds of carbon. Although, Sn and Pb have hardly any tendency for catenation.

9. **Allotropy** It is the tendency of an element to exist in different forms. Almost all members of this group show allotropy, e.g.

- Carbon exists in crystalline forms (e.g. diamond and graphite) and microcrystalline forms, (e.g. coal, coke, charcoal, carbon black etc.) Microcrystalline forms were previously regarded as amorphous.

  Amorphous = without definite structure, All the microcrystalline forms have finely divided graphite structure.

  - Si also exists in two allotropic forms, i.e. grey crystalline form and brown amorphous powder. These forms differ in particle size and content of impurities. The amorphous variety fuses on strong heating and solidifies on cooling to give the crystalline form.
  - Germanium exists in two crystalline forms, while tin exists in three solid forms namely grey tin, white tin and rhombic tin. Out of these, white tin is the most common form of tin as it shows the stability at room temperature.

$$\text{Grey} \overset{18°\text{C}}{\rightleftharpoons} \text{White} \overset{161°\text{C}}{\rightleftharpoons} \text{Rhombic}$$

The densities of the three forms are 5.74, 7.32 and 6.55 g/cc respectively. White tin is not only the heaviest but also the most stable form. The conversion of white tin into grey tin takes place very slowly at 18°C (transition temperature). However, if the temperature is low as –50°C and a small amount of grey tin is also present, the conversion becomes very rapid. This conversion is known as **tin pest or tin disease.**

10. **Oxidation state and nature of compounds** All the elements in common, have the oxidation state of +4 except C. C shows only +4 oxidation state but other elements also show +2 oxidation state. **The stability of +2 oxidation state increases while that of +4 oxidation state it decrease on moving down the group.**

- This is done due to inert pair effect.
- In the case of lead, Pb^{2+} compounds are more stable than Pb^{4+} compounds. The Pb^{4+} compounds. act as oxidising agents.

$$\underset{\substack{\text{Less stable}\\ \text{(oxidising agent)}}}{Pb^{4+}} + 2e^- \longrightarrow \underset{\text{More stable}}{Pb^{2+}}$$

- Due to its small sizes, the M^{4+} ions of Pb have more covalent character than the electrovalent in their compounds. (The covalent nature in the compounds of Pb^{4+} ions can be explained on the basis of high polarisation produced by such ions).
- The compounds of Ge^{2+} are unstable while compounds of Ge^{4+} are stable. Thus, the compounds of Ge^{2+} get oxidised into Ge^{4+} easily and act as a reducing agent.

$$\underset{\substack{\text{Less stable}\\ \text{(reducing agent)}}}{Ge^{2+}} \xrightarrow{-2e} \underset{\text{More stable}}{Ge^{4+}}$$

- The compounds of Sn^{2+} are less stable than Sn^{4+}. Thus, Sn^{2+} compounds also act as reducing agents. The order is follows as

$$Ge^{2+} < Sn^{2+} < Pb^{2+}$$
$$Ge^{4+} > Sn^{4+} > Pb^{4+}$$

Chemical Properties

The elements of this group are relatively less reactive and with in a group reactivity does not increase or decrease in a proper way. Lead often appears more unreactive than expected. Various chemical properties of this group are as follows

1. **Reactivity toward oxygen** Elements of group 14 form oxides when heated in presence of oxygen. These are mainly of two types, i.e. MO (monoxide) and MO_2 (dioxide).
2. **Reaction with water** C, Si and Ge do not react with water while Sn reacts with steam and forms SnO_2 and H_2.

$$Sn(s) + 2H_2O(g) \xrightarrow{\Delta} SnO_2(g) + 2H_2(g)$$

Lead also remains unaffected due to the formation of a protective film of lead oxide over its surface.

3. **Reactivity toward halides** Except carbon all the elements of this group form halides of type MX_2 and MX_4 ($X =$ F, Cl, Br, I) on reacting with halogen under suitable conditions.

Hydrides

All the elements of this group form covalent hydrides. The number of stable hydrides and the ease of their formation decreases on moving down the group. Owing to which their tendency to act as reducing agent increases down the group. Decreasing order of stability

$$CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$$

Hydrides of different elements of the groups are discussed as :

1. Hydrides of Carbon

Carbon forms a number of hydrides which are known as **hydrocarbons.** We study them completely in 'organic chemistry'.

2. Hydrides of Silicon

- These hydrides are similar to those of carbon which are less stable and much less in number. These are called **silanes** and have the general formula Si_nH_{2n+2}. Silanes up to $n = 8$ are known. The first two members are colourless gases while 3rd and subsequent members are liquids. SiH_4 is stable at room temperature and the thermal stability of silanes decreases with increasing chain length.

Some important facts related to silanes are as follows

- Silanes are produced by the action of acids on metallic silicides as,

$$Mg_2Si + 4HCl \longrightarrow 2MgCl_2 + SiH_4$$

- Silanes are much less stable than corresponding alkanes and their structure is analogous to that of alkanes. Infact they are spontaneously inflammable and explosive in air.
- They decompose slowly when brought in contact with water as,

$$SiH_4 + 3H_2O \longrightarrow H_2SiO_3 + 4H_2\uparrow$$

- These are soluble in strong alkali solutions in the presence of air and evolve hydrogen gas.
- Silanes, being oxidised easily, have strong reducing properties. These are reduce permangnate to Mn (II), Hg (II) to Hg (I) or even Hg (0); Fe (III) to Fe (II) and copper (II) to copper hydride.
- With Cl_2 and Br_2, they react with violent explosion even at ordinary temperatures. But treatment of SiH_4 with HCl or HBr at 100°C in the presence of $AlCl_3$ as a catalyst results in substitution of hydrogen atoms by chlorine or bromine as,

$$SiH_4 + HCl \xrightarrow{AlCl_3} \underset{\text{Halo (chloro) silane}}{SiH_3Cl} + H_2\uparrow$$

3. Hydrides of Germanium

These hydrides are called **germanes** and have the general formula, $[Ge_nH_{2n+2}]$. Germanes upto $n = 5$ are known. Three hydrides are more commonly known, i.e. monogermane (GeH_4), digermane (Ge_2H_6) and trigermane (Ge_3H_8). Some points related to germanes are as follows

- These are prepared by the same way as silanes and the mixture contains mono, di and trigermanes. From the mixture individual germanes can be separated by fractional distillation.

- First two germanes are colourless gases while higher members are liquids. These are less volatile and less reactive than corresponding silanes, e.g. in comparison to SiH_4, the GeH_4 does not ignite when brought in contact with air. Also unlike silanes, they are not attacked by water.
- Monogermane unlike monosilane is not attacked by 30% NaOH or KOH. Digermane evolves hydrogen under these conditions. At higher temperatures these decompose to give germanium and hydrogen.

4. Hydrides of Tin

Two hydrides of tin namely **monostannane** (SnH_4) and **distannane** (Sn_2H_6) are known.

Important points related to stannanes or tin are as follows

- SnH_4 is obtained as a gas by reducing tin (IV) chloride with ethereal $Li[AlH_4]$. It is also formed by the action of atomic hydrogen on metallic Sn or by the action of $SnCl_2$ with $NaBH_4$.
- SnH_4 is not stable and decomposes slowly even at room temperature into Sn and hydrogen. Decomposition is easier above 145°C. It is resistant to dilute aqueous acids and alkalies.

There is some doubt about the existence of lead hydride although, it is claimed that it is formed in minute quantities as a gas when a lead magnesium alloy is dissolved in dilute acids.

Halides

The elements of group 14 form MX_4 and MX_2 type of halides (where, $X = F, Cl, Br, I$) such as,

1. Tetrahalides (MX_4)

All the tetrahalides (i.e. MX_4) have covalent nature and are sp^3 hybridised.

The thermal stability of halides of different this group elements with a common halogen decreases with increasing atomic number.

$$CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$$

The thermal stability of tetrahalides of the same element decreases with increase in molecular mass of the tetrahalide.

$$CF_4 > CCl_4 > CBr_4 > CI_4$$

Other facts related to tetrahalides of element of this group are as follows.

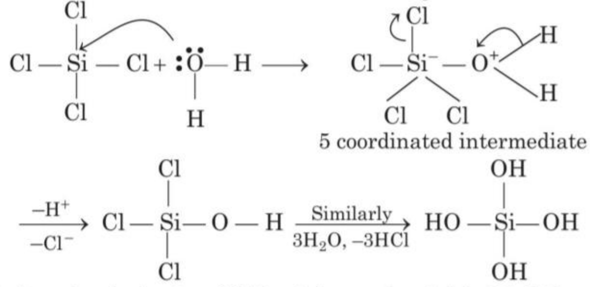
- The tetrafluorides of C, Si and Ge are gases while of Sn and Pb are solids. The last two have more ionic character than the first three.
- All the tetrachlorides of group 14 elements are liquids with $PbCl_4$ having lesser tendency to become liquid. CCl_4 is used for preparing freons such as $CFCl_3, CF_2Cl_2$ which are used in refrigeration.
- CBr_4 is a solid, while tetrabromides of Si, Ge and Sn are liquids.
- The tetraiodides of first four elements are solids. However, $PbBr_4$ and PbI_4 are unknown.

  $PbBr_4$ and PbI_4 compounds does not exist. This is due to the of strong oxidising nature of Pb^{4+}. The ions Br^- and I^- are reducing agents, i.e. in the presence of these ions, Pb^{4+} ions are reduced to Pb^{2+} ions.

$$Pb^{4+} + 2Br^- \longrightarrow Pb^{2+} + Br_2$$
$$Pb^{4+} + 2I^- \longrightarrow Pb^{2+} + I_2$$

- Due to the absence of *d*-orbitals. The tetrahalides of C are not hydrolysed by water under normal conditions while the tetrahalides of other elements are readily hydrolysed due to the availability of empty *d*-orbitals in them.

  The mechanism of hydrolysis of $SiCl_4$ is as,



Infact, hydrolysis of SiF_4 ultimately yields H_2SiF_6 (fluorosilicic acid).

$$3SiF_4 + 2H_2O \longrightarrow SiO_2 + \underset{\text{Fluorosilicic acid}}{2H_2SiF_6}$$

Fluorosilicic acid is a strong acid and exists largely in ionised state as,

$$H_2SiF_6 + 2H_2O \longrightarrow 2H_3O^+ + [SiF_6]^{2-}$$

(GeF_4 also undergoes hydrolysis in the same manner).

- The tetrahalides of carbon do not form complexes because of the unavailability of empty *d*-orbitals while tetrahalides of other elements form the complexes like $[SiF_6]^{2-}$, $[GeF_6]^{2-}$, $[SnCl_6]^{2-}$. These ions involve sp^3d^2 hybridisation with octahedral structure.

2. Dihalides (MX_2)

Carbon does not form dihalides while silicon along with Ge, Sn and Pb form dihalides of MX_2 type. These dihalides are more ionic in character. These dihalides can be prepared as,

$$SiCl_4 + Si \xrightarrow[1100°C]{\text{Above}} 2SiCl_2$$

$$GeX_4 + Ge \xrightarrow{\Delta} \underset{\text{(Strong reducing agent)}}{2GeX_2}$$

$$SnCl_4 + Sn \xrightarrow{\Delta} \underset{\text{(Anhydrous Tin chloride)}}{2SnCl_2}$$

($SnCl_2$ on reaction with weak alkali followed by dehydration in the absence of air, gives SnO).

$$Pb(NO_3)_2 + 2HF \longrightarrow \underset{\text{ppt.}}{PbF_2\downarrow} + 2HNO_3$$

The stability of dihalides increases on moving down the group. $PbCl_2 > PbCl_4$ (stability).

Lead dihalides are sparingly soluble in cold water that's why these are obtained differently from other dihalides.

Some trihalides of C, Si and Ge are also known. e.g. $CHCl_3, SiHCl_3, GeHCl_3$ etc. Lead and tin do not form such compounds.

Example 3. *Consider the following statements*

I. *Lead (II) chloride reacts with* Cl_2 *to give lead (IV) chloride*

II. *Lead (IV) chloride is highly unstable towards heat.*

III. PbI_4 *exists.*

The incorrect statement(s) is/are

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

Sol. (c)

(I) Due to inert pair effect, Pb is more stable in $+2$ state than in $+4$ oxidation state. Therefore, lead (II) chloride does not react with Cl_2 to give lead (IV) chloride. (incorrect)

(II) Lead (IV) chloride on heating decomposes to give lead (II) chloride and Cl_2 because lead in $+2$ oxidation state is more stable than in $+4$ oxidation state. (correct)

$$PbCl_4(l) \xrightarrow{\Delta} PbCl_2(s) + Cl_2(g)$$

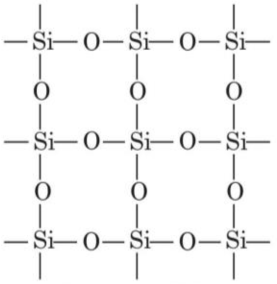
(III) Due to strong oxidising power of Pb^{4+} ion and reducing power of I^- ion, PbI_4 does not exist. (incorrect)

Oxides

- The 14th group elements form two types of oxides, namely, **monoxides** of formula MO, e.g. CO, SiO, GeO, SnO and PbO and **dioxides** of formula MO_2, e.g. $CO_2, SiO_2, GeO_2, SnO_2$ and PbO_2. Lead also forms Pb_3O_4 which infact is a mixed oxide of PbO and PbO_2, i.e. $2PbO \cdot PbO_2$.
- Acidic character of dioxides decreases and basic character increases, on moving down the group.

$$\underbrace{CO_2,\ SiO_2}_{\text{Acidic}}\quad \underbrace{GeO_2, SnO_2}_{\text{Amphoteric}}\quad \underbrace{PbO_2}_{\text{Weakly basic}}$$

- CO_2 is a gas and SiO_2 is a hard solid with a very high melting point. It is due to the fact that smaller atom of C (radius 0.77 Å) does not permit the oxygen to combine with another C-atom while fairly large atom of silica (1.17 Å) permits the sharing of single oxygen atom between two Si atoms as shown below



Structure of SiO_2

- Among monoxide CO is neutral, GeO is acidic, SnO and PbO are amphoteric.

Unique Behaviour of Carbon

The properties of carbon are quite different from other members of the group this is due to

- size of carbon is smallest among the group
- it has high electronegativity
- it has high ionisation enthalpy
- of the non-availability d-orbitals

Its unique properties are as follows

- Its melting and boiling points are very high as compared to other members of the group.
- It has maximum tendency of catenation.
- It has a high tendency of formation of $p\pi$-$p\pi$ multiple bonds either with its own atoms (e.g. $C=C, C\equiv C$) or with other atoms such as O, N, S (e.g. $C=O, C\equiv N, C=S$ etc.) while other member of this group have a tendency of $d\pi$-$p\pi$ bonding.
- Maximum covalency of carbon is four while other members can expand their covalency upto 6.
- Carbon remains unaffected by alkalies while other members reacts with alkali.

Similarities of Carbon with Si

Some following characteristics of carbon exhibits resemblance with silicon are as,

- Carbon is the essential constituent of the animal and vegetable kingdom (organic) while silicon is the essential constituent of the mineral kingdom (inorganic).
- Both of these elements, possess an electronic configuration ending with $ns^2\ np^2$ configuration and show a tetracovalency.
- They are both typical non-metals and form oxides, hydrides, etc. The higher oxides of both these elements are acidic in nature.
- Carbon and silicon both atoms possess catenation property. Some other similarities are given in table below.

Similarity between the Compounds of C and Si

Compounds	Carbon	Silicon
Dioxides	CO_2, acidic formed by burning carbon in air of oxygen.	SiO_2, acidic, formed by burning silicon in air or oxygen
Acids	H_2CO_3 (carbonic acid), $(COOH)_2$ (oxalic acid)	H_2SiO_3 (meta-silicic acid) $(SiOOH)_2$ (silico-oxalic acid)
Hydrides	CH_4 Methane C_2H_6 Ethane	SiH_4 Silico-methane Si_2H_6 Silico-ethane
Halides	CCl_4, CI_4	$SiCl_4$, SiI_4
Other compounds	$CHCl_3$ (chloroform) $CHBr_3$, CHI_3, etc.	$SiHCl_3$ (silico-chloroform) $SiHBr_2$, $SiHI_3$, etc.

Points of Difference with Si

Inspite of many similarities, there are some dissimilarities which are as follows

- Carbon dioxide is a gas while silica is a hard solid.
- Carbon tetrachloride and chloroform are stable liquids while the corresponding compounds of silicon are not so stable and are easily hydrolysed.
- Hydrides of carbon, (e.g. CH_4,C_2H_6) are very stable while those of silicon, (e.g. SiH_4) are easily decomposed by the common reagents, like alkalies, silver nitrate, etc.
- Oxalic acid, $(COOH)_2$ is much more stable than silico-oxalic acid $(SiOOH)_2$.
- The maximum covalence of carbon is four, while that of silicon is six.
- Carbon does not melt at any temperature, silicon does melt at high temperature.
- Silicon is a bad conductor of electricity while some forms of carbon are good conductors.

Example 4. *The stability of dihalides of* Si, Ge, Sn *and* Pb *increases steadily in the sequence*

(a) $GeX_2 < SiX_2 < SnX_2 < PbX_2$
(b) $SiX_2 < GeX_2 < PbX_2 < SnX_2$
(c) $SiX_2 < GeX_2 < SnX_2 < PbX_2$
(d) $PbX_2 < SnX_2 < GeX_2 < SiX_2$

Sol. *(c)* Due to inert pair effect, the stability of +2 oxidation state increases as we move down this group.

$\therefore \quad SiX_2 < GeX_2 < SnX_2 < PbX_2$

Allotropes of Carbon

Carbon shows allotropism due to the property of catenation and $p\pi$-$p\pi$ bond formation. It exists in two following allotropic forms.

I. Crystalline Forms of Carbon

These allotropes have well defined crystal structures. Diamond, graphite and fullerens are crystalline forms of carbon.

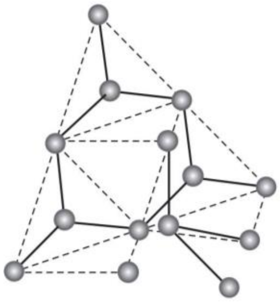
1. Diamond

It is the purest form of carbon and occurs in nature in free state. It is one of the best known and most saveht after gemstones. It is solid form of the element carbon with its atoms arranged in a crystal structure called diamond cubic.

Structure

Diamond has a three dimensional giant structure in which each C-atoms are sp^3 hybridised and arranged tetrahedrally (means it consists of number of tetrahedral unit). In each tetrahedral unit a central carbon atom is linked with other four C-atoms placed at the four corners of the tetrahedron through a strong covalent bond.

The C-atoms of each tetrahedron are also linked with neighbouring C-atom of each tetrahedrons through C—C covalent bond.



Structure of diamond

Properties

On the basis of its structure, diamond exhibits following properties.

- It is very hard, have high density and unusually high melting point (close to 3500°C).
- Due to unavailability of free electrons, it is a bad conductor of electricity.
- It has high thermal conductivity due to lattice vibrations.
- It has very high refractive index (2.417) and density (3.15 g/cm^2 at 25°C).
- It is transparent to X-rays.
- It is insoluble in all solvents.
- Diamond is used as a gemstone on the account of reflection and refraction of light. Impure diamonds (black) are used in knives for cutting glass and rock drilling equipment.

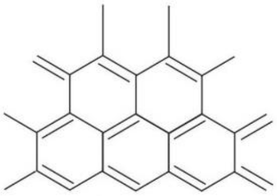
2. Graphite

It is a grey coloured allotrope of carbon. It is a crystalline form of the element carbon with its atoms arranged in a hexagonal structure. It occurs naturally in this forms and is the most stable form of carbon under standard conditions.

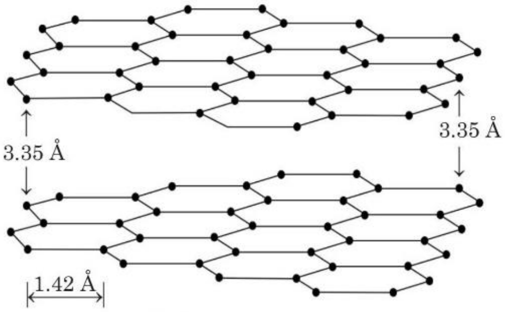
Structure

Graphite has a **two dimensional structure**. In this case, only 3 of the 4 valence electrons of C participate in bonding. Thus, hybridisation is sp^2 having 3 covalent bonds with other 3 C-atoms in the same plane. The 4th electron of C does not participate in the bonding and remains free.

This electron is responsible for electrical conductivity of graphite. In fact, the structure of graphite is two dimensional sheet like, consisting a number of hexagonal rings fused together as shown in the figure below



(a) Hexagonal layer structure of graphite



(b) Bonding in graphite

The sheet or layers are held together by relatively weak van der Waals' forces. The C—C bond distance is 1.42 Å. The distance between two successive layers is 3.36 Å.

This structure is less compact than diamond and since the bonding between layers involve only the **van der Waals' forces** (weak forces) hence, these layers can slide over each other. This gives softness, greasiness and lubricating character to graphite.

Properties

- Graphite is thermodynamically more stable than diamond and its free energy of formation is 1.9 kJ, less than diamond.

$$\text{Graphite} \xrightarrow[\text{50000-60000 atm}]{1600°\text{C}} \text{Diamond}$$

- When graphite is heated with vapours of K, Rb, Cs at 300°C, it forms C_8M. Graphite is diamagnetic but C_8M is paramagnetic.
- Due to delocalised electron density throughout the layer structure, graphite acts as good conductor of heat and electricity.
- The average value of C—C bond order in graphite is 1.33.
- Its melting point is high.
- It is chemically more active than diamond.
- It is inert to both alkalies and dilute acids.
- On heating in air at 700-800°C, it gives CO_2.

Uses

Graphite is used

- for lining and marking electrodes of electric furnaces.
- in making refractory crucibles.
- in making lead pencils.
- as a moderator in nuclear reactor.
- as a lubricant in machinery.

3. Fullerene

These are the recently discovered allotropes of carbon. Due to their resemblance with geodesic domes designed which is built by the American architect **Robert Buckminster Fuller** they are called as fullerene (or Buckminster fullerenes). The credit of the discovery of fullerenes goes to **HW kroto**, **RF curl** and **RE smalley**.

Preparation

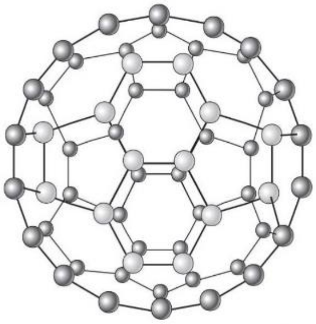
Fullerene are prepared from graphite as,

$$\text{Graphite} \xrightarrow[\text{He or Ar}]{\text{Electric arc}} \text{vaporised C} \xrightarrow{\text{Condense}} \text{fullerene}$$

$$\text{soot } (C_{60} \text{ mainly} + C_{70} \text{ little})$$

Structure

Fullerenes are large cage like spheroidal molecules with general formula C_{2n} (where $n \geq 30$). Two important member are C_{60} and C_{70}. C_{60} fullerene looks like a soccer ball (so called bucky ball) and contains 20, six membered and 12, five membered rings of carbon atoms.



Structure of C_{60}, Buckminster fullerene

Six membered rings are fused with both six membered as well as five membered rings while five membered rings are attached only with six membered rings.

Each carbon atom in the structure, forms three σ bonds with other three carbon atoms and the fourth electron remains free. These free electrons delocalise and provide some aromatic character to the molecule.

On the other hand, C_{70} have rugby ball like structure. It consists of 12 five membered and 25 six membered rings.

Fullerenes act as wonderful lubricants and the alkali compounds of C_{60} are used as super conducting substance at the temperature range of 10-40 K.

II. Microcrystalline Forms of Carbon

Coke, coal, charcoal, lamp black, gas carbon etc., belong to this form of carbon.

1. **Coal** It is formed by the slow carbonisation of vegetable matter buried under the earth centuries ago, in limited supply of air under high temperature and pressure. Peat (60% C), lignite (70% C), bituminous (78% C) and anthracite (90% C) are different varities of coal. Out of these, bituminous is the most common and anthracite is purest variety.
2. **Coke** It is a greyish black hard solid and is obtained by destructive distillation of coal.
3. **Charcoal** Depending upon the source from which it is obtained, animal charcoal, wood charcoal, sugar charcoal, and activated charcoal. Wood charcoal adsorbs colouring matter and odoriferous gases, thus used in decolourising sugar solutions and in gas masks.
4. **Lamp black or carbon black** It is the most pure amorphous form, contains about 98-99% carbon. Lamp black is used for making printer ink, black paint, varnishes and carbon papers.
5. **Gas carbon** It is scraped from the walls of a container used for destructive distillation of coal.

Physical Properties of Allotropes of Carbon

	Crystalline forms			Microcrystalline forms			
Property	**Diamond**	**Graphite**	**Fullerene**	**Coal**	**Charcoal**	**Animal charcoal**	**Lamp black**
Colour	Colourless transparent	Grey	—	Black	Black	Black	Black
Carbon content	100%	95–97%	—	60-90%	68-85%	8-10%	98-99%
Density (g cm^{-3})	3.51	2.25	—	—	1.4-1.7	—	—
Hardness	Hardest substance	Soft marks the paper	Medium	Hard mass	Soft	Soft	Soft
Electrical Conductivity	Bad conductor	Good conductor	Good conductor	Bad conductor	Bad conductor	Bad conductor	Bad conductor

Oxides of Carbon

Carbon forms two oxide, i.e. carbon monoxide and carbon dioxide. Their preparation methods, properties, structure and uses are described below.

1. Carbon Monoxide, CO

It is found in small amounts in volcanic gases, chimney gases, exhaust gases of internal combustion engines and coal gas.

Methods of Preparation

- Carbon monoxide is obtained by burning C in limited supply of oxygen. Pure CO can be obtained by heating HCOOH with H_2SO_4 where, H_2SO_4 acts as, dehydrating agent.
- It is also prepared by

  –heating carbonates of Ca, Ba or Mg with Zn

  $$MgCO_3 + Zn \longrightarrow MgO + ZnO + CO$$

  –heating potassium ferrocyanide with conc. H_2SO_4.

  $$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 6CO + 3(NH_4)_2SO_4$$
- Carbon monoxide is obtained in the form of water gas and producer gas when air (moist) is passed over a bed of white hot coke. The following reactions may occur.

  $$2C + O_2 \longrightarrow 2CO_2; C + O_2 \longrightarrow CO_2$$

  $$C + H_2O \longrightarrow \underbrace{CO + H_2}_{\text{Water gas}}$$

Carbon dioxide is reduced by passing the mixture over heated charcoal.

$$CO_2 + \underset{\text{(Charcoal)}}{C} \longrightarrow 2CO$$

The CO produced, always consists of N_2, H_2, CO_2, etc.

Properties

- It is a colourless and odourless gas.
- It is slightly soluble in water.
- Its density is nearly equal to the density of air.
- It is highly poisonous in nature. One part in 100 parts of air causes death in few minutes. The poisonous nature of CO is due to the fact that it combines with haemoglobin (a red colouring matter of blood which is carrier of oxygen) to form carboxy-haemoglobin which is not capable to absorb oxygen and as a result of this, suffocation takes place.
- It is an essential constituent of gaseous fuels like water gas, producer gas etc.
- CO is highly combustible gas and produces CO_2 on combustion, along with a large amount of heat.

  $$CO + \frac{1}{2}O_2 \longrightarrow CO_2 + \text{Heat}$$
- It is a good reducing agent and reduces metal oxides to metals as

  $$Fe_2O_3 + 3CO \xrightarrow{823\text{ K}} 2Fe + 3CO_2$$
- It gives phosgene when reacts with Cl_2 in sunlight.
- It forms metal carbonyls with transition metals like Ni, Fe, Co, etc.

Structure

The structure of CO can be represented as,

$$C \overset{\leftarrow}{=} O$$

Two pairs of electrons are considered to be shared between carbon and oxygen. Oxygen also donates a lone pair to carbon resulting to a coordinate bond. The properties of CO can be explained satisfactorily if we consider CO as the resonance hybrid of following three structures.

$$C{=}\ddot{\underset{\cdot\cdot}{O}} \longleftrightarrow \overset{-}{C}{\equiv}\overset{+}{O}\!: \longleftrightarrow :\!\overset{+}{C}{-}\ddot{\underset{\cdot\cdot}{O}}\!:^{-}$$

Uses

CO is used

- as industrial fuels, as water gas and producer gas
- as reducing agent in many metallurgical processes.
- in the purification of Ni by Mond's process.

2. Carbon Dioxide, CO_2

CO_2 is present in atmosphere to the extent of 0.03-0.05 per cent. It comes to the atmosphere from animal breathing, decay of vegetable matter, burning of carbon and carbonous matter, etc. It is also utilised by plants in photosynthesis.

Methods of Preparation

CO_2 is obtained by burning C in air (excess). In laboratory, it can be prepared by the action of cold dilute HCl on $CaCO_3$ (marble).

Properties

- CO_2 is colourless gas with a faint pungent smell and slight acidic taste. It dissolves in water forming H_2CO_3 as,

  $$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

  H_2CO_3 is a weak acid and dissolves in alkalies to form salts as,

  $$H_2CO_3 + 2NaOH \longrightarrow Na_2CO_3 + 2H_2O$$
- It turns lime water milky which disappears, if CO_2 is passed for a long time due to the formation of soluble calcium bicarbonate.
- It reacts with liquid NH_3 at 473 K and 220 atm, and gives ammonium carbonate which subsequently decomposes to give urea.
- **Solid CO_2 is commonly called "dry ice".** It is a soft white snow like compound with specific gravity 1.53 and m.p. –56.6°C at 5.2 atm pressure. It is produced by evaporating liquid CO_2 at 20°C and 70 atm pressure to a pressure less than 5.2 atm.

Structure

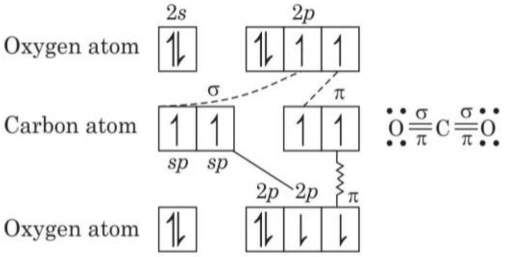
Structure of CO_2 is considered as resonance hybrid of following three structures that are shown below

$$O{=}C{=}O \longleftrightarrow \overset{-}{O}{-}C{\equiv}\overset{+}{O} \longleftrightarrow \overset{+}{O}{\equiv}C{-}\overset{-}{O}$$

(linear structure of CO_2)

The formation of the molecule can be explained on the basis of hybridisation. Carbon is *sp*-hybridised. The hybrid orbitals form sigma bonds with *p*-orbitals of each oxygen atoms.

The unhybridised two *p*-orbitals of carbon atom form two π-bonds with two oxygen atoms.



Uses

CO_2 is used

- in a refrigerant under the commercial name **Drikold.**
- as a substitute of ice in cold drinks and in ice cream preparation.
- in hospitals, it is used for surgical operations of sores.
- as important constituent of carbogen (a mixture of 95% O_2 and 5% CO_2) is used for artifical respiration.
- as a fire extinguisher.

Example 5. *The C — C bond length is maximum in*

(JEE Main 2019)

(a) graphite
(b)
(c)
(d) diamond

Sol. (*d*) The C—C bond length is maximum in diamond having value 154 pm.

Here, each carbon atom undergoes sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. It has a rigid three dimensional network of carbon atoms.

C—C bond length within the layers of graphite is 141.5 pm.

In C_{60}, C—C distances between single and double bonds are 143.5 pm and 138.3 pm respectively.

Compounds of Silicon

Silicon forms several compounds, some important of them are as follows

1. Silicon Tetrachloride

Its chemical formula is $SiCl_4$. It is also called as tetrachlorosilane. Its preparation, methods and properties are as follows

Methods of Preparation

$SiCl_4$ is prepared by heating Si or SiC with Cl_2.

$$Si(s) + 2Cl_2(g) \xrightarrow{\Delta} SiCl_4(l)$$

$$SiC(s) + 4Cl_2(g) \xrightarrow{\Delta} SiCl_4(l) + CCl_4(l)$$

Properties and Uses

- It is a volatile liquid with boiling point 330.57 K.
- On hydrolysis, it gives silicic acid $Si(OH)_4$ which on further heating form silica gel.

$$SiCl_4 + 2H_2O \xrightarrow{\Delta} \underset{\text{Silicic acid}}{Si(OH)_4} \xrightarrow{\Delta} \underset{\text{Silica gel}}{SiO_2 \cdot xH_2O}$$

(Silica gel being very porous is used as a catalyst in petroleum industry and as an adsorbent in column chromatography).

- On reduction, it gets converted into Si. The silicon obtained is ultrapure and is used for making transistors, computer chips and solar cells.

2. Silica

SiO_2 is commonly called as silica. It occurs in earth's crust as crystalline quartz, tridymite and crystoballite. The amorphous form of silica is **Kieselguhr**.

Methods of Preparation

- It is obtained by heating silicon in oxygen as,

$$Si + O_2 \longrightarrow SiO_2$$

- Pure SiO_2 is prepared in its amorphous forms as a white powder by reacting $SiCl_4$ or SiF_4 with water as

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$$
$$SiF_4 + 2H_2O \longrightarrow SiO_2 + 4HF$$

The latter method is normally less used as SiO_2 further reacts with HF to form H_2SiF_6 (fluorosilicic acid).

Properties

- SiO_2 is insoluble in water and in all acids except HF with which it reacts to form SiF_4 as,

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

If we take HF in excess, SiF_4 further reacts with it to form fluorosilicic acid as

$$SiF_4 + 2HF \longrightarrow H_2SiF_6$$

- SiO_2 melts in oxyhydrogen flame above 1875 K to colourless glass, called quartz glass. It has remarkably low coefficient of expansion. Red hot quartz when plunged into water does not shatter to pieces.
- SiO_2 is acidic and dissolves in hot conc. alkalies to form sodium silicate as,

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

- It acts as a powerful acid anhydride and combines with bases and many metallic oxides to form silicates as,

$$SiO_2 + Na_2O \longrightarrow Na_2SiO_3 \uparrow$$
$$SiO_2 + CaO \longrightarrow CaSiO_3 \uparrow$$

- It also reacts with carbonates of many metals at high temperatures forming silicates with liberation of CO_2 as,

$$SiO_2 + Na_2CO_3 \longrightarrow Na_2SiO_3 + CO_2 \uparrow$$
$$SiO_2 + CaCO_3 \longrightarrow CaSiO_3 + CO_2 \uparrow$$

- When heated with carbon in an electric furnace, it is reduced to **carborundum** or **silicon carbide** as,

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

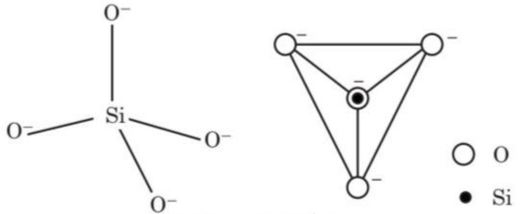
Uses

Silica is used

- as an adsorbent in column chromatography.
- as a catalyst in petroleum industry.
- as a humidity detector.
- as Kieselguhr, in filtration plants and as an inert support or filler.

3. Silicates

Silicates are minerals of silicon, mica, asbestos, cement, bricks, tiles, porcelains, glass, pottery, etc., are made from silicates. The basic building unit of all silicates is the tetrahedral SiO_4^{4-} ion. The three dimensional tetrahedral structure is represented by a planar structure for convenience



Structure of SiO_4^{4-} ion

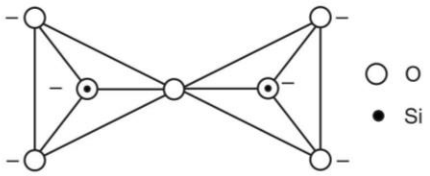
All silicates involve Si—O bonds of following two types

- Terminal Si—O bonds in which oxygen is bonded to a silicon and not other atom.
- Bridging Si— O—Si bonds in which oxygen is bonded to two silicon atoms.

On the basis of the way, the SiO_4^{4-} tetrahedral units are linked together, the silicates minerals are classified into following types

(i) **Orthosilicates** These are contains discrete SiO_4^{4-} units in which oxygen atoms are found to associate only with metal ions, e.g. **zircon** ($ZrSiO_4$), **wellimite** (Zn_2SiO_4) and **phenacite** (Be_2SiO_4) etc.

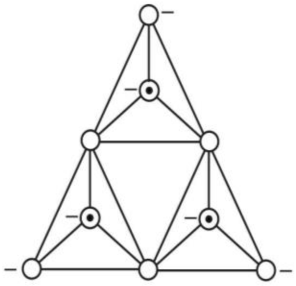
(ii) **Pyrosilicates** Two SiO_4^{4-} tetrahedrons share a corner oxygen atom. They contain $[Si_2O_7]^{6-}$ ions as discrete units. These are also called **island structures.** These silicates are not very common. e.g. **thorteveitite** ($Sc_2Si_2O_7$) and **hemimorphite** $[Zn_4(OH)_2Si_2O_7]$.



$Si_2O_7^{6-}$ (Anion of pyrosilicate)

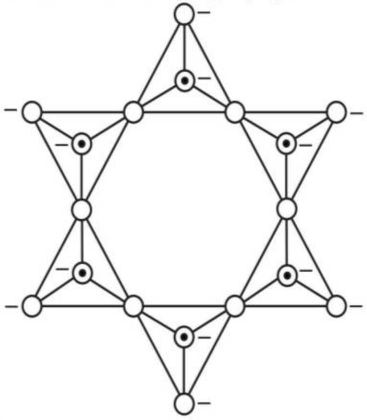
(iii) **Cyclic silicates** Two oxygen atoms of each tetrahedron are shared to form a ring with general formula $[SiO_3]_n^{2n-}$. The ring may be of

- Three membered ring in which discrete units are $[Si_3O_9]^{6-}$, e.g. **wollastonite** $Ca_3Si_3O_9$, **bentonite** $BaTi[Si_3O_9]$ etc.



$Si_3O_9^{6-}$ ion (Anion of three membered cyclic silicate)

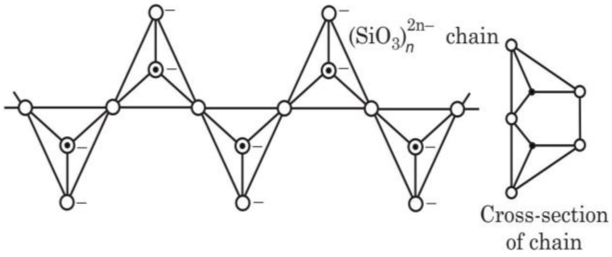
- Six membered ring in which discrete units are $[Si_6O_{18}]^{12-}$, e.g. **beryl** $(Be_3Al_2Si_6O_8)$



$Si_6O_{18}^{12-}$ ion (Anion of six membered cyclic silicates)

(iv) **Chain silicates** Two oxygen atoms per tetrahedron are shared to form an extensively long chain. The primary units is $[SiO_3]^{2-}$ and the general formula is $[SiO_3]_n^{2n-}$. Two types of chain silicates may be formed. as,

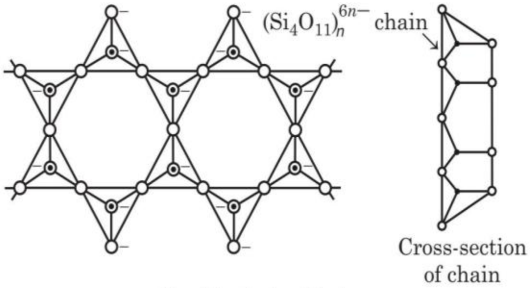
- **Single chain silicates,** in which $[SiO_3]_2^{4-}$ combines to form a chain like polymer, these are also called pyroxenes, e.g. **diopside** $[CaMg(SiO_3)_2]$.



Single chain silicates

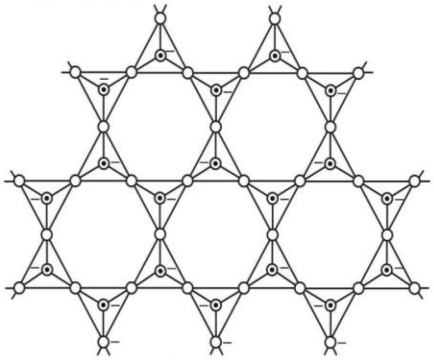
- **Double chain silicates,** in which $[Si_4O_{11}]^{6-}$ are primary units. Two simple chains are joined together through one of the four oxygen atom of SiO_4 tetrahedra. These structures are known as **amphiboles**.

Some tetrahedra share three oxygen. e.g. **termolite** $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$, **asbestos** $CaMg_3O(Si_4O_{11})$.



Double chain silicates

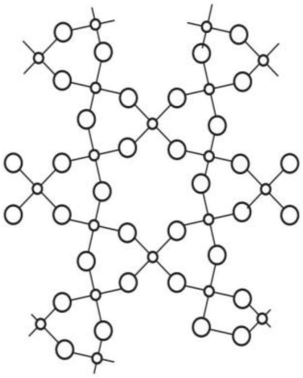
(v) **Sheet silicates** Three oxygen atoms per tetrahedron are shared to form an infinite plane sheet, containing $[Si_2O_5]_n^{2n-}$. e.g. **kaolinite** $[Al(OH)_4Si_2O_5]$, talc $[Mg_3(OH)_2(Si_2O_5)_2]$, mica minerals, etc.



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

(vi) **Three dimensional silicates** All the four oxygen atoms are shared in each tetrahedron to form an infinite three dimensional structure. Each oxygen atom is bonded to two silicon atoms. Each silicon atom (sp^3-hybridised) is surrounded tetrahedrally by four oxygen atoms and each oxygen atom is linked covalently to two silicon atoms. These silicates are neutral.

Various forms of silica occur in three dimensional silicate structure, have general formula $(SiO_3)_n^{2n-}$.



Three dimensional structure of silica

4. Zeolites

These are microporous aluminosilicate having general formula $M_{x/n}[AlO_2]_x[SiO_2]_y \cdot mH_2O$.

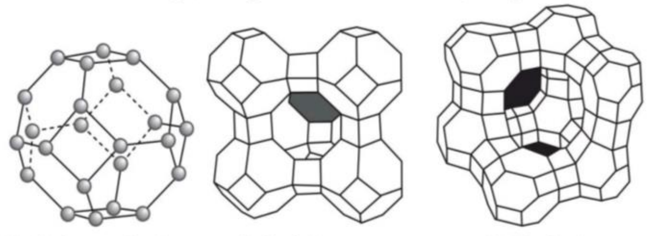
Preparation

Aluminosilicates are obtained by substituting some of the silicon atoms in a three dimensional network silicate by Al^{3+} ions. The negative charge carried by aluminosilicate framework is neutralised by exchangeable cations of valence *n*, while *m* water molecules fill the voids.

Structure

The **cubo** octahedron shown in figure (a) is the building block of zeolites and also called the **sodalite cage.** The sodalite cages in figure (b) are linked to each other through four membered rings to produce two or three dimensional network of inter connected channels and cavities. As a consequence of such packing, the zeolites are highly porous.

When sodalite cages are linked through double six-membered rings, Faujasite is obtained (in figure (c).



(a) Cubo octahedron (b) Sodalite cages (c) Faujasite

The three dimensional structure of zeolites

Uses

Zeolites are used as

- molecular seives and can separate molecules of different sizes.
- as catalyst due to their porous structure.

5. Silicones

Silicones are organo-silicon polymers containing ...... O—Si—O ...... linkages. These may be linear silicones, cyclic silicones and cross-linked silicones.

Methods of Preparation

These are prepared by the hydrolysis of alkyl or aryl derivatives of $SiCl_4$ like $RSiCl_3$, R_2SiCl_2 and R_3SiCl followed by polymerisation of obtained product.

This method consists of the following steps as,

***Step* I Preparation of alkyl or aryl derivatives of silicon tetrachloride.** Examples of such derivatives are $RSiCl_3$, R_2SiCl_2 and R_3SiCl where *R* is an alkyl (e.g. CH_3, C_2H_5 etc.,) or aryl (e.g. C_6H_5) group.

Preparation of some of the above derivative are as follows

- **Methyl chlorosilanes** [like $(CH_3)SiCl_3$, $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$] are prepared by heating methyl chloride, CH_3Cl with Si, catalysed by Cu, at 300°C. This reaction gives a mixture of methyl chlorosilanes.

$$2CH_3Cl + Si \xrightarrow[300°C]{Cu}$$

$$\underbrace{(CH_3)SiCl_3 + (CH_3)_2SiCl_2 + (CH_3)_3SiCl}_{\text{Mixture of methyl chlorosilanes + other compounds}}$$

- **Alkyl or aryl chlorosilanes** can also be obtained by the action of Grignard reagent on $SiCl_4$.

$$\underset{\text{(Grignard reagent)}}{RMgCl} + SiCl_4 \longrightarrow RSiCl_3 + MgCl_2$$

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

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

['*R*' stands for $—CH_3$, $—C_2H_5$ or $—C_6H_5$ groups].

***Step* II Preparation of alkyl or aryl hydroxy derivatives of silicon tetrachloride** (called silanols or silandiols) These silanols are obtained by the hydrolysis of $RSiCl_3$, R_2SiCl_2 and R_3SiCl respectively.

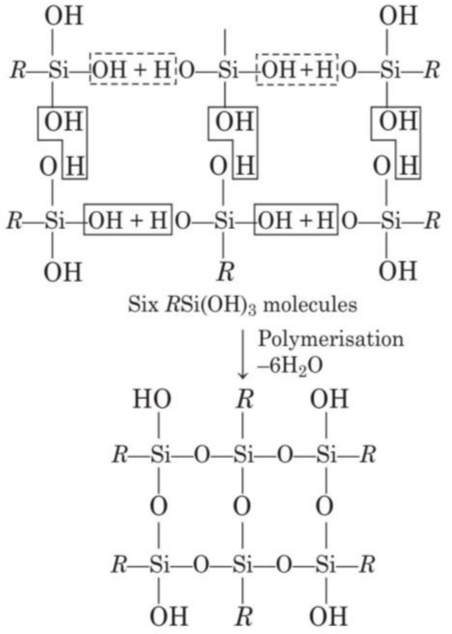
e.g.

$$RSiCl_3 + 3H \cdot OH \xrightarrow{\text{Hydrolysis}} RSi(OH)_3 + 3HCl$$

$$R_2SiCl_2 + 2H \cdot OH \xrightarrow{\text{Hydrolysis}} R_2Si(OH)_2 + 2HCl$$

***Step* III Polymerisation of alkyl or aryl hydroxy derivatives** The type of silicon obtained depends on the nature of alkyl or aryl hydroxy derivative and the way in which the hydroxy derivative undergoes polymerisation. e.g.

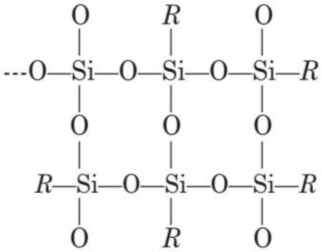
***Case* I** When many molecules of alkyl trihydroxy silane, $RSi(OH)_3$ undergoes polymerisation, a cross-linked two dimensional silicone is obtained as,



Six $RSi(OH)_3$ molecules

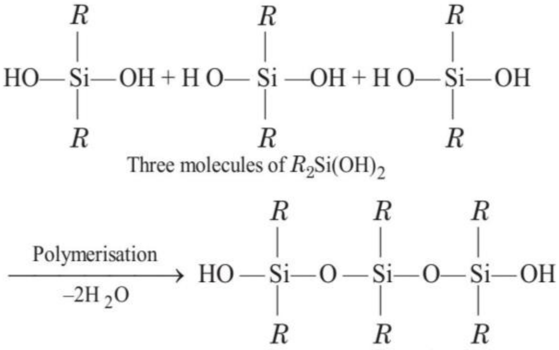
Polymerisation $-6H_2O$

Since, an active OH group is present at each end of the chain, polymerisation continues on both the ends and hence, the length of the chain increases. The increase in the length of the chain produce cross-linked silicone as shown below



Two dimensional cross-linked silicone

***Case* II** When many molecules of dialkyl dihydroxysilane, $R_2Si(OH)_2$ undergo polymerisation, a straight chain (linear) or cyclic (ring) silicone is obtained as,

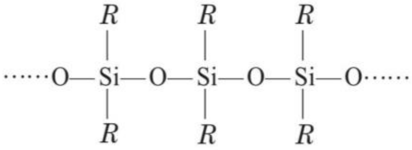


$$HO-\underset{R}{\overset{R}{Si}}-OH + HO-\underset{R}{\overset{R}{Si}}-OH + HO-\underset{R}{\overset{R}{Si}}-OH \xrightarrow[-2H_2O]{\text{Polymerisation}} HO-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-OH$$

Three molecules of $R_2Si(OH)_2$

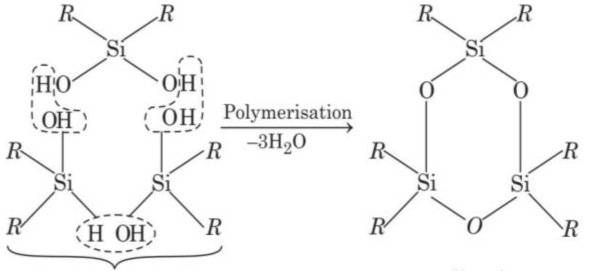
(Straight chain)

Since, an active OH group is present at each end of the chain, polymerisation continues and hence, the length of the chain increases and gives rise to the formation of long chain silicon, as shown below



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

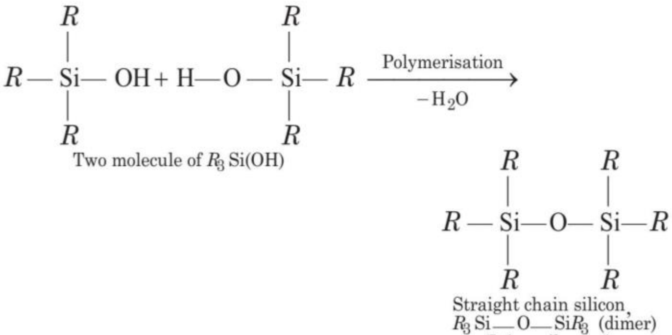
Linear or straight chain silicone (thermoplastic polymer)



Three molecules of $R_2Si(OH)_2$

cyclic trimer

***Case* III** When two molecules of trialkyl monohydroxysilane, $R_3Si(OH)$ undergo polymerisation, a straight chain silicon (dimer) is obtained as,



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

Two molecule of $R_3Si(OH)$

Straight chain silicon, $R_3Si-O-SiR_3$ (dimer)
(It is a siloxane)

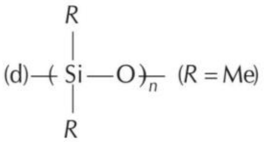
Properties and Uses

Important properties and uses of silicones are as follows

- They have high **thermal stability** in the absence of air and with stand temperature up to 250-300°C.
- They remain unaffected by most of the chemical reagents, such as weak acids, alkalies and salt solution. Thus, **silicones are chemically inert.**
- Many of low molecular weight silicones dissolve in solvents like C_6H_6, ether and CCl_4.
- They do not become too viscous on cooling and are, therefore, used for low temperature lubrication.

Example 6. *The basic structural unit of feldspar, zeolites, mica and asbestos is* ***(JEE Main 2019)***

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



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

Sol. (c) The basic structural unit of feldspar, zeolites, mica and asbestos is $(SiO_4)^{4-}$. These all are silicates.

Example 7. *The amorphous form of silica is* ***(JEE Main 2019)***

(a) tridymite
(b) Kieselguhr
(c) cristobalite
(d) quartz

Sol. (b) Silica occurs in nature in several amorphous and crystalline forms. Kieselguhr is the amorphous form of silica. Quartz, tridymite and cristobalite are crystalline forms of silica.

Example 8. *The one that is extensively used as a piezoelectric material is* ***(JEE Main 2019)***

(a) quartz
(b) tridymite
(c) amorphous silica
(d) mica

Sol. (a) Piezoelectric materials are those materials that produce an electric current when they are placed under mechanical stress. Crystalline solids can be used as piezoelectric material hence, quartz is a correct answer.

Practice Exercise

ROUND I Topically Divided Problems

Physical and Chemical Properties of Group 13

1. The reason for small radius of Ga compared to Al is

(a) poor screening effect of *d* and *f*-orbitals
(b) presence of higher orbitals
(c) increase in nuclear charge
(d) (a) and (c) both are correct

2. The strongest oxidising agent among the given is

(a) SiO_2 (b) GeO_2
(c) SnO_2 (d) PbO_2

3. Ionisation enthalpy ($\Delta_i H_1 \text{kJ mol}^{-1}$) for the elements of group 13 follows the order. *(NCERT Exemplar)*

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

4. Aluminium is usually found in +3 oxidation state. In contrast, thallium exists in +1 and +3 oxidation states. This is due to *(JEE Main 2019)*

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

5. In aqueous solution, GaCl disproportionates to

(a) $GaCl_2$ and $GaCl_3$ (b) Ga and $GaCl_3$
(c) $GaCl_2$ and Ga (d) $GaCl_3$ and $GaCl_5$

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

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

7. Which of the following is true for an element *R* present in III-A group of the periodic table ?

(a) It has oxidation state of +4
(b) It is gas at room temperature
(c) It forms R_2O_3 type of oxides
(d) It forms RX_2 type of halides

8. Which of the following is the electron deficient molecule?

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

9. Which of the following is a Lewis acid ?

(a) $AlCl_3$ (b) $MgCl_2$ *(NCERT Exemplar)*
(c) $CaCl_2$ (d) $BaCl_2$

10. Which of the following oxides is strongly basic?

(a) Tl_2O (b) B_2O_3 (c) Al_2O_3 (d) Ga_2O_3

11. A non-metallic element of group 13, used in making bullet proof vests is extremely hard solid of black colour. It can exist in many allotropic forms and has unusually high melting point. Its trifluoride acts as *(NCERT Exemplar)*

(a) Lewis base (b) Lewis acid
(c) Bronsted acid (d) Bronsted base

12. BF_3 exists but BH_3 doesn't because of the absence of

(NCERT Exemplar)

(a) back bonding in BF_3 (b) back bonding in BH_3
(c) *d* orbital in B (d) None of the above

13. Boron can't form which one of the following anions? *(AIEEE 2011)*

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

14. BCl_3 exists as monomer whereas $AlCl_3$ dimerises through halogen bridging. This is because of the *(NCERT Exemplar)*

(a) small size of B atom as compare to Al
(b) absence of *d*-orbital in B atom
(c) $p\pi$- $p\pi$ back bonding in $AlCl_3$
(d) $p\pi$- $p\pi$ back bonding in BCl_3

15. 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 *(NCERT Exemplar)*

(a) sp^3, tetrahedral (b) sp^3, square planar
(c) sp^3d^2, octahedral (d) dsp^2, square planar

16. Purification of aluminium done by electrolytic refining is known as

(a) Hoope's process (b) Serpeck's process
(c) Hall's process (d) Baeyer's process

17. In purification of bauxite by Hall's process, bauxite ore is
(a) fused with Na_2CO_3
(b) heated with NaOH solution at 50°C
(c) heated with $NaHCO_3$
(d) fused with coke and heated at 1800°C in a current of nitrogen

18. In extraction of aluminium, the electrolyte is
(a) fused cryolite with felspar
(b) pure alumina in molten state
(c) fused cryolite with fluorspar
(d) pure alumina with bauxite and molten cryolite6

19. The function of fluorspar in the electrolytic reduction of alumina dissolved in fused cryolite (Na_3AlF_6) is
(a) to decrease the rate of oxidation of carbon at the anode
(b) to lower the temperature of the melt and to make the fused mixture very conducting
(c) as a catalyst
(d) None of the above

20. Anodising can be done by electrolysing dilute H_2SO_4 with Al as anode, this result in
(a) the formation of protective oxide layer
(b) the formation of $Al_2(SO_4)_3$ and SO_2 gas
(c) the formation of AlH_3 and SO_2 gas
(d) the formation of $Al(HSO_3)$ and H_2 gas

21. Which one of the following is correct statement ?
(a) The hydroxide of aluminium is more acidic than that of boron.
(b) The hydroxide of boron is basic, while that of aluminium is amphoteric
(c) The hydroxide of boron is acidic, while that of aluminium is amphoteric
(d) The hydroxide of boron and aluminium are amphoteric

22. The element which exists in liquid state for a wide range of temperature and can be used for measuring high temperature is *(NCERT Exemplar)*
(a) B (b) Al (c) Ga (d) In

Compounds of Elements of Group 13

23. Which of the following is known as inorganic benzene?
(a) Borazine (b) Phosphonitrilic acid
(c) Boron nitride (d) *p*-dichlorobenzene

24. Boron nitride has the structure of the type
(a) graphite type
(b) diamond type
(c) Both diamond and graphite type
(d) NaCl type

25. Boric acid is slippery due to
(a) banana bonds (b) hydrogen bonds
(c) van der Waals' forces (d) None of these

26. Which of the following compounds are formed when BCl_3 is treated with water ?
(a) B_2O_3 + HCl (b) B_2H_6 + HCl
(c) H_3BO_3 + HCl (d) None of these

27. Boric acid is an acid because its molecule
(a) contains replaceable H^+ ion *(NCERT Exemplar)*
(b) gives up a proton
(c) accepts OH^- from water releasing proton
(d) combines with proton from water molecule

28. In the structure of diborane *(NCERT Exemplar)*
(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

29. The number of 2-centre-2-electron and 3-centre-2-electron bonds in , respectively, are *(JEE Main 2019)*
(a) 4 and 2 (b) 2 and 4 (c) 2 and 2 (d) 2 and 1

30. Which of the following statements is/are correct ?
(a) Boric acid is Lewis base
(b) Hybridisation of boron in boric acid is sp^3
(c) Boric acid molecule held together by hydrogen bonding
(d) All of the above

31. Which statements about anhydrous aluminium chloride is correct?
(a) It is a strong Lewis base
(b) It is not easily hydrolysed
(c) Its Al—Cl bond is ionic
(d) It sublimes at 100°C

32. Heating of an aqueous solution of aluminium chloride to dryness will give *(AIEEE 2005)*
(a) $Al(OH)Cl_2$ (b) Al_2O_3
(c) Al_2Cl_6 (d) $AlCl_3$

33. Alum is widely used to purify water since
(a) it forms complex with clay particles *(AIEEE 2002)*
(b) it coagulates the mud particles
(c) it exchanges Ca^{2+} and Mg^{2+} ions present in hard water
(d) its sulphate ion is water purifier

34. Alum are used as mordant in dyeing because
(a) dye is adsorbed on $Al(OH)_3$ which is deposited on fibre in the hydrolysis process
(b) dye is adsorbed on KOH formed due to hydrolysis
(c) Both (a) and (b)
(d) None of the above

35. The dimeric structure of aluminium chloride disappears, when
(a) it dissolves in water (b) it dissolves in benzene
(c) it reacts with R_3N (d) Both (a) and (c)

36. Which of the following is obtained when aluminium oxide and carbon is strongly heated in dry chlorine gas?
(a) Aluminium chloride
(b) Hydrated aluminium chloride
(c) Anhydrous aluminium chloride
(d) None of the above

37. Carborundum is obtained when silica is heated at high temperature with
(a) carbon (b) carbon monoxide
(c) carbon dioxide (d) calcium carbonate

Physical and Chemical Properties of Group 14

38. Monosilane on coming in contact with air burns with a luminous flame producing vortex rings. These rings are of
(a) SiO_2 (b) SiO (c) Si (d) H_2SiO_3

39. Lead pipes are not suitable for drinking water because
(a) a layer of lead dioxide is deposited over pipes
(b) lead forms basic lead carbonate
(c) lead reacts with water containing air to form $Pb(OH)_2$
(d) lead reacts with air to form litharge

40. A tetravalent element forms monoxide and dioxide with oxygen. When air is passed over heated element (1273 K), producer gas is obtained. Monoxide of the element is a powerful reducing agent and reduces ferric oxide to iron. Identify the element. *(NCERT Exemplar)*
(a) Lead (b) Carbon (c) Tin (d) Silicon

41. The most commonly used reducing agent is *(NCERT Exemplar)*
(a) $AlCl_3$ (b) $PbCl_2$ (c) $SnCl_4$ (d) $SnCl_2$

42. The element that does not show catenation is *(JEE Main 2019)*
(a) Ge (b) Sn (c) Si (d) Pb

43. The element that shows greater ability to form $p\pi$-$p\pi$ multiple bonds, is *(JEE Main 2019)*
(a) Ge (b) Si (c) Sn (d) C

44. The correct order of catenation is *(JEE Main 2019)*
(a) $C > Sn > Si \approx Ge$
(b) $Si > Sn > C > Ge$
(c) $C > Si > Ge \approx Sn$
(d) $Ge > Sn > Si > C$

45. In SiF_6^{2-} and $SiCl_6^{2-}$ which one is known and why ?
(a) SiF_6^{2-} because of small size of F
(b) SiF_6^{2-} because of large size of F
(c) $SiCl_6^{2-}$ because of small size of Cl
(d) $SiCl_6^{2-}$ because of large size of Cl

46. Which of the following statement is correct with respect to the property of elements in the carbon family with an increase in the atomic number? Their
(a) atomic size decreases
(b) stability of +2 oxidation state increases
(c) metallic character decreases
(d) ionisation energy increases

47. The stability of hydrides of carbon family is in the order
(a) $CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$
(b) $CH_4 < SiH_4 < GeH_4 < SnH_4 < PbH_4$
(c) $CH_4 > SnH_4 > GeH_4 > SiH_4 > PbH_4$
(d) None of the above

Allotropes of Carbon and Important Compounds of Group 14

48. The different layers in graphite are held together by
(a) metallic bonding (b) covalent bonding
(c) ionic bonding (d) van der Waals' forces

49. Quartz is extensively used as a piezoelectric material as it contains *(NCERT Exemplar)*
(a) Pb (b) Si
(c) Ti (d) Sn

50. Carbon suboxide, C_3O_2 has
(a) bent structure
(b) trigonal planar structure
(c) linear structure
(d) distorted tetrahedral structure

51. Solid CO_2 is known as dry ice, because
(a) it evaporates at 40°C
(b) it melts at 0°C
(c) its boiling points is more than 199°C
(d) it evaporates at – 78°C without melting

52. Which of the following statements are correct?
(a) Fullerenes have dangling bonds
(b) Fullerenes are cage-like molecules
(c) Graphite is thermodynamically less stable allotrope of carbon
(d) Graphite is slippery and hard and therefore used as a dry lubrication in machines

53. Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behaviour is that graphite *(AIEEE 2003)*
(a) is a non-crystalline substance
(b) is an allotropic form of diamond
(c) has molecules of variable molecular masses like polymers
(d) has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interplate bonds

54. Name of the structure of silicates in which three oxygen atoms of $[SiO_4]^{4-}$ are shared is
(a) pyrosilicate
(b) sheet silicate
(c) linear chain silicate
(d) three dimensional silicate

55. Among the following substituted silanes the one which will give rise to cross-linked silicone polymer on hydrolysis is *(AIEEE 2008)*
(a) R_4Si (b) $RSiCl_3$ (c) R_2SiCl_2 (d) R_3SiCl

56. Which of the following product is formed 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

57. Me_3SiCl is used during polymerisation of organo silicones because *(NCERT Exemplar)*
(a) the chain length of organo silicone polymers can be controlled by adding Me_3SiCl
(b) Me_3SiCl improves the quality and yield of the polymer
(c) Me_3SiCl acts as a catalyst during polymerisation
(d) of (a) and (b) both

58. Silicon has a strong tendency to form polymers like silicones. The chain length of silicone polymer can be controlled by adding *(NCERT Exemplar)*
(a) $MeSiCl_3$ (b) Me_2SiCl_2 (c) Me_3SiCl (d) Me_4Si

ROUND II Mixed Bag

1. Which of the following is not true about potash alum?
(a) Its aqueous solution is basic
(b) It is used in dyeing industries
(c) On heating it melts to give water of crystallisation
(d) Its empirical formula is $KAl(SO_4)_2 \cdot 12H_2O$

2. The number of pentagons in C_{60} and trigons (triangles) in white phosphorus, respectively, are *(JEE Main 2019)*
(a) 20 and 3 (b) 12 and 4
(c) 20 and 4 (d) 12 and 3

3. The hydride that is not electron deficient is *(JEE Main 2019)*
(a) (b)
(c) (d)

4. Which of the following statements is incorrect ?
(a) Boron exhibits +3 oxidation state only
(b) In Ga +3 oxidation state is more stable than +1 oxidation state
(c) In Sn +2 oxidation state is more stable than +4 oxidation state
(d) In Tl +1 oxidation state is more stable than +3 oxidation state

5. Boric acid is used in carom 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 can be powdered to a very small grain size
(d) H-bonding in H_3BO_3 give it a layered structure

6. When aqueous solution of borax is acidified with hydrochloric acid, a white crystalline solid is formed which is soapy to touch. The nature of the solid is *(NCERT Exemplar)*
(a) acidic
(b) basic
(c) neutral
(d) depends upon the nature of solvent

7. When BCl_3 is treated with water, it hydrolysis and forms $[B(OH)_4]^-$ only whereas $AlCl_3$ in acidified aqueous solution forms $[Al(H_2O)_6]^{3+}$ ion. The hybridisation of boron and aluminium in these species is respectively. *(NCERT Exemplar)*
(a) sp^3, sp^3d (b) sp^3, sp^3d^2
(c) sp^3d, sp^3d^2 (d) sp^2, sp^3d^2

8. Which one of the following statements about the zeolite is false?

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

9. $B(OH)_3 + NaOH \rightleftharpoons$

$NaBO_2 \cdot 2H_2O$ or $Na[B(OH)_4$ 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

10. For purification of alumina, the modern processes most useful when (i) the impurity present is a lot of iron oxides and (ii) the impurity present is a lot of silica, are

(a) for (i) Hall's process; for (ii) Baeyer's process
(b) for (i) Serpeck's process; for (ii) Baeyer's process
(c) for (i) Hall's process; for (ii) Serpeck's process
(d) for (i) Baeyer's process; for (ii) Serpeck's process

11. Which one of the following is the correct statement? ***(AIEEE 2008)***

(a) Boric acid is a protonic acid
(b) Beryllium exhibits coordination number of six
(c) Chlorides of both beryllium and aluminium have bridged chloride structures in solid phase
(d) $B_2H_6 \cdot 2NH_3$ is known as 'inorganic benzene'

12. A metal, *M* forms chlorides in its +2 and +4 oxidation states. Which of the following statements about these chlorides is correct? ***(AIEEE 2006)***

(a) MCl_2 is more volatile than MCl_4
(b) MCl_2 is more soluble in anhydrous ethanol than MCl_4
(c) MCl_2 is more ionic than MCl_4
(d) MCl_2 is more easily hydrolysed than MCl_4

13. In silicon dioxide, ***(AIEEE 2005)***

(a) there are double bonds between silicon and oxygen atoms
(b) silicon atom is bonded to two oxygen atoms
(c) each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms
(d) each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms

14. A compound (*A*) of boron reacts with NMe_3 to give an adduct (*B*) which on hydrolysis gives a compound (*C*) and hydrogen gas. Compound (*C*) is an acid. The adduct (*B*) is ***(NCERT Exemplar)***

(a) $B_3N_3H_6$ (b) $2BH_3 \cdot NMe_3$
(c) $BH_3 \cdot 2NMe_3$ (d) $BH_3 \cdot NMe_3$

15. The soldiers of Napolean army while at Alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White metallic tin buttons got converted to grey powder. This transformation is related to

(a) a change in the crystalline structure of tin
(b) an interaction with nitrogen of the air at very low temperatures
(c) a change in the partial pressure of oxygen in the air
(d) an interaction with water vapour contained in the humid air

16. Suppose you have to determine the percentage of carbon dioxide in a sample of a gas available in a container. Which is the best absorbing material for the carbon dioxide?

(a) Heated copper oxide
(b) Cold, solid calcium chloride
(c) Cold, solid calcium hydroxide
(d) Heated charcoal

17. Which of the following statements about H_3BO_3 is not correct?

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

18. The chloride that cannot get hydrolysed is ***(JEE Main 2019)***

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

19. The order of acidic strength of boron trihalides is

(a) $BF_3 < BCl_3 < BBr_3 < BI_3$ (b) $BI_3 < BBr_3 < BCl_3 < BF_3$
(c) $BCl_3 < BBr_3 < BI_3 < BF_3$ (d) $BBr_3 < BCl_3 < BF_3 < BI_3$

20. B has a smaller first ionisation enthalpy than Be. Consider the following statements :

I. It is easier to remove 2*p*-electron than 2*s* electron
II. 2*p* electron of B is more shielded from the nucleus by the inner core of electrons than the 2*s* electrons of Be
III. 2*s* electron has more penetration power than 2*p* electron

IV. atomic radius of B is more than Be (atomic number B = 5, Be = 4)

The correct statements are

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

21. Consider the statements among (I) to (IV) regarding silicones

I. They are polymers with hydrophobic character.
II. They are biocompatible.
III. In general, they have high thermal stability and low dielectric strength.
IV. Usually, they are resistant to oxidation and used as greases. *(JEE Main 2019)*

Choose the correct statements and mark the correct option.

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

22. Identify the compound Z in the following reaction sequence.

$$A + 2HCl + 5H_2O \longrightarrow 2NaCl + X$$

$$X \xrightarrow[370\text{ K}]{\Delta} HBO_2 \xrightarrow[>370\text{ K}]{\Delta} Z$$

(NCERT Exemplar)

(a) Borax (b) Orthoboric acid
(c) Metaboric acid (d) Boron trioxide

23. 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 *(AIEEE 2009)*

(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 $p\pi$ - $p\pi$ 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 $p\pi$ - $p\pi$ interaction between B and F in BF_3 than that between C and F in CF_4

24. In the following reaction sequence,

$$\text{Metal } (A) + N_2 \xrightarrow{\Delta} (B) \xrightarrow{+H_2O} (C) + (D)$$

white ppt. (C) is formed and gas (D) is evolved. White ppt. (C) dissolves in NaOH solution, while gas (D) gives white fumes in HCl. Metal A is

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

Numeric Value Questions

25. The value obtained when we add the oxidation number of boron and number of H_2O molecule present in the compound $Na_2[B_2CO_2(OH)_2 \cdot xH_2O]$ is ....

26. In diborane, the one highest H–B–H angle are nearly ...... (in degree).

27. C_{60}, an allotrope of carbon contains x hexagonal and y pentagons rings of carbon atoms. The product of x and y will be ....

28. The number of B—O—B bonds present in structure of borax is/are ....

29. A certain salt (x) gives the following tests:

(i) Its aqueous solution is alkaline to litmus.
(ii) On strong heating, it swells to give a glassy bead.
(iii) When conc. H_2SO_4 is added to a hot conc. solution of (x), white crystal of (z) separate out. (z) is a boron salt and contain x number of B atoms in its formula unit.
The value of x will be ....

30. A compound of 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 hydride. The sum of the number of B atoms present in the molecular formulae of compounds X and Y are ....

31. Consider the following information regarding compounds X

(i) Compound (X) on reduction with $LiAlH_4$ gives a hydride (Y) along with other products.
(ii) The compounds (Y) reacts with air explosively resulting in boron trioxide.
The percentage of hydrogen present in compound X is ....

32. A white crystalline compound 'A' swell up on heating and gives coloured flame aqueous solution gives following reaction.

(i) A white ppt. with $BaCl_2$ in the presence of HCl.
(ii) It gives white ppt. when treated with excess of NH_4OH. The ppt. dissolve in NaOH and reappears on boiling with conc. solution of NH_4Cl.
(iii) It gives yellow ppt. with cobalt nitrate solution.

The compound (A) contains ...... number of water of crystalisation.

Answers

Round I

1. (d)	**2.** (d)	**3.** (d)	**4.** (c)	**5.** (c)	**6.** (b)	**7.** (c)	**8.** (d)	**9.** (a)	**10.** (a)
11. (b)	**12.** (b)	**13.** (a)	**14.** (b)	**15.** (a)	**16.** (a)	**17.** (a)	**18.** (d)	**19.** (b)	**20.** (a)
21. (c)	**22.** (c)	**23.** (a)	**24.** (a)	**25.** (b)	**26.** (c)	**27.** (c)	**28.** (b)	**29.** (a)	**30.** (c)
31. (d)	**32.** (b)	**33.** (b)	**34.** (a)	**35.** (d)	**36.** (c)	**37.** (a)	**38.** (a)	**39.** (c)	**40.** (b)
41. (d)	**42.** (d)	**43.** (d)	**44.** (c)	**45.** (a)	**46.** (b)	**47.** (a)	**48.** (d)	**49.** (b)	**50.** (c)
51. (d)	**52.** (b)	**53.** (d)	**54.** (b)	**55.** (b)	**56.** (d)	**57.** (a)	**58.** (c)		

Round II

1. (c)	**2.** (b)	**3.** (c)	**4.** (c)	**5.** (d)	**6.** (a)	**7.** (b)	**8.** (b)	**9.** (a)	**10.** (d)
11. (c)	**12.** (c)	**13.** (d)	**14.** (b)	**15.** (a)	**16.** (c)	**17.** (d)	**18.** (b)	**19.** (a)	**20.** (a)
21. (d)	**22.** (d)	**23.** (c)	**24.** (b)	**25.** (6)	**26.** (120°)	**27.** (240)	**28.** (5)	**29.** (4)	**30.** (5)
31. (21.7)	**32.** (24)								

Solutions

Round I

2. For Pb, the more stable oxidation state is +2 but in PbO_2, it is in +4 oxidation state thus PbO_2 has great tendency to get reduced into PbO (+2 OS). Therefore, it acts as an oxidising agent.

3. Due to its small size and lowest shielding effect, IE is highest for boron and decreases from B to Tl, But not in a regular manner.

IE of Ga is greater than that of Al because of poor shielding of 10 *d*-electrons, while IE of Tl is higher than that of In because of the poor shielding effect of 14 *f* electrons present in the inner energy shell.

Thus, the correct order is option (d), i.e.
$B > Al < Ga > In < Tl$

4. Due to inert pair effect, group-13 elements (ns^2np^1) show + 3 and + 1 oxidation states in their compounds. Stability order of these oxidation states will be as,

$B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}$ (**+ 3 oxidation states**)

B^{3+} does not exist in free states. All B(III) compounds are covalent.

$B^+ < Al^+ < Ga^+ < In^+ < Tl^+$ (+ 1 oxidation states)

B^+ does not exist in ionic as well covalent compounds.

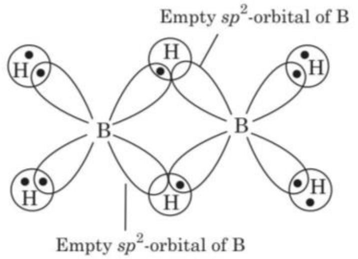
6. The presence of two oxidation states in p-block elements is due to the inert pair effect. Due to the presence of poor shielding *d* and *f*-orbitals, as we move from Ga to Tl, effective nuclear charge of these elements increases so as to hold the valence ns^2 electrons tightly.

It causes difficulty to the ionisation of ns^2-electrons and it remains inert, only np^1-electron ionises to give + 1 oxidation state.The stability order of + 3 and + 1 oxidation states of group 13 elements will be

$$B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} >> Tl^{3+}$$
(order of + 3 oxidation state)

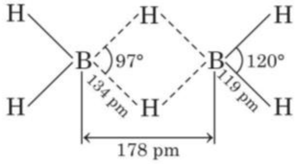
$$B^+ << Al^+ < Ga^+ < In^+ < Tl^+$$
(order of + 1 oxidation state)

8. B_2H_6



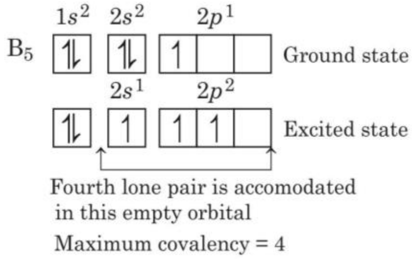
11. The given characteristics for B and its trifluoride is BF_3. Because of the presence of electron deficient boron atom, it acts as Lewis acid.

12. Boron fluoride exists as BF_3. Due to its small size, B atom cannot coordinate to 4 small fluoride ions and hence, cannot form the dimeric molecule. On the other hand, boron hydride exists as B_2H_6. This is due to the fact that hydrogen atom in BH_3 has no electron to form $p\pi$-$p\pi$ back bonding. Thus, boron possesses incomplete octet and BH_3 is dimerised to form B_2H_6 molecule with covalent and three centre bonds.



Structure of diborane, B_2H_6

13. Electronic configuration of B_5 is

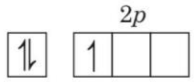


Maximum covalency = 4

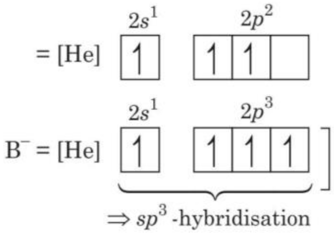
Due to absence of 2*d*-orbital, maximum covalency is four. Thus, i.e. BF_6^{3-} is not formed.

14. Due to the absence of *d*-orbitals in B-atom. BCl_3 does not dimerise but in $AlCl_3$, Al contains empty *d*-orbital so it is capable to undergo dimerisation.

$_5B = [He]\, 2s^2 2p^1$



In first excited state



These four sp^3-hybridised orbitals overlap with four OH^- orbitals to form 4*s*-bonds

Hence, its hybridisation is sp^3 and geometry is tetrahedral.

17. In Hall's process,

$$Al_2O_3 \cdot 2H_2O + Na_2CO_3 \longrightarrow 2NaAlO_2 + CO_2 + 2H_2O$$

$$2NaAlO_2 + 3H_2O + CO_2 \xrightarrow{333K} 2Al(OH)_3 \downarrow + Na_2CO_3$$

$$2Al(OH)_3 \xrightarrow{1475\text{ K}} Al_2O_3 + 3H_2O$$

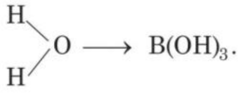
20. Anodising of Al results in the formation of a protective oxide layer over Al surface.

22. Gallium, (Ga) due to its unusual structure to exists as Ga_2 molecules and thus has low melting point. It exists as liquid upto 2000°C and hence, used in high temperature thermometry.

26. BCl_3 is completely hydrolysed by water, yielding boric acid and hydrochloric acid.

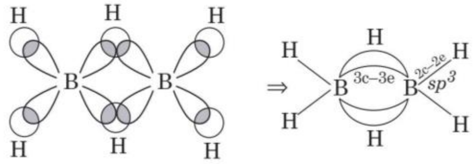
$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$

27. H_3BO_3, due to the presence of electron deficient B atom, in aqueous medium coordinates with a water molecule to form hydrated species



B^{3+} ion pulls the σ electron density of coordinated O atom towards itself, which in turn pulls th3e σ-electron density of the O—H bond of attached water molecule towards itself. This facilitates the removal of H^+. Thus, H_3BO_3 behaves as weak Lewis acid.

29. The structure of B_2H_6 can be shown as



In B_2H_6, four 2-centre-2-electron (2*c* — 2*e*) bonds are present in the same plane and two 3-centre-2-electron (3*c*—2*e*) bonds are present in another plane.

30. Boric acid is a Lewis acid, in it boron possesses sp^2-hybridisation and their molecules are held together by hydrogen bonding.

31. $AlCl_3$ exists as Al_2Cl_6 (dimer). It is covalent and gets easily hydrolysed. It is a Lewis acid and due to covalent bonding it has lower melting point.

32. Aqueous solution of $AlCl_3$ is acidic due to hydrolysis.

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

On strongly heating $Al(OH)_3$ is converted into Al_2O_3.

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

33. Mud is colloidal charged solution which on treatment with alum (Al^{3+}) gets neutralised or coagulated.

35. Due to its high heat of hydration in water, it dimerises. It forms complex of type R_3NAlCl_3 with R_3N.

36. When aluminium oxide and carbon are heated in the presence of dry chlorine gas they result in the formation of anhydrous aluminium chloride.

$$Al_2O_3 + 3Cl_2 + 3C \xrightarrow{\Delta} \underset{\text{Anhydrous}}{2AlCl_3} + 3CO\uparrow$$

37. Silica on heating with carbon at high temperature gives carborundum (silicon carbide).

$$SiO_2 + 3C \xrightarrow{\Delta} \underset{\text{Carborundum}}{SiC} + 2CO$$

Carborundum is very hard substance.

38. Monosilane (e.g. SiH_4) on coming in contact with air burns with a luminous flame producing vortex ring. These rings are of silica as,

$$SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$$

40. According to the given information, the element is carbon. Its two oxides are carbon monoxide (CO) and carbon dioxide (CO_2).

Producer gas is formed when air is passed over heated carbon at 1273 K

$$2C + \underbrace{O_2 + N_2}_{\text{From air}} \longrightarrow \underbrace{2CO + N_2}_{\text{Producer gas}}$$

Carbon monoxide (CO) is a powerful reducing agent. It reduces fesic oxide into iron.

$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$
$$FeO + CO \longrightarrow Fe + CO_2$$

41. Sn^{4+} is more stable than Sn^{2+}. Sn^{2+} have a greater tendency to get converted into Sn^{4+} by losing two electrons hence, it is used as reducing agent.

42. On moving down the group, catenation tendency decreases due to decrease in element bond strength.

Catenation tendency in group 14 elements is highest in carbon while silicon has second highest tendency of catenation among all elements of family due to higher bond energy. The decreasing tendency of catenation among group 14 elements is as follows

$$C >> Si > Ge \approx Sn$$

However, Pb does not show catenation.

45. In SiF_6^{2-} and $SiCl_6^{2-}$, SiF_6^{2-} is known due to the small size of F atoms.

The small six F atoms can be easily accommodated around Si atom to form SiF_6^{2-} while in $SiCl_6^{2-}$, six large Cl atoms cannot be accommodated around Si atom.

46. In carbon family the stability of +2 oxidation state increases on moving down the group in the Periodic table with an increase in atomic number due to screening effect.

47. The stability of hydrides of carbon family decreases down the group, hence order is

$$CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$$

50. Carbon suboxide has linear structure with C—C bond length equal to 130 Å and C—O bond length equal to 120 Å.

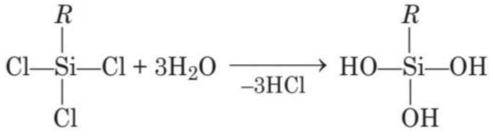
$$O{=}C{=}C{=}C{=}O \longleftrightarrow {}^{-}O{-}C{\equiv}C{-}C{\equiv}O^{+}$$

52. Fullerenes are cage-like molecules and graphite is the thermodynamically most stable allotrope of carbon. It is slippery and soft and hence, used as a dry lubricant in machines.

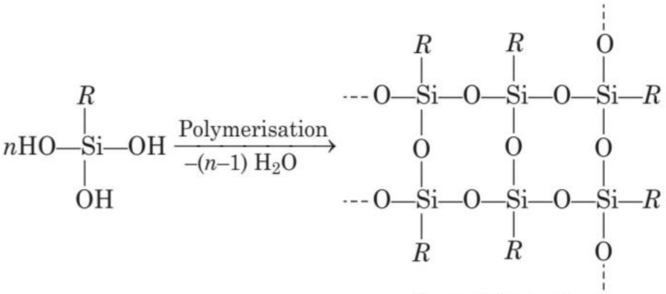
53. C-atoms form covalently bonded plates (layers). Layers are bonded weakly together, that's why one layer can slide over other and cause lubricacy. It cannot be melted easily as large number of atoms being bonded strongly in the layer form big entity.

54. Sheet silicates are formed when three oxygen atoms (bridging O-atoms) of each $(SiO_4)^{4-}$ unit are shared. Hence, the general formula of sheet silicates is $(Si_2O_5)^{2n-}$.

55. Hydrolysis of alkyltrichlorosilanes followed by condensation polymerisation gives cross-linked silicones.



$$Cl{-}\underset{Cl}{\overset{R}{Si}}{-}Cl + 3H_2O \xrightarrow[-3HCl]{} HO{-}\underset{OH}{\overset{R}{Si}}{-}OH$$



Cross-linked silicone

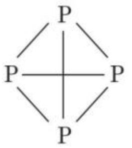
56. When Si is heated with CH_3Cl at high temperature in the presence of Cu as a catalyst, a mixture of mono-, di- and trimethylchlorosilanes along with a small amount of tetramethylsilane is formed.

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

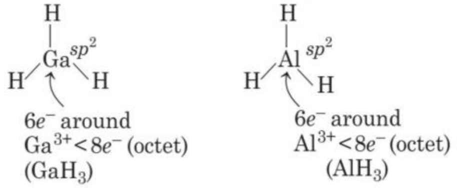
58. The product obtained by the hydrolysis of Me_3SiCl contains only one —OH group which when subjected to polymerisation makes the polymer incapable for further polymerisation, controls the chain length.

Round II

2. In C_{60} (Buckminster fullerene), twenty hexagons and twelve pentagons are present which are interlocked resulting a shape of soccer ball. Every ring in this structure is aromatic and P_4 is.

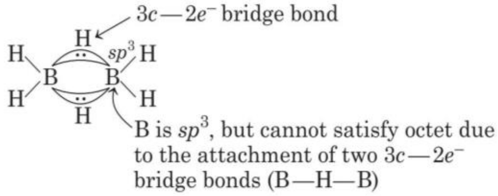


3. GaH_3, AlH_3 and B_2H_6 are the hydrides of group-13 having (ns^2np^1), whereas SiH_4 is an hydride of group 14.



$6e^-$ around $Ga^{3+} < 8e^-$ (octet) (GaH_3)

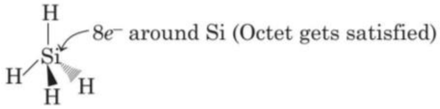
$6e^-$ around $Al^{3+} < 8e^-$ (octet) (AlH_3)



$3c - 2e^-$ bridge bond

B is sp^3, but cannot satisfy octet due to the attachment of two $3c - 2e^-$ bridge bonds (B—H—B)

So, B_2H_6, AlH_3 and GaH_3 are electron deficient hydrides. But, SiH_4 is an electron rich hydride of group 14 having (ns^2np^2), i.e. these hydrides can have the required number of electrons to write their conventional Lewis structures.



6. When an aqueous solution of borax is acidified with HCl, boric acid is formed.

$$\underset{\text{Borax}}{Na_2B_4O_7} + 2HCl + 5H_2O \longrightarrow 2NaCl + \underset{\text{Boric acid}}{4H_3BO_3}$$

Boric acid is a white crystalline solid. It is soapy to touch because of its planar layered structure. Boric acid is a weak monobasic acid. It is not a protonic acid but acts as a Lewis acid by accepting electrons from a hydroxyl ion.

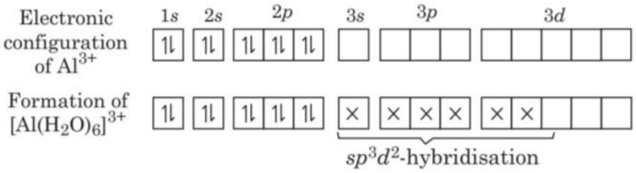
$$B(OH)_3 + 2HOH \longrightarrow [B(OH)_4]^- + H_3O^+$$

7. BCl_3 on hydrolysis in water forms tetrahedral $[B(OH)_4]^-$ species; in which the hybridisation state of B is sp^3.

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

$AlCl_3$ in acidified aqueous solution forms octahedral $[Al(H_2O)_6]^{3+}$ ion.

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



In this complex, the $3d$ orbitals of Al are involved and the hybridisation state of Al is sp^3d^2.

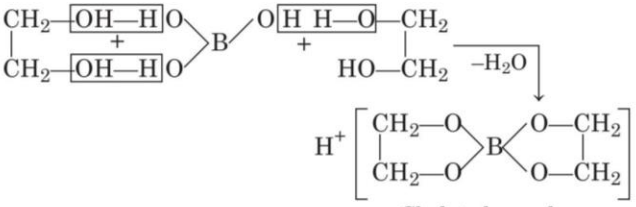
9. $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 \cdot H_2O$ or $Na^+[B(OH)_4]^-$

This reaction is reversible reaction because sodium metaborate, $Na^+[B(OH)_4]^-$ formed by the reaction between $B(OH)_3$ and NaOH gets hydrolysed to regenerate $B(OH)_3$ and NaOH.

$$Na^+[B(OH)_4]^- \xrightarrow[\text{hydrolysis}]{} NaOH + B(OH)_3$$

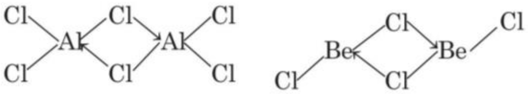
If, some quantity of polyhydroxy compounds like *cis*-1,2-diol, catechol, glycerol etc., is added to the reaction mixture the $B(OH)_3$ combines with such polyhydroxy compounds to give chelated complex compound.

Due to complex compound formation, stability increases and due to higher stability of complex, reaction moves in forward direction.

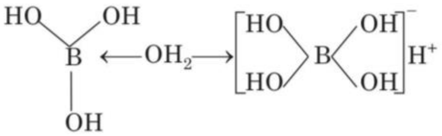


Chelated complex compound

11. Chlorides of both beryllium and aluminium have bridged structures in solid phase



Boric acid is not a protonic acid.



Borazole, inorganic benzene is $B_3N_3H_6$

i.e. $B_3N_3H_6$ is also known as inorganic benzene.

12. In MCl_2, oxidation state of $M = +2$

In MCl_4, oxidation state of $M = +4$

Higher the oxidation state, smaller the size.

Greater the polarising power, greater the covalent characteristic.

Hence, MCl_4 is more covalent and MCl_2 is more ionic.

14. Since, compound '*A*' of boron reacts with NMe_3 to form an adduct '*B*'.

Thus, compound '*A*' is a Lewis acid. Since, adduct '*B*' on hydrolysis gives an acid '*C*' and hydrogen gas, therefore, '*A*' is B_2H_6 and '*C*' is boric acid.

$$\underset{\text{Diborane }(A)}{B_2H_6} + 2NMe_3 \longrightarrow \underset{\text{Adduct }(B)}{2BH_3 \cdot NMe_3}$$

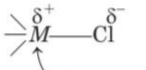
$$BH_3 \cdot NMe_3 + 3H_2O \longrightarrow \underset{\text{Boric acid }(C)}{H_3BO_3} + NMe_3 + 3H_2\uparrow$$

15. As temperature decreases, white tin (β-form) changes to grey tin (α-form).

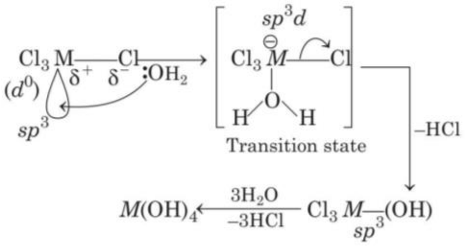
$$\alpha\text{-Sn} \underset{}{\overset{13.2°C}{\rightleftharpoons}} \beta\text{-Sn}$$

α-Sn has a much lower density.

18. The compounds given are the tetrahalides (MCl_4) of group 14 elements. For the hydrolysis, (nucleophilic substitution) of MCl_4, the nature of the M—Cl bond should be as,



It must expand its covalency beyond 4 by the use of its vacant *d*-orbital which will accommodate the lone pair of electrons of H_2O (the nucleophile).



Here, M can be Si, Sn and Pb because they have vacant nd-orbital. But, carbon is a member of second period

($n = 2, l = 0, 1$), it does not have d-orbital ($l = 2$). So, CCl_4 will not be hydrolysed hence correct option is (b).

19. Boron trihalide are Lewis acid. The increasing order of their acidic strength is as follows

$$BF_3 < BCl_3 < BBr_3 < BI_3$$

20. Statement I, II and III are correct whereas statement IV is incorrect. It's correct statement is as atomic radius of B is less than Be.

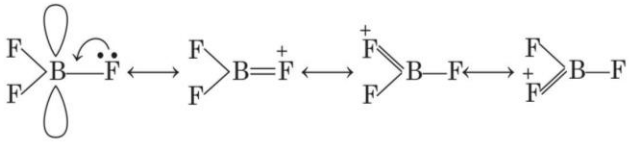
22. (i) $\underset{\text{Borax }(A)}{Na_2B_4O_7} + 2HCl + 5H_2O \longrightarrow 2NaCl + \underset{\substack{\text{Orthoboric acid}\\(X)}}{4H_3BO_3}$

(ii) $\underset{(X)}{H_3BO_3} \xrightarrow{\Delta,\ 370\text{ K}} \underset{\text{Metaboric acid}}{HBO_2} + H_2O$

$$4HBO_2 \xrightarrow[-H_2O]{\Delta,\ >370\text{ K}} \underset{\text{Tetraboric acid}}{[H_2B_4O_7]}$$

$$\xrightarrow{\text{Red heat}} \underset{\substack{\text{Boron trioxide}\\(Z)}}{2B_2O_3} + H_2O$$

23. In BF_3 there is significant $p\pi$- $p\pi$ interaction between unshared p-orbital (having no electron) over boron and the lone pair of electron over fluorine in $2p$ orbital.



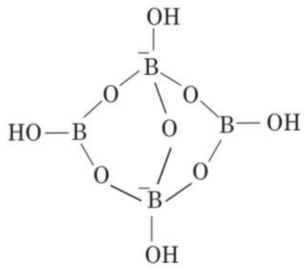
24. $\underset{(A)}{2Al} + N_2 \xrightarrow{\Delta} \underset{(B)}{2AlN}$

$$AlN + 3H_2O \longrightarrow \underset{(C)}{Al(OH)_3} + \underset{(D)}{NH_3}$$

25. The more representative formula of $NaBO_3$ is $Na_2[B_2CO_2^-(OH)_4]{\cdot}6H_2O$ with O_2 signifying peroxide linkage and with a +3 oxidation number.

27. C_{60} an allotrope of carbon contains 20 hexagonal and 12 pentagonal rings of carbon atoms. Thus, the product of x and y is 240.

28. Borax contains the tetrhedral unit, i.e. $[B_4O_5(OH)_4]^{2-}$ and its structure can be shown as



29. (X) is borax, $Na_2B_4O_7 \cdot 10H_2O$ as its aqueous solution is weakly alkaline, it gives a glassy bead on strong heating. The reactions are as follows

(i) $Na_2B_4O_7 + 7H_2O \rightleftharpoons \underset{\text{Strong}}{2NaOH} + \underset{\text{Weak}}{4H_3BO_3}$

Due to the presence of a strong base (NaOH), the aqueous solution is alkaline to litmus.

(ii) $\underset{(X)}{Na_2B_4O_7} \xrightarrow[\text{Swells}]{\Delta} 2NaBO_2 + \underset{\text{Glassy bead}}{B_2O_3}$

(iii) $Na_2B_4O_7 \cdot 10H_2O + H_2SO_4$

$$\longrightarrow Na_2SO_4 + \underset{\substack{\text{White crystal}\\(Z)}}{4H_3BO_3} + 5H_2$$

Thus, the value of x is 4.

30. $B_3N_3H_6$ or borazine is called inorganic benzene. It is obtained by heating diborane with NH_3.

$$\underset{(X)}{3B_2H_6} + 6NH_3 \longrightarrow \underset{\substack{(Y)\\\text{Inorganic benzene}}}{2B_3N_3H_6} + 12H_2\uparrow$$

Diborane is also prepared by treating BF_3 with $LiAlH_4$.

$$4BF_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

Thus, the sum number of boron present in B_2H_6 and $B_3N_3H_6$ is 5.

31. $\underset{(X)}{4BCl_3} + 3LiAlH_4 \longrightarrow \underset{(Y)}{2B_2H_6} + 3AlCl_3 + 3LiCl$

Percentage of hydrogen in $B_2H_6 = \dfrac{6}{27.62} \times 100 = 21.72$

$$B_2H_6 + 3O_2 \xrightarrow{\text{Explosion}} \underset{\text{Boron trioxide}}{B_2O_3} + 3H_2O$$

32. Compound 'A' is **potash alum**.

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$$

It swells on heating due to evolution of water molecule.

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

$$\xrightarrow[\text{Swellsup}]{\Delta} K_2SO_4 \cdot Al_2(SO_4)_3 + 24H_2O$$

It gives violet colour to the flame due to potassium salt.

(i) The solution consists of sulphate ion which combine with Ba^{2+} ion to form white ppt of $BaSO_4$.

$$Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4$$

(ii) $Al_2(SO_4)_3 + 6NH_4OH \longrightarrow \underset{\text{ppt.}}{2Al(OH)_3} + 3(NH_4)_2SO_4$

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

$$NaAlO_2 + NH_4Cl + H_2O \longrightarrow \underset{\text{ppt.}}{Al(OH)_3} + NaCl + NH_3$$

(iii) Potassium salt gives yellow ppt with cobalt nitrite solution.

$$2K_2SO_4 + Na_4[Co(NO_2)_6] \longrightarrow \underset{\text{Yellow ppt.}}{K_4[Co(NO_2)_6]}$$

$$+ 2Na_2SO_4$$

The water of installisation in the given formula is 24.