

BRUSH UP for NEET/JEE 2020

Brush up your concepts to get high rank in NEET/JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

Unit 6

The *p*-Block Elements

INTRODUCTION

- Elements having outer electronic configuration of the type $ns^2 np^1$ to $ns^2 np^6$, with all other inner orbitals completely filled, are termed as *p*-block elements. In other words, the elements in which the last electron enters into any of the outermost *p*-orbitals are called *p*-block elements. Thus, the general outer electronic configuration of the *p*-block elements is $ns^2 np^{1-6}$.
- The elements belonging to the group 13 to 18 of the long form of periodic table are *p*-block elements. The *p*-block elements include metals, non-metals and metalloids.

GROUP 13 ELEMENTS : BORON FAMILY

- Group 13 of the periodic table contains six elements, boron (B), aluminium (Al), gallium (Ga), indium (In), thallium (Tl) and Nihonium (Nh).

Electronic Configuration

- Their valence shell electronic configuration is $ns^2 np^1$.

Element	Symbol	Electronic configuration [noble gas] $ns^2 np^1$
Boron	${}_5\text{B}$	$[\text{He}]2s^2 2p^1$
Aluminium	${}_{13}\text{Al}$	$[\text{Ne}]3s^2 3p^1$
Gallium	${}_{31}\text{Ga}$	$[\text{Ar}]3d^{10} 4s^2 4p^1$
Indium	${}_{49}\text{In}$	$[\text{Kr}]4d^{10} 5s^2 5p^1$
Thallium	${}_{81}\text{Tl}$	$[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^1$
Nihonium	${}_{113}\text{Nh}$	$[\text{Rn}]5f^{14} 6d^{10} 7s^2 7p^1$

General Physical Properties

- **Atomic radii and ionic radii :**
 - Group 13 elements and their ions have smaller size than the corresponding group 2 elements because of the increase in nuclear charge.
 - Their atomic and ionic radii increase on going down the group with an exception at gallium.

Element	Metallic radius (Å)	Ionic radius	
		M^{3+} (Å)	M^+ (Å)
B	0.885	0.27	–
Al	1.43	0.535	–
Ga	1.225	0.620	1.20
In	1.67	0.800	1.40
Tl	1.70	0.885	1.50

- **Melting and boiling points :**
 - Melting points of group 13 elements do not vary regularly due to structural changes in the elements. The melting point decreases from B to Ga and then increases from Ga to Tl.

Element	Melting point (°C)	Boiling point (°C)
B	2300	2550
Al	660	2467
Ga	30	2240
In	157	2050
Tl	303	1470

- Boron shows a very high melting point because it exists as a giant covalent polymer crystal structure consisting of icosahedral units.

- **Ionisation enthalpy :** The first ionisation enthalpy values of group 13 elements are lower than the corresponding alkaline earth metals, due to the fact that removal of electron is easy. [$ns^2 np^1$ configuration].

On moving down the group, *I.E.* decreases from B to Al, but the next element Ga has slightly higher ionisation enthalpy than Al due to the poor shielding of intervening *d*-electrons. It again decreases in In and then increases in the last element Tl.

- **Oxidation states :**

Valence electronic configuration $ns^2 np^1$, suggests that these elements are expected to show +1 and +3 oxidation states.

Element	Oxidation state
B	+3
Al	+1, +3
Ga	+1, +3
In	+1, +3
Tl	+1, +3

- As we move down in the group, stability of +1 oxidation state increases due to the fact that the two *s*-electrons in the outer shell tend to remain paired and do not participate in bonding (inert pair effect).
- The stability of +3 oxidation state decreases from aluminium to thallium.
Thus, $B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}$
 $Tl^+ > In^+ > Ga^+ > Al^+ > B^+$
 $Ga^{3+} > Ga^+$ while $Tl^+ > Tl^{3+}$

- **Electropositive or metallic character :**

- Group 13 elements are less electropositive than alkali metals and alkaline earth metals due to their higher ionisation energies.
- The electropositive character first increases down the group from boron to aluminium and then decreases from aluminium to thallium. Al shows higher metallic character than B due to its larger size and lower ionisation energy. Decrease in the electropositive character beyond Al is due to poor shielding by *d*-electrons, so that the valence electrons cannot be easily removed.
- Electropositive character can also be explained on the basis of their respective electrode potential.
- Because of high ionisation energy and small size, B is considered as non-metal.

- **Electronegativity :**

- Group 13 elements are more electronegative than group 1 elements (alkali metals) and group 2 (alkaline earth metals).
- Electronegativity first decreases from B to Al and then increases due to poor shielding by *d*-electrons.

Element	B	Al	Ga	In	Tl
Pauling's electronegativity	2.0	1.5	1.6	1.7	1.8

TRENDS IN CHEMICAL PROPERTIES

- **Oxides and hydroxides :**

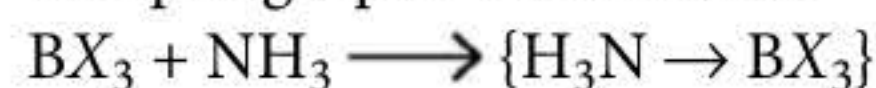
All the elements of group 13 form oxides with formula M_2O_3 and hydroxides with formula $M(OH)_3$. Reactivity of these elements towards oxygen increases down the group.

Oxides	Hydroxides	Nature
B_2O_3	$B(OH)_3$	acidic
Al_2O_3	$Al(OH)_3$	amphoteric
Ga_2O_3	$Ga(OH)_3$	amphoteric
In_2O_3	$In(OH)_3$	basic
Tl_2O_3	$Tl(OH)_3$	strongly basic

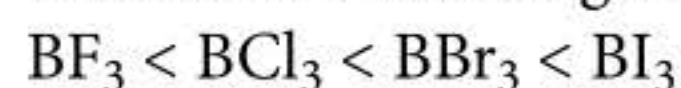
As we moves down the group, the atomic size of elements goes on increasing whereas, the ionisation energy decreases. As a result, the strength of *M* – *O* bond goes on decreasing accounting for the increase in basic character down the group or conversely explains the decrease in acidic character.

- **Halides :** Group 13 elements form trihalides (MX_3). Monohalides of thallium are also given as TlF, TlCl, TlBr and TlI.

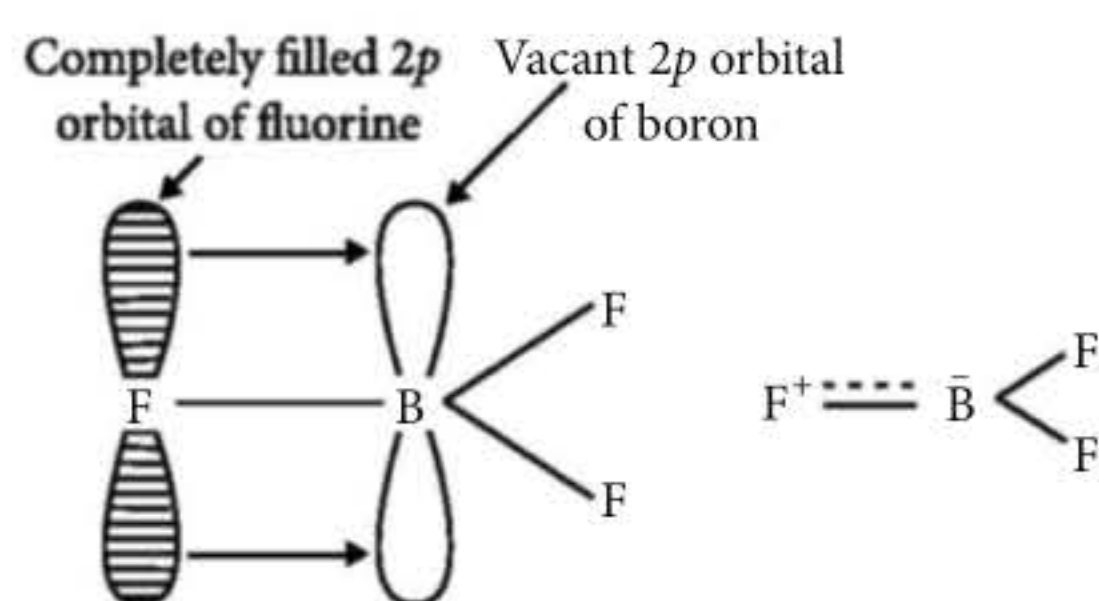
- Due to small size and high electronegativity, all boron halides are covalent and sp^2 hybridised.
- Boron halides BX_3 are electron deficient compounds having six electrons in the outermost orbit thus function as Lewis acid by accepting a pair of electrons.



The Lewis acid strength follows the order :



This order can be explained on the basis of back bonding or back donation. In BF_3 , there is donation of electron from unutilized $2p$ -orbitals of fluorine to a vacant $2p$ -orbital of B.

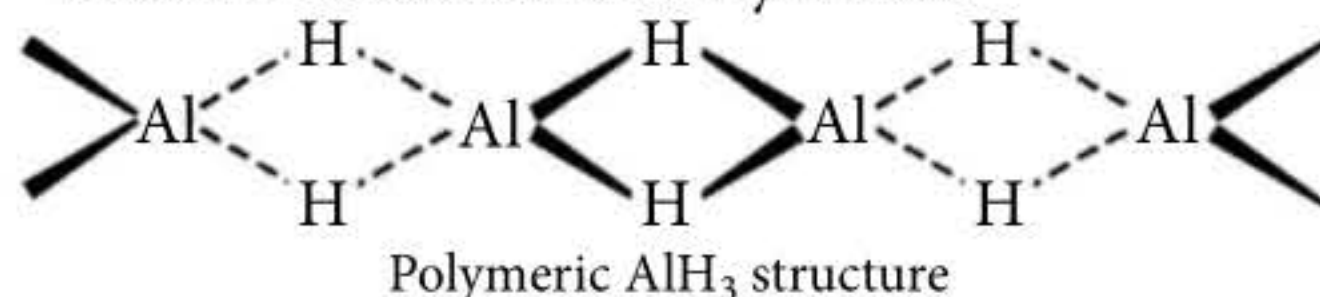


Thus, B–F bond has some double bond character.

- Lewis acid character of halides of group 13 elements decreases in the order : $BX_3 > AlX_3 > GaX_3 > InX_3$

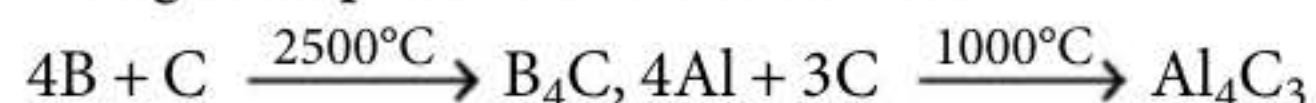
- **Formation of hydrides :**

- None of the group 13 elements reacts directly with hydrogen. However a number of hydrides of these elements are known.
- Boron forms a number of stable covalent hydrides with general formula B_nH_{n+4} (nido-boranes e.g., B_2H_6) and B_nH_{n+6} (arachno-boranes e.g., B_4H_{10}). These are called boranes and are electron deficient compounds.
- The simplest and most important boron hydride is diborane (B_2H_6).
- Other members of this group also form a stable hydride but they are polymeric in nature e.g., $(AlH_3)_n$, $(GaH_3)_n$, $(InH_3)_n$ and contain $M - H_b - M$ bridge bond. Their stability decreases as we move down the group due to corresponding decrease in strength of $M - H$ bond as the size of atom increases.
- Thallium does not form hydrides.

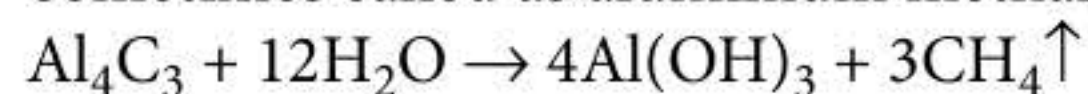


- **Formation of carbides :**

- Boron and aluminium on heating with carbon at high temperature form carbides.



- Boron carbide is covalent in nature.
- Aluminium carbide is ionic carbide. On hydrolysis it gives methane, hence it is sometimes called as aluminium methanide.



Anomalous Properties of Boron

- Due to the smallest size, high ionisation energy, absence of vacant d -orbitals and high electronegativity boron shows anomalous behaviour as compared to other members of the group.

Property	Boron	Other elements of group 13
Metallic behaviour	Non-metal	Metals
Maximum covalency	4	6
Allotropy	Exhibits	Do not exhibit
Oxidation states	Only +3	+1, +3
Compounds	Only covalent	Both ionic and covalent
Halides	Monomeric	Polymeric
Aqueous solution	No ionisation	Form cations
Oxides and hydroxides	Acidic	Amphoteric or basic
Action of non-oxidising acids	No action	React
Combination with metals	Forms boride	Do not combine (form alloy)

PEEP INTO PREVIOUS YEARS

1. Which one of the following elements is unable to form MF_6^{3-} ion?
(a) Ga (b) Al (c) B (d) In
(NEET 2018)

2. Consider the following standard electrode potentials (E° in volts) in aqueous solution,

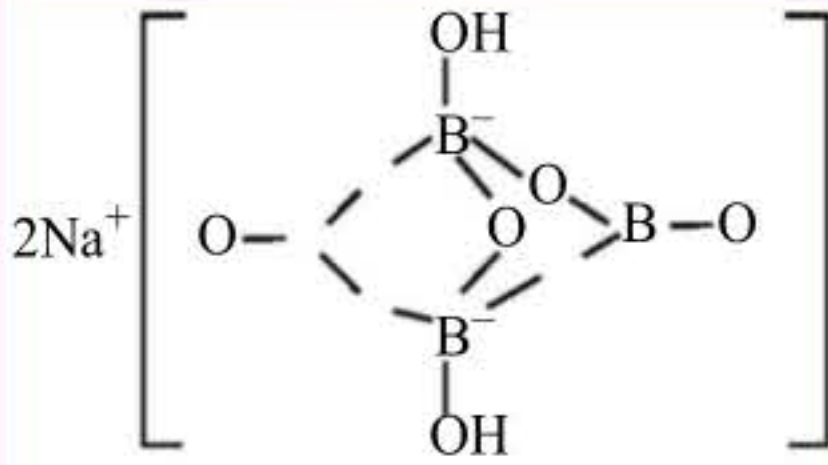
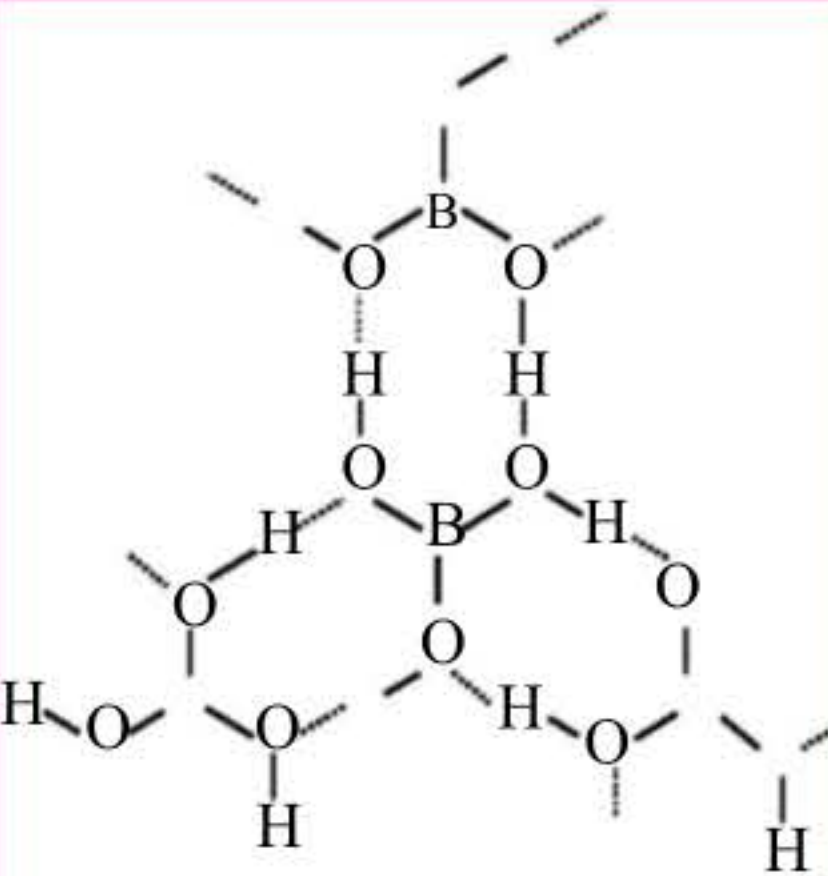
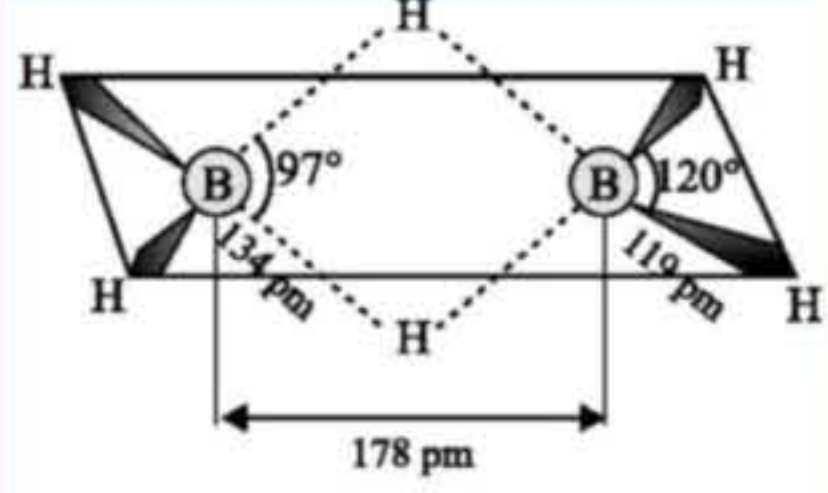
Element	M^{3+}/M	M^+/M
Al	-1.66	+0.55
Tl	+1.26	-0.34

Based on these data, which of the following statements is correct?

- (a) Tl^+ is more stable than Al^+ .
 - (b) Tl^{3+} is more stable than Al^{3+} .
 - (c) Al^+ is more stable than Al^{3+} .
 - (d) Tl^+ is more stable than Al^{3+} .

(JEE Main Online 2017)
3. The increasing order of atomic radii of the following group 13 elements is
(a) $Al < Ga < In < Tl$ (b) $Ga < Al < In < Tl$
(c) $Al < In < Ga < Tl$ (d) $Al < Ga < Tl < In$
(JEE Advanced 2016)

SOME IMPORTANT COMPOUNDS OF GROUP 13 ELEMENTS

	Preparation	Properties	Structure
Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)	$\text{Ca}_2\text{B}_6\text{O}_{11} + 2\text{Na}_2\text{CO}_3 \xrightarrow{\Delta} \text{Na}_2\text{B}_4\text{O}_7 + 2\text{NaBO}_2 + 2\text{CaCO}_3$ <p style="text-align: center;">Colemanite</p> $4\text{NaBO}_2 + \text{CO}_2 \rightarrow \text{Na}_2\text{B}_4\text{O}_7 + \text{Na}_2\text{CO}_3$ $4\text{H}_3\text{BO}_3 + \text{Na}_2\text{CO}_3 \xrightarrow{\Delta} \text{Na}_2\text{B}_4\text{O}_7 + 6\text{H}_2\text{O} + \text{CO}_2$	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \xrightarrow{\Delta} \text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$ $\text{Na}_2\text{B}_4\text{O}_7 \xrightarrow{\Delta} 2\text{NaBO}_2 + \text{B}_2\text{O}_3$ <p style="text-align: center;">Transparent glassy bead</p> $\text{Na}_2\text{B}_4\text{O}_7 + 2\text{NaOH} \rightarrow 4\text{NaBO}_2 + \text{H}_2\text{O}$ $\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{B}_4\text{O}_7$	
	Uses : <ul style="list-style-type: none"> It is used as water softener and cleansing agent. In the laboratory it is used for borax bead test. 		
Orthoboric acid (H_3BO_3)	$\text{Na}_2\text{B}_4\text{O}_7 + 2\text{HCl} + 5\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{BO}_3 + 2\text{NaCl}$ $\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_2\text{SO}_4 + 5\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{BO}_3 + \text{Na}_2\text{SO}_4$ $\text{Ca}_2\text{B}_6\text{O}_{11} + 4\text{SO}_2 + 11\text{H}_2\text{O} \rightarrow 2\text{Ca}(\text{HSO}_3)_2 + 6\text{H}_3\text{BO}_3$ $\text{B}_2\text{H}_6 + 6\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{BO}_3 + 6\text{H}_2$ $\text{BN} + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{BO}_3 + \text{NH}_3$	$\text{H}-\text{OH} + \text{B}(\text{OH})_3 \rightarrow [\text{B}(\text{OH})_4]^- + \text{H}^+;$ <p style="text-align: center;">$\text{p}K_a = 9.25$</p> $\text{H}_3\text{BO}_3 \xrightarrow{370\text{ K}} \text{HBO}_2 + \text{H}_2\text{O}$ $\text{HBO}_2 \xrightarrow{410\text{ K}} \text{H}_2\text{B}_4\text{O}_7 + \text{H}_2\text{O}$ <p style="text-align: center;">Red heat</p> $2\text{B}_2\text{O}_3 + \text{H}_2\text{O}$ $\text{B}(\text{OH})_3 + 3\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{B}(\text{OC}_2\text{H}_5)_3 + 3\text{H}_2\text{O}$ <p style="text-align: center;">Triethyl borate</p>	
	Uses : <ul style="list-style-type: none"> It is used in the manufacture of heat resistant borosilicate glass. The aqueous solution of boric acid is used as a mild antiseptic especially as eye wash under the name <i>boric lotion</i>. 		
Diborane (B_2H_6)	$2\text{NaBH}_4 + \text{I}_2 \xrightarrow{\text{Diglyme}} \text{B}_2\text{H}_6 + 2\text{NaI} + \text{H}_2$ $2\text{BF}_3 + 6\text{NaH} \xrightarrow{450\text{ K}} \text{B}_2\text{H}_6 + 6\text{NaF}$ $4\text{BF}_3 \cdot \text{Et}_2\text{O} + 3\text{LiAlH}_4 \xrightarrow{\text{Diethyl ether}} 2\text{B}_2\text{H}_6 + 3\text{LiF} + 3\text{AlF}_3 + 4\text{Et}_2\text{O}$	$\text{B}_2\text{H}_6 + 3\text{O}_2 \rightarrow \text{B}_2\text{O}_3 + 3\text{H}_2\text{O};$ <p style="text-align: center;">$\Delta_c H^\circ = -1976\text{ kJ mol}^{-1}$</p> $\text{B}_2\text{H}_6 + 6\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{BO}_3 + 6\text{H}_2$ $\text{B}_2\text{H}_6 + 6\text{CH}_3\text{OH} \rightarrow 2\text{B}(\text{OCH}_3)_3 + 6\text{H}_2$ $\text{B}_2\text{H}_6 + 2\text{NaH} \xrightarrow{\text{Diethyl ether}} 2\text{NaBH}_4$ $\text{B}_2\text{H}_6 + 2\text{LiH} \xrightarrow{\text{Diethyl ether}} 2\text{LiBH}_4$ $\text{B}_2\text{H}_6 + 2\text{KOH} + 2\text{H}_2\text{O} \rightarrow 2\text{KBO}_2 + 6\text{H}_2$ $\text{B}_2\text{H}_6 + 2\text{NMe}_3 \rightarrow 2\text{BH}_3 \cdot \text{NMe}_3$ $3\text{B}_2\text{H}_6 + 6\text{NH}_3 \xrightarrow{\text{low temp}} 3[\text{BH}_2(\text{NH}_3)_2]^+ [\text{BH}_4]^- \xrightarrow{473\text{ K}} 2\text{B}_3\text{N}_3\text{H}_6 + 12\text{H}_2$ <p style="text-align: center;">Borazine</p>	
	Uses : <ul style="list-style-type: none"> It is used for preparing a number of borohydrides such as LiBH_4, NaBH_4, etc. It is used as a reducing agent in organic reactions. 		

Aluminium chloride (AlCl ₃)	$2\text{Al} + 3\text{Cl}_2 \longrightarrow 2\text{AlCl}_3$ $2\text{Al} + 6\text{HCl} \longrightarrow 2\text{AlCl}_3 + 3\text{H}_2$ $\text{Al}_2\text{O}_3 + 3\text{C} + 3\text{Cl}_2 \xrightarrow{100^\circ\text{C}} 2\text{AlCl}_3 + 3\text{CO}$	<p>Anhydrous AlCl₃ fumes in moist air due to hydrolysis and the resulting solution is acidic.</p> $\text{AlCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{Al}(\text{OH})_3 + 3\text{HCl}$ $\text{AlCl}_3 + 3\text{NH}_4\text{OH} \longrightarrow \text{Al}(\text{OH})_3 \downarrow + 3\text{NH}_4\text{Cl}$ <p style="text-align: center;">Gelatinous ppt. (Insoluble in excess NH₄OH)</p> $\text{AlCl}_3 + 3\text{NaOH} \longrightarrow \text{Al}(\text{OH})_3 \downarrow + 3\text{NaCl}$ <p style="text-align: center;">(Soluble in excess NaOH)</p> $\text{Al}(\text{OH})_3 + \text{NaOH} \longrightarrow \text{NaAlO}_2 + 2\text{H}_2\text{O}$ <p style="text-align: center;">(Sodium metaaluminate)</p>	
	<p>Uses :</p> <ul style="list-style-type: none"> Anhydrous AlCl₃ is used as a catalyst in Friedel-Craft's reaction and in cracking of petroleum. 		

PEEP INTO PREVIOUS YEARS

- Diborane (B₂H₆) reacts independently with O₂ and H₂O to produce, respectively
 - HBO₂ and H₃BO₃
 - B₂O₃ and H₃BO₃
 - B₂O₃ and [BH₄]⁻
 - H₃BO₃ and B₂O₃

(JEE Main 2019)
- The green colour produced in the borax bead test of a chromium(III) salt is due to
 - CrB
 - Cr₂O₃
 - Cr(BO₂)₃
 - Cr₂(B₄O₇)₃

(JEE Advanced 2019)
- Boric acid is an acid because its molecule
 - contains replaceable H⁺ ion
 - gives up a proton
 - accepts OH⁻ from water releasing proton
 - combines with proton from water molecule.

(NEET Phase-II 2016)

POINTS FOR EXTRA SCORING

- Gallium is a low melting solid (m.pt = 29.8°C) and readily supercools *i.e.*, remains liquid even at temperatures several degrees below its melting point.
- Boron nitride has a layer structure resembling graphite, in which hexagonal ring consists of alternating of boron and nitrogen atoms.
- Corundum (an α-form of Al₂O₃) an extremely hard substance is used as jeweller's rouge to polish glass.

- Boron halides do not exist as dimer due to small size of boron atom which makes it unable to coordinate four large-sized halide ions.
- In thallium triiodide (TlI₃), thallium is in (+1) oxidation state and anion is I₃⁻.
- Thallium is the highly toxic element amongst the group 13 members.
- The anhydrous alum is called burnt alum.

GROUP 14 ELEMENTS : CARBON FAMILY

- Group 14 of the periodic table contains six elements, carbon (C), silicon (Si), germanium (Ge), tin (Sn), lead (Pb) and Flerovium (Fl).

Electronic Configuration

- Their valence shell electronic configuration is ns^2np^2 .

Element	Symbol	Electronic configuration [noble gas] ns^2np^2
Carbon	₆ C	[He] 2s ² 2p ²
Silicon	₁₄ Si	[Ne] 3s ² 3p ²
Germanium	₃₂ Ge	[Ar] 3d ¹⁰ 4s ² 4p ²
Tin	₅₀ Sn	[Kr] 4d ¹⁰ 5s ² 5p ²
Lead	₈₂ Pb	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ²
Flerovium	₁₁₄ Fl	[Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ²

General Physical Properties

- Atomic radii :**
 - The atomic radii of group 14 elements are smaller than those of corresponding elements

of group 13, because as we move from left to right in a period, effective nuclear charge increases, consequently, the size of the atom decreases.

- The atomic radii of group 14 elements increase regularly on moving down the group mainly due to increase in the number of shells.

- **Melting and boiling points :**

- The melting and boiling points of group 14 elements are much higher than those of the elements of group 13. It is because these form four covalent bonds with each other and hence there exists strong binding forces between their atoms both in the solid as well as in the liquid state.
- The melting and boiling points decrease on descending the group from carbon to lead because the $M-M$ bond becomes weaker as the atom size increases.

- **Ionization enthalpy :**

- The first ionization potential of group 14 elements are higher than those of corresponding elements of group 13 due to increased nuclear charge.
- Due to increase in the atomic radii of these elements from C to Pb the ionisation enthalpy decreases on moving down the group.
- Due to ineffective shielding of valence electrons by d - and f -orbitals the sequence for ionization energy is

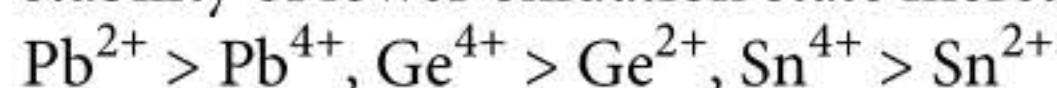


- **Oxidation state :**

Element	Oxidation state
C	+4
Si	+4
Ge	+2, +4
Sn	+2, +4
Pb	+2, +4

The stability of +2 state increases from Ge to Pb, *i.e.*, $Ge^{2+} < Sn^{2+} < Pb^{2+}$ but for +4 oxidation state it is $Ge^{4+} > Sn^{4+} > Pb^{4+}$.

As we move down, inert pair effect increases and stability of lower oxidation state increases.



- **Electropositive character or metallic character :**

Group 14 elements are less electropositive than group 13 elements.

Element	Metallic character
C	Non-metal
Si	Non-metal
Ge	Metalloid
Sn	Metal
Pb	Metal

- **Catenation (Tendency to form chains) :**

- Catenation is the property of elements to form long chains or rings by self-linking of their own atoms through covalent bonds.
- The tendency for catenation decreases in the order $C \gg Si > Ge \approx Sn \gg Pb$
- Carbon shows a remarkable catenation due to smaller size and high electronegativity, so that C-C bond is extremely stable.

- **Allotropy :** All the elements of group 14 except Pb show allotropy.

CHEMICAL PROPERTIES

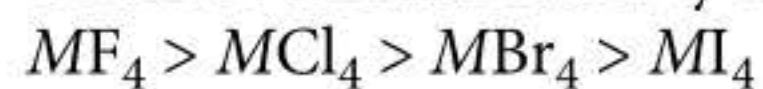
- **Hydrides :** All members of the group form covalent hydrides. Their number and ease of formation decreases down the group. Hydrides of carbon are called *hydrocarbons* (alkanes, alkenes or alkynes). Hydrides of Si and Ge are known as *silanes* and *germanes*. The only hydrides of Sn and Pb are SnH_4 (stannane) and PbH_4 (plumbane).

- Their thermal stability decreases down the group.
- Their reducing character increases down the group.

- **Halides :** All the elements give tetrahedral and covalent halides of the type MX_4 except $PbBr_4$ and PbI_4 .

Thermal stability: $CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$

Order of thermal stability with common metals :

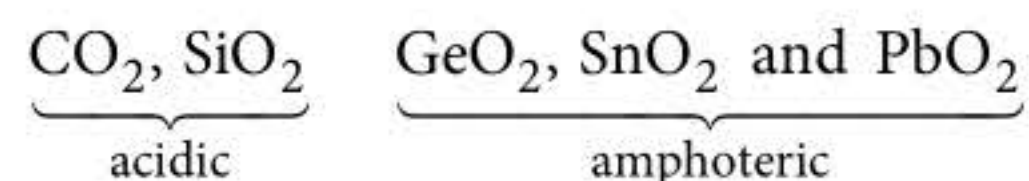


Except CX_4 other tetrahalides can hydrolysed due to the presence of vacant d -orbitals.



Ease of hydrolysis : $SiX_4 > GeX_4 > SnX_4 > PbX_4$

- **Oxides :** They form two type of oxides, mono-oxides of the type MO and dioxides of the type MO_2 .



SiO_2 is a solid with three dimensional network in which Si is bonded to four oxygen atoms tetrahedrally and covalently.

- **Carbides :**

- The binary compounds of carbon with elements other than hydrogen are called *carbides*.
- Ionic carbides are formed by the most electropositive metals such as alkali and alkaline earth metals and Al.
- Both Be_2C and Al_4C_3 are called methanides because they react with H_2O yielding methane.
- Covalent carbides are formed by Si and B.
- SiC (carborundum) has a diamond like structure, hence it is called *artificial diamond*.
- Interstitial carbides are formed by transition elements in which C-atoms occupy interstitial positions in the close-packed arrays of metal atoms. W, Zr, Ti, Ta and Mo can form interstitial carbides.

Allotropes of Carbon

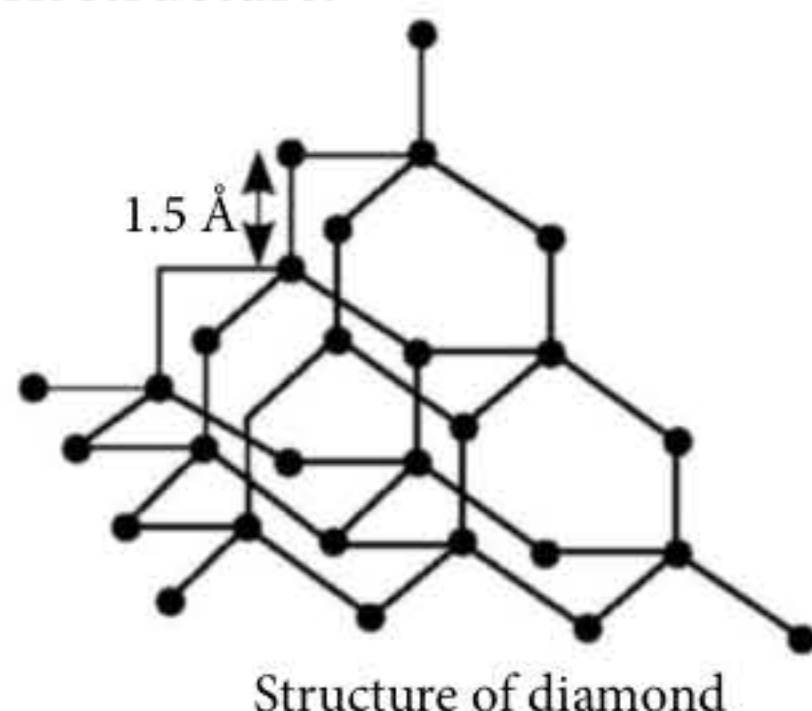
- The allotropic forms of carbon are :
 - Crystalline form : diamond and graphite.
 - Amorphous form : coal, charcoal, lampblack, etc.

Diamond :

- It is a transparent, crystalline substance with very high refractive index.
- It is the purest form of carbon found naturally and can also be made artificially.
- Diamond is the hardest natural substance known and is a bad conductor of electricity.

Structure :

- Each carbon atom of diamond is bonded to four other carbon atoms, through sp^3 hybridised orbitals, situated at the corners of a regular tetrahedron, with C - C bond length of 1.54 Å and bond angle of 109.5° .
- This gives diamond a three-dimensional network structure.

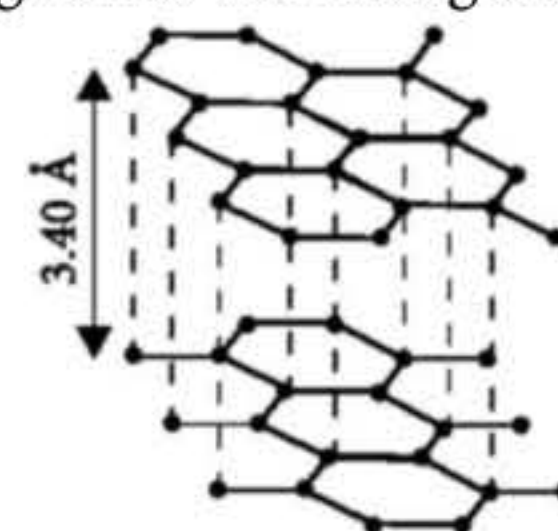


- **Graphite :**

- It is a dark grey, crystalline solid which is soft and greasy to touch. It possesses a metallic lustre.
- It is also known as '*plumbago*' (black lead) as it leaves a black mark on paper.
- It is a good conductor of electricity and its conductivity increases with rise in temperature.

- **Structure :**

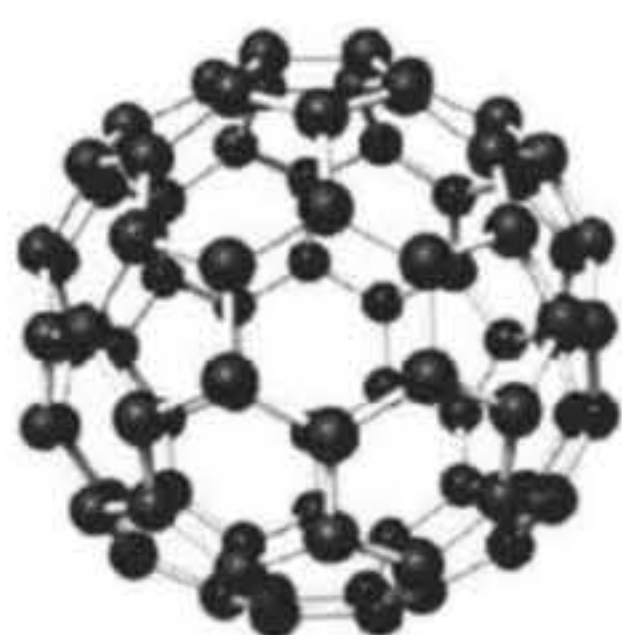
- It has a two dimensional sheet like structure with each carbon atom being covalently bonded to three carbon atoms through sp^2 hybridised orbitals, forming a planar hexagonal structure.
- The fourth electron of each carbon forms a $\pi(\pi)$ bond with partial overlap with that of the neighbouring carbon.
- The C - C bond length is 1.42 Å, shorter than that in diamond. The π -electrons are free to move (mobile electrons) and account for the electrical conductivity.
- The adjacent hexagonal layers (sheets) are held by weak van der Waals' forces thus, making it easy for the layers to slide over one another, accounting for its soft and greasy texture.



Structure of graphite

Fullerenes

- Fullerenes are made by heating graphite in an electric arc in the presence of inert gases such as helium or argon. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules. C_{60} molecule has a shape like soccer ball and called Buckminsterfullerene.
- It contains twenty, six-membered rings and twelve, five-membered rings. A six membered ring is fused with six or five membered ring but a five membered ring can only be fused with six membered ring. All the carbon atoms are equal and they undergo sp^2 hybridisation. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C-C distances of 143.5 pm and 138.3 pm, respectively. Spherical fullerenes are also called *bucky balls* in short.



Structure of Buckminsterfullerene

Anomalous Properties of Carbon

- Carbon differs from other elements of group 14 because of its smaller size, high electronegativity, absence of d -orbitals and high tendency of catenation.

Property	Carbon	Other elements
Hardness	hardest (diamond)	less hard
M.pt. and B.pt.	high	low
Maximum covalency	4	6
Multiple bonds	$p\pi-p\pi$ (high extent)	$p\pi-d\pi$ (low extent)
Catenation	very high tendency	very low
Tetrahalides	does not undergo hydrolysis	undergo hydrolysis

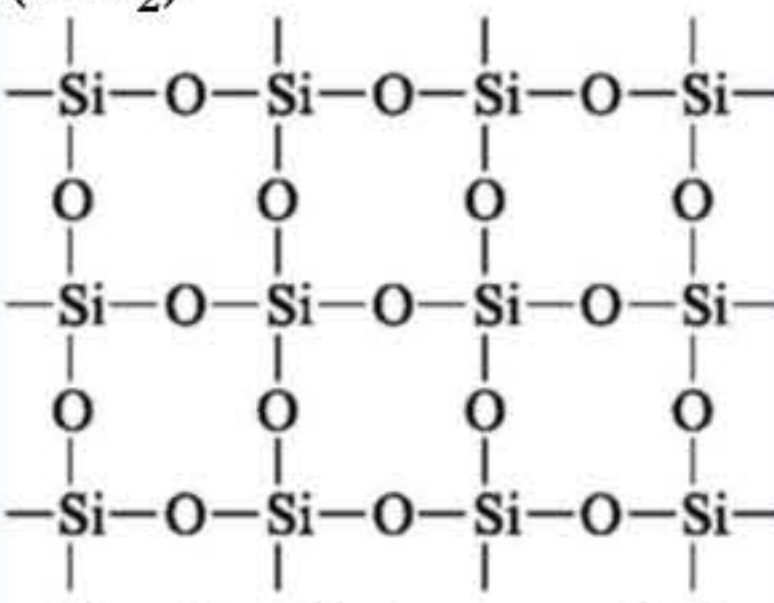
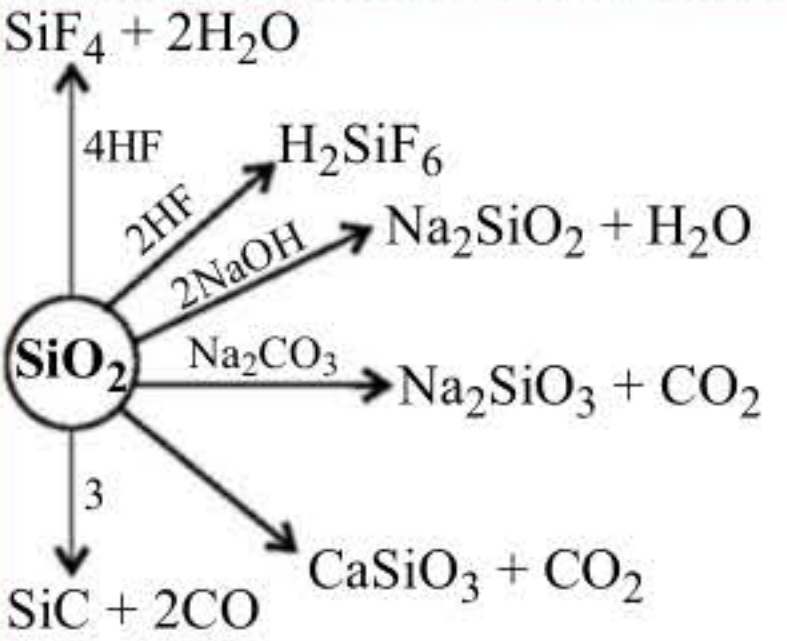
PEEP INTO PREVIOUS YEARS

7. Which of the following is incorrect statement?
 (a) SnF_4 is ionic in nature.
 (b) PbF_4 is covalent in nature.
 (c) SiCl_4 is easily hydrolysed.
 (d) GeX_4 ($X = \text{F, Cl, Br, I}$) is more stable than GeX_2 .
 (NEET 2019)
8. A tin chloride 'Q' undergoes the following reactions (not balanced)
 $\text{Q} + \text{Cl}^- \rightarrow \text{X}$
 $\text{Q} + \text{Me}_3\text{N} \rightarrow \text{Y}$
 $\text{Q} + \text{CuCl}_2 \rightarrow \text{Z} + \text{CuCl}$
 X is monoanion having pyramidal geometry. Both Y and Z are neutral compounds. Choose the correct option(s).
 (a) The central atom in X is sp^3 hybridized.
 (b) There is a coordinate bond in Y.
 (c) The oxidation state of the central atom in Z is +2.
 (d) The central atom in Z has one lone pair of electrons.
 (JEE Advanced 2019)
9. In graphite and diamond, the percentage of p -characters of the hybrid orbitals in hybridisation are respectively
 (a) 33 and 75
 (b) 50 and 75
 (c) 33 and 25
 (d) 67 and 75
 (JEE Main Online 2018)

SOME IMPORTANT COMPOUNDS OF GROUP 14 ELEMENTS

Compound	Preparation	Properties	Uses
Carbon monoxide (CO) $:\text{C}\equiv\text{O}:^+ \leftrightarrow :\text{C}=\ddot{\text{O}}:$ or $:\text{C}\equiv\text{O}:$	Incomplete combustion of carbon and carbon containing compounds. $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$ Commercially CO is obtained as water gas ($\text{H}_2 + \text{CO}$) and producer gas ($\text{CO} + \text{N}_2$). $\text{C}_{(s)} + \text{H}_2\text{O}_{(g)} \xrightarrow{200-1000^\circ\text{C}} \underbrace{\text{CO}_{(g)} + \text{H}_2}_{\text{Water gas}}$	It is neutral towards litmus. It is colourless odourless and tasteless neutral oxide. Reactions: $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$ (Phosgene) $\text{CO} + \text{Fe}_3\text{O}_4 \xrightarrow{1073\text{ K}} 2\text{Fe} + 3\text{CO}_2$ $\text{CO} + 2[\text{Ag}(\text{NH}_3)_2]^+ + \text{OH}^- \rightarrow 2\text{Ag}\downarrow + \text{CO}_2 + \text{H}_2\text{O} + 4\text{NH}_3$ $\text{CO} + \text{ZnO} \xrightarrow{2\text{H}_2} \text{Zn} + \text{CO}_2$ $\text{CO} + \text{Ni} \xrightarrow{323\text{ K}} \text{Ni}(\text{CO})_4$ $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$	In the form of producer gas ($\text{N}_2 + \text{CO}$) and water gas ($\text{H}_2 + \text{CO}$), it is used as fuel. In the metallurgy of nickel. As a reducing agent. For the manufacture of methyl alcohol and synthetic petrol

	$2C_{(s)} \xrightarrow[\text{Air}]{\substack{2g \text{ N}_2g \\ 1000^\circ\text{C}}} \xrightarrow[\text{Producer gas}]{g \quad g}$ $Fe_2O_3 + 3C \xrightarrow{\Delta} 2Fe + 3CO_2$ $ZnO + CO \xrightarrow{\Delta} Zn + CO_2$ $HCOOH \xrightarrow[373 \text{ K}]{\text{Conc. H}_2\text{SO}_4} CO + H_2O$ $\begin{array}{c} \text{COOH} \\ \\ \text{COOH} \end{array} + H_2SO_4 \xrightarrow{\text{Heat}} CO_2 + CO + H_2O$		
<p>Silicones (Si—O—Si) linkage $(R_2SiO)_n$</p> $-O-\left[\begin{array}{c} R \\ \\ Si \\ \\ R \end{array} -O-\left[\begin{array}{c} R \\ \\ Si \\ \\ R \end{array} -R-$	$2RMgCl + SiCl_4 \rightarrow R_2SiCl_2 + 2MgCl_2$ <p style="text-align: center;">Dialkyldichloro silane</p> $R_2SiCl_2 \xrightarrow[-2HCl]{+2H_2O} R_2Si(OH)_2$ <p style="text-align: center;">Dialkyldihydro silane</p> <p style="text-align: center;">-H₂O Polymerisation</p> $\left[\begin{array}{c} R \quad R \\ \quad \\ -O-Si-O-Si-O- \\ \quad \\ R \quad R \end{array} \right]_n$ <p style="text-align: center;">Silicone</p>	<p>Silicone polymers are highly stable towards heat. High dielectric strength. Polymers of silicon with low molecular weight are soluble in organic solvents.</p> <p>They are not affected by weak acids, alkalies, salt solutions and resistant to oxidation.</p> <p>They are water repellents and good electrical insulators.</p>	<p>Silicone polymers are used as sealant, greases, varnishes and these can be used even at very low temperatures (of the order of -40°C).</p> <p>These are used as lubricants at both high and low temperatures.</p> <p>Silicone rubbers are very useful because they retain their elasticity at lower temperatures as compared to other rubbers. They are also mixed in paints to make them damp resistant.</p>
<p>Carbon dioxide (CO₂)</p> $:\ddot{O}=\overset{\ominus}{C}=\ddot{O}:^+ \leftrightarrow ^+O\equiv C-O: \leftrightarrow ^-O-C\equiv O^+$	$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $C_3H_{8(s)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}$ $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$ $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$ $NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2\uparrow + H_2O$		<p>In aerated waters, e.g., in soda water, etc.</p> <p>CO₂ is used in extinguishing fire.</p> <p>Solid carbon dioxide (dry ice) is used as refrigerant.</p> <p>In the manufacture of sodium carbonate and sodium bicarbonate by the Solvay's process.</p>

<p>Silicon dioxide or silica (SiO₂)</p>  <p>Three-dimensional structure of SiO₂</p>	$\text{Si} + \text{O}_2 \longrightarrow \text{SiO}_2$ $\text{SiCl}_4 + 2\text{H}_2\text{O} \longrightarrow \text{SiO}_2 + 4\text{HCl}$ $\text{SiF}_4 + 2\text{H}_2\text{O} \longrightarrow \text{SiO}_2 + 4\text{HF}$		<p>As quartz, it is used as a piezoelectric material. In the form of silica gel, it act as drying agent. It also supports chromatographic materials and catalysts.</p>
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PEEP INTO PREVIOUS YEARS

10. Which of the following compounds is used in cosmetic surgery?

- (a) Silica (b) Silicates
(c) Silicones (d) Zeolites

(Odisha NEET 2019)

11. Lithium aluminium hydride reacts with silicon tetrachloride to form

- (a) LiCl, AlCl₃ and SiH₄
(b) LiCl, AlH₃ and SiH₄
(c) LiH, AlCl₃ and SiCl₂
(d) LiH, AlH₃ and SiH₄

(JEE Main Online 2018)

12. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are

- (a) CH₃SiCl₃ and Si(CH₃)₄
(b) (CH₃)₂SiCl₂ and (CH₃)₃SiCl
(c) (CH₃)₂SiCl₂ and CH₃SiCl₃
(d) SiCl₄ and (CH₃)₃SiCl (JEE Advanced 2015)

POINTS FOR EXTRA SCORING

- Graphite can be converted into diamond at $\approx 55 \times 10^3$ atmospheric pressure.
- Chemical composition of ordinary glass is Na₂SiO₃ · CaSiO₃ · 4SiO₂.
- PbO is called litharge, Red lead (Pb₃O₄) is a mixed oxide.

Answer Key For Peep Into Previous Years

- | | | | | | | | | | | | |
|----|-----|----|-------|----|-----|-----|-----|-----|-----|-----|-----|
| 1. | (c) | 2. | (a) | 3. | (b) | 4. | (b) | 5. | (c) | 6. | (c) |
| 7. | (b) | 8. | (a,b) | 9. | (d) | 10. | (c) | 11. | (a) | 12. | (b) |

WRAP it up!

- AlCl₃ is an electron deficient compound but AlF₃ is not. This is because
 - atomic size of F is smaller than Cl which makes AlF₃ more covalent
 - AlCl₃ is a covalent compound while AlF₃ is an ionic compound
 - AlCl₃ exists as a dimer but AlF₃ does not
 - Al in AlCl₃ is in sp³ hybrid state but Al in AlF₃ is in sp² state.
- Aqueous solution of borax acts as a buffer because
 - it contains weak acid and its salt with strong base
 - it contains tribasic acid and strong base
 - it contains number of neutral water molecules
 - none of these.
- Borosilicate glass has the special property of being
 - transparent
 - uncrackable
 - resistant of heat
 - tough
- Which of the following exists in gaseous form in nature?
 - ClF₃
 - BF₃
 - IF₃
 - ICl