

**Question 11.1:**

Discuss the pattern of variation in the oxidation states of

(i) B to Tl and (ii) C to Pb.

Answer

(i) B to Tl

The electronic configuration of group 13 elements is $ns^2 np^1$. Therefore, the most common oxidation state exhibited by them should be +3. However, it is only boron and aluminium which practically show the +3 oxidation state. The remaining elements, i.e., Ga, In, Tl, show both the +1 and +3 oxidation states. On moving down the group, the +1 state becomes more stable. For example, Tl (+1) is more stable than Tl (+3). This is because of the inert pair effect. The two electrons present in the s-shell are strongly attracted by the nucleus and do not participate in bonding. This inert pair effect becomes more and more prominent on moving down the group. Hence, Ga (+1) is unstable, In (+1) is fairly stable, and Tl (+1) is very stable.

Group 13 element	Oxidation state
B	+3
Al	+3
Ga, In, Tl	+1, +3

The stability of the +3 oxidation state decreases on moving down the group.

(ii) C to Pb

The electronic configuration of group 14 elements is $ns^2 np^2$. Therefore, the most common oxidation state exhibited by them should be +4. However, the +2 oxidation state becomes more and more common on moving down the group. C and Si mostly show the +4 state. On moving down the group, the higher oxidation state becomes less stable. This is because of the inert pair effect. Thus, although Ge, Sn, and Pb show both the +2 and +4 states, the stability of the lower oxidation state increases and that of the higher oxidation state decreases on moving down the group.

Group 14 element	Oxidation state
C	+4



Si	+4
Ge, Sn, Pb	+2, +4

stability of +2 state increases →

C Si Ge Sn Pb

← stability of +4 state decreases

Question 11.2:

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

Answer

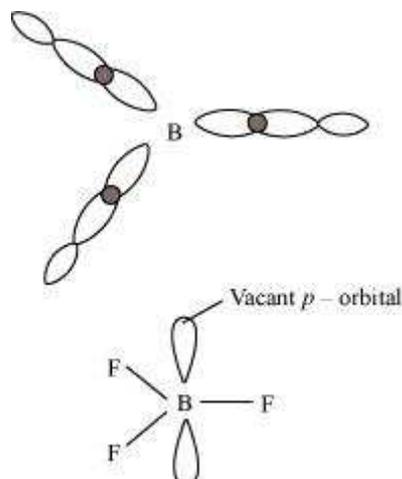
Boron and thallium belong to group 13 of the periodic table. In this group, the +1 oxidation state becomes more stable on moving down the group. BCl_3 is more stable than TlCl_3 because the +3 oxidation state of B is more stable than the +3 oxidation state of Tl. In Tl, the +3 state is highly oxidising and it reverts back to the more stable +1 state.

Question 11.3:

Why does boron trifluoride behave as a Lewis acid?

Answer

The electric configuration of boron is $ns^2 np^1$. It has three electrons in its valence shell. Thus, it can form only three covalent bonds. This means that there are only six electrons around boron and its octet remains incomplete. When one atom of boron combines with three fluorine atoms, its octet remains incomplete. Hence, boron trifluoride remains electron-deficient and acts as a Lewis acid.

**Question 11.4:**

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

Answer

Being a Lewis acid, BCl_3 readily undergoes hydrolysis. Boric acid is formed as a result.



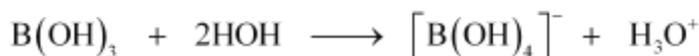
CCl_4 completely resists hydrolysis. Carbon does not have any vacant orbital. Hence, it cannot accept electrons from water to form an intermediate. When CCl_4 and water are mixed, they form separate layers.

**Question 11.5:**

Is boric acid a protic acid? Explain.

Answer

Boric acid is not a protic acid. It is a weak monobasic acid, behaving as a Lewis acid.



It behaves as an acid by accepting a pair of electrons from OH^- ion.

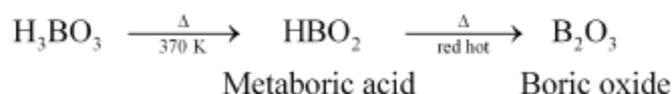
Question 11.6:

Explain what happens when boric acid is heated.

Answer



On heating orthoboric acid (H_3BO_3) at 370 K or above, it changes to metaboric acid (HBO_2). On further heating, this yields boric oxide B_2O_3 .

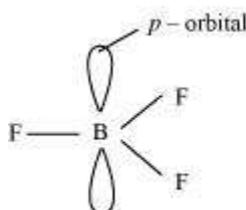
**Question 11.7:**

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

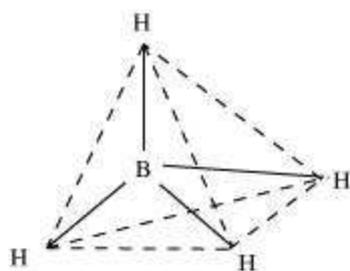
Answer

(i) BF_3

As a result of its small size and high electronegativity, boron tends to form monomeric covalent halides. These halides have a planar triangular geometry. This triangular shape is formed by the overlap of three sp^2 hybridised orbitals of boron with the sp orbitals of three halogen atoms. Boron is sp^2 hybridised in BF_3 .

**(ii) BH_4^-**

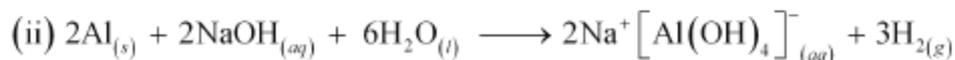
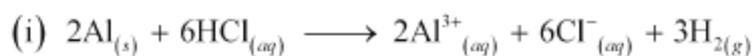
Boron-hydride ion (BH_4^-) is formed by the sp^3 hybridisation of boron orbitals. Therefore, it is tetrahedral in structure.

**Question 11.8:**

Write reactions to justify amphoteric nature of aluminium.

Answer

A substance is called amphoteric if it displays characteristics of both acids and bases. Aluminium dissolves in both acids and bases, showing amphoteric behaviour.

**Question 11.9:**

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

Answer

In an electron-deficient compound, the octet of electrons is not complete, i.e., the central metal atom has an incomplete octet. Therefore, it needs electrons to complete its octet.

(i) BCl_3

BCl_3 is an appropriate example of an electron-deficient compound. B has 3 valence electrons. After forming three covalent bonds with chlorine, the number of electrons around it increases to 6. However, it is still short of two electrons to complete its octet.

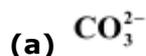
(ii) $SiCl_4$

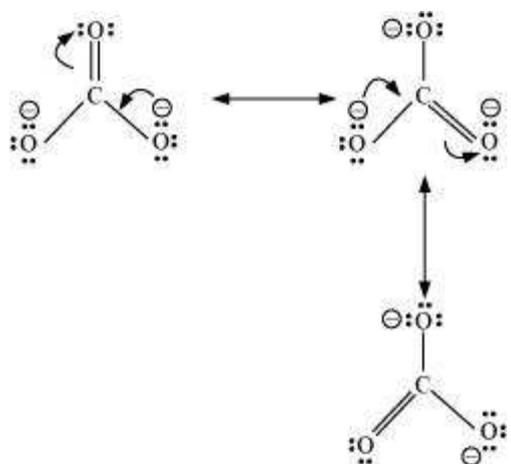
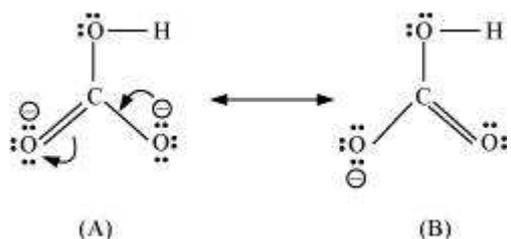
The electronic configuration of silicon is $ns^2 np^2$. This indicates that it has four valence electrons. After it forms four covalent bonds with four chlorine atoms, its electron count increases to eight. Thus, $SiCl_4$ is not an electron-deficient compound.

Question 11.10:

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

Answer



**(b) HCO₃⁻ ion**

There are only two resonating structures for the bicarbonate ion.

Question 11.11:

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

Answer

The state of hybridisation of carbon in:

(a) CO_3^{2-}

C in CO_3^{2-} is sp^2 hybridised and is bonded to three oxygen atoms.

(b) Diamond

Each carbon in diamond is sp^3 hybridised and is bound to four other carbon atoms.

(c) Graphite

Each carbon atom in graphite is sp^2 hybridised and is bound to three other carbon atoms.

**Question 11.12:**

Explain the difference in properties of diamond and graphite on the basis of their structures.

Answer

Diamond	Graphite
It has a crystalline lattice.	It has a layered structure.
In diamond, each carbon atom is sp^3 hybridised and is bonded to four other carbon atoms through a σ bond.	In graphite, each carbon atom is sp^2 hybridised and is bonded to three other carbon atoms through a σ bond. The fourth electron forms a π bond.
It is made up of tetrahedral units.	It has a planar geometry.
The C–C bond length in diamond is 154 pm.	The C–C bond length in graphite is 141.5 pm.
It has a rigid covalent bond network which is difficult to break.	It is quite soft and its layers can be separated easily.
It acts as an electrical insulator.	It is a good conductor of electricity.

Question 11.13:

Rationalise the given statements and give chemical reactions:

- Lead(II) chloride reacts with Cl_2 to give PbCl_4 .
- Lead(IV) chloride is highly unstable towards heat.
- Lead is known not to form an iodide, PbI_4 .

Answer

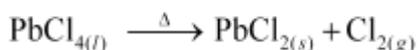
(a) Lead belongs to group 14 of the periodic table. The two oxidation states displayed by this group is +2 and +4. On moving down the group, the +2 oxidation state becomes



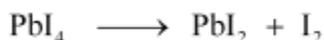
more stable and the +4 oxidation state becomes less stable. This is because of the inert pair effect. Hence, PbCl_4 is much less stable than PbCl_2 . However, the formation of PbCl_4 takes place when chlorine gas is bubbled through a saturated solution of PbCl_2 .



(b) On moving down group IV, the higher oxidation state becomes unstable because of the inert pair effect. Pb(IV) is highly unstable and when heated, it reduces to Pb(II) .



(c) Lead is known not to form PbI_4 . Pb (+4) is oxidising in nature and I^- is reducing in nature. A combination of Pb(IV) and iodide ion is not stable. Iodide ion is strongly reducing in nature. Pb(IV) oxidises I^- to I^2 and itself gets reduced to Pb(II) .

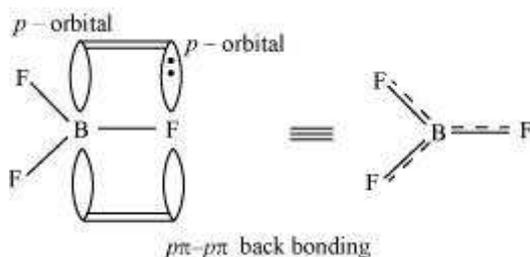


Question 11.14:

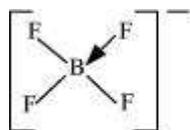
Suggest reasons why the B–F bond lengths in BF_3 (130 pm) and BF_4^- (143 pm) differ.

Answer

The B–F bond length in BF_3 is shorter than the B–F bond length in BF_4^- . BF_3 is an electron-deficient species. With a vacant p -orbital on boron, the fluorine and boron atoms undergo $p\pi-p\pi$ back-bonding to remove this deficiency. This imparts a double-bond character to the B–F bond.



This double-bond character causes the bond length to shorten in BF_3 (130 pm). However, when BF_3 coordinates with the fluoride ion, a change in hybridisation from sp^2 (in BF_3) to sp^3 (in BF_4^-) occurs. Boron now forms 4 σ bonds and the double-bond character is lost. This accounts for a B–F bond length of 143 pm in BF_4^- ion.



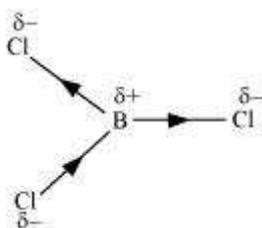
Tetrahedral structure

Question 11.15:

If B–Cl bond has a dipole moment, explain why BCl₃ molecule has zero dipole moment.

Answer

As a result of the difference in the electronegativities of B and Cl, the B–Cl bond is polar in nature. However, the BCl₃ molecule is non-polar. This is because BCl₃ is trigonal planar in shape. It is a symmetrical molecule. Hence, the respective dipole-moments of the B–Cl bond cancel each other, thereby causing a zero-dipole moment.

**Question 11.16:**

Aluminium trifluoride is insoluble in anhydrous HF but dissolves on addition of NaF. Aluminium trifluoride precipitates out of the resulting solution when gaseous BF₃ is bubbled through. Give reasons.

Answer

Hydrogen fluoride (HF) is a covalent compound and has a very strong intermolecular hydrogen-bonding. Thus, it does not provide ions and aluminium fluoride (AlF) does not dissolve in it. Sodium fluoride (NaF) is an ionic compound and when it is added to the mixture, AlF dissolves. This is because of the availability of free F⁻. The reaction involved in the process is:



When boron trifluoride (BF₃) is added to the solution, aluminium fluoride precipitates out of the solution. This happens because the tendency of boron to form complexes is much



more than that of aluminium. Therefore, when BF_3 is added to the solution, B replaces Al from the complexes according to the following reaction:

**Question 11.17:**

Suggest a reason as to why CO is poisonous.

Answer

Carbon monoxide is highly-poisonous because of its ability to form a complex with haemoglobin. The CO–Hb complex is more stable than the O_2 –Hb complex. The former prevents Hb from binding with oxygen. Thus, a person dies because of suffocation on not receiving oxygen. It is found that the CO–Hb complex is about 300 times more stable than the O_2 –Hb complex.

Question 11.18:

How is excessive content of CO_2 responsible for global warming?

Answer

Carbon dioxide is a very essential gas for our survival. However, an increased content of CO_2 in the atmosphere poses a serious threat. An increment in the combustion of fossil fuels, decomposition of limestone, and a decrease in the number of trees has led to greater levels of carbon dioxide. Carbon dioxide has the property of trapping the heat provided by sunrays. Higher the level of carbon dioxide, higher is the amount of heat trapped. This results in an increase in the atmospheric temperature, thereby causing global warming.

Question 11.19:

Explain structures of diborane and boric acid.

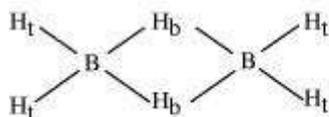
Answer

(a) Diborane

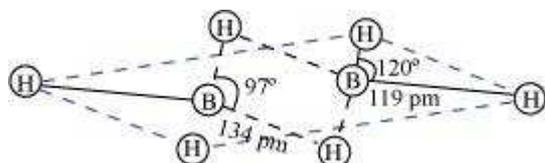
B_2H_6 is an electron-deficient compound. B_2H_6 has only 12 electrons – 6 e^- from 6 H atoms and 3 e^- each from 2 B atoms. Thus, after combining with 3 H atoms, none of the boron atoms has any electrons left. X-ray diffraction studies have shown the structure of diborane as:



H_t = terminal hydrogen
 H_b = bridging hydrogen

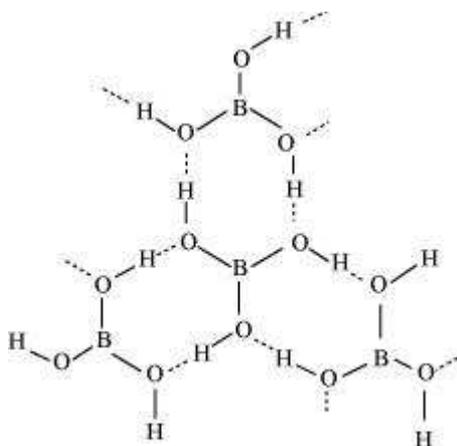


2 boron and 4 terminal hydrogen atoms (H_t) lie in one plane, while the other two bridging hydrogen atoms (H_b) lie in a plane perpendicular to the plane of boron atoms. Again, of the two bridging hydrogen atoms, one H atom lies above the plane and the other lies below the plane. The terminal bonds are regular two-centre two-electron ($2c - 2e^-$) bonds, while the two bridging (B-H-B) bonds are three-centre two-electron ($3c - 2e^-$) bonds.



(b) Boric acid

Boric acid has a layered structure. Each planar BO_3 unit is linked to one another through H atoms. The H atoms form a covalent bond with a BO_3 unit, while a hydrogen bond is formed with another BO_3 unit. In the given figure, the dotted lines represent hydrogen bonds.



Question 11.20:

What happens when

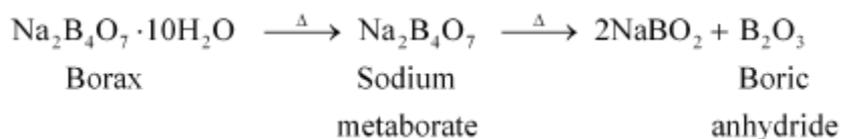
- Borax is heated strongly,
- Boric acid is added to water,



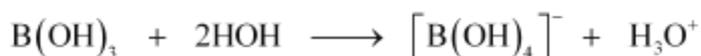
- (c) Aluminium is treated with dilute NaOH,
(d) BF_3 is reacted with ammonia?

Answer

(a) When heated, borax undergoes various transitions. It first loses water molecules and swells. Then, it turns into a transparent liquid, solidifying to form a glass-like material called borax bead.



(b) When boric acid is added to water, it accepts electrons from OH^- ion.



(c) Al reacts with dilute NaOH to form sodium tetrahydroaluminate(III). Hydrogen gas is liberated in the process.



(d) BF_3 (a Lewis acid) reacts with NH_3 (a Lewis base) to form an adduct. This results in a complete octet around B in BF_3 .



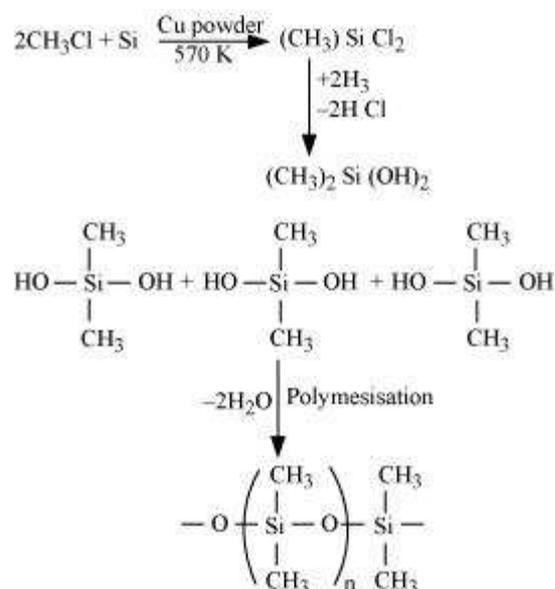
Question 11.21:

Explain the following reactions

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

Answer

(a) When silicon reacts with methyl chloride in the presence of copper (catalyst) and at a temperature of about 537 K, a class of organosilicon polymers called methyl-substituted chlorosilanes (MeSiCl_3 , Me_2SiCl_2 , Me_3SiCl , and Me_4Si) are formed.



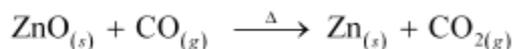
(b) When silicon dioxide (SiO_2) is heated with hydrogen fluoride (HF), it forms silicon tetrafluoride (SiF_4). Usually, the Si-O bond is a strong bond and it resists any attack by halogens and most acids, even at a high temperature. However, it is attacked by HF.



The SiF_4 formed in this reaction can further react with HF to form hydrofluorosilicic acid.



(c) When CO reacts with ZnO, it reduces ZnO to Zn. CO acts as a reducing agent.



(d) When hydrated alumina is added to sodium hydroxide, the former dissolves in the latter because of the formation of sodium meta-aluminate.



Question 11.22:

Give reasons:

- Conc. HNO_3 can be transported in aluminium container.
- A mixture of dilute NaOH and aluminium pieces is used to open drain.
- Graphite is used as lubricant.
- Diamond is used as an abrasive.
- Aluminium alloys are used to make aircraft body.



(vi) Aluminium utensils should not be kept in water overnight.

(vii) Aluminium wire is used to make transmission cables.

Answer

(i) Concentrated HNO_3 can be stored and transported in aluminium containers as it reacts with aluminium to form a thin protective oxide layer on the aluminium surface. This oxide layer renders aluminium passive.

(ii) Sodium hydroxide and aluminium react to form sodium tetrahydroxoaluminate(III) and hydrogen gas. The pressure of the produced hydrogen gas is used to open blocked drains.



(iii) Graphite has a layered structure and different layers of graphite are bonded to each other by weak van der Waals' forces. These layers can slide over each other. Graphite is soft and slippery. Therefore, graphite can be used as a lubricant.

(iv) In diamond, carbon is sp^3 hybridised. Each carbon atom is bonded to four other carbon atoms with the help of strong covalent bonds. These covalent bonds are present throughout the surface, giving it a very rigid 3-D structure. It is very difficult to break this extended covalent bonding and for this reason, diamond is the hardest substance known. Thus, it is used as an abrasive and for cutting tools.

(v) Aluminium has a high tensile strength and is very light in weight. It can also be alloyed with various metals such as Cu, Mn, Mg, Si, and Zn. It is very malleable and ductile. Therefore, it is used in making aircraft bodies.

(vi) The oxygen present in water reacts with aluminium to form a thin layer of aluminium oxide. This layer prevents aluminium from further reaction. However, when water is kept in an aluminium vessel for long periods of time, some amount of aluminium oxide may dissolve in water. As aluminium ions are harmful, water should not be stored in aluminium vessels overnight.

(vii) Silver, copper, and aluminium are among the best conductors of electricity. Silver is an expensive metal and silver wires are very expensive. Copper is quite expensive and is also very heavy. Aluminium is a very ductile metal. Thus, aluminium is used in making wires for electrical conduction.

**Question 11.23:**

Explain why is there a phenomenal decrease in ionisation enthalpy from carbon to silicon?

Answer

Ionisation enthalpy of carbon (the first element of group 14) is very high (1086 kJ/mol). This is expected owing to its small size. However, on moving down the group to silicon, there is a sharp decrease in the enthalpy (786 kJ). This is because of an appreciable increase in the atomic sizes of elements on moving down the group.

Question 11.24:

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

Answer

Atomic radius (in pm)	
Aluminium	143
Gallium	135

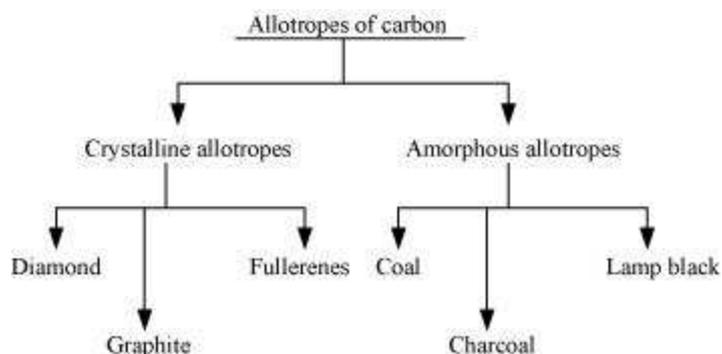
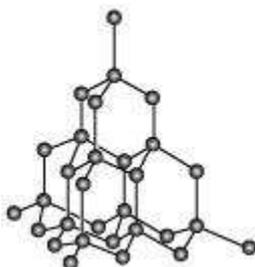
Although Ga has one shell more than Al, its size is lesser than Al. This is because of the poor shielding effect of the $3d$ -electrons. The shielding effect of d -electrons is very poor and the effective nuclear charge experienced by the valence electrons in gallium is much more than it is in the case of Al.

Question 11.25:

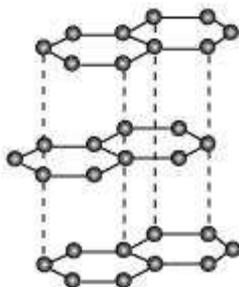
What are allotropes? Sketch the structure of two allotropes of carbon namely diamond and graphite. What is the impact of structure on physical properties of two allotropes?

Answer

Allotropy is the existence of an element in more than one form, having the same chemical properties but different physical properties. The various forms of an element are called allotropes.

**Diamond:**

The rigid 3-D structure of diamond makes it a very hard substance. In fact, diamond is one of the hardest naturally-occurring substances. It is used as an abrasive and for cutting tools.

Graphite:

It has sp^2 hybridised carbon, arranged in the form of layers. These layers are held together by weak van der Waals' forces. These layers can slide over each other, making graphite soft and slippery. Therefore, it is used as a lubricant.

Question 11.26:

(a) Classify following oxides as neutral, acidic, basic or amphoteric:

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

(b) Write suitable chemical equations to show their nature.



Answer

(1) CO = Neutral

(2) B₂O₃ = Acidic

Being acidic, it reacts with bases to form salts. It reacts with NaOH to form sodium metaborate.



(3) SiO₂ = Acidic

Being acidic, it reacts with bases to form salts. It reacts with NaOH to form sodium silicate.



(4) CO₂ = Acidic

Being acidic, it reacts with bases to form salts. It reacts with NaOH to form sodium carbonate.



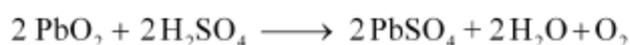
(5) Al₂O₃ = Amphoteric

Amphoteric substances react with both acids and bases. Al₂O₃ reacts with both NaOH and H₂SO₄.



(6) PbO₂ = Amphoteric

Amphoteric substances react with both acids and bases. PbO₂ reacts with both NaOH and H₂SO₄.



(7) Tl₂O₃ = Basic

Being basic, it reacts with acids to form salts. It reacts with HCl to form thallium chloride.



**Question 11.27:**

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

Answer

Thallium belongs to group 13 of the periodic table. The most common oxidation state for this group is +3. However, heavier members of this group also display the +1 oxidation state. This happens because of the inert pair effect. Aluminium displays the +3 oxidation state and alkali metals display the +1 oxidation state. Thallium displays both the oxidation states. Therefore, it resembles both aluminium and alkali metals.

Thallium, like aluminium, forms compounds such as $TlCl_3$ and Tl_2O_3 . It resembles alkali metals in compounds Tl_2O and $TlCl$.

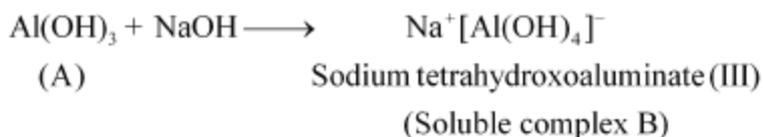
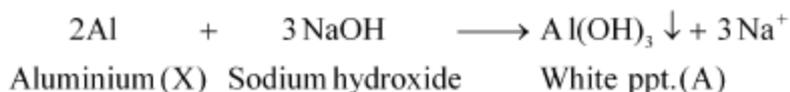
Question 11.28:

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

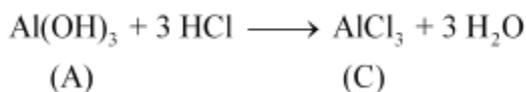
Answer

The given metal X gives a white precipitate with sodium hydroxide and the precipitate dissolves in excess of sodium hydroxide. Hence, X must be aluminium.

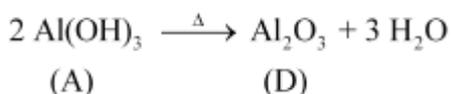
The white precipitate (compound A) obtained is aluminium hydroxide. The compound B formed when an excess of the base is added is sodium tetrahydroxoaluminate(III).



Now, when dilute hydrochloric acid is added to aluminium hydroxide, aluminium chloride (compound C) is obtained.



Also, when compound A is heated strongly, it gives compound D. This compound is used to extract metal X. Aluminium metal is extracted from alumina. Hence, compound D must be alumina.

**Question 11.29:**

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

Answer

(a) Inert pair effect

As one moves down the group, the tendency of *s*-block electrons to participate in chemical bonding decreases. This effect is known as inert pair effect. In case of group 13 elements, the electronic configuration is $ns^2 np^1$ and their group valency is +3. However, on moving down the group, the +1 oxidation state becomes more stable. This happens because of the poor shielding of the ns^2 electrons by the *d*- and *f*- electrons. As a result of the poor shielding, the ns^2 electrons are held tightly by the nucleus and so, they cannot participate in chemical bonding.

(b) Allotropy

Allotropy is the existence of an element in more than one form, having the same chemical properties but different physical properties. The various forms of an element are called allotropes. For example, carbon exists in three allotropic forms: diamond, graphite, and fullerenes.

(c) Catenation

The atoms of some elements (such as carbon) can link with one another through strong covalent bonds to form long chains or branches. This property is known as catenation. It is most common in carbon and quite significant in Si and S.

Question 11.30:

A certain salt X, gives the following results.

(i) Its aqueous solution is alkaline to litmus.



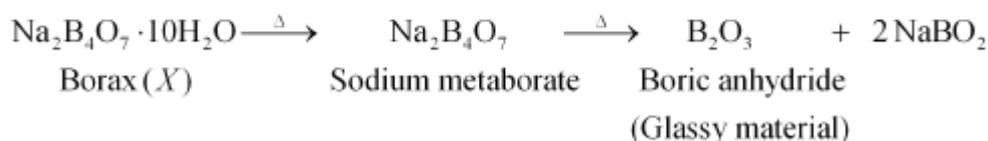
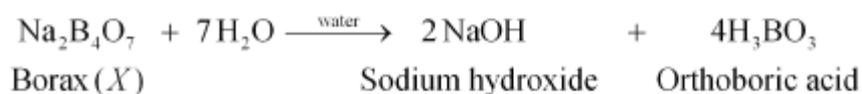
- (ii) It swells up to a glassy material Y on strong heating.
(iii) When conc. H_2SO_4 is added to a hot solution of X, white crystal of an acid Z separates out.

Write equations for all the above reactions and identify X, Y and Z.

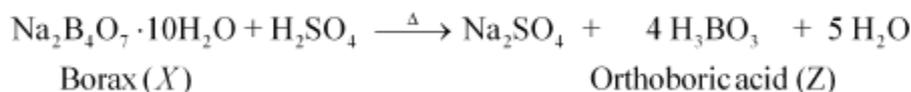
Answer

The given salt is alkaline to litmus. Therefore, X is a salt of a strong base and a weak acid. Also, when X is strongly heated, it swells to form substance Y. Therefore, X must be borax.

When borax is heated, it loses water and swells to form sodium metaborate. When heating is continued, it solidifies to form a glassy material Y. Hence, Y must be a mixture of sodium metaborate and boric anhydride.



When concentrated acid is added to borax, white crystals of orthoboric acid (Z) are formed.

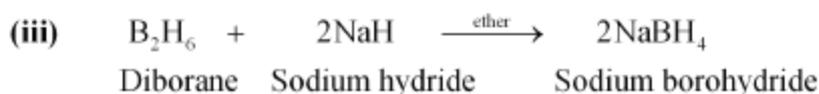
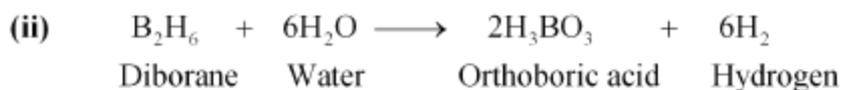
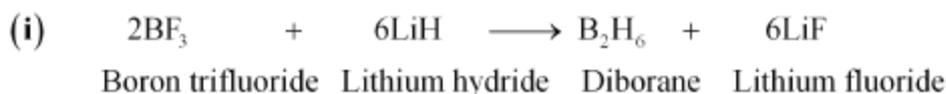


Question 11.31:

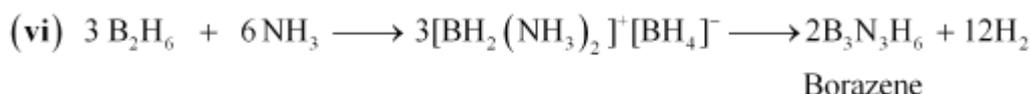
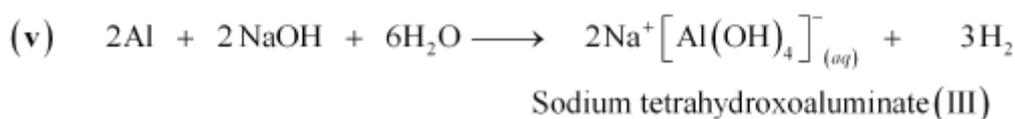
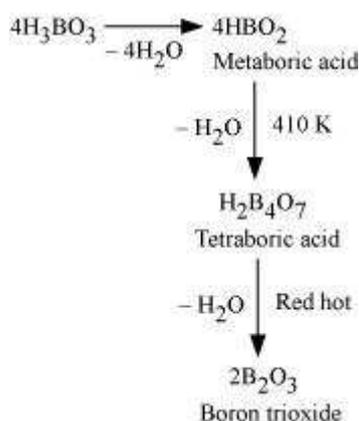
Write balanced equations for:

- (i) $\text{BF}_3 + \text{LiH} \rightarrow$
(ii) $\text{B}_2\text{H}_6 + \text{H}_2\text{O} \rightarrow$
(iii) $\text{NaH} + \text{B}_2\text{H}_6 \rightarrow$
(iv) $\text{H}_3\text{BO}_3 \xrightarrow{\Delta}$
(v) $\text{Al} + \text{NaOH} \rightarrow$
(vi) $\text{B}_2\text{H}_6 + \text{NH}_3 \rightarrow$

Answer



(iv)



Question 11.32:

Give one method for industrial preparation and one for laboratory preparation of CO and CO₂ each.

Answer

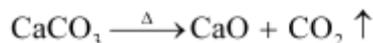
Carbon dioxide

In the laboratory, CO₂ can be prepared by the action of dilute hydrochloric acid on calcium carbonate. The reaction involved is as follows:





CO₂ is commercially prepared by heating limestone. The reaction involved is as follows:

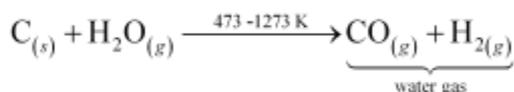


Carbon monoxide

In the laboratory, CO is prepared by the dehydration of formic acid with conc. H₂SO₄, at 373 K. The reaction involved is as follows:



CO is commercially prepared by passing steam over hot coke. The reaction involved is as follows:



Question 11.33:

An aqueous solution of borax is

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

Answer

(c) Borax is a salt of a strong base (NaOH) and a weak acid (H₃BO₃). It is, therefore, basic in nature.

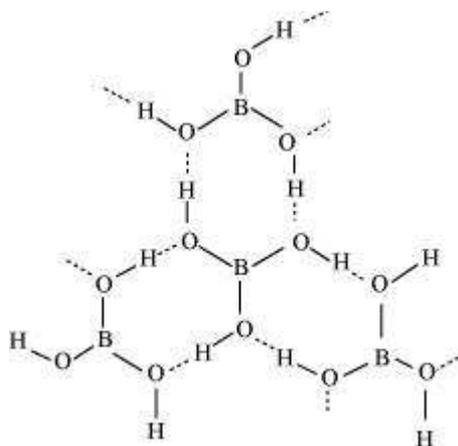
Question 11.34:

Boric acid is polymeric due to

- (a) its acidic nature (b) the presence of hydrogen bonds
(c) its monobasic nature (d) its geometry

Answer

(b) Boric acid is polymeric because of the presence of hydrogen bonds. In the given figure, the dotted lines represent hydrogen bonds.

**Question 11.35:**

The type of hybridisation of boron in diborane is

- (a) sp (b) sp^2 (c) sp^3 (d) dsp^2

Answer

(c) Boron in diborane is sp^3 hybridised.

Question 11.36:

Thermodynamically the most stable form of carbon is

- (a) diamond (b) graphite
(c) fullerenes (d) coal

Answer

(b) Graphite is thermodynamically the most stable form of carbon.

Question 11.37:

Elements of group 14

- (a) exhibit oxidation state of +4 only
(b) exhibit oxidation state of +2 and +4
(c) form M^{2-} and M^{4+} ion
(d) form M^{2+} and M^{4+} ions

Answer

(b) The elements of group 14 have 4 valence electrons. Therefore, the oxidation state of the group is +4. However, as a result of the inert pair effect, the lower oxidation state



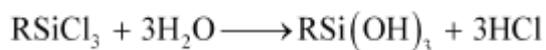
becomes more and more stable and the higher oxidation state becomes less stable. Therefore, this group exhibits +4 and +2 oxidation states.

Group 14 element	Oxidation state
C	+4
Si	+4
Ge, Sn, Pb	+2, +4

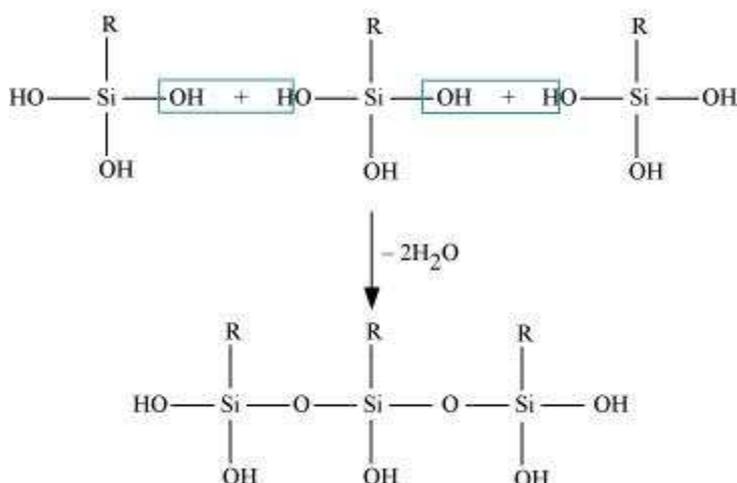
Question 11.38:

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

Answer

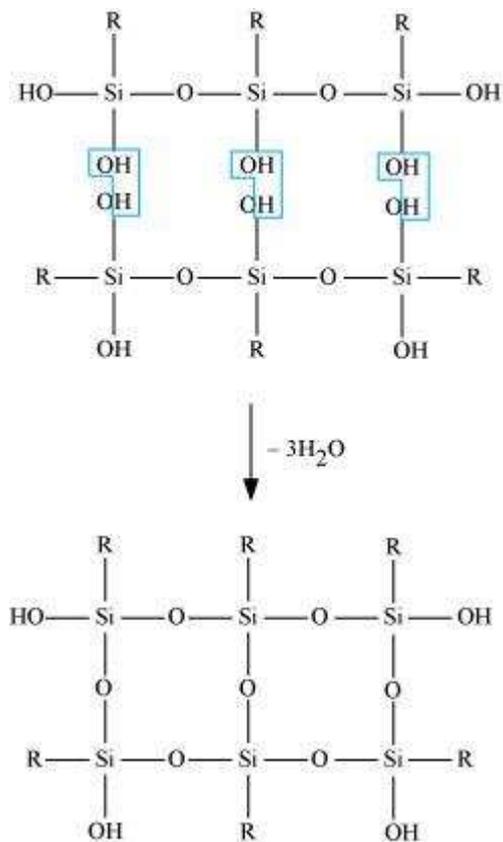


(i)





(ii)

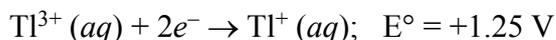


UNIT-11

p-BLOCK ELEMENTS

Group-13 Elements

- **Inert pair effect** : It is the reluctance of the *s*-electrons of the valence shell to take part in bonding. It arises due to poor or ineffective shielding of the *ns*² electrons of the valence shell by the intervening *d*- and/or *f*-electrons. Inert pair effect increases down a group and thus the elements present in the lower part of the group show lower oxidation states which is two units less than the highest group oxidation state. In group 13 elements, inert pair effect is more pronounced in Tl.
- **Oxidation states** : B and Al show an oxidation state of +3 only while Indium and thallium show oxidation states of both +1 and +3. Further due to inert pair effect, as we move down the group, the stability of +3 oxidation state decreases while that of +1 oxidation state increases. For Tl, it is the +1 oxidation state which is more stable than +3 as shown by the redox potential data :



The decrease in stability of +3 oxidation state with increasing atomic number is due to decrease in bond energy with increase in size from Al to Tl. As a result, the energy required to unpair the *ns*² electrons is not compensated by the energy released in forming two additional bonds.

Stability of +1 oxidation state follows the trend : Ga < In < Tl

- **Halides** : All the elements of group 13 (except thallium which preferably forms thallos monohalides) form trihalides of the general formula MX₃ where X = F, Cl, Br and I.
All the boron trihalides, *i.e.*, BF₃, BCl₃, BBr₃ and BI₃ and aluminium trihalides *i.e.*, AlCl₃, AlBr₃ and AlI₃ (AlF₃ being ionic) are covalent compounds. Whereas boron trihalides exist as only monomers, aluminium trihalides exist as dimers.
- **Nature of Trihalides** : The trihalides of group 13 elements have only six electrons in the valence shell and hence have a strong tendency to accept a pair of electrons to acquire the nearest inert gas configuration. Consequently trihalides of group 13 elements behave as Lewis acids.

Group-14 Elements

- **Oxidation states :** All the elements show an oxidation state of +4. However, as we move down the group from C to Pb, the stability of +4 oxidation state decrease while that of +2 oxidation state increases due to inert pair effect. Thus, +4 oxidation state is important for C and Si while +2 state becomes increasingly important for Ge, Sn and Pb. The stability of the divalent state increases in the sequence $\text{Ge} < \text{Sn} < \text{Pb}$.
- **Catenation :** The property of self-linking of an atoms of an element through covalent bonds to form straight or branched chains and rings of different sizes is called **catenation**. The tendency of an element to form chains depends upon the strength of the element-element bond. Amongst the group 14 elements, C – C bond strength (348 KJ mol^{-1}) is maximum, therefore, carbon shows maximum tendency for catenation. As we move down the group, the element-element bond strength decreases very rapidly, *i.e.*,

Element-Element	C – C	Si – Si	Ge – Ge	Sn – Sn
Bond strength (kJ mol^{-1})	348	297	260	240

Therefore, the tendency for catenation decreases in the order $\text{C} > > > \text{Si} > \text{Ge} \approx \text{Sn} > > \text{Pb}$.

Lead however, do not show any tendency for catenation.

$p\pi$ - $p\pi$ and $p\pi$ - $d\pi$ multiple bonding : Amongst group 14 elements, carbon shows a pronounced ability to form $p\pi$ - $p\pi$ multiple bonds with itself (*e.g.*, in graphite) and with other elements especially nitrogen and oxygen. Silicon and other heavier elements of this group show negligible tendency of this type. This is the reason that silicon exists only in the diamond structure.

$p\pi$ - $d\pi$ multiple bonding has been observed particularly in case of silicon linked to oxygen and nitrogen. Thus trimethylamine, $\text{N}(\text{CH}_3)_3$ is pyramidal (N is sp^3 -hybridized) and is more basic whereas similar silicon compound trisilylamine, $\text{N}(\text{SiH}_3)_3$ is planar (N is sp^2 -hybridized) and is less basic. In this case, the lone pair of nitrogen atom is transferred to the empty d -orbital of silicon ($p\pi$ - $d\pi$ overlapping) leading to the planar structure.

- **Chemical Properties**

Nature of bonding : The compounds of group 14 elements which show an oxidation state of +4 are covalent while those which show an oxidation of +2 are ionic in nature. Further, as we move down the group, the tendency of the elements to form covalent compounds decreases but the tendency to form ionic compounds increases.

Formation of halides :

(i) Tetrahalides : All the elements of group 14 form tetrahalides of the general formula, MX_4 where $X = F, Cl, Br$ or I . All these tetrahalides are covalent compounds and have tetrahedral structures. The stability of these tetrahalides decreases as we move from C to Pb , *i.e.*,



(ii) Dihalides : All the elements of group 14 form dihalides of the formula, MX_2 where $X = F, Cl, Br$ or I . The stability of these dihalides increases as we move down the group from C to Pb . Thus, the dihalides of tin and Pb , *i.e.*, $SnCl_2$ and $PbCl_2$ are quite stable. Dihalides are generally ionic in nature and behave as reducing agents, the reducing character (of M^{2+} species) decreases in the order *e.g.*, $GeCl_2 > SnCl_2 > PbCl_2$.

• **Formation of oxides :** All the elements of this group form two types of oxides : (i) monoxides and (ii) dioxide.

(i) Monoxides : All the elements of group 14 form monoxides of the general formula MO , *i.e.*, CO, SiO, GeO, SnO and PbO . These oxides except SiO and GeO are quite stable. CO is neutral while SnO and GeO are amphoteric.

(ii) Dioxides : All these elements form dioxides of the general formula, MO_2 *i.e.*, $CO_2, SiO_2, GeO_2, SnO_2$ and PbO_2 . All these dioxides can be prepared by heating the elements in oxygen except lead which forms lead monoxide. CO_2 is a monomeric, linear molecule and hence exists as a gas while the dioxides of all other elements are crystalline solids with high melting points due to the formation of three dimensional network of bond.

• **Silicones :** Silicones are synthetic organosilicon compounds containing repeated R_2SiO units held by $Si - O - Si$ linkages. Since the empirical formula R_2SiO (where $R = CH_3$ or C_6H_5 group) is similar to that of a ketone (R_2CO), the name silicones have been given to these materials.

Short chains silicones are oily liquids, medium chains silicones behave as viscous oils, jellies and greases and those with very long chains behave as rubbery elastomers and resins.

Silicones are water repellent, heat resistant, chemically inert, resistant to oxidation and attack by organic acids and good electrical insulators.

Silicones are used for making water proof papers, wool, textiles, wood, etc., as lubricants at high and low temperatures, as antifoaming agents, as sealants. Being biocompatible they are also used in surgical and cosmetic plants.

1 - MARK QUESTIONS

1. Write the general electronic configuration of *p*-block elements.
2. Mention two important ores of boron.
3. Write the resonance structure of CO_3^{2-} .
4. Write the chemical formula of inorganic benzene.
5. Mention the hybridisation state of carbon in diamond and graphite.
6. Why boric acid (H_3BO_3) is a monobasic acid ?
7. Diamond is covalent, yet it has high melting point. Why ?
8. White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.
9. Why does boron trifluoride behave as a Lewis acid ?
10. Atomic radius of gallium (135 pm) is less than that of aluminium (143 pm). Why ?
11. Boron cannot form B^{3+} ions. Why ?
12. The +1 oxidation state gets progressively stabilized from Ga to Tl. Give chemical reaction in support of this observation.
13. Why is anhydrous AlCl_3 used as catalyst in several organic reactions ?
14. Aluminium is highly electropositive metal but nitric acid renders it passive. Why ?
15. Name the element of group 13 which forms only covalent compounds.
16. Draw the structure of Al_2Cl_6 .
17. Mention an industrial application of silicones.
18. Name a zeolite catalyst used to convert alcohols directly into gasoline.
19. Electronegativity of group 13 elements is in the order $\text{B} > \text{Al} > \text{Ga} > \text{In} > \text{Tl}$. Explain this trend.
20. Why is boric acid considered as a weak acid ?
21. Write the isotopes of Boron.
22. Write the general electronic configuration of group 13 and group-14 elements.

23. Boron is a non-metal yet it has very high melting point why?
24. AlCl_3 exist in dimeric form in solid state and vapour phase. Why?
25. Boron can't show covalency more than 4. Why ?

2 - MARK QUESTIONS

1. How is diborane prepared in the laboratory ? Give its structure.
2. Account for the following :
 - (a) BCl_3 exist but BH_3 does not.
 - (b) Aluminium alloys are used to make aircraft body.
3. Mention two similarities and two dissimilarities between B and Al.
4. What happens when :
 - (a) Borax is heated strongly.
 - (b) Boric acid is added to water.
5. B – Cl bond has a dipole moment. Explain why BCl_3 molecule has zero dipole moment ?
6. Write balanced chemical equations for :
 - (a) $\text{BF}_3 + \text{LiH} \rightarrow$
 - (b) $\text{B}_2\text{H}_6 + \text{NH}_3 \rightarrow$
7. Write chemical reactions to justify amphoteric nature of aluminium.
8. The +1 oxidation state in group 13 and +2 oxidation state in group 14 become more and more stable with increasing atomic number. Explain why ?
9. Arrange the hydrides of group 14 elements in increasing order of :
 - (a) thermal stability
 - (b) reducing power
10. $[\text{SiF}_6]^{2-}$ is known whereas $[\text{SiCl}_6]^{2-}$ not. Give appropriate reason.
11. Account for the following :
 - (a) CO_2 is a gas while SiO_2 is a solid at room temperature.
 - (b) Solid CO_2 is known as dry ice.
12. Write the composition of water gas. How it can be synthesized ?
13. How do you agree with phenomenon concept of inert pair effect ? Justify your answer.

14. What are silicones ? How are they manufactured ? Give the chemical equation involved.
15. Explain with suitable reasons :
- CCl_4 is resistant to hydrolysis but SiCl_4 is readily hydrolysed.
 - In group 14, the tendency for catenation decreases with increasing atomic number.

3 - MARK QUESTIONS

- List two important properties in which boron differs from the rest of the members of group. Mention the main reasons for the difference.
- Write balanced chemical equations for :
 - $\text{BF}_3 + \text{NaH} \xrightarrow{450\text{ K}}$
 - $\text{Fe}_2\text{O}_3 + 3\text{CO} \xrightarrow{\Delta}$
 - $\text{CaCO}_3 + 2\text{HCl} \rightarrow$
- Identify X, Y and Z in the following chemical equations :

$$\text{Z} + 3\text{LiAlH}_4 \rightarrow \text{X} + 3\text{LiF} + 3\text{AlF}_3$$

$$\text{X} + 6\text{H}_2\text{O} \rightarrow \text{Y} + 6\text{H}_2$$

$$\text{X} + 3\text{O}_2 \xrightarrow{\Delta} \text{B}_2\text{O}_3 + 3\text{HO}_2$$

[Ans. Z = BF_3 , X = B_2H_6 , Y = H_3BO_3]
- Select the member(s) of group 14 that :
 - forms the most acidic dioxide.
 - is commonly found in +2 oxidation state.
 - used as semiconductor.
- What are allotropes ? Sketch the structure of two allotropes of carbon namely diamond and graphite.
 - List two main differences in the properties of diamond and graphite on the basis of their structure.
- Write one method for industrial preparation and one for laboratory preparation of CO. Suggest a reason as to why CO is poisonous.
- Give suitable reasons for the following :

- (a) CO_2 turns lime water milky, but if passed for a long time, the solution becomes clear again.
 - (b) Graphite is used as a lubricant but diamond is used as an abrasive.
 - (c) Graphite is a good conductor of electricity but diamond is insulator.
8. A salt A, gives the following results :
- (a) Its aqueous solution is alkaline to litmus
 - (b) It swells up to a glassy material B on strong heating.
 - (c) When conc. H_2SO_4 is added to a hot solution of A, white crystals an acid C separates out. Write equations for all the above reactions and identify A, B and C.
9. Suggest reasons for the following observations :
- (a) Excessive content of CO_2 is responsible for global warming
 - (b) Boron is unable to form BF_6^{3-} ion.
 - (c) A boron carbide rod is used in nuclear reactor.
10. (i) How orthoboric acid is prepared? Give its structure.
(ii) What happens when—
(a) It is dissolved in water. (b) It is heated.
11. Give reasons of the following –
- (a) In diborane, two B–H–B bonds are different from common covalent bonds.
 - (b) Aluminium metal shows amphoteric behaviour.
 - (c) Quartz is used to develop extremely accurate clocks.

5 - MARK QUESTIONS

1. (a) Draw the structure of diborane.
(b) Define the term inert pair effect. Explain your answer with the help of lead chlorides.
(c) (i) Which is more ionic, SnCl_2 or SnCl_4 ?
(ii) PbO_2 is a strong oxidising agent. Assign a reason for this.
2. (a) Account for the following :
- (i) The first ionization enthalpy of carbon is greater than that of boron but the reverse is true for second ionization enthalpy.

- (ii) PbCl_4 is less stable than SnCl_4 but PbCl_2 is more stable than SnCl_2 .
- (iii) Gallium has higher ionization enthalpy than aluminium.
- (b) Identify the compounds X and Y in the following reactions :
- (i) $\text{Na}_2\text{B}_4\text{O}_7 + 2\text{HCl} + 5\text{H}_2\text{O} \rightarrow 2\text{NaCl} + \text{X}$
- (ii) $\text{X} \xrightarrow[370 \text{ K}]{\Delta} \text{HBO}_2 \xrightarrow[> 370 \text{ K}]{\Delta} \text{Y}$
3. Compare the general trends in the following properties of the elements in groups 13 and 14 :
- Atomic size
 - Ionization enthalpy
 - Metallic character
 - Oxidation states
 - Nature of halides
4. When metal 'X' is treated with sodium hydroxide, a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound (A) is soluble in dilute HCl to form compound (C). The compound (A) when heated strongly gives (D), which is used to extract metal. Identify (X), (A), (B), (C) and (D). Write chemical equations to support their identities.
5. Assign reasons :
- Aluminium alloys are used to make body.
 - Conc. HNO_3 can be transported in aluminium containers.
 - Aluminium utensils should not be kept overnight.
 - Aluminium wire is used to make transmission cables.
 - A mixture of dilute NaOH and aluminium pieces is used to open drain.
6. Name the following —
- The crystalline form of silica used in modern-radio and T.V. broadcasting and mobile-radio communication!
 - The oxide of carbon which forms a complex with haemoglobin 300 times more faster than O_2 .
 - The allotrope of Carbon which has $\Delta_f H^\circ = 0$.
 - Group 13 element which is used to measure high temperature !
 - A type of polymer which is semiorganic in nature !