

Q 11.1

Discuss the pattern of variation in the oxidation states of

(i) C to Pb

(ii) B to Tl

Ans:

(i) C to Pb

The electronic configuration of group 14 elements is $ns^2 np^2$. Hence, the most common oxidation state exhibited by them should be +4. Upon moving down the group, the +2 oxidation state becomes increasingly common and the relatively higher oxidation states become less stable. This is because of the inert pair effect. Si and C mostly exhibit the +4 state. Although Sn, Ge and Pb show the +4 and +2 states, the stability of higher oxidation states decrease while 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 ←

(ii) B to Tl

Group 13 elements have their electronic configuration of $ns^2 np^1$ and the oxidation state exhibited by these elements should be 3. Apart from these two electrons boron and aluminium, other elements of this group exhibit both +1 and +3 oxidation states. Boron and aluminium show oxidation state of +3 due to the inert pair effect. The two electrons, which are present in the S-shell do not participate in bonding as they are strongly attracted by the nucleus. As we move down the group, the inert pair effect becomes more prominent. Therefore Ga (+1) is unstable and Tl (+1) is very stable

On moving down the group, the stability of the +3 oxidation state gets decreased.

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

Q 11.2

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

Ans:

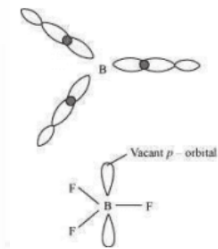
Thallium and boron belong to group 13 of the periodic table and +1 oxidation state becomes more stable as we move down the group. Boron is more stable than thallium because +3 state of thallium is highly oxidizing and it reverts back to a more stable +1 state.

Q 11.3

Why does boron trifluoride behave as a Lewis acid ?

Ans:

The electronic configuration of boron is $ns^2 np^1$. It contains 3 electrons in its valence shell. Thus, it can form only 3 covalent bonds which mean that there are only 6 electrons around boron and its octet remains incomplete. When 1 of the boron's atom combines with 3 fluorine atoms, its octet (8) remains incomplete. Therefore, boron trifluoride remains electron-deficient and acts as Lewis acid.

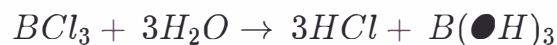


Q 11.4

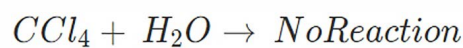
Consider the compounds, BCl_3 and CCl_4 . How will they behave with water? Justify.

Ans:

Since it is a Lewis acid, BCl_3 readily undergoes hydrolysis to form boric acid.



On the other hand, CCl_4 does not undergo hydrolysis readily. Since carbon does not possess any vacant orbitals, it cannot accept any electrons from water in order to form an intermediate. When CCl_4 and water are mixed, separate layers are formed.

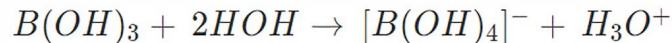


Q 11.5

Is boric acid a protic acid? Explain.

Ans:

Boric acid is a weak monobasic acid which behaves as a Lewis acid. So, it is not a protic acid.



It behaves as a Lewis acid by accepting an electron pair from the OH^- ion.

Q 11.6

Explain what happens when boric acid is heated

Ans:

Upon heating orthoboric acid at a temperature of 370 K or above, it is converted into metaboric acid and, upon further heating, yields boric oxide (B_2O_3).



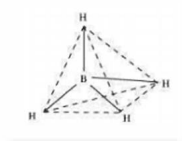
Q 11.7

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

Ans:

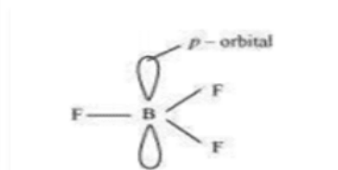
(i) BH_4^-

BH_4^- has a tetrahedral structure which is accounted for by the sp^3 hybridized orbitals.



(ii) BF_3

Boron tends to form monomeric covalent halides because of its small size and high electronegativity. These halides of boron usually have a planar triangular geometry, which can be explained by the overlap of three sp^2 hybridized orbitals of boron with the sp orbitals of 3 halogen atoms. It can be noted that boron is sp^2 hybridized in BF_3 .



Q 11.8

Write reactions to justify amphoteric nature of aluminium

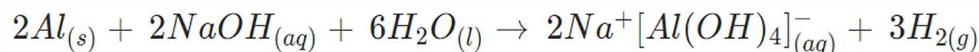
Ans:

Amphoteric substances are substances that exhibit both acidic and basic qualities. Since aluminium dissolves in both acids and bases, it is said to have an amphoteric nature.

(i)



(ii)



Q 11.9

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

Ans:

Electron-deficient compounds are chemical compounds with incomplete octets that tend to acquire 1 or more electrons to complete their octet configurations.

(i) $SiCl_4$

Silicon has 4 valence electrons (its electronic configuration is $2s^2 2p^2$). Its octet is completed after forming four single bonds with four different chlorine atoms. Therefore, $SiCl_4$ is not an electron-deficient compound.

(ii) BCl_3

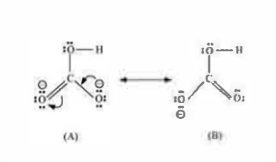
BCl_3 is a good example of an electron-deficient compound. Since boron has three valence electrons, it forms 3 single bonds with chlorine, giving the boron atom a total of 6 electrons in the outermost shell. However, it is still short of 2 electrons to complete its octet.

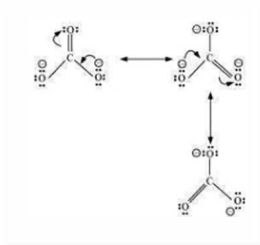
Q 11.10

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

Ans:

(a) HCO_3^-





There are only 2 resonating structures for the bicarbonate ion.

Q 11.11

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

Ans:

The state of hybridization of carbon in:

(a) Graphite

Each carbon atom in graphite is hybridized with sp^2 and is bound to 3 other atoms of carbon.



C in CO_3^{2-} is sp^2 hybridized and is bonded to 3 oxygen atoms.

(c) Diamond

Each diamond carbon is hybridized by sp^3 and is bound to 4 additional carbon atoms.

Q 11.12

Explain the difference between the properties of graphite and diamond on their structure basis.

Ans:

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.

Q 11.13

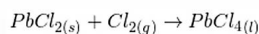
Rationalize the given statements and give chemical reactions:

- 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 .

Ans:

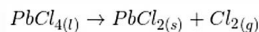
(a)

Lead is a member of group 14 of the periodic table. The two oxidation states this group shows are + 2 and + 4. The + 2 oxidation state becomes more stable when moving down the group, and the oxidation status + 4 becomes less stable. This is due to the inert pair effect. So $PbCl_4$ is significantly less stable than $PbCl_2$. However, $PbCl_4$ formation occurs when the chlorine gas is bubbled through a $PbCl_2$ saturated solution.



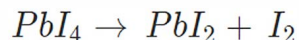
(b)

Due to the inert pair effect, the higher oxidation state becomes unstable when moving down group IV.



(c)

Lead is not known for forming PbI_4 . In nature, Pb (+ 4) is oxidizing, and I reduce in nature. A Pb(IV) and iodide ion combination is not stable. Iodide ion reduces sharply in nature. Pb(IV) oxidizes I⁻ to I₂, and reduces itself to Pb(II).

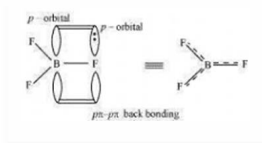


Q 11.14

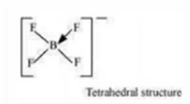
Suggest reasons why the B–F bond lengths in BF_3 (130 pm) and (143 pm) differ.

Ans:

In BF_3 , the length of the B–F bond is shorter than that of the B–F bond in BF_4^- . BF_3 is a species that has an electron deficiency. The fluorine and boron atoms undergo p_n–p_n back-bonding with a vacant p-orbital on boron to remove this deficiency. This endows the B–F bond with a double bond character.



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

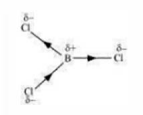


Q 11.15

If B–Cl bond has a dipole moment, explain why BCl_3 molecule has zero dipole moment.

Ans:

The B – Cl bond is naturally polar because of the difference in the electronegativities of Cl and B. Yet the molecule of BCl_3 is non-polar. That is because the shape of BCl_3 is trigonal planar. The molecule is asymmetrical. So the respective B – Cl bond dipole moments cancel each other, creating a zero dipole moment.

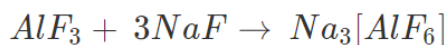


Q 11.16

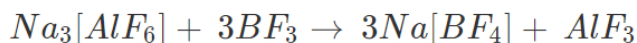
Aluminum trifluoride is insoluble in anhydrous HF but dissolves when NaF is added. It precipitates out of the resulting solution when gaseous BF_3 (boron trifluoride) is bubbled through. Give reasons.

Ans:

Hydrogen fluoride is a covalent compound with a very strong intermolecular bonding to hydrogen. Thus, it does not provide ions and does not dissolve aluminum fluoride in it. Sodium fluoride is an ionic compound, and AlF₃ dissolves when added to the mixture. This is because of the Free F⁻ available. The reaction involved in the process is:



When boron trifluoride is added to the solution, aluminum fluoride becomes precipitated out of solution. This is because the boron's tendency to form complexes is much greater than that of aluminum. So, when boron trifluoride is added to the solution, B replaces Al of the complexes by the following reaction:



Q 11.17:

Suggest a reason as to why CO is poisonous.

Ans:

Given its ability to form a complex with hemoglobin, carbon monoxide is highly poisonous. The former impedes binding with oxygen by Hb. Consequently, a person dies due to suffocation on not receiving oxygen. The complex CO – Hb is more stable than the complex O₂–Hb. The CO – Hb complex is found to be roughly 300 times more stable than the O₂–Hb complex.

Q 11.18

How is the excessive content of CO₂ responsible for global warming?

Ans:

Carbon dioxide is a gas that is necessary for our survival. The increased CO₂ content in the environment, however, poses a serious threat. An increase in fossil fuel combustion, calcareous decomposition, and a decrease in the number of trees has resulted in higher carbon dioxide levels. Carbon dioxide has the property of trapping the heat that sun rays provide. The higher the carbon dioxide level, the greater the amount of heat that is trapped. This leads to an increase in atmospheric temperature which causes global warming.

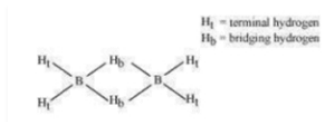
Q 11.19

Explain the structures of diborane and boric acid.

Ans:

(a) Diborane

B₂H₆ is a compound that lacks an electron. B₂H₆ only has 12 electrons – 6 e⁻ of 6 H atoms and 3 e⁻ of 2 B atoms each. So none of the boron atoms have any electrons left after being mixed with 3 H atoms. X-ray diffraction studies showed the diborane structure as:

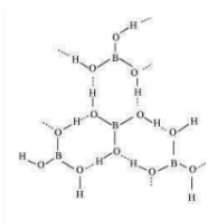


Two boron and four-terminal atoms of hydrogen (H_t) lie in one direction, while the other two bridging atoms of hydrogen (H_b) are in the surface perpendicular to the plane of boron atoms. Once, of the two atoms of hydrogen bridging, one atom of H lies above the plane, and the other below the plane. The terminal bonds are regular two-center two-electron (2c – 2e⁻) bonds, while the two bridgings (B–H–B) bonds are three-center two-electron (3c – 2e⁻) bonds.



(b) Boric acid

Boric acid is structured in a layered form. Each planar unit BO_3 is connected by atoms H to each other. The H atoms form a covalent bond with a BO_3 unit whereas another BO_3 unit forms a hydrogen bond. The dotted lines, in the given figure, represent hydrogen bonds.



Q 11.20

What happens when

(i) Aluminum is treated with dilute NaOH,

(ii) BF_3 is reacted with ammonia,

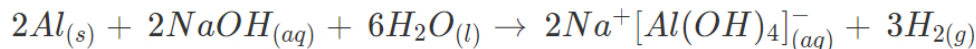
(iii) Boric acid is added to water,

(iv) Borax is heated strongly.

Ans:

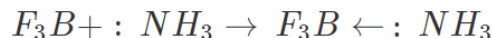
(i) Aluminum is treated with dilute NaOH

Aluminum reacts to sodium tetrahydroxoaluminate(III) by forming dilute NaOH. In this process, hydrogen gas is liberated.



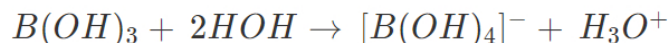
(ii) BF_3 is reacted with ammonia

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



(iii) Boric acid is added to water

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



(iv) Borax is heated strongly

Borax undergoes various transformations when heated. It is losing molecules and swells of water at first. Then it becomes a translucent liquid, which solidifies to form a glass-like material called a borax bead.

Q 11.21

Explain the following reactions

(i) CO is heated with ZnO;

(ii) Silicon is heated with methyl chloride at high temperature in the presence of copper;

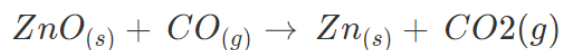
(iii) Hydrated alumina is treated with aqueous NaOH solution;

(iv) Silicon dioxide is treated with hydrogen fluoride.

Ans:

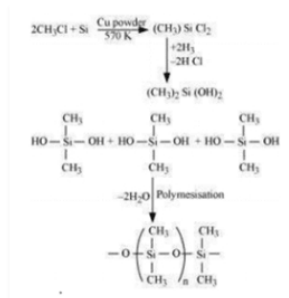
(i) CO is heated with ZnO

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



(ii) Silicon is heated with methyl chloride at high temperature in the presence of copper

A class of organosilicon polymers called methyl-substituted chlorosilane MeSiCl₃, Me₂SiCl₂, Me₃SiCl, and Me₄Si are formed when silicon reacts with methyl chloride in the presence of copper (catalyst) and at a temperature of about 537 K.



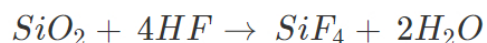
(iii) Hydrated alumina is treated with aqueous NaOH solution

When sodium hydroxide is added to hydrated alumina, the former dissolves in the latter due to the sodium meta-aluminate formation.



(iv) Silicon dioxide is treated with hydrogen fluoride.

When the hydrogen fluoride (HF) heats silicon dioxide (SiO₂), it forms silicon tetrafluoride (SiF₄). The Si – O bond is usually a strong bond, avoiding any attack by halogens and most acids even at high temperatures. It is being attacked by HF though.



The SiF₄ formed in this reaction can further react with HF to form hydro-fluorosilicic acid.



Q 11.22

Give reasons:

- (i) Diamond is used as an abrasive
- (ii) A mixture of dilute NaOH and aluminium pieces is used to open drain.
- (iii) Aluminum alloys are used to make aircraft bodies.
- (iv) Conc. HNO₃ can be transported in an aluminium container.
- (v) Aluminum wire is used to make transmission cables.
- (vi) Graphite is used as the lubricant.
- (vii) Aluminum utensils should not be kept in water overnight.

Ans:

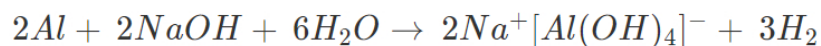
(i) Diamond is used as an abrasive

Carbon is sp³ hybridized in Diamond. With the help of strong covalent bonds, each carbon atom is bound to four other carbon atoms. These covalent bonds exist all over the surface, giving it a very rigid 3-D structure. This extended covalent bonding is very hard to break and for this reason, diamond is the

hardest known substance. It is therefore used as an abrasive and for cutting instruments.

(ii) A mixture of dilute NaOH and aluminum pieces is used to open the drain.

Sodium hydroxide and aluminum react to form aluminate (III) sodium tetra hydroxy and hydrogen gas.



(iii) Aluminum alloys are used to make aircraft bodies.

Aluminum has a high resistance to tensile and is light. It may also be alloyed to different metals such as Si, Mg, Cu, Mn and Zn. It is very ductile and very malleable. Hence, it is used in the design of aircraft bodies.

(iv) Conc. HNO₃ can be transported in an aluminum container.

As it reacts with aluminum to form a thin protective oxide layer on the aluminum surface, concentrated HNO₃ can be stored and transported in aluminum containers.

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

Gold, copper, and aluminum are amongst the best electricity conductors. Silver is a costly metal, and very delicate gold links. Copper is pretty expensive, and heavy too. A very ductile metal, aluminium. Aluminum is thus used for making wires for electrical conduction.

(vi) Graphite is used as the lubricant.

Graphite has a layered structure, and the forces of weak van der Waals bind different layers of graphite together. These layers may slide one over another. Graphite is slippery and soft. Graphite can, therefore, be utilized as a lubricant.

(vii) Aluminum utensils should not be kept in water overnight.

The oxygen in water reacts to create a thin layer of aluminum oxide with aluminum. This layer prevents further reaction from aluminum. Nevertheless, some amount of aluminum oxide can dissolve in water if the water is held in an aluminum vessel for long periods of time. Water should not be stored overnight in aluminum vessels because aluminum ions are harmful.

Q 11.23

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

Ans:

Carbon ionizing enthalpy (the first element in group 14) is very high (1086 kJ / mol). That is expected because of its small size. However, there is a sharp decrease in enthalpy (786 kJ) when moving down the group to silicon. This is due to a considerable increase in the atomic sizes of elements when the group is moving down.

Q 11.24

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

Ans:

Atomic radius (in pm)	
Aluminium	143
Gallium	135

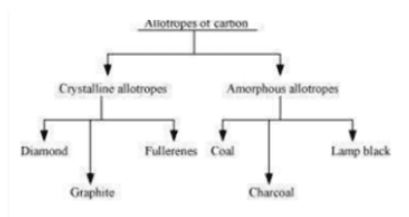
Although Ga has more than one shell than Al, it is smaller in size than Al. This is because the 3d-electrons have poor shielding effect. The shielding effect of d-electrons is very poor, and the effective nuclear charge experienced in gallium by the valence electrons is far more than in Al.

Q 11.25

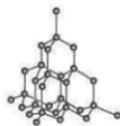
What are allotropes? Sketch the structure of two allotropes of carbon namely diamond and graphite. What is the impact of structure on the physical properties of two allotropes?

Ans:

Allotropy is the presence of an element in more than one form, having different physical properties but the same chemical properties.

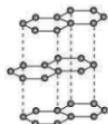


Diamond:



Diamond's solid 3-D structure makes it a really strong material. Diamond is probably one of the most difficult naturally occurring substances. It is used as an abrasive and as a tool for cutting.

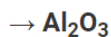
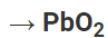
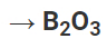
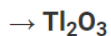
Graphite:



It has hybridized carbon sp^2 , structured in layer form. These layers are held together by the forces of weak van der Waals. These layers may slide over each other, making graphite slippery and soft. Consequently, it is used as a lubricant.

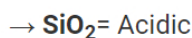
Q 11.26

(A) Classify the following oxides as Acidic, Neutral, Amphoteric or basic.

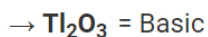
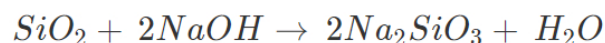


(B) Write suitable chemical equations to show their nature.

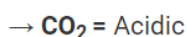
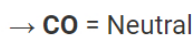
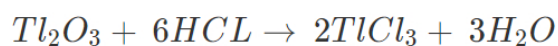
Ans:



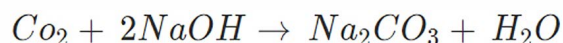
Being acidic, it reacts with bases to form salts. It reacts with NaOH to form sodium silicate.



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

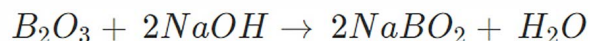


Being acidic, it reacts with bases to form salts. It reacts with NaOH to form sodium carbonate.



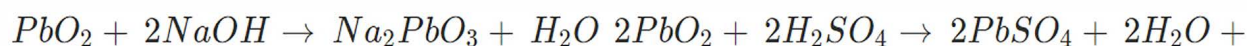
→ B_2O_3 = Acidic

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



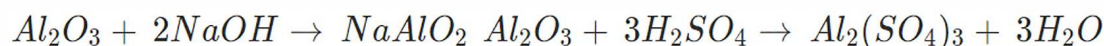
→ PbO_2 = Amphoteric

Amphoteric substances react with both acids and bases. PbO_2 reacts with both NaOH and H_2SO_4 .



→ Al_2O_3 = Amphoteric

Amphoteric substances react with both acids and bases. Al_2O_3 reacts with both NaOH and H_2SO_4 .



Q 11.27

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

Ans:

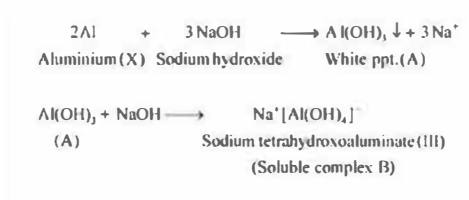
Thallium is a part of the periodic table group 13. For this group, the most common oxidation state is + 3. Heavier members of this group, however, also display the state of oxidation + 1. This is due to the inert pair effect. Aluminum shows the state of oxidation + 3 and alkali metals show the state of oxidation + 1. Thallium demonstrates the oxidation state of both. Hence, it is similar to both aluminum and alkali metals. Thallium forms compounds such as $TlCl_3$ and Tl_2O_3 , like aluminum. It is akin to alkali metals in Tl_2O and $TlCl$ compounds.

Q 11.28

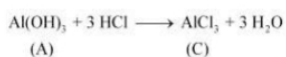
When metal X is treated with sodium hydroxide, a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound (A) is soluble in dilute HCl to form compound (C). The compound (A) when heated strongly gives (D), which is used to extract the metal. Identify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

Ans:

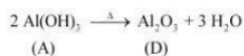
The given metal X gives sodium hydroxide to a white precipitate, and the precipitate dissolves exceeding sodium hydroxide. X must, therefore, be made of aluminum. The obtained white precipitate (compound A) is hydroxide from aluminum. Sodium tetrahydroxy aluminate(III) is the compound B formed when an excess of base is added.



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



As well, it gives compound D when compound A is heated strongly. Uses this compound to extract metal X. Extracts aluminum metal from alumina. Therefore alumina must be compound D.



Q 11.29

What do you understand by

(a) Inert pair effect

(b) Allotropy and

(c) Catenation?

Ans:

(a) Inert pair effect

As one moves down the group, s-block electrons decrease their tendency to participate in chemical bonding. This effect is called the inert pair effect. The electronic configuration for group 13 elements is $ns^2 np^1$, and its group valence is + 3. However, the oxidation state of + 1 becomes more stable when moving down the group. This is because the ns^2 electrons are poorly shielded by the d- and f- electrons. The ns^2 electrons are held tightly by the nucleus as a result of poor shielding, and thus they can not engage in chemical bonding.

(b) Allotropy

Allotropy is the presence of an element in more than one form, having different physical properties but the same chemical properties. The different forms of an element are called allotropes. Carbon occurs in three allotropic forms, for example, diamond, graphite, and fullerenes.

(c) Catenation

Some elements or atoms (such as carbon) may connect with each other via strong covalent bonds to form long chains or branches. This characteristic is known as catenation. It is most common in carbon, and important in Si and S.

Q 11.30

A certain salt X gives the following results.

(i) Its aqueous solution is alkaline to litmus.

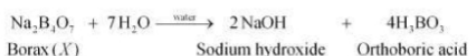
(ii) It swells up to a glassy material Y on strong heating.

(iii) When conc. H_2SO_4 is added to a hot solution of X, a white crystal of an acid Z separates out.

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

Ans:

The salt given to litmus is alkaline. X is, therefore, a salt with a strong base, and a weak acid. Once X is heated excessively, it also swells to form material Y. Hence X has to be borax. When heated, borax loses water and swells in order to form sodium metaborate. When heating is continued, the forming of a glassy material Y solidifies. Thus, Y must be a mixture of metaborate sodium and boric anhydride.





The CO is prepared commercially by passing steam over hot coke:



Q 11.33

An aqueous solution of borax is

- (a) Basic
- (b) Amphoteric
- (c) Neutral
- (d) Acidic

Ans:

a) Borax is a potent base salt (NaOH) and a weak acid (H₃BO₃). Therefore it is fundamental in nature.

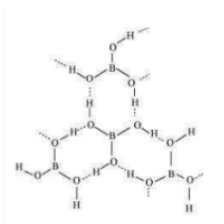
Q 11.34

Boric acid is polymeric due to

- (a) Its acidic nature
- (b) Its geometry
- (c) Its monobasic nature
- (d) The presence of hydrogen bonds

Ans:

(d) Boric acid is polymeric due to the hydrogen bonds. The dotted lines in the given figure represent hydrogen bonds.



Q 11.35

The type of hybridization of boron in diborane is

- (a) sp
- (b) sp³
- (c) sp²
- (d) dsp³

Ans:

(b) Boron in diborane is sp³ hybridized.

Q 11.36

Thermodynamically the most stable form of carbon is

- (a) Diamond
- (b) Coal
- (c) Fullerenes
- (d) Graphite

Ans:

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

Q 11.37

Elements of group 14

(a) exhibit oxidation state of +2 and +4

(b) exhibit oxidation state of +4 only

(c) form M^{2-} and M^{4+} ion

(d) form M^{2+} and M^{4+} ions

Ans:

(a) Group 14 elements possess 4 valence electrons. Consequently, group oxidation status is + 4. However, the lower oxidation state becomes increasingly stable due to the inert pair effect, 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

Q 11.38

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

Ans:

