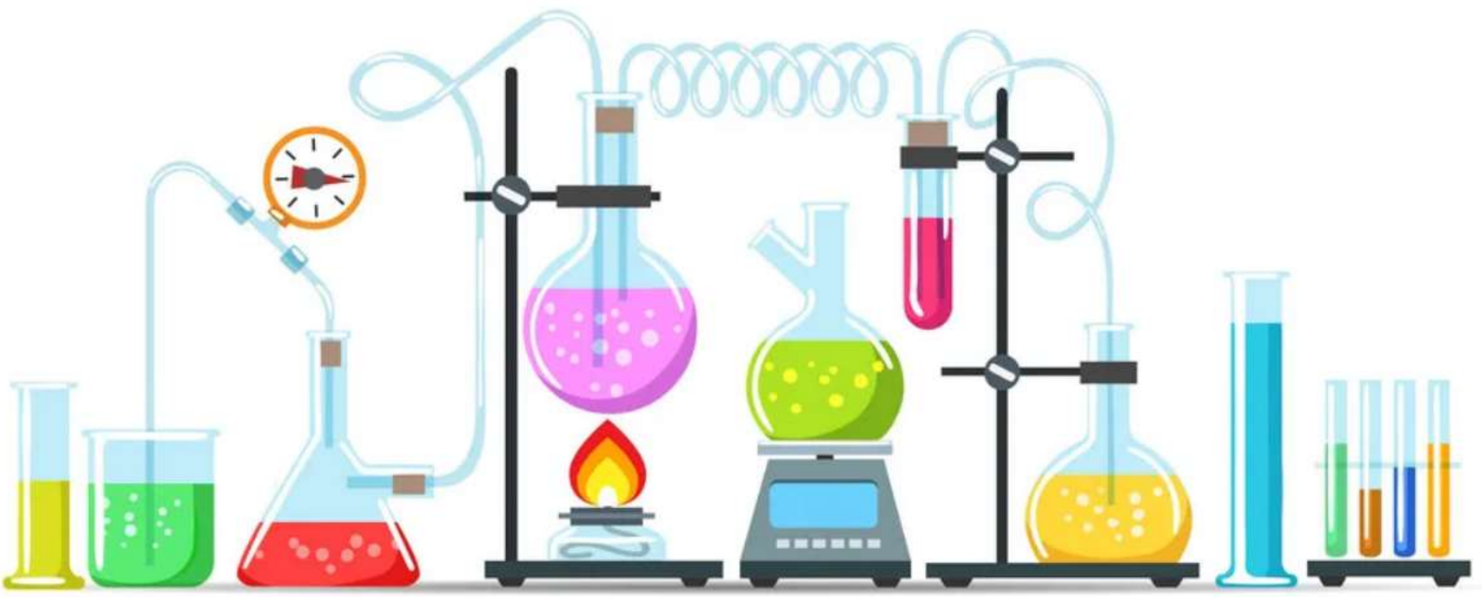
CHEMISTRY



THE P-BLOCK ELEMENTS

Introduction

The elements in which last electron enters into p-subshell are called as p-block elements. The number of p-orbitals is three and, therefore, the maximum number of electrons that can be accommodated in a set of p-orbitals is six, hence p-block contains six groups.

Boron Family

Group III A contains six elements: Boron, aluminium, gallium, indium, thallium and ununtrium. The penultimate shell (next to the outermost) conains $1s^2$ in boron, $2s^2$ $2p^6$ (8 electrons) in aluminium and $(n–1)s^2(n–1)p^6(n–1)d^{10}$ (18 electrons) in other elements.

Boron is a non-metal and always form covalent bonds. Boron family is known as most heterogeneous family as there is no regular trend in all properties, as it comes after d-block, lanthanoid contraction, poor shielding of d-orbital, they have large deviation in properties.

1. **Physical Properties**

The atomic radius, ionic radius and density increases when one moves from top to bottom in a group in periodic table. While melting point decreases from B to Ga and then increases from (Ga to In). Ionisation energy decreases from B to Al, but shows a reverse trend in going from Al to Ga.

2. **Chemical Properties**

i. **Reaction with air:** Impure boron in air forms oxide while pure boron is less reactive.

$4B + 3O_2 \longrightarrow 2B_2O_3$

ii. **Reaction with water:** Boron is not affected by water or steam under ordinary conditions. However, Aluminium reacts with cold water if oxide layer is not present on its surface.

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

iii. **Reaction with acids:** Boron is not affected by non-oxidising acids like HCl and dilute H_2SO_4 while other elements dissolve and liberate H_2 gas.

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

iv. **Reaction with alkalies:** Boron, Aluminium, Gallium react with alkali solutions whereas

Indium and Thallium are not affected by alkalies.

$2B + 6NaOH \longrightarrow 2Na2BO_3 + 3H_2$

Anomalous Properties of Boron

Boron, the first member of group 13 elements, shows anomalous behaviour and differ from rest of the members of its family. The main reason for this difference are:

- Exceptionally small atomic and ionic size.
- High ionization enthalpy.
- Absence of d orbital in its valence shell.
- It has higher melting and boiling point than those of the other members of its group.

Compounds of Boron

1. **Borax/ Sodium Tetraborate ($Na_2B_4O_7 \cdot 10H_2O$)**

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

Preparation:

From Boric acid: Boric acid is neutralised with sodium carbonate and the resulting solution is cooled to get crystals of borax.

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

Properties:

i. It gets hydrolysed with water to form an alkaline solution

$Na_2B_4O_7 + 7H_2O \longrightarrow 2NaOH + H_3BO_3$

ii. **Borax bead test:** On heating borax first swells up due to elimination of water molecules. On further heating it melts to a liquid which then solidifies to a transparent glassy mass.

$Na_2B_4O_7.10H_2O \longrightarrow Na_2B_4O_7 + 10H_2O$

$Na_2B_4O_7 \longrightarrow 2NaBO_2 + B_2O_3$

iii. It is a useful primary standard for titration against acids.

$Na_2[B_4O_5(OH)_4]\cdot 8H_2O + 2HCl \longrightarrow 2NaCl + 4H_3BO_3 + 5H_2O$

2. **Diborane: B_2H_6**

The simplest boron hydride known, is diborane. It is prepared by treating boron trifluoride with $LiAlH_4$ in diethyl ether.

Preparation

$3LiAlH_4 + 4BCl_3 \longrightarrow 3LiCl + 3AlCl_3 + B_2H_6$

Properties

i. Stable at low temperature only, colourless and highly toxic.

ii. $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$

iii. $B_2H_6 + 6Cl_2 \longrightarrow 2BCl_3 + 6HCl$

iv. $B_3H_6 + 2Me_3N \longrightarrow 2[Me_3N.BH_3]$

Uses of Boron and Aluminium and Their Compounds

Boron Compounds

Boron is a hard solid having high melting point low density and very low electrical conductivity. Some important boron compounds are:

1. **Boron fibers:** It is mixed with plastic to form a material which is lighter than aluminium but tougher and stiffer than steel hence it is used in body armour, missiles and aircrafts.
2. **Boron-10 (^{10}B) isotope:** Boron carbide rods or boron steel are used to control nuclear reactions as neutron absorbers.

   ${}_5B^{10} + {}_0n^1 \longrightarrow {}_5B^{11}$
3. **Borax:** It is used in manufacture of enamels and glazes for pottery and tiles. It is also used in making optical glasses and also borosilicate glasses which is very resistant to heat and shock. It is used as an antispectic.
4. **Boric acid:** It is used in glass industry, in food industry as preservative. It is also used as an antiseptic and eye wash under the name 'boric lotion'. It is also used in manufacture of enamels and glazes for pottery.
5. **Boron carbide:** Hardest boron compound.

Aluminium Compounds

Aluminium and its alloy are used in packing industry, utensil industry, aeroplane and transportation industry etc.

1. **Alumina ($Al2O_3$):**
   a) Used in chromatography.
   b) Used in making bauxite bricks which are used for lining furnaces.
2. **Aluminium chloride ($AlCl_3$):** Used in manufacture of dyes, drugs and perfumes and also in manufacture of gasoline. It is also used as catalyst in Friedel Craft reaction.
3. **Potash Alum. [K_2SO_4-$Al_2(SO_4)_3$-24 H_2O]:** Used in purification of water, leather tanning, as antiseptic and as a mordant.

Group 14 Elements : The Carbon Family

Group IV A contains six elements: carbon, silicon, germanium, tin, lead and ununquadium. The penultimate shell (prior to outermost) contains $1s^2$ -grouping in carbon, $2s^22p^6$ (8 electrons) in silicon and $(n–1)s^2(n–1)p^6(n–1)d^{10}$ (18 electrons) in other elements. This shows why carbon differs from silicon in some respects and these two differ from rest of the members of this group. General electronic configuration is ns^2np^2.

1. Atomic and Physical Properties

The important properties of carbon family are discussed below:

i. **Atomic Radii:** The atomic radii of group 14 elements are less than the corresponding elements of group 13. However, the atomic radii increases down the family.

ii. **Ionisation Energies:** The higher ionisation energies than group 13 are due to the higher nuclear charge and smaller size of atoms of group 14 elements. While moving down the group, the ionisation energies decreases till Sn.

   C > Si > Ge > Sn < Pb

iii. **Oxidation state and valency:** The elements of group 14 show tetravalency by sharing four of its valence electrons. Therefore, they have oxidation state of +4. In addition, Ge, Sn and Pb also show +2 oxidation state.

iv. **Catenation:** Catenation is ability of like atoms to link with one another through covalent bonds. Tendency decreases from C to Pb. It is due to the decreasing M-M single bond energy. Thus, the tendency for catenation decreases as:

   C > Si > Ge > Sn > Pb

v. **Allotropy:** All the elements of the carbon family with the exception of lead exhibit allotropy. Carbon exists as two important allotropic forms diamond and graphite.

2. Chemical Properties

i. **Reactivity towards air:** All members of this group form monoxide of the general formula

MO such as CO, SiO, SnO and PbO. All members of this group form dioxides of molecular formula MO_2 such as CO_2, SiO_2, GeO_2, SnO_2 and PbO_2.

ii. **Reactivity towards water:** In this family three members i.e., carbon, silicon and germanium are affected by water while lead is not affected by water due to formation of protective oxide film, but tin decomposes with steam into tin dioxide and hydrogen gas.

iii. **Reactivity towards halogen:** These elements form two types of hallides - MX_2 and MX_4. Most of the MX_4 are covalent. SnF_4 and PbF_4 are ionic in nature.

Anomalous Behaviour of Carbon

Carbon shows anomalous behaviour due to its smaller size, higher electronegativity, higher ionization enthalpy and unavailability of d orbitals. Carbon atom forms double or triple bonds involving pπ-pπ bonding. Carbon has also the property to form closed chain compounds with O, S and N atoms as well as forming pπ-pπ multiple bonds with other elements particularly N, S and O. When we move down the group size increases and electronegativity decreases hence catenation tendency decreases. Order is:

$C >> Si > Ge \approx S$

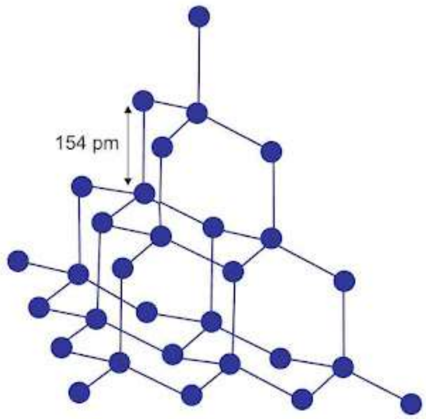
Allotropes of Carbon

Carbon shows allotropism due to catenation and pπ-pπ bond formation. Carbon exists in two allotropic forms – crystalline and amorphous. The crystalline forms are diamond and graphite while the amorphous forms are coal, charcoal and lamp-black. The third form is fullerenes discovered by Kroto, Smalley and Curl.

Note: Tin has maximum number of allotropes.

Diamond

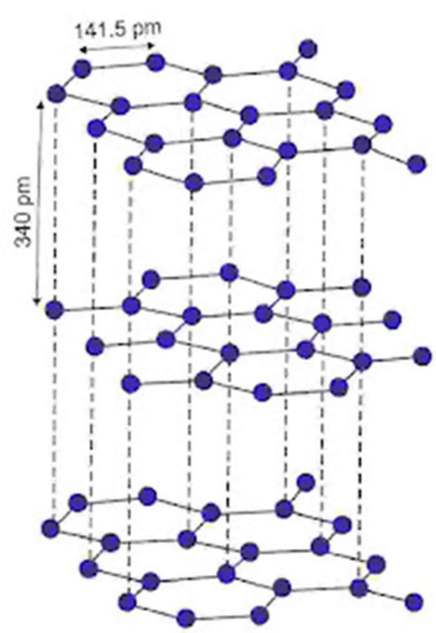
In diamond each carbon is joined to other four carbon tetrahedrally and carbon-carbon bond length is 1.54Å and bond angle is 109˚28′ having sp3 hybridisation on each carbon. All four electrons in carbon are involved in bonding hence, it is bad conductor of electricity. Diamond is an excellent thermal conductor.



It is hardest natural substance known. It is transparent and has a specific gravity 3.52 and its refractive index is high (2.45). Difficult to break due to extented covalent bonding. Diamond is used for making cutters. Blades of diamond are used in eye surgery and as an abrasive for sharpening hard tools. Impure diamonds (black) are used in knives for cutting glass.

Graphite

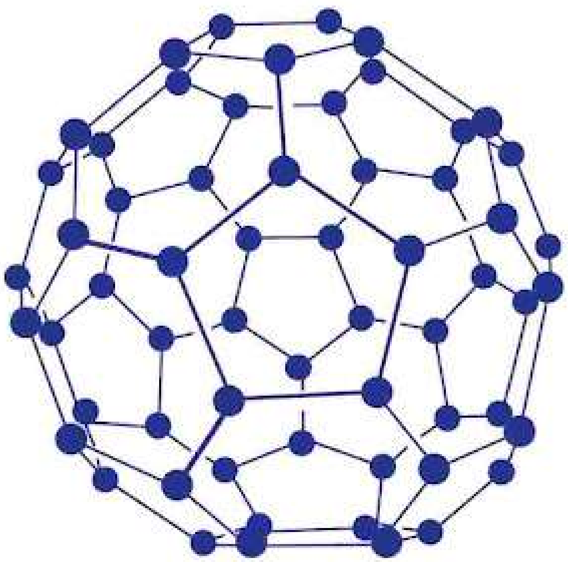
Each carbon is sp^2 hybridised. It has layered structure. These layers are attracted by van der Waals force. Each carbon has one free electron in p-orbital, so it is a good conductor of electricity. All electrons get delocalized in one layer and form π-bond. Electron jumps from one orbital to another hence it is a good conductor of heat and electricity. In graphite carbon-carbon bond length is 141.5 pm and distance between adjacent graphite layer is 340 pm.



Graphite is used as a lubricant at high temperature. Oil gets burn or denatured at high temperature but graphite does not get denatured even at high temperature so, preferred over oil and grease.

Fullerene

It was made as a result of action of a laser beam or strong heating of a sample of graphite in presence of inert atmosphere. The sooty material mainly contains C_{60} with C_{70} (small amount). Most common fullerene is C_{60} called Buckminsterfullerene which has football-like structure. It contains 20 six-membered ring and 12 five-membered ring. It is used to make ball bearings.



Coal

It is the crude form of carbon. It has been formed in nature as a result of slow decomposition of vegetable matter under the influence of heat, pressure and limited supply of air. The successive stages of transformation are peat, lignite, bituminous, steam coal and anthracite. Bituminous is hard stone, burns with smoky flame. The superior quality is anthracite which burns with non-smoky flame.

Uses of carbon

- **Graphite:** In making lead pencils, electrodes of electric furnances, as a moderator in nuclear reactor, as a lubricant in machinery.
- **Charcoal:** In removing offensive odour from air, in removing fused oil from crude spirit, in decolourising sugar syrup, in gas masks etc.
- **Carbon black:** For making printing inks, black paints, Indian inks, boot polishes and ribbons of typewriters.
- **Coal:** For the manufacture of coal gas, coal tar, coke, and synthetic petrol.

Allotropes of Carbon

1. **Carbon Monoxide (CO)**

Preparation: Carbon monoxide is majorly prepared by

$2C + O_2 \longrightarrow 2CO$

Properties:

i. Burns with blue flame

$2CO + O_2 \longrightarrow 2CO_2$

ii. $CO + Cl2 \longrightarrow COCl_2$ (Phosgene)

iii. $CO + 2H_2 \longrightarrow CH_3OH$

iv. Many of the transition metals form metal carbonyls

$Ni + 4CO \longrightarrow Ni(CO)_4$

2. **Carbon Dioxide (CO_2)**

Preparation:

Carbon dioxide is mostly prepared by decomposition of carbonates and bicarbonates:

i. $CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$

ii. $CaCO3 \longrightarrow CaO + CO2$

Properties:

Carbon dioxide is an acidic, colourless gas. The important properties are:

i. $Zn + CO_2 \longrightarrow ZnO + CO$

ii. $2Mg + CO_2 \longrightarrow 2MgO + C$

iii. $2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$

iv. $Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$

Summary-

1. **Allotropes:** Those compounds which have different physical properties but similar chemical properties are called allotropes e.g., diamond and graphite.
2. **Catenation:** Tendency of carbon atom to link with itself to form long chain is called catenation.
3. **Inert pair effect:** Decrease in tendency of ns^2 electron pair to participate in bond formation with increase in atomic number is called inert pair effect.
4. **Silicones:** It is organosilicon compound containing repeated R_2SiO units.
5. **Silicates:** Compounds in which anions are either discrete SiO_4^{-4} units or a number of such units combine together through corners.
6. **Alums:** All double sulphates having one monovalent basic radical and one trivalent basic radical.
7. **Boranes:** Hydrides of boron are called as boranes.

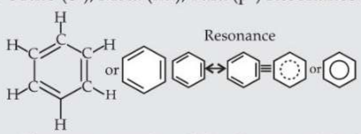
MIND MAP : LEARNING MADE SIMPLE CHAPTER - 13

Hydrocarbons

Compounds of Carbon and Hydrogen

Aromatic Hydrocarbon

- Types: Benzenoids – contain benzene ring, Non-benzenoids – does not contain benzene ring.
- Isomerism: Ortho (o-), Meta (m-), Para (p-) Resonance and
- Structure:



- Aromaticity: Planarity, complete delocalisation of the TT–electros in the ring, presence of (4n + 2) π electrons in the ring where n is an integer (n = 0,1,2,......) (Huckel rule)

Preparation:
- Cyclic polymerisation of ethyne

$C_6H_5COONa + NaOH \xrightarrow[\Delta]{CaO} C_6H_6 + Na_2CO_3$

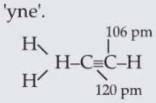
$C_6H_5OH + Zn \xrightarrow{\Delta} C_6H_6 + ZnO$

Mechanism of Electrophilic substitution reactions

(i) Generation of Electrophile
(ii) Formation of carbocation intermediate
(iii) Removal of proton

Alkenes (C_nH_{2n-2})

- IUPAC name: replacing 'ane' by the suffix 'yne'.
- Shows position and chain isomerism



Preparation:

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

$CaO + 3C \longrightarrow CaC_2 + CO$

$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

$CH_2Br-CH_2Br + KOH \xrightarrow[-KBr,\ -H_2O]{alcohol} H_2C=CHBr \xrightarrow[-NaBr,\ -NH_3]{NaNH_2} CH\equiv CH$

Physical Properties:
- First three members are gases, next eight are liquids and higher ones are solids.
- Colourless, ethyne has characteristic odour and other are odourless.
- Lighter than water, immiscible with water but soluble in organic solvents.
- m.p, b.p. and density increase with increase in molar mass.

Chemical Properties:

$HC\equiv CH + Na \longrightarrow HC\equiv CNa + 1/2H_2$

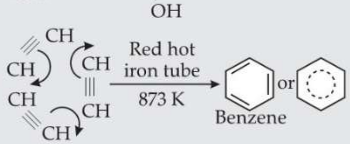
$HC\equiv CH + H_2 \xrightarrow{Pt/Pd/Ni} [H_2C=CH_2] \xrightarrow{H_2} CH_3-CH_3$

$CH_3-C\equiv CH + Br_2 \longrightarrow [CH_3CBr=CHBr] \xrightarrow{Br_2} CH_3-CBr_2-CHBr_2$

$HC\equiv C-H + HBr \longrightarrow [CH_2C=CH-Br] \longrightarrow CHBr_2-CH_3$

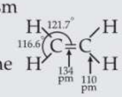
$HC\equiv CH + H_2O \xrightarrow[333\,K]{Hg^{2+}/H^+} [CH_2=C(OH)-H] \xrightarrow{Isomersation} CH_3-C(=O)-H$

Polymerisation



Alkenes (C_2H_{2n})

- Shows structural and geometrical isomerism



Preparation:

$RC\equiv CR' + H_2 \xrightarrow{Pd/C}$ R(H)C=C(H)R' cis-Alkene

$RC\equiv CR' + H_2 \xrightarrow{Na/Liquid\ NH_3}$ R(H)C=C(H)R' trans-Alkene

$H_3C-CH_2X \xrightarrow[\Delta]{Alc.KOH} H_2C=CH_2$

$CH_2Br-CH_2Br + Zn \longrightarrow CH_2=CH_2 + ZnBr_2$

$H_3CCH_2OH \xrightarrow[\Delta]{conc.H_2SO_4} CH_2=CH_2 + H_2O$

- Physical Properties :
  - Ethene is a colourless gas with faint sweet smell.
  - All other are colourless and odourless, insoluble in water but fairly soluble in non-polar solvents.
  - Increase in b.p. with increased molecular size.
- Chemical Properties:

$CH_2=CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2-CH_2Br$

$CH_2=CH_2 + HBr \longrightarrow CH_3CH_2Br$

$CH_3-CH=CH_2 + HBr \xrightarrow{Markovnikov\ rule}$ $CH_3-CH(Br)-CH_3$ / $CH_3-CH_2-CH_2-Br$

$H_3C-C(CH_3)=CH_2 + H_2O \xrightarrow{H^+} (CH_3)_3C-OH$

$CH_3-CH=CH-CH_3 \xrightarrow{KMnO_4/H^+} 2CH_3COOH$

$n(CH_2=CH_2) \xrightarrow[Catalyst]{HighTemp/Pressure} (CH_2-CH_2)_n$

$n(CH_3-CH=CH_2) \xrightarrow[Catalyst]{HighTemp/Pressure} (CH-CH_2)_n$

Physical Properties:

- Non-polar, usually colourless liquids or solids with characteristic aroma.
- Immiscible with water but miscible with organic solvents.
- Burns with sooty flame.

Chemical Properties:

$C_6H_6 + conc.\ HNO_3 + conc.\ H_2SO_4 \xrightarrow{323-333K} C_6H_5NO_2 + H_2O$

$C_6H_6 + Cl_2 \xrightarrow{Anhyd.\ AlCl_3} C_6H_5Cl + HCl$; $C_6H_5Cl + H_2SO_4 \xrightarrow{\Delta} C_6H_4(Cl)SO_3H + H_2O$

$C_6H_6 + CH_3Cl \xrightarrow{Anhyd.\ AlCl_3} C_6H_5CH_3 + HCl$

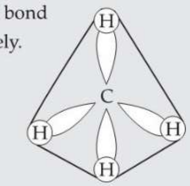
$C_6H_6 + CH_3COCl \xrightarrow{Anhyd.\ AlCl_3} C_6H_5COCH_3 + HCl$

Classification

- **Saturated:** Contain C-C and C-H single bonds. (alkanes)
- **Unsaturated:** Contain C-C multiple bonds.
- **Aromatic**: Contain cyclic compounds

Alkene (C_2H_{2n-2})

- H-C-H bond angles – 190.5, C-C and C-H bond lengths are 154 pm and 112 pm respectively.
- Shows structural and chain isomerism.



Preparation :

$CH_2=CH_2 + H_2 \xrightarrow{pt/pd/Ni} CH_3-CH_3$

$CH_3Cl + H_2 \xrightarrow{zn,H^+} CH_4 + HCl$

Wurtz reaction :

$CH_3Br + 2Na + BrCH_3 \xrightarrow{Dryether} CH_3-CH_3 + 2NaBr$

$CH_3COO^-Na^+ + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$

$2CH_3COONa + 2H_2O \longrightarrow C_2H_6 + 2CO_2 + H_2 + 2NaOH$

- Physical Properties:

Non-polar, weak van der Waals forces, colourless, odourless.
B.P. increases with increases in molecular size.

Chemical Properties:

$CH_4 \xrightarrow[hv/-HCl]{+Cl_2} CH_3Cl + \xrightarrow[hv/-HCl]{+Cl_2} CH_2Cl_2 \xrightarrow[hv/-HCl]{+Cl_2} CHCl_3 \xrightarrow[hv/-HCl]{+Cl_2}$

$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$

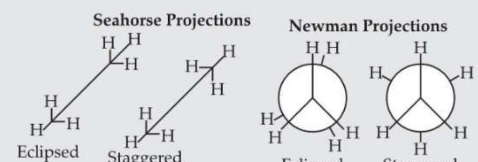
$2CH_4 + O_2 \xrightarrow{Cu/523K/100atm} 2CH_3OH$

$CH_4 + O_2 \xrightarrow[\Delta]{Mn_2O_3} HCHO + H_2O$

$CH_4(CH_2)_4CH_3 \xrightarrow{Anhyd.AlCl_3/HCl} CH_3-CH(CH_3)-(CH_2)_2-CH_3 + CH_3-CH_2-CH(CH_3)-CH_2-CH_3$

$CH_4 + H_2O \xrightarrow[\Delta]{Ni} CO + 3H_2$

$C_6H_{14} \xrightarrow{733\,K}$ $C_6H_{12} + H_2$ / $C_uH_8 + C_2H_6$ / $C_3H_6 + C_2H_4 + CH_4$



Important Questions

Multiple Choice questions-

Question 1. Consider the following statement about Ozone I. O3 is formed by the interaction of fluorine. II. It turns tetramethyl base paper as violet. III. It turns benzidine paper as brown. The correct set of true statement is

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

Question 2. In the compound of type ECl3, where E = B, P, As, or Bi, the angle Cl – E – Cl for different E are ion the order:

(a) B = P = As = Bi
(b) B > P > As > Bi
(c) B < P = As = Bi
(d) B < P < As < Bi

Question 3. In white phosphorous(P_4) molecule, which one is not correct:

(a) 6P-P single bonds are present
(b) 4P-P single bonds are present
(c) 4 lone pair of electrons is present
(d) P-P-P bond angle is 60°

Question 4. All the elements of oxygen family are

(a) Non metals
(b) Metalloids
(c) Radioactive
(d) Polymorphic

Question 5. Which of the following will not produce hydrogen gas?

(a) Reaction between Fe and dil. HCl
(b) Reaction between Zn and NaOH
(c) Reaction between Zn and conc. H_2SO_4
(d) Electrolysis of NaCl in Nelsons cell

Question 6. Amorphous form of Silica is

(a) Tridymite
(b) Kieselguhr
(c) Cristobalite
(d) Quartz

Question 7. Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behavior is that graphite.

(a) Has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interpolate bonds
(b) Is a non – crystalline substance
(c) Is an allotropic from of carbon
(d) Has molecules of variable molecular masses like polymers.

Question 8. Borax is used as a cleansing agent because on dissolving in water, it gives

(a) Alkaline solution
(b) Acidic solution
(c) Bleaching solution
(d) Amphoteric solution.

Question 9. Among the C-X bond (where, X = Cl, Br, I) the correct decreasing order of bond energy is

(a) C−I > C−Cl > C−Br
(b) C−I > C−Br > C−Cl
(c) C−Cl > C−Br > C−I
(d) C−Br > C−Cl > C−I

Question 10. On heating boron with caustic potash, the pair of products formed are

(a) Potassium Borate + Dihydrogen
(b) Potassium Borate + Water
(c) Potassium Borate + H_2
(d) Borax + Dihydrogen.

Question 11. Which of the following statements regarding ozone is not correct?

(a) The oxygen-oxygen bond length in ozone is identical with that of molecular oxygen
(b) The ozone is response hybrid of two structures
(c) The ozone molecule is angular in shape
(d) Ozone is used as a germicide and disinfectant for the purification of air.

Question 12. There is no S-S bond in

(a) $S_2O^{2-}4$
(b) $S_2O^{2-}5$
(c) $S_2O^{2-}3$
(d) $S_2O^{2-}7$

Question 13. Which is strongest Lewis acid?

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

Question 14. Fertilizer having the highest nitrogen percentage is:

(a) Calcium cyanamide
(b) Urea
(c) Ammonium nitrate
(d) Ammonium sulphate

Question 15. In general, the Boron Trihaides act as

(a) Strong reducing agent
(b) Lewis Acids
(c) Lewis Bases
(d) Dehydrating Agents

Very Short:

1. Do boron halides form additional compounds with amines?
2. How does boron interact with NaOH?
3. What is the oxidation state of C in

(a) CO

(b) HCN

(c) H_2CO_3

(d) CaC_2

4. What is the state of hybridization of C in

(a) CO_3^{2-}

(b) CCl_4

(c) diamond

(d) Graphite?

5. Give two examples of electron-deficient compounds.
6. Arrange the following halides of boron in the increasing order of acidic character
7. What is dry ice? Why is it so-called?
8. Write balanced equations to show hydrolysis reactions of CO_3^{2-} and HCO_3^{-}.
9. Why boron does not form B3+ ion?
10. Which oxide of carbon is an anhydride of carbonic acid?

Short Questions:

1. Although boric acid $B(OH)_3$ contains three hydroxyl groups, yet it behaves as a monobasic acid. Explain.

2. $SiCl_4$ forms $[SiCl_6]^{2-}$ while CCl4 does not form $[CCl_6]^{2-}$ Explain.
3. Why does not silicon form an analogue of graphite?
4. Why carbon forms covalent compounds whereas lead forms ionic compounds?
5. How is borax prepared from?
6. Mention three important uses of borax.

Long Questions:

1. SiCl. forms $[SiCl]^{2-}$ while CClL does not form $[CCl]^{2-}$. Explain
2. Borazine is more reactive than benzene. Why?
3. (i) What are the different oxidation states exhibited by the group 14 elements? Discuss the stability of their oxidation states.

   (ii) What type of oxides are formed by group 14 elements? Which of them are acidic, neutral or basic?
4. (a) $[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ is not known. Give reasons

   (b) Select the member (s) of group 14 that

   (i) forms the most acidic oxide

   (ii) is commonly found in the +2-oxidation state

   (iii) used as a semi-conductor.

   (c) Explain why a diamond that is covalent has a high melting point?

   (d) Discuss the reaction of silica with

   (i) NaOH

   (ii) HE
5. (a) Carbon exhibits catenation, whereas silicon does not. Explain.

   (b) How does boron differ from aluminum.

   (c) Write the similarities between boron and silicon.

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): If Aluminium atoms replace a few silicon atoms in three

   dimensional network of silicon dioxide, the overall structure acquires a negative charge.

   Reason (R) : Aluminium is trivalent while silicon is tetravalent.

   (i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

Assertion (A): Silicon's are water repelling in nature.

Reason (R) : Silicon's are organosilicon polymers, which have (–R2SiO–) as

repeating unit.

(i) A and R both are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) A and R both are not true.

(iv) A is not true but R is true.

Case Study Based Question:

1. The heavier members of 13 and 14 groups besides the group oxidation state also show another oxidation state which is two units less than the group oxidation state. Down the group (↓), the stability of higher oxidation state decreases and that of lower oxidation state increases. This concept which is commonly called inert pair effect has been used to explain many physical and chemical properties of the element of these groups.

(1) Heavier members of groups 13 exhibit oxidation state

(a) +3 only

(b) +1 only

(c) +1 and +3 both

(d) +1, +2, +3

(2) Which among the following is the strongest oxidising agent?

(a) SiO_2

(b) GeO_2

(c)SnO_2

(d) PbO_2

(3) Which among the following is the strongest reducing agent?

(a) GaCl

(b) InCl

(c) BCl_3

(d) TlCl

(4) The strongest reductant among the following is

(a) $SnCl_2$

(b) $SnCl_4$

(c) $PbCl_2$

(d) $GeCl_2$

(5) Which of the following statement is wrong?

(a) Tl(III) salt undergo disproportionation.

(b) CO is used as a reducing agent.

(c) CO_2 is a greenhouse gas.

(d) SiO_2 is a covalent solid.

Answer Key:

MCQ

1. (b) I, II and III
2. (b) B > P > As > Bi
3. (a) 6P-P single bonds are present
4. (d) Polymorphic
5. (c) Reaction between Zn and conc. H_2SO_4
6. (c) Cristobalite
7. (a) Has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interpolate bonds
8. (a) Alkaline solution
9. (c) C−Cl > C−Br > C−I
10. (a) Potassium Borate + Dihydrogen
11. (a) The oxygen-oxygen bond length in ozone is identical with that of molecular oxygen
12. (d) $S_2O^{2-}_7$
13. (a) BF_3
14. (b) Urea
15. (b) Lewis Acids

Very Short Answer:

1. Boron halides are Lewis's acids and hence accept a pair of electrons from amines to form additional compounds.

2. 2B + 6NaOH → 2Na3BO3 + 3H2.

3. (a) + 2

(b) +2

(c) +4

(d) -1

4. (a) sp^2

(b) sp^3

(c) sp^3

(d) sp^2

5. BF_3 and B_2H_6.

6. $BF_3 < BCl_3 < BBr_3 < BI_3$.

7. Solid CO_2 is known as dry ice. It does not wet a piece of paper/cloth and sublimes without melting. Therefore, it is called dry ice.

8. $CO3^{2-} + H_2O \rightleftharpoons OH^- + HCO^{3-}$

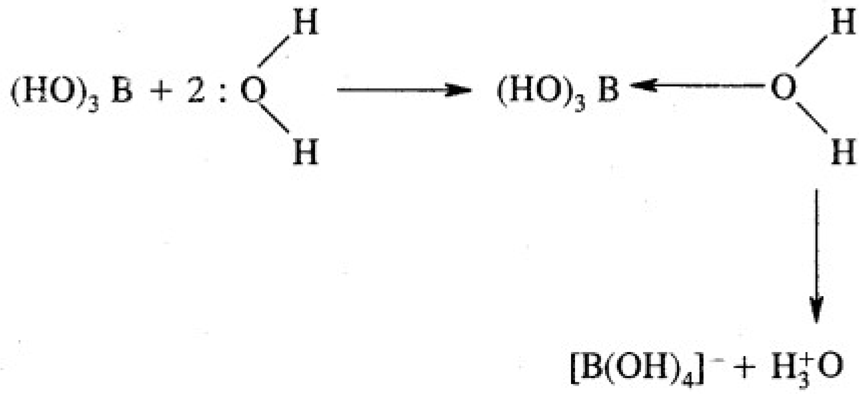
$HCO_3^- + H_2O \rightleftharpoons OH^- + H_2CO_3$.

9. Boron has a very high sum of the first three ionisation enthalpies. Hence it cannot lose three electrons to form a B^{3+} ion.

10. CO_2, because H_2CO_3 acid decomposes to give H_2O and CO_2.

Short Answer:

Ans: 1.



Hydrated species

$B(OH)_3$ is not a protonic acid.

It behaves as a Lewis acid because it abstracts a pair of electrons from hydroxyl ion.

Ans: 2. Carbon does not have d-orbitals and hence C. Cl_4 does not combine with Cl^- ions to give $[CCl_6]^{2-}$, On the other hand, silicon has vacant 3d-orbitals and thus can expand its covalency from 4 to 6. Therefore, $SiCl_4$ combines with CL ions to form $[SiCl_6]^{2-}$

$SiCl_4 + 2Cl^- \rightarrow [SiCl_6]^{2-}$

Ans: 3. In graphite, C is sp^2 hybridised and each C is linked to three other C atoms forming hexagonal rings. Thus, graphite has a two-dimensional sheet-like structure.

Silicon, on the other hand, does not form an analogue of C because of the following two reasons:

1. Silicon has a much lesser tendency for catenation than C as Si-Si bonds are much weaker than C-C bonds.
2. Silicon because of its larger size than C undergoes sp3 hybridisation.

Ans: 4. Carbon cannot lose electrons to form C4 because the sum of four ionisation enthalpies is very high. It cannot gain four electrons to form C4 because energetically it is not favorable. Hence C forms only covalent compounds. Down the group 14, ionisation enthalpies decrease, Pb being the last element has so low I.E. that it can lose electrons to form ionic compounds.

Ans: 5. (I) Borax is also called sodium tetraborate decahydrate (Na2B4O7.10H2O). It can be prepared as follows:

From colemanite: Powdered mineral is boiled with sodium carbonate solution and filtered. The filtrate is concentrated and then cooled when crystals of borax.

$Ca_2B_6O_{11} + 2Na_2CO_3 \rightarrow Na_2B4O_7 + 2NaBO_2 + 2CaCO_3$.

The mother-liquor which contains sodium meta-borate is treated with a current of C02, to convert it into borax which separates out.

$4NaBO_2 + CO_2 \rightarrow Na_2B4O_7 + Na_2CO_3$

(ii) **From Tincal:** Tincal obtained from dried up lakes is boiled with water. The solution is filtered to get rid of insoluble impurities of clay, sand etc. The filtrate is concentrated to get the crystals of borax.

(iii) **From boric acid:** Boric acid is neutralised with sodium carbonate and the resulting solution is concentrated and cooled to get the crystals of borax $Na_2B4O7.10H_2O$.

$4H3BO_3 + Na_2CO_3 \rightarrow Na_2B4O_7 + 6H_2O + CO_2 \uparrow$

Ans: 6. It is used:

- As a flux soldering and welding in industry.
- In the manufacture of borosilicate glass (or pyrex glass).
- In making enamels and glazes.
- In stiffening of candle wicks.
- In softening of water.
- In a qualitative analysis for borax bead test in the laboratory.

Long Answer:

Ans: 1. Carbon does not have d-orbitals, hence CCl_4 does not combine with Cl ions to form $[CCl_6]^{2-}$. On the other hand, silicon has vacant 3-d orbitals & thus $SiCl_4$ combines with Cl^- ions to form

[Sicy2-

$SiCl_4 + 2Cl^- \rightarrow [SiCl_6]^{2-}$

In other words, carbon shows a fixed covalency of 4 but silicon exhibits varying covalency from 4 to 6.

Ans: 2. Both Borazine & Benzene are isoelectronic. In benzene C = C bonds are non-polar while N=B bonds in borazine are polar in nature due to the presence of a co-ordinate bond between N & B atoms. As a result, addiction is quite frequent in borazine while it is less in benzene because of delocalization of π-electron charge.

Ans: 3. (i) The group 14 elements have four electrons in the outermost shell. The common oxidation states exhibited by these elements are +4 and +2. Since the sum of the first four ionisation enthalpies is very high, compounds in the +4-oxidation state are generally covalent in nature. In heavier members such as Ge, Sn and Pb, the tendency to show +2 oxidation state increases. It is due to the inability of ns2 electrons of the valence shell to participate in bonding.

The relative stabilities of these two oxidation states vary down the group. C and Si mostly show a +4 oxidation state. Ge forms stable compounds in the +4 state and only a few compounds in the +2 state. Sn forms compounds in both oxidation states (Sn in +2 state is a reducing agent).

Lead compounds in the +2 state are stable and in the +4 state are strong oxidising agents. In the tetravalent state, the number of electrons around the central atom in a molecule (e.g., carbon in CCl_4) is eight. Being electron precise molecules, they are normally not expected to act as an electron acceptor or electron donor.

Although carbon cannot exceed its covalence of more than 4, other elements of the group can do so. It is because of the presence of d-orbital in them. Due to this, their halides undergo hydrolysis and have a tendency to form complexes by accepting electron pairs from donor species. For example, the species like SiF_5^-, SiF_6^-, $[GeCl_6]^{2-}$, $[Sn(OH)_6]^{2-}$ exist where the hybridisation of the central atom is sp^3d^2.

(ii) All members when heated in oxygen form oxides. There are -mainly two types of oxides, i. e., monoxide and dioxide of formula MO and MO_2 respectively. SiO only exists at high temperature. Oxides in the higher oxidation state of elements are generally more acidic than those in the lower oxidation state. The dioxides-CO_2, SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

Ans: 4. (a) (i) $[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ does not exist.

The main reasons are (i) six large chlorine atoms cannot be accommodated around silicon atom due to the limitation of their size.

(ii) Interactions between lone pairs of a chlorine atom and silicon atom are not very strong

(b) (i) The most acidic dioxide is formed by carbon (CO2).

(ii) Lead is mostly found in the +2 oxidation state in its compounds.

(iii) Silicon and germanium are used as semiconductors.

(c) Though diamond has covalent bonding in it, yet it has a high melting point, because a diamond has a 3-dimensional network involving strong C—C bond, which are very difficult to break and in turn, it has a high melting point.

(d) (i) SiO_2 reacts with HF as follows:

$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$

(ii) SiO_2 reacts with HF as follows:

$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$.

Ans: 5. (a) Carbon shows catenation because of its smaller size, high bond energy of C – C bond, the possibility of sp, sp^2, sp^3 hybridisation and formation of multiple bonds C-C (1σ), C = C (1σ + 1π),- C = C (1σ + 2π). On the other hand, silicon shows only limited catenation because of its large atomic radius, low bond energy of Si-Si bond and absence of multiple bonds between Si atoms.

(b) Difference between boron and aluminum:

1. Boron is a non-metal but aluminum is a metal.
2. Boron is a semi-conductor while aluminum is a good conductor of electricity.
3. Boron forms a number of hydrides called boranes, but Al forms a polymeric hydride.
4. Halides of boron (except BF_3) are readily hydrolysed by water whereas halides of A1 are only partially hydrolysed by water.
5. B_2O_3 is acidic, but Al_2O_3 is amphoteric.
6. Boron hydroxide $B(OH)_3$ is acidic, but $Al(OH)_3$ is amphoteric.

(c) Similarities between boron and silicon:

1. Both are non-metals.
2. Both are semi-conductors
3. Boron and silicon form a number of covalent hydrides which have similar properties. For example, they spontaneously catch fire on exposure to air and are readily hydrolysed by water.
4. The halides of boron and silicon are readily hydrolysed by water.
5. Boron trioxide (B_2O_3) and silicon dioxide (SiO_2) are acidic in nature. These dissolve in alkali solution forming borates and silicates.

Assertion Reason Answer:

1. (i) Both A and R are correct and R is the correct explanation of A.
2. (ii) Both A and R are correct but R is not the correct explanation of A.

Case Study Answer:

1. **Answer:**

(1) (c) +1 and +3 both

(2) (d) PbO_2

(3) (c) BCl_3

(4) (d) $GeCl_2$

(5) (a) Tl(III) salt undergo disproportionation.