ALLEN CAREER INSTITUTE OVERSEAS

CHEMISTRY

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# MODULE-4


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CHAPTER 1

# REDOX & EQUIVALENT CONCEPTS (STOICHIOMETRY-II)

## Chapter 01 Contents


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# IMPORTANT NOTES

CHAPTER 1

# REDOX & EQUIVALENT CONCEPTS (STOICHIOMETRY-II)

## 1. OXIDATION & REDUCTION

Let us do a comparative study of oxidation and Reduction ;

| | **Oxidation** | | **Reduction** |
|---|---|---|---|
| (1) | Addition of oxygen | (i) | Removal of oxygen |
| **e.g.** | $2Mg + O_2 \rightarrow 2MgO$ | **e.g.** | $CuO + C \rightarrow Cu + CO$ |
| (2) | Removal of Hydrogen | (ii) | Addition of Hydrogen |
| **e.g.** | $H_2S + Cl_2 \rightarrow 2HCl + S$ | **e.g.** | $S + H_2 \rightarrow H_2S$ |
| (3) | Increase in positive charge | (iii) | Decrease in positive charge |
| **e.g.** | $Fe^{2+} \rightarrow Fe^{3+} + e^-$ | **e.g.** | $Fe^{3+} + e \rightarrow Fe^{2+}$ |
| (4) | Increase in oxidation number | (iv) | Decrease in oxidation number |
| | (+2) (+4) | | (+7) (+2) |
| | $SnCl_2 \rightarrow SnCl_4$ | | $MnO_4^- \rightarrow Mn^{2+}$ |
| (5) | Removal of electron | (v) | Addition of electron |
| **e.g.** | $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$ | **e.g.** | $Fe^{3+} + e^- \rightarrow Fe^{2+}$ |

## 2. Oxidation Number :

- It is an imaginary or apparent charge gained by an element when it goes from its elemental free state to combined state in molecules.
- It is calculated on basis of a arbitrary set of rules.
- It is a relative charge in a particular bonded state.

### 2.1 Rules governing oxidation number :

The following rules are helpful in calculating oxidation number of the elements in their different compounds. It is remember that the basis of these rule is the electronegativity of the element.

- **Fluorine atom :**

  Fluorine is most electronegativity atom (known). It always has oxidation no. equal to –1 in all its compounds.

- **Oxygen atom :**

  In general and as well as in its oxides, oxygen atom has oxidation number equal to –2.

**In case of :**

(i) peroxide (e.g. $H_2O_2$, $Na_2O_2$) is –1

(ii) super oxide (e.g. $KO_2$) is – ½

(iii) ozonide ($KO_3$) is – ⅓

(iv) oxygen fluoride $OF_2$ is +2 & in $O_2F_2$ is +1

- **Hydrogen atom :**

  In general, H atom has oxidation number equal to +1. But in metallic hydrides (e.g. NaH, KH) it is –1.

- **Halogen atom :**

  In general, all halogen atom (Cl, Br, I) has oxidation number equal to –1.

  But if halogen atom is attached with an more electronegative atom than halogen atom then it will show positive oxidation numbers.

  e.g. $K\overset{+5}{Cl}O_3$ $H\overset{+5}{I}O_3$ $H\overset{+7}{Cl}O_4$ $K\overset{+5}{Br}O_3$

- **Metals :**

  (a) Alkali metal (Li, Na, K, Rb, .....) always have oxidation number +1.

  (b) Alkaline earth metal (Be, Mg, Ca .....) always have oxidation number +2.

**Note :** Metal may have positive or zero oxidation number.

(c) Aluminium always have +3 oxidation number

- Oxidation number of an element in free state or in allotropic forms is always zero.

  e.g. $\overset{0}{O_2}, \overset{0}{S_8}, \overset{0}{P_4}, \overset{0}{O_3}$

- Sum of the charges of elements in a molecule is zero.
- Sum of the charges of all elements in an ions is equal to the charge on the ion.
- If the group no. of an element in periodic table is n then its oxidation number may vary from n to n – 8 (but it is mainly applicable in p-block elements)

  e.g. N-atom belongs to v group in the periodic table therefore as per rule its oxidation number may vary from

  –3 to +5 $(\overset{-3}{N}H_3, \overset{+2}{N}O, \overset{+3}{N_2}O_3, \overset{+4}{N}O_2, \overset{+5}{N_2}O_5)$

---

***Ex.1 Calculate oxidation number of underlined element $Na_2S_2O_3$ :***

**Sol.** Let oxidation number of S-atom is x. Now work accordingly with the rules given before.

$(+1) \times 2 + (x) \times 2 + (-2) \times 3 = 0$

$x = +2$

***Ex.2 $Na_2S_4O_6$ :***

**Sol.** Let oxidation number of S-atom is x

$(+1) \times 2 + (x) \times 2 + (-2) \times 6 = 0$

$x = +2.5$

- It's important to note here that $Na_2S_2O_3$ have two S-atom and there are four S-atom in $Na_2S_4O_6$ but sulphur atom in both the compound have +2 or +2.5 oxidation number, it is the average charge (O. No.) Which reside on each sulphur atom therefore we should work to calculate the individual oxidation number of each sulphur atom in these compound.

***Ex.3 Calculate the O.S. of all the atoms in the following species :***

***(i) $ClO^-$, (ii) $NO_2^-$, (iii) $NO_3^-$ (iv) $CCl_4$ (v) $K_2CrO_4$ and (vi) $KMnO_4$***

**Sol.** (i) In $ClO^-$, the net charge on the species is –1 and therefore the sum of the oxidation states of Cl and O must be equal to –1. Oxygen will have an O.S. of –2 and if the O.S. of Cl is assumed to be 'x' then x – 2 should be equal to –1.

x is + 1

(ii) $NO_2^-$ : $(2 \times -2) + x = -1$ (where 'x' is O.S. of N)

$\therefore$ x = +3

(iii) $NO_3^-$ : $x + (3 \times -2) = -1$ (where 'x' is O.S. of N)

x = +5

(iv) In $CCl_4$, Cl has an O.S. of –1

$x + 4 \times -1 = 0$

$\therefore$ x = +4 (where 'x' is O.S. of C)

(v) $K_2CrO_4$ : K has O.S. of +1 and O has O.S. of –2 and let Cr has O.S. 'x' then, $2 \times +1 + x + 4 \times -2 = 0$

$\therefore$ x = +6

(vi) $KMnO_4$ : $+1 + x + (4 \times -2) = 0$

$\therefore$ x = +7 (where x is O.S. of Mn).

## 2.2 MISCELLANEOUS EXAMPLES

In order to determine the exact or individual oxidation number we need to take help from the structures of the molecules. Some special cases are discussed as follows :

- The structure of $CrO_5$ is

From the structure it is evident that in $CrO_5$ there are two peroxide linkages and one double bond.

The contribution of each peroxide linkage is –2. Let the O.N. of Cr is x.

$\therefore$ $x + (-2)2 + (-2) = 0$ or x = 6

$\therefore$ O.N. of Cr = +6**Ans.**

$K_3CrO_8$

From the structure it is evident that in $CrO_8^{-3}$ there are four peroxide linkages.

The contribution of each peroxide linkage is –2. Let the O.N. of Cr is x.

$\therefore$ $x + (-2)4 = -3$ or $x = +5$

$\therefore$ O.N. of Cr = +5 **Ans.**

- The strcuture of $H_2SO_5$ is

From the structure, it is evident that in $H_2SO_5$. there are one peroxide linkage, two sulphur - oxygen double bond and one OH group. Let the O.N. of S = x.

$\therefore$ $+1 - 2 + x + (-2)\,2 + (-2) + 1 = 0$

or $x + 2 - 8 = 0$

or $x - 6 = 0$

or $x = 6$

$\therefore$ O.N. of S in $H_2SO_5$ is +6 **Ans**

## 2.3 PARADOX OF FRACTIONAL OXIDATION NUMBER

Fractional oxidation state is the average oxidation state of the element under examination and the structural parameters reveal that the element for whom fractional oxidation state is realised is actually present in different oxidation states. Structure of the species $C_3O_2$, $Br_3O_8$ and $S_4O_6^{2-}$ reveal the following bonding situations.

- The element marked with asterisk in each species is exhibiting the different oxidation state (oxidation number) from rest of the atoms of the same element in each of the species. This reveals that in $C_3O_2$, two carbon atoms are present in +2 oxidation state each whereas the third one is present in zero oxidation state and the average is 4/3. However the realistic picture is +2 for two terminal carbons and zero for the middle carbon.

$$O = \overset{+2}{C} = \overset{0}{C^*} = \overset{+2}{C} = O$$

Structure of $C_3O_2$

(Carbon suboxide)

- Likewise in $Br_3O_8$, each of the two terminal bromine atoms are present in +6 oxidation state and the middle bromine is present in +4 oxidation state. Once again the average, that is different from reality is 16/3.

Structure of $Br_3O_8$ (tribromooctaoxide)

- In the same fashion, in the species $S_4O_6^{2-}$, is 2.5, whereas the reality being +5,0,0 and +5 oxidation number respectively for each sulphur.

Structure of $S_4O_6^{2-}$ (tetrathionate ion)

## 3.1 OXIDISING AND REDUCING AGENT

### 3.1 Oxidising agent or Oxidant :

Oxidising agents are those compound which can oxidise others and reduced itself during the chemical reaction. Those reagents whose O.N. decrease or which gain electrons in a redox reaction are termed as oxidants

e.g. $KMnO_4$, $K_2Cr_2O_7$, $HNO_3$, conc. $H_2SO_4$ etc, are powerful oxidising agents.

### 3.1 Reducing agent or Reductant :

Redusing agents are those compound which can reduce others and oxidise itself during the chemical reaction. Those reagents whose O.N. increase or which loses electrons in a redox reaction are termed as reductants.

e.g. KI, $Na_2S_2O_3$ are powerful reducing agents.

**Note :** There are some compounds also which can work both oxidising agent and reducing agent.

e.g. $H_2O_2$, $NO_2^-$

## 3.3 HOW TO IDENTIFY WHETHER A PARTICULAR SUBSTANCE IS AN OXIDISING OR REDUCING AGENT

***Ex.4. Identify the species undergoing oxidation and reduction***

*(i)* $\underbrace{N_2}_{(R)} + \overbrace{H_2 \longrightarrow NH_3}^{(O)}$

*(ii)* $\underbrace{Zn + HCl \longrightarrow ZnCl_2}_{(O)} + \overbrace{H_2}^{(R)}$

*(iii)* $\underbrace{Mg + O_2 \longrightarrow MgO}$ (R)

*(iv)* $\overbrace{Zn + NaOH}^{(O)} \longrightarrow \underbrace{Na_2ZnO_2 + H_2}_{(R)}$

*(v)* $\overbrace{H_2SO_4 + Mg \longrightarrow MgSO_4 + SO_2}^{(R)} + H_2O$ (O)

*(vi)* $H_2SO_4 + NaOH \longrightarrow Na_2SO_4 + H_2O$

*Neither O & R*

(vii) $\overbrace{Cl_2 + NaOH \longrightarrow NaCl}^{(R)} + NaClO_3 + H_2O$

(O)

(viii) $\overbrace{FeCl_3 + SnCl_2 \longrightarrow FeCl_2}^{(R)} + SnCl_4$

(O)

(ix) $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$

*No oxidation and no reduction.*

## 4 REDOX REACTION

A reaction in which oxidation and reduction simultaneously take place.

In all redox reactions the total increase in oxidation number must equal the total decrease in oxidation number.

e.g. $10\overset{+2}{Fe}SO_4 + 2K\overset{+7}{Mn}O_4 + 8H_2SO_4 \longrightarrow 5\overset{+3}{Fe_2}(SO_4)_3 + 2\overset{+2}{Mn}SO_4 + K_2SO_4 + 8H_2O$

## 5. TYPE OF REACTION

### 5.1 Combination Reactions :

When two or more element combine to form compound then such reaction are redox reaction.

For example

$$A + B \longrightarrow C$$

(a) $3\overset{0}{Mg}(s) + \overset{0}{N_2}(g) \xrightarrow{\Delta} \overset{+2}{Mg_3}\overset{-3}{N_2}(s)$

(b) $\overset{0}{C}(s) + \overset{0}{O_2}(g) \xrightarrow{\Delta} \overset{+4}{C}\overset{-2}{O_2}(g)$

(c) $\overset{-4}{C}\overset{+1}{H_4}(g) + 2\overset{0}{O_2}(g) \xrightarrow{\Delta} \overset{+4}{C}\overset{-2}{O_2}(g) + 2\overset{+1}{H_2}\overset{-2}{O}(\ell)$

(d) $\overset{0}{Li}(s) + \overset{0}{N_2}(g) \xrightarrow{\Delta} \overset{+1}{Li_3}\overset{-3}{N}(s)$

In reaction (c), there is no change in the oxidation number of hydrogen.

## 5.2 Decomposition Reactions :

Decomposition reactions are opposite of combination. Decomposition reactions are those in which when a molecule breaks down to form two or more components, at least one of them must be in the elemental state. For example :

(a) $2\overset{+1}{K}\overset{+5}{Cl}\overset{-2}{O_3}(s) \xrightarrow{\Delta} 2\overset{+1}{M}\overset{-1}{Cl}(s) + 3\overset{0}{O_2}(g)$

(b) $\overset{+2}{Ca}\overset{-1}{H_2} \xrightarrow{\Delta} \overset{0}{Ca}(s) + \overset{0}{H_2}(g)$

(c) $2\overset{+1}{Na}\overset{-1}{H}(s) \xrightarrow{\Delta} 2\overset{0}{Na}(s) + \overset{0}{H_2}(g)$

(d) $\overset{+1}{H_2}\overset{-2}{O}(\ell) \xrightarrow{\Delta} 2\overset{0}{H_2}(g) + \overset{0}{O_2}(g)$

Exception :

$$\overset{+2}{Ca}\overset{+4}{C}\overset{-2}{O_3}(s) \xrightarrow{\Delta} \overset{+2}{Ca}\overset{-2}{O}(s) + \overset{+4}{C}\overset{-2}{O_2}(g)$$

## 5.3 Displacement Reactions :

A reaction in which an atom or iron in a compund is replaced by an atom or ion of another element is called a displacement reaction. It may be denoted as :

$$X + YZ \longrightarrow XZ + Y$$

## 5.4 Disproportionation reactions :

A redox reaction in which a same element present in a particular compound in a definite oxidation state is oxidized as well as reduced simultaneously is a disproportionation reactions.

Disproportionation reactions are a special type of redox reactions. One of the reactants in a disproportionation reaction always contains **an element that can exist in at least three oxidation states.** The element in the form of reacting substance is in the intermediate oxidation state and both higher and lower oxidation states of that element are formed in the reaction.

$$2\overset{+1}{H_2}\overset{-1}{O_2}(aq) \longrightarrow H_2O(\ell) + O_2(g)$$

$$\overset{0}{S_8}(s) + 12OH^-(aq) \longrightarrow 4\overset{-2}{S^{2-}}(aq) + 2\overset{+2}{S_2}O_3^{2-}(aq) + 6H_2O(\ell)$$

$$\overset{0}{Cl_2}(g) + 2OH^-(aq) \longrightarrow \overset{+1}{ClO^-}(aq) + \overset{-1}{Cl^-}(aq) + H_2O(\ell)$$

- **Consider following reactions :**

(a) $2KClO_3 = 2KCl + 3O_2$

$KClO_3$ plays a role of oxidant and reductant both. Because same element is not oxidised and reduced. Here, Cl present in $KClO_3$ is reduced and O present in $KClO_3$ is oxidized. So **its not a disproportion reaction** although it looks like one.

(b) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

Nitrogen in this compound has –3 and +3 oxidation number so it is not a definite value, so its not a disproportion reaction. Its a example of **comproportionation reaction** which is a class of redox reaction in which a element from two different oxidation state gets converted into a single oxidation state.

(c) $4KClO_3 \longrightarrow 3KClO_4 + KCl$

Its a case of disproportionation reaction in which Cl is the atom disproportionating.

- **List of some important disproportionation reaction :**

1. $H_2O_2 \longrightarrow H_2O + O_2$
2. $X_2 + OH^-$ (dil.) $\longrightarrow X^- + XO^-$
3. $X_2 + OH^-$ (conc.) $\longrightarrow X^- + XO_3^-$

**$F_2$ does not (can not) undergo disproportionation as it is the most electronegative element.**

$F_2 + NaOH$ (dil) $\longrightarrow F^- + OF_2$

$F_2 + NaOH$ concentration (dil) $\longrightarrow F^- + O_2$

- Reverse of disproportionation is called Comproportionation. In some of the disproportionation reactions by changing the medium (from acidic to basic or reverse) the reaction goes in backward direction and can be taken as an example of Comproportionation.

$$I^- + IO_3^- + H^+ \longrightarrow I_2 + H_2O \text{ (acidic)}$$

## 6. BALANCING OF REDOX REACTION

All balanced equations must satisfy two criteria

**1. Atom balance (mass balance) :**

That is there should be the same number of atoms of each kind in reactant and products side.

**2. Charge balance :**

That is the sum of actual charges on both side of the equation must be equal

There are two methods for balancing the redox equations

(a) Oxidation - number change method

(b) Ion electron method or half cell method

**(a) Oxidation number change method :**

This method was given by Jonson. In a balanced redox reaction, total increase in oxidation number must be equal to total decreases in oxidation number. This equivalence provides the basis for balancing redox reactions.

The general procedure involves the following steps :

(i) Select the atom in oxidising agent whose oxidation number decreases and indicate the gain of electrons.

(ii) Select the atom in reducing agent whose oxidation number increases and write the loss of electrons.

(iii) Now cross multiply i.e. multiply oxidising agent by the number of loss of electrons and reducing agent by number of gain of electrons.

(iv) Balance the number of atoms on both sides whose oxidation numbers change in the reaction.

(v) In order to balance oxygen atoms, add $H_2O$ molecules to the side deficient in oxygen. Then balance the number of H atoms by adding $H^+$ ions in the hydrogen.

***Ex.5 Write the skeleton equation for each of the following processes and balance them by ion electron method :***

***(i) Permanganate ion oxidizes oxalate ions in acidic medium to carbon dioxide and gets reduced itself to $Mn^{2+}$ ions.***

***(ii) Chlorine reacts with base to form chlorate ion, chloride ion and water in acidic medium.***

**Sol.** (i) The skeleton equation for the process :

$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$

◆ **Step (1)** : Indicating oxidation number :

$$\overset{+7}{Mn}\overset{-2}{O_4^-} + \overset{+3}{C_2}O_4^{2-} \longrightarrow Mn^{2+} + \overset{+4}{C}\overset{-2}{O_2} + \overset{+1}{H_2}\overset{-2}{O}$$

◆ **Step (2)** : Writing oxidation and reduction half reaction :

$$\overset{+3}{C_2}O_4^{2-} \longrightarrow 2\overset{+4}{C}O_2 \qquad \text{(Oxidation half)}$$

$$\overset{+7}{Mn}O_4^- \longrightarrow Mn^{2+} \qquad \text{(Reduction half)}$$

◆ **Step (3)** : Adding electrons to make the difference in O.N.

$$\overset{+3}{C_2}O_4^{2-} \longrightarrow 2\overset{+4}{C}O_2 + 2e^-$$

$$\overset{+7}{Mn}O_4^- + 5e^- \longrightarrow Mn^{2+}$$

◆ **Step (4)** : Balancing 'O' atom by adding $H_2O$ molecules

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

$$MnO_4^- + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

◆ **Step (5)** : Balancing H atom by adding $H^+$ ions

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

$$MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

- **Step (6)** : Multiply the oxidation half reaction by 2 and reduction half reaction by 5 to equalize the electrons lost and gained and add the two half reactions.

$[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$

$[MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O] \times 2$

---

$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$

(ii) The skeleton equation for the given process :

$Cl_2 + OH^- \longrightarrow Cl^- + ClO_3^- + H_2O$

- **Step (1) :** Indicate the oxidation number of each atom

$\overset{0}{Cl_2} + \overset{-2}{O}H^- \longrightarrow Cl^- + \overset{+5}{Cl}O_3^- + \overset{+1}{H_2}\overset{-2}{O}$

Thus, chlorine is the only element which undergoes the change in oxidation number. It decreases its oxidation number from 0 to 1 and also increases its oxidation number from 0 to 5.

- **Step (2) :** Write the oxidation and reduction half reactions

$\overset{0}{Cl_2} \longrightarrow 2\overset{+5}{Cl}O_3^-$ (Oxidation half)

$\overset{0}{Cl_2} \longrightarrow 2Cl^-$ (Reduction half)

- **Step (3) :** Add electrons to make up for the difference in O.N.

$\overset{0}{Cl_2} \longrightarrow 2\overset{+5}{Cl}O_3^- + 10e^-$

$\overset{0}{Cl_2} + 2e^- \longrightarrow 2Cl^-$

- **Step (4) :** Balance O atoms by adding $H_2O$ molecules

$Cl_2 + 6H_2O \longrightarrow 2(ClO_3)^- + 10e^-$

$Cl_2 + 2e^- \longrightarrow Cl^-$

- **Step (5) :** Since medium is basic, balance H atoms by adding $H_2O$ molecules to the side falling short of H atoms and equal number of $OH^-$ ions to the other side.

$Cl_2 + 6H_2O + 12OH^- \longrightarrow 2ClO_3^- + 10e^- + 12H_2O$

$Cl_2 + 2e^- \longrightarrow 2Cl^-$

- **Step (6) :** Multiply the reduction half reaction by 5 and add two half reactions.

$Cl_2 + 5H_2O + 2OH^- \longrightarrow 2ClO_3^- + 10e^- + 12H_2O$

$[Cl_2 + 2e^- \longrightarrow 2Cl^-] \times 5$

---

$Cl_2 + 5Cl_2 + 12OH^- \longrightarrow 2ClO_3^- + 10Cl^- + 6H_2O$

or, $6Cl_2 + 12OH^- \longrightarrow 2ClO_3^- + 10Cl^- + 6H_2O$

or, $3Cl_2 + 6OH^- \longrightarrow ClO_3^- + 5Cl^- + 3H_2O$

***Ex.6 Balance the following chemical reaction by oxidation number method and write their skeleton equation :***

***(i) The nitrate ions in acidic medium oxidize magnesium to $Mg^{2+}$ ions but itself gets reduced to nitrous oxide.***

**Sol.** (i) The skeleton equation for the given process is

$$Mg + NO_3^- \longrightarrow Mg^{2+} + N_2O + H_2O$$

- **Step (1) :** $\overset{0}{Mg} + (\overset{+5}{N}\overset{-2}{O_3})^- \longrightarrow Mg^{2+} + \overset{+1}{N_2}\overset{-2}{O} + \overset{+1}{H_2}\overset{-2}{O}$

  Multiply $NO_3^-$ by 2 to equalize N atoms

- **Step (2) :** O.N. increases by 2 per Mg atom

  $$\overset{0}{Mg} + 2NO_3^- \longrightarrow Mg^{2+} + \overset{+1}{N_2}O + H_2O$$

  $4 \times 2 = 8$

  O.N. decreases by 4 per N atom

- **Step (3) :** Equalize increase/decrease in O.N. by multiplying Mg by 4 and $2NO_3^-$ by 1.

  $$4Mg + 2NO_3^- \longrightarrow Mg^{2+} + N_2O + H_2O$$

- **Step (4) :** Balance atoms other than O and H

  $$4Mg + 2NO_3^- \longrightarrow 4Mg^{2+} + N_2O + H_2O$$

- **Step (5) :** Balance O atoms

  $$4Mg + 2NO_3^- \longrightarrow 4Mg^{2+} + N_2O + H_2O + 4H_2O$$

- **Step (6) :** Balance H atoms as is done in acidic medium.

  $$4Mg + 2NO_3^- + 10H^+ \longrightarrow 4Mg^{2+} + N_2O + 5H_2O$$

**(b) Ion electron method or half cell method :**

By this method redox equation are balanced in two different medium

(a) Acidic medium (b) Basic medium

- **Balancing in acidic medium**

Students are advised to follow the following steps to balance the redox reactions by ion electron method in acidic medium.

***Ex.7 Balance the following redox reaction.***

$$FeSO_4 + KMnO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + MnSO_4 + H_2O$$

**Sol :** **Step-I** assign the oxidation No. to each elements present in the reaction.

$$\overset{+2}{Fe}\,\overset{+6}{S}\,\overset{-2}{O_4} + \overset{+1}{K}\overset{+7}{Mn}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{+6}{S}\overset{-2}{O_4} \longrightarrow \overset{+3}{Fe_2}(\overset{+6}{S}\overset{-2}{O_4})_3 + \overset{+2}{Mn}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{-2}{O}$$

**Step-II** Now convert the reaction in ionic form by eliminating the elements or species which are not going either oxidation or reduction

$$Fe^{2+} + \overset{+7}{Mn}O_4^- \longrightarrow Fe^{3+} + Mn^{2+}$$

**Step-III** Now identify the oxidation / reduction occurring into the reaction.

undergoes reduction

$$Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$$

undergoes oxidation

**Step-IV** Split the ionic reaction in two half one for oxidation and other for reduction

$$Fe^{2+} \xrightarrow{\text{oxidation}} Fe^{3+} \quad \Big| \quad MnO_4^- \xrightarrow{\text{Reduction}} Mn^{2+}$$

**Step-V** Balance the atom other than oxygen and hydrogen atom in both half reactions

$$Fe^{2+} \rightarrow Fe^{3+} \quad \Big| \quad MnO_4^- \rightarrow Mn^{2+}$$

Fe & Mn atom are balanced in both side.

**Step-VI** Now balance O & H atom by $H_2O$ & $H^+$ respectively by the following way for one excess oxygen atom add one $H_2O$ on the other side and two $H^+$ on the same side.

$$Fe^{2+} \longrightarrow Fe^{3+} \quad \text{(no oxygen atom)} \qquad \text{.....(i)}$$

$$8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O \qquad \text{.....(ii)}$$

**Step VII** Now see equation (i) & (ii) is balanced atomwise. Now balance both equations chargewise to balance the charge add electrons to the electrically positive side.

$$Fe^{2+} \xrightarrow{\text{oxidation}} Fe^{3+} + e^- \qquad \text{.....(1)}$$

$$5e^- + 8H^+ + MnO_4^- \xrightarrow{\text{Reduction}} Mn^{2+} + 4H_2O \qquad \text{.....(2)}$$

**Step VIII** The number of electrons gained and lost in each half-reaction are equalised by multiply suitable factor in both the half reaction and finally the half reactions are added to give the over all balanced reaction.

Here we multiply equation (i) by 5 and (ii) by one

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \qquad .....(1) \times 5$$

$$5e^- + 8H^+ + MnO_4^- \rightarrow M^{2+} + 4H_2O \qquad .....(2) \times 1$$

$$5Fe^{2+} + 8H^+ + MnO_4^- \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

(Here at this stage you will get balanced redox reaction in ionic form)

**Step IX** Now convert the ionic reaction in to molecular form by adding the elements or species which are removed instep (II).

Now by some manipulation you will get

$$5\ FeSO_4 + KMnO_4 + 4H_2SO_4 \rightarrow \frac{5}{2}\ Fe_2(SO_4)_3 + MnSO_4 + 4H_2O \qquad \text{or}$$

$$10\ FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O + K_2SO_4$$

**7. Equivalent weight (E) :**

$$\text{Eq. wt (E)} = \frac{\text{Molecular weight}}{\text{valency factor (v.f)}} = \frac{\text{Mol. wt.}}{\text{n} - \text{factor}}$$

$$\text{no of Equivalents} = \frac{\text{mass of a sample}}{\text{eq. wt. of that species}}$$

- Equivalent mass is a pure number when expressed in gram, it is called gram equivalent mass.
- The equivalent mass of substance may have different values under different conditions.

**8. Valency factor calculation :**

- **For Acids :**

  valence factor = number of replaceable $H^+$ ions

**Solved Examples :**

**Ex :** HCl, $H_2SO_4$ $H_3PO_4$ $H_3PO_3$

{see there are only two replaceable $H^+$ ions}

| | | | | |
|---|---|---|---|---|
| **Sol :** valence→ factor | 1 | 2 (assume 100% dissociation) | 3 | 2 |
| Eq.wt.→ | $\frac{M}{1}$ | $\frac{M}{2}$ | $\frac{M}{3}$ | $\frac{M}{2}$ |

**Self practice problems :**

**1.** Find the valence factor for following acids

(i) $CH_3COOH$ (ii) $NaH_2PO_4$ (iii) $H_3BO_3$

**Answers :**

**1.** (i) 1 (ii) 2 (iii) 1

**8.2 For Base :**

v.f. = number of replicable $OH^-$ ions

**Solved Examples :**

**Ex :** NaOH KOH

**Sol :** v.f.→ 1 1

E.→ $\frac{M}{1}$ $\frac{M}{1}$

**Self practice problems :**

**1.** Find the valence factor for following bases

(i) $Ca(OH)_2$ (ii) CsOH (iii) $Al(OH)_3$

**Answers :**

**1.** (i) 2 (ii) 1 (iii) 3

**8.3 Acid - base reaction :**

In case of acid base reaction, the valence factor is the actual number of $H^+$ or $OH^-$ replaced in the reaction. The acid or base may contain more number of replaceable $H^+$ or $OH^-$ than actually replaced in reaction.

v.f. for base is the number of $H^+$ ion form the acid replaced by per molecule of the base.

***Ex.9*** $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

***Base*** ***Acid***

**Sol :** valency factor of base = 1

valency factor of acid = 2

Here two molecule of NaOH replaced $2H^+$ ion from the $H_2SO_4$ therefore per molecule of NaOH replaced only one $H^+$ ion of acid so v.f. = 1

- v.f. for acid is number of $OH^-$ replaced for the base by per molecule of acid

***Ex.10*** $NaOH + H_3PO_4 \rightarrow NaH_2PO_4 + H_2O$

***Base*** ***Acid***

**Sol :** valence factor of acid = 1

here one of molecule of $H_3PO_4$ replaced one $OH^-$ from NaOH therefore v.f. for $H_3PO_4$ is = 1

$$E = \frac{\text{mol. wt. of } H_3PO_4}{1}$$

***Ex.11*** $2NaOH + H_3PO_4 \rightarrow Na_2HPO_4 + 2H_2O$

***Base*** ***Acid***

**Sol :** valence factor of acid = 2

here one of molecule of $H_3PO_4$ replaced two $OH^-$ from NaOH therefore v.f. for $H_3PO_4$ is = 2

$$E = \frac{\text{mol. wt. of } H_3PO_4}{2}$$

***Ex.12*** $Al(OH)_3 + HCl \rightarrow Al(OH)_2Cl + H_2O$

***Base*** ***Acid***

**Sol :** valence factor of base = 1

here one of molecule of $Al(OH)_3$ replaced one $H^+$ from HCl therefore v.f. for $Al(OH)_3$ is = 1

$$E = \frac{\text{mol. wt. of } Al(OH)_3}{1}$$

---

**8.4 For Salts :**

v.f. = Total number of positive charge or negative charge present into the compound.

**Solved Examples :**

| ***Ex.13*** | $Na_2CO_3$ | $Fe_2(SO_4)_3(2Fe^{3+} + 3SO_4^{2-})$ | $FeSO_4.7H_2O$ |
|---|---|---|---|
| **Sol :** V.f. | 2 | $2 \times 3 = 6$ | 2 |
| E. | $\frac{M}{2}$ | $\frac{M}{6}$ | $\frac{M}{2}$ |

---

**8.5 Eq. wt. of oxidising / reducing agents in redox reaction :**

The equivalent weight of an oxidising agent is that weight which accepts one mole electron in a chemical reaction.

(a) Equivalent wt. of an oxidant (get reduced)

$$= \frac{\text{Mol.wt.}}{\text{No. of electrons gained by one mole}}$$

***Ex.14*** ***In acidic medium***

$$6e^- + Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$

***Eq. wt. of*** $K_2Cr_2O_7 = \dfrac{\text{Mol. wt of } K_2Cr_2O_7}{6} = \dfrac{\text{Mol. wt.}}{6}$

**Note :** [6 in denominator indicates that 6 electrons were gained by $Cr_2O_7^{2-}$ as it is clear from the given balanced equation]

(b) Similarly equivalent wt. of a reductant (gets oxidised)

$$= \frac{\text{Mol. wt.}}{\text{No. of electrons lost by one mole}}$$

---

***Ex.15*** ***In acidic medium,***

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

***Here, Total electrons lost = 2***

***So, eq. wt.*** $= \dfrac{\text{Mol. wt.}}{2}$

***(c)*** ***In different condition a compound may have different equivalent weights. Because, it depends upon the number of electrons gained or lost by that compound in that reaction.***

**Ex.15** (i) $MnO_4^- \longrightarrow Mn^{2+}$ (acidic medium)

(+7) (+2)

Here 5 electrons are taken so eq. wt. $= \dfrac{\text{Mol.wt.of } KMnO_4}{5} = \dfrac{158}{5} = 31.6$

(ii) $MnO_4^- \longrightarrow Mn^{+4}$ (neutral medium)

(+7) (+4)

Here, only 3 electrons are gained, so eq. wt. $= \dfrac{\text{Mol.wt.of } KMnO_4}{3} = \dfrac{158}{3} = 52.7$

(iii) $MnO_4^- \longrightarrow MnO_4^{-2}$ (alkaline medium)

(+7) (+6)

Here, only one electron is gained, so eq. wt. $= \dfrac{\text{Mol.wt.of } KMnO_4}{1} = 158$

**Note :** It is important to note that $KMnO_4$ acts as an oxidant in every medium although with different strength which follows the order.

acidic medium > neutral medium > alkaline medium

***Ex.16*** $2S_2O_3^{--} \longrightarrow S_4O_6^{--} + 2e^-$

***(Reducing agent)***

***equivalent weight of*** $S_2O_3^{--} = \frac{2M}{2} = M$

---

- **Questions based on Equivalent weight :**

**1.** Molecular weight of $KMnO_4$ in acidic medium and neutral medium will be respectively :

(A) 7 × equivalent wt. and 2 × equivalent wt. (B) 5 × equivalent wt. and 3 × equivalent wt.

(C) 4 × equivalent wt. and 5 × equivalent wt. (D) 2 × equivalent wt. and 4 × equivalent wt.

**2.** In acidic medium, equivalent weight of $K_2Cr_2O_7$ (Mol. wt. = M) is –

(A) M/3 (B) M/4 (C) M/6 (D) M/2

**Answers :**

**(1)** B **(2)** A **(3)** C

---

## 9. NORMALITY

Normality of solution is defined as the number of equivalent of solute present in one litre (1000 mL) solutions. Let a solution is prepared by dissolving W g of solute of eq. wt. E in V mL water.

- No. of equivalent of solute = $\frac{W}{E}$
- V mL of solution have $\frac{W}{E}$ equivalent of solute
- 1000 mL solution have $\frac{W \times 1000}{E \times VmL}$
- **Normality (N) =** $\frac{W \times 1000}{E \times VmL}$
- **Normality (N) = Molarity × Valence factor**

Normality (N) = molarity × Valence factor (n)

**or** N × V (in mL) = M × V (in mL) × n

**or** milli equivalents = millimoles × n

## 10. LAW OF EQUIVALENCE

The law states that one equivalent of an element combine with one equivalent of the other, and in a chemical reaction equivalent and mill equivalent of reactants react in equal amount to give same no. of equivalent or milli equivalents of products separately.

**According :**

(i) $aA + bB \rightarrow mM + nN$

m.eq of A = m.eq of B = m.eq of M = m.eq of N

(ii) In a compound $M_xN_y$

m.eq of $M_xN_y$ = m.eq of M = m.eq of N

***Ex.17 The number of moles of oxalate ions oxidized by one mole of $MnO_4^-$ ion in acidic medium.***

***(A)*** $\frac{5}{2}$ ***(B)*** $\frac{2}{5}$ ***(C)*** $\frac{3}{5}$ ***(D)*** $\frac{5}{3}$

**Sol :** Equivalents of $C_2O_4^{2-}$ = equivalents of $MnO_4^-$

x (mole) × 2 = 1 × 5

$x = \frac{5}{2}$

***Ex.18 What volume of 6 M HCl and 2 M HCl should be mixed to get two litre of 3 M HCl ?***

**Sol.** Let, the volume of 6 M HCl required to obtain 2 L of 3M HCl = x L

∴ Volume of 2 M HCl required = (2 – x) L

| $M_1V_1$ | + | $M_2V_2$ | = | $M_3V_3$ |
|---|---|---|---|---|
| 6M HCl | | 2M HCl | | 3M HCl |

$6 \times (x) + 2 \times (2 - x) = 3 \times 2$

$\Rightarrow 6x + 4 - 6x = 6 \Rightarrow 4x = 2$

∴ x = 0.5 L

Hence, volume of 6 M HCl required = 0.5 L

Volume of 2M HCl required = 1.5 L

***Ex.19 In a reaction vessel, 1.184 g of NaOH is required to be added for completing the reaction. How many millilitre of 0.15 M NaOH should be added for this requirement ?***

**Sol.** Amount of NaOH present in 1000 mL of 0.15 M NaOH = 0.15 × 40 = 6 g

∴ 1 mL of this solution contain NaOH $= \frac{6}{1000} \times 10^{-3}$ g

∴ 1.184 g of NaOH will be present in $= \frac{1}{6 \times 10^{-3}} \times 1.184 = 197.33$ mL

***Ex.20 What weight of $Na_2CO_3$ of 85% purity would be required to prepare 45.6 mL of 0.235N $H_2SO_4$?***

**Sol.** Meq. of $Na_2CO_3$ = Meq. of $H_2SO_4$ = 45.6 × 0.235

$$\therefore \quad \frac{W_{Na_2CO_3}}{E_{Na_2CO_3}} \times 1000 = 45.6 \times 0.235$$

$$\Rightarrow \quad \frac{W_{Na_2CO_3}}{106/2} \times 1000 = 45.6 \times 0.235$$

$$\therefore \quad W_{Na_2CO_3} = 0.5679 \text{ g}$$

For 85 g of pure $Na_2CO_3$, weighed sample = 100 g

$\therefore$ For 0.5679 g of pure $Na_2CO_3$, weighed sample $= \frac{100}{85} \times 0.5679$

= 0.6681 g

---

**10.1 Drawbacks of Equivalent concept :**

(i) Since equivalent weight of a substance for example oxidising or reducing agent may be variable hence it is better to use mole concept.

e.g. $5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 2H_2O$

$\therefore$ Eq. wt of $MnO_4^- = \frac{MnO_4^-(\text{mol.wt.})}{5}$

e.g. $3e^- + 2H_2O + MnO_4^- \rightarrow MnO_2 + 4OH^-$

$\therefore$ Eq. wt. of $MnO_4^- = \frac{MnO_4^-}{3}$

**Thus the no. of equivalents of $MnO_4^-$ will be different in the above two cases but no. of moles will be same.**

(ii) **Normality of any solution depends on reaction while molarity does not.**

For example.

Consider 0.1 mol $KMnO_4$ dissolved in water to make 1L solution. Molarity of this solution is 0.1 M. However, its normality is not fixed. It will depend upon the reaction in which $KMnO_4$ participates, e.g. If $KMnO_4$ forms $Mn^{2+}$, normality = 0.1 × 5 = 0.5 N. This same sample of $KMnO_4$, if employed in a reaction giving $MnO_2$ as product (Mn in +4 state) will have normality 0.1 × 3 = 0.3 N.

(iii) **The concept of equivalents is handy, but it should be used with care.** One must never equate equivalents in a sequence which involves same element in more than two oxidation states. Consider an example $KIO_3$ reacts with KI to liberate iodine and liberated iodine is titrated with standard hypo solution, The reaction are

(i) $IO_3^- + I^- \longrightarrow I_2$

(ii) $I_2 + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + I^-$

meq of hypo = meq of $I_2$ = meq of $IO_3^-$ + meq of $I^-$

$\because$ $IO_3^-$ react with $I^- \Rightarrow$ meq of $IO_3^-$ = meq of $I^-$

- meq of hypo = 2 × meq of $IO_3^-$

This is wrong. Note that $I_2$ formed by (i) have v.f. = 5/3 & reacted in equation (ii) have v.f. = 2.

$\because$ v.f. of $I_2$ in both the equation are different therefore we cannot equate m.eq is sequence.

In this type of case students are advised to use mole concept.

---

***Ex.21 How many milliliters of 0.02000 M $KMnO_4$ solution would be required to exactly titrate 25.00 mL of 0.2000 M $Fe(NO_3)_2$ solution?***

**Sol : Method - 1 : Mole concept method**

Starting with 25.00 mL of 0.2000M$Fe^{2+}$, we can write.

Millimoles of $Fe^{2+}$ = 25.00 × 0.2000

and in volume V (in milliliters of the $MnO_4^-$)

Millimoles of $MnO_4^-$ = V (0.02000)

The balanced reaction is :

$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5\,Fe^{3+} + 4H_2O$

This requires that at the equivalent point,

$$\frac{V(0.02000)}{1} = \frac{(25.00)(0.2000)}{5} \qquad V = 50.00 \text{ mL}$$

**Method - 2 : Equivalent Method :**

Equivalents of $MnO_4^-$ = 5 × moles of $MnO_4^-$

Normality $MnO_4^-$ = 5 × molarity of $MnO_4^-$

For $Fe^{2+}$, moles and equivalents are equal,

At the equivalence point,

Equivalents of $MnO_4^-$ = Equivalents of $Fe^{2+}$

or $V_{MnO_4^-}$ × Normality of $MnO_4^-$

= $V_{Fe^{2+}}$ × Normality of $Fe^{2+}$

For 0.02000 M $MnO_4^-$ solution

Normality of $MnO_4^-$ = (5) (0.02000) = 0.1 N and for 0.2000 M $Fe^{2+}$ solution

Normality of $Fe^{2+}$ = 0.2000 N $\quad V_{MnO_4^-} = (25.00 \text{ mL})\left(\frac{0.2000}{0.1000}\right) = 50.00\,\text{mL}$

## 10.2 FOR ACID-BASE (NEUTRALIZATION REACTION) OR REDOX REACTION

$N_1V_1 = N_2V_2$ is always true.

But $M_1V_1 = M_2V_2$ (may or may not be true )

But $M_1 \times n_1 \times V_1 = M_2 \times n_2 \times V_2$ (always true where n terms represent n-factor).

## 10.3 SOME OXIDIZING AGENTS/REDUCING AGENTS WITH EQ. WT.

| Species | Changed to | Reaction | Electrons exchanged or change in O.N. | Eq. wt. |
|---|---|---|---|---|
| $MnO_4^-$ (O.A.) | $Mn^{+2}$ in acidic medium | $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ | 5 | $E = \frac{M}{5}$ |
| $MnO_4^-$ (O.A.) | $MnO_2$ in neutral medium | $MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$ | 3 | $E = \frac{M}{3}$ |
| $MnO_4^-$ (O.A.) | $MnO_4^{2-}$ in basic medium | $MnO_4^- + e^- \longrightarrow MnO_4^{2-}$ | 1 | $E = \frac{M}{1}$ |
| $Cr_2O_7^{2-}$(O.A.) | $Cr^{3+}$ in acidic medium | $CrO_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ | 6 | $E = \frac{M}{6}$ |
| $MnO_2$(O.A.) | $Mn^{2+}$ in acidic medium | $MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$ | 2 | $E = \frac{M}{2}$ |
| $Cl_2$(O.A.) in bleaching powder | $Cl^-$ | $Cl_2 + 2e^- \longrightarrow 2Cl^-$ | 2 | $E = \frac{M}{2}$ |
| $CuSO_4$(O.A.) in iodometric titration | $Cu^+$ | $Cu^{2+} + e^- \longrightarrow Cu^+$ | 1 | $E = \frac{M}{1}$ |
| $S_2O_3^{2-}$ (R.A.) | $S_4O_6^{2-}$ | $2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$ (for two molecules) | 2 | $E=\frac{2M}{2}=M$ |
| $H_2O_2$(O.A.) | $H_2O$ | $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$ | 2 | $E = \frac{M}{2}$ |
| $H_2O_2$(R.A.) | $O_2$ | $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$ (O.N. of oxygen in $H_2O_2$ is –1 per atom) | 2 | $E = \frac{M}{2}$ |
| $Fe^{2+}$(R.A.) | $Fe^{3+}$ | $Fe^{2+} \longrightarrow Fe^{3+} + e^-$ | 1 | $E = \frac{M}{1}$ |

**Ex.22** ***To find the n-factor in the following chemical changes.***

*(i)* $KMnO_4 \xrightarrow{H^+} Mn^{2+}$ *(ii)* $KMnO_4 \xrightarrow{H_2O} Mn^{4+}$

*(iii)* $KMnO_4 \xrightarrow{OH^-} Mn^{6+}$ *(iv)* $K_2Cr_2O_7 \xrightarrow{H^+} Cr^{3+}$

*(v)* $C_2O_4^{2-} \rightarrow CO_2$ *(vi)* $FeSO_4 \rightarrow Fe_2O_3$

*(vii)* $Fe_2O_3 \rightarrow FeSO_4$

**Sol.** (i) In this reaction, $KMnO_4$ which is an oxidizing agent, itself gets reduced to $Mn^{2+}$ under acidic conditions.

$n = |1 \times (+7) - 1 \times (+2)| = 5$

(ii) In this reaction, $KMnO_4$ gets reduced to $Mn^{4+}$ under neutral or slightly (weakly) basic conditions.

$n = |1 \times (+7) - 1 \times (+4)| = 3$

(iii) In this reaction, $KMnO_4$ gets reduced to $Mn^{6+}$ under basic conditions.

$n = |1 \times (+7) - 1 \times (+6)| = 1$

(iv) In this reaction, $K_2Cr_2O_7$ which acts as an oxidizing agent reduced to $Cr^{3+}$ under acidic conditions. (It does not react under basic conditions.)

$n = |2 \times (+6) - 2 \times (+3)| = 6$

(v) In this reaction, $C_2O_4^{2-}$ (oxalate ion) gets oxidized to $CO_2$ when it is reacted with an oxidizing agent.

$n = |2 \times (+3) - 2 \times (+4)| = 2$

(vi) In this reaction, ferrous ions get oxidized to ferric ions.

$n = |1 \times (+2) - 1 \times (+3)| = 1$

(vi) In this reaction, ferric ions are getting reduced to ferrous ions.

$n = |2 \times (+3) - 2 \times (+2)| = 2$

**Ex.23** ***Calculate the molar ratio in which the following two substances would react ?***

***$Ba_3(PO_4)_2$ and $AlCl_3$***

**Sol.** n-factor of $Ba_3(PO_4)_2 = 3 \times (+2) = 6 = n_1$

While n-factor of $AlCl_3 = 1 \times (+3) = 3 = n_2$

$\frac{n_1}{n_2} = \frac{6}{3}$ If $\frac{n_1}{n_2} = \frac{x}{y}$

Molar ratio $= \frac{y}{x}$ (inverse of equivalent ratio)

$\therefore$ Molar ratio in which $Ba_3(PO_4)_2$ and $AlCl_3$ will react = 3 : 6 = 1 : 2

## 10.4 APPLICATIONS OF THE LAW OF EQUIVALENCE

### 10.4.1 Simple Titration

In this, we can find the concentration of unknown solution by reacting it with solution of known concentration (standard solution).

For example, let there be a solution of substance A of unknown concentration. We are given solution of another substance B whose concentration is known ($N_1$). We take a certain known volume of A in a flask ($V_2$) and then we add B to A slowly till all the A is consumed by B (this can be known with the help of indicators). Let us, assume that the volume of B consumed is $V_1$. According to the law of equivalence, the number of g equivalents of B at the end point.

$\therefore N_1V_1 = N_2V_2$, where $N_2$ is the conc. of A.

From this we can calculate the value of $N_2$.

**Ex.24** ***1.20 g sample of $Na_2CO_3$ and $K_2CO_3$ was dissolved in water to form 100 mL of a Solution. 20 mL of this solution required 40 mL of 0.1 N HCl for complete neutralization. Calculate the weight of $Na_2CO_3$ in the mixture. If another 20 mL of this solution is treated with excess of $BaCl_2$ what will be the weight of the precipitate ?***

**Sol.** Let, weight of $Na_2CO_3$ = x g

Weight of $K_2CO_3$ = y g

$\therefore$ x + y = 1.20 g .....(i)

For neutralization reaction of 100 mL

Meq. of $Na_2CO_3$ + Meq. of $K_2CO_3$ = Meq. of HCl

$$\Rightarrow \frac{x}{106} \times 2 \times 1000 + \frac{y}{138} \times 2 \times 1000 = \frac{40 \times 0.1 \times 100}{20}$$

$\therefore$ 69 x + 53 y = 73.14 .....(ii)

From Eqs. (i) and (ii), we get

x = 0.5962 g

y = 0.604 g

Solution of $Na_2CO_3$ and $K_2CO_3$ gives ppt. of $BaCO_3$ with $BaCl_2$

(Meq. of $Na_2CO_3$ + Meq. of $K_2CO_3$) in 20 mL = Meq. of $BaCO_3$

$\Rightarrow$ Meq. of HCl for 20 mL mixture = Meq. of $BaCO_3$

$\Rightarrow$ Meq. of $BaCO_3$ = 40 × 0.1 = 4

$$\frac{W_{BaCO_3}}{M_{BaCO_3}} \times 1000 = 40 \times 0.1 = 4$$

$$\frac{W_{BaCO_3}}{197} \times 2 \times 1000 = 4$$

$\therefore$ $W_{BaCO_3}$ = 0.394 g

## 10.4.2 BACK TITRATION

Back titration is used to calculate % purity of a sample. Let us assume that we are given an impure solid substance C weighing w gs and we are asked to calculate the percentage of pure C in the sample. We will assume that the impurities are inert. We are provided with two solutions A and B, where the concentration of B is known ($N_1$) and that of A is not known. This type of titration will work only if the following condition is satisfied, i.e. the nature of compounds A, B and C should be such that A and B can react with each other. A and C can react with each other but the product of A and C should not react with B.

Now, we take a certain volume of A in a flask ( the g equivalents of A taken should be ≥ g equivalents of C in the sample and this can be done by taking A in excess). Now, we perform a simple titration using B. Let us assume that the volume of B used is $V_1$. In another beaker, we again take the solution of A in the same volume as taken earlier. Now, C is added to this and after the reaction is completed, the solution is being titrated with B. Let us assume that the volume of B used up is $V_2$. Gram equivalents of B used in the first titration = $N_1V_1$.

∴ gm. equivalents of A initially = $N_1V_1$

gm. equivalents of B used in the second titration = $N_1V_2$

∴ gm. equivalents of A left in excess after reacting with C = $N_1V_2$

gm. equivalents of A that reacted with C = $N_1V_1 - N_1V_2$

If the n-factor of C is x, then the moles of pure C = $\frac{N_1V_1 - N_1V_2}{x}$

∴ The weight of C = $\frac{N_1V_1 - N_1V_2}{x} \times$ Molecular weight of C

∴ Percentage of C = $\frac{N_1V_1 - N_1V_2}{x} \times \frac{\text{Molecular wt. of C}}{w} \times 100$

## SOME REDOX TITRATIONS (EXCLUDING IODOMETRIC / IODIMETRIC)

| Estimation of | By titrating with | Reactions | Relation between O.A. and R.A. |
|---|---|---|---|
| $Fe^{2+}$ | $MnO_4^-$ | $Fe^{2+} \longrightarrow Fe^{3+} + e^-$<br>$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ | $5Fe^{2+} \equiv MnO_4^-$<br>Eq. wt. $Fe^{2+}$ = M/1<br>Eq. wt. $MnO_4^-$ = M/5 |
| $Fe^{2+}$ | $Cr_2O_7^{2-}$ | $Fe^{2+} \longrightarrow Fe^{3+} + e^-$<br>$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ | $6Fe^{2+} \equiv Cr_2O_7^{2-}$<br>Eq. wt. $Cr_2O_7^{2-}$ = M/6 |
| $C_2O_4^{2-}$ | $MnO_4^-$ | $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$<br>$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$ | $5C_2O_4^{2-} \equiv 2MnO_4^-$<br>Eq. wt. $C_2O_4^{2-}$ = M/2<br>Eq. wt. $MnO_4^-$ = M/5 |
| $H_2O_2$ | $MnO_4^-$ | $H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$<br>$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ | $5H_2O_2 \equiv 2MnO_4^-$<br>Eq. wt. $H_2O_2$ = M/2<br>Eq. wt. $MnO_4^-$ = M/5 |
| $As_2O_3$ | $MnO_4^-$ | $As_2O_3 + 5H_2O \rightarrow 2AsO_4^{3-} + 10H^+ + 4e^-$ | Eq. wt. $As_2O_3$ = M/4 |
| $AsO_3^{3-}$ | $BrO_3^-$ | $AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e^-$<br>$BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$ | Eq. wt. $AsO_3^{3-}$ = M/2<br>Eq. wt. $BrO_3^-$ = M/6 |

### 10.4.3 Iodometric and Iodimetric Titration :

The reduction of free iodine to iodide ions and oxidation of iodide ions to free iodine occurs in these titrations.

$I_2 + 2e^- \longrightarrow 2I^-$ (reduction)

$2I^- \longrightarrow I_2 + 2e^-$ (oxidation)

These are divided into two types :

**(i) Iodometic Titration :**

In iodometric titrations, an oxidizing agent is allowed to react in neutral medium or in acidic medium with excess of potassium iodide to liberate free iodine.

$$KI + \text{oxidizing agent} \longrightarrow I_2$$

Free iodine is titrated against a standard reducing agent usually with sodium thiosulphate. Halogen, dichromates, cupric ion, peroxides etc., can be estimated by this method.

$$I_2 + 2NaS_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

$$K_4Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O + 3I_2$$

**(ii) Iodimetric Titration**

These are the titrations in which free iodine is used as it is difficult to prepare the solution of iodine (volatile and less soluble in water), it is dissolved in KI solution :

$$KI + I_2 \longrightarrow KI_3 \text{ (Potassium triiodide)}$$

This solution is first standardized before using with the standard solution of substance such as sulphite, thiosulphate, arsenite etc, are estimated.

In iodimetric and iodometric titration, starch solution is used as an indicator. Starch solution gives blue or violet colour with free iodine. At the end point, the blue or violet colour disappears when iodine is completely changed to iodide.

## SOME IODOMETRIC TITRATIONS (TITRATING SOLUTIONS IS $Na_2S_2O_3.5H_2O$)

| Estimation of | Reaction | Relation between O.A. and R.A. |
|---|---|---|
| $I_2$ | $I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$<br>or<br>$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$ | $I_2 = 2I \equiv 2Na_2S_2O_3$<br>Eq. wt. of $Na_2S_2O_3 = M/1$ |
| $CuSO_4$ | $2CuSO_4 + 4KI \longrightarrow 2Cu_2I_2 + 2K_2SO_4 + I_2$<br>$Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$<br>(White ppt.) | $2CuSO_4 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$<br>Eq. wt. of $CuSO_4 = M/1$ |
| $CaOCl_2$ | $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$<br>$Cl_2 + 2KI \longrightarrow 2KCl + I_2$<br>$CaOCl_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$<br>$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$ | Eq. wt. of $CaOCl_2 = M/2$ |
| $MnO_2$ | $MnO_2 + 4HCl(conc) \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$<br>$Cl_2 + 2KI \longrightarrow 2KCl + I_2$<br>or<br>$MnO_2 + 4H^+ + 2Cl^- \longrightarrow Mn^{2+} + 2H_2O + Cl_2$<br>$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$ | $MnO_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$<br>Eq. wt. of $MnO_2 = M/2$ |
| $IO_3^-$ | $IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$ | $IO_3^- \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$<br>Eq. wt. of $IO_3^- = M/6$ |
| $H_2O_2$ | $H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$ | $H_2O_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$<br>Eq. wt. of $H_2O_2 = M/2$ |
| $Cl_2$ | $Cl_2 + 2I^- \longrightarrow 2CI^- + I_2$ | $Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$<br>Eq. wt. of $Cl_2 = M/2$ |
| $O_3$ | $O_3 + 6I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$ | $O_3 \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$<br>Eq. wt. of $O_3 = M/6$ |
| $Cr_2O_7^{2-}$ | $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 3I_2 + 2Cr^{3+} + 7H_2O$ | $Cr_2O_7^{2-} \equiv 3I_2 \equiv 6I$<br>Eq. wt. of $Cr_2O_7^{2-}$ |
| $MnO_4^-$ | $2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2MnO_4^- + 5I_2 + 8H_2O$ | $2MnO_4^- \equiv 5I_2 \equiv 10I$<br>Eq. wt. of $MnO_4^- = M/5$ |
| $BrO_3^-$ | $BrO_3^- + 6I^- + 6H^+ \longrightarrow Br^- + 3I_2 + 3H_2O$ | $BrO_3^- \equiv 3I_2 \equiv I_2$<br>Eq. wt. of $BrO_3^- = M/6$ |
| As(V) | $H_3AsO_4 + 2I^- + 2H^+ \longrightarrow H_3AsO_3 + H_2O + I_2$ | $H_3AsO_4 \equiv I_2 \equiv 2I$<br>Eq. wt. of $H_3AsO_4 = M/2$ |

## SOME IODIMETRIC TITRATION (TITRATING SOLUTIONS IS $I_2$ IN KI)

| Estimation of | Reaction | Relation between O.A. and R.A. |
|---|---|---|
| $H_2S$ (in acidic medium) | $H_2S + I_2 \longrightarrow S + 2I^- + 2H^+$ | $H_2S \equiv I_2 \equiv 2I$<br>Eq. wt. of $H_2S = M/2$ |
| $SO_3^{2-}$ (in acidic medium) | $SO_3^{2-} + I_2 + H_2O \longrightarrow SO_3^{2-} + 2I^- + 2H^+$ | $SO_3^{2-} \equiv I_2 \equiv 2I$<br>Eq. wt. of $SO_3^{2-} = M/2$ |
| $Sn^{2+}$ (in acidic medium) | $Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$ | $Sn^{2+} \equiv I_2 \equiv 2I$<br>Eq. wt. of $Sn^{2+} = M/2$ |
| As(III) (at pH = 8) | $H_2AsO_3^- + I_2 + H_2O \longrightarrow HAsO_4^{2-} + 2I^- + 2H^+$ | $H_2AsO_3^- \equiv I_2 \equiv 2I$<br>Eq. wt. of $H_2AsO_3^- = M/2$ |
| $N_2H_4$ | $N_2H_4 + 2I_2 \longrightarrow N_2 + 4H^+ + 4I^-$ | $N_2H_4 \equiv 2I_2 \equiv 4I$<br>Eq. wt. of $N_2H_4 = M/4$ |

## 11. HARDNESS OF WATER :

**Hard water** does not give lather with soap. Water free from soluble salts of calcium and magnesium is called **Soft water**. It gives lather with soap easily.

Hard water forms scum/precipitate with soap. Soap containing sodium stearate ($C_{17}H_{35}COONa$) reacts with hard water to precipitate out Ca/Mg stearate.

$$2C_{17}H_{35}COONa(aq) + M^{2+}(aq) \rightarrow (C_{17}H_{35}COO)_2M \downarrow +2Na^+(aq);\ M \text{ is Ca/Mg}$$

**Hardness of water is of two types**

(a) Temporary Hardness

(b) Permanent Hardness

**Temporary Hardness :-**

This is due to presence of bicarbonate of calcium and magnesium. Rain water dissolves a small quantities of $CO_2$ from the atmospher forming a very dilute solution of carbonic acid.

This water attacks Ca and Mg carbonate in any rock

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

Temporary hardness in water is easily removed by boiling, as the bicarbonates decomposes readily and the insoluble carbonates are precipitated.

$$Ca(HCO_3)_2 \xrightarrow{Boil} CaCO_3 + H_2O + CO_2$$

(Insoluble)

$$Mg(HCO_3)_2 \xrightarrow{Boil} MgCO_3 + H_2O + CO_2$$

(Insoluble)

Temporarily hardness can also be removed by clark's process which involves the addition of slaked lime Ca(OH)

$$Ca(HCO_3)_2 + Ca(OH)_2 \xrightarrow{Boil} 2CaCO_3 + 2H_2O$$

(Insoluble)

**Permanent Hardness :-** Permanent hardness is due to presence of sulphates and chlorides of both calcium and magnesium. This type of hardness cannot be removed by boiling or by $Ca(OH)_2$;. Substance used to remove the hardness of water are known as water softener. This various water softeners are -

**(i)** **Washing soda :-** It removes both the temporary and permanent hardness by converting soluble Ca and Mg compounds into insoluble Carbonates.

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$

$$C\ aSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$

$$Ca(HCO_3)_2 + Na_2CO_3 \longrightarrow CaCO_3 + NaHCO_3$$

(Insoluble) (Insoluble)

**(ii)** **Permutit:** Permutit is technical name given to certain hydrated silicates of aluminium and sodium.or sodium alumunium orthosilicate or sodium zeolite.

**Example :** $Na_2\ Al_2\ Si_2\ O_8\ xH_2O$.

$$Na_2\ Al_2\ Si_2\ O_8\ xH_20 + Ca^{+2} \longrightarrow Ca\ Al_2\ Si_2\ O_8\ xH_2O + 2Na^{\oplus}$$

$$Na_2\ Al_2\ Si_2\ O_8\ xH_2O + Mg^{+2} \longrightarrow Mg\ Al_2\ Si_2\ O_8\ xH_2O + 2Na^{\oplus}$$

These ions can be re-exchanged by treating it with brine (NaCl) solution.

$$Ca\ Al_2\ Si_2\ O_8\ xH_2O + 2NaCl \longrightarrow Na_2\ Al_2\ Si_2\ O_8\ xH_2O + CaCl_2$$

This method is useful for the removal of both temporary and permanent hardness of water.

**(iii)** **CALGON:** Tlie complex salt of metaphosphoric acid, sodium hexametaphosphate $(Na_4(PO_3)_6)$ is called Calgon. It is represented as $Na_2[Na_4(PO_3)_6]$.

$$2CaSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Ca_2(PO_3)_6] + Na_2SO_4$$

$$2MgSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Mg_2(PO_3)_6] + Na_2SO_4$$

**(iv) Ion exchange Resins:-** Ion exchange resins are the most popular water softener these days. This resins are synthetic substance. The cation exchanger consists of granular insoluble organic acid resins having giant molecules with $-SO_3H$ or -COOH groups while the anion exchanges contains giant organic molecules with basic groups derived from amine. Ion exchange resins removes all soluble mineral from water.

| Cation exchanger | | Cation exchanger |
|---|---|---|
| Remove cation like | | Remove anion like |
| $Na^+$, $Mg^{2+}$ or $Ca^{2+}$ | | $SO_4^{2-}$, $Cl^-$ or $NO_3^+$ |
| and furnish $H^+$ | | and furnish $OH^-$ |
| $H^+ + OH^-$ | $\longrightarrow$ | $H_2O$ |
| $Ca^{2+} + RH_2$ | $\longrightarrow$ | $R_2Ca + 2H^+$ |

The water coming from cation exchanger is acidic due to $H^+$. This water is then passed through another bed containing anion exchanger. This exchanger removes anion like $Cl^-$, $SO_4^{2-}$, $NO_3$ by exchanging with OH– ions.

**Reaction at Cation exchanger :**

$$Ca^{+2} + RH_2 \longrightarrow R_2Ca + 2H^{\oplus}$$

$$Mg^{+2} + RH_2 \longrightarrow R_2Mg + 2H^{\oplus}$$

**Reaction at Anion exchanger :**

$$R.(OH)_2 + Cl^- \longrightarrow RC1_2 + OH^-$$

$$R.(OH)_2 + SO_4^{2-} \longrightarrow RSO_4 + OH^-$$

**NOTE :** Degree of Hardness of water is measured in terms of ppm of $CaCO_3$ which is defined as number of parts of $CaCO_3$ by mass present in one million parts by mass of water whose equivalent is equal to the gram equivalent of various calcium & magnesium salts.

For **example** consider the sample of hard water which is found to contain 36 mg of $MgSO_4$ per kg of water.

gm equivalent of $CaCO_3$ = gm eq. of $MgSO_4$

$$\frac{W_{CaCO_3}}{100} \times 2 = \frac{36 \times 10^{-3}}{120} \times 2$$

$W_{CaCO_3} = 3 \times 10^{-2}$gm

degree of hardness = ppm of $CaCO_3$ = $\frac{3 \times 10^{-2}}{1000} \times 10^6 = 30$

## 12. GLOSSARY

**Aliquot.** A portion of the whole, usually a simple fraction. A portion of a sample withdraw from a volumetric flask with a pipet is called an aliquot.

**Analytical concentration.** The total number of moles per litre of a solute regardless of any reactions that might occur when the solute dissolves. Used synonymously with formality.

**Equivalent.** The amount of a substance which furnishes or reacts with 1 mol of $H^+$ (acid-base), 1 mol of electrons (redox), or 1 mol of a univalent cation (precipitation and complex formation).

**Equivalent weight.** The weight in grams of one equivalent of a substance.

**Equivalence point.** The point in a titration where the number of equivalents of titrant is the same as the number of equivalents of analyte.

**End point.** The point in a titration where an indicator changes color.

**Formula weight.** The number of formula weights of all the atoms in the chemical formula of a substance.

**Formality.** The number of formula weights of solute per litre of solution; synonymous with analytical concentration.

**Indicator.** A chemical substance which exhibits different colors in the presence of excess analyte or titrant.

**Normality.** The number of equivalents of solute per litre of solution.

**Primary standard.** A substance available in a pure form or state of known purity which is used in standardizing a solution.

**Standardization.** The process by which the concentration of a solution is accurately ascertained.

**Standard solution.** A solution whose concentration has been accurately determined.

**Titrant.** The reagent (a standard solution) which is added from a buret to react with the analyte.

## SOME MORE SOLVED EXAMPLES

**Ex.25** A 3.00 g sample containing $Fe_3O_4$, $Fe_2O_3$ and an inert impure substance, is treated with excess of KI solution in presence of dilute $H_2SO_4$. The entire iron is converted into $Fe^{2+}$ along with the liberation of iodine. The resulting solution is diluted to 100 mL. A 20 mL of the diluted solution require 11 mL of 0.5 M $Na_2S_2O_3$ solution to reduce the iodine present. A 50 mL of diluted solution after complete extraction of the iodine requires 12.80 mL of 0.25 $KMnO_4$ solution in dilute $H_2SO_4$ medium for the oxidation of $Fe^{2+}$. Calculate the percentages of $Fe_2O_3$ and $Fe_3O_4$ in the original sample.

**Sol.** Let number of moles of $Fe_3O_4$ is 'a' and no. of moles of $Fe_2O_3$ is 'b' in 3 gram sample.

Now, 'a' moles $Fe_3O_4$ means (a moles $Fe_2O_3$ + a mole of FeO)

So, in sample (a + b) moles $Fe_2O_3$ and 'a' mole FeO present.

$Fe_2O_3 + KI + \xrightarrow{H_2SO_4} FeSO_4 + I_2 + K_2SO_4 + H_2O$

No. of gram equivalent of $Fe_2O_3$ = no. of gram equivalent of $I_2$

$n_{Fe_2O_3} \times n_{f(Fe_2O_3)} = n_{I_2} \times n_{f(I_2)}$

$(a + b) \times 2 = n_{I_2} \times 2$

$n_{I_2} = (a + b)$ moles.

Now, solution is diluted to 100 ml

So, $[I_2] = \frac{n}{V_{litre}} = \frac{(a+b)}{100/1000} = 10(a+b)$

$[Fe^{2+}] = \left(\frac{n(Fe^{2+})}{V_{litre}}\right) = \frac{(3a+2b)}{100/1000} = 10(3a + 2b)$

Now 20 ml of this solution titrated with 11 ml, 0.5 M $Na_2S_2O_3$

$I_2 + Na_2S_2O_3 \rightarrow NaI + Na_2S_4O_6$

No. of gram equivalent of $I_2$ = no. of gram equivalent of $Na_2S_2O_3$

$(N \times V)_{I_2} = (N \times V)_{Na_2S_2O_3}$

$(M \times n_f \times V)_{I_2} = (M \times n_f \times V)_{Na_2S_2O_3}$

$10 (a + b) \times 2 \times 20 = 0.5 \times 1 \times 11$

$a + b = \frac{11}{800}$ ..... (i)

50 ml of solution after extraction of $I_2$ allowed to oxidation

of $Fe^{2+}$ by 12.80 ml, 0.25 M $KMnO_4$.

$Fe^{2+} + KMnO_4 + H_2SO_4 \rightarrow Fe^{3+} + MnSO_4 + K_2SO_4 + H_2O$

no. of gram equivalent of $Fe^{2+}$ = no. of gram equivalent of $KMnO_4$.

$(M \times n_f \times V)_{Fe^{2+}} = (M \times n_f \times V)_{KMnO4}$

$10(3a + 2b) \times 1 \times 50 = 0.25 \times 5 \times 12.80$

$3a + 2b = \frac{16}{500}$ .....(ii)

By (i) & (ii)

a = 0.0045 moles

b = 0.00925 moles

so % $Fe_2O_3 = \frac{Wt(Fe_2O_3)}{Total\ wt.} \times 100 = \frac{b \times 160}{3} \times 100 = \frac{0.00925 \times 160}{3} \times 100 = 49.33\%$.

% $Fe_2O_3 = \frac{Wt(Fe_2O_3)}{Total\ wt.} \times 100 = \frac{a \times 232}{3} \times 100 = \frac{0.0045 \times 232}{3} \times 100 = 34.8\ \%$

**Ex.26** Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of $KMnO_4$ (20 mL) acidified with dilute $H_2SO_4$. The same volume of $KMnO_4$ solution is just decolorized by 10 mL of $MnSO_4$ in neutral medium simultaneously forming a dark brown precipitate of hydrated $MnO_2$. The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute $H_2SO_4$. Write the equations involved in the reactions and calculate the molarity of $H_2O_2$.

**Sol.** Let molarity of $H_2O_2$ solution is $M_1$

20 ml, $M_1$ molar $H_2O_2$ react with 20 ml $KMnO_4$ in $H_2SO_4$ solution

$H_2O_2 + KMnO_4 + H_2SO_4 \rightarrow MnSO_4 + K_2SO_4 + H_2O + O_2$

no. of gram equivalent of $H_2O_2$ = no. of gram equivalent of $KMnO_4$

$(M \times n_f \times V)_{H_2O_2} = (M \times n_f \times V)_{KMnO_4}$

$M_1 \times 2 \times 20 = M_{KMnO_4} \times 5 \times 20$ .....(i)

20 ml $KMnO_4$ decolourise by 10 ml $MnSO_4$ in neutral medium.

$KMnO_4 + MnSO_4 + H_2O \rightarrow MnO_2 + H_2SO_4 + KHSO_4$

no. of gram equivalent of $KMnO_4$ = no. of gram equivalent of $MnO_2$

$M_{KMnO_4} \times 3 \times 20ml$ = no. of gram equivalent of $MnO_2$

$M_{KMnO_4} \times 3 \times 20 \times 10^{-3} = n_{MnO_2} \times 6/5$ .....(ii)

and obtained $MnO_2$ dissolved in 10 ml, 0.2 M $Na_2C_2O_4$

$MnO_2 + Na_2C_2O_4 + H_2SO_4 \rightarrow MnSO_4 + CO_2 + Na_2SO_4 + H_2O$

no. of gram equivalent of $MnO_2$ = no. of gram equivalent of $Na_2C_2O_4$

$n_{MnO_2} \times 2 = 0.2 \times 2 \times 10 \times 10^{-3}$

$n_{MnO_2} = 2 \times 10^{-3}$ moles .....(iii)

From equaiton (ii)

$M_{KMnO_4} \times 3 \times 20 \times 10^{-3} = 2 \times 10^{-3} \times \frac{6}{5}$

$M_{KMnO_4} = \frac{2}{50}$

From equation (1)

$M_1 \times 2 \times 20 = \frac{2}{50} \times 5 \times 20$

$M_1 = 0.1M$

**Ex.27** One litre of a mixture of $O_2$ and $O_3$ ($O_3 \longrightarrow O_2 + O^{2-}$) at 1 atm and 273 K was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 ml of M/10 sodium thiosulphate solution for titration. What is the percent of ozone in the mixture ? Ultraviolet radiation of wave length 300 nm can decompose ozone. Assuming that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture ?

**Sol.** Let in 1 litre mixture x litre is $O_2$ and y litre is $O_3$ at NTP

excess KI reduce $O_3$ into $O_2$ and $O^{2-}$

$KI + O_3 + H_2O \rightarrow I_2 + O_2 + KOH$

no. of gram equivalent of $O_3$ = no. of gram equivalent of $I_2$

$(n \times n_f)_{O_3} = (n \times n_f)_{I_2}$

$\frac{y}{22.4} \times 2 = n_{I_2} \times 2$

$n_{I_2} = \frac{y}{22.4}$ .....(1)

Now, released $I_2$ required 40 ml , $\frac{1}{10}$ M $Na_2S_2O_3$

$I_2 + Na_2S_2O_3 \rightarrow NaI + Na_2S_4O_6$

No. of gram equivalent of $I_2$ = no. of gram equivalent of $Na_2S_2O_3$

$$n_{I_2} \times 2 = \frac{1}{10} \times 1 \times 40 \times 10^{-3}$$

$n_{I_2} = 2 \times 10^{-3}$ moles

Now from equation (1)

$$\frac{y}{22.4} = 2 \times 10^{-3}$$

$y = (44.8 \times 10^{-3})$ litre = 0.0448 litre

$x = 1 - y = 1 - 0.0448 = 0.9552$ litre

$$\% \text{ (by wt)} = \frac{wt(O_3)}{wt.(total)} \times 100$$

$$= \frac{n(O_3) \times 48}{n(O_3) \times 48 + n(O_2) \times 32} \times 100$$

$$= \frac{\frac{y}{22.4} \times 48}{\frac{y}{22.4} \times 48 + \frac{x}{22.4} \times 32} \times 100$$

$$= \frac{3y}{3y + 2x} \times 100$$

$$= \frac{3 \times 0.0448}{3 \times 0.048 + 2 \times 0.9552} \times 100$$

$$= \frac{0.1344}{2.0448} \times 100 = 6.57\ \%$$

One photon required for breaking of one $O_3$ bond in to $O_2$ & O

$O_3 \xrightarrow{hv} O_2 + O$

So. no. of photon required = no. of $O_3$ bonds break

= no. of $O_3$ molecules

$$= n_{O_3} \times N_A = \frac{0.0448}{22.4} \times 6 \times 10^{23}$$

$= 1.2 \times 10^{21}$ photons.

**Ex.28** A mixture of FeO and $Fe_2O_3$ is reacted with acidified $KMnO_4$ solution having a concentration of 2/5 M, 100 mL of which was used. The solution was then titrated with Zn dust which converted $Fe^{3+}$ of the solution to $Fe^{2+}$. The $Fe^{2+}$ required 1000 mL of 2/15 M $K_2Cr_2O_7$ solution. Find the % by mol of FeO and $Fe_2O_3$.

**Sol.** Let no. of moles of FeO is x millimoles & $Fe_2O_3$ is y millimoles in mixture.

$FeO + KMnO_4 + H_2SO_4 \rightarrow MnSO_4 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$

no. of milligram equivalent of FeO = no. of milli gram equivalent of $KMnO_4$.

$$x \times 1 = \frac{2}{5} \times 5 \times 100$$

x = 200 m moles.

Zn - dust convert all $Fe^{3+}$ to $Fe^{2+}$

So no. of millimoles of $Fe^{2+}$ in solution is = (x + 2y).

$Fe^{2+} + K_2Cr_2O_7 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Fe^{3+} + K_2SO_4 + H_2O$

no. of milli gram equivalent of $Fe^{2+}$ = no. of milligram equivalent of $K_2Cr_2O_7$

$$(x + 2y) \times 1 = \frac{2}{15} \times 6 \times 1000$$

$$(200 + 2y) = \frac{2}{15} \times 1000$$

y = 300 millimoles.

$$\% \text{ FeO (by moles)} = \frac{x}{x+y} \times 100 = \frac{200}{500} \times 100 = 40\%$$

% $Fe_2O_3$ (by moles) = 60%

**Ex.29** A substance of crude copper is boiled in $H_2SO_4$ till all the copper has reacted. The impurities are inert to the acid. The $SO_2$ liberated in the action is passed into 100 mL of 0.4 M acidified $KMnO_4(SO_2 \rightarrow SO_4^{-2})$. The solution of $KMnO_4$ after passage of $SO_2$ is allowed to react with oxalic acid and requires 25 mL of 1 M oxalic acid. If the purity of copper is 95.25%, what was the weight of the sample?

**Sol.** let given sample is w gram and no. of moles of Cu in given sample is x millimoles.

$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$

x millimoles x millimoles

$SO_2 + KMnO_4 + H_2SO_4 \rightarrow MnSO_4 + H_2O + SO_3 + K_2SO_4$

no. of milligram eq. of $SO_2$ = no. of milli gram eq. of $KMnO_4$

x × 2 = no. of gram eq. of $KMnO_4$

left $KMnO_4$ reduced by $H_2C_2O_4$

$KMnO_4 + H_2SO_4 + H_2C_2O_4 \rightarrow MnSO_4 + CO_2 + H_2O + K_2SO_4$

no. of milligram eq. of $KMnO_4$(left)

= no. of mill gram equ. of $H_2C_2O_4$

$= 1 \times 2 \times 25$

So, total milligram eq. of $KMnO_4$ = milligram eq. of $SO_2$ + milligram eq. of $H_2C_2O_4$

$0.4 \times 5 \times 100 = x \times 2 + 1 \times 2 \times 25$

x = 75 millimoles

wt(Cu) = 95.25% of W

$$75 \times 10^{-3} \times 63.5 = \frac{95.25}{100} \times W$$

$\Rightarrow$ W = 5 gram.

**Ex.30** $H_2O_2$ is reduced rapidly by $Sn^{2+}$, the products being $Sn^{4+}$ and water. $H_2O_2$ decomposes slowly at room temperature to yield $O_2$ and water. Calculate the volume of $O_2$ produced at 273 K and 1.00 atm when 200 g of 10.0 % by mass $H_2O_2$ in water is treated with 88.2 mL of 1 M $Sn^{2+}$ and then the mixture is allowed to stand until no further reaction occurs.

**Sol.** Let x millimoles of $H_2O_2$ react with 1M, 88.2 ml $Sn^{2+}$

$H_2O_2 + Sn^{2+} \rightarrow Sn^{4+} + H_2O$

no. of milligram equivalent of $H_2O_2$

= no. of milligram eq. of $Sn^{2+}$

$x_{millimole} \times 2 = 1 \times 2 \times 88.2$

x = 88.2 millimoles

Total given moles of $H_2O_2$ is

$$n_{total} = \frac{W(H_2O_2)}{34} = \frac{10\% \text{ of } 200 \text{ gram}}{34}$$

$$= \frac{20}{34} \text{moles}$$

= 0.5882 moles

= 588.2 millimoles.

so. no. of moles of $H_2O_2$ that decomposed to $O_2$

= 588.2 – 88.2

= 500 millimoles

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$$

$$n(O_2) \text{ released} = \frac{1}{2} \times 500 = 250 \text{ millimoles}$$

$V_{O_2}$ (at 1atm, 273 K) = $250 \times 10^{-3} \times 22.4 = 5.6$ litre.

**Ex.31** 0.84 g iron ore containing x percent of iron was taken in a solution containing all the iron in ferrous condition. The solution required x ml of a dichromatic solution for oxidizing the iron content to ferric state. Calculate the normality of dichromatic solution.

**Sol.** Let Normality of $K_2Cr_2O_7$ solution is N

$$Fe^{2+} + K_2Cr_2O_7 + H^+ \rightarrow Fe^{3+} + Cr^{3+} + H_2O$$

no. of gram eq. of $Fe^{2+}$ = no. of gram eq. of $K_2Cr_2O_7$

$$n_{Fe^{2+}} \times 1 = N \times x \times 10^{-3}$$

$$\frac{W_{Fe^{2+}}}{56} \times 1 = N \times x \times 10^{-3}$$

$$\frac{\frac{x}{100} \times 0.84}{56} \times 1 = N \times x \times 10^{-3}$$

N = 0.15

**Ex.32** 5 g of pyrolusite (impure $MnO_2$) were heated with conc. HCl and $Cl_2$ evolved was pssed through excess of KI solution. The iodine liberated required 40 mL of N/10 hypo solution. Find the % of $MnO_2$ in the pyrolusite.

**Sol.** Let moles of $MnO_2$ in 5 gram sample is x.

$$MnO_2 + HCl \rightarrow MnCl_2 + Cl_2 + H_2O$$

no. of gram eq. of $MnO_2$ = no. of gram equivalent of $Cl_2$

$x \times 2 = n_{(Cl_2)} \times 2$

$x = n_{(Cl_2)}$

so $n_{I_2} = n_{Cl_2} = x$

evolved $Cl_2$ passes through KI that released $I_2$

$Cl_2 + 2\,KI \rightarrow I_2 + 2KCl$

x moles x moles

Evaled $I_2$ required 40 ml , $\frac{N}{10}$ $Na_2S_3O_3$

$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$

no. of gram equivalent of $I_2$ = no. of gram equivalent of hypo

$x \times 2 = \frac{1}{10} \times 40 \times 10^{-3}$

$x = 2 \times 10^{-3}$ moles

$\%\ MnO_2 = \frac{wt.(MnO_2)}{total\ wt.} \times 100$

$= \frac{x \times 87}{5} \times 100 = \frac{2 \times 10^{-3} \times 87}{5} \times 100$

= 3.48 %

**Ex.33** A 458 g sample containing $Mn_3O_4$ was dissolved and all manganese was converted to $Mn^{2+}$. In the presence of fluoride ion, $Mn^{2+}$ is titrated with 3 lit of $KMnO_4$ solution (which was 1.25 N against oxalate in acidic medium), both reactants being converted to a complex of Mn(III), What was the % of $Mn_3O_4$ in the sample ?

**Sol.** $KMnO_4 + H_2C_2O_4 + H_2SO_4 \rightarrow CO_2 + MnSO_4 + K_2SO_4 + H_2O$

3 litre, M molar

Normality $(KMnO_4)$ = Molarity $\times n_f$

$1.25 = M \times 5$

$M = 0.25$

Let x moles of $Mn_3O_4$ present in 458 gram sample

$Mn_3O_4 \rightarrow 3Mn^{2+}$

xmole 3xmoles

$Mn^{2+} + KMnO_4 \rightarrow Mn^{3+}$

no. of gram eq. of $Mn^{2+}$ = no. of gram eq. $KMnO_4$

$3x \times 1 = (M \times n_f \times V)_{KMnO_4}$

$3x \times 1 = 0.25 \times 4 \times 3$

x = 1 moles

$$\% \ Mn_3O_4 \text{ (by wt)} = \frac{w(Mn_3O_4)}{w_{total}} \times 100$$

$$= \frac{1 \times 229}{458} \times 100 = 50\%$$

**Ex.34** 80 gm of a sample of Anhydrous $CuSO_4$ was dissolved in water and made to 250 mL. 25 mL of this solution after taking usual precaution was treated with a little excess of KI solution. A white ppt. of $Cu_2I_2$ and iodine was evolved. The iodine so evolved required 40 mL of 1 M hypo solution. What is the approximate purity of $CuSO_4$ solution? **[Mol. wt. of $CuSO_4$ = 160]**

**Sol.** Let 80 gram sample contains x moles of $CuSO_4$ that desolve in 250 ml solution

So 25 ml solution contain (x/10) moles $CuSO_4$

$$CuSO_4 + KI \rightarrow Cu_2I_2 + I_2$$

no. of gram eq. of $CuSO_4$ = no. of gram eq. of $I_2$

$$\frac{x}{10} \times 1 = n_{(I_2)} \times 2$$

$$n_{(I_2)} = \frac{x}{20}$$

Evalved $I_2$ required 40 ml, 1M hypo solution

$$I_2 + Na_2S_2O_3 \rightarrow NaI + Na_2S_4O_6$$

no. of gram eq. of $I_2$ = no. of gram eq. of hypo

$n(I_2) \times 2 = 1 \times 1 \times 40 \times 10^{-3}$

$$\frac{x}{20} \times 2 = 40 \times 10^{-3}$$

$x = 40 \times 10^{-2}$ moles

$$\% \ CuSO_4 \text{ (by mass)} = \frac{wt(CuSO_4)}{wt\ total} \times 100$$

$$= \frac{40 \times 10^{-2} \times 160}{80} \times 100 = 80\%$$

# EXERCISE (S-1)

## OXIDATION NUMBER

**1.** Calculate oxidation number of underlines elements in the following compounds

(a) $H_2\underline{S}_2O_7$ (b) $H_4\underline{P}_2O_7$ (c) $\underline{S}_2O_3^{2-}$ (d) $\underline{C}H_4$

(e) $\underline{C}Cl_4$ (f) $Ca\underline{O}_2$ (g) $\underline{Z}nO_2^{2-}$ (h) $\underline{Cr}O_2Cl_2$

(i) $Ca(\underline{Cl}O_2)_2$

**2.** Classify each of the following unbalanced half–reactions as either an oxidation or a reduction :

(a) $O_2(g) \longrightarrow OH^-(aq)$ (b) $H_2O_2(aq) \longrightarrow O_2(g)$

(c) $MnO_4^-(aq) \longrightarrow MnO_4^{2-}(aq)$ (d) $CH_3OH(aq) \longrightarrow CH_2O(aq)$

**3.** Identify the oxidant and reductant in the following reactions :

(a) $Zn(s) + \frac{1}{2}O_2(g) \longrightarrow ZnO(s)$

(b) $Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$

(c) $10H^+(aq) + 4Zn(s) + NO_3^-(aq) \longrightarrow 4Zn^{2+}(aq) + NH_4^+(aq) + 3H_2O(\ell)$

## BALANCING OF REDOX

**4.** Balance the following redox reactions by oxidation number method :

(i) $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$ (Acidic medium)

(ii) $Br_2 + H_2O_2 \longrightarrow BrO_3^- + H_2O$ (Acidic medium)

(iii) $MnO_4^- + Fe^{+2} \longrightarrow Mn^{+2} + Fe^{+3}$ (Acidic medium)

(iv) $MnO_2 + Cl^- \longrightarrow Mn^{+2} + Cl_2 + H_2O$ (Acidic medium)

(v) $ClO^- + CrO_2^- \xrightarrow{OH^-} Cl^- + CrO_4^{2-} + H_2O$ (Basic medium)

**5.** Balance the following redox reactions by half-reaction method (Ion electron method):

(i) $MnO_4^-(aq) + I^-(aq) \longrightarrow MnO_2(s) + I_2(s)$ (in basic medium)

(ii) $MnO_4^-(aq) + SO_2(g) \longrightarrow Mn^{2+}(aq) + HSO_4^-(aq)$ (in acidic solution)

(iii) $H_2O_2(aq) + Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + H_2O(l)$ (in acidic solution)

(iv) $Cr_2O_7^{2-}(aq.) + SO_2(g) \longrightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$ (in acidic solution)

**6.** Find the valence factor for the following acid/bases -

(1) $CH_3COOH$ (2) $NaH_2PO_4$ (3) $H_3BO_3$

(4) NaOH (5) $Ca(OH)_2$ (6) CsOH

**7.** Find the n-factor of underlined species in the following non redox reaction.

(1) $NaOH + \underline{H_3PO_4} \longrightarrow NaH_2PO_4 + H_2O$

(2) $NaOH + \underline{H_2SO_4} \longrightarrow NaHSO_4 + H_2O$

(3) $\underline{Ca(OH)_2} + HCl \longrightarrow Ca(OH)Cl + H_2O$

(4) $\underline{Na_2CO_3} + HCl \longrightarrow NaHCO_3 + NaCl$

(5) $\underline{\mathbf{Na_2CO_3}} + HCl \longrightarrow NaCl + H_2O + CO_2$

**8.** What will be the equivalent wt. of $H_3PO_4$ in each of the reaction?

$H_3PO_4 + OH^- \longrightarrow H_2PO_4^- + H_2O$

$H_3PO_4 + 2OH^- \longrightarrow HPO_4^{2-} + 2H_2O$

$H_3PO_4 + 3OH^- \longrightarrow PO_4^{3-} + 3H_2O$

**9.** What is the equivalent weight of $HNO_3$ in following reaction ?

$HNO_3 + H_2S \longrightarrow H_2O + NO + S$

**10.** Find out the equivalent weight of the underlined species in the following reaction :

(i) $\underline{ClO_3^-} + Fe^{2+} + H^+ \longrightarrow Cl^- + Fe^{3+} + H_2O$

(ii) $CuO + \underline{NH_3} \longrightarrow Cu + N_2 + H_2O$

**11.** Find out the $n_{factor}$ of $(NH_4)_2Cr_2O_7$ in the following decomposition reaction.

$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + N_2(g) + H_2O$

**12.** Find out the $n_{factor}$ of $IO_3^-$ in the following disproportionation reaction.

$I_2 \xrightarrow{OH^-} IO_3^- + I^-$

## ACID BASE TITRATION

**13.** How many millilitre of 0.5 M $H_2SO_4$ are needed to dissolve 0.5 g of copper II carbonate ?

**[JEE 1999]**

**14.** An aqueous solution of 6.3 g of oxalic acid dihydrate is made upto 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is : **[JEE 2001]**

**15.** Calculate volume of 1N $H_3PO_4$ required to react with 20 ml 2N $Ca(OH)_2$ solution

**16.** Calculate volume of 1N $H_2SO_4$ required to react with 20 ml 1 M $Al(OH)_3$ solution

**17.** Calculate volume of 0.4 M NaOH required to react with following mixture

$HCl(1\ mol) + H_2SO_4\ (2\ mol)$

**18.** Calculate volume of 0.2 M $H_2SO_4$ required to react with following mixture

$NaOH(1\ mol) + Ca(OH)_2\ (2\ mol)$

**19.** How many litre of 0.1N HCl are required to react completely with 19 gm mixture of $Na_2CO_3$ and $NaHCO_3$ containing equimolar amount of two ?

**20.** $H_3PO_4$ is a tri basic acid and one of its salt is $NaH_2PO_4$. What volume in ml of 1 M NaOH solution should be added to 12 g of $NaH_2PO_4$ to convert it into $Na_3PO_4$ ?

## REDOX TITRATION

**21.** Calculate the normality of a solution containing 50 mL of 5 M solution of $K_2Cr_2O_7$ in acidic medium.

**22.** A 5.0 $cm^3$ solution of $H_2O_2$ liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of $H_2O_2$ solution in terms of volume strength at STP. **[JEE' 1995]**

**23.** Calculate the normality of a solution containing 15.8 g of $KMnO_4$ in 50 mL acidic solution.

**24.** 20 mL of $H_2O_2$ after acidification with dil $H_2SO_4$ required 30 mL of $\frac{N}{12}$ $KMnO_4$ for complete oxidation. The strength of $H_2O_2$ solution is [Molar mass of $H_2O_2$ = 34]

**25.** It required 40 ml of 1 M $Ce^{4+}$ to titrate 20 ml of 1 M $Sn^{2+}$ to $Sn^{4+}$. What is the oxidation state of cerium in the product.

**26.** A volume of 10.0 ml of 1 M $SeO_2$ reacted with exactly 20 ml of 2 M $CrSO_4$. In the reaction, $Cr^{2+}$ was oxidized to $Cr^{3+}$. To what oxidation state was selenium converted by the reaction.

**27.** Potassium acid oxalate $K_2C_2O_4.\ 3H_2C_2O_4.4H_2O$ can be oxidized by $MnO_4^-$ in acid medium. Calculate the volume of 0.1 M $KMnO_4$ reacting in acid solution with 5.08 gm of the acid oxalate.

**28.** A 1 g sample of $H_2O_2$ solution containing x% $H_2O_2$ by mass requires x $cm^3$ of a $KMnO_4$ solution for complete oxidation under acidic condition. Calculate the normality of $KMnO_4$ solution.

**29.** Metallic tin in the presence of HCl is oxidized by $K_2Cr_2O_7$ to stannic shloride, $SnCl_4$. What volume of deci-normal dichromate solution would be reduced by 11.9 gm of tin [Sn = 119]

**30.** Calculate the number of millimoles of $K_2Cr_2O_7$ which will completely react with 40 ml 0.1 MKI Solution.

**31.** Find the number of moles of $KMnO_4$ needed to oxidise one mole $Cu_2S$ in acidic medium. The reaction is : $Cu_2S + KMnO_4 \longrightarrow Cu^{2+} + Mn^{2+} + SO_2$

**32.** 0.4 M $KMnO_4$ solution completely reacts with 0.05 M $FeSO_4$ solution under acidic conditions. The volume of $FeSO_4$ used is 50 mL. What volume of $KMnO_4$ was used ?

## BACK TITRATION

**33.** 50 gm of a sample of $Ca(OH)_2$ is dissolved in 50 ml of 0.5 N HCl solution. The excess of HCl was titrated with 0.3N NaOH. The volume of NaOH used was 20cc. Calculate % purity of $Ca(OH)_2$.

**34.** 10 g $CaCO_3$ were dissolved in 250 ml of 1 M HCl. What volume of 2 M KOH would be required to neutralise excess HCl.

**35.** 20 g of a sample of $Ba(OH)_2$ is dissolved in 10 mL of 0.5 N HCl solution : The excess of HCl was titrated with 0.1 N NaOH. The volume of NaOH used was 20 cc. Calculate the percentage of $Ba(OH)_2$ in the sample. (Ba = 137)

**36.** To 50 L of 0.2 N NaOH, 2.5 L of 2N HCl and 15 L of 0.1 N $FeCl_3$ solutions are added. What weight of $Fe_2O_3$ can be obtained from the precipitate? Also report the normality of NaOH left in resultant solution :

## HARDNESS OF WATER

**37.** Softening of hard water by using sodium aluminium silicate (zeolite) is due to -

Adsorption of ..... and .....ions of hard water, replacing ..... ions

**38.** One litre of a sample of hard water contains 10 mg of $CaCl_2$ & 9.5 mg of $MgCl_2$. What is degree of hardness in terms of ppm of $CaCO_3$ ?

## EXERCISE (O-1)

**1.** The oxidation number of phosphorus in $Ba(H_2PO_2)_2$ is :

(A) +3 (B) +2 (C) +1 (D) –1

**2.** The oxidation states of the most electronegative element in the products of the reaction of $BaO_2$ with dilute $H_2SO_4$.

(A) 0 and –1 (B) –1 and –2 (C) –2 and 0 (D) –2 and +2

**3.** In the coordination compound, $K_4[Ni(CN)_6]$, the oxidation state of nickel is **[AIEEE-03]**

(A) +1 (B) +2 (C) –1 (D) 0

**4.** The oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$ is - **[AIEEE-05]**

(A) +2 (B) +3 (C) 0 (D) +1

**5.** Oxidation number of Cl in $CaOCl_2$ (bleaching powder is ) **[AIEEE-02]**

(A) Zero, since it contains $Cl_2$ (B) –1, since it contains $Cl^-$

(C) +1, since it contains $ClO^-$ (D) +1 and –1 since it contains $ClO^-$ and $Cl^-$

**6.** The oxidation number of sulphur in $S_8$, $S_2F_2$ and $H_2S$ respectively are :

(A) 0, +1 and –2 (B) +2, +1 and –2

(C) 0, +1 and +2 (D) –2, +1 and –2

**7.** The incorrect order of decreasing oxidation number of S in compounds is :-

(A) $H_2S_2O_7 > Na_2S_4O_6 > Na_2S_2O_3 > S_8$ (B) $H_2SO_5 > H_2SO_3 > SCl_2 > H_2S$

(C) $SO_3 > SO_2 > S_8 > H_2S$ (D) $H_2SO_4 > SO_2 > H_2S > H_2S_2O_8$

**8.** Which of the following is a redox? **[AIEEE-02]**

(A) $2NaAg(CN)_2 + Zn \longrightarrow Na_2Zn(CN)_4 + 2Ag$

(B) $BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$

(C) $N_2O_5 + H_2O \longrightarrow 2HNO_3$

(D) $AgNO_3 + KI \longrightarrow AgI + KNO_3$

**9.** Which reaction does not represent autoredox or disproportionation?

(A) $Cl_2 + OH^- \longrightarrow Cl^- + ClO_3^- + H_2O$

(B) $2H_2O_2 \longrightarrow H_2O + O_2$

(C) $2Cu^+ \longrightarrow Cu^{+2} + Cu$

(D) $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$

**10.** Which of the following is not a redox reaction?

(A) $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$ (B) $2BaO + O_2 \rightarrow 2BaO_2$

(C) $2KClO_3 \rightarrow 2KCl + 3O_2$ (D) $SO_2 + 2H_2S \rightarrow 2H_2O + 3S$

**11.** $H_2O_2$ acts as a reducing agent in:

(A) $FeCl_2 + HCl + H_2O_2 \longrightarrow FeCl_3 + H_2O$

(B) $Cl_2 + H_2O_2 \longrightarrow HCl + O_2$

(C) $HI + H_2O_2 \longrightarrow I_2 + H_2O$

(D) $H_2SO_3 + H_2O_2 \longrightarrow H_2SO_4 + H_2O$

**12.** Match List-I (Compounds) with List-II (Oxidation states of nitrogen) and select answer using the codes given below the lists :-

| **List-I** | | **List-II** | |
|---|---|---|---|
| (a) | $NaN_3$ | 1. | +5 |
| (B) | $N_2H_2$ | 2. | +2 |
| (C) | NO | 3. | –1/3 |
| (D) | $N_2O_5$ | 4. | –1 |

**Code :**

| | (a) | (B) | (C) | (D) |
|---|---|---|---|---|
| (A) | 3 | 4 | 2 | 1 |
| (B) | 4 | 3 | 2 | 1 |
| (C) | 3 | 4 | 1 | 2 |
| (D) | 4 | 3 | 1 | 2 |

**13.** $MnO_4^-$ is good oxidising agent in different medium changing to - **[AIEEE-02]**

$MnO_4^- \longrightarrow Mn^{2+}$

$\longrightarrow MnO_4^{2-}$

$\longrightarrow MnO_2$

$\longrightarrow Mn_2O_3$

Changes in oxidation number respectively are -

(A) 1, 3, 4, 5 (B) 5, 4, 3, 2 (C) 5, 1, 3, 4 (D) 2, 6, 4, 3

**14.** In the reaction,

$$xHI + yHNO_3 \longrightarrow NO + I_2 + H_2O$$

(A) x = 3, y = 2 (B) x = 2, y = 3 (C) x = 6, y = 2 (D) x = 6, y = 1

**15.** The number of electrons to balance the following equation :-

$NO_3^- + 4H^+ + e^- \rightarrow 2H_2O + NO$ is

(A) 5 (B) 4 (C) 3 (D) 2

**16.** Number of moles of electrons taken up when 1 mole of $NO_3^-$ ions is reduced to 1 mole of $NH_2OH$ is

(A) 2 (B) 4 (C) 5 (D) 6

**17.** For the redox reaction,

$$MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$$

the correct coefficients of the reactants for the balanced reaction are :

| | $MnO_4^-$ | $C_2O_4^{2-}$ | $H^+$ |
|---|---|---|---|
| (A) | 2 | 5 | 16 |
| (B) | 16 | 5 | 2 |
| (C) | 5 | 16 | 2 |
| (D) | 2 | 16 | 5 |

**18.** In a redox reaction, the equivalent weight of $HNO_2$ is found to be 23.5. The reaction products might contain

(A) $NO_2$ (B) NO (C) $NH_3$ (D) $HNO_3$

**19.** When $N_2$ is converted into $NH_3$, the equivalent weight of nitrogen will be :

(A) 1.67 (B) 2.67 (C) 3.67 (D) 4.67

**20.** The equivalent mass of $MnSO_4$ is half its molecular mass when it is converted to : **[JEE 1998]**

(A) $Mn_2O_3$ (B) $MnO_2$ (C) $MnO_4^-$ (D) $MnO_4^{2-}$

**21.** When $KBrO_3$ ion reacts with $Br^-$ ion in acid solution $Br_2$ is liberated.The equivalent weight of $KBrO_3$ in this reaction is

(A) M/8 (B) M/3 (C) M/5 (D) M/6

**22.** In the reaction $CrO_5 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + H_2O + O_2$ one mole of $CrO_5$ will liberate how many moles of $O_2$ :-

(A) 5/2 (B) 5/4 (C) 9/2 (D) 7/4

**23.** A solution of $KMnO_4$ is reduced to $MnO_2$. The normality of solution is 0.6. The molarity is :

(A) 1.8M (B) 0.6M (C) 0.1M (D) 0.2M

**24.** The normality of 0.3 M phosphorus acid ($H_3PO_3$) is :

(A) 0.1 (B) 0.9 (C) 0.3 (D) 0.6

**25.** 0.52 g of a dibasic acid required 100 mL of 0.2 N NaOH for complete neutralization. The equivalent weight of acid is

(A) 26 (B) 52 (C) 104 (D) 156

**26.** What is the equivalent weight of $H_2SO_4$ in the reaction ?

$$H_2SO_4 + NaI \rightarrow Na_2SO_4 + I_2 + H_2S + H_2O$$

(A) 12.25 (B) 49 (C) 61.25 (D) None of these

**27.** 125 mL of 63% (w/v) $H_2C_2O_4.\ 2H_2O$ is made to react with 125 mL of a 40% (w/v) NaOH solution. The resulting solution is :-

(A) neutral (B) acidic (C) strongly acidic (D) alkaline

**28.** The mass of oxalic acid crystals ($H_2C_2O_4.\ 2H_2O$) required to prepare 50 mL of a 0.2 N solution is:-

(A) 4.5 g (B) 6.3 g (C) 0.63 g (D) 0.45 g

**29.** If 25 mL of a $H_2SO_4$ solution reacts completely with 1.06 g of pure $Na_2CO_3$, what is the normality of this acid solution :

(A) 1 N (B) 0.5 N (C) 1.8 N (D) 0.8 N

**30.** The number of moles of $KMnO_4$ that will be required to react with 2 mol of ferrous oxalate is

(A) $\frac{6}{5}$ (B) $\frac{2}{5}$ (C) $\frac{4}{5}$ (D) 1

**31.** The oxidation state of chromium in the final product formed by the reaction between Kl and acidified potassium dichromate solution is - **[AIEEE-05]**

(A) +6 (B) +4 (C) +3 (D) +2

**32.** The number of mole of $KMnO_4$ that will need to react completely with one mole ferrous oxalate in acidic solution is : **[JEE 1997]**

(A) 2/5 (B) 3/5 (C) 4/5 (D) 1

**33.** The number of mole of $KMnO_4$ that will be needed to react with one mole of sulphite ion in acidic solution is : **[JEE 1997]**

(A) 2/5 (B) 3/5 (C) 4/5 (D) 1

**34.** What volume of 0.1 M $KMnO_4$ is needed to oxidize 100 mg of $FeC_2O_4$ in acid solution ?

(A) 4.1 mL (B) 8.2 mL (C) 10.2 mL (D) 4.6 mL

**35.** What volume of 6 M $HNO_3$ is needed to oxidize 8 g of $Fe^{2+}$ to $Fe^{3+}$, $HNO_3$ gets converted to NO?

(A) 8 mL (B) 7.936 mL (C) 32 mL (D) 64 mL

**36.** The minimum quantity of $H_2S$ needed to precipitate 63.5 g of $Cu^{2+}$ will be nearly.

(A) 63.5 g (B) 31.75 g (C) 34 g (D) 2.0 g

**37.** The volume of 1.5 $MH_3PO_4$ solution required to neutralize exactly 90 mL of a 0.5 M Ba $(OH)_2$ solution is :-

(A) 10 mL (B) 30 mL (C) 20 mL (D) 60 mL

**38.** Hydrogen peroxide in aqueous solution decomposes on warming to give oxygen according to the equation

$$2H_2O_2\,(aq) \longrightarrow 2H_2O\,(\ell) + O_2\,(g)$$

Under conditions where 1 mole of gas occupies 24 $dm^3$. 100 $cm^3$ of XM solution of $H_2O_2$ produces 3 $dm^3$ of $O_2$. Thus X is :-

(A) 2.5 (B) 1 (C) 0.5 (D) 0.25

**39.** A mixture of $NaHC_2O_4$ and $KHC_2O_4 \cdot H_2C_2O_4$ required equal volumes of 0.2 N $KMnO_4$ and 0.12 N NaOH separately. What is the molar ratio of $NaHC_2O_4$ and $KHC_2O_4 \cdot H_2C_2O_4$ in the mixture ?

(A) 6 : 1 (B) (C) 1 : 3 (D) none

**40.** Volume $V_1$ mL of 0.1 $MK_2Cr_2O_7$ is needed for complete oxidation of 0.678 g $N_2H_4$ in acidic medium. The volume of 0.3 M $KMnO_4$ needed for same oxidation in acidic medium will be :-

(A) $\frac{2}{5}V_1$ (B) $\frac{5}{2}V_1$ (C) 113 $V_1$ (D) can't say

**41.** $As_2O_3$ is oxidised to $H_3AsO_4$ by $KMnO_4$ in acidic medium. Volume of 0.02M $KMnO_4$ required for this purpose by 1mmol of $As_2O_3$ will be

(A) 10 mL (B) 20 mL (C) 40 mL (D) 80 mL

**42.** When ozone is passed through dry KOH, $KO_3$ is obtained and $O_2$ is liberated. In this reaction _____ is oxidised and _____ is reduced.

(A) hydrogen, oxygen (B) potassium, oxygen

(C) oxygen, oxygen (D) oxygen, hydrogen

**43.** 100 ml of 0.1M $NaAl(OH)_2CO_3$ is neutralised by 0.25 N HCl to form NaCl, $AlCl_3$ and $CO_2$. Volume of HCl required is

(A) 10 mL (B) 40 mL (C) 100mL (D) 160 mL

**44.** x mmol of $XeF_4$ quantitatively oxidized KI to $I_2$ and liberated Xe, alongwith formation of KF. This iodine required 20 ml of decinormal hypo solution for exact titration. The value of x is

(A) 0.5 (B) 1.0 (C) 2.0 (D) 5.0

**45.** Temporary hardness is due to $HCO_3^-$ of $Mg^{2+}$ and $Ca^{2+}$. It is removed by addition of CaO.

$$Ca(HCO_3)_2 + CaO \rightarrow 2CaCO_3 + H_2O$$

Mass of CaO required to precipitate 2 g $CaCO_3$ is :-

(A) 2.00 (B) 0.56 g (C) 0.28 g (D) 1.12 g

**46.** 0.3 g of an oxalate salt was dissolved in 100 mL solution. The solution required 90 mL of N/20 $KMnO_4$ for complete oxidation. The % of oxalate ion in salt is :-

(A) 33% (B) 66% (C) 70% (D) 40%

## EXERCISE (O-2)

**1.** If 10 g of $V_2O_5$ is dissolved in acid and is reduced to $V^{2+}$ by zinc metal, how many mole $I_2$ could be reduced by the resulting solution if it is further oxidised to $VO^{2+}$ ions ?

**[Assume no change in state of $Zn^{2+}$ ions] (V = 51, O = 16, I = 127) :**

(A) 0.11 mole of $I_2$ (B) 0.22 mole of $I_2$ (C) 0.055 mole of $I_2$ (D) 0.44 mole of $I_2$

**2.** The number of moles of $Cr_2O_7^{2-}$ needed to oxidize 0.136 equivalents of $N_2H_5^+$ by the reaction $N_2H_5^+ + Cr_2O_7^{2-} \rightarrow N_2 + Cr^{3+} + H_2O$ is

(A) 0.136 (B) 0.068 (C) 0.0227 (D) 0.272

**3.** Dichloroacetic acid ($CHCl_2COOH$) is oxidized to $CO_2$, $H_2O$ and $Cl_2$ by 600 meq of an oxidizing agent. Same amount of acid can neutralize how many moles of ammonia to form ammonium dichloroacetate?

(A) 0.0167 (B) 0.1 (C) 0.3 (D) 0.6

**4.** $HNO_3$ oxidises $NH_4^+$ ions to nitrogen and itself gets reduced to $NO_2$. The moles of $HNO_3$ required by 1 mol of $(NH_4)_2SO_4$ is :-

(A) 4 (B) 5 (C) 6 (D) 2

**5.** During the disproportionation of iodine to iodide and iodate ions, the ratio of iodate and iodide ions formed in alkaline medium is :-

(A) 1 : 5 (B) 5 : 1 (C) 3 : 1 (D) 1 : 3

**6.** When arsenic sulphide is boiled with NaOH, sodium arsenite and sodium thioarsenite are formed

$x\ As_2S_3 + y\ NaOH \longrightarrow Na_3AsO_3 + x\ Na_3AsS_3 + \frac{y}{2}\ H_2O$. What are the values of x and y ?

(A) 1, 6 (B) 2, 8 (C) 2, 6 (D) 1, 4

**7.** 35 mL sample of hydrogen peroxide gives of 500 mL of $O_2$ at 27°C and 1 atm pressure. Volume strength of $H_2O_2$ sample will be :-

(A) 10 volume (B) 13 volumes (C) 11 volume (D) 12 volume

**8.** An element A in a compound ABD has oxidation number $A^{n-}$. It is oxidised by $Cr_2O_7^{2-}$ in acid medium. In the experiment $1.68 \times 10^{-3}$ moles of $K_2Cr_2O_7$ were used for $3.26 \times 10^{-3}$ moles of ABD. The new oxidation number of A after oxidation is :-

(A) 3 (B) 3 – n (C) n – 3 (D) +n3

**9.** 50g of pure $CaCO_3$ is heated to liberate $CO_2$. Liberated $CO_2$ required 0.4 mol of moist ammonia to yield only $(NH_4)_2CO_3$. Find the volume of $CO_2$ liberated at STP adding excess dil. HCl to this heated residue.

(A) zero (B) 4.42 L (C) 6.81 L (D) 6.72 L

**10.** For the reaction

$I^- + ClO_3^- + H_2SO_4 \rightarrow Cl^- + HSO_4^- + I_2$

The correct statement(s) in the balanced equation is / are :

(A) Stoichiometric coefficient of $HSO_4^-$ is 6

(B) Iodide is oxidized

(C) Sulphur is reduced

(D) $H_2O$ is one of the products

**11.** A sample of $KMnO_4$ solution required 50 ml when titrated against 3 mmol of oxalic acid. The normality of same solution in reaction with alkaline $H_2O_2$ is

(A) 0.120 N (B) 0.060 N (C) 0.072 N (D) 0.036 N

## Assertion Reason Type

**12.** **Statement–1 :-** Moles of $KMnO_4$ required for oxidation of $Fe^{2+}$ in acidic and basic medium will be different.

**Statement–2 :-** Final oxidation state to which $Mn^{7+}$ will be reduced will be different in case of acidic and basic medium.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

**13.** **Statement–1 :-** Mass of a particular substance that combine with 8 gm of oxygen is said to be equivalent weight of substance.

**Statement–2 :-**x gm of metal gave y gm of its oxide, so equivalent weight of metal is $\left(\frac{x}{y-x}\right)\times 8$

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

**14.** **Statement–1 :-** Degree of hardness of water is measured in terms of ppm of $CaCO_3$.

**Statement–2 :-** If water contains 120 ppm of $MgSO_4$, and 2ppm NaCl, its hardness in terms of $CaCO_3$ > 100 ppm.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

## MATCH THE COLUMN

**15.** **Column-I** **Column-II**

(A) $\underline{P_2H_4} \longrightarrow PH_3 + P_4H_2$ (p) $E = \frac{3M}{4}$

(B) $\underline{I_2} \longrightarrow I^- + IO_3^-$ (q) $E = \frac{3M}{5}$

(C) $MnO_4^- + Mn^{2+} + H_2O \longrightarrow \underline{Mn_3O_4} + H^+$ (r) $E = \frac{15M}{26}$

(D) $\underline{H_3PO_2} \longrightarrow PH_3 + H_3PO_3$ (s) $E = \frac{5M}{6}$

**Paragraph for Q.16 to Q.19**

Equivalent weight $= \frac{\text{Molecular weight / Atomic weight}}{\text{n – factor}}$

n-factor is very important in redox as well as non-redox reactions. With the help of n-factor we can predicts the molar ratio of the reactant species taking part in reactions. The reaciprocal of n-factor's ratio of the reactants is the molar ratio of the reactants.

In general n-factor of acid/base is number of moles of $H^+$ /$OH^-$ furnished per mole of acid/ base. n-factor of a reactant is no. of moles of electrons lost or gained per mole of reactant.

**Example 1 :**

1. In acidic medium : $KMnO_4$ (n = 5) $\longrightarrow Mn^{2+}$
2. In neutral medium : $KMnO_4$ (n = 3) $\longrightarrow Mn^{2+}$
3. In basic medium : $KMnO_4$ (n = 1) $\longrightarrow Mn^{6+}$

**Example 2 :** $FeC_2O_4 \longrightarrow Fe^{3+} + 2CO_2$

Total no. of moles of $e^-$ lost by 1 mole of $FeC_2O_4 = 1 + 1 \times 2 \Rightarrow 3$

$\therefore$ n-factor of $FeC_2O_4 = 3$

**16.** n-factor of $Ba(MnO_4)_2$ in acidic medium is :

(A) 2 (B) 6 (C) 10 (D) none of these

**17.** For the reaction,

$$H_3PO_2 + NaOH \longrightarrow NaH_2PO_2 + H_2O$$

What is the equivalent weight of $H_3PO_2$ ? (mol. wt. is M)

(A) M (B) M/2

(C) M/3 (D) none of these

**18.** For the reaction, $Fe_{0.95}O$ (molar mass : M) $\longrightarrow Fe_2O_3$. What is the eq. wt. of $Fe_{0.95}O$ ?

(A) $\frac{M}{0.85}$ (B) $\frac{M}{0.95}$

(C) $\frac{M}{0.8075}$ (D) none of these

**19.** In the reaction, $xVO + yFe_2O_3 \longrightarrow FeO + V_2O_5$. What is the value of x and y respectively?

(A) 1, 1 (B) 2, 3

(C) 3, 2 (D) none of these

## Table type question :

| **Column-I (1 mole of each oxidizing) agent is taken)** | **Column-II (oxidation number** | **Column-III (Reducing agents)** |
|---|---|---|
| (A) $KMnO_4$ (acidic) | (P) O.N of Mn = 4 | (1) 3 mole of $FeSO_4$ |
| (B) $KMnO_4$ (neutral) | (Q) O.N of Mn = 7 | (2) 0.5 mole of $I_2$ changes to $HIO_3$ |
| (C) $MnO_2$ (acidic) | (R) O.N of Cr = 6 | (3) 1 mole of $K_2C_2O_4$ |
| (D) $K_2CrO_4$ (acidic) | (S) O.N of Cr = 7 | (4) 1.5 mole $K_2SO_3$ |

**20.** Which of the following is correct

(A) A ; P ; 2 (B) A ; Q ; 4 (C) B ; Q ; 1 (D) B ; Q ; 3

**21.** Which of the following is correct

(A) A ; Q ; 3 (B) C ; P ; 3 (C) C ; P ; 4 (D) C ; Q ; 1

**22.** Which of the following is correct

(A) D ; R ; 1 (B) D ; R ; 2 (C) D ; S ; 1 (D) D ; R ; 4

## EXERCISE (JM)

**1.** Given : **[JEE(Main-online)-2013]**

$$X\ Na_2\ HAsO_3 + Y\ NaBrO_3 + ZHCl \rightarrow NaBr + H_3AsO_4 + NaCl$$

The values of X, Y and Z in the above redox reaction are respectively :

(1) 2, 1, 3 (2) 3, 1, 6 (3) 2, 1, 2 (4) 3, 1, 4

**2.** Consider the following reaction : **[JEE(Main)-2013]**

$$xMnO_4^- + yC_2O_4^{2-} + zH^+ \rightarrow xMn^{2+} + 2yCO_2 + \frac{z}{2}\ H_2O$$

The values of x, y and z in the reaction are respectively :-

(1) 5,2 and 16 (2) 2,5 and 8 (3) 2, 5 and 16 (4) 5,2 and 8

**3.** How many electrons are involved in the following redox reaction ? **[JEE(Main-online)-2014]**

$Cr_2O_7^{2-} + Fe^{2+} + C_2O_4^{2-} \rightarrow Cr^{3+} + Fe^{3+} + CO_2$ (Unbalanced)

(1) 3 (2) 4 (3) 5 (4) 6

**4.** Consider the reaction **[JEE(Main-online)-2014]**

$$H_2SO_{3(aq)} + Sn^{4+}_{(aq)} + H_2O_{(l)} \rightarrow Sn^{2+}_{(aq)} + HSO^-_{4(aq)} + 3H^+_{(aq)}$$

Which of the following statements is correct?

(1) $H_2SO_3$ is the reducing agent because it undergoes oxidation

(2) $H_2SO_3$ is the reducing agent because it undergoes reduction

(3) $Sn^{4+}$ is the reducing agent because it undergoes oxidation

(4) $Sn^{4+}$ is the oxidizing agent because it undergoes oxidation

**5.** In which of the following reaction $H_2O_2$ acts as a reducing agent ? **[JEE(Main)-2014]**

(a) $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (b) $H_2O_2 - 2e^- \rightarrow O_2 + 2H^+$

(c) $H_2O_2 + 2e^- \rightarrow 2OH^-$ (d) $H_2O_2 + 2OH^- - 2e^- \rightarrow O_2 + 2H_2O$

(1) (a), (c) (2) (b), (d) (3) (a), (b) (4) (c), (d)

**6.** The molecular formula of a commercial resin used for exchanging ions in water softening is $C_8H_7SO_3Na$ (Mol. w.t 206). What would be the maximum uptake of $Ca^{2+}$ ions by the resin when expressed in mole per gram resin ? **[JEE(Main)-2015]**

(1) $\frac{2}{309}$ (2) $\frac{1}{412}$ (3) $\frac{1}{103}$ (4) $\frac{1}{206}$

**7.** The volume of 0.1N dibasic acid sufficient to neutralize 1 g of a base that furnishes 0.04 mole of $OH^-$ in aqueous solution is : **[JEE(Main)-OnLine-2016]**

(1) 400 mL (2) 200 mL (3) 600 mL (4) 800 mL

**8.** Which of the following reactions is an example of a redox reaction ? **[JEE(Main)-2017]**

(1) $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$ (2) $XeF_2 + PF_5 \rightarrow [XeF]^+PF_6^-$

(3) $XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$ (4) $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$

**9.** In which of the following reaction, hydrogen peroxide acts as an oxidizing agent ? **[JEE(Main)-OnLine-2017]**

(1) $I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$

(2) $HOCl + H_2O_2 \rightarrow H_3O^+ + Cl^- + O_2$

(3) $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$

(4) $2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$

**10.** In $KO_2$, the nature of oxygen species and the oxidation state of oxygen atom are, respectively **[JEE(Main)-OnLine-2018]**

(1) Superoxide and –1/2 (2) Oxide and -–2

(3) Peroxide and –1/2 (4) Superoxide and –1

**11.** In the reaction of oxalate with permaganate in acidic medium, the number of electrons involved in producing one molecule of $CO_2$ is : **[JEE(Main)-(Jan.)-2019]**

(1) 10 (2) 2 (3) 1 (4) 5

**12.** The chemical nature of hydrogen preoxide is :- **[JEE(Main)-(Jan.)-2019]**

(1) Oxidising and reducing agent in acidic medium, but not in basic medium.

(2) Oxidising and reducing agent in both acidic and basic medium

(3) Reducing agent in basic medium, but not in acidic medium

(4) Oxidising agent in acidic medium, but not in basic medium.

**13.** The hardness of a water sample (in terms of equivalents of $CaCO_3$) containing $10^{-3}$ M $CaSO_4$ is : (molar mass of $CaSO_4$ = 136 g $mol^{-1}$) **[JEE(Main)-(Jan.)-2019]**

(1) 100 ppm (2) 50 ppm (3) 10 ppm (4) 90 ppm

**14.** 50 mL of 0.5 M oxalic acid is needed to neutralize 25 mL of sodium hydroxide solution. The amount of NaOH in 50 mL of the given sodium hydroxide solution is : **[JEE(Main)-(Jan.)-2019]**

(1) 4 g (2) 2 g (3) 8 g (4) 1 g

**15.** In order to oxidise a mixture one mole of each of $FeC_2O_4$, $Fe_2(C_2O_4)_3$, $FeSO_4$ and $Fe_2(SO_4)_3$ in acidic medium , the number of moles of $KMnO_4$ required is - **[JEE(Main)-(April)-2019]**

(1) 3 (2) 2 (3) 1 (4) 1.5

**16.** The correct order of the oxidation states of nitrogen in NO, $N_2O$, $NO_2$ and $N_2O_3$ is :

(1) $NO_2 < N_2O_3 < NO < N_2O$ **[JEE(Main)-(April)-2019]**

(2) $NO_2 < NO < N_2O_3 < N_2O$

(3) $N_2O < N_2O_3 < NO < NO_2$

(4) $N_2O < NO < N_2O_3 < NO_2$

**17.** An example of a disproportionation reaction is : **[JEE(Main)-(April)-2019]**

(1) $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$

(2) $2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$

(3) $2CuBr \rightarrow CuBr_2 + Cu$

(4) $2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$

**18.** 100 mL of a water sample contains 0.81 g of calcium bicarbonate and 0.73 of magnesium bicarbonate. The hardness of this water sample expressed in terms of equivalents of $CaCO_3$ is: (molar mass of calcium bicarbonate is 162 g $mol^{-1}$ and magnesium bicarbonate is 146 $gmol^{-1}$)

(1) 1,000 ppm

(2) 10,000 ppm **[JEE(Main)-(April)-2019]**

(3) 100 ppm

(4) 5,000 ppm

**19.** 25 ml of the given HCl solution requires 30 mL of 0.1 M sodium carbonate solution. What is the volume of this HCl solution required to titrate 30 mL of 0.2 M aqueous NaOH solution?

**[JEE(Main)-(Jan)-2019]**

(1) 25 mL (2) 50 mL (3) 12.5 mL (4) 75 mL

**20.** Oxidation number of potassium in $K_2O$, $K_2O_2$ and $KO_2$ , respectively, is :

**[JEE(Main)-(Jan)-2020]**

(1) +1, +4 and +2

(2) +1, +2 and +4

(3) +1, +1 and +1

(4) +2 , +1 and $+\frac{1}{2}$

**21.** The compound that cannot act both as oxidising and reducing agent is : **[JEE(Main)-(Jan)-2020]**

(1) $H_2O_2$ (2) $H_2SO_3$ (3) $HNO_2$ (4) $H_3PO_4$

**22.** The hardness of a water sample containing $10^{-3}$ M $MgSO_4$ expressed as $CaCO_3$ equivalents (in ppm) is _____. **(molar mass of $MgSO_4$ is 120.37 g/mol)** **[JEE(Main)-(Jan)-2020]**

## EXERCISE (JA)

**1.** Reduction of the metal centre in aqueous permanganate ion involves - **[JEE-2011]**

(A) 3 electrons in neutral medium (B) 5 electrons in neutral medium

(C) 3 electrons in alkaline medium (D) 5 electrons in acidic medium

**2.** Reaction of $Br_2$ with $Na_2CO_3$ in aqueous solution gives sodium bromide and sodium bromate with evolution of $CO_2$ gas. The number of sodium bromide molecules involved in the balanced chemical equation is. **[JEE- 2011]**

**3.** Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen-

(A) $HNO_3$, NO, $NH_4Cl$, $N_2$ (B) $HNO_3$, NO, $N_2$, $NH_4Cl$ **[JEE- 2012]**

(C) $HNO_3$, $NH_4Cl$, NO, $N_2$ (D) NO, $HNO_3$, $NH_4Cl$, $N_2$

**4.** 25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N $Na_2S_2O_3$ was used to reach the end point. The molarity of the household bleach solution is **[JEE- 2012]**

(A) 0.48 M (B) 0.96 M (C) 0.24 M (D) 0.024 M

**5.** In neutral or faintly alkaline solution, 8 moles permanganate anion quantitatively oxidize thiosulphate anions to produce X moles of a sulphur containing product. the magnitude of X is **[JEE- 2016]**

**6.** To measure the quantity of $MnCl_2$ dissolved in an aqueous solution, it was completely converted to $KMnO_4$ using the reaction, **[JEE- 2018]**

$MnCl_2 + K_2S_2O_8 + H_2O \rightarrow KMnO_4 + H_2SO_4 + HCl$ (equation not balanced).

Few drops of concentrated HCl were added to this solution and gently warmed. Further, oxalic acid (225 g) was added in portions till the colour of the permanganate ion disappeared. The quantity of $MnCl_2$ (in mg) present in the initial solution is _____.

**(Atomic weights in g mol$^{-1}$ : Mn = 55, Cl = 35.5)**

# ANSWER KEY

## EXERCISE (S-1)

1. (a) +6 (b) +5 (c) +2 (d) –4
   (e) +4 (f) –1 (g) +2 (h) +6
   (i) +3

2. (a) Reduction (b) Oxidation
   (c) Reduction (d) Oxidation

3. (a) Oxidant : $O_2$ ; Reductant : Zn
   (b) Oxidant : $H^+$ ; Reductant : Zn
   (c) Oxidant : $NO_3^-$ ; Reductant : Zn

4. (i) $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$
   (ii) $Br_2 + 5H_2O_2 \longrightarrow 2BrO_3^- + 4H_2O + 2H^+$
   (iii) $MnO_4^- + 5Fe^{+2} + 8H^+ \longrightarrow Mn^{+2} + 5Fe^{+3} + 4H_2O$
   (iv) $MnO_2 + 2Cl^- + 4H^+ \longrightarrow Mn^{+2} + Cl_2 + 2H_2O$
   (v) $3ClO^- + 2CrO_2^- + 2OH^- \longrightarrow 3Cl^- + 2CrO_4^{2-} + H_2O$

5. (i) $2MnO_4^- + 6I^- + 4H_2O \longrightarrow 2MnO_2 + 3I_2 + 8OH^-$
   (ii) $H^+ + 2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5HSO_4^-$
   (iii) $2Fe^{2+} + H_2O_2 + 2H^+ \longrightarrow 2Fe^{3+} + 2H_2O$
   (iv) $Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$

6. Ans. (1) 1 (2) 2 , 1 (3) 1
   (4) 1 (5) 2 (6) 1

7. (1) 1 (2) 1 (3) 1 (4) 1 (5) 2

8. 98, 49, 32.67 9. Ans.21 10. Ans. (i) $\frac{83.5}{6}$ ; (ii) $\frac{17}{3}$

11. Ans. 6 12. Ans.5 13. Ans.(8.097 mL)

14. Ans.(40) 15. Ans.40 ml 16. Ans.60 ml 17. Ans.12.5 L

18. Ans.12.5 L 19. Ans. V = 3 lit. 20. Ans. 200 mL 21. Ans. 30 N

22. Ans.(4.48) 23. Ans. 10 N 24. Ans.2.12 g/L 25. Ans.+ 3

26. Ans.Zero 27. Ans.V = 160 ml 28. Ans.0.588 N 29. Ans.4 lit.

30. Ans. $\frac{2}{3}$ 31. Ans. 8/5 32. Ans. 1.25 mL 33. Ans.1.406%

34. Ans.V = 25 mL 35. Ans.1.28% 36. Ans.40 g , 0.0518N

37. Ans.($Ca^{2+}$ , $Mg^{2+}$, $Na^+$) 38. Ans.(19.09)

## EXERCISE (O-1)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1. | Ans. (C) | 2. | Ans. (B) | 3. | Ans. (B) | 4. | Ans. (B) |
| 5. | Ans. (D) | 6. | Ans. (A) | 7. | Ans. (D) | 8. | Ans. (A) |
| 9. | Ans. (D) | 10. | Ans. (A) | 11. | Ans. (B) | 12. | Ans. (A) |
| 13. | Ans. (C) | 14. | Ans. (C) | 15. | Ans. (C) | 16. | Ans. (D) |
| 17. | Ans. (A) | 18. | Ans. (D) | 19. | Ans. (D) | 20. | Ans. (B) |
| 21. | Ans. (C) | 22. | Ans. (D) | 23. | Ans. (D) | 24. | Ans. (D) |
| 25. | Ans. (A) | 26. | Ans. (C) | 27. | Ans. (D) | 28. | Ans. (C) |
| 29. | Ans. (D) | 30. | Ans. (A) | 31. | Ans. (C) | 32. | Ans. (B) |
| 33. | Ans. (A) | 34. | Ans. (A) | 35. | Ans. (B) | 36. | Ans. (C) |
| 37. | Ans. (C) | 38. | Ans. (A) | 39. | Ans. (D) | 40. | Ans. (A) |
| 41. | Ans. (C) | 42. | Ans. (C) | 43. | Ans. (D) | 44. | Ans. (A) |
| 45. | Ans. (B) | 46. | Ans. (B) | | | | |

## EXERCISE (O-2)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1. | Ans. (A) | 2. | Ans. (C) | 3. | Ans. (B) | 4. | Ans. (C) |
| 5. | Ans. (A) | 6. | Ans. (A) | 7. | Ans. (B) | 8. | Ans. (B) |
| 9. | Ans. (C) | 10. | Ans. (A,B,D) | 11. | Ans. (C) | 12. | Ans. (A) |
| 13. | Ans. (B) | 14. | Ans. (C) | 15. | (A) $\rightarrow$ s ; (B) $\rightarrow$ q ; (C) $\rightarrow$ r ; (D) $\rightarrow$ p | | |
| 16. | Ans. (C) | 17. | Ans. (A) | 18. | Ans. (A) | 19. | Ans. (B) |
| 20. | Ans. (C) | 21. | Ans. (B) | 22. | Ans. (A,D) | | |

## EXERCISE (JM)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1. | Ans. (2) | 2. | Ans. (3) | 3. | Ans. (4) | 4. | Ans. (1) |
| 5. | Ans. (2) | 6. | Ans. (2) | 7. | Ans. (1) | 8. | Ans. (1) |
| 9. | Ans. (3) | 10. | Ans. (1) | 11. | Ans. (3) | 12. | Ans. (2) |
| 13. | Ans. (1) | 14. | Ans. (1) | 15. | Ans. (2) | 16. | Ans. (4) |
| 17. | Ans. (3) | 18. | Ans. (2) | 19. | Ans. (1) | 20. | Ans. (3) |
| 21. | Ans. (4) | 22. | Ans. (100) | | | | |

## EXERCISE (JA)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1. | Ans. (A,C,D) | 2. | Ans. (5) | 3. | Ans. (B) | 4. | Ans. (C) |
| 5. | Ans. (6) | 6. | Ans. (126) | | | | |

CHAPTER 2

# HYDROGEN & IT'S COMPOUNDS

## Chapter 02 Contents


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# IMPORTANT NOTES

# CHAPTER 2 HYDROGEN & IT'S COMPOUNDS

## POSITION OF HYDROGEN IN THE PERIODIC TABLE

Hydrogen is the first element in the periodic table. However, its placement in the periodic table has been a subject of discussion in the past. As you know by now that the elements in the periodic table are arranged according to their electronic configurations. Hydrogen has electronic configuration $1s^1$. On one hand, its electronic configuration is similar to the outer electronic configuration ($ns^1$) of alkali metals , which belong to the first group of the periodic table. On the other hand, like halogens (with $ns^2np^5$ configuration belonging to the seventeenth group of the periodic table), it is short by one electron to the corresponding noble gas configuration, helium ($1s^2$). Hydrogen, therefore, has resemblance to alkali metals, which lose one electron to form unipositive ions, as well as with halogens, which gain one electron to form uninegative ion. Like alkali metals, hydrogen forms oxides, halides and sulphides. However, unlike alkali metals, it has a very high ionization enthalpy and does not possess metallic characteristics under normal conditions. In fact, in terms of ionization enthalpy, hydrogen resembles more with halogens, $\Delta_i H$ of Li is 520 kJ $mol^{-1}$, F is 1680 kJ $mol^{-1}$ and that of H is 1312 kJ $mol^{-1}$. Like halogens, it forms a diatomic molecule, combines with elements to form hydrides and a large number of covalent compounds. However, in terms of reactivity, it is very low as compared to halogens.

Inspite of the fact that hydrogen, to a certain extent resembles both with alkali metals and halogens, it differs from them as well. Now the pertinent question arises as where should it be placed in the periodic table? Loss of the electron from hydrogen atom results in nucleus ($H^+$) of ~$1.510^{-3}$ pm size. This is extremely small as compared to normal atomic and ionic sizes of 50 to 200pm. As a consequence, $H^+$ does not exist freely and is always associated with other atoms or molecules. Thus, it is unique in behaviour and is, therefore, best placed separately in the periodic table.

## DIHYDROGEN, $H_2$

### Occurrence

Dihydrogen is the most abundant element in the universe (70% of the total mass of the universe) and is the principal element in the solar atmosphere. The giant planets Jupiter and Saturn consist mostly of hydrogen. However, due to its light nature, it is much less abundant (0.15% by mass) in the earth's atmosphere. Of course, in the combined form it constitutes 15.4% of the earth's crust and the oceans. In the combined form besides in water, it occurs in plant and animal tissues, carbohydrates, proteins, hydrides including hydrocarbons and many other compounds.

- **Isotopes of Hydrogen**

Hydrogen has three isotopes: **protium**, ${}^{1}_{1}H$, **deuterium**, ${}^{2}_{1}H$ or D and **tritium**, ${}^{3}_{1}H$ or T. These isotopes differ from one another in respect of the presence of neutrons. Ordinary hydrogen, protium, has no neutrons, deuterium (also known as heavy hydrogen) has one and tritium has two neutrons in the nucleus. In the year 1934, an American scientist, Harold C. Urey, got Nobel Prize for separating hydrogen isotope of mass number 2 by physical methods.

The predominant form is protium. Terrestrial hydrogen contains 0.0156% of deuterium mostly in the form of HD. The tritium concentration is about one atom per 1018 atoms of protium. Of these isotopes, only tritium is radioactive and emits low energy $\beta^-$ particles.

**Atomic and Physical Properties of Hydrogen**

| Property | Hydrogen | Deuterium | Tritium |
|---|---|---|---|
| Relative abundace (%) | 99.985 | 0.0156 | $10^{-15}$ |
| Relative atomic mass (g $mol^{-1}$) | 1.008 | 2.014 | 3.016 |
| Melting point / K | 13.96 | 18.73 | 20.62 |
| Boiling point /K | 20.39 | 23.67 | 25.0 |
| Density / $gL^{-1}$ | 0.09 | 0.18 | 0.27 |
| Enthalpy of fusion/KJ $mol^{-1}$ | 0.117 | 0.197 | – |
| Enthalpy of vaporization/kJ $mol^{-1}$ | 0.904 | 1.226 | – |
| Enthalpy of bond dissociation/kJ $mol^{-1}$ at 298.2K | 435.88 | 443.35 | – |
| Internuclear distance/pm | 74.14 | 74.14 | – |
| Ionization enthalpy/kJ $mol^{-1}$ | 1312 | – | – |
| Electron gain enthalpy/kJ $mol^{-1}$ | –73 | – | – |
| Covalent radius/pm | 37 | – | – |
| Ionic radius($H^-$)/ pm | 208 | | |

Since the isotopes have the same electronic configuration, they have almost the same chemical properties. The only difference is in their rates of reactions, mainly due to their different enthalpy of bond dissociation. However, in physical properties these isotopes differ considerably due to their large mass differences.

- **Different forms of Hydrogen :**

**(a) Based on oxidation Number.**

There are three types of hydrogen

| | $H^+$ | $H^-$ | $H$ |
|---|---|---|---|
| | Proton | Hydride | Atomic hydrogen |
| Number of electron | 0 | 2 | 1 |
| Oxidation number | +1 | –1 | 0 |
| Formation | $H \rightarrow H^+ + e^-$ | $H + e^- \rightarrow H^-$ | $H_2 \xrightarrow{\Delta} 2H$ |

**Note :** In the aqueous state proton ($H^+$) exist as $H^+ (H_2O)_n$

Where n is a large number.

If $n = 1 \longrightarrow H_3O^+$

$n = 2 \longrightarrow H^+(H_2O)_2$

**(b) Based on reactivity :**

Hydrogen
↓
Atomic Hydrogen
↓
Simple atomic H | Nascent hydrogen | Adsorbed/Occluded

- **Atomic hydrogen :**

**(i) Simple atomic hydrogen –** It is formed by simple dissociation of hydrogen.

$$H_2 \underset{}{\overset{3000\text{-}5000}{\rightleftharpoons}} 2H$$

Favourable condition – Favourable condition are high temp & low pressure.

**(ii) Nascent hydrogen –** Hydrogen at the moment of its birth it called nascent hydrogen means which forms at the instant is known as Nascent hydrogen.

It is formed only by some specific chemical reaction.

(a) Acid + Metals $\quad Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$

(b) Base + amphoteric metal (Be, Zn, Al, Ga, Pb, Sn) $\quad 2NaOH + Be \longrightarrow Na_2BeO_2 + 2H$

(c) $C_2H_5OH$ + Alkali metal

$$C_2H_5OH + Na \longrightarrow C_2H_5ONa + H$$

**(iii) Adsorbed/Occluded hydrogens**

Adsorbed H is hydrogen present at the outer surface of metal.

- **Occlusion :** The property of metal to adsorb any gas is called occlusion.

**Reactivity order**

Atomic hydrogen > Nascent hydrogen > Molecular hydrogen

**(iii) Based on Nuclear spin (Nuclear isomers)**

Hydrogen → Ortho, Para

**(a) Ortho hydrogen :** The molecular form of hydrogen having same spin of nucleus is called ortho hydrogen.

**(b) Para hydrogen :** The molecular form of hydrogen having opposite spin of nucleus is called para hydrgen.

In ortho hydrogen spin of nucleus is same, so they will repel each other & because of this repulsion, internal energy of ortho hydrogen increases. So ortho hydrogen has more internal energy.

- **Stability of ortho & Para hydrogen**

Stability of ortho & para hydrogen depends upon temperature condition.

At low temp : para hydrogen is more stable than ortho hydrogen while at high temp ortho hydrogen is more stable than para hydrogen.

$$P_{H_2} \underset{T\downarrow}{\overset{T\uparrow}{\rightleftharpoons}} O_{H_2}$$

| | Ortho | Para |
|---|---|---|
| At high temperature | 75% | 25% |
| At absolute zero temp. | 0 | 100% |

- **Imp. Note :**

(i) We can obtain 100% pure para hydrogen at low temp but can't ortho because at high temp parahydrogen will dissociate into atomic hydrogen.

(ii) Ortho & Para hydrogen differs only in physical properties but have same chemical properites.

## PREPARATION OF DIHYDROGEN, $H_2$

There are a number of methods for preparing dihydrogen from metals and metal hydrides.

- **Laboratory Preparation of Dihydrogen**

(i) It is usually prepared by the reaction of granulated zinc with dilute hydrochloric acid.

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$

(ii) It can also be prepared by the reaction of zinc with aqueous alkali.

$$Zn + 2NaOH \rightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2$$

- **Commercial Production of Dihydrogen**

The commonly used processes are outlined below :

(i) Electrolysis of acidified water using platinum electrodes gives hydrogen.

$$2H_2O(\ell) \xrightarrow[\text{Trances of acid/base}]{\text{Electrolysis}} 2H_2(g) + O_2(g)$$

(ii) High purity (>99.95%) dihydrogen is obtained by electrolysing warm aqueous barium hydroxide solution between nickel electrodes.

(iii) It is obtained as a byproduct in the manufacture of sodium hydroxide and chlorine by the electrolysis of brine solution. During electrolysis, the reactions that take place are:

at anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

at cathode: $2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

The overall reaction is

$$2Na^+(aq) + 2Cl^-(aq) + 2H_2O(\ell) \rightarrow Cl_2(g) + H_2(g) + 2Na^+(aq) + 2OH^-(aq)$$

(iv) Reaction of steam on hydrocarbons or coke at high temperatures in the presence of catalyst yields hydrogen.

$$C_nH_{2n-2} + nH_2O \xrightarrow[\text{Ni}]{1270\text{ K}} nCO + (2n-1)H_2$$

e.g.,

$$CH_4(g) + H_2O(g) \xrightarrow[\text{Ni}]{1270\text{ K}} CO(g) + 3H_2(g)$$

The mixture of CO and $H_2$ is called *water gas*. As this mixture of CO and $H_2$ is used for the synthesis of methanol and a number of hydrocarbons, it is also called *synthesis gas or* **'syngas'**. Nowadays 'syngas' is produced from sewage, saw-dust, scrap wood, newspapers etc. The process of producing 'syngas' from coal is called *'coal gasification'*.

$$C(s) + H_2O(g) \xrightarrow{1270K} CO(g) + H_2(g)$$

The production of dihydrogen can be increased by reacting carbon monoxide of syngas mixtures with steam in the presence of iron chromate as catalyst ($Fe_2O_3$ and $Cr_2O_3$).

$$CO(g) + H_2O(g) \xrightarrow[\text{catalyst}]{673K} CO_2(g) + H_2(g)$$

This is called water-gas shift reaction **/Bosch process**. Carbon dioxide is removed by scrubbing with sodium arsenite solution. Presently ~77% of the industrial dihydrogen is produced from petro-chemicals, 18% from coal, 4% from electrolysis of aqueous solutions and 1% from other sources.

## ❑ PROPERTIES OF DIHYDROGEN

- **Physical Properties**

Dihydrogen is a colourless, odourless, tasteless, combustible gas. It is lighter than air and insoluble in water. Its other physical properties alongwith those of deuterium are given in Table.

- **Chemical Properties**

The chemical behaviour of dihydrogen (and for that matter any molecule) is determined, to a large extent, by bond dissociation enthalpy. The H–H bond dissociation enthalpy is the highest for a single bond between two atoms of any element. What inferences would you draw from this fact ? It is because of this factor that the dissociation of dihydrogen into its atoms is only ~0.081% around 2000K which increases to 95.5% at 5000K. Also, it is relatively inert at room temperature due to the high H–H bond enthalpy. Thus, the atomic hydrogen is produced at a high temperature in an electric arc or under ultraviolet radiations. Since its orbital is incomplete with $1s^1$ electronic configuration, it does combine with almost all the elements. It accomplishes reactions by (i) loss of the only electron to give $H^+$, (ii) gain of an electron to form $H^-$, and (iii) sharing electrons to form a single covalent bond.

The chemistry of dihydrogen can be illustrated by the following reactions:

- ***Reaction with halogens :*** It reacts with halogens, $X_2$ to give hydrogen halides HX,

$$H_2(g) + X_2(g) \rightarrow 2HX(g) \ (X = F, Cl, Br, I)$$

While the reaction with fluorine occurs even in the dark, with iodine it requires a catalyst.

- ***Reaction with dioxygen:*** It reacts with dioxygen to form water. The reaction is highly exothermic.

$$2H_2(g) + O_2(g) \xrightarrow{\text{catalyst or heating}} 2H_2O(\ell);\ \Delta H^{\ominus} = -285.9\ \text{kJ mol}^{-1}$$

- ***Reaction with dinitrogen:*** With dinitrogen it forms ammonia.

$$3H_2(g) + N_2(g) \xrightarrow[\text{Fe}]{673K/200atm} 2NH_3(g)\ ;\ \Delta H^{\ominus} = -92.6\ \text{kJ mol}^{-1}$$

This is the method for the manufacture of ammonia by the Haber process.

- ***Reactions with metals :*** With many metals it combines at a high temperature to yield the corresponding hydrides.

$$H_2(g) + 2M(g) \rightarrow 2MH(s)\ ;$$

where M is an alkali metal

- ***Reactions with metal ions and metal oxides:*** It reduces some metal ions in aqueous solution and oxides of metals (less active than iron) into corresponding metals.

$$H_2(g) + Pd^{2+}(aq) \rightarrow Pd(s) + 2H^+(aq)$$

$$yH_2(g) + M_xO_y(s) \rightarrow xM(s) + yH_2O(\ell)$$

- ***Reactions with organic compounds:*** It reacts with many organic compounds in the presence of catalysts to give useful hydrogenated products of commercial importance. For example :

(i) Hydrogenation of vegetable oils using nickel as catalyst gives edible fats (margarine and vanaspati ghee)

(ii) Hydroformylation of olefins yields aldehydes which further undergo reduction to give alcohols.

$$H_2 + CO + RCH = CH_2 \rightarrow RCH_2CH_2CHO$$

$$H_2 + RCH_2CH_2CHO \rightarrow RCH_2CH_2CH_2OH$$

**Problem-1**

Comment on the reactions of dihydrogen with (i) chlorine, (ii) sodium, and (iii) copper(II) oxide.

**Solution**

(i) Dihydrogen reduces chlorine into chloride ($Cl^-$) ion and itself gets oxidised to $H^+$ ion by chlorine to form hydrogen chloride. An electron pair is shared between H and Cl leading to the formation of a covalent molecule.

(ii) Dihydrogen is reduced by sodium to form NaH. An electron is transferred from Na to H leading to the formation of an ionic compound, $Na^+H^-$.

(iii) Dihydrogen reduces copper(II) oxide to copper in zero oxidation state and itself gets oxidised to $H_2O$, which is a covalent molecule.

**Uses of Dihydrogen**

The largest single use of dihydrogen is in the synthesis of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers.

- Dihydrogen is used in the manufacture of vanaspati fat by the hydrogenation of polyunsaturated vegetable oils like soyabean, cotton seeds etc. . It is used in the manufacture of bulk organic chemicals, particularly methanol.

$$CO(g) + 2H_2(g) \xrightarrow[\text{catalyst}]{\text{cobalt}} CH_3OH(\ell)$$

- It is widely used for the manufacture of metal hydrides.
- It is used for the preparation of hydrogen chloride, a highly useful chemical.
- In metallurgical processes, it is used to reduce heavy metal oxides to metals.
- Atomic hydrogen and oxy-hydrogen torches find use for cutting and welding purposes. Atomic hydrogen atoms (produced by dissociation of dihydrogen with the help of an electric arc) are allowed to recombine on the surface to be welded to generate the temperature of 4000 K.
- It is used as a rocket fuel in space research.
- Dihydrogen is used in fuel cells for generating electrical energy. It has many advantages over the conventional fossil fuels and electric power. It does not produce any pollution and releases greater energy per unit mass of fuel in comparison to gasoline and other fuels.

## ❑ HYDRIDES

Dihydrogen, under certain reaction conditions, combines with almost all elements, except noble gases, to form binary compounds, called **hydrides**. If 'E' is the symbol of an element then hydride can be expressed as $EH_x$ (e.g., $MgH_2$) or $E_mH_n$ (e.g., $B_2H_6$).

The hydrides are classified into three categories :

(i) Ionic or saline or saltlike hydrides

(ii) Covalent or molecular hydrides

(iii) Metallic or non-stoichiometric hydrides

- **Ionic or Saline Hydrides**

These are stoichiometric compounds of dihydrogen formed with most of the *s*-block elements which are highly electropositive in character. However, significant covalent character is found in the lighter metal hydrides such as LiH, $BeH_2$ and $MgH_2$. In fact $BeH_2$ and $MgH_2$ are polymeric in structure. The ionic hydrides are crystalline, non-volatile and nonconducting in solid state. However, their melts conduct electricity and on electrolysis liberate dihydrogen gas at anode, which confirms the existence of $H^-$ ion.

$$2H^-\,(\text{melt}) \xrightarrow{\text{anode}} H_2(g) + 2e^-$$

Saline hydrides react violently with water producing dihydrogen gas.

$$NaH(s) + H_2O(aq) \rightarrow NaOH(aq) + H_2(g)$$

Lithium hydride is rather unreactive at moderate temperatures with $O_2$ or $Cl_2$. It is, therefore, used in the synthesis of other useful hydrides, e.g.,

$$8LiH + Al_2Cl_6 \rightarrow 2LiAlH_4 + 6LiCl$$

$$2LiH + B_2H_6 \rightarrow 2LiBH_4$$

- **Covalent or Molecular Hydride**

Dihydrogen forms molecular compounds with most of the *p*-block elements. Most familiar examples are $CH_4$, $NH_3$, $H_2O$ and HF. For convenience hydrogen compounds of nonmetals have also been considered as hydrides. Being covalent, they are volatile compounds. Molecular hydrides are further classified according to the relative numbers of electrons and bonds in their Lewis structure into :

**(i) electron-deficient, (ii) electron-precise, and (iii) electron-rich hydrides.**

An electron-deficient hydride, as the name suggests, has too few electrons for writing its conventional Lewis structure. Diborane ($B_2H_6$) is an example. In fact all elements of group 13 will form electron-deficient compounds. They act as Lewis acids i.e., electron acceptors.

Electron-precise compounds have the required number of electrons to write their conventional Lewis structures. All elements of group 14 form such compounds (e.g., $CH_4$) which are tetrahedral in geometry.

Electron-rich hydrides have excess electrons which are present as lone pairs. Elements of group 15-17 form such compounds. ($NH_3$ has 1- lone pair, $H_2O$ – 2 and HF –3 lone pairs). They will behave as Lewis bases i.e., electron donors. The presence of lone pairs on highly electronegative atoms like N, O and F in hydrides results in hydrogen bond formation between the molecules. This leads to the association of molecules.

**Problem -2**

Would you expect the hydrides of N, O and F to have lower boiling points than the hydrides of their subsequent group members ? Give reasons.

**Solution**

On the basis of molecular masses of $NH_3$, $H_2O$ and HF, their boiling points are expected to be lower than those of the subsequent group member hydrides. However, due to higher electronegativity of N, O and F, the magnitude of hydrogen bonding in their hydrides will be quite appreciable. Hence, the boiling points $NH_3$, $H_2O$ and HF will be higher than the hydrides of their subsequent group members.

- **Metallic or Non-stoichiometric (or Interstitial ) Hydrides**

These are formed by many *d*-block and *f*-block elements. However, the metals of group 7, 8 and 9 do not form hydride. Even from group 6, only chromium forms CrH. These hydrides conduct heat and electricity though not as efficiently as their parent metals do. Unlike saline hydrides, they are almost always nonstoichiometric, being deficient in hydrogen. For example, $LaH_{2.87}$, $YbH_{2.55}$, $TiH_{1.5–1.8}$, $ZrH_{1.3–1.75}$, $VH_{0.56}$, $NiH_{0.6–0.7}$, $PdH_{0.6–0.8}$ etc. In such hydrides, the law of constant composition does not hold good.

Earlier it was thought that in these hydrides, hydrogen occupies interstices in the metal lattice producing distortion without any change in its type. Consequently, they were termed as interstitial hydrides. However, recent studies have shown that except for hydrides of Ni, Pd, Ce and Ac, other hydrides of this class have lattice different from that of the parent metal. The property of absorption of hydrogen on transition metals is widely used in catalytic reduction / hydrogenation reactions for the preparation of large number of compounds. Some of the metals (e.g., Pd, Pt) can accommodate a very large volume of hydrogen and, therefore, can be used as its storage media. This property has high potential for **hydrogen storage** and as a **source of energy**.

## WATER

A major part of all living organisms is made up of water. Human body has about 65% and some plants have as much as 95% water. It is a crucial compound for the survival of all life forms. It is a solvent of great importance. The distribution of water over the earth's surface is not uniform. The estimated world water supply is given in Table.

**Estimated World Water Supply**

| Source | % of total |
|---|---|
| Oceans | 97.33 |
| Saline lakes and inland seas | 0.008 |
| Polar ice and glaciers | 2.04 |
| Ground water | 0.61 |
| Lakes | 0.009 |
| Soil moisture | 0.005 |
| Atomspheric water vapour | 0.001 |
| Rivers | 0.001 |

- **Physical Properties of Water**

It is a colourless and tasteless liquid. Its physical properties are given in Table along with the physical properties of heavy water. The unusual properties of water in the condensed phase (liquid and solid states) are due to the presence of extensive hydrogen bonding between water molecules.

This leads to high freezing point, high boiling point, high heat of vaporisation and high heat of fusion in comparison to $H_2S$ and $H_2Se$. In comparison to other liquids, water has a higher specific heat, thermal conductivity, surface tension, dipole moment and dielectric constant, etc. These properties allow water to play a key role in the biosphere.

**Physical Properties of $H_2O$ and $D_2O$**

| Property | $H_2O$ | $D_2O$ |
|---|---|---|
| Molecular mass (g $mol^{-1}$) | 18.0151 | 20.0276 |
| Melting point/K | 273.0 | 276.8 |
| Boiling point/K | 373.0 | 374.4 |
| Enthalpy of formation/kJ $mol^{-1}$ | –285.9 | –294.6 |
| Enthalpy of vaporisation (373K)/kJ$mol^{-1}$ | 40.66 | 41.61 |
| Enthalpy of fusion/kJ $mol^{-1}$ | 6.01 | - |
| Temp of max. density/K | 276.98 | 284.2 |
| Density(298K)/g $cm^{-3}$ | 1.0000 | 1.1059 |
| Viscosity/centipoise | 0.8903 | 1.107 |
| Dielectric constant/$C^2/N.m^2$ | 78.39 | 78.06 |
| Electrical conductivity (293K/$ohm^{-1}$ $cm^{-1}$) | $5.7 \times 10^{-8}$ | - |

The high heat of vaporisation and heat capacity are responsible for moderation of the climate and body temperature of living beings. It is an excellent solvent for transportation of ions and molecules required for plant and animal metabolism. Due to hydrogen bonding with polar molecules, even covalent compounds like alcohol and carbohydrates dissolve in water.

- **Structure of Water**

In the gas phase water is a bent molecule with a bond angle of 104.5° and O–H bond length of 95.7 pm as shown in Fig (a).

$H_2O$ molecule

*(a) The bent structure of water; (b) the water molecule as a dipole and (c) the orbital overlap picture in water molecule.*

It is a highly polar molecule, (Fig (b)). Its orbital overlap picture is shown in Fig. (c). In the liquid phase water molecules are associated together by hydrogen bonds.

The crystalline form of water is ice. At atmospheric pressure ice crystallises in the hexagonal form, but at very low temperatures it condenses to cubic form. Density of ice is less than that of water. Therefore, an ice cube floats on water. In winter season ice formed on the surface of a lake provides thermal insulation which ensures the survival of the aquatic life. This fact is of great ecological significance.

- **Structure of Ice**

Ice has a highly ordered three dimensional hydrogen bonded structure as shown in Fig. Examination of ice crystals with X-rays shows that each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 276 pm. Hydrogen bonding gives ice a rather open type structure with wide holes. These holes can hold some other molecules of appropriate size interstitially.

**The Structure of Ice**

- **Chemical Properties of Water**

Water reacts with a large number of substances. Some of the important reactions are given below.

***(1) Amphoteric Nature :***

It has the ability to act as an acid as well as a base i.e., it behaves as an amphoteric substance. In the Brönsted sense it acts as an acid with $NH_3$ and a base with $H_2S$.

$H_2O(\ell) + NH_3(aq) \rightarrow OH^-(aq) + NH_4^+(aq)$

$H_2O(\ell) + H_2O(aq) \rightarrow H_3O^+(aq) + HS^-(aq)$

The auto-protolysis (self-ionization) of water takes place as follows :

$H_2O(\ell) + H_2O(\ell) \rightarrow H_3O^+(aq) + OH^-(aq)$

| acid-1 | base-2 | acid-2 | base-1 |
|---|---|---|---|
| (acid) | (base) | (conjugate acid) | (conjugate base) |

***(2) Redox Reactions Involving Water:***

Water can be easily reduced to dihydrogen by highly electropositive metals.

$$2H_2O(\ell) + 2Na(s) \rightarrow 2NaOH(aq) + H_2(g)$$

Thus, it is a great source of dihydrogen.

Water is oxidised to $O_2$ during photosynthesis.

$$6CO_2(g) + 12H_2O(\ell) \rightarrow C_6H_{12}O_6(aq) + 6H_2O(\ell) + 6O_2(g)$$

With fluorine also it is oxidised to $O_2$.

$$2F_2(g) + 2H_2O(\ell) \rightarrow 4H^+ (aq) + 4F^-(aq) + O_2(g)$$

***(3) Hydrolysis Reaction:***

Due to high dielectric constant, it has a very strong hydrating tendency. It dissolves many ionic compounds. However, certain covalent and some ionic compounds are hydrolysed in water.

$$P_4O_{10}(s) + 6H_2O(\ell) \rightarrow 4H_3PO_4 (aq)$$

$$SiCl_4(\ell) + 2H_2O(\ell) \rightarrow SiO_2(s) + 4HCl(aq)$$

$$N^{3-}(s) + 3H_2O(\ell) \rightarrow NH_3(g) + 3OH^-(aq)$$

***(4) Hydrates Formation:***

From aqueous solutions many salts can be crystallised as hydrated salts. Such an association of water is of different types viz.,

(i) coordinated water e.g.,

$[Cr(H_2O)_6]^{3+}\ 3Cl^-$

(ii) interstitial water e.g., $BaCl_2.2H_2O$

(iii) hydrogen-bonded water e.g.,

$[Cu(H_2O)_4]^{2+}\ SO_4^{2-}.\ H_2O$ in $CuSO_4.5H_2O$.

**Problem -3**

The number of water molecule(s) directly bonded to the metal centre in $CuSO_4.\ 5H_2O$ is - **[JEE 2009]**

**Solution.**

- **Hard and Soft Water**

Rain water is almost pure (may contain some dissolved gases from the atmosphere). Being a good solvent, when it flows on the surface of the earth, it dissolves many salts. Presence of calcium and magnesium salts in the form of hydrogencarbonate, chloride and sulphate in water makes water **'hard'**. **Hard water** does not give lather with soap. Water free from soluble salts of calcium and magnesium is called **Soft water**. It gives lather with soap easily.

Hard water forms scum/precipitate with soap. Soap containing sodium stearate ($C_{17}H_{35}COONa$) reacts with hard water to precipitate out Ca/Mg stearate.

$$2C_{17}H_{35}COONa(aq) + M^{2+}(aq) \rightarrow (C_{17}H_{35}COO)_2M \downarrow + 2Na^+(aq) \text{ ; M is Ca/Mg}$$

It is, therefore, unsuitable for laundry. It is harmful for boilers as well, because of deposition of salts in the form of scale. This reduces the efficiency of the boiler. The hardness of water is of two types:

(i) temporary hardness, and (ii) permanent hardness.

- **Temporary Hardness :**

Temporary hardness is due to the presence of magnesium and calcium hydrogencarbonates. It can be removed by :

***(i)*** ***Boiling :*** During boiling, the soluble $Mg(HCO_3)_2$ is converted into insoluble $Mg(OH)_2$ and $Ca(HCO_3)_2$ is changed to insoluble $CaCO_3$. It is because of high solubility product of $Mg(OH)_2$ as compared to that of $MgCO_3$, that $Mg(OH)_2$ is precipitated. These precipitates can be removed by filtration. Filtrate thus obtained will be soft water.

$$Mg(HCO_3)_2 \xrightarrow{\text{Heating}} Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$

$$Ca(HCO_3)_2 \xrightarrow{\text{Heating}} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

***(ii)*** ***Clark's method :*** In this method calculated amount of lime is added to hard water. It precipitates out calcium carbonate and magnesium hydroxide which can be filtered off.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$$

- **Permanent Hardness**

It is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in water. Permanent hardness is not removed by boiling. It can be removed by the following methods:

***(i) Treatment with washing soda (sodium carbonate) :*** Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates.

$$MCl_2 + Na_2CO_3 \rightarrow MCO_3 \downarrow + 2NaCl \text{ (m + Mg, Ca)}$$

$$MSO_4 + Na_2CO_3 \rightarrow MCO_3 \downarrow + Na_2SO_4$$

***(ii) Calgon's method :*** Sodium hexametaphosphate ($Na_6P_6O_{18}$), commercially called 'calgon', when added to hard water, the following reactions take place.

$$Na_6P_6O_{18} \rightarrow 2Na^+ + Na_4P_6O_{18}^{2-} \text{ (M = Mg. Ca)}$$

$$M^{2+} + Na_4P_6O_{18}^{2-} \rightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+$$

The complex anion keeps the $Mg^{2+}$ and $Ca^{2+}$ ions in solution.

**(iii) Ion-exchange method (By Zeolite) :** This method is also called zeolite / permutit process.

$[Na_2Al_2Si_2O_8.\ xH_2O]$

$[Na_2O.Al_2O_3.2SiO_2.xH_2O]$

Hydrated sodium aluminium silicate is zeolite/ permutit. For the sake of simplicity, sodium aluminium silicate ($NaAlSiO_4$) can be written as NaZ. When this is added in hard water, exchange reactions take place.

$$2NaZ(s) + M^{2+}(aq) \rightarrow MZ_2(s) + 2Na^+(aq) \text{ (M=Mg, Ca)}$$

Permutit/zeolite is said to be exhausted when all the sodium in it is used up. It is regenerated for further use by treating with an aqueous sodium chloride solution.

$$MZ_2(s) + 2NaCl(aq) \rightarrow 2NaZ(s) + MCl_2(aq)$$

**(iv) Ion exchange method (By synthetic resins ) :** Ion exchanges resins are the most popular water softener these days. This resins are synthetic substance. The **cation exchanger** consists of granular insoluble organic acid resins having giant molecules with $-SO_3H$ or $-COOH$ groups (represented as RH) while the **anion exchanger** contains giant organic molecules with basic groups derived from amine (represented as ROH). Ion exchange resins remove all soluble mineral from water.

**Reaction at Cation exchanger**

$$Ca^{2+} + RH \longrightarrow R_2Ca + 2H^{\oplus}$$

$$Mg^{2+} + RH \longrightarrow R_2Mg + 2H^{\oplus}$$

**Reaction at Anion exchanger**

$$ROH + Cl^- \longrightarrow RCl + OH^-$$

$$2ROH + SO_4^{2-} \longrightarrow R_2SO_4 + 2OH^-$$

The water coming from cation exchanger is acidic due to $H^{\oplus}$. This water is then passed through another bed containing anion exchanger. This exchanger removes anion like $Cl^-$, $SO_4^{2-}$, $NO_3^-$ by exchanging with $OH^-$ ions.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$$

This water is free from impurities & can be used for drinking purpose.

After some times when both resin gets exhausted process is stopped.

**Regenration of resin :**

(i) Cation exchange resin : We use dil acid.

$$2HCl + R_2Ca \longrightarrow RH + CaCl_2$$

(ii) Anion exchange resin : We use dil NaOH solution

$$NaOH + RCl \longrightarrow NaCl + ROH$$

## HYDROGEN PEROXIDE ($H_2O_2$)

**This article has been taken in p-block chapter.**

## HEAVY WATER, $D_2O$ :

It can be prepared by exhaustive electrolysis of water or as a by-product in some fertilizer industries.

- **Physical properties :**

(a) Heavy water is a colourles, odourless and tasteless mobile liquid,

(b) Nearly all the physical constants are higher than the corresponding values of ordinary water.

It is used for the preparation of other deuterium compounds, for example:

$$CaC_2 + 2D_2O \rightarrow C_2D_2 + Ca(OD)_2$$

$$SO_3 + D_2O \rightarrow D_2SO_4$$

$$Al_4C_3 + 12D_2O \rightarrow 3CD_4 + 4Al(OD)_3$$

- **Uses :** It is extensively used as a moderator & coolant in nuclear reactors and in exchange reactions for the study of reaction mechanisms. **As a neutron moderator :** Fission in uranium-235 is brought by slow speed neutrons. The substances which are used for slowing down the speed of neutrons are called moderators. Heavy water is used for this purpose in nuclear reactors.

## DIHYDROGEN AS A FUEL

Dihydrogen releases large quantities of heat on combustion. The data on energy released by combustion of fuels like dihydrogen, methane, LPG etc. are compared in terms of the same amounts in mole, mass and volume, are shown in Table.

From this table it is clear that on a mass for mass basis dihydrogen can release more energy than petrol (about three times). Moreover, pollutants in combustion of dihydrogen will be less than petrol. The only pollutants will be the oxides of dinitrogen (due to the presence of dinitrogen as impurity with dihydrogen).

This, of course, can be minimised by injecting a small amount of water into the cylinder to lower the temperature so that the reaction between dinitrogen and dioxygen may not take place. However, the mass of the containers in which dihydrogen will be kept must be taken into consideration. A cylinder of compressed dihydrogen weighs about 30 times as much as a tank of petrol containing the same amount of energy. Also, dihydrogen gas is converted into liquid state by cooling to 20K. This would require expensive insulated tanks. Tanks of metal alloy like $NaNi_5$, $Ti–TiH_2$, $Mg–MgH_2$ etc. are in use for storage of dihydrogen in small quantities. These limitations have prompted researchers to search for alternative techniques to use dihydrogen in an efficient way.

In this view Hydrogen Economy is an alternative. The basic principle of hydrogen economy is the transportation and storage of energy in the form of liquid or gaseous dihydrogen. Advantage of hydrogen economy is that energy is transmitted in the form of dihydrogen and not as electric power. It is for the first time in the history of India that a pilot project using dihydrogen as fuel was launched in October 2005 for running automobiles. Initially 5% dihydrogen has been mixed in CNG for use in four-wheeler vehicles. The percentage of dihydrogen would be gradually increased to reach the optimum level.

Nowadays, it is also used in fuel cells for generation of electric power. It is expected that economically viable and safe sources of dihydrogen will be identified in the years to come, for its usage as a common source of energy.

**The Energy Released by Combustion of Various Fuels in Moles, Mass and Volume**

| Energy released on Combustion in kJ state) | Dihydrogen in gaseous state) | Dihydrogen (in liuqid) | LPG | $CH_4$ gas | Octance (in liuquid state) |
|---|---|---|---|---|---|
| per mole | 286 | 285 | 2220 | 880 | 5511 |
| per gram | 143 | 142 | 50 | 53 | 47 |
| per litre | 12 | 9968 | 25590 | 35 | 34005 |

## EXERCISE (S-1)

### Integer Type

**1.** Find out the sum of protons, electrons and neutrons in the heaviest isotope of hydrogen.

**2.** Find out the number of following orders which are correct against the mentioned properties :

(i) $H_2 < D_2 < T_2$ (Number of protons)

(ii) $H_2 < D_2$ (Bond energy)

(iii) $H_2 < D_2 < T_2$ (Boiling point)

(iv) $H_2 < D_2 < T_2$ (No. of neutrons)

**3.** Find out the number of following orders which are **NOT** correct against the mentioned properties:

(i) $CaH_2 < BeH_2$ (Electrical conductance in molten condition)

(ii) $LiH < NaH < CsH$ (Ionic character)

(iii) $H_2 < D_2 < F_2$ (Bond dissociation enthalpy)

(iv) $NaH < MgH_2 < H_2O$ (Reducing property)

**4.** What is the oxidation state of oxygen of $H_2O_2$ in the final product when it reacts with $ClO_3^-$.

**5.** Find out the value of 'x' in ion $[H_xO_4]^+$ :

## EXERCISE (O-1)

### DIHYDROGEN

**1.** The sum number of neutrons and protons in one of the isotopes of hydrogen is :-

(A) 3 (B) 4 (C) 5 (D) 6

**2.** The catalyst used in Bosch process of manufacture of $H_2$ is :-

(A) Finely divided Ni (B) $V_2O_5$ (C) Pb (D) $Fe_2O_3 + Cr_2O_3$

**3.** The most abundant isotope of hydrogen is :-

(A) Tritium (B) Deuterium (C) Protium (D) Para hydrogen

**4.** The n/p ratio for $_1H^1$ is :-

(A) 1 (B) 2 (C) 3 (D) Zero

**5.** Ordinary hydrogen at high temperature is a mixture of :-

(A) 75% o-Hydrogen + 25% p-Hydrogen (B) 25% o-Hydrogen + 75% p-Hydrogen

(C) 50% o-Hydrogen + 50% p-Hydrogen (D) 1% o-Hydrogen + 99% p-Hydrogen

**6.** Hydrogen is behave as :-

(A) Electropositive

(B) Electronegative

(C) Both electropositive as well as elecctro-negative

(D) Neither electropositive nor electronegative

**7.** At high temperature Para hydrogen is :-

(A) Less stable than ortho hydrogen

(B) More stable than ortho hydrogen

(C) As stable as ortho hydrogen

(D) None of these

**8.** When the same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide, the ratio of volumes of hydrogen evolved is :-

(A) 1 : 1 (B) 1 : 2 (C) 2 : 1 (D) 9 : 4

**9.** The lightest gas is :-

(A) Nitrogen (B) Helium (C) Oxygen (D) Hydrogen

**10.** The ratio of electron, proton and neutron in tritium is :-

(A) 1 : 1 : 1 (B) 1 : 1 : 2 (C) 2 : 1 : 1 (D) 1 : 2 : 1

**11.** The nuclei of tritium ($H^3$) atom would contain neutrons :-

(A) 1 (B) 2 (C) 3 (D) 4

**12.** The adsorption of hydrogen by metals is called :-

(A) Dehydrogenation (B) Hydrogenation (C) Occlusion (D) Adsorption

**13.** At absolute zero :-

(A) Only para hydrogen exists (B) Only ortho hydrogen exists

(C) Both para and ortho hydrogen exist (D) None

## WATER ($H_2O$)

**14.** Only temporary hardness in water is removed by :-

(A) Boiling (B) Filtration (C) Calgon's process (D) None of these

**15.** Both temporary and permanent hardness is removed on boiling water with :-

(A) $Ca(OH)_2$ (B) $Na_2CO_3$ (C) $CaCO_3$ (D) CaO

**16.** Temporary hardness is caused due to the presence of :-

(A) $CaSO_4$ (B) $CaCl_2$ (C) $CaCO_3$ (D) $Ca(HCO_3)_2$

**17.** High boiling point of water is due to :-

(A) Its high specific heat (B) Hydrogen bonding

(C) High dielectric constant (D) Low dissociation constant

**18.** Calgon is an industrial name given to :-

(A) Normal sodium phosphate (B) Sodium meta-aluminate

(C) Sodium hexametaphosphate (D) Hydrated sodium aluminium silicate

**19.** Permutit is :-

(A) Hydrated sodium aluminium silicate (B) Sodium hexametaphosphate

(C) Sodium silicate (D) Sodium meta-aluminate

**20.** Heavy water has found application in atomic reactor as :-

(A) Coolant (B) Moderator

(C) Both coolant and moderator (D) Neither coolant nor moderator

**21.** Calgon (a water softener) is :-

(A) $Na_2[Na_4(PO_3)_6]$ (B) $Na_4[Na_2(PO_3)]_6$ (C) $Na_2[Na_4(PO_4)]_6$ (D) $Na_4[Na_2(PO_4)_6]$

**22.** The hardness of water is due to.....metal ions

(A) $Ca^{2+}$ and $Na^+$ (B) $Mg^{2+}$ and $K^+$ (C) $Ca^{2+}$ and $Mg^{2+}$ (D) $Zn^{2+}$ and $Ba^{2+}$

**23.** The formula of heavy water is :-

(A) $H_2O^{18}$ (B) $D_2O$ (C) $T_2O$ (D) $H_2O^{17}$

**24.** Pure de-mineralised water can be obtained by -

(A) $Na^+$ cation exchanger and $Cl^-$ anion exchanger

(B) $H^+$ cation exchanger only

(C) $H^+$ cation exchanger and $OH^-$ anion exchanger

(D) $Na^+$ cation exchanger only

## HYDROGEN PEROXIDE ($H_2O_2$)

**25.** The bleaching properties of $H_2O_2$ are due to its :-

(A) Reducing properties (B) Oxidising properties

(C) Unstable nature (D) Acidic nature

**26.** Hydrogen peroxide has a :-

(A) Linear structure (B) Pyramidal structure

(C) Closed book type structure (D) Half open book type structure

**27.** Hydrogen peroxide is a :-

(A) Liquid (B) Gas (C) Solid (D) Semi-solid

**28.** Which of the following is a true structure of $H_2O_2$ ?

(A)

(B)

(C)
(D)

**29.** Decomposition of $H_2O_2$ is retarded by :-

$2H_2O_2(\ell) \rightarrow 2H_2O(\ell) + O_2(g)$

(A) Acetanilide (B) $MnO_2$

(C) Zinc (D) Finely divided metals

**30.** $H_2O_2$ is :-

(A) An oxiding agent
(B) Both oxidising and reducing agent
(C) Reducing agent
(D) None of the above

**31.** $H_2O_2$ is always stored in black bottles because :-

(A) It is highly unstable
(B) Its enthalpy of decomposition is high
(C) It undergoes auto-oxidation on prolonged standing
(D) None of these

**32.** Acidified solution of $K_2Cr_2O_7$ on treatment with $H_2O_2$ yields :-

(A) $CrO_3 + H_2O + O_2$
(B) $Cr_2O_2 + H_2O + O_2$
(C) $CrO_5 + H_2O + K_2SO_4$
(D) $H_2Cr_2O_7 + H_2O + O_2$

**33.** $H_2O_2$ restores the colour of old lead paintings, blackened by the action of $H_2S$ gas by :-

(A) Converting $PbO_2$ to Pb
(B) By oxidising PbS to $PbSO_4$
(C) Converting $PbCO_3$ to Pb
(D) Oxidising $PbSO_3$ to $PbSO_4$

**34.** The reaction, $H_2S + H_2O_2 \longrightarrow S + 2H_2O$ manifests:

(A) Acidic nature of $H_2O_2$
(B) Alkaline nature of $H_2O_2$
(C) Oxidising nature of $H_2O_2$
(D) Reducing nature of $H_2O_2$

**35.** Hydrogen peroxide is now generally prepared on industrial scale by the :-

(A) Action of $H_2SO_4$ on barium peroxide
(B) Action of $H_2SO_4$ on sodium peroxide
(C) auto-oxidation of 2-alklylanthraquinols
(D) Burning hydrogen in excess of oxygen

## EXERCISE (O-2)

**1.** Which of the following is / are same for Ortho and Para hydrogen ?

(A) In the number of protons

(B) In the molecular mass

(C) In the nature of spins of nucleus

(D) In the nature of spins of electrons

**2.** In Bosch's process which gas is **NOT** utilised for the production of hydrogen :-

(A) Producer gas (B) Water gas (C) Coal gas (D) Natural gas

**3.** The gas(es) used in the hydrogenation of oils in presence of nickel as a catalyst is / are :-

(A) Methane (B) Ethane (C) Ozone (D) Hydrogen

**4.** Water softening by Clarke's process does **NOT** uses :-

(A) Calcium bicarbonate (B) Sodium bicarbonate

(C) Potash alum (D) Calcium hydroxide

**5.** Which of the following produces hydrolith with dihydrogen ?

(A) Mg (B) Al (C) Cu (D) Ca

**6.** Which process is/are used to remove permanent hardness?

(A) Boiling (B) Clark's method

(C) On reaction with with NaOH (D) Permutit process

**7.** Ionic hydrides is/are usually :-

(A) Good electrically conductors when solid (B) Easily reduced

(C) Good reducing agents (D) Liquid at room temperature

**8.** Which of the following will produce hydrogen gas?

(A) Reaction between Fe and dil. HCl

(B) Reaction between Zn and conc. $H_2SO_4$

(C) Reaction between Zn and NaOH

(D) Electrolysis of NaCl (aq.) in Nelson's cell

**9.** Ortho-hydrogen and para-hydrogen resembles in which of the following property?

(A) Thermal conductivity (B) Magnetic properties

(C) Chemical properties (D) Heat capacity

**10.** Which of the following statements concerning protium, deuterium and tritium is / are true?

(A) They are isotopes of each other

(B) They have similar electronic configurations

(C) They exist in the nature in the ratio of 1 : 2 : 3

(D) Their mass numbers are in the ratio of 1 : 2 : 3

**11.** Ionic hydrides are formed by :-

(A) Transition metals

(B) Elements of very high electropositivity

(C) Elements of very low electropositivity

(D) Metalloids

**12.** Which of the following statements is/are correct?

(A) Atomic hydrogen is obtained by passing hydrogen gas through an electric arc

(B) 30% (w/v) or 100V $H_2O_2$ solution is not called per hydrol.

(C) Finely divided palladium absorbs large volume of hydrogen gas.

(D) Ortho and para hydrogen have same physical properties.

**13.** Which hydride is/are an ionic hydride?

(A) $NH_3$ (B) $H_2S$ (C) $TiH_{1.73}$ (D) NaH

**14.** Which of the following hydride is/are "electron-precise' type ?

(A) HF (B) $H_2O$ (C) $SiH_4$ (D) $PH_3$

**15.** Hydrogen peroxide can act as a :-

(A) A reducing agent (B) An oxidising agent

(C) A dehydrating agent (D) A bleaching agent

## EXERCISE (JM)

**1.** Which one of the following processes will produce hard water :- **[AIEEE 2003]**

(1) Saturation of water with $CaSO_4$ (2) Addition of $Na_2SO_4$ to water

(3) Saturation of water with $CaCO_3$ (4) Saturation of water with $MgCO_3$

**2.** Very pure hydrogen (99.9%) can be made by which of the following processes?

(1) Reaction of salt like hydrides with water **[AIEEE 2012]**

(2) Reaction of methane with steam

(3) Mixing natural hydrocarbons of high molecular weight

(4) Electrolysis of water

**3.** In which of the following reaction $H_2O_2$ acts as a reducing agent ? **[JEE(Main) 2014]**

(a) $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (b) $H_2O_2 - 2e^- \rightarrow O_2 + 2H^+$

(c) $H_2O_2 + 2e^- \rightarrow 2OH^-$ (d) $H_2O_2 + 2OH^- - 2e^- \rightarrow O_2 + 2H_2O$

(1) (a), (c) (2) (b), (d) (3) (a), (b) (4) (c), (d)

**4.** Which of the following statements about $Na_2O_2$ is **not** correct ? **[JEE(Main) 2014]**

(1) $Na_2O_2$ oxidises $Cr^{3+}$ to $CrO_4^{2-}$ in acid medium

(2) It is diamagnetic in nature

(3) It is the super oxide of sodium

(4) It is a derivative of $H_2O_2$

**5.** Hydrogen peroxide acts both as an oxidising and as a reducing agent depending upon the nature of the reacting species. In which of the following cases $H_2O_2$ acts as a reducing agent in acid medium ? :- **[JEE(Main)Online-2014]**

(1) $MnO_4^-$ (2) $SO_3^{2-}$ (3) KI (4) $Cr_2O_7^{2-}$

**6.** Permanent hardness in water cannot be cured by: **[JEE(Main)Online-2015]**

(1) Treatment with washing soda (2) Calgon's method

(3) Boiling (4) Ion exchange method

**7.** From the following statements regarding $H_2O_2$, choose the incorrect statement :

(1) It has to be stored in plastic or wax lined glass bottles in dark **[JEE(Main)Online-2015]**

(2) It has to be kept away from dust

(3) It can act only as an oxidizing agent

(4) It decomposes on exposure to light

**8.** In which of the following reaction, hydrogen peroxide acts as an oxidizing agent ?

(1) $I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$ **[JEE(Main)-2017]**

(2) $HOCl + H_2O_2 \rightarrow H_3O^+ + Cl^- + O_2$

(3) $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$

(4) $2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$

**9.** Hydrogen peroxide oxidises $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ in acidic medium but reduces $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ in alkaline medium. The other products formed are, respectively :

(1) $(H_2O + O_2)$ and $(H_2O + OH^-)$ **[JEE(Main) -2018]**

(2) $H_2O$ and $(H_2O + O_2)$

(3) $H_2O$ and $(H_2O + OH^-)$

(4) $(H_2O + O_2)$ and $H_2O$

**10.** The chemical nature of hydrogen preoxide is :- **[JEE(Main) -2019]**

(1) Oxidising and reducing agent in acidic medium, but not in basic medium.

(2) Oxidising and reducing agent in both acidic and basic medium

(3) Reducing agent in basic medium, but not in acidic medium

(4) Oxidising agent in acidic medium, but not in basic medium.

**11.** The total number of isotopes of hydrogen and number of radioactive isotopes among them, respectively, are : **[JEE(Main) -2019]**

(1) 2 and 0 (2) 3 and 2 (3) 3 and 1 (4) 2 and 1

**12.** The correct statements among (a) to (d) regarding $H_2$ as a fuel are : **[JEE(Main) -2019]**

(a) It produces less pollutant than petrol

(b) A cylinder of compressed dihydrogen weighs ~ 30 times more than a petrol tank producing the same amount of energy

(c) Dihydrogen is stored in tanks of metal alloys like $NaNi_5$

(d) On combustion, values of energy released per gram of liquid dihydrogen and LPG are 50 and 142 kJ, respectively

(1) b and d only (2) a, b and c only (3) b, c and d only (4) a and c only

**13.** The correct statements among (a) to (b) are: **[JEE(Main) -2019]**

(a) saline hydrides produce $H_2$ gas when reacted with $H_2O$.

(b) reaction of $LiAH_4$ with $BF_3$ leads to $B_2H_6$.

(c) $PH_3$ and $CH_4$ are electron - rich and electron-precise hydrides, respectively.

(d) HF and $CH_4$ are called as molecular hydrides.

(1) (c) and (d) only (2) (a), (b) and (c) only

(3) (a), (b), (c) and (d) (4) (a), (c) and (d) only

**14.** In comparison to the zeolite process for the removal of permanent hardness, the synthetic resins method is : **[JEE(Main) -2020]**

(1) less efficient as it exchanges only anions

(2) more efficient as it can exchange only cations

(3) less efficient as the resins cannot be regenerated

(4) more efficient as it can exchange both cations as well as anions

**15.** Hydrogen has three isotopes (A), (B) and (C). If the number of neutron(s) in (A), (B) and (C) respectively, are (x), (y) and (z), the sum of (x), (y) an (z) is : **[JEE(Main) -2020]**

(1) 4 (2) 3 (3) 2 (4) 1

**16.** Among the statements (a) - (d), the correct ones are - **[JEE(Main) -2020]**

(a) Decomposition of hydrogen peroxide gives dioxygen

(b) Like hydrogen peroxide, compounds , such as $KClO_3$, $Pb(NO_3)_2$ and $NaNO_3$when heated liberated dioxygen

(c) 2-Ethylanthraquinone is useful for the industrial preparation of hydrogen peroxide.

(d) Hydrogen peroxide is used for the manufacture of sodium perborate

(1) (a), (b) and (c) only (2) (a) and (c) only

(3) (a), (b) , (c) and (d) (4) (a), (c) and (d) only

## EXERCISE (JA)

**1.** When zeolite (hydrated sodium aluminium silicate) is treated with hard water, the sodium ions are exchanged with :- **[IIT 1990]**

(A) $H^+$ ions (B) $Ca^{2+}$ ions (C) $SO_4^{2-}$ ions (D) $OH^-$ ions

**2.** Which of the following statement is correct?

(A) Hydrogen has same ionisation potential as sodium

(B) H has same electronegativity as halogens

(C) It will not be liberated at anode

(D) H has oxidation state + 1, zero and – 1

**3.** Polyphosphates are used as water softening agent becuase they :- **[IIT 2002]**

(A) Form soluble complexes with anionic species

(B) Precipitate anionic species

(C) Form soluble complexes with cationic species

(D) Precipitate cationic species.

**4.** Hydrogen peroxide in its reaction with $KIO_4$ and $NH_2OH$ respectively, is acting as a

(A) reducing agent, oxidising agent **[JEE Adv. 2014]**

(B) reducing agent, reducing agent

(C) oxidising agent, oxidising agent

(D) oxidising agent, reducing agent

**5.** Which of the following combination will produce $H_2$ gas? **[JEE Adv. 2017]**

(A) Zn metal and NaOH(aq.)

(B) Au metal and NaCN(aq.) in the presence of air

(C) Cu metal and conc. $HNO_3$

(D) Fe metal and conc. $HNO_3$

# ANSWER KEY

## EXERCISE (S-1)

| Que. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Ans. | 4 | 3 | 3 | 0 | 9 |

## EXERCISE (O-1)

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | A | D | C | D | A | C | A | A | D | B | B | C | A | A | B |
| Que. | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Ans. | D | B | C | A | C | A | C | B | C | B | D | A | B | A | B |
| Que. | 31 | 32 | 33 | 34 | 35 | | | | | | | | | | |
| Ans. | C | C | B | C | C | | | | | | | | | | |

## EXERCISE (O-2)

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | A,B,D | A,C,D | D | A,B,C | D | D | C | A,C,D | C | A,B,D |
| Que. | 11 | 12 | 13 | 14 | 15 | | | | | |
| Ans. | B | A,C | D | C | A,B,D | | | | | |

## EXERCISE (JM)

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | 1 | 4 | 2 | 3 | 1 | 3 | 3 | 3 | 2 | 2 |
| Que. | 11 | 12 | 13 | 14 | 15 | 16 | | | | |
| Ans. | 3 | 2 | 3 | 4 | 2 | 3 | | | | |

## EXERCISE (JA)

| Que. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Ans. | B | D | C | A | A |

CHAPTER 3

# s-BLOCK ELEMENTS

## Chapter 03 Contents


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# IMPORTANT NOTES

CHAPTER 3

# s-BLOCK ELEMENTS

## OBJECTIVES

**After studying this unit you will be able to :**

- Describe the general characteristics of the alkali metals and their compounds;
- Explain the general characteristics of the alkaline earth metals and their compounds;
- Describe the manufacture, properties and uses of industrially important sodium and calcium compounds including Portland cement :
- Appreciate the biological significance of sodium, potassium, magnesium and calcium.

The *s*-block elements of the Periodic Table are those in which the last electron enters the outermost *s*-orbital. As the *s*-orbital can accommodate only two electrons, two groups (1 & 2) belong to the s-block of the Periodic Table. Group 1 of the Periodic Table consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are collectively known as the *alkali metals*. These are so called because they form hydroxides on reaction with water which are strongly alkaline in nature. The elements of Group 2 include beryllium, magnesium, calcium, strontium, barium and radium. These elements with the exception of beryllium are commonly known as the *alkaline earth metals*. These are so called because their oxides and hydroxides are alkaline in nature and these metal oxides are found in the earth's crust*.

Among the alkali metals sodium and potassium are abundant and lithium, rubidium and caesium have much lower abundances. Francium is highly radioactive; its longest-lived isotope 223Fr has a half-life of only 21 minutes. Of the alkaline earth metals calcium and magnesium rank fifth and sixth in abundance respectively in the earth's crust. Strontium and barium have much lower abundances. Beryllium is rare and radium is the rarest of all comprising only 10–10 per cent of igneous rocks.

The general electronic configuration of *s*-block elements is [noble gas]*ns*1 for alkali metals and [noble gas] $ns^2$ for alkaline earth metals.

* *The thin, rocky outer layer of the Earth is crust.* † *A type of rock formed from magma (molten rock) that has cooled and hardened.*

Lithium and beryllium, the first elements of Group 1 and Group 2 respectively exhibit some properties which are different from those of the other members of the respective group. In these anomalous properties they resemble the second element of the following group. Thus, lithium shows similarities to magnesium and beryllium to aluminium in many of their properties. This type of diagonal similarity is commonly referred to as *diagonal relationship* in the periodic table.

The diagonal relationship is due to the similarity in ionic sizes and /or charge/radius ratio of the elements. Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.

## 10.1 GROUP 1 ELEMENTS : ALKALI METALS

The alkali metals show regular trends in their physical and chemical properties with the increasing atomic number. The atomic, physical and chemical properties of alkali metals are discussed below.

### 10.1.1 Electronic Configuration

All the alkali metals have one valence electron, $ns^1$ outside the noble gas core. The loosely held *s*-electron in the outermost valence shell of these elements makes them the most electropositive metals. They readily lose electron to give monovalent $M^+$ ions. Hence they are never found in free state in nature.

| Element | Symbol | Electronic configuration |
|---|---|---|
| Lithium | Li | $1s^2s^1$ |
| Sodium | Na | $1s^2\ 2s^2 2p^6 3s^1$ |
| Potassium | K | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ |
| Rubidium | Rb | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$ |
| Caesium | Cs | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6\ 4d^{10} 5s^6 5p^6 6s^1$ or [Xe] $6s^1$ |
| Francium | Fr | $[Rn]7s^1$ |

### 10.1.2 Atomic and Ionic Radii

Li < Na < K < Rb < Cs

Increase down the group, because value of n (principal quantum number) increases.

### 10.1.3 Ionization Enthalpy

Li > Na > K > Rb > Cs.

This is because the effect of increasing size outweighs the increasing nuclear charge, and the outermost electron is very well screened from the nuclear charge.

### 10.1.4 Hydration Enthalpy

The hydration enthalpies of alkali metal ions decrease with increase in ionic sizes.

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

$Li^+$ has maximum degree of hydration and for this reason lithium salts are mostly hydrated,

e.g., $LiCl \cdot 2H_2O$

### 10.1.5 Physical Properties

(i) All the alkali metals are silvery white, soft and light metals.

(ii) Because of the large size, these elements have low density which increases down the group from Li to Cs. However, potassium is lighter than sodium.

Li < **K** < Na < Rb < Cs.

(iii) The melting and boiling points of the alkali metals are low indicating weak metallic bonding due to the presence of only a single valence electron in them.

(iv) The alkali metals and their salts impart characteristic colour to an oxidizing flame. This is because the heat from the flame excites the outermost orbital electron to a higher energy level. When the excited electron comes back to the ground state, there is emission of radiation in the visible region as given below :

| Metal | Li | Na | K | Rb | Cs |
|---|---|---|---|---|---|
| Colour | Crimson red | Yellow | Violet | Red violet | Blue |
| $\lambda$/nm | 670.8 | 589.2 | 766.5 | 780.0 | 455.5 |

(v) Alkali metals can therefore, be detected by the respective flame tests and can be determined by flame photometry or atomic absorption spectroscopy.

(vi) These elements when irradiated with light, the light energy absorbed may be sufficient to make an atom lose electron.

**Table : Atomic and Physical Properties of the Alkali Metals**

| Property | Lithium Li | Sodium Na | Potassium K | Rubidium Rb | Caesium Cs | Francium Fr |
|---|---|---|---|---|---|---|
| Atomic number | 3 | 11 | 19 | 37 | 55 | 87 |
| Atomic mass (g $mol^{-1}$) | 6.94 | 22.99 | 39.10 | 85.47 | 132.91 | (223) |
| Electronic configuration | $[He]2s^1$ | $[Ne]\ 3s^1$ | $[Ar]\ 4s^1$ | $[Kr]\ 5s^1$ | $[Xe]\ 6s^1$ | $[Rn]\ 7s^1$ |
| Ionization enthalpy/kJ $mol^{-1}$ | 520 | 496 | 419 | 403 | 376 | ~375 |
| Hydration enthalpy/kJ $mol^{-1}$ | –506 | –406 | –330 | –310 | –276 | - |
| Metallic radius/pm | 152 | 186 | 227 | 248 | 265 | - |
| Ionic radius $M^+$/pm | 76 | 102 | 138 | 152 | 167 | (180) |
| m.p./K | 454 | 371 | 336 | 312 | 302 | - |
| b.p/K | 1615 | 1156 | 1032 | 961 | 944 | - |
| Density / g $cm^{-3}$ | 0.53 | 0.97 | 0.86 | 1.53 | 1.90 | - |
| Standard Potentials $E^{\ominus}$ /V for ($M^+$/M) | –3.04 | –2.714 | –2.925 | –2.930 | –2.927 | - |
| Occurrence in lithosphere | 18* | 2.27** | 1.84** | 78-12* | 2-6* | ~$10^{-18}$* |

**ppm (part per million), ** percentage by weight; † Lithosphere: The Earth's outer layer: its crust and part of the upper mantle.*

This property makes caesium and potassium useful as electrodes in photoelectric cells.

### 10.1.6 Chemical Properties

The alkali metals are highly reactive due to their large size and low ionization enthalpy. The reactivity of these metals increases down the group.

***(i)*** ***Reactivity towards air :*** The alkali metals tarnish in dry air due to the formation of their oxides which in turn react with moisture to form hydroxides. They burn vigorously in oxygen forming oxides. Lithium forms monoxide, sodium forms peroxide, the other metals form superoxides. The superoxide $O_2^-$ ion is stable only in the presence of large cations such as K, Rb, Cs.

$$4Li + O_2 \rightarrow 2Li_2O \text{ (oxide)}$$

$$2Na + O_2 \rightarrow Na_2O_2 \text{ (peroxide)}$$

$$M + O_2 \rightarrow MO_2 \text{ (superoxide)}$$

(M = K, Rb, Cs)

In all these oxides the oxidation state of the alkali metal is +1. Lithium shows exceptional behaviour in reacting directly with nitrogen of air to form the nitride, $Li_3N$ as well. Because of their high reactivity towards air and water, **alkali metals are normally kept in kerosene oil.**

**Problem 10.1**

What is the oxidation state of K in $KO_2$ ?

**Solution**

The superoxide species is represented as $O_2^-$ ; since the compound is neutral, therefore, the oxidation state of potassium is +1.

***(ii)*** ***Reactivity towards water :*** The alkali metals react with water to form hydroxide and dihydrogen.

$$2M + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2$$

(M = an alkali metal)

It may be noted that although lithium has most negative $E^\ominus$ value , its reaction with water is less vigorous than that of sodium which has the least negative $E^\ominus$ value among the alkali metals. This behaviour of lithium is attributed to its small size and very high hydration energy. Other metals of the group react explosively with water.

They also react with proton donors such as alcohol, gaseous ammonia and alkynes.

***(iii)*** ***Reactivity towards dihydrogen:*** The alkali metals react with dihydrogen at about 673K (lithium at 1073K) to form hydrides. All the alkali metal hydrides are ionic solids with high melting points.

$$2M + H_2 \rightarrow 2M^+H^-$$

*(iv)* ***Reactivity towards halogens :*** The alkali metals readily react vigorously with halogens to form ionic halides, M+X–. However, lithium halides are somewhat covalent. It is because of the high polarisation capability of lithium ion (The distortion of electron cloud of the anion by the cation is called polarisation). The Li+ ion is very small in size and has high tendency to distort electron cloud around the negative halide ion. Since anion with large size can be easily distorted, among halides, lithium iodide is the most covalent in nature.

*(v)* ***Reducing nature :*** The alkali metals are strong reducing agents, lithium being the most and sodium the least powerful. The standard electrode potential ( $E^{\ominus}$ ) which measures the reducing power represents the overall change :

$M(s) \rightarrow M(g)$ sublimationenthalpy

$M(g) \rightarrow M^{+}(g) + e^{-}$ ionizationenthalpy

$M^{+}(g) + H_2O \rightarrow M^{+}(aq)$ hydrationenthalpy

With the small size of its ion, lithium has the highest hydration enthalpy which accounts for its high negative $E^{\ominus}$ value and its high reducing power.

**Problem 10.2**

The $E^{\ominus}$ for $Cl_2/Cl^{-}$ is +1.36, for $I_2/I^{-}$ is + 0.53, for $Ag^{+}$ /Ag is +0.79, $Na^{+}$/Na is –2.71 and for Li+ /Li is – 3.04. Arrange the following ionic species in decreasing order of reducing strength :

$I^{-}$, Ag, $Cl^{-}$, Li, Na

**Solution**

The order is Li > Na > I– > Ag > Cl–

*(vi)* ***Solutions in liquid ammonia :*** The alkali metals dissolve in liquid ammonia giving deep blue solutions which are conducting in nature.

$$M+(x + y)NH_3 \rightarrow [M(NH_3)_x]^{+} + [e(NH_3)y]^{-}$$

The blue colour of the solution is due to the ammoniated electron which absorbs energy in the visible region of light and thus imparts blue colour to the solution. The solutions are paramagnetic and on standing slowly liberate hydrogen resulting in the formation of amide.

$M^{+}_{(am)} + e^{-} + NH_3(1) \rightarrow MNH_{2(am)} + ½H_2(g)$ (where 'am' denotes solution in ammonia.) In concentrated solution, the blue colour changes to bronze colour and becomes diamagnetic.

*(vii)* ***Reaction with $H_2$***

They react with $H_2$ forming metal hydride with formula MH which are of ionic nature. Stability of hydride decreases down the group.

***(viii) Reaction with $N_2$***

Only Lithium reacts with $N_2$ to form ionic lithium nitride $Li_3N$.

$$3Li + \frac{3}{2}N_2 \rightarrow Li_3N$$

***(ix) Sulphides***

All metals react with S forming sulphides such as $Na_2S$ and $Na_2S_n$ (n = 2, 3, 4, 5 or 6). The polysulphide ions are made from zig-zag chains of sulphur atoms.

***(x) Crown Ethers and Cryptands :***

Dibenzo-18-Crown-6

Cryptand - 222

[Na (Cryptand 222)]$^+$ $Na^-$

[$Cs^+$(Cryptand - 222)]

[Contains $Na^-$ (sodide ion)]

[(Cyrptand-222)$e^-$] [electride]

**10.1.7 Uses :**

Lithium metal is used to make useful alloys, for example with lead to make 'white metal' bearings for motor engines, with aluminium to make aircraft parts, and with magnesium to make armour plates. It is used in thermonuclear reactions.

Lithium is also used to make electrochemical cells. Sodium is used to make a Na/Pb alloy needed to make $PbEt_4$ and $PbMe_4$. These organolead compounds were earlier used as anti-knock additives to petrol, but nowadays vehicles use lead-free petrol. Liquid sodium metal is used as a coolant in fast breeder nuclear reactors. Potassium has a vital role in biological systems. Potassium chloride is used as a fertilizer. Potassium hydroxide is used in the manufacture of soft soap. It is also used as an excellent absorbent of carbon dioxide. Caesium is used in devising photoelectric cells.

## 10.2 GENERAL CHARACTERISTICS OF THE COMPOUNDS OF THE ALKALI METALS

All the common compounds of the alkali metals are generally ionic in nature. General characteristics of some of their compounds are discussed here.

### 10.2.1 Oxides and Hydroxides

On combustion in excess of air, lithium forms mainly the oxide, $Li_2O$ (plus some peroxide $Li_2O_2$), sodium forms the peroxide, $Na_2O_2$ (and some oxide $Na_2O$) whilst potassium, rubidium and caesium form the superoxides, $MO_2$. Under appropriate conditions pure compounds $M_2O$, $M_2O_2$ and $MO_2$ may be prepared. The increasing stability of the peroxide or superoxide, as the size of the metal ion increases, is due to the stabilisation of large anions by larger cations through lattice energy effects. These oxides are easily hydrolysed by water to form the hydroxides according to the following reactions :

$$M_2O + H_2O \rightarrow 2M^+ + 2OH^-$$

$$M_2O_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2$$

$$2MO_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2 + O_2$$

The oxides and the peroxides are colourless when pure, but the superoxides are yellow or orange in colour. The superoxides are also paramagnetic. Sodium peroxide is widely used as an oxidising agent in inorganic chemistry.

**Problem 10.3**

Why is $KO_2$ paramagnetic ?

**Solution**

The superoxide $O_2^-$ is paramagnetic because of one upaired electron in $\pi^*2p$ molecular orbital. The hydroxides which are obtained by the reaction of the oxides with water are all white crystalline solids. The alkali metal hydroxides are the strongest of all bases and dissolve freely in water with evolution of much heat on account of intense hydration.

***Sodium Oxide ($Na_2O$) :***

***Preparation :***

(i) It is obtained by burning sodium at 180°C in a limited supply of air or oxygen and distilling off the excess of sodium in vacuum.

$$2Na + \frac{1}{2}O_2 \xrightarrow{180^\circ} Na_2O$$

(ii) By heating sodium peroxide, nitrate or nitrite with sodium.

$$Na_2O_2 + 2Na \xrightarrow{\Delta} 2Na_2O$$

$$2NaNO_3 + 10Na \xrightarrow{\Delta} 6Na_2O + N_2$$

$$2NaNO_2 + 6Na \xrightarrow{\Delta} 4Na_2O + N_2$$

***Properties :***

**(i)** It is white amorphous mass.

**(ii)** It decomposes at 400°C into sodium peroxide and sodium

$$2Na_2O \xrightarrow{400°C} Na_2O_2 + 2Na$$

**(iii)** It dissolve violently in water, yielding caustic soda.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

***Sodium Peroxides ($Na_2O_2$) :***

***Preparation:*** It is formed by heating the metal in excess of air or oxygen at 300°, which is free from moisture and $CO_2$.

$$2Na + O_2 \longrightarrow Na_2O_2$$

***Properties:***

**(i)** It is a pale yellow solid, becoming white in air from the formation of a film of NaOH and $Na_2CO_3$.

**(ii)** In cold water (~0°C) produces $H_2O_2$ but at room temperature produces $O_2$. In ice-cold mineral acids also produces $H_2O_2$.

$$Na_2O_2 + 2H_2O \xrightarrow{\sim 0°C} 2NaOH + H_2O_2$$

$$2Na_2O_2 + 2H_2O \xrightarrow{25°C} 4NaOH + O_2$$

$$Na_2O_2 + H_2SO_4 \xrightarrow{\sim 0°C} Na_2SO_4 + H_2O_2$$

**(iii)** It reacts with $CO_2$, giving sodium carbonate and oxygen and hence its use for purifying air in a confined space e.g. submarine, ill-ventilated room,

$$2Na_2O_2 + 2CO_2 \longrightarrow 2Na_2CO_3 + O_2$$

**(iv)** It is an oxidising agent and oxidises charcoal, CO, $NH_3$, $SO_2$.

$3Na_2O_2 + 2C \longrightarrow 2Na_2CO_3 + 2Na$ [deposition of metallic Na]

$$CO + Na_2O_2 \longrightarrow Na_2CO_3$$

$$SO_2 + Na_2O_2 \longrightarrow Na_2SO_4$$

$$2NH_3 + 3Na_2O_2 \longrightarrow 6NaOH + N_2$$

**(v)** It contains peroxide ion $[-O-O-]^{-2}$

***Uses:***

**(i)** For preparing $H_2O_2$, $O_2$

**(ii)** Oxygenating the air in submarines

**(iii)** Oxidising agent in the laboratory.

***Oxides of Potassium :***

| | $K_2O$, | $K_2O_2$, | $K_2O_3$, | $KO_2$ | and | $KO_3$ |
|---|---|---|---|---|---|---|
| ***Colours :*** | White | White | Red | Bright Yellow | | Orange Solid |

***Preparation :***

**(i)** $2KNO_3 + 10K \xrightarrow{\text{heating}} 6K_2O + N_2$

** $K_2O \xrightarrow{\text{heating}} K_2O$

(White) (Yellow)

** $K_2O + H_2O \longrightarrow 2KOH$

**(ii)** $2K + O_2 \xrightarrow[\text{air at 300°C}]{\text{Controlled}} K_2O_2$ [Props: Similar with $Na_2O_2$]

**(iii)** Passage of $O_2$ through a blue solution of K in liquid $NH_3$ yields oxides $K_2O_2$ (white), $K_2O_3$ (red) and $KO_2$ (deep yellow) i.e

$$\text{K in liq. } NH_3 \xrightarrow{O_2} \underset{\text{white}}{K_2O_2} \longrightarrow \underset{\text{red}}{K_2O_3} \longrightarrow \underset{\text{yellow}}{KO_2}$$

** $KO_2$ reacts with $H_2O$ and produces $H_2O_2$ and $O_2$ both

$$2KO_2 + 2H_2O \xrightarrow{\sim 0°C} 2KOH + H_2O_2 + O_2$$

**$KO_3$ :** KOH + $O_3$ (ozonised oxygen) $\xrightarrow{-10°\text{to}-15°C}$ $KO_3$

(Dry powdered) (orange solid)

### 10.2.2 Halides

The alkali metal halides, MX, (X=F,Cl,Br,I) are all high melting, colourless crystalline solids. They can be prepared by the reaction of the appropriate oxide, hydroxide or carbonate with aqueous hydrohalic acid (HX). All of these halides have high negative enthalpies of formation; the $\Delta_f H^\ominus$ values for fluorides become less negative as we go down the group, whilst the reverse is true for $\Delta_f H^\ominus$ for chlorides, bromides and iodides. For a given metal $\Delta_f H^\ominus$ always becomes less negative from fluoride to iodide.

The standard enthalpies of formation of the halides of Group 1 elements at 298 K

### 10.2.3 Salts of Oxo-Acids

Oxo-acids are those in which the acidic proton is on a hydroxyl group with an oxo group attached to the same atom e.g., carbonic acid, $H_2CO_3$ ($OC(OH)_2$; sulphuric acid, $H_2SO_4$ ($O_2S(OH)_2$). The alkali metals form salts with all the oxo-acids. They are generally soluble in water and thermally stable.

Their carbonates ($M_2CO_3$) and in most cases the hydrogencarbonates ($MHCO_3$) also are highly stable to heat. As the electropositive character increases down the group, the stability of the carbonates and hydorgencarbonates increases. Lithium carbonate is not so stable to heat; lithium being very small in size polarises a large $CO_3^{2-}$ ion leading to the formation of more stable $Li_2O$ and $CO_2$. Its hydrogencarbonate does not exist as a solid.

## 10.3 ANOMALOUS PROPERTIES OF LITHIUM

The anomalous behaviour of lithium is due to the : (i) exceptionally small size of its atom and ion, and (ii) high polarising power (i.e., charge/ radius ratio). As a result, there is increased covalent character of lithium compounds which is responsible for their solubility in organic solvents. Further, lithium shows diagonal relationship to magnesium which has been discussed subsequently.

### 10.3.1 Points of Difference between Lithium and other Alkali Metals

**(i)** Lithium is much harder. Its m.p. and b.p. are higher than the other alkali metals.

**(ii)** Lithium is least reactive but the strongest reducing agent among all the alkali metals. On combustion in air it forms mainly monoxide, $Li_2O$ and the nitride, $Li_3N$ unlike other alkali metals.

**(iii)** LiCl is deliquescent and crystallises as a hydrate, $LiCl.2H_2O$ whereas other alkali metal chlorides do not form hydrates.

**(iv)** Lithium hydrogencarbonate is not obtained in the solid form while all other elements form solid hydrogencarbonates.

**(v)** Lithium unlike other alkali metals forms no ethynide on reaction with ethyne.

**(vi)** Lithium nitrate when heated gives lithium oxide, $Li_2O$, whereas other alkali metal nitrates decompose to give the corresponding nitrite.

$$4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$$

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

**(vii)** LiF and $Li_2O$ are comparatively much less soluble in water than the corresponding compounds of other alkali metals.

### 10.3.2 Points of Similarities between Lithium and Magnesium

The similarity between lithium and magnesium is particularly striking and arises because of their similar sizes : atomic radii, Li = 152 pm, Mg = 160 pm; ionic radii : $Li^+$ = 76 pm, $Mg^{2+}$= 72 pm. The main points of similarity are :

**(i)** Both lithium and magnesium are harder and lighter than other elements in the respective groups.

**(ii)** Lithium and magnesium react slowly with water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride, $Li_3N$ and $Mg_3N_2$, by direct combination with nitrogen.

**(iii)** The oxides, $Li_2O$ and MgO do not combine with excess oxygen to give any superoxide.

**(iv)** The carbonates of lithium and magnesium decompose easily on heating to form the oxides and $CO_2$. Solid hydrogencarbonates are not formed by lithium and magnesium.

**(v)** Both LiCl and $MgCl_2$ are soluble in ethanol.

**(vi)** Both LiCl and $MgCl_2$ are deliquescent and crystallise from aqueous solution as hydrates, $LiCl{\cdot}2H_2O$ and $MgCl_2{\cdot}8H_2O$.

## 10.4 SOME IMPORTANT COMPOUNDS OF SODIUM

Industrially important compounds of sodium include sodium carbonate, sodium hydroxide, sodium chloride and sodium bicarbonate. The large scale production of these compounds and their uses are described below :

***Sodium Carbonate (Washing Soda),*** **$Na_2CO_3 \cdot 10H_2O$**

Sodium carbonate is generally prepared by **Solvay Process**. In this process, advantage is taken of the low solubility of sodium hydrogencarbonate whereby it gets precipitated in the reaction of sodium chloride with ammonium hydrogencarbonate. The latter is prepared by passing $CO_2$ to a concentrated solution of sodium chloride saturated with ammonia, where ammonium carbonate followed by ammonium hydrogencarbonate are formed.

The equations for the complete process may be written as:

$$2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2\,CO_3$$

$$(NH_4)_2\,CO_3 + H_2O + CO_2 \rightarrow 2NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$$

Sodium hydrogencarbonate crystal separates. These are heated to give sodium carbonate.

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

In this process $NH_3$ is recovered when the solution containing $NH_4Cl$ is treated with $Ca(OH)_2$. Calcium chloride is obtained as a by-product.

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + H_2O$$

It may be mentioned here that Solvay process cannot be extended to the manufacture of potassium carbonate because potassium hydrogencarbonate is too soluble to be precipitated by the addition of ammonium hydrogencarbonate to a saturated solution of potassium chloride.

***Properties :*** Sodium carbonate is a white crystalline solid which exists as a decahydrate, $Na_2CO_3 \cdot 10H_2O$. This is also called washing soda. It is readily soluble in water. On heating, the decahydrate loses its water of crystallisation to form monohydrate. Above 373K, the monohydrate becomes completely anhydrous and changes to a white powder called soda ash.

$$Na_2CO_2.10H_2O \xrightarrow{375K} Na_2CO_3.H_2O + 9H_2O$$

$$Na_2CO_3.H_2O \xrightarrow{>373K} Na_2CO_3 + H_2O$$

Carbonate part of sodium carbonate gets hydrolysed by water to form an alkaline solution.

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$$

***Uses:*** **(i)** It is used in water softening, laundering and cleaning.

**(ii)** It is used in the manufacture of glass, soap, borax and caustic soda.

**(iii)** It is used in paper, paints and textile industries.

**(iv)** It is an important laboratory reagent both in qualitative and quantitative analysis.

**Note:** $K_2CO_3$ cannot be prepared by **Solvey process** because $KHCO_3$ is soluble in water and cannot be separated form $NH_4Cl$.

***Sodium Chloride,* NaCl**

The most abundant source of sodium chloride is sea water which contains 2.7 to 2.9% by mass of the salt. In tropical countries like India, common salt is generally obtained by evaporation of sea water. Approximately 50 lakh tons of salt are produced annually in India by solar evaporation. Crude sodium chloride, generally obtained by crystallisation of brine solution, contains sodium sulphate, calcium sulphate, calcium chloride and magnesium chloride as impurities. Calcium chloride, $CaCl_2$, and magnesium chloride, $MgCl_2$ are impurities because they are deliquescent (absorb moisture easily from the atmosphere).

To obtain pure sodium chloride, the crude salt is dissolved in minimum amount of water and filtered to remove insoluble impurities. The solution is then saturated with hydrogen chloride gas. Crystals of pure sodium chloride separate out. Calcium and magnesium chloride, being more soluble than sodium chloride, remain in solution.

Sodium chloride melts at 1081K. It has a solubility of 36.0 g in 100 g of water at 273 K. The solubility does not increase appreciably with increase in temperature.

***Uses :***

**(i)** It is used as a common salt or table salt for domestic purpose.

**(ii)** It is used for the preparation of $Na_2O_2$, NaOH and $Na_2CO_3$.

**(iii)** It is used to prepare freezing mixture in laboratory [Ice-common salt mixture is called freezing mixture and temperature goes down to –23°C.]

**(iv)** For melting ice and snow on road.

***Sodium Hydroxide (Caustic Soda),* NaOH**

Sodium hydroxide is generally prepared commercially by the electrolysis of sodium chloride in Castner-Kellner cell. A brine solution is electrolysed using a mercury cathode and a carbon anode. Sodium metal discharged at the cathode combines with mercury to form sodium amalgam. Chlorine gas is evolved at the anode. (The anodes are now made of steel coated with titanium. Titanium is very resistance to corrosion)

**Cathode :** $Na^+ + e^- \xrightarrow{Hg} Na - \text{ amalgam}$

**Anode :** $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$

The amalgam is treated with water to give sodium hydroxide and hydrogen gas.

$$2Na\text{-amalgam} + 2H_2O \rightarrow 2NaOH + 2Hg + H_2$$

Sodium hydroxide is a white, translucent solid. It melts at 591 K. It is readily soluble in water to give a strong alkaline solution. Crystals of sodium hydroxide are deliquescent. The sodium hydroxide solution at the surface reacts with the $CO_2$ in the atmosphere to form $Na_2CO_3$.

***Uses :*** It is used in

**(i)** The manufacture of soap, paper, artificial silk and a number of chemicals,

**(ii)** In petroleum refining,

**(iii)** In the purification of bauxite,

**(iv)** In the textile industries for mercerising cotton fabrics, (v) for the preparation of pure fats and oils, and

**(vi)** As a laboratory reagent.

***Sodium Hydrogencarbonate (Baking Soda),* $NaHCO_3$**

Sodium hydrogencarbonate is known as baking soda because it decomposes on heating to generate bubbles of carbon dioxide (leaving holes in cakes or pastries and making them light and fluffy).

Sodium hydrogencarbonate is made by saturating a solution of sodium carbonate with carbon dioxide. The white crystalline powder of sodium hydrogencarbonate, being less soluble, gets separated out.

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$$

Sodium hydrogencarbonate is a mild antiseptic for skin infections. **It is used in fire extinguishers.**

***Potassium carbonate,* $K_2CO_3$**

It is also called potash or pearl ash. It cannot be made by the use of solvay process as potassium bicarbonate is more soluble than sodium bicarbonate. However, it can be prepared by **Le-Blanc process**. KCl is first converted into $K_2SO_4$. Potassium sulphate ($K_2SO_4$) is then heated with $CaCo_3$ and carbon.

$$KCl + H_2SO_4 \longrightarrow KHSO_4 + HCl$$

$$KHSO_4 + KCl \longrightarrow K_2SO_4 + HCl$$

$$K_2SO_4 + CaCO_3 + 2C \longrightarrow K_2CO_3 + CaS + 2CO_2$$

It is a white powder , deliquescent in nature. It is highly soluble in water.

**Uses :** It is used in the manufacture of hard glass. The mixture of $K_2CO_3$ and $Na_2CO_3$ is used a **fusion mixture** in laboratory.

## 10.5 BIOLOGICAL IMPORTANCE OF SODIUM AND POTASSIUM

A typical 70 kg man contains about 90 g of Na and 170 g of K compared with only 5 g of iron and 0.06 g of copper. Sodium ions are found primarily on the outside of cells, being located in blood plasma and in the interstitial fluid which surrounds the cells. These ions participate in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and amino acids into cells. Sodium and potassium, although so similar chemically, differ quantitatively in their ability to penetrate cell membranes, in their transport mechanisms and in their efficiency to activate enzymes.

Thus, potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and, with sodium, are responsible for the transmission of nerve signals.

There is a very considerable variation in the concentration of sodium and potassium ions found on the opposite sides of cell membranes. As a typical example, in blood plasma, sodium is present to the extent of 143 $mmolL^{-1}$, whereas the potassium level is only 5 $mmolL^{-1}$ within the red blood cells. These concentrations change to 10 $mmolL^{-1}$ ($Na^+$) and 105 $mmolL^{-1}$ ($K^+$). These ionic gradients demonstrate that a discriminatory mechanism, called the sodium-potassium pump, operates across the cell membranes which consumes more than one-third of the ATP used by a resting animal and about 15 kg per 24 h in a resting human.

## 10.6 GROUP 2 ELEMENTS : ALKALINE EARTH METALS

The group 2 elements comprise beryllium, magnesium, calcium, strontium, barium and radium. They follow alkali metals in the periodic table. These (except beryllium) are known as alkaline earth metals. The first element beryllium differs from the rest of the members and shows diagonal relationship to aluminium. The atomic and physical properties of the alkaline earth metals are shown in Table.

### 10.6.1 Electronic Configuration

These elements have two electrons in the *s* -orbital of the valence shell. Their general electronic configuration may be represented as [noble gas] $ns^2$. Like alkali metals, the compounds of these elements are also predominantly ionic.

| Element | Symbol | Electronic configuration |
|---|---|---|
| Beryllium | Be | $1s^2 2s^2$ |
| Magnesium | Mg | $1s^2 2s^2 2p^6 3s^2$ |
| Calcium | Ca | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ |
| Strontium | Sr | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$ |
| Barium | Ba | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$ or [Xe] $6s^2$ |
| Radium | Ra | [Rn]$7s^2$ |

### 10.6.2 Atomic and Ionic Radii

The atomic and ionic radii of the alkaline earth metals are smaller than those of the

**Table : Atomic and Physical Properties of the Alkaline Earth Metals**

| Property | Beryllium Be | Magnesium mg | Calcium Ca | Strontium Sr | Barium Ba | Radium Ra |
|---|---|---|---|---|---|---|
| Atomic number | 4 | 12 | 20 | 38 | 56 | 88 |
| Atomic mass (g $mol^{-1}$) | 9.01 | 24.31 | 40.08 | 87.62 | 137.33 | 226.03 |
| Electronic configuration | [He]$2s^2$ | [Ne] $3s^2$ | [Ar] $4s^2$ | [Kr] $5s^2$ | [Xe] $6s^2$ | [Rn] $7s^2$ |
| Ionization enthalpy (I)/kJ $mol^{-1}$ | 899 | 737 | 590 | 549 | 503 | 509 |
| Ionization enthyalpy(II) kJ $mol^{-1}$ | 1757 | 1450 | 1145 | 1064 | 965 | 979 |
| Hydration enthalpy/kJ $mol^{-1}$ | –2494 | –1921 | –1577 | –1443 | –1305 | - |
| Metallic radius/pm | 111 | 160 | 197 | 215 | 222 | - |
| Ionic radius $M^+$/pm | 31 | 72 | 100 | 118 | 135 | 148 |
| m.p./K | 1560 | 924 | 1124 | 1062 | 1002 | 973 |
| b.p/K | 2745 | 1363 | 1767 | .1655 | 2078 | (1973) |
| Density / g $cm^{-3}$ | 1.84 | 1.74 | 1.55 | 2.63 | 3.59 | (5.5) |
| Standard Potentials $E^-$ / V for ($M^{+2}$/M) | –1.97 | –2.36 | –2.84 | –2.89 | –2.92 | –2.92 |
| Occurrence in lithosphere | 2* | 2.76** | 4.6** | 384* | 390* | $10^{-6}$* |

**ppm (part per million); ** percentage by weight :*

Corresponding alkali metals in the same periods. This is due to the increased nuclear charge in these elements. Within the group, the atomic and ionic radii increase with increase in atomic number.

### 10.6.3 Ionization Enthalpies

***Ionization Enthalpy***

Be > Mg > Ca > Sr > Ba

Down the group IE decreases due to increase in size

**Q.** $IE_1$ of AM < $IE_1$ of AEM

$IE_2$ of AM > $IE_2$ of AEM

[where AM = Alkali metal, AEM = Alkaline earth metal]

***Reason*** **:** $IE_1$ of AEM is large due to increased nuclear charge in AEM as compared to AM but $IE_2$ of AM is large because second electron in AM is to be removed from cation which has already acquired noble gas configuration.

### 10.6.4 Hydration Enthalpies

Like alkali metal ions, the hydration enthalpies of alkaline earth metal ions decrease with increase in ionic size down the group.

$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Thus, compounds of alkaline earth metals are more extensively hydrated than those of alkali metals, e.g., $MgCl_2$ and $CaCl_2$ exist as $MgCl_2.6H_2O$ and $CaCl_2 \cdot 6H_2O$ while NaCl and KCl do not form such hydrates.

### 10.6.5 Physical Properties

**(i)** The alkaline earth metals, in general, are silvery white, lustrous and relatively soft but harder than the alkali metals. Beryllium and magnesium appear to be somewhat greyish.

**(ii)** The melting and boiling points of these metals are higher than the corresponding alkali metals due to smaller sizes. The trend is, however, not systematic.

**(iii)** Because of the low ionisation enthalpies, they are strongly electropositive in nature. The electropositive character increases down the group from Be to Ba.

**(iv)** Calcium, strontium and barium impart characteristic brick red, crimson and apple green colours respectively to the flame. In flame the electrons are excited to higher energy levels and when they drop back to the ground state, energy is emitted in the form of visible light. The electrons in beryllium and magnesium are too strongly bound to get excited by flame. Hence, these elements do not impart any colour to the flame. The flame test for Ca, Sr and Ba is helpful in their detection in qualitative analysis and estimation by flame photometry.

**(v)** The alkaline earth metals like those of alkali metals have high electrical and thermal conductivities which are typical characteristics of metals.

### 10.6.6 Chemical Properties

The alkaline earth metals are less reactive than the alkali metals. The reactivity of these elements increases on going down the group.

***(i)*** ***Reactivity towards air :*** Beryllium and magnesium are kinetically inert to oxygen and water because of the formation of an oxide film on their surface. However, powdered beryllium burns brilliantly on ignition in air to give BeO and $Be_3N_2$. Magnesium is more electropositive and burns with dazzling brilliance in air to give MgO and $Mg_3N_2$. Calcium, strontium and barium are readily attacked by air to form the oxide and nitride.

**(ii)** ***Reactivity towards water.***

***Reaction with $H_2O$ :*** AEM have lesser tendency to react with water as compared to AM. They form hydroxides and liberate $H_2$ on reaction with $H_2O$

$$M + 2H_2O \xrightarrow{\Delta} M(OH)_2 + H_2$$

* Be is inert towards water.

* Magnesium react as

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

or $$Mg + H_2O \rightarrow MgO + H_2O$$

MgO forms protective layer, that is why it does not react readily unless layer is removed amalgamating with Hg. Other metals react quite readily (Ca, Sr, Ba).

**Note:** $Be(OH)_2$ is amphoteric but other hydroxides are basic in nature.

**(iii)** ***Reactivity towards the halogens :*** All the alkaline earth metals combine with halogen at elevated temperatures forming their halides.

$$M + X_2 \rightarrow MX_2 \ (X = F, Cl, Br, I)$$

Thermal decomposition of $(NH_4)_2BeF_4$ is the best route for the preparation of $BeF_2$, and $BeCl_2$ is conveniently made from the oxide.

$$BeO + C + Cl_2 \xrightleftharpoons{600-800\,K} BeCl_2 + CO$$

**(iv)** ***Reactivity towards hydrogen :*** All the elements except beryllium combine with hydrogen upon heating to form their hydrides, $MH_2$. $BeH_2$, however, can be prepared by the reaction of $BeCl_2$ with $LiAlH_4$.

$$2BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$$

**(v)** ***Reactivity towards acids :*** AEM react with acids & liberate $H_2$

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$

Be is amphoteric as it also react with NaOH, other metals do not react as they are purely basic.

$$Be + 2NaOH \rightarrow Be(OH)_2 \xrightarrow{\text{excess NaOH}} [Be(OH)_4]^{2-}$$

**(vi)** ***Reducing nature :*** Like alkali metals, the alkaline earth metals are strong reducing agents. This is indicated by large negative values of their reduction potentials. However their reducing power is less than those of their corresponding alkali metals. Beryllium has less negative value compared to other alkaline earth metals. However, its reducing nature is due to large hydration energy associated with the small size of $Be^{2+}$ ion and relatively large value of the atomization enthalpy of the metal.

***(vii)*** ***Solutions in liquid ammonia :*** Like alkali metals, the alkaline earth metals dissolve in liquid ammonia to give deep blue black solutions forming ammoniated ions.

$$M + (x + y)\ NH_3 \rightarrow [M(NH_3)_x]^{2+} + 2[e(NH_3)_y]^{-} \text{ (except : Be and Mg)}$$

From these solutions, the ammoniates, $[M(NH_3)_6]^{2+}$ can be recovered.

**10.6.7 Uses :**

**Be :** Beryllium is used in the manufacture of alloys. Copper-beryllium alloys are used in the preparation of high strength springs. Metallic beryllium is used for making windows of X-ray tubes.

**Mg :** Magnesium forms alloys with aluminium, zinc, manganese and tin. Magnesium-aluminium alloys being light in mass are used in air-craft construction. Magnesium (powder and ribbon) is used in flash powders and bulbs, incendiary bombs and signals. A suspension of magnesium hydroxide in water (called *milk of magnesia*) is used as antacid in medicine. Magnesium carbonate is an ingredient of toothpaste.

**Ca :** Calcium is used in the extraction of metals from oxides which are difficult to reduce with carbon. Calcium and barium metals, owing to their reactivity with oxygen and nitrogen at elevated temperatures, have often been used to remove air from vacuum tubes.

**Ra :** Radium salts are used in radiotherapy, for example, in the treatment of cancer.

## 10.7 GENERAL CHARACTERISTICS OF COMPOUNDS OF THE ALKALINE EARTH METALS

The dipositive oxidation state ($M^{2+}$) is the predominant valence of Group 2 elements. The alkaline earth metals form compounds which are predominantly ionic but less ionic than the corresponding compounds of alkali metals. This is due to increased nuclear charge and smaller size. The oxides and other compounds of beryllium and magnesium are more covalent than those formed by the heavier and large sized members (Ca, Sr, Ba). The general characteristics of some of the compounds of alkali earth metals are described below.

***(i)*** ***Oxides and Hydroxides :***

The alkaline earth metals burn in oxygen to form the monoxide, MO which, except for BeO, have rock-salt structure. The BeO is essentially covalent in nature. The enthalpies of formation of these oxides are quite high and consequently they are very stable to heat. BeO is amphoteric while oxides of other elements are ionic in nature. All these oxides except BeO are basic in nature and react with water to form sparingly soluble hydroxides.

$$MO + H_2O \rightarrow M(OH)_2$$

The solubility, thermal stability and the basic character of these hydroxides increase with increasing atomic number from $Mg(OH)_2$ to $Ba(OH)_2$. The alkaline earth metal hydroxides are, however, less basic and less stable than alkali metal hydroxides. Beryllium hydroxide is amphoteric in nature as it reacts with acid and alkali both.

$$Be(OH)_2 + 2OH^- \rightarrow [Be(OH)_4]^{2-}$$

Beryllate ion

$$Be(OH)_2 + 2HCl \rightarrow 2H_2O + BeCl_2$$

***(ii)*** ***Halides :***

Except for beryllium halides, all other halides of alkaline earth metals are ionic in nature. Beryllium halides are essentially covalent and soluble in organic solvents. Beryllium chloride has a chain structure in the solid state as shown below:

In the vapour phase $BeCl_2$ tends to form a chloro-bridged dimer which dissociates into the linear monomer at high temperatures of the order of 1200 K. The tendency to form halide hydrates gradually decreases (for example, $MgCl_2 \cdot 8H_2O$, $CaCl_2 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$) down the group. The dehydration of hydrated chlorides, bromides and iodides of Ca, Sr and Ba can be achieved on heating; however, the corresponding hydrated halides of Be and Mg on heating suffer hydrolysis. The fluorides are relatively less soluble than the chlorides owing to their high lattice energies.

***(iii)*** ***Salts of Oxoacids :*** The alkaline earth metals also form salts of oxoacids. Some of these are :

***Carbonates :*** Carbonates of alkaline earth metals are insoluble in water and can be precipitated by addition of a sodium or ammonium carbonate solution to a solution of a soluble salt of these metals. The solubility of carbonates in water decreases as the atomic number of the metal ion increases. All the carbonates decompose on heating to give carbon dioxide and the oxide. Beryllium carbonate is unstable and can be kept only in the atmosphere of $CO_2$. The thermal stability increases with increasing cationic size.

***Sulphates :*** The sulphates of the alkaline earth metals are all white solids and stable to heat. $BeSO_4$, and $MgSO_4$ are readily soluble in water; the solubility decreases from $CaSO_4$ to $BaSO_4$. The greater hydration enthalpies of $Be^{2+}$ and $Mg^{2+}$ ions overcome the lattice enthalpy factor and therefore their sulphates are soluble in water.

***Nitrates :*** The nitrates are made by dissolution of the carbonates in dilute nitric acid. Magnesium nitrate crystallises with six molecules of water, whereas barium nitrate crystallises as the anhydrous salt. This again shows a decreasing tendency to form hydrates with increasing size and decreasing hydration enthalpy. All of them decompose on heating to give the oxide like lithium nitrate.

$$2M(NO_3)_2 \rightarrow 2MO + 4NO_2 + O_2$$

(M + Be, Mg, Ca, Sr, Ba)

**Problem 10.4**

Why does the solubility of alkaline earth metal hydroxides in water increase down the group?

**Solution**

Among alkaline earth metal hydroxides, the anion being common the cationic radius will influence the lattice enthalpy. Since lattice enthalpy decreases much more than the hydration enthalpy with increasing ionic size, the solubility increases as we go down the group.

**Problem 10.5**

Why does the solubility of alkaline earth metal carbonates and sulphates in water decrease down the group?

**Solution**

The size of anions being much larger compared to cations, the lattice enthalpy will remain almost constant within a particular group. Since the hydration enthalpies decrease down the group, solubility will decrease as found for alkaline earth metal carbonates and sulphates.

## 10.8 ANOMALOUS BEHAVIOUR OF BERYLLIUM

Beryllium, the first member of the Group 2 metals, shows anomalous behaviour as compared to magnesium and rest of the members. Further, it shows diagonal relationship to aluminium which is discussed subsequently.

**(i)** Beryllium has exceptionally small atomic and ionic sizes and thus does not compare well with other members of the group. Because of high ionisation enthalpy and small size it forms compounds which are largely covalent and get easily hydrolysed.

**(ii)** Beryllium does not exhibit coordination number more than four as in its valence shell there are only four orbitals. The remaining members of the group can have a coordination number of six by making use of *d*-orbitals.

**(iii)** The oxide and hydroxide of beryllium, unlike the hydroxides of other elements in the group, are amphoteric in nature.

### 10.8.1 Diagonal Relationship between Beryllium and Aluminium

The ionic radius of $Be^{2+}$ is estimated to be 31 pm; the charge/radius ratio is nearly the same as that of the $Al^{3+}$ ion. Hence beryllium resembles aluminium in some ways. Some of the similarities are:

**(i)** Like aluminium, beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.

**(ii)** Beryllium hydroxide dissolves in excess of alkali to give a beryllate ion, $[Be(OH)_4]^{2-}$ just as aluminium hydroxide gives aluminate ion, $[Al(OH)_4]^-$.

**(iii)** The chlorides of both beryllium and aluminium have $Cl^-$ bridged chloride structure in vapour phase. Both the chlorides are soluble in organic solvents and are strong Lewis acids. They are used as Friedel Craft catalysts.

**(iv)** Beryllium and aluminium ions have strong tendency to form complexes, $BeF_4^{2-}, AlF_6^{3-}$

## 10.9 SOME IMPORTANT COMPOUNDS OF CALCIUM

Important compounds of calcium are calcium oxide, calcium hydroxide, calcium sulphate, calcium carbonate and cement. These are industrially important compounds. The large scale preparation of these compounds and their uses are described below.

***Calcium Oxide or Quick Lime,* CaO**

It is prepared on a commercial scale by heating limestone ($CaCO_3$) in a rotary kiln at 1070-1270 K.

$$CaCO_3 \xrightleftharpoons{\text{heat}} CaO + CO_2$$

The carbon dioxide is removed as soon as it is produced to enable the reaction to proceed to completion. Calcium oxide is a white amorphous solid. It has a melting point of 2870 K. On exposure to atmosphere, it absorbs moisture and carbon dioxide.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$CaO + CO_2 \rightarrow CaCO_3$$

The addition of limited amount of water breaks the lump of lime. This process is called *slaking of lime*. Quick lime slaked with soda gives solid sodalime. Being a basic oxide, it combines with acidic oxides at high temperature.

$$CaO + SiO_2 \rightarrow CaSiO_3$$

$$6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$$

***Uses :*** **(i)** It is an important primary material for manufacturing cement and is the cheapest form of alkali.

**(ii)** It is used in the manufacture of sodium carbonate from caustic soda.

**(iii)** It is employed in the purification of sugar and in the manufacture of dye stuffs.

***Calcium Hydroxide (Slaked lime),*** **$Ca(OH)_2$**

Calcium hydroxide is prepared by adding water to quick lime, CaO.

It is a white amorphous powder. It is sparingly soluble in water. The aqueous solution is known as *lime water* and a suspension of slaked lime in water is known as *milk of lime*.

When carbon dioxide is passed through lime water it turns milky due to the formation of calcium carbonate.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

On passing excess of carbon dioxide, the precipitate dissolves to form calcium hydrogencarbonate.

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca\,(HCO_3)_2$$

Milk of lime reacts with chlorine to form hypochlorite, a constituent of bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \rightarrow CaCl_2 + Ca(OCl)_2 + 2H_2O$$

***Uses:*** **(i)** It is used in the preparation of mortar, a building material.

**(ii)** It is used in white wash due to its disinfectant nature.

**(iii)** It is used in glass making, in tanning industry, for the preparation of bleaching powder and for purification of sugar.

***Calcium Carbonate,*** **$CaCO_3$**

Calcium carbonate occurs in nature in several forms like limestone, chalk, marble etc. It can be prepared by passing carbon dioxide through slaked lime or by the addition of sodium carbonate to calcium chloride.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$$

Excess of carbon dioxide should be avoided since this leads to the formation of water soluble calcium hydrogencarbonate.

Calcium carbonate is a white fluffy powder. It is almost insoluble in water. When heated to 1200 K, it decomposes to evolve carbon dioxide.

$$CaCO_3 \xrightarrow{1200K} CaO + CO_2$$

It reacts with dilute acid to liberate carbon dioxide.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

***Uses:*** It is used as a building material in the form of marble and in the manufacture of quick lime. Calcium carbonate along with magnesium carbonate is used as a flux in the extraction of metals such as iron. Specially precipitated $CaCO_3$ is extensively used in the manufacture of high quality paper. It is also used as an antacid, mild abrasive in tooth paste, a constituent of chewing gum, and a filler in cosmetics.

***Calcium Sulphate (Plaster of Paris),*** **$CaSO_4 \cdot ½ H_2O$**

It is a hemihydrate of calcium sulphate. It is obtained when gypsum, $CaSO_4 \cdot 2H_2O$, is heated to 393 K.

$$2(CaSO_4.2H_2O) \rightarrow 2(CaSO_4).H_2O + 3H_2O$$

Above 393 K, no water of crystallisation is left and anhydrous calcium sulphate, $CaSO_4$ is formed. This is known as 'dead burnt plaster'.

It has a remarkable property of setting with water. On mixing with an adequate quantity of water it forms a plastic mass that gets into a hard solid in 5 to 15 minutes.

***Uses:*** The largest use of Plaster of Paris is in the building industry as well as plasters. It is used for immoblising the affected part of organ where there is a bone fracture or sprain. It is also employed in dentistry, in ornamental work and for making casts of statues and busts.

***Cement:*** Cement is an important building material. It was first introduced in England in 1824 by Joseph Aspdin. It is also called **'Portland cement'** because it resembles with the natural limestone quarried in the Isle of Portland, England.

Cement is a product obtained by combining a material rich in lime, CaO with other material such as clay which contains silica, $SiO_2$ along with the oxides of aluminium, iron and magnesium. The average composition of Portland cement is :

CaO, 50-60%; $SiO_2$, 20-25%; $Al_2O_3$, 5-10%; MgO, 2-3%; $Fe_2O_3$, 1-2% and $SO_3$, 1-2%. For a good quality cement, the ratio of silica ($SiO_2$) to alumina ($Al_2O_3$) should be between 2.5 and 4 and the ratio of lime (CaO) to the total of the oxides of silicon ($SiO_2$) aluminium ($Al_2O_3$) and iron ($Fe_2O_3$) should be as close as possible to 2.

The raw materials for the manufacture of cement are limestone and clay. When clay and lime are strongly heated together they fuse and react to form 'cement clinker'. This clinker is mixed with 2-3% by weight of gypsum ($CaSO_4 \cdot 2H_2O$) to form cement. Thus important ingredients present in Portland cement are dicalcium silicate ($Ca_2SiO_4$) 26%, tricalcium silicate ($Ca_3SiO_5$) 51% and tricalcium aluminate ($Ca_3Al_2O_6$) 11%.

***Setting of Cement :*** When mixed with water, the setting of cement takes place to give a hard mass. This is due to the hydration of the molecules of the constituents and their rearrangement. The purpose of adding gypsum is only to slow down the process of setting of the cement so that it gets sufficiently hardened.

***Uses:*** Cement has become a commodity of national necessity for any country next to iron and steel. It is used in concrete and reinforced concrete, in plastering and in the construction of bridges, dams and buildings.

## 10.10 BIOLOGICAL IMPORTANCE OF MAGNESIUM AND CALCIUM

An adult body contains about 25 g of Mg and 1200 g of Ca compared with only 5 g of iron and 0.06 g of copper. The daily requirement in the human body has been estimated to be 200 – 300 mg. All enzymes that utilise ATP in phosphate transfer require magnesium as the cofactor. The main pigment for the absorption of light in plants is chlorophyll which contains magnesium. About 99 % of body calcium is present in bones and teeth. It also plays important roles in neuromuscular function, interneuronal transmission, cell membrane integrity and blood coagulation. The calcium concentration in plasma is regulated at about 100 $mgL^{-1}$. It is maintained by two hormones: calcitonin and parathyroid hormone. Do you know that bone is not an inert and unchanging substance but is continuously being solubilised and redeposited to the extent of 400 mg per day in man? All this calcium passes through the plasma.

**Summary :** The ***s*-Block** of the periodic table constitutes **Group1** (alkali metals) and **Group 2** (alkaline earth metals). They are so called because their oxides and hydroxides are alkaline in nature. The alkali metals are characterised by one *s*-electron and the alkaline earth metals by two *s*-electrons in the valence shell of their atoms. These are highly reactive metals forming monopositive **($M^+$)** and dipositve **($M^{2+}$)** ions respectively.

There is a regular trend in the physical and chemical properties of the alkali metal with increasing atomic numbers. The **atomic** and **ionic** sizes increase and the **ionization enthalpies** decrease systematically down the group.

Somewhat similar trends are observed among the properties of the alkaline earth metals. The first element in each of these groups, lithium in Group 1 and beryllium in Group 2 shows similarities in properties to the second member of the next group. Such similarities are termed as the **'diagonal relationship'** in the periodic table.

As such these elements are anomalous as far as their group characteristics are concerned.

The alkali metals are silvery white, soft and low melting. They are highly reactive. The compounds of alkali metals are predominantly ionic. Their oxides and hydroxides are soluble in water forming strong alkalies. Important compounds of sodium includes sodium carbonate, sodium chloride, sodium hydroxide and sodium hydrogencarbonate. Sodium hydroxide is manufactured by **Castner-Kellner** process and sodium carbonate by **Solvay** process.

The chemistry of alkaline earth metals is very much like that of the alkali metals. However, some differences arise because of reduced atomic and ionic sizes and increased cationic charges in case of alkaline earth metals. Their oxides and hydroxides are less basic than the alkali metal oxides and hydroxides. Industrially important compounds of calcium include calcium oxide (lime), calcium hydroxide (slaked lime), calcium sulphate **(Plaster of Paris),** calcium carbonate (limestone) and cement. **Portland cement** is an important constructional material.

It is manufactured by heating a pulverised mixture of limestone and clay in a rotary kiln. The clinker thus obtained is mixed with some gypsum (2-3%) to give a fine powder of cement. All these substances find variety of uses in different areas.

Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in **biological fluids**. These ions perform important **biological functions** such as maintenance of ion balance and nerve impulse conduction.

## FEW IMPORTANT POINTS

(i) Magnesium Peroxide ($MgO_2$) and Calcium Peroxide ($CaO_2$) are obtained by passing $H_2O_2$ in a suspension of $Mg(OH)_2$ and $Ca(OH)_2$.

(ii) $MgO_2$ is used as an antiseptic in tooth paste and as a bleaching agent.

(iii) Preperation of NaOH : Caustication of $Na_2CO_3$ (Gossage's method):

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3\downarrow$$

(suspension)

Since the $K_{sp}$ ($CaCO_3$) < $K_{sp}$ ($Ca(OH)_2$), the reaction shifts towards right.

(iv) As a reagent KOH is less frequently used but in absorption of $CO_2$, KOH is preferably used compared to NaOH. Because $KHCO_3$ formed is soluble whereas $NaHCO_3$ is sparingly soluble and may therefore choke the tubes of apparatus used.

(v) Calcium hydroxide is used as a mortar.

[Mortar is a mixture of slaked lime (1 Part) and sand (3 Parts) made into paste with water.]

(vi) NaCl is used to prepare freezing mixture in laboratory [Ice-common salt mixture is called freezing mixture and temperature goes down to –23°C.]

(vii) On heating $MgCl_2 \cdot 6H_2O$ undergoes hydrolysis as follows:

$$MgCl_2 \cdot 6H_2O \xrightarrow{\Delta} Mg(OH)Cl + HCl + 5H_2O$$

$$Mg(OH)Cl \longrightarrow MgO + HCl$$

** Hence, Anh. $MgCl_2$ cannot be prepared by heating this hydrate.

** Because of the formation of HCl , sea water cannot be used in marine boilers which corrodes the iron body.

(viii) Anhydrous $MgCl_2$ can be prepared by heating a double salt like $MgCl_2 . NH_4Cl . 6H_2O$ as follows:

$$MgCl_2 . NH_4Cl . 6H_2O \xrightarrow[\Delta]{-H_2O} MgCl_2 . NH_4Cl \xrightarrow[\Delta]{\text{strong}} MgCl_2 + NH_3 + HCl$$

(ix) Sorel Cement is a mixture of MgO and $MgCl_2$ (paste like) which set to hard mass on standing, this is used in dental filling, flooring etc.

(x) Anh. $CaCl_2$ is used in drying gases and organic compounds but not $NH_3$ or alcohol due to the formation of $CaCl_2 . 8NH_3$ and $CaCl_2 . 4C_2H_5OH$.

(xi) One interesting feature of the solubility of glauber's salt is; when crystallised at below 32.4°C, then $Na_2SO_4 . 10H_2O$ is obtained but above 32.4°C, $Na_2SO_4$ (anh.) comes out.

(xii) Leblanc Process (Preparation of $Na_2CO_3$) :

$$NaCl + H_2SO_4 \text{ (conc.)} \xrightarrow{\text{mild heating}} NaHSO_4 + HCl$$

$$NaCl + NaHSO_4 \xrightarrow[\text{heated}]{\text{Strongly}} \underset{\text{(Salt Cake)}}{Na_2SO_4} + HCl$$

$$Na_2SO_4 + 4C \longrightarrow Na_2S + 4CO\uparrow$$

$$Na_2S + CaCO_3 \longrightarrow Na_2CO_3 + CaS$$

## EXERCISE (S-1)

### NUMERIC GRID TYPE QUESTIONS :

**1.** Find the number of compounds from the following in which the element in the anionic part is in the minimum oxidation state of it

$$LiH,\ Mg_3Bi_2,\ Al_4C_3,\ Ca_3P_2,\ BaO_2$$

**2.** How many nitrate groups are present in 1 molecule of Basic beryllium nitrate?

**3.** Consider the following order :

(1) $CH_4 < CCl_4 < CF_4$ : E.N. of central atom C

(2) $Mg^{+2} < K^+ < S^{-2} < Se^{-2}$ : Ionic radius

(3) $Be^{+2}_{(aq)} > Mg^{+2}_{(aq)} > Ca^{+2}_{(aq)}$ : Ionic mobility

(4) $Be^{+2} > Li^+ > Al^{+3}$ : Hydrated size

(5) Be > Li > Cs : Reducing power

(6) $F^{\ominus}_{(aq)} > Cl^{\ominus}_{(aq)} > Br^{\ominus}_{(aq)}$ : Electrical conductance in infinite dilute solution

Then calculate value of $|x - y|^2$, where x and y are correct and incorrect orders respectively.

**4.** Consider the following elements :

Li, Cs, Mg, Pb, Al, N

- $x$ = number of elements which can form MO type of oxides.
- $y$ = the highest oxidation state shown by any one of them.
- $z$ = the number of elements which can form amphoteric oxide(s).

Find the sum of $x$, $y$ and $z$.

***Fill your answer as sum of digits till you get the single digit answer.***

**5.** Find the number of s-block elements which can produce ammoniated cation and ammoniated electron with liquid ammonia.

Li, Na, K, Rb, Cs, Ca, Sr, Ba

**6.** How many of the following metal chlorides impart characteristic colour to the oxidising flame?

$LiCl,\ NaCl,\ KCl,\ BeCl_2,\ MgCl_2,\ CaCl_2,\ SrCl_2,\ BaCl_2$

# EXERCISE (O-1)

## SELECT THE CORRECT ALTERNATIVE (ONLY ONE CORRECT ANSWER)

### Alkali metals

**1.** $Cs^+$ ions impart violet colour to Bunsen flame. This is due to the fact that the emitted radiations are of -

(A) high energy
(B) lower frequencies
(C) longer wave-lengths
(D) zero wave number

**2.** The reaction of an element A with water produces combustible gas B and an aqueous solution of C. When another substance D reacts with this solution C also produces the same gas B. D also produces the same gas even on reaction with dilute $H_2SO_4$ at room temperature. Element A imparts golden yellow colour to Bunsen flame. Then, A, B, C and D may be identified as

(A) Na, $H_2$, NaOH and Zn
(B) K, $H_2$, KOH and Zn
(C) K, $H_2$, NaOH and Zn
(D) Ca, $H_2$, $CaCOH_2$ and Zn

**3.** Which of the following carbonate of alkali metals has the least thermal stability?

(A) $Li_2CO_3$
(B) $K_2CO_3$
(C) $Cs_2CO_3$
(D) $Na_2CO_3$

**4.** The alkali metals which form normal oxide, peroxide as well as super oxides are

(A) Na, Li
(B) K, Li
(C) Li, Cs
(D) K, Rb

**5.** The pair of compounds, which cannot exist together in a solution is

(A) $NaHCO_3$ and NaOH
(B) $Na_2CO_3$ and NaOH
(C) $NaHCO_3$ and $Na_2CO_3$
(D) $NaHCO_3$ and $H_2O$

**6.** Solution of sodium metal in liquid ammonia is a strong reducing agent due to presence of

(A) solvated sodium ions
(B) solvated hydrogen ions
(C) sodium atoms or sodium hydroxide
(D) solvated electrons

**7.** The order of solubility of lithium halides in non-polar solvents follows the order

(A) LiI > LiBr > LiCl > LiF
(B) LiF > LiI > LiBr > LiCl
(C) LiCl > LiF > LiI > LiBr
(D) LiBr > LiCl > LiF > LiI

**8.** The salt which finds uses in qualitative inorganic analysis is

(A) $CuSO_4 \cdot 5H_2O$ or $ZnSO_4 \cdot 5H_2O$
(B) $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
(C) $Na(NH_4)HPO_4 \cdot 4H_2O$
(D) $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

**9.** Fire extinguishers contain

(A) conc. $H_2SO_4$ solution
(B) $H_2SO_4$ and $NaHCO_3$ solutions
(C) $NaHCO_3$ solution
(D) $CaCO_3$ solution

**10.** $CsBr_3$ contains

(A) Cs–Br covalent bonds
(B) $Cs^{3+}$ and $Br^-$ ions
(C) $Cs^+$ and $Br_3^-$ ions
(D) $Cs^{3+}$ and $Br_3^{3-}$ ions

**11.** $Na + Al_2O_3 \xrightarrow{\text{High temperature}} X \xrightarrow[\text{water}]{CO_2 \text{ in}} Y$; compound Y is

(A) $NaAlO_2$
(B) $NaHCO_3$
(C) $Na_2CO_3$
(D) $Na_2O_2$

**12.** aq. $NaOH + P_4$ (white) $\longrightarrow PH_3 + X$; compound X is

(A) $NaH_2PO_2$
(B) $NaHPO_4$
(C) $Na_2CO_3$
(D) $NaHCO_3$

**13.** When $K_2O$ is added to water, the solution becomes basic in nature because it contains a significant concentration of

(A) $K^+$
(B) $O^{2-}$
(C) $OH^-$
(D) $O_2^{2-}$

**14.** The order of melting point of chlorides of alkali metals is

(A) LiCl > NaCl > KCl < CsCl
(B) LiCl > NaCl > KCl > CsCl
(C) NaCl > KCl > CsCl > LiCl
(D) LiCl > NaCl > CsCl > KCl

**15.** $NaOH(Solid) + CO \xrightarrow{200°C} X$; product X is

(A) $NaHCO_3$
(B) $Na_2CO_3$
(C) HCOONa
(D) $H_2CO_3$

**16.** The aqueous solutions of lithium salts are poor conductor of electricity rather than other alkali metals because of

(A) high ionisation energy
(B) high electronegativity
(C) lower ability of $Li^+$ ions to polarize water molecules
(D) higher degree of hydration of $Li^+$ ions

**17.** In $LiAlH_4$, metal Al is present in

(A) anionic part
(B) cationic part
(C) in both anionic and cationic part
(D) neither in cationic nor in anionic part

**18.** Which one of the following fluoride of alkali metals has the highest lattice energy?

(A) LiF
(B) CsF
(C) NaF
(D) KF

**19.** Crown ethers and cryptands form

(A) complexes with alkali metals

(B) salts of alkali metals

(C) hydroxides of alkali metals used for inorganic quantitative analysis

(D) organic salts of alkali metals

**20.** The correct order of degree of hydration of $M^+$ ions of alkali metals is

(A) $Li^+ < K^+ < Na^+ < Rb^+ < Cs^+$ (B) $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

(C) $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$ (D) $Cs^+ < Rb^+ < Na^+ < K^+ < Li^+$

**21.** The commercial method of preparation of potassium by reduction of molten KCl with metallic sodium at 850°C is based on the fact that

(A) potassium is solid and sodium distils off at 850 °C

(B) potassium being more volatile and distils off thus shifting the reaction forward

(C) sodium is less reactive than potassium at 850 °C with respect to $Cl_2$

(D) sodium has less affinity to chloride ions in the presence of potassium ion

## Alkaline earth metals

**22.** The 'milk of magnesia' used as an antacid is chemically

(A) $Mg(OH)_2$ (B) MgO (C) $MgCl_2$ (D) $MgO + MgCl_2$

**23.** An alkaline earth metal (M) gives a salt with chlorine, which is soluble in water at room temperature. It also forms an insoluble sulphate whose mixture with a sulphide of a transition metal is called 'lithopone' -a white pigment. Metal M is

(A) Ca (B) Mg (C) Ba (D) Sr

**24.** The hydroxide of II$^{nd}$ A metal, which has the lowest value of solubility product ($K_{sp}$) at normal temperature (25°C) is

(A) $Ca(OH)_2$ (B) $Mg(OH)_2$ (C) $Sr(OH)_2$ (D) $Be(OH)_2$

**25.** Which of the following metal is inert towards reaction with $H_2O$?

(A) Be (B) Na (C) Ca (D) K

**26.** $Mg_2C_3 + H_2O \longrightarrow X$ (organic compound). Compound X is

(A) $C_2H_2$ (B) $CH_4$ (C) propyne (D) ethene

**27.** The hydration energy of $Mg^{2+}$ is

(A) more than that of $Mg^{3+}$ ion (B) more than that of $Na^{+}$ ion

(C) more than that of $Al^{3+}$ ion (D) more than that of $Be^{2+}$ ion

**28.** The correct order of second ionisation potentials (IP) of Ca, Ba and K is

(A) K > Ca > Ba (B) Ba > Ca > K (C) K > Ba > Ca (D) K = Ba = Ca

**29.** EDTA is used in the estimation of

(A) $Mg^{2+}$ ions (B) $Ca^{2+}$ ions

(C) both $Ca^{2+}$ and $Mg^{2+}$ ions (D) $Mg^{2+}$ ions but not $Ca^{2+}$ ions

**30.** The correct order of solubility is

(A) $CaCO_3 < KHCO_3 < NaHCO_3$ (B) $KHCO_3 < CaCO_3 < NaHCO_3$

(C) $NaHCO_3 < CaCO_3 < KHCO_3$ (D) $CaCO_3 < NaHCO_3 < KHCO_3$

**31.** The complex formation tendency of alkaline earth metals decreases down the group because

(A) atomic size increases

(B) availability of empty d and f-orbitals increases

(C) nuclear charge to volume ratio increases

(D) all the above

**32.** The alkaline earth metals, which do not impart any colour to Bunsen flame are

(A) Be and Mg (B) Mg and Ca (C) Be and Ca (D) Be and Ba

**33.** $Y \xleftarrow{\Delta, 205°C} CaSO_4 \cdot 2H_2O \xrightarrow{\Delta, 120°C} X$. X and Y are respectively

(A) plaster of paris, dead burnt plaster

(B) dead burnt plaster, plaster of paris

(C) CaO and plaster of paris

(D) plaster of paris, mixture of gases

**34.** A metal M readily forms water soluble sulphate, and water insoluble hydroxide $M(OH)_2$. Its oxide MO is amphoteric, hard and having high melting point. The alkaline earth metal M must be

(A) Mg (B) Be (C) Ca (D) Sr

**35.** The purpose of addition of gypsum in the cement is -

(A) To slow down the process of setting of the cement

(B) To fasten the process of setting of the cement

(C) Not to affect the process of setting of the cement by any means

(D) None of these

**36.** (Milky Cloud) C $\xleftarrow{CO_2}$ A + $Na_2CO_3$ $\longrightarrow$ B + C

The chemical formulae of A and B are

(A) NaOH and $Ca(OH)_2$ (B) $Ca(OH)_2$ and NaOH

(C) NaOH and CaO (D) CaO and $Ca(OH)_2$

**37.** The correct order of basic-strength of oxides of alkaline earth metals is

(A) BeO > MgO > CaO > SrO (B) SrO > CaO > MgO > BeO

(C) BeO > CaO > MgO > SrO (D) SrO > MgO > CaO > BeO

**38.** $X \xrightarrow{N_2,\Delta} Y \xrightarrow{H_2O} Z(\text{colourless gas}) \xrightarrow[CuSO_4]{} T(\text{blue colour})$

Then, substances Y and T are

(A) Y = $Mg_3N_2$ and T = $CuSO_4 \cdot 5H_2O$ (B) Y = $Mg_3N_2$ and T = $CuSO_4 \cdot 4NH_3$

(C) Y = $Mg(NO_3)_2$ and T = CuO (D) Y = MgO and T = $CuSO_4 \cdot 4NH_3$

**39.** Weakest base among KOH, NaOH, $Ca(OH)_2$ and $Zn(OH)_2$ is

(A) $Ca(OH)_2$ (B) KOH (C) NaOH (D) $Zn(OH)_2$

**40.** If X and Y are the second ionisation potentials of alkali and alkaline earth metals of same period, then -

(A) X > Y (B) X < Y (C) X = Y (D) X << Y

**41.** In Castner-Kellner cell if cathode is made up of graphite instead of mercury, then product that will be obtained first at cathode will be -

(A) Na-amalgam (B) Na only (C) $H_2$ gas (D) NaOH

**42.** $Na^+$ ion can form complex with which of the following ligand?

(A) Cryptands (B) Crown ether (C) Both (A) and (B) (D) None

**43.** $X + C + Cl_2 \xrightarrow[\text{of about 1000 K}]{\text{High temperature}} Y + CO$ ; $Y + 2H_2O \rightarrow Z + 2HCl$

Compound Y is found in polymeric chain structure and is an electron deficient molecule. Y must be

(A) BeO (B) $BeCl_2$ (C) $BeH_2$ (D) $AlCl_3$

**44.** $BeCl_2 + LiAlH_4 \longrightarrow X + LiCl + AlCl_3$

(A) X is LiH (B) X is $BeH_2$

(C) X is $BeCl_2 \cdot 2H_2O$ (D) None

**45.** The order of thermal stability of carbonates of IIA group is

(A) $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$

(B) $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$

(C) $CaCO_3 > SrCO_3 > BaCO_3 > MgCO_3$

(D) $MgCO_3 = CaCO_3 > SrCO_3 = BaCO_3$

**46.** A pair of substances which gives all the same products on reaction with water is

(A) Mg and MgO (B) Sr and SrO (C) Ca and $CaH_2$ (D) Be and BeO

**47.** A metal which is soluble in both water and liquid $NH_3$ separately -

(A) Cr (B) Mn (C) Ba (D) Al

**48.** $Be_2C + H_2O \longrightarrow BeO + X$

$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + Y$; then X and Y are respectively

(A) $CH_4$, $CH_4$ (B) $CH_4$, $C_2H_6$ (C) $CH_4$, $C_2H_2$ (D) $C_2H_2$, $CH_4$

**49.** Which of the following groups of elements have chemical properties that are most similar?

(A) Na, K, Ca (B) Mg, Sr, Ba (C) Be, Al, Ca (D) Be, Ra, Cs

**50.** $MgBr_2$ and $MgI_2$ are soluble in acetone because of

(A) Their ionic nature (B) Their coordinate nature

(C) Their metallic nature (D) Their covalent nature

# EXERCISE (O-2)

## SELECT THE CORRECT ALTERNATIVES

## (ONE OR MORE THEN ONE CORRECT ANSWERS)

### Alkali metals

**1.** Nitrogen dioxide can be prepared by heating -

(A) $KNO_3$ (B) $AgNO_3$ (C) $Pb(NO_3)_2$ (D) $Cu(NO_3)_2$

**2.** Which of the following compounds are not paramagnetic in nature?

(A) $KO_2$ (B) $K_2O_2$ (C) $Na_2O_2$ (D) $RbO_2$

**3.** The golden yellow colour associated with NaCl to Bunsen flame can be explained on the basis of

(A) low ionisation potential of sodium

(B) emission spectrum

(C) photosensitivity of sodium

(D) sublimation of metallic sodium of yellow vapours

**4.** $KO_2$ finds use in oxygen cylinders used for space and submarines. The fact(s) related to such use of $KO_2$ is/are

(A) it produces $O_2$ (B) it produces $O_3$

(C) it absorbs $CO_2$ (D) it absorbs both CO and $CO_2$

**5.** The compound(s) which have –O–O– bond(s) is/are

(A) $BaO_2$ (B) $Na_2O_2$ (C) $CrO_5$ (D) $Fe_2O_3$

**6.** Highly pure dilute solution of sodium in ammonia

(A) shows blue colouration due to solvated electrons

(B) shows electrical conductivity due to both solvated electrons as well as solvated sodium ions

(C) shows red colouration due to solvated electrons but a bad conductor of electricity

(D) produces hydrogen gas or carbonate

**7.** Sodium metal is highly reactive and can be stored under

(A) toluene (B) kerosene oil (C) alcohol (D) benzene

### Alkaline earth metals

**8.** The compound(s) of II$^{nd}$ A metals, which are amphoteric in nature is/are

(A) BeO (B) MgO (C) $Be(OH)_2$ (D) $Mg(OH)_2$

**9.** The correct statement is/are

(A) $BeCl_2$ is a covalent compound

(B) $BeCl_2$ is an electron deficient molecule

(C) $BeCl_2$ can form dimer

(D) the hybrid state of Be in $BeCl_2$ is $sp^2$

**10.** Which of the following substance(s) is/are used in laboratory for drying purposes?

(A) anhydrous $P_2O_5$ (B) graphite

(C) anhydrous $CaCl_2$ (D) $Na_3PO_4$

**11.** $Na_2SO_4$ is water soluble but $BaSO_4$ is insoluble because

(A) the hydration energy of $Na_2SO_4$ is higher than that of its lattice energy

(B) the hydration energy of $Na_2SO_4$ is less than that of its lattice energy

(C) the hydration energy of $BaSO_4$ is less than that of its lattice energy

(D) the hydration energy of $BaSO_4$ is higher than that of its lattice energy

**12.** Which of the following statements are false?

(A) $BeCl_2$ is a linear molecule in the vapour state but it is polymeric form in the solid state

(B) Calcium hydride is called hydrolith.

(C) Carbides of both Be and Ca react with water to form acetylene

(D) Oxides of both Be and Ca are amphoteric.

**13.** Which of the following are ionic carbides?

(A) $CaC_2$ (B) $Al_4C_3$ (C) SiC (D) $Be_2C$

**14.** Which of the following orders are **CORRECT** :

(A) AgCl > AgF : Covalent character order

(B) BaO > $BaF_2$ : Melting point order

(C) $BeF_2$ > $BaF_2$ : Solubility order

(D) $LiNO_3$ < $RbNO_3$ : Thermal stability order

**15.** Which of the following statements are **CORRECT** :

(A) Mg is present in chlorophyll

(B) Alkaline earth metals does not form super oxide

(C) $NaHCO_3$ is known as baking soda

(D) Permanent hardness of water is removed by boiling

**16.** Which of the following carbides on hydrolysis does not form methane?

(A) $Be_2C$ (B) $CaC_2$ (C) $SrC_2$ (D) $Mg_2C_3$

**17.** Select the incorrect order for given properties :

(A) Thermal stability : $BaSO_4 > SrSO_4 > CaSO_4$

(B) Solubility : $BaSO_4 > SrSO_4 > CaSO_4$

(C) Thermal stability : $Li_2CO_3 < Na_2CO_3 < K_2CO_3$

(D) Solubility : $Li_2CO_3 > Na_2CO_3 > K_2CO_3$

**18.** The correct statement(s) is/are

(A) Mg cannot form complexes

(B) Be can form complexes due to a very small atomic size

(C) the first ionisation potential of Be is higher than that of Mg

(D) Mg forms an alkaline hydroxide while Be forms amphoteric oxides

**19.** Which of the following is are the characteristic of barium?

(A) It produce water soluble sulphide, sulphite and sulphate

(B) It is a silvery white metal

(C) It forms $Ba(NO_3)_2$ which is used in preparation of green fire

(D) It produce blue-black solution in liquid ammonia

## EXERCISE (JM)

**1.** A metal M readily forms its sulphate $MSO_4$ which is water soluble. It forms oxide MO which becomes inert on heating. It forms insoluble hydroxide which is soluble in NaOH. The metal M is:- **[AIEEE-2002]**

(1) Mg (2) Ba (3) Ca (4) Be

**2.** $KO_2$ is used in space and submarines because it **[AIEEE-2002]**

(1) Absorbs $CO_2$ and increase $O_2$ concentration

(2) Absorbs moisture

(3) Absorbs $CO_2$

(4) Produces ozone

**3.** In curing cement plasters, water is sprinkled from time to time. This helps in :- **[AIEEE-2003]**

(1) Hydrating sand and gravel mixed with cement

(2) Converting sand into silicate

(3) Developing interlocking needle like crystals of hydrated silicates

(4) Keeping it cool

**4.** The solubilities of carbonates decreases down the magnesium group due to decrease in-

(1) Inter-ionic attraction (2) Entropy of solution formation **[AIEEE-2003]**

(3) Lattice energy of solids (4) Hydration energy of cations

**5.** The substance not likely to contain $CaCO_3$ is :- **[AIEEE-2003]**

(1) Sea shells (2) Dolomite

(3) A marble statue (4) Calcined gypsum

**6.** One mole of magnesium nitride on reaction with excess of water gives :- **[AIEEE-2004]**

(1) Two mole of $HNO_3$ (2) Two mole of $NH_3$

(3) 1 mole of $NH_3$ (4) 1 mole of $HNO_3$

**7.** Berylium and aluminium exhibit many properties which are similar. But the two elements differ in - **[AIEEE-2004]**

(1) Exhibiting maximum covalency in compounds

(2) Forming polymeric hydrides

(3) Forming covalent halides

(4) Exhibiting amphoteric nature in their oxides.

**8.** The ionic mobility of alkali metal ioins in aqueous solution is maximum for :- **[AIEEE-2006]**

(1) $Rb^+$ (2) $Li^+$ (3) $Na^+$ (4) $K^+$

**9.** The products obtained on heating $LiNO_3$ will be :- **[AIEEE-2011]**

(1) $LiNO_2 + O_2$ (2) $Li_2O + NO_2 + O_2$

(3) $Li_3N + O_2$ (4) $Li_2O + NO + O_2$

**10.** What is the best description of the change that occurs when $Na_2O(s)$ is dissolved in water ? **[AIEEE-2011]**

(1) Oxidation number of sodium decreases

(2) Oxide ion accepts sharing in a pair of electrons

(3) Oxide ion donates a pair of electrons

(4) Oxidation number of oxygen increases

**11.** Which of the following on thermal-decomposition yields a basic as well as an acidic oxide ? **[AIEEE-2012]**

(1) $NH_4NO_3$ (2) $NaNO_3$ (3) $KClO_3$ (4) $CaCO_3$

**12.** Fire extinguishers contain $H_2SO_4$ and which one of the following :-**[JEE MAIN-2012, Online]**

(1) $CaCO_3$ (2) $NaHCO_3$ and $Na_2CO_3$

(3) $Na_2CO_3$ (4) $NaHCO_3$

**13.** Based on lattice energy and other considerations, which one of the following alkali metal chloride is expected to have the highest melting point ? **[JEE MAIN-2012, Online]**

(1) RbCl (2) LiCl (3) KCl (4) NaCl

**14.** Which one of the following will react most vigorously with water ? **[JEE MAIN-2012, Online]**

(1) Li (2) K (3) Rb (4) Na

**15.** A metal M on heating in nitrogen gas gives Y. Y on treatment with $H_2O$ gives a colourless gas which when passed through $CuSO_4$ solution gives a blue colour, Y is :- **[JEE MAIN-2012, Online]**

(1) $NH_3$ (2) MgO (3) $Mg_3N_2$ (4) $Mg(NO_3)_2$

**16.** The correct statement for the molecule, $CsI_3$, is : **[JEE(Main)-2014]**

(1) it contains $Cs^{3+}$ and $I^-$ ions

(2) it contains $Cs^+$, $I^-$ and lattice $I_2$ molecule

(3) it is a covalent molecule

(4) it contains $Cs^+$ and $I_3^-$ ions

**17.** Which of the following statements about $Na_2O_2$ is **not** correct ? **[JEE MAIN-2014, Online]**

(1) $Na_2O_2$ oxidises $Cr^{3+}$ to $CrO_4^{2-}$ in acid medium

(2) It is diamagnetic in nature

(3) It is the super oxide of sodium

(4) It is a derivative of $H_2O_2$

**18.** Amongst LiCl, RbCl, $BeCl_2$ and $MgCl_2$ the compounds with the greatest and the least ionic character, respectively are : **[JEE MAIN-2014, Online]**

(1) RbCl and $MgCl_2$ (2) LiCl and RbCl

(3) $MgCl_2$ and $BeCl_2$ (4) RbCl and $BeCl_2$

**19.** The correct order of thermal stability of hydroxides is : **[JEE(Main)Online-2015]**

(1) $Ba(OH)_2 < Sr(OH)_2 < Ca(OH)_2 < Mg(OH)_2$

(2) $Mg(OH)_2 < Sr(OH)_2 < Ca(OH)_2 < Ba(OH)_2$

(3) $Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

(4) $Ba(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Mg(OH)_2$

**20.** Which of the alkaline earth metal halides given below is essentially covalent in nature :- **[JEE(Main)Online-2015]**

(1) $SrCl_2$ (2) $CaCl_2$ (3) $BeCl_2$ (4) $MgCl_2$

**21.** Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy ? **[JEE(Main)-2015]**

(1) $BaSO_4$ (2) $SrSO_4$ (3) $CaSO_4$ (4) $BeSO_4$

**22.** The commercial name for calcium oxide is : **[JEE(Main)-2016]**

(1) Quick lime (2) Milk of lime (3) Limestone (4) Slaked lime

**23.** The correct order of the solubility of alkaline-earth metal sulphates in water is : **[JEE(Main)-2016]**

(1) Mg < Sr < Ca < Ba (2) Mg < Ca < Sr < Ba

(3) Mg > Ca > Sr > Ba (4) Mg > Sr > Ca > Ba

**24.** The main oxides formed on combustion of Li, Na and K in excess of air are respectively : **[JEE(Main)-2016]**

(1) $Li_2O$, $Na_2O_2$ and $KO_2$ (2) $Li_2O$, $Na_2O$ and $KO_2$

(3) $LiO_2$, $Na_2O_2$ and $K_2O$ (4) $Li_2O_2$, $Na_2O_2$ and $KO_2$

**25.** Both lithium and magnesium display several similar properties due to the diagonal relationship ; however, the one which is incorrect is : **[JEE(Main)-2017]**

(1) Both form basic carbonates

(2) Both form soluble bicarbonates

(3) Both form nitrides

(4) Nitrates of both Li and Mg yield NO2 and O2 on heating

**26.** Which of the following ions does **not** liberate hydrogen gas on reaction with dilute acids? **[JEE(Main)-2017 on line]**

(1) $Ti^{2+}$ (2) $Cr^{2+}$

(3) $Mn^{2+}$ (4) $V^{2+}$

**27.** In $KO_2$, the nature of oxygen species and the oxidation state of oxygen atom are, respectively **[JEE(Main)ONLINE-2018]**

(1) Superoxide and –1/2 (2) Oxide and -–2

(3) Peroxide and –1/2 (4) Superoxide and –1

## EXERCISE (JA)

**1.** The species that do not contain peroxide linkage are - **[JEE 1992]**

(A) $PbO_2$ (B) $H_2O_2$ (C) $SrO_2$ (D) $BaO_2$

**2.** Read the following statement and explanation and answer as per the options given below :

**Statement-1 :** The alkali metals can form ionic hydrides which contain the hydride ion $H^-$.

**Statement-2 :** The alkali metals have low electronegativity ; their hydrides conduct electricity when fused and liberate hydrogen at the anode. **[JEE 1994]**

(A) Both 1 and 2 are true and 2 is the correct explanation of 1.

(B) Both 1 and 2 are true but 2 is not the correct explanation of 1.

(C) 1 is true but 2 is false.

(D) 1 is false but 2 is true.

**3.** The following compounds have been arranged in order of their increasing thermal stabilities. Identify the correct order. **[JEE 1996]**

$K_2CO_3$(I) $MgCO_3$(II) $CaCO_3$(III) $BeCO_3$(IV)

(A) I < II < III < IV (B) IV < II < III < I

(C) IV < II < I < III (D) II < IV < III < I

**4.** Property of all the alkaline earth metals that increase with their atomic number is - **[JEE 1997]**

(A) ionisation energy (B) solubility of their hydroxides

(C) solubility of their sulphate (D) electronegativity

**5.** Highly pure dilute solution of sodium in liquid ammonia - **[JEE 1998]**

(A) shows blue colour (B) exhibits electrical conductivity

(C) produces sodium amide (D) produces hydrogen gas

**6.** The set representing the correct order of first ionization potential is - **[JEE 2001S]**

(A) K > Na > Li (B) Be > Mg > Ca (C) B > C > N (D) Ge > Si > C

### Asseration and Reason

**7.** This questions contains statement-1 (asseration) and statement-2 (reason) and has 4 choices (a), (b), (c) and (d) out of which only one is correct.

**Statement-1 :** Alkali metals dissolve in liquid ammonia to give blue solutions, because.

**Statement-1 :** Alkali metals is liquid ammonia give solvated species of the type $[M(NH_3)_n]^+$ (M = alkali metals). **[JEE 2007]**

(A) Both 1 and 2 are true and 2 is the correct explanation of 1.

(B) Both 1 and 2 are true but 2 is not the correct explanation of 1.

(C) 1 is true but 2 is false.

(D) 1 is false but 2 is true.

**8.** The compound(s) formed upon combustion of sodium metal in excess air is (are) **[JEE 2009]**

(A) $Na_2O_2$ (B) $Na_2O$ (C) $NaO_2$ (D) NaOH

# ANSWER KEY

## EXERCISE (S-1)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1.** | **(4)** | **2.** | **(6)** | **3.** | **(4)** | **4.** | (10), OMR - (1) |
| **5.** | **(8)** | **6.** | **(6)** | | | | |

Except Be & Mg other s-block metals impart characteristic colour to oxidising flame.

## EXERCISE (O-1)

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1.** | (A) | **2.** | (A) | **3.** | (A) | **4.** | (D) | **5.** | (A) | **6.** | (D) |
| **7.** | (A) | **8.** | (C) | **9.** | (B) | **10.** | (C) | **11.** | (C) | **12.** | (A) |
| **13.** | (C) | **14.** | (C) | **15.** | (C) | **16.** | (D) | **17.** | (A) | **18.** | (A) |
| **19.** | (A) | **20.** | (C) | **21.** | (B) | **22.** | (A) | **23.** | (C) | **24.** | (D) |
| **25.** | (A) | **26.** | (C) | **27.** | (B) | **28.** | (A) | **29.** | (C) | **30.** | (D) |
| **31.** | (A) | **32.** | (A) | **33.** | (A) | **34.** | (B) | **35.** | (A) | **36.** | (B) |
| **37.** | (B) | **38.** | (B) | **39.** | (D) | **40.** | (A) | **41.** | (C) | **42.** | (C) |
| **43.** | (B) | **44.** | (B) | **45.** | (A) | **46.** | (C) | **47.** | (C) | **48.** | (C) |
| **49.** | (B) | **50.** | (D) | | | | | | | | |

## EXERCISE (O-2)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1.** | (B),(C), (D) | **2.** | (B),(C) | **3.** | (A),(B) | **4.** | (A),(C) |
| **5.** | (A),(B),(C) | **6.** | (A), (B) | **7.** | (A), (B),(D) | **8.** | (A),(C) |
| **9.** | (A),(B),(C) | **10.** | (A),(C) | **11.** | (A), (C) | **12.** | (C),(D) |
| **13.** | (A),(B),(D) | **14.** | (A),(B),(C),(D) | **15.** | (A),(B),(C) | **16.** | (B),(C),(D) |
| **17.** | (B), (D) | **18.** | (B),(C),(D) | **19.** | (B),(C),(D) | | |

## EXERCISE (JM)

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1.** | (4) | **2.** | (1) | **3.** | (3) | **4.** | (4) | **5.** | (4) | **6.** | (2) | **7.** | (1) |
| **8.** | (1) | **9.** | (2) | **10.** | (3) | **11.** | (4) | **12.** | (4) | **13.** | (4) | **14.** | (3) |
| **15.** | (3) | **16.** | (4) | **17.** | (3) | **18.** | (4) | **19.** | (3) | **20.** | (3) | **21.** | (4) |
| **22.** | (1) | **23.** | (3) | **24.** | (1) | **25.** | (1) | **26.** | (3) | **27.** | (1) | | |

## EXERCISE (JA)

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1.** | A | **2.** | A | **3.** | B | **4.** | B | **5.** | A,B | **6.** | B | **7.** | B |
| **8.** | A,B | | | | | | | | | | | | |

CHAPTER 4

# p–BLOCK GROUP–13 & 14

## Chapter 04 Contents


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# IMPORTANT NOTES

CHAPTER 4

# p–BLOCK GROUP–13 & 14

## BORON FAMILY

## 1.0 INTRODUCTION

**(i)** Group 13 to 18 of the periodic table of elements constitute the p–block. The p–block contains metals, metalloids as well as non–metals.

**(ii)** The p–block elements have general valence shell electronic configuration $ns^2\ np^{1-6}$.

**(iii)** The first member of each group from 13–17 of the p–block elements differ in many respects from the other members of their respective groups because of small size, high electronegativity and absence of d–orbitals.

**(iv)** The first member of a group also has greater ability to form $p\pi$–$p\pi$ multiple bonds to itself (e.g. C = C, C ≡ C, N ≡ N) and to element of second row (e.g C = O, C = N, C ≡ N, N = O) compared to the other members of the same group.

**(v)** The highest oxidation state of p–block element is equal to the group number minus 10. Moving down the group, the oxidation state two less than the highest group oxidation state and becomes more stable in groups 13 to 16 due to inert pair effect (reluctance of s-subshell electrons to participate in chemical bonding)

## 2.0 GROUP 13 ELEMENTS : THE BORON FAMILY

Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron, and gallium, indium and thallium are almost exclusively metallic in character,

### 2.1 Electronic Configuration

The valence shell electronic configuration of these elements is $ns^2\ np^1$.

### 2.2 Atomic Radii

On moving down the group, for each successive member one extra shell of electrons is added and therefore, atomic radius is expected to increase. Atomic radius of Ga is less than that of Al. The presence of additional 10 d-electrons offer only poor screening effect for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

### 2.3 Ionization Enthalpy

The ionisation enthalpy values do not decrease smoothly down the group. The decreases from B to Al is associated with increases in size. The observed discontinuity in the ionisation enthalpy values between Al and Ga and between In and TI are due to the non-availability of d- and f-electrons, which have low screening effect, to compensate the increase in nuclear charge. The sum of the first three ionisation enthalpies for each of the elements is very high.

## 2.4 Electronegativity

Down the group, electronegativity first decreases from B to Al and then increases marginally. This is because of the discrepancies in atomic size of the elements.

## 2.5 Physical Properties

Boron is non-metallic in nature . It is extremely hard and black coloured solid. It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point. Rest of the member are soft metals with low melting point and high electrical conductivity. Gallium with low melting point (303 K), could exist in liquid state during summer. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures. Density of the elements increases down the group from boron to thallium.

## 2.6 Chemical Properties

- **OXIDATION STATE AND TRENDS IN CHEMICAL REACTIVITY**

Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form + 3 ions and compel it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases, and is therefore able to form $Al^{3+}$ ions. However, down the group, due to poor shielding, effective nuclear charge holds ns electrons tightly (responsible for inert pair effect) and thereby, restricting their participation in bonding. As a result of this only p-orbital electron may be involved in bonding. In fact in Ga, In and Tl, both + 1 and + 3 oxidations states are observed. The relative stability of + 1 oxidation state progressively increases for heavier elements: Al < Ga < In < Tl. In thallium +1 oxidation state is predominant and + 3 oxidation state highly oxidising in character. The compound in +1 oxidation state, as expected from energy considerations, are more ionic than those in + 3 oxidations state.

In trivalent state, the number of electrons around the central atom in a molecule of the compounds of these elements (e.g., boron in $BF_3$) will be only six. Such **electron deficient** molecules have tendency to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids. The tendency to behave as Lewis acid decreases with the increases in the size down the group. $BCl_3$ easily accepts a lone pair of electrons from ammonia to form $BCl_3.NH_3$. In trivalent state most of the compounds being covalent are hydrolysed in water. The trichloride on hydrolysis in water form tetrahedral $[M(OH)_4]^-$ species; Aluminium chloride in acidified aqueous solution form octahedral $[Al(H_2O)_6]^{3+}$ ion. $AlX_3$ (X = Cl, Br) exists as dimer in vapour state (at lower temperature) and in non-polar solvent like benzene. However, when the halides dissolved in water, the high enthalpy of hydration is sufficient to break the covalent dimer into $[M.6H_2O]^{3+}$ and $3X^-$ ions.

**(i) Reactivity towards air :** Boron is unreactive in crystalline form. Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack. Amorphous boron and aluminium metal on heating in air form $B_2O_3$ and $Al_2O_3$ respectively. With dinitrogen at high temperature they form nitrides.

$$2E(s) + 3\,O_2\,(g) \xrightarrow{\Delta} 2\,E_2O_3(s)\ ;\ 2E(s) + N_2(g) \xrightarrow{\Delta} 2\,EN\,(s).$$

The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in their properties.

**(ii) Reactivity towards acids and alkalies :** Boron does not react with acids and alkalies even at moderate temperature; but aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character.

Aluminium dissolved in dilute HCl and liberates dihydrogen. However, concentrated nitric acid renders aluminium passive by forming protective oxide layer on the surface . Aluminium also reacts with aqueous alkali and liberates dihydrogen .

$$2\,Al(s) + 6\,HCl(aq) \longrightarrow 2\,Al^{3+}\,(aq) + 6\,Cl^{-}(aq) + 3\,H_2(g)$$

$$2Al(s) + 2NaOH\,(aq) + 6H_2O\,(\ell) \longrightarrow 2Na^{+}\,[Al(OH)_4]^{-}\,(aq) + 3H_2(g)$$

Sodium tetrahydroxoaluminate (III)

**(a)** $Al(OH)_3$ is amphoteric and reacts principally as a base. However, $Al(OH)_3$ shows some acidic properties when it dissolves in NaOH forming aluminate. The $Al(OH)_3$ is reprecipitated by the addition of $CO_2$, showing that the acidic properties are very weak.

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightleftharpoons CO_3^{2-} + 2H^{+}\ ;\ 2Al^{3+} + 3CO_3^{2-} + 3H_2O \rightarrow 2Al(OH)_3 + 3CO_2$$

In concentrated solutions above 1.5 M and pH greater than 13, it exists as dimer $[(OH)_3Al—O—Al(OH)_3]^{2-}$

**(b)** Aluminates are important constituents of portland cement.

**(c)** $Ga_2O_3$ and $Ga(OH)_3$ are both amphoteric compounds. $Tl_2O_3$ and $In_2O_3$ are completely basic and form neither hydrates nor hydroxides.

**(iii) Reactivity towards halogens :** These elements react with halogen to form trihalides (except $TlI_3$ ).

$$2E(s) + 3X_2\,(g) \rightarrow 2EX_3\,(s) \quad (X = F, Cl\ Br, I)$$

- **ANOMALOUS PROPERTIES OF BORON**

The tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water. Species like tetrahedral $[M(OH)_4]^{-}$ and octahedral $[M(H_2O)_6]^{3+}$, except in boron, exist in aqueous medium. It is due to the absence of d orbitals that the maximum covalence of boron is 4. Since the d-orbitals are available with Al and other elements, the maximum covalence can be expected beyond 4.

## 3.0 BORON (B)

### 3.1 Occurrence

**Boron occurs in nature in the form of the following minerals:**

**(i)** Borax $(Na^+)_2B_4O_7^{2-}.10H_2O$. (boron is part of an anionic complex), (ii) Boric acid $H_3BO_3$,

**(ii)** Kernite $Na_2B_4O_7.4H_2O$ & (iv) Colemanite $Ca_2B_6O_{11}.5H_2O$

**Extraction of Boron :**

**Modern method (electrolytic method) :**

Electrolysis of a fused mixture of magnesium oxide and magnesium fluoride with boric anhydride at 1100°C gives boron. The magnesium reduced at cathode which react with boric anhydride.

$$2MgO \longrightarrow 2Mg + O_2 \quad \text{at cathode}$$

$$B_2O_3 + 3\,Mg \longrightarrow 2B + 3MgO$$

**Note :-** Crystalline boron can be obtained by the reduction of $B_2O_3$ with aluminium powder.

$$B_2O_3 + 2Al \longrightarrow 2B\ (\text{crystalline}) + Al_2O_3.$$

### 3.2 Properties

**Physical Properties :**

**(i)** Elemental boron exists in the structures of $B_{12}$ **(icosahedral)** units which is shown in fig.

It is hard solid (MP = 2300ºC) and bad conductor of heat and electricity.

**(ii)** It exists in five forms, four of which are crystalline and one is amorphous. All crystalline forms are very hard made up of clusters of $B_{12}$ units. All crystalline forms are black in appearance and chemically inert. However, it is attacked at high temperature by strong oxidising agents such as a mixture of hot concentrated $H_2SO_4$ and $HNO_3$ or $Na_2O_2$. But amorphous form is brown and chemically active.

**Chemical Properties :**

**(i)** Reaction with air : Burns in air or oxygen forming $B_2O_3$.

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

Also burns in nitrogen at white heat.

$$2B + N_2 \longrightarrow 2BN \; ; \quad BN + 3H_2O \xrightarrow{\text{High temperature, pressure}} H_3BO_3 + NH_3$$

**(ii)** Action of alkalies and acids

$$2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2$$

$$2B + 6NaOH \xrightarrow{\text{fused}} 2Na_3BO_3 + 3H_2$$

$$2B + 3H_2SO_4 \text{ (hot \& concentrated)} \longrightarrow 2H_3BO_3 + 3SO_2$$

$$2B + 6HNO_3 \text{ (hot \& concentrated)} \longrightarrow 2H_3BO_3 + 6NO_2$$

**(iii)** Reaction with Mg and Ca

$$3Mg + 2B \longrightarrow Mg_3B_2 \quad ; \quad 3Ca + 2B \longrightarrow Ca_3B_2$$

$Mg_3B_2$ on consequent hydrolysis gives diborane.

$$Mg_3B_2 + 6HCl \xrightarrow{\text{hydrolysis}} 3MgCl_2 + B_2H_6 \quad ; \quad B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

## 4.0 COMPOUNDS OF BORON

### 4.1 Boron Trioxide ($B_2O_3$)

- **Preparation**

$$\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow{100^oC} HBO_2 \xrightarrow{160^oC} H_2B_4O_7 \xrightarrow{\text{red hot}} B_2O_3$$

- **Properties**

It is an acidic oxide and is anhydride of boric acid and it reacts with alkalies or bases to form borates.

$$3Na_2O + B_2O_3 \rightarrow 2Na_3BO_3 \text{ (sodium orthoborate).}$$

It reacts with water slowly to form orthoboric acid.

$$H_2O + B_2O_3 \longrightarrow 2HBO_2 \; ; \quad HBO_2 + H_2O \longrightarrow H_3BO_3$$

When heated with transition metal salts, it forms coloured compounds.

$$3B_2O_3 + Cr_2(SO_4)_3 \xrightarrow{\Delta} 3SO_3 \uparrow + 2Cr(BO_2)_3\text{(green)}$$

$$2B_2O_3 + 2Cu(NO_3)_2 \xrightarrow{\Delta} 4NO_2 \uparrow + O_2 \uparrow + 2Cu(BO_2)_2 \text{ (blue)}$$

## 4.2 Orthoboric Acid ($H_3BO_3$)

- **Preparation**

**(i)** It is precipitated by treating a concentrated solution of borax with sulphuric acid.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3 \downarrow$$

**(ii)** From Colemanite: Powdered colemanite is suspended in water and excess $SO_2$ is passed through it.On filtering and cooling the filtrate, white crystals of $H_3BO_3$ are obtained.

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

- **Properties**

It is a weak monobasic acid soluble in water and in aqueous solution the boron atom completes its octet by accepting $OH^-$ from water molecules:

$$B(OH)_3(aq) + 2H_2O(\ell) \rightleftharpoons [B(OH)_4]^-(aq) + H_3O^+(aq). \qquad pK = 9.25.$$

It, therefore, functions as a Lewis acid and not as a proton donor like most acids.

Since $B(OH)_3$ only partially reacts with water to form $H_3O^+$ and $[B(OH)_4]^-$, it behaves as a weak acid. Thus $H_3BO_3$ can not be titrated satisfactorily with NaOH as a sharp end point is not obtained. If certain organic polyhydroxy compounds such as glycerol, mannitol or sugars are added to the titration mixture, then $B(OH)_3$ behaves as a strong monobasic acid and it can be now titrated with NaOH and the end point is detected using phenolphthalein as indicator (pH = 8.3 - 10.0).

The added compound must be a cis-diol, to enhance the acid properties. The cis-diol forms very stable complex with the $[B(OH)_4]^-$, thus removing it from solution. The reaction is reversible and thus removal of one of the products shifts the equilibrium in the forward direction and thus all the $B(OH)_3$ reacts with NaOH; in effect it acts as a strong acid in the presence of the cis-diol.

$$B(OH)_3 + NaOH \longrightarrow Na[B(OH)_4] + NaBO_2 + 2H_2O$$

Ethanol does not form similar complex but catechol, salicylic acids, mannitol form similar complexes.

When heated it first forms metaboric acid ($HBO_2$) and then boron trioxide.

$$\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow{100^oC} HBO_2 \xrightarrow{160^oC} H_2B_4O_7 \xrightarrow{\text{red hot}} B_2O_3$$

Orthoboric acid is greasy to touch less soluble in cold water but more soluble in hot water. In the solid state, the $B(OH)_3$ units are hydrogen bonded together in to two dimensional sheets with almost hexagonal symmetry. The layered are quite a large distance apart (3.18 Å) and thus the crystal breaks quite easily into very fine particles.

- **Test for Borate radical**

When boric acid is heated with ethyl alcohol, the evolved gas is burned forming a **green edged flame**.

$$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\text{ethyl borate (volatile)}}{B(OC_2H_5)_3} + 3H_2O$$

- **Uses**

**(i)** It is an antiseptic and its water solution is used as an eyewash.

**(ii)** It is also used in glass, enamel and pottery industry.

## 4.3 Borax ($Na_2B_4O_7.10H_2O$)

- **Preparation**

It is found in nature but can also be prepared by the following methods.

**(i)** **From Colemanite :** When colemanite powder is heated with $Na_2CO_3$ solution, the following reaction occurs with the precipitation of $CaCO_3$.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3\downarrow + Na_2B_4O_7 + 2NaBO_2$$

The filtrate is cooled when white crystals of borax are precipitated. The mother liquor on treatment with $CO_2$ converts $NaBO_2$ to $Na_2B_4O_7$ which precipitates out on crystallization.

$$4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$$

**(ii)** From orthoboric acid : Borax is obtained by the action of $Na_2CO_3$ on orthoboric acid.

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

**Structure of borax :**

It is made up of two triangular and two tetrahedral units. The ion and water molecules are associated with metal ions. Out of 10 water molecules of crystallisation ,8 are attached to $Na^+$ and rest two with boron atoms.

- **Properties**

**(i)** Borax is a white powder, less soluble in cold water, more soluble in hot water.

**(ii)** Its aqueous solution is alkaline because of its hydrolysis to weak acid $H_3BO_3$ and strong alkali NaOH.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 4H_3BO_3 + 2NaOH$$

**(iii)** **Action of heat :** When borax powder is heated, it first swells due to loss of water in the form of steam but at 740°C it becomes converted into colourless transparent borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10\ H_2O\uparrow$$

$$Na_2B_4O_7 \xrightarrow{740^oC} 2NaBO_2 + B_2O_3 \text{ (borax bead)}$$

**(iv)** Oxidation of boric acid or sodium metaborate with $H_2O_2$.

$$Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + 2H_2O_2 + 6H_2O \longrightarrow Na_2[(OH)_2B\ (O—O)_2B(OH)_2].6H_2O$$

Sodium per oxoborate is used as a brightner in washing powder. In very hot water (over 80ºC) the peroxide linkages —O—O— break down to give $H_2O_2$.

**(v)** It is a useful primary standard for titrating against acids. One mole of it reacts with two moles of acid. This is because when borax is dissolved in water both $B(OH)_3$ and $[B(OH)_4]^-$ are formed, but only the $[B(OH)_4]^-$ reacts with HCl.

$$[B_4O_5(OH)_4]^{2-} + 5H_2O \rightleftharpoons 2B(OH)_3 \text{ (weak acid)} + 2[B(OH)_4]^- \text{ (salt)}$$

$$2[B(OH)_4]^- + 2H_3O^+ \longrightarrow 2B(OH)_3 + 4H_2O$$

On cooling, the white flakes of boric acid are obtained

Borax is also used as a buffer since its aqueous solution contain equal amounts of week acid and its salt.

- **Borax-bead test**

Borax reacts with certain metal salts such as, $Ni^{2+}$, $Co^{2+}$, $Cr^{3+}$, $Cu^{2+}$, $Mn^{2+}$ etc. to form coloured metaborates. The colour of the metaborates can be used to identify the metallic ions (cations) in salts.

$$Na_2B_4O_7{\cdot}10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{740^oC} \underbrace{2NaBO_2 + B_2O_3}_{\text{glassy mass}};\ CuO + B_2O_3 \longrightarrow Cu(BO_2)_2 \text{ (blue bead)}$$

- **Uses**

**(i)** in borax bead test,

**(ii)** in purifying gold,

**(iii)** as flux during welding of metals and

**(iv)** in production of glass.

## 4.4 Diborane ($B_2H_6$)

Binary compounds of B with H are called boron hydrides or boranes. These compounds form following two types of series :

$B_nH_{n+4}$ - $B_2H_6$, $B_5H_9$, $B_6H_{10}$, $B_{10}H_{14}$

$B_nH_{n+6}$ - $B_4H_{10}$, $B_5H_{11}$, $B_6H_{12}$, $B_9H_{15}$

The chemistry of diborane has aroused considerable interest because of its usefulness in many synthetic reactions and also because the elucidation of its structure helped to clarify the basic concepts about the structure of electron deficient compounds.

- **Preparation**

**(i)** $4BF_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 2B_2H_6 + 3Li\,[AlF_4]$

**(ii)** $2NaBH_4 + I_2 \xrightarrow{\text{ether}} B_2H_6 + 2NaI + H_2$

**(iii)** $3NaBH_4 + 4BF_3 \xrightarrow[450\,K]{\text{ether}} 3NaBF_4 + 2B_2H_6$

**(iv)** $2BF_3 + 6NaH \xrightarrow{453\,K} B_2H_6 + 6NaF$ (Industrial method)

**Structure of diborane :** The structure of diborane is shown in fig. The four terminal hydrogen atoms and the two boron atoms lie in one plane. There are two bridging hydrogen atoms are out of plane i.e. one on either side of plane.

The four terminal B-H bonds are regular two centre-two electron bonds while the two bridge (B-H-B) bonds are different and can be described in terms of three centre - two $e^-$ bonds.

**The structure of diborane $B_2H_6$**

*Bonding in diborane* : Each B atom uses $sp^3$ hybrids for bonding. Out of the four $sp^3$ hybrids on each B atom, one is without an electron shown in broken lines. The terminal B-H bonds are normal 2c-2e bonds but the two bridge bonds are 3c-2e bonds. The 3c-2e bridge bonds are also referred to as **banana bonds or tau bonds.**

- **Properties**

**(i)** $B_2H_6$ is colourless gas and highly reactive (boiling point 183 K).

**(ii)** Controlled pyrolysis of diborane leads to most of the higher boranes.

It catches fire spontaneously in air and explodes with $O_2$. Reaction with oxygen is extremely exothermic.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O \qquad \Delta H = -2160 \text{ kJ mol}^{-1}$$

Mixtures of diborane with air or oxygen inflame spontaneously producing large amount of heat. Diborane has a higher heat of combustion per unit weight of fuel than most other fuels. It is therefore used as a rocket fuel.

At red-heat the boranes decomposes to boron and hydrogen.

**(iii)** Reaction with water is instantaneous.

$$B_2H_6 + 6H_2O \longrightarrow 2B(OH)_3 + 6H_2$$

Dibroane is also hydrolysed by weaker acids (e.g. alcohols) or aqueous alkali.

$$B_2H_6 + 6ROH \longrightarrow 2B(OR)_3 + 6H_2$$

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

**(iv)** Reaction with HCl replaces a terminal H with Cl.

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

**(v)** Reaction with chlorine gives the trichloride.

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

**(vi)** The electron deficient 3c-2e BHB bridges are sites of nucleophilic attack.

Small amines such as $NH_3$, $CH_3NH_2$ and $(CH_3)_2NH$ give unsymmetrical cleavage of diborane.

$$B_2H_6 + 2NH_3 \longrightarrow [H_2B\ (NH_3)_2]^+\ [BH_4]^-$$

Large amines such as $(CH_3)_3N$ and pyridine give symmetrical cleavage of diborane.

$$2(CH_3)_3N + B_2H_6 \longrightarrow 2H_3B \longleftarrow N(CH_3)_3$$

$$B_2H_6 + 2Me_3P \longrightarrow 2Me_3PBH_3$$

$$B_2H_6 + 2CO \xrightarrow{200^oC,\ 20\ atm} 2BH_3CO \text{ (borane carbonyl)}$$

The boronium ion products $[H_2BL_2]^+$, are tetrahedral and can undergo substitution by other bases

$$[H_2B(NH_3)_2]^+ + 2PR_3 \longrightarrow [H_2B(PR_3)_2]^+ + 2NH_3$$

The reaction with ammonia depends on conditions.

$$B_2H_6 + NH_3 \xrightarrow[\text{low temperature}]{\text{Excess } NH_3} B_2H_6 . 2NH_3 \text{ or } [H_2B(NH_3)_2]^+ [BH_4]^- \text{ (ionic compound).}$$

$$\xrightarrow[\text{higher temperature (> 200°C)}]{\text{Excess } NH_3} (BN)_x \text{ boron nitride.}$$

$$\xrightarrow[\text{higher temperature (200°C)}]{\text{Ratio } 2NH_3 : 1\, B_2H_6} B_3N_3H_6 \text{ borazine.}$$

Borazole

Borazine is much more reactive than benzene. Borazine readily undergoes addition reactions which do not occur with benzene. Borazine also decomposes slowly and may be hydrolysed to $NH_3$ and boric acid at elevated temperature. If heated with water, $B_3N_3H_6$ hydrolyses slowly.

$$B_3N_3H_6 + 9H_2O \longrightarrow 3NH_3 + 3H_3BO_3 + 3H_2O$$

**Boron nitride :**

**(i) Preparation :**

By heating boron in the atmosphere of nitrogen

(a) $2B + N_2 \longrightarrow 2BN$

(b) $2B + 2NH_3 \longrightarrow 2BN + 3H_2$

(c) $Na_2B_4O_7 + 2NH_4Cl \longrightarrow 2BN + 2NaCl + B_2O_3 + 4H_2O$

(d) $2BCl_3 + 8\ NH_3 \longrightarrow 2BN + 6NH_4Cl$

**(ii) Properties :**

(a) It gets decomposed when heated in steam under pressure to yield ammoina.

$2BN + 3H_2O \longrightarrow B_2O_3 + 2NH_3$

(b) The structure of BN is similar to the structure of graphite. So it is called Inorganic graphite.

(c) It is not affected by mineral acids except HF

$BN + 4HF \longrightarrow NH_4BF_4$

(d) It is not affected by alkali also, but when fused with $K_2CO_3$, it gives potassium cyanate & metaborate

$$BN + K_2CO_3 \longrightarrow KCNO + KBO_2$$

## 5.0 ALUMINIUM (Al)

**(i)** It is a silvery metal with a density of 2.7 g/cc, having a melting point of 660°C, and is a good conductor of heat and electricity. It is malleable and ductile.

**(ii)** Action of air: Dry air has no action on aluminium. But moist air forms a thin layer of $Al_2O_3$ on its surface and it loses its luster. At very high temperatures it burns to form $Al_2O_3$ and AlN.

**(iii)** Reaction with halogens : When gaseous halogens are passed over aluminium, its halide are formed in an anhydrous form. $2Al + 3Cl_2 \longrightarrow 2AlCl_3$

**(iv)** Action of alkalies: When warmed with concentrated NaOH, it liberates $H_2$ gas and a colourless solution of sodium meta-aluminate is formed.

$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2\uparrow$$

**(v)** Action of acids: Aluminium reacts with dilute $H_2SO_4$ and dilute HCl but concentrated $HNO_3$ does not react with aluminium because aluminium becomes passive by the action of concentrated $HNO_3$ forming a protective oxide layer on the surface.

$$2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2\uparrow ; 2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2\uparrow$$

**(vi)** Reaction with $N_2$ : When $N_2$ gas is passed over heated aluminium, aluminium nitride is formed. Hot aluminium thus acts as an absorbing agent for $N_2$.

$$2Al + N_2 \longrightarrow 2AlN$$

AlN reacts with hot water to form $Al(OH)_3$ and $NH_3$

- **Uses**

**(i)** for manufacture of cooking and household utensils.

**(ii)** as aluminium plating for tanks, pipes, iron bars and other steel objects to prevent corrosion.

**(iii)** for manufacture of aluminium cables.

**(iv)** for making precision instruments, surgical apparatus, aircraft bodies, rail coaches, motorboats, car.

## 6.0 COMPOUNDS OF ALUMINIUM

### 6.1 Aluminium Oxide ($Al_2O_3$)

It is also called alumina. It occurs in nature in the form of bauxite and corundum. It is also found in the form of gems. Some important aluminium oxide gems are :

(A) Oriental Topaz-yellow ($Fe^{3+}$), (B) Sapphire-blue ($Fe^{2+/3+}$ / $Ti^{4+}$),

(C) Ruby-red ($Cr^{3+}$), (D) Oriental Emerald-green ($Cr^{3+}$ / $V^{3+}$)

- **Preparation**

Pure $Al_2O_3$ is obtained by igniting $Al_2(SO_4)_3$, $Al(OH)_3$ or ammonium alum.

$$Al_2(SO_4)_3 \xrightarrow{\Delta} Al_2O_3 + 3SO_3\uparrow \quad ; \quad 2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O\uparrow$$

- **Properties**

It is a white amorphous powder insoluble in water but soluble in acids (forming eg., $AlCl_3$) as well as alkalies (forming e.g., $NaAlO_2$), Thus amphoteric in nature. It is a polar covalent compound. Exists in two forms $\alpha$-$Al_2O_3$ or corundum and $\gamma$-$Al_2O_3$.

Addition of $Cr_2O_3$ or $Fe_2O_3$ makes alumina coloured.

$$\gamma\text{-}Al_2O_3 \xrightarrow[\Delta]{1000°C} \alpha\text{-}Al_2O_3$$

- **Uses**

**(i)** It is used for the extraction of aluminium.

**(ii)** It is used for making artificial gems.

**(iii)** $\alpha$-$Al_2O_3$ is used in making furnace linings. It is a refractory material.

**(iv)** Corundum is extremely hard and is used as 'Jewellers rouge' to polish glass.

### 6.2 Aluminium Chloride ($AlCl_3.6H_2O$)

It is a colourless crystalline solid, soluble in water. It is covalent. Anhydrous $AlCl_3$ is a deliquescent white solid.

- **Preparation**

**(i) By dissolving aluminium, $Al_2O_3$, or $Al(OH)_3$ in dilute HCl :**

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2\uparrow ;$$
$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O;$$
$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

The solution obtained is filtered and crystallized when the crystals of $AlCl_3.6H_2O$ are obtained.

**(ii)** Anhydrous $AlCl_3$ is obtained by the action of $Cl_2$ on heated aluminium.

**(iii)** By heating a mixture of $Al_2O_3$ and coke and passing chlorine over it.

$$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 \text{ (anhydrous)} + 3CO\uparrow$$

- **Properties**

**(i) Action of heat :** Hydrated salt when heated strongly is converted to $Al_2O_3$.

$$2AlCl_3.6H_2O \xrightarrow{\Delta} Al_2O_3 + 6HCl\uparrow + 3H_2O$$

**(ii) Action of moisture on anhydrous $AlCl_3$ :** When exposed to air, anhydrous $AlCl_3$ produces white fumes of HCl

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

**(iii) Action of $NH_3$ :** Anhydrous $AlCl_3$ absorbs $NH_3$ since the former is a Lewis acid.

$$AlCl_3 + 6NH_3 \longrightarrow AlCl_3.6NH_3 \text{ (white solid)}$$

**(iv) Action of NaOH solution :** When NaOH solution is added dropwise to an aqueous $AlCl_3$ solution, a gelatinous precipitate of $Al(OH)_3$ is first formed which dissolves in excess of NaOH solution to give a colourless solution of sodium meta-aluminate.

$$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3\downarrow + 3NaCl\ ;$$

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

This reaction is important as a test to distinguish between an aluminium salt from salts of Mg, Ca, Sr, and Ba. (When NaOH solution is added to their salt solutions, a white precipitate of hydroxide forms which does not dissolve in excess of NaOH).

**(v) Action of $NH_4OH$ solution :** When $NH_4OH$ solution is added to a solution of $AlCl_3$, a white precipitate of $Al(OH)_3$ is formed which does not dissolve in excess of $NH_4OH$.

$$AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3\downarrow \text{ (white gelatinous)} + 3NH_4Cl$$

This reaction is important as a test to distinguish an Al salt from a Zn salt. (With a Zn salt a white precipitate of $Zn(OH)_2$ is formed which dissolves in excess of $NH_4OH$ solution).

**(vi) Hydrolysis with water :** When $AlCl_3$ is dissolved in water, it undergoes hydrolysis rapidly to produce $Al(OH)_3$ which is a weak base and HCl which is a strong acid. Hence the solution is acidic to litmus.

$$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5OH]^{+2} + H^+$$

The complex cation has a high tendency to get dimerised.

$$2[Al(H_2O)_5OH]^{2+} \longrightarrow [(H_2O)_4Al\langle^{OH}_{OH}\rangle Al(H_2O)_4]^{+4} + 2H_2O$$

**(vii)** $4LiH + AlCl_3 \longrightarrow LiAlH_4 + 3LiCl$

## 7.0 ALUMS ; $M_2SO_4.\ M'_2(SO_4)_3.\ 24H_2O$ or $MM'(SO_4)_2.\ 12H_2O$

(a) Alums are double sulphates with their general formula $R_2SO_4.M_2(SO_4)_3.24H_2O$ where R = monovalent radical like $Na^+$, $K^+$, $NH_4^+$ and M = Trivalent radical like $Al^{+3}$, $Cr^{+3}$. $Fe^{+3}$.

(b) The different alums are -

| | | | |
|---|---|---|---|
| (i) | Potash alum | - | $K_2SO_4.Al_2(SO_4)_3.24H_2O$ |
| (ii) | Chrome alum | - | $K_2SO_4\ Cr_2(SO_4)_3.\ 24\ H_2O$ |
| (iii) | Iron alum | - | $(NH_4)_2SO_4.\ Fe_2(SO_4)_3.\ 24H_2O$ |
| (iv) | Ammonium alum | - | $(NH_4)_2SO_4.\ Al_2(SO_4)_3.\ 24H_2O$ |

(c) In alums each metal ion is surrounded by six water molecules.

(d) Lithium does not form alum because Li ion is too small to have a coordination number of six.

(e) **Pseudo alums** : Double sulphates of divalent ions and trivalent ions with 24 water molecules in their crystals are known as **pseudo alums**.

Eg. $MSO_4.X_2\ (SO_4)_3.24H_2O$

M = divalent or Bivalent ion

X = Trivalent metal ion

**(ii) Properties :**

(a) It is a white crystalline solid highly soluble in water.

(b) On heating it undergoes dehydration and swells up.

(c) It is highly acidic in aqueous solution due to the hydrolysis of aluminium sulphate to sulphuric acid

(d) It is a double salt and its aqueous solution gives reaction of all the constituents ions $K^+$, $Al^{+3}$, $SO_4^{-2}$.

**(iii) Uses :**

(i) Alum is used to stop bleeding.

(ii) It is used for purification of water.

(iii) It is used as a mordant in dyeing industry.

(iv) Alum is used for tanning of leather.

## Illustrations

**Illustration 1.** Explain why aluminium, though an electropositive metal, finds extensive use as a structural material.

**Solution.** (a) being electropositive reacts with air or oxygen to form protective layer of $Al_2O_3$ on its surface which protects it form further action.

(b) Cheap and light metal and forms alloys with other metal which are not easily corrode.

**Illustration 2.** Discuss the pattern of variation in oxidation states of the following :

(i) Al to TI (ii) Si to Pb (iii) P to Bi

**Solution.** (i) Al has no d-or f-electrons. Therefore, it does not exhibit inert pair effect and consequenty, it shows an oxidation state of +3 only due to the presence of two electrons in the s-and one electron in the p-orbital of the valence shell. As we move down the group from Ga to TI, the stability of +1 oxidation state increases while that of =3 oxidation decreases due to inert pair effect. For

(ii) In group 14 common oxidation states are +2 and +4.

(iii) In group 15 common oxidation states are +3 and +5.

**Illustration 3.** How is $LiAlH_4$ prepared ? What is its important uses ?

**Solution.** $4LiH + AlCl_3 \xrightarrow{\text{Dry ether}} Li^+[AlH_4]^- + 3LiCl.$

Reducing agent in organic chemistry.

**Illustration 4.** What happens when NaOH (aq) is added drop wise to a solution of $GaCl_3$ in water ?

**Solution.** $GaCl_3 + 3NaOH \longrightarrow Ga(OH)_3 \downarrow + 3NaCl$

$Ga(OH)_3 + NaOH \longrightarrow NaGaO_2 + 2H_2O$

**Illustration 5.** Give formula of the following :

(i) Felspar (ii) Cryolite (iii) Jeweller's borax (iv) Corundum

(v) Colemanite

**Solution.** (i) $KAlSi_3O_8$ (ii) $Na_3AlF_6$ (iii) $Na_2B_4O_7.5H_2O$

(iv) $Al_2O_3$ (v) $Ca_2B_6O_{11}.5H_2O$

**Illustration 6.** Answer the following :

(i) What is the outer electronic configuration of group IIA elements ?

(ii) Name the first two elements of group IIIA.

(iii) What is Tincal ?

(iv) What is thermite mixture ?

(v) What is inorganic benzene ?

(vi) Name the two metals present in common alum.

(vii) Name the aluminium compound used in Friedel Craft's reaction.

**Solution.** (i) $ns^2\ np^1$

(ii) Boron and aluminium

(iii) It is a mineral of boron. Its composition is $Na_2B_4O_7.10H_2O$

(iv) Mixture containing 1 part Al powder and 3 parts $Fe_2O_3$ or $Cr_2O_3$

(v) Borazole or borazine, $B_3N_3H_6$ is known as inorganic benzene

(vi) Common alum is the double sulphate of potassium and aluminium. Its composition is, $K_2SO_4.Al_2(SO_4)_3.24H_2O$

(vii) Anhydrous aluminium chloride, $AlCl_3$.

## BEGINNER'S BOX-1

### Group – 13 [Boron Family]

**1.** The decrease in stability of higher oxidation state in p–block with increasing atomic number is due to:

(A) increase in bond energy as going down the group.

(B) the reluctance of s-sub shell electrons to participate in the chemical bonding.

(C) both are correct.

(D) none is correct.

**2.** $B^{3+}$ ion cannot exist in aqueous solution because of its :

(A) strong reducing ability (B) strong oxidizing ability.

(C) small size and large charge. (D) large size and small charge.

**3.** From the $B_2H_6$ all the following can be prepared except :

(A) $H_3BO_3$ (B) $[BH_2(NH_3)_2]^+ [BH_4]^-$

(C) $B_2(CH_3)_6$ (D) $NaBH_4$

**4.** Boric acid is polymeric due to :

(A) its acidic nature
(B) the presence of hydrogen bonds
(C) its monobasic nature
(D) its geometry

**5.** The number of possible isomers for disubstituted borazine, $B_3N_3H_4X_2$ is :

(A) 3
(B) 4
(C) 6
(D) 2

**6.** In the following reaction : $B(OH)_3 + H_2O \rightarrow [B(OH)_4]^- + H^+$:

(A) $B(OH)_3$ is a Lewis acid.
(B) $B(OH)_3$ is a Lewis base.
(C) $B(OH)_3$ is amphoteric.
(D) none is correct.

**7.** When borax is dissolved in water :

(A) $B(OH)_3$ is formed only
(B) $[B(OH)_4]^-$ is formed only
(C) both $B(OH)_3$ and $[B(OH)_4]^-$ are formed
(D) $[B_3O_3(OH)_4]^-$ is formed only

**8.** The bonds present in borazole are :

(A) $12\sigma, 3\pi$
(B) $9\sigma, 6\pi$
(C) $6\sigma, 6\pi$
(D) $9\sigma, 9\pi$

**9.** Borax is prepared by treating colemanite with :

(A) $NaNO_3$
(B) NaCl
(C) $Na_2CO_3$
(D) $NaHCO_3$

**10.** Diborane reacts with water to form :

(A) $HBO_2$
(B) $H_3BO_3$
(C) $H_3BO_3 + H_2$
(D) $H_2$

**11.** Borax on heating with cobalt oxide forms a blue bead of :

(A) $Co(BO_2)_2$
(B) $CoBO_2$
(C) $Co_3(BO_3)_2$
(D) $Na_3Co(BO_3)_2$

**12.** Aluminium vessels should not be washed with materials containing washing soda because :

(A) washing soda is expensive
(B) washing soda is easily decomposed
(C) washing soda reacts with aluminium to form soluble aluminate
(D) washing soda reacts with aluminium to form insoluble aluminium oxide

# CARBON FAMILY

## 8.0 INTRODUCTION

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14. Naturally occurring carbon contains two stable isotopes: $^{12}C$ and $^{13}C$. In addition to these third isotopes, $^{14}C$ is also presents , it is a radioactive isotope with half-life 5770 years and used for radiocarbon dating. Silicon is a very important component of ceramics, glass and cement. Germanium exists only in traces. Tin occurs mainly as cassiterite, $SnO_2$ and lead as galena, PbS. Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.

## 8.1 Electronic Configuration

The valence shell electronic configuration of these elements is $ns^2 np^2$.

## 8.2 Covalent Radius

There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed. This is due to the presence of completely filled d and f orbitals in heavier members.

## 8.3 Ionization Enthalpy

The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electron is visible here also. In general the ionisation enthalpy decreases down the group. Small decreases in $\Delta_i H$ from Si to Ge to Sn and slight increase in $\Delta_i H$ from Sn to Pb is the consequence of poor shielding effects of intervening d and f–orbitals and increase in size of the atom.

## 8.4 Electronegativity

Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity value for elements from Si to Pb are almost the same. Carbon has higher electronegativity as compared to other elements of the group. As a result it can accept electrons and can form negative ions of type $C_2^{2-}$ in acetylides and $C^{4-}$ in methanides.

## 8.5 Physical Properties

All group 14 members are solids. Carbon and silicon are non-metals, germanium is metalloid whereas tin and lead are soft metals with low melting points. Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13 due to stronger metallic bonding.

## 8.6 Chemical Properties

- **Oxidation states and trends in chemical reactivity**

The group 14 elements have four electrons in outermost shell. The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states. Since the sum of the first four ionization enthalpies is very high, compound in +4 oxidation state are generally covalent in nature. In heavier members the tendency to show +2 oxidation state increases in the sequence Ge < Sn < Pb. It is due to the inability of $ns^2$ electrons of valence shell to participate in bonding (inert pair effect). The relative stabilities of these two oxidation states vary down the group. Carbon cannot exceed its covalence 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 tendency to form complexes by accepting electron pairs from donor species. For example, the species like $SiF_6^{2-}$. $[GeCl_6]^{2-}$, $[Sn(OH)_6]^{2-}$ and $[Pb(OH)_6]^{2-}$ exist in solutions as covalently bonded complex ions.

**(i) Reactivity towards oxygen :** 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 higher oxidation states of elements are generally more acidic than those in 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.

**(ii) Reactivity towards water :** Carbon , silicon and germanium are not affected by water . Tin decomposes steam to form dioxide and dihydrogen gas. Lead is unaffected by water, probably because of a protective oxide film formation.

**(iii) Reactivity towards halogen :** These elements can form halides of formula $MX_2$ and $MX_4$ (where X = F, Cl Br, I). Except carbon all other members react directly with halogen under suitable condition to make halides. Most of the $MX_4$ are covalent in nature. Exceptions are $SnF_4$ and $PbF_4$, which are ionic in nature. $PbI_4$ does not exist because Pb–I bond initially formed during the reaction does not release enough energy to unpair $6s^2$ electrons and excite one of them to higher orbital to have four unpaired electrons around lead atom. Heavier members Ge to Pb are able to make halides of formula $MX_2$. Stability of dihalides increases down the group. Except $CCl_4$ other tetrachlorides are easily hydrolysed by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecules in d orbital.

## 8.7 Anomalous Behaviour of Carbon

Like first member of other groups, carbon also differs from rest of the members of its group. It is due to its smaller size, higher electronegativity, higher ionisation enthalpy and unavailability of d orbitals. Carbon accommodate only four pairs of electrons around it and thus this would limit the maximum covalence to four whereas other members can expand their covalence due to the presence of d orbitals, Carbon also has unique ability to form pπ-pπ multiple bonds with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are C = C, C ≡ C, C = O, C = S and C ≡ N. Heavier elements do not form pπ-pπ bonds because their atomic orbital are too large and diffuse to have effective overlapping.

**Catenation :** Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation. This is because C–C bonds are very strong. Down the group the size increases tendency to show catenation decreases. This can be clearly seen from bond enthalpies values. The order of catenation is C >> Si > Ge ≈ Sn. Lead does not show catenation. Due to the property of catenation and pπ-pπ bonds formation, carbon is able to show allotropic forms.

| **Bond** | **Bond enthalpy (kJ mol$^{-1}$)** |
|---|---|
| C—C | 348 |
| Si—Si | 297 |
| Ge—Ge | 260 |
| Sn—Sn | 240 |

## 8.8 Allotropic Form of Carbon

**(1) Diamond :**

(a) Three dimensional polymeric structure.

(b) In diamond each carbon is in $sp^3$ hybridized state and is linked to four other neighbouring carbon atoms held at the corners of a regular tetrahedron by covalent bonds.

(c) In this structure C — C distance is 1.54 Å with a bond angle of 109.5°.

(d) Due to these strong covalent bonds, diamond is the hardest substance having abnormally high melting point (3600° C) and is extremely inert, chemically.

(e) It has very high refractive index (2.5), i.e. light rays are slowed down by the tightly bound electron.

(g) Due to unavailability of mobile electrons it is non-conductor of electricity.

**(2) Graphite :**

(a) Unlike diamond, it has a two dimensional **laminar** structure.

(b) The adjacent layers of sheet are held together by weak vander Waal forces.

(c) Here each carbon atom is in $sp^2$ hybridised state and is thus attached to three other carbon atoms by three σ bonds forming a hexagonal planar structure.

(d) The fourth electron present in an unhybridised p-orbital of each carbon atom of a hexagonal unit then overlap with each other to form a π bond.

(e) The C—C bond length in graphite is shorter (1.42 Å) than that of diamond (1.54Å)

(f) Since π-electrons ($\pi - e^-$) are free to move through out the entire layers, graphite is a good conductor of electricity. Its conductivity increases with temperature.

(g) It is a soft greasy, dark greyish coloured crystalline solid having density of 2.5 g $mL^{-1}$

(h) Since it leaves a black mark on paper it is called black lead or plumbago

(i) It is thermodynamically more stable than diamond and its free energy of formation is 1.9 kJ less than diamond.

$$\text{Graphite} \xrightarrow[50{,}000\text{-}60{,}000\ \text{atm}]{1600°C} \text{Diamond}$$

**(3) Amorphous**

(a) **Coal**

(i) Naturally form & artificially.

(ii) It is found in different form.

e.g. Peat, Lignite, Bituminous, Anthracite

(iii) Max percent of C = Anthracite, Min. percent of C = Peat

(iv) Calorific value Max. in = Anthracite

**Uses :** As a fuel & manufacture of coal gas, coaltar & Coke

(b) **Charcoal**

(i) This form is obtained by heating wood, cellulose or any other carbonous matter in a limited supply of air

(ii)

(iii) Charcoal $\xrightarrow{H_2O}$ Activated charcoal

(iv) By this process absorption capacity of charcoal is increased which is known as activation of charcoal.

(v) Charcoal is most active form of carbon due to its larger surface area.

(c) **Lamp black or carbon black or Soot**

(i) Highly soft black powder

(ii) It is obtained by bursting substance which contain carbon such as kerosene oil, petrolium, turpentine oil, acetylene etc. in a limited supply of air.

(iii) Contain 98 to 99% C

(iv) It is soft black powder used for making printing inks, ribbon of type writers.

**(4) Other Most important form**

(i) That is bucky balls or buck minster fullerene.

(ii) It has the formula $C_{60}$ form by hexa & pentagonal ring of carbon.

(iii) This structure is foot ball type.

(iv) **Formation**

$$\text{Graphite} \xrightarrow{\text{evaporation by laser}} \text{fullerene } (C_n)$$

$$\text{Graphite} \xrightarrow[\text{electric arc}]{\text{Inert gas}} \text{Fullerene } (C)_n$$

Fullerene normally contain $C_{60}$ with smaller quantity of $C_{70}$

(v) **Structure of $C_{60}$**

- $C_{60}$ is also called buckminster fullerene in honour of robert buckminster fuller.
- Shape of $C_{60}$ is Soccer ball & $C_{70}$ is Rugby ball.
- $C_{70}$ & $C_{60}$ having hexagonal & pentagonal unit.

Graphite is thermodynamically most stable allotrope of carbon and, therefore, $\Delta_f H$ values of diamond and fullerene, $C_{60}$ are 1.90 and 38.1 kJ $mol^{-1}$, respectively.

Diamond is unaffected by halogens but graphite reacts with $F_2$ at 500ºC forming intercalation compounds or graphite fluoride $(CF)_n$.

Diamond is unaffected by concentrated acids but graphite changes to Mellitic acid also called benzene hexa-carboxylic acid with hot concentrated $HNO_3$ and to graphite oxide with a hot concentrated $HF/HNO_3$.

(Mellitic acid)

Si, Ge and Sn also have a diamond type of structure. Ge liquid expands when it forms the solid. This property is unique to Ga, Ge and Bi.

$$\alpha\text{-Sn} \underset{}{\overset{32^\circ C}{\rightleftharpoons}} \beta\text{-Sn}$$

grey tin (Diamond structure) — white tin (Metallic)

**Chemical Properties of Carbon :**

**(1) Action of air**

All the allotropic forms of carbon burn in air or oxygen forming carbon dioxide (when oxygen supply is sufficient) and carbon monoxide (when oxygen supply is insufficient)

$$C + O_2 \longrightarrow CO_2 \quad ; \ \Delta H = -ve \qquad 2C + O_2 \longrightarrow 2CO \ ; \ \Delta H = -ve$$

**(2) Reducing properties**

Carbon is a strong reducing agent. It reduces many metallic oxides to corresponding metals, water to hydrogen at high temp.

$$PbO + C \longrightarrow Pb + CO$$

$$\underset{\text{red hot}}{C} + \underset{\text{Steam}}{H_2O} \longrightarrow CO + H_2$$

$$3C + Fe_2O_3 \longrightarrow 2Fe + 3CO$$

$$4C + BaSO_4 \longrightarrow BaS + 4CO$$

**(3) Formation of carbides**

When heated with certain oxides, it forms the corresponding carbides

$$CaO + 3C \xrightarrow{2000°C} CaC_2 + CO\uparrow \qquad 2Al_2O_3 + 9C \xrightarrow{2000°C} Al_4C_3 + 6CO\uparrow$$

$$3C + SiO_2 \xrightarrow{2000°C} SiC + 2CO\uparrow$$

- **Uses of carbon**

Graphite fibres embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircraft and canoes. Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis. Crucibles made from graphite are inert to dilute acids and alkalies. Being highly porous and having enormous surface area activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminators and in air conditioning system to control odour. Carbon black is used as black pigment in black ink and as filler in automobile tyres. Coke is used as a fuel and largely as a reducing agent in metallurgy. Diamond is a precious stone and used in jewellery. It is measured in carats (1 carat = 200 mg.).

## 9.0 OXIDES OF CARBON

### 9.1 Carbon Monoxide (CO)

- **Preparation**

**(i)** It is formed together with $CO_2$, when carbon or carbonaceous matter is oxidized by air or oxygen. It is also produced when $CO_2$ is reduced by red- hot carbon; this reaction is of importance in metal extractions.

$$C(s) + CO_2(g) \longrightarrow 2CO(g)$$

**(ii)** In the laboratory it can be prepared by dehydrating methanoic acid with concentrated sulphuric acid.

$$HCOOH\ (liq) \xrightarrow[\text{conc.}H_2SO_4]{373K} CO(g) + H_2O$$

**(iii)** If oxalic acid is dehydrated in the same way, $CO_2$ is formed as well.

$$H_2C_2O_4 \xrightarrow[-H_2O]{\text{conc. } H_2SO_4, \Delta} CO + CO_2$$

**(iv)** On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and $H_2$ thus produced is known as water gas or synthesis gas.

$$C\,(s) + H_2O\,(g) \xrightarrow{473\text{–}1273K} CO\,(g) + H_2(g) \text{ (water gas).}$$

When air is used instead of steam, a mixture of CO and $N_2$ is produced, which is called producer gas.

$$2\,C\,(s) + O_2\,(g) + 4\,N_2\,(g) \xrightarrow{1273K} 2\,CO\,(g) + 4\,N_2\,(g) \text{ (Producer gas).}$$

Water gas and producer gas are very important industrial fuels. Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat.

**(v)** $K_4Fe(CN)_6 + 6H_2SO_4$ (concentrated) $+ 6H_2O \xrightarrow{\Delta} 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

- **Properties**

**(i)** Carbon monoxide is a colourless, odourless gas which burns in air with a blue flame, forming $CO_2$. It is sparingly soluble in water and is a neutral oxide. CO is toxic, because it forms a complex with haemoglobin in the blood and this complex is more stable than oxy-haemoglobin. This prevents the haemoglobin in the red blood corpuscles from carrying oxygen round the body. This causes oxygen deficiency, leading to unconsciousness and then death.

$$Hb—O_2 + CO \longrightarrow Hb—CO + O_2$$

Ordinary gas masks are no protection against the gas, since it is not readily adsorbed on active charcoal. In the presence of air, a mixture of manganese (IV) oxide and copper(II) oxide catalytically oxidizes it to $CO_2$, and this mixed catalyst is used in the breathing apparatus worn by rescue teams in mine disasters.

**(ii)** Carbon monoxide is a powerful reducing agent, being employed industrially in the extraction of iron and nickel .

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 2CO_2(g)\ ; \qquad NiO(s) + CO(g) \longrightarrow Ni(s) + CO_2(g)$$

**(iii)** CO is readily absorbed by an ammonical solution of copper (I) chloride to give $CuCl.CO.2H_2O$. It reduces an ammonical solution of silver nitrate to silver (black) and, in the absence of other gaseous reducing agents, this serves as a test for the gas. It can be estimated by reaction with iodine pentoxide, the iodine which is produced quantitatively being titrated with standard sodium thiosulphate solution.

$$5CO(g) + I_2O_5(s) \longrightarrow I_2(s) + 5CO_2(g)$$

## 9.2 Carbon Dioxide ($CO_2$)

- **Preparation**

**(i)** In the laboratory it can be conveniently made by the action of dilute hydrochloric acid on marble chips :

$$CO_3^{2-}(aq) + 2H^+(aq) \longrightarrow CO_2(g) + H_2O(\ell)$$

**(ii)** Industrially it is produced as a by-product during the manufacture of quicklime and in fermentation processes:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)\ ;\ C_6H_{12}O_6(aq)\{glucose\} \longrightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

- **Properties**

**(i)** It is a colourless, odourless and heavy gas which dissolves in its own volume of water at ordinary temperature and pressure. Like all gases, it dissolves much more readily in water when the pressure is increased and this principle is used in the manufacture of soda water and fizzy drinks.

**(ii)** $CO_2$ is easily liquefied (critical temperature = 31.1°C) and a cylinder of the gas under pressure is a convenient fire extinguisher. When the highly compressed gas is allowed to expand rapidly solid carbon dioxide ('dry ice') is formed. Solid carbon dioxide sublimes at –78°C and, since no massy liquid is produced, it is a convenient means of producing low temperatures.

**(iii)** Carbon dioxide is the acid anhydride of carbonic acid, which is a weak dibasic acid and ionises in two steps as follows :

$$H_2CO_3(aq) + H_2O\ (\ell) \rightleftharpoons HCO_3^-(aq) + H_3O^+\ (aq)$$

$$HCO_3^-\ (aq) + H_2O\ (\ell) \rightleftharpoons CO_3^{2-}\ (aq) + H_3O^+\ (aq)$$

$H_2CO_3 / HCO_3^-$ buffer system helps to maintain pH of blood between 7.26 to 7.42.

A solution of carbonic acid in water will slowly turn blue litmus red and when the solution is boiled, all the $CO_2$ is evolved.

**(iv)** Carbon dioxide, which is normally present to the extent of ~ 0.03% by volume in the atmosphere, is removed from it by the process known as photosynthesis. It is the process by which green plants convert atmospheric $CO_2$ into carbohydrates such as glucose. The overall chemical change can be expressed as :

$$6\ CO_2 + 12\ H_2O \xrightarrow[\text{Chlorophyll}]{h\upsilon} C_6H_{12}O_6 + 6\ O_2 + 6\ H_2O$$

By this process plants make food for themselves as well as for animals and human beings. But the increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years seem to increase the $CO_2$ content of the atmosphere. This may lead to increase in green house effect and thus, raise the temperature of the atmosphere which might have serious consequences.

**(v)** Gaseous $CO_2$ is extensively used to carbonate soft drinks. Being heavy and non–supporter of combustion it is used as fire extinguisher. A substantial amount of $CO_2$ is used to manufacture urea.

## 9.3 Carbides

Carbides are binary compounds in which carbon combines with the elements of lower or about equal electronegativity.

Carbides are of three types according to the type of bonding

(i) Salt like carbides (ionic carbides)

(ii) Covalent carbides (giant molecular carbides)

(iii) Interstitial carbides.

**(I) Salt like carbides (ionic carbides)/Electrovalent carbides :**

(a) These are formed by strong electropositive elements of groups 1, 2 and 13 (except B), coinage metals, Zn, Cd.

(b) These are transparent crystalline substances and do not conduct electric current in the solid state.

(c) These are easily hydrolysed by water or dilute acids to give aliphatic hydrocarbons,

(i) **Methanides** (**Methides**) – Methanides are the carbides which give methane on hydrolysis.

They contain $C^{4-}$ ions.

$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$

$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$

$C^{-4} + 4H^+ \longrightarrow CH_4$

(ii) **Acetylides** – These are the carbides which yield acetylene on hydrolysis.

They contain the ion $C_2^{2-}$. e.g. : $CaC_2$

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

$C_2^{2-} + 2H^+ \longrightarrow C_2H_2$

Most of these carbides have ionic NaCl - type of structure.

(iii) **Allylides** – These carbides give methylacetylene or allylene ($CH_3–C\equiv CH$) on hydrolysis.

They contain $C_3^{4-}$ ions. The only example of this class is $Mg_2C_3$

$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3–C\equiv CH$

**(II) Covalent carbides (giant molecular carbides)**

(a) Covalent carbides are the compounds of carbon with elements having similar electronegativity.

(b) These are covalent, polymeric, thermally stable, extremely hard, high melting and technically inert solid.

(c) $B_4C$ and SiC are two main covalent carbides. SiC is known as carborundum.

**(III) Interstitial carbides/metallic carbides/Refractory carbides :**

Transition metals like Ti, Zr, Hf, V, Nb, Ta and Mo form these carbides. The metals retains their **close packed lattice** and carbons are incorporated in their interstitial spaces.These carbides are extremly hard and have very high melting points. The carbides of V and Ta are very hard hence they are used for manufacture of high speed cutting tools.

## 10.0 SILICON

Silicon is the second most abundant element occurring in the earth's crust (about 28 per cent by weight) as the oxide, silica, in a variety of forms, e.g., sand, quartz and flint, and as silicates in rocks and clays.

- **Preparation**

**(i)** The element is obtained from silica by reduction with carbon in an electric furnace.

$$SiO_2(s) + 2C(s) \longrightarrow Si(s) + 2CO(g)$$

Extremely pure silicon is obtained from 'chemically' pure silicon by the method of zone refining.

**(ii)** $SiO_2 + 2Mg \xrightarrow{\Delta} 2MgO + Si$

- **Properties**

Silicon is a very high melting-point solid with the same structure as diamond. The non-existence of an allotrope with the graphite structure clearly shows the inability of silicon atoms to multiple bond with themselves. In the massive form, silicon is chemically rather unreactive but powdered silicon is attacked by the halogens and alkalies.It is not attacked by acids except hydrofluoric acid, with which it forms hexafluorosilicic acid:

$$Si(s) + 6HF(g) \longrightarrow H_2SiF_6(aq) + 2H_2(g)$$

$$Si(powdered) + 2Cl_2(g) \longrightarrow SiCl_4(liq.)$$

$$Si(powdered) + 2OH^-(aq) + H_2O(liq) \longrightarrow SiO_3^{2-}(aq) + 2H_2(g)$$

## 11.0 COMPOUNDS OF SILICON

### 11.1 Silicon Dioxide ($SiO_2$)

Silicon dioxide, commonly known as silica, occurs in several crystallographic forms. Quartz, cristobalite and tridymite are some of the crystalline forms of silica, and they are interconvertable at suitable temperature. Silicon dioxide is a covalent, three-dimensional network solid in which each silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms. Each oxygen atom in turn covalently bonded to another silicon atoms. Each corner is shared with another tetrahedron. The entire crystal may be considered as giant molecule in which eight membered rings are formed with alternates silicon and oxygen atoms. Silica in its normal form is almost non-reactive because of very high Si–O bond enthalpy. It resists the attack by halogens, dihydrogen and most of the acids and metals even at elevated temperatures. However, it is attacked by HF and NaOH.

$$SiO_2 + 2\,NaOH \longrightarrow Na_2SiO_3 + H_2O\ ; \qquad SiO_2 + 4\,HF \longrightarrow SiF_4 + 2\,H_2O$$

Quartz is extensively used as a piezoelectric material ; it has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications. Silica gel used as a drying agent and as a support for chromatographic materials and catalysts. Kieselghur, an amorphous form of silica is used in filtration plants.

## 11.2 Silicates

Binary compounds of silicon with oxygen are called silicates but they contain other metals also in their structures.

**(i)** Since the electronegativity difference between O & Si is about 1.7, so Si–O bond can be considered 50% ionic & 50% covalent.

**(ii)** If we calculate the radius ratio then, $\frac{r_{Si^{4+}}}{r_{O^{2-}}} = 0.29$

It suggests that the coordination number of silicon must be 4 and from VBT point of view we can say that Si is $sp^3$ hybridized. Therefore silicate structures must be based upon $SiO_4^{4-}$ tetrahedral units.

**(iii)** $SiO_4^{4-}$ tetrahedral units may exist as discrete units or may polymerise into larger units by sharing corners.

## 11.3 Classification of Silicates

**(A) Orthosilicates :** These contain discrete $[SiO_4]^{4-}$ units i.e., there is no sharing of corners with one another as shown is figure.

e.g. Zircon ($ZrSiO_4$), Forsterite of Olivine ($Mg_2SiO_4$), Willemite ($Zn_2SiO_4$)

**(B) Pyrosilicate :** In these silicates two tetrahedral units are joined by sharing oxygen at one corner thereby giving $[Si_2O_7]^{6-}$ units.

e.g. Thorteveitite ($Sc_2Si_2O_7$), Hemimorphite ($Zn_3(Si_2O_7)\ Zn(OH)_2H_2O$)

(–) charge will be present on the oxygen atoms which is bonded with one Si atom.

**(C) Cyclic silicates :** If two oxygen atoms per tetrahedron are shared to form closed rings such that the structure with general formula $(SiO_3^{2-})_n$ or $(SiO_3)_n^{2n-}$ is obtained, the silicates containing these anions are called cyclic silicates. $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$ anions are the typical examples of cyclic silicates.

$Si_3O_9^{6-}$

$Si_6O_{18}^{12-}$

**(D) Chain silicates :** Chain silicates may be further classified into simple chain & double chain compounds. In case of simple chains two corners of each tetrahedron are shared & they form a long chain of tetrahedron. Their general formula is also same as the cyclic silicates i.e. $(SiO_3)_n^{2n-}$

Similarly, double chain silicates can be drawn in which two simple chains are joined together by shared oxygen. Such compounds are also known as amphiboles. The asbestos mineral is a well known example of double chain silicates. The anions of double chain silicates have general formula $(Si_4O_{11})_n^{6n}$

e.g., Synthetic silicates ($Li_2SiO_3$, $Na_2SiO_3$), Spodumene ($LiAl(SiO_3)_2$), Enstatite ($MgSiO_3$), Diopside ($CaMg(SiO_3)_2$ ), Tremolite ($Ca_2Mg_5(Si_4O_{11})_2(OH)_2$ ), etc.

**(E) Two dimensional sheet silicates :** In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent $SiO_4^{4-}$ tetrahedrals. Such sharing forms two dimension sheet structure with general formula $(Si_2O_5)_n^{2n-}$

e.g. Talc $(Mg(Si_2O_5)_2\ Mg(OH)_2$ , Kaolin $Al_2(OH)_4\ (Si_2O_5)$

**(F) Three dimensional sheet silicates :** These silicates involve all four oxygen atom in sharing with adjacent $SiO_4^{4-}$ tetrahedral units.

e.g. Quartz, Tridymite, Crystobalite, Feldspar, Zeolite and Ultramarines.

## 11.4 Silicones

Silicones are synthetic organosilicon compounds having repeated $R_2SiO$ units held by Si – O – Si linkages. These compounds have the general formula $(R_2SiO)_n$ where R = alkyl or aryl group. The silicones are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes and their subsequent polymerisation. The alkyl or aryl substituted chlorosilanes are prepared by the following reactions.

(a) $RCl + Si \xrightarrow[300^oC]{Cu} R_3SiCl + R_2SiCl_2 + RSiCl_3$

(b) $RMgCl + SiCl_4 \longrightarrow RSiCl_3 + MgCl_2$

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

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

After fractional distillation, the silane derivatives are hydrolysed and the 'hydroxides' immediately condense by intermolecular elimination of water. The final product depends upon the number of hydroxyl groups originally bonded to the silicon atom:

In this manner several molecules may combine to form a long chain polymer whose both the ends will be occupied by –OH groups. Such compounds are generally represented from the following formula.

The polymer chain depicted above is terminated by incorporating a small quantity of the monochlorosilane derivative into the hydrolysis mixture.

Silicones can be prepared from the following types of compounds only.

(i) $R_3SiCl$ (ii) $R_2SiCl_2$ (iii) $RSiCl_3$

Silicones from the hydrolysis of $(CH_3)_3$ SiCl

$$(CH_3)_3\ SiCl \xrightarrow{H_2O} (CH_3)_3\ Si\ (OH)$$

Silicones from the hydrolysis of a mixture of $(CH_3)_3$ SiCl & $(CH_3)_2$ $SiCl_2$

The dichloro derivative will form a long chain polymer as usual. But the growth of this polymer can be blocked at any stage by the hydrolysis product of mono-chloro derivative.

Silicones from the hydrolysis of trichloro derivative.

When a compound like $CH_3SiCl_3$ undergoes hydrolysis, a complex cross-linked polymer is obtained as chain can grow in three places as

The hydrocarbon layer along the silicon-oxygen chain makes silicones water-repellent.

Silicones find a variety of applications because of their chemical inertness, water repelling nature, heat resistance and good electrical insulation property.

Products having the physical properties of oils, rubbers and resins can be produced using silicones. Silicone varnishes are such excellent insulators and so heat-resistance that insulating wiring with them enabled motors to work over-loads that would have set fire to the insulation formerly used. Silicone fluids are used as hydraulic systems of planes as they are thermally stable and their viscosity alters very little with temperature. Silicone rubbers are used in placed of ordinary rubber as they retain their elasticity at much lower temperature than ordinary rubber.

## 12.0 COMPOUNDS OF TIN

### 12.1 Stannous Oxide (SnO)

- **Preparation**

By heating stannous hydroxide, $Sn(OH)_2$, in absence of air.

$$Sn(OH)_2 \longrightarrow SnO + H_2O\uparrow$$

- **Properties**

SnO is an amphoteric dark grey or black solid oxide, insoluble in water. It dissolves in acids to form stannous salts.

$$SnO\ (basic) + 2H^+ \longrightarrow Sn^{2+} + H_2O\ ;$$

$$SnO\ (acidic) + 4OH^- + H_2O \longrightarrow [Sn(OH)_6]^{4-} \text{ or } SnO_2^{2-}\ (stannite)$$

Stannites are only known in aqueous solutions.

### 12.2 Stannous Chloride ($SnCl_2 \cdot 2H_2O$)

- **Preparation**

**(i)** $Sn + 2HCl\ (concentrated) \longrightarrow SnCl_2(aq) + H_2\uparrow$

**(ii)** $SnO + 2HCl \longrightarrow SnCl_2(aq) + H_2O$

The solution on crystallization gives colourless crystals of $SnCl_2 \cdot 2H_2O$.

- **Properties**

**(i)** It is a colourless solid soluble in water. It is soluble in alcohol and ether also.

**(ii)** **Reducing agent :** It is a stronger reducing agent.

(a) It reduces ferric chloride, $FeCl_3$ to ferrous chloride, $FeCl_2$.

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$

(b) It also reduces $CuCl_2$ to CuCl (white).

**(iii)** $SnCl_2$ partly hydrolyses in water forming the basic chloride, Sn(OH)Cl.

$$SnCl_2 + H_2O \longrightarrow Sn(OH)Cl\ (white)\downarrow + HCl$$

As it produces a weak base and strong acid its aqueous solution is acidic. Its hydrolysis can be prevented by adding concentrated HCl to it during the process of its preparation.

## 13.0 COMPOUNDS OF LEAD

### 13.1 Litharge (PbO)

PbO is prepared by heating Pb at 180°C. It is a volatile yellow organic solid.

$$2Pb + O_2 \xrightarrow{\Delta} 2PbO$$

It is an amphoteric oxide and dissolves in acids as well as in alkalies.

It is used in rubber industry and in the manufacture of flint glasses, enamels, and storage batteries.

## 13.2 Lead Dioxide ($PbO_2$)

- **Preparation**

  $Pb_3O_4 + 4HNO_3$ (dilute) $\longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

- **Properties**

  It is a chocolate / dark brown coloured insoluble solid.

  **(i)** On heating at 440°C it gives the monoxide.

  $2PbO_2 \xrightarrow{440°C} 2PbO + O_2$

  **(ii)** $PbO_2$ is an oxidising agent and reduced to PbO since stability of Pb(II) > Pb(IV) based on inert pair effect.

  **(a)** It oxidizes HCl to $Cl_2$.

  $PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2\uparrow$

  **(b)** It oxidises Mn salt to permanganic acid.

  $2MnSO_4 + 5PbO_2 + 6HNO_3 \longrightarrow 2HMnO_4 + 2PbSO_4 + 3Pb(NO_3)_2 + 2H_2O$

  **(iii)** It reacts with concentrated $HNO_3$ to evolve oxygen gas.

  $PbO_2 + 2HNO_3 \longrightarrow Pb(NO_3)_2 + 1/2O_2 + H_2O$

  $PbO_2 + H_2SO_4 \longrightarrow PbSO_4 + 2H_2O + O_2$

- **Uses**

  It is used in match industry for making ignition surface of match boxes, in the preparation of $KMnO_4$ and in explosives.

## 13.3 Red Lead ($Pb_3O_4$)

- **Preparation**

  It is prepared by heating PbO at 450°C for a long time.

  $6PbO + O_2 \xrightarrow{450°C} 2Pb_3O_4$

- **Properties**

  **(i)** It is a red powder insoluble in water but when heated with concentrated $HNO_3$ it gives a red precipitate of $PbO_2$.

  $Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2\downarrow + 6H_2O$

  **(ii)** When heated above 550°C, it decomposes into PbO.

  $Pb_3O_4 \xrightarrow{\Delta} 6PbO + O_2\uparrow$

- **Uses**

  It is used as an oxidizing agent, for making metal protecting paints like red oxide paint, for making special lead cement and for making flint glass.

## 13.4 Lead Chloride ($PbCl_2$)

- **Preparation**

  $Pb(OH)_2 \cdot PbCO_3$ (basic lead carbonate) $+ 4HCl \longrightarrow 2PbCl_2\downarrow + CO_2\uparrow + 3H_2O$

- **Properties**

  It is a white crystalline solid, insoluble in cold water but soluble in boiling water. It dissolves in concentrated HCl forming a complex ion.

  $2\,HCl + PbCl_2 \rightleftharpoons H_2PbCl_4$ (chloroplumbous acid)

- **Uses**

  It is used for making pigments for paints.

## 14.0 GLASS

**(1)** Glass is a hard, brittle, transparent, amorphous solid or supercooled liquid made up of silicates of Na, Ca and other metals like Pb, Zn etc.

**(2)** Being amorphous solid (not a true solid) it has no sharp melting and melts at high temperature.

**(3)** Glass has no definite chemical formula, however it may be represented as :

$$xM_2O.yM'O.6SiO_2$$

where M = alkali metals Na, K

M' = bivalent metals Ca, Pb, Zn etc. x and y are integers.

**(4)** $CaO + Na_2CO_3 + 6SiO_2 \xrightarrow{1700K} \underset{\text{Glass}}{Na_2SiO_3} + CaSiO_3 + 4SiO_2 + CO_2$

## 14.1 Different Types of Glass

**(i)** **Soda or Soft glass or Sodalime glass :** It is mixture Na & Ca silicates, used for formation of tubes, plates and common glassware.

**(ii)** **Potash or Hard glass :** It is a mixture of potassium and calcium silicates. It fuses with difficulty. It is more resistant to the action of water and acids. It is used for making hard glass apparatus.

**(iii)** **Flint glass :** It is mixture of potassium and lead silicates. It has a very high refractive index and is used for making electric bulbs and optical instruments.

**(iv)** **Crooke's glass :** It is a optical glass containing $CeO_2$ which prevents the entry of UV rays.

**(v)** **Pyrex glass or borasil or borosilicate glass :** It is used to make lab appliances ,as it is resistant to heat, shock and common reagents. It is a mixture of zinc and barium boro silicates and alumina silicate.

Small part of $SiO_2$ is replaced by boric oxide/borax.

Low coeficient and thermal expansion, can with stand sudden change in temperature so used for making lab glass wares.

## 14.2 Etching of Glass

Glass is attacked by hydrofluoric acid to form soluble fluorosilicates. This property is used in the etching of glass. The glass to be etched is coated with a thin layer of wax and the design to be produced is scratched with a needle or stylus. An aqueous solution of hydrofluoric acid is applied to the exposed part. After sometime it is placed in water and wax is removed from the surface. The marks are engraved on the exposed parts. This is called as etching of glass.

## Illustrations

**Illustration 7.** What is the importance of ultra pure elemental silicon ? How is it obtained ?

**Solution.** Ultra pure elemental silicon is used for making semiconductors.

$$SiCl_4\,(pure) + 2H_2(g) \xrightarrow{\Delta} Si(s) + 4HCl(g)$$

$$SiHCl_3(s) + H_2(g) \xrightarrow{\Delta} Si(s) + 3HCl(g)$$

$$SiH_4(g) \xrightarrow[\text{Pyrolysis}]{675\ K} Si(s) + 2H_2(g)$$

**Illustration 8.** Write balanced equations for the following reactions :

(A) SnO is treated with dil. $HNO_3$

(B) Tin is treated with an excess of chlorine gas.

(C) Lead sulphide is heated in air.

**Solution.** (A) $SnO + 2HNO_3 \longrightarrow Sn(NO_3)_2 + H_2O$

(B) $Sn + 2Cl_2 \xrightarrow{\Delta} SnCl_4$

(C) $2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$ ; $PbS + 2O_2 \longrightarrow PbSO_4$

**Illustration 9.** What are silicates ? How are they classified ?

**Solution.** Silicates are oxoanion of Si. They are of types like ortho silicate, pyro silicate, chain and ring silicate, 2D and 3D silicate.

**Illustration 10.** What are silicones ? How are they manufactured ?

**Solution.** Silicons are polymers which produced by condensation polymerization.

**Illustration 11.** How far do you agree with the phenomenon concept of inert pair effect ? Justify your answer.

**Solution.** Inert pair effect is due to the ineffectively shielding of the s-electrons of the valence shell by the d-and f-electrons of the inner shells.

**Illustration 12.** Why alkali metals should not be used for drying $CCl_4$ and other chlorocarbons?

**Solution.** They violently react with alkali metals according to following reactions.

$$CCl_4(\ell) + 4Na(s) \longrightarrow 4NaCl(s) + C(s)$$

**Illustration 13.** Why in reactions of HCl & $SO_2$ , $PbO_2$ shows oxidising nature? Explain.

**Solution.** $\overset{IV}{P}bO_2 + 4HCl \longrightarrow \overset{II}{P}bCl_2 + Cl_2$ ; $\overset{IV}{P}bO_2 + SO_2 \longrightarrow \overset{II}{P}bSO_4$

**Illustration 14.** Dilute HCl is preferred over dilute $H_2SO_4$ for the preparation of $CO_2$ from lime stone. Explain.

**Solution.** $CaSO_4$ formed with $H_2SO_4$ forms a protective layer over lime stone and then reaction slowly ceases and stop. But $CaCl_2$ is soluble.

**Illustration 15.** $PbCl_4$ is less stable than $SnCl_4$ . Explain.

**Solution.** $PbCl_4$ is less stable than $SnCl_4$ due to more effective inert pair effect in lead. Pb–Cl bond length is more then that of Sn–Cl.

## BEGINNER'S BOX-2

### Group – 14 [Carbon Family]

**1.** Diamond and graphite are :

(A) isomers (B) isotopes (C) allotropes (D) none of the above

**2.** Which of the following is a good conductor of electricity ?

(A) Diamond (B) Graphite (C) Coal (D) None

**3.** CO forms a volatile compound with :

(A) nickel (B) copper (C) sodium (D) aluminium

**4.** CO is absorbed by :

(A) $CHCl_3$ (B) pyrogallol

(C) $CCl_4$ (D) ammoniacal solution of copper (I) chloride

**5.** Elements of group 14 :

(A) exhibit oxidation state of +4 only (B) exhibit oxidation state of +2 and +4

(C) form $M^{-2}$ and $M^{4+}$ ions (D) form $M^{2+}$ and $M^{4+}$ ions

**6.** $CO_2$ in water behaves as :

(A) weak dibasic acid $H_2CO_3$ (B) weak monobasic acid $HO - CO_2H$

(C) weak diacid base $CO(OH)_2$ (D) weak monoacid base $HO - CO_2H$

**7.** Allylides are ionic carbides. They contains :

(A) $C^{4-}$ ions (B) $C_2^{2-}$ ions (C) $C_3^{3-}$ ions (D) $C_3^{4-}$ ions

**8.** Methanides are :

(A) $Mg_2C_3$ , $Be_2C$, $Al_4C_3$ and $CaC_2$
(B) $Mg_2C_3$ , $Be_2C$ and $Al_4C_3$
(C) $Be_2C$, $Al_4C_3$ and $CaC_2$
(D) $Be_2C$ and $Al_4C_3$

**9.** The oxide which is not a reducing agent is :

(A) $CO_2$ (B) $NO_2$ (C) $SO_2$ (D) $ClO_2$

**10.** $CCl_4$ is inert towards hydrolysis but $SiCl_4$ is readily hydrolysed because

(A) carbon cannot expand its octet but silicon can expand its octet
(B) ionisation potential of carbon is higher than silicon
(C) carbon forms double and triple bonds
(D) electronegativity of carbon is higher than that of silicon

**11.** A colourless gas which burns with blue flame and reduces CuO to Cu is :

(A) $N_2$ (B) CO (C) $CO_2$ (D) $NO_2$

**12.** Which of the following compound is obtained on heating potassium ferrocyanide with concentrated $H_2SO_4$?

(A) $CO_2$ (B) CO (C) $C_2H_2$ (D) $(CN)_2$

**13.** Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behaviour is that graphite.

(A) is a non-crystalline substance.
(B) is an allotropic form of diamond
(C) has molecules of variable molecular masses like polymers
(D) has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interplate bonds.

**14.** In silicon dioxide :

(A) there are double bonds between silicon and oxygen atoms
(B) silicon atom is bonded to two oxygen atoms
(C) each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms
(D) each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms

**15.** Select incorrect statemen (s) :

(A) Interstitial carbides are formed by metalloids like Si and B
(B) Covalent carbides are formed by metalloids
(C) CO and $CN^-$ both are fatal due to complex formation with Fe(III) present in blood
(D) SiC is called carborundum

## GOLDEN KEY POINTS

- **Atomic and physical properties**

| Element | | | B | Al | Ga | In | Tl |
|---|---|---|---|---|---|---|---|
| Atomic Number | | | 5 | 13 | 31 | 49 | 81 |
| Atomic Mass | | | 10.81 | 26.98 | 69.72 | 114.82 | 204.38 |
| Electronic configuration | | | [He] $2s^2\ 2p^1$ | [Ne] $3s^2\ 3p^1$ | [Ar] $3d^{10}\ 4s^2 4p^1$ | [Kr] $4d^{10}\ 5s^2\ 5p^1$ | [Xe] $4f^{14}\ 5d^{10}\ 6s^2 6p^1$ |
| Atomic Radius / pm | | | 85 | 143 | 135 | 167 | 170 |
| Ionic Radius $M^{3+}$ / pm | | | 27 | 53.5 | 62 | 80 | 88.5 |
| Ionization enthalpy (kJ $mol^{-1}$) | $\Delta_i H_1$ | I | 801 | 577 | 579 | 558 | 589 |
| | $\Delta_i H_2$ | II | 2427 | 1816 | 1979 | 1820 | 1971 |
| | $\Delta_i H_3$ | III | 3659 | 2744 | 2962 | 2704 | 2877 |
| Electronegativity | | | 2.0 | 1.5 | 1.6 | 1.7 | 1.8 |
| Density/[$gcm^{-3}$ (at 293 K)] | | | 2.35 | 2.70 | 5.90 | 7.31 | 11.85 |
| Melting point / K | | | 2453 | 933 | 303 | 430 | 576 |
| Boiling point / K | | | 3923 | 2740 | 2676 | 2353 | 1730 |

- **Atomic and Physical Properties**

| Element | | | C | Si | Ge | Sn | Pb |
|---|---|---|---|---|---|---|---|
| Atomic Number | | | 6 | 14 | 32 | 50 | 82 |
| Atomic Mass | | | 12.01 | 28.09 | 72.60 | 118.71 | 207.2 |
| Electronic configuration | | | [He] $2s^2\ 2p^2$ | [Ne] $3s^2\ 3p^2$ | [Ar] $3d^{10}\ 4s^2\ 4p^2$ | [Kr] $4d^{10}\ 5s^2\ 5p^2$ | [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$ |
| Atomic Radius / pm | | | 77 | 118 | 122 | 140 | 146 |
| Ionic Radius $M^{+4}$ / pm | | | – | 40 | 53 | 69 | 78 |
| Ionization enthalpy (kJ $mol^{-1}$) | $\Delta_i H_1$ | I | 1086 | 786 | 761 | 708 | 715 |
| | $\Delta_i H_2$ | II | 2352 | 1577 | 1537 | 1411 | 1450 |
| | $\Delta_i H_3$ | III | 4620 | 3228 | 3300 | 2942 | 3081 |
| Electronegativity | | | 2.5 | 1.8 | 1.8 | 1.8 | 1.9 |
| Melting point / K | | | 4373 | 1693 | 1218 | 505 | 600 |
| Boiling point / K | | | – | 3550 | 3123 | 2896 | 2024 |

## ANSWERS

### BEGINNER'S BOX-1

**1.** (B) **2.** (C) **3.** (C) **4.** (B) **5.** (B) **6.** (A) **7.** (C) **8.** (A)
**9.** (C) **10.** (C) **11.** (A) **12.** (C)

### BEGINNER'S BOX-2

**1.** (C) **2.** (B) **3.** (A) **4.** (D) **5.** (B) **6.** (A) **7.** (D) **8.** (D)
**9.** (A) **10.** (A) **11.** (B) **12.** (B) **13.** (D) **14.** (D) **15.** (A)

# EXERCISE (S-1)

## SECTION - 1 : NUMERICAL ANSWER BASED QUESTIONS

**1.** What is the value of X in the given chemical formula of crystalline borax?

$Na_2\ [B_4O_5(OH)_4]\ X\ H_2O$

**2.** The structure of $B_3N_3H_6$ is as follows

How many derivative structure of $B_3N_3H_4X_2$ can be derived from the basic structure, by the replacement of two hydrogen atoms ?

**3.** Find the maximum number of atoms that lie in the one plane in $Be_2H_3CH_3$.

**4.** How many statement/s is/are correct ?

(i) $B_2$ solid does not exist, boron have basic building $B_{12}$ icosahedral units made up of polyhedron having 20 faces and 12 corners.

(ii) In alum each metal ion is surrounded by six water molecules.

(iii) Graphite is used as dry lubricant in machines running at high temperature in place of oil.

(iv) Fullerene contains twenty, six-membered rings and twelve, five-membered rings.

**5.** Calculate value of $|x + y - z|$ for the following silicate $[Si_xO_{y+z}]^{z-}$ anion.

## SECTION - 2 : MATRIX - MATCH QUESTIONS

**Match the Column**

**6.**

| **Column – I** | **Column – II** |
|---|---|
| (A) Colemanite | (p) $Na_3AlF_6$ |
| (B) Cryolite | (q) $KAI(SO_4)_2.12H_2O$ |
| (C) Bauxite | (r) $Ca_2B_6O_{11}.5H_2O$ |
| (D) Borax | (s) $Na_2B_4O_7.10H_2O$ |
| (E) Potash alum | (t) $Al_2O_3.2H_2O$ |

**7.**

| **Column - I** | **Column- II** |
|---|---|
| (A) $BBr_3 + H_2 \longrightarrow$ | (p) Borax bead test |
| (B) $Na_2B_4O_7.\ 10\ H_2O + CuSO_4 \rightarrow$ | (q) Hydrolysis |
| (C) $AlCl_3 + H_2O \longrightarrow$ | (r) Reduction |
| (D) $Cr_2O_3 + Al \longrightarrow$ | (s) White fumes |

## EXERCISE (O-1)

### SINGLE CHOICE CORRECT QUESTIONS

**1.** The borax bead is chemically :

(A) $B_2O_3$ (B) $Na_2B_4O_7$ (C) $Na_3BO_3$ (D) $B_2O_3 + NaBO_2$

**2.** Borax bead test is responded by :

(A) divalent metals (B) heavy metals

(C) light metals (D) metal which forms coloured metaborates

**3.** On the addition of mineral acid to an aqueous solution of borax, the compound formed is:

(A) borodihydride (B) orthoboric acid (C) metaboric acid (D) pyroboric acid

**4.** An aqueous solution of borax is :

(A) neutral (B) amphoteric (C) basic (D) acidic

**5.** The product obtained in the reaction of diborane with excess of ammonia at low temperature is :

(A) $B_2H_6.\ NH_3$ (B) $B_2H_6.\ 2NH_3$ (C) $(BN)_x$ (D) Borazine

**6.** Aluminium is more reactive than iron. But aluminium is less easily corroded than iron because:

(A) aluminium is a noble metal

(B) oxygen forms a protective oxide layer on aluminium surface

(C) iron unergoes reaction easily with water

(D) iron forms both mono and divalent ions

**7.** Aluminium does not react with:

(A) NaOH (B) conc. HCl (C) $N_2$ (D) conc. $HNO_3$

**8.** The dissolution of $Al(OH)_3$ by a solution of NaOH results in the formation of :

(A) $[Al(H_2O)_4(OH)]^{2+}$ (B) $[Al(H_2O)_2(OH)_4]^-$ (C) $[Al(H_2O)_3(OH)_3]$ (D) $[Al(H_2O)_6(OH)_3]$

**9.** $Al_2O_3$ can be converted to anhydrous $AlCl_3$ by heating :

(A) hydrated $Al_2O_3$ with $Cl_2$ gas (B) $Al_2O_3$ with aqueous HCl

(C) $Al_2O_3$ with NaCl in solid state (D) a mixture of $Al_2O_3$ and carbon in dry $Cl_2$ gas

**10.** Which of the following statement is correct for diborane ?

(A) $NH_3$ and small amines like $CH_3NH_3$ give unsymmetrical cleavage of diborane.

(B) Large amines such as $(CH_3)_3N$ and pyridine gives symmetrical cleavage of diborane.

(C) Small as well as large amines both gives symmetrical cleavage of diborane.

(D) (A) and (B) both

**11.** $BF_3$ on hydrolysis forms :

(A) $H_3BO_3$ (B) $HBF_4$ (C) both (A) and (B) (D) none of these

**12.** Which of the following statements about anhydrous aluminium chloride is correct ?

(A) It exists as $AlCl_3$ molecule (B) It is not easily hydrolysed

(C) It sublimes at 100ºC under vacuum (D) It is a strong Lewis base

**13.** Which reaction cannot give anhydrous $AlCl_3$ ?

(A) Heating of $AlCl_3.6H_2O$

(B) Passing dry HCl over heated aluminium powder

(C) Passing dry $Cl_2$ over heated aluminium powder

(D) Heating a mixture of alumina and coke in a current of dry $Cl_2$

**14.** Silicon reacts with hot solution of NaOH forming :

(A) $Si(OH)_4$ (B) $Si(OH)_2$ (C) $SiO_2$ (D) $Na_4SiO_4$

**15.** The structural unit present in pyrosillicates is :

(A) $Si_3O_9^{6-}$ (B) $SiO_4^{4-}$ (C) $Si_2O_7^{6-}$ (D) $(Si_2O_5^{2-})_n$

**16.** Unlike $PbCl_4$, $PbI_4$ and $PbBr_4$ are not found because :

(A) bromine and iodine are more electronegative than chlorine.

(B) iodine and bromine are smaller in size.

(C) larger iodine and bromine are able to reduce $Pb^{4+}$ to $Pb^{2+}$ or Pb.

(D) the statement is incorrect.

**17.** $Me_2SiCl_2 \xrightarrow{H_2O} (A) \xrightarrow{\text{condensation}} (B)$.

The nature of product (B) may be

(A) only linear polymers (B) cyclic products

(C) (A) and (B) both (D) none of these

**18.** When steam is passed through red hot coke :

(A) $CO_2$ and $H_2$ are obtained (B) CO and $N_2$ are formed

(C) CO and $H_2$ are obtained (D) petrol gas is obtained

**19.** Which of the following facts regarding boron and silicon is not true?

(A) Boron and silicon are semiconductors.

(B) Boron and silicon form halides which are not hydrolysed.

(C) Boron and silicon react with magnesium to form magnesium boride and magnesium silicide which are decomposed by acids to give volatile borane and silane, respectively.

(D) Both boron and silicon react with alkali to form borates and silicates containing $BO_4$ and $SiO_4$ tetrahedral units, respectively.

## EXERCISE (O-2)

### SECTION - 1 : MULTIPLE CHOICE CORRECT QUESTIONS

**1.** $B(OH)_3 + NaOH \longrightarrow Na[B(OH)_4]$ (aq).

Then addition of which of the following proceeds the reaction in the forward direction.

(A) Glycerol (B) Mannitol (C) Catachol (D) Ethanol

**2.** The carbide which does/do not give propyne on hydrolysis is/are :

(A) $Al_4C_3$ (B) $CaC_2$ (C) $Fe_3C$ (D) $Mg_2C_3$

**3.** Which of the following reactions are is correct ?

(A) $CF_4 + 2F^- \rightarrow [CF_6]^{2-}$ (B) $SiF_4 + 2F^- \rightarrow [SiF_6]^{2-}$

(C) $GeCl_4 + 2Cl^- \rightarrow [GeCl_6]^{2-}$ (D) $SnCl_4 + 2Cl^- \rightarrow [SnCl_6]^{2-}$

**4.** Which species exist:

(A) $[BF_6]^{3-}$ (B) $[AlF_6]^{3-}$ (C) $[GaF_6]^{3-}$ (D) $[InF_6]^{3-}$

**5.** Borax bead test is given by:

(A) An aluminium salt (B) A cobalt salt (C) A copper salt (D) A nickel salt

**6.** Identify the statement that is/are correct as far as structure of diborane is concerned:

(A) There are two bridging hydrogen atoms in diborane

(B) Each boron atom forms four bonds in diborane

(C) The hydrogen atoms are not in the same plane in diborane

(D) All B-H bonds in diborane are similar

**7.** Which is/are correct ?

(A) Al acts as a reducing agent

(B) Oxide of Al is highly basic.

(C) Al forms a number of alloys with other metals

(D) Al is ionic in all its compounds

**8.** Which is/are true in case of $BF_3$ ?

(A) It is volatile liquid even at room temperature

(B) It is Lewis acid

(C) It has planar geometry

(D) It forms adduct with $NH_3$

**9.** Select the correct statement(s) .

(A) The graphite is diamagnetic and diamond is paramagnetic in nature.

(B) Graphite acts as a metallic conductor along the layers of carbon atoms and as semi-conductor perpendicular to the layers of the carbon atoms.

(C) Graphite is less denser than diamond

(D) $C_{60}$ is called as Buckminster fullerene

**10.** Carbon monoxide is prepared by :

(A) heating formic acid with conc. $H_2SO_4$

(B) heating potassium ferrocyanide with conc $H_2SO_4$

(C) heating malonic acid with $P_4O_{10}$

(D) hydrolysis of $Mg_2C_3$

**11.** Select the correct statement(s)

(A) Carborundum on strong heating does not melt but dissociates to give volatile silicon and graphite.

(B) Graphite crystallised in presence of alkali metals is found to be much more conducting.

(C) Carbon monoxide burns with blue flame.

(D) The oxidation state of central carbon atom in carbon sub-oxide is two.

**12.** Which of the following give(s) ethyne on reaction with water?

(A) $Al_2(C_2)_3$ (B) $Al_4C_3$ (C) $SrC_2$ (D) $Mg_2C_3$

**13.** Select the correct statement(s)

(A) Double chain silicates are known as amphiboles.

(B) In cyclic silicates two oxygen atoms per tetrahedron are shared.

(C) Orthosilicates contain discrete $(SiO_4)^{4-}$ units.

(D) Asbestos mineral is a double chain silicate and mica is a sheet silicate.

## SECTION - 2 : COMPREHENSION BASED QUESTIONS
## (SINGLE CHOICE CORRECT QUESTION)

**Comprehension-1**

**14.** 'D' is

(A) HF + KF (B) $CaF_2 + H_2SO_4$ (C) KF (D) $SF_6$

**15.** Which of the following reactions also produces 'A' ?

(A) $BCl_3 + NH_3 \xrightarrow{\Delta}$ (B) $B + NH_3 \xrightarrow{\Delta}$

(C) $BCl_3 + H_2 + Al \xrightarrow{\Delta}$ (D) $NaBH_4 + I_2 \longrightarrow$

**Comprehension-2**

The name 'Silica' covers an entire group of minerals, which have the general formula $SiO_2$, The most common of which is quartz. Quartz is a framework silicate with $SiO_4$ tetrahedral arranged in spirals. the spirals can turn in a clockwise or anticlockwise direction – a feature that results in there being two mirror images, optically active, varieties of quartz.

**16.** The following pictures represent various silicate anions. Their formulae are respectively –

(A) $SiO_3^{2-}$ $Si_3O_7^{2-}$ (B) $SiO_4^{4-}$ $Si_3O_{10}^{8-}$ (C) $SiO_4^{2-}$ $Si_3O_9^{2-}$ (D) $SiO_3^{4-}$ $Si_3O_7^{8-}$

**17.** $Si_3O_9^{6-}$ (having three tetrahedral) is represented as –

(A)

(B)

(C) Both (D) None of these

**18.** The silicate anion in the mineral kaolinite is a chain of three $SiO_4$ tetrahedral that share corners with adjacent tetrahedral. The mineral also contains $Ca^{2+}$ ions, $Cu^{2+}$ ions, and water molecules in a 1:1:1 ratio. Mineral is represented as –

(A) $CaCuSi_3O_{10} \cdot H_2O$ (B) $CaCuSi_3O_{10} \cdot 2H_2O$

(C) $Ca_2Cu_2Si_3O_{10} \cdot 2H_2O$ (D) None of these

## EXERCISE (JM)

**1.** Select the incorrect statement. **[AIEEE 2009]**

(1) Silicones are hydrophobic in nature.

(2) Si–O–Si linkages are moisture sensitive.

(3) $SnI_4$ is an orange solid on account of charge transfer.

(4) Silicones are resistant to most chemicals due to high strength of the Si–C bond and stable silica like structure of Si–O–Si–O–Si.

**2.** The catenation tendency of C, Si and Ge is in the order Ge < Si < C. The bond energies (in kJ $mol^{-1}$) of C — C, Si —Si and Ge—Ge bonds are respectively : **[JEE MAINS - ONLINE - 2013]**

(1) 348, 260, 297 (2) 348, 297, 260 (3) 297, 348, 260 (3) 260, 297, 348

**3.** In the following sets of reactants which two sets best exhibit the amphoteric character of $Al_2O_3.\ xH_2O$ ? **[JEE MAINS - ONLINE - 2014]**

**Set-1 :** $Al_2O_3.xH_2O(s)$ and $OH^-$ (aq) **Set-2 :** $Al_2O_3.xH_2O(s)$ and $H_2O$ ($\ell$)

**Set-3 :** $Al_2O_3.xH_2O(s)$ and $H^+$ (aq) **Set-4 :** $Al_2O_3.xH_2O(s)$ and $NH_3$ (aq)

(1) 1 and 2 (2) 2 and 4 (3) 1 and 3 (4) 3 and 4

**4.** Example of a non three-dimensional silicate is : **[JEE MAINS - ONLINE - 2014]**

(1) Beryls (2) Zeolites (3) Feldspars (4) Ultramarines

**5.** Match the items in **Column I** with its main use listed in **Column II**: **[JEE MAINS - ONLINE - 2016]**

| | Column-I | | Column-I |
|---|---|---|---|
| (A) | Silica gel | (i) | Transistor |
| (B) | Silicon | (ii) | Ion-exchanger |
| (C) | Silicone | (iii) | Drying agent |
| (D) | Silicate | (iv) | Sealant |

(1) (A)-(iii), (B)-(i), (C)-(iv), (D)-(ii) (2) (A)-(iv), (B)-(i), (C)-(ii), (D)-(iii)

(3) (A)-(ii), (B)-(iv), (C)-(i), (D)-(iii) (4) (A)-(ii), (B)-(i), (C)-(iv), (D)-(iii)

**6.** The number of 2-centre-2-electron and 3-centre-2-electron bonds in $B_2H_6$, respectively, are : **[JEE MAINS - ONLINE - 2019]**

(1) 2 and 4 (2) 2 and 1 (3) 2 and 2 (4) 4 and 2

**7.** Which of the following is not and example of heterogeneous catalytic reaction ? **[JEE MAINS - ONLINE - 2019]**

(1) Ostwald's process (2) Haber's process

(3) Combustion of coal (4) Hydrogenation of vegetable oils

**8.** The hydride that is NOT electron deficient is:- **[JEE MAINS - ONLINE - 2019]**

(1) $B_2H_6$ (2) $AlH_3$ (3) $SiH_4$ (4) $GaH_3$

**9.** The relative stability of +1 oxidation state of group 13 elements follows the order :- **[JEE MAINS - ONLINE - 2019]**

(1) Al < Ga < Tl < In (2) Tl < In < Ga < Al

(3) Al < Ga < In < Tl (4) Ga < Al < In < Tl

**10.** The chloride that CANNOT get hydrolysed is : **[JEE MAINS - ONLINE - 2019]**

(1) $SiCl_4$ (2) $SnCl_4$ (3) $PbCl_4$ (4) $CCl_4$

**11.** The element that does NOT show catenation is: **[JEE MAINS - ONLINE - 2019]**

(1) Sn (2) Ge (3) Si (4) Pb

**12.** In the Hall-Heroult process, aluminium is formed at the cathode. The cathode is made out of : **[JEE MAINS - ONLINE - 2019]**

(1) Platinum (2) Carbon (3) Pure aluminium (4) Copper

**13.** The one that is extensively used as a piezoelectric material is : **[JEE MAINS - ONLINE - 2019]**

(1) Quartz (2) Amorphous silica (3) Mica (4) Tridymite

**14.** Aluminium is usually found in +3 oxidation stagte. In contarast, thallium exists in +1 and +3 oxidation states. This is due to : **[JEE MAINS - ONLINE - 2019]**

(1) lanthanoid contraction (2) lattice effect

(3) diagonal relationship (4) inert pair effect

**15.** Diborane ($B_2H_6$) reacts independently with $O_2$ and $H_2O$ to produce, respectively **[JEE MAINS - ONLINE - 2019]**

(1) $HBO_2$ and $H_3BO_3$ (2) $H_3BO_3$ and $B_2O_3$

(3) $B_2O_3$ and $H_3BO_3$ (4) $B_2O_3$ and $[BH_4]^-$

**16.** Excessive release of $CO_2$ into the atomosphere results in : **[JEE MAINS - ONLINE - 2019]**

(1) polar vortex (2) depletion of ozone

(3) formation of smog (4) global warming

**17.** The amorphous form of silica is : **[JEE MAINS - ONLINE - 2019]**

(1) quartz (2) kieselguhr

(3) cristobalite (4) tridymite

**18.** The correct order of catenation is : **[JEE MAINS - ONLINE - 2019]**

(1) C > Si > Ge ≈ Sn (2) C > Sn > Si ≈ Ge

(3) Ge > Sn > Si > C (4) Si > Sn > C > Ge

**19.** The synonym for water gas when used in the production of methanol is :- **[JEE MAINS - ONLINE - 2019]**

(1) natural gas (2) laughing gas (3) syn gas (4) fuel gas

**20.** The number of pentagons in $C_{60}$ and trigons (triangles) in white phosphorus, respectively, are: **[JEE MAINS - ONLINE - 2019]**

(1) 12 and 3 (2) 20 and 4 (3) 12 and 4 (4) 20 and 3

## EXERCISE (JA)

**1.** **Statement-1 :** $Pb^{+4}$ compounds are stronger oxidizing agents than $Sn^{4+}$ compounds

**Statement-2 :** The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to 'inert pair effect'. **[JEE 2008]**

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

**2.** The Coordination number of Al in the crystalline state of $AlCl_3$ is ? **[JEE 2009]**

**3.** In the reaction, $2\mathbf{X} + B_2H_6 \longrightarrow [BH_2(\mathbf{X})_2]^+ [BH_4]^-$

the amine(s) **X** is(are) : **[JEE 2009]**

(A) $NH_3$ (B) $CH_3NH_2$ (C) $(CH_3)_2NH$ (D) $(CH_3)_3N$

**4.** The value of n in the molecular formula $Be_nAl_2Si_6O_{18}$ is : **[JEE 2010]**

**5.** With respect to graphite and diamond, which of the statement (s) given below is (are) correct ?

(A) Graphite is harder than diamond. **[JEE 2012]**

(B) Graphite has higher electrical conductivity than diamond

(C) Graphite has higher thermal conductivity than diamond.

(D) Graphite has higher C-C bond order than diamond.

**6.** The correct statement(s) for orthoboric acid is/are **[JEE Advanced 2014]**

(A) It behaves as a weak acid in water due to self ionization

(B) Acidity of its aqueous solution increases upon addition of ethylene glycol

(C) It has a three dimensional structure due to hydrogen bonding

(D) It is weak electrolyte in water

**7.** Three moles of $B_2H_6$ are completely reacted with methanol. The number of moles of boron containing product formed is **[JEE Advanced 2015]**

**8.** The crystalline form of borax has **[JEE Advanced 2016]**

(A) tetranuclear $[B_4O_5(OH)_4]^{2-}$ unit

(B) all boron atoms in the same plane.

(C) equal number of $sp^2$ and $sp^3$ hybridized boron atoms

(D) one terminal hydroxide per boron atom

# ANSWER KEY

## EXERCISE (S-1)

### NUMERICAL ANSWER BASED QUESTIONS

**1.** (8) **2.** (4) **3.** (7) **4.** (4) **5.** (0)

### MATRIX MATCH QUESTIONS

**6.** (A) - (r), (B) - (p), (C) - (t), (D) - (s), (E) - (q) **7.** (A) - (r), (B) - (p), (C) - (qs), (D) - (r)

## EXERCISE (O-1)

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | D | D | B | C | B | B | D | B | D | D | C | C | A | D | C |
| Que. | 16 | 17 | 18 | 19 | | | | | | | | | | | |
| Ans. | C | A | C | B | | | | | | | | | | | |

## EXERCISE (O-2)

### MULTIPLE CHOICE CORRECT QUESTIONS

**1.** (ABC) **2.** (ABC) **3.** (BCD) **4.** (BCD)
**5.** (BCD) **6.** (ABC) **7.** (AC) **8.** (BCD)
**9.** (BCD) **10.** (AB) **11.** (ABC) **12.** (AC)
**13.** (ABCD)

### COMPREHENSION BASED QUESTIONS

**14.** (B) **15.** (D) **16.** (B) **17.** (B) **18.** (C)

## EXERCISE (JM)

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | 2 | 2 | 3 | 1 | 1 | 4 | 3 | 3 | 3 | 4 | 4 | 2 | 1 | 4 | 3 |
| Que. | 16 | 17 | 18 | 19 | 20 | | | | | | | | | | |
| Ans. | 4 | 2 | 1 | 3 | 3 | | | | | | | | | | |

## EXERCISE (JA)

**1.** (C) **2.** (6) **3.** (ABC) **4.** (3) **5.** (BD)
**6.** (BD) **7.** (6) **8.** (ACD)

CHAPTER 5

# GOC, STRUCTURAL & CONFORMATIONAL ISOMERISM

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# IMPORTANT NOTES

CHAPTER 5

# GOC, STRUCTURAL & CONFORMATIONAL ISOMERISM

## 1.0 ELECTRONIC EFFECTS

There are four effect which affect the chemical reaction are –

**(i)** Inductive effect

**(ii)** Mesomeric effect

**(iii)** Hyper conjugation

**(iv)** Electromeric effect

### 1.1 Inductive Effect

- Polarity developed in Carbon–chain due to the **shifting of σ bond** electron as a result of electronegativity difference is known as inductive effect,.
- Discovered by scientist **Ingold.**
- It is effective upto 3 or 4 carbons. After 3 or 4 carbons it becomes neutralized.

  So Magnitude of I effect $\propto \frac{1}{\text{distance}}$

- Inductive effect is measure with respect to hydrogen atom that means inductive effect of hydrogen is always zero.
- It is a permanent effect.
- Some atoms or groups have a greater tendency to attract the shared electron of the covalent bond.Such atoms or groups acquire partial negative charge by receiving electron density from the covalent bonds of the chain. Therefore, these are classified as the groups exerting **negative inductive (– I) effect.**
- If shifting of electron takes place from carbon chain to group or away from the carbon chain or towards the group , then it is known as **(–) I** effects.

$C_1(\delta+) > C_2(\delta\delta+) > C_3(\delta\delta\delta+)$

- Due to –I effect positive charge develops over carbon chain or carbon chain becomes electron deficient Group which shows (–) I are -

  The decreasing order of negative inductive effect of some important atoms and groups is given below :

**Order of – I effect** $\overset{\oplus}{O}R_2 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -SO_3H > -CN >$

$-COOH > -X > -OH > -OR > -NH_2 > -C_6H_5 > -H$

- Some groups are electron donor and therefore acquire partial positive charge by increasing electron density in the covalent bonds of a chain. Such groups exert **positive inductive (+ I) effect.**
- if shifting of electron takes place from group to carbon chain or away from the group or towards the carbon chain then it known as **(+) I effect**

(II)

$C_1(\delta-) > C_2(\delta\delta-) > C_3(\delta\delta\delta-)$

- Due to +I effect electron density increase on carbon chain or negative charge comes on carbon chain Group which shows +I effect are. All alkyl groups, all anionic groups.
- In alkyl groups megnitude of **+I effect $\propto$ size of alkyl group**

  $-CH_3 < -CH_2CH_3 < -CH_2CH_2CH_3 < -CH_2CH_2CH_2CH_3$

  In isomeric alkyl group megnitude of **+I effect $\propto$ number of branches**.

- **Application of I-effect**

**(A) Stability of carbocation :**

**(i)** If number of + I groups increases then stability of carbocation increases.

**(ii)** If number of –I groups decreases then stability of carbocation increases.

**(iii)** Therefore

$$\text{Stability of Carbocation} \propto \text{No. of} + \text{I groups}$$

$$\text{Stability of carbocation} \propto \frac{1}{\text{No. of} - \text{I groups}}$$

**Example :** Stability order :

**Solution.** Reason : More no. of +I group.
more stable carbocation.

**(B) Stability of carbon free radical**

**(i)** If number of + I groups increases then stability of free radical increases.

**(ii)** If number of –I groups decreases then stability of free radical increases.

**(iii)** Therefore

$$\boxed{\text{Stability of free radical} \propto \text{No. of} + \text{I groups}}$$

$$\boxed{\text{Stability of free radical} \propto \frac{1}{\text{No. of} - \text{I groups}}}$$

**Example :** Stability order :

**Solution.** Reason : More no. of +I group.
more stable carbocation.

**(C) Stability of carbanion :**

**(i)** If number of – I groups increases then stability of carbanion increases.

**(ii)** If number of +I groups decreases then stability of carbanion increases.

$$\boxed{\text{Stability of Carbanion} \propto \text{No. of} - \text{I groups}}$$

$$\boxed{\text{Stability of Carbanion} \propto \frac{1}{\text{No. of} + \text{I groups}}}$$

**Example :**

(1) $\overset{\ominus}{C}H_2-\underset{\underset{F}{|}}{CH}-CH_2-CH_3$ (2) $\overset{\ominus}{C}H_2-CH_2-\underset{\underset{F}{|}}{CH}-CH_3$ (3) $\overset{\ominus}{C}H_2-CH_2-CH_2-CH_2-F$

-I is $\propto$ distance

So stability order 1 > 2 > 3

**(D) Acidic strength :**

**(i)** If No. of – I groups increases then acidic strength increases.

**(ii)** If No. of + I groups increases then acidic strength decreases.

$$\boxed{\text{acidic strength} \propto \text{No. of -I groups} \propto \frac{1}{\text{No. of} + \text{I groups}}}$$

**Example :**

(i)

+I of $-CH_3$
so anion is less stable

–I of –Cl, so anion is more stable
and corresponding acid is more acidic.

**(ii)** $CH_3-CH_2-\underset{\underset{F}{|}}{CH}-COOH > CH_3-\underset{\underset{F}{|}}{CH}-CH_2-COOH > \underset{\underset{F}{|}}{CH_2}-CH_2-CH_2-COOH$

minimum distance of –F from –COOH, so maximum –I of F. So maximum acidic strength.

**(E) Basic strength :**

**(i)** If No. of + I groups increases then basic strength increases.

**(ii)** If No. of – I groups increases then basic strength decreases.

$$\text{Basic strength} \propto \text{No. of } +\text{I groups} \propto \frac{1}{\text{No. of } -\text{I groups}}$$

**Example :**

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH > CH_3-\underset{\underset{CH_3}{|}}{CH}-OH > CH_3-CH_2-OH$$

Maximum +I.

Maximum tendency to donate l.p.

Maximum basic strength.

## Illustrations

**Illustration 1.** Explain— Basicity order in aqueous solution and in liquid phase.

$Et_2\ NH > Et_3\ N > Et\ NH_2$

**Solution.** Tertiary amine is less basic then secondary due to following reasons :

(i) **Steric hindrance :** In tertiary amines ($R_3N$) , three alkyl groups attached to N are bulkier and as such exert steric hindrance.

(ii) **Decrease in hydration :**

**In tertiary amine** **In secondary amine**

Protonated t–amine can form H–bonding with water molecule only at one point [less stable]

Protonated s–amine can form H–bonding with water molecules at two points (more stable)

3° amine are less stable as compare to 2° amine due to low hydration so less basic.

**But in gaseous phase basic order is** $R_3\ddot{N} > R_2\ddot{N}H > R\ddot{N}H_2 > \ddot{N}H_3$

Some other basic order of different amine if alkyl group would be change (in aq. medium)

| Alkyl groups (R–) | Relative base strength |
|---|---|
| **(i)** $CH_3$ – | $R_2NH > RNH_2 > R_3N > NH_3$ |
| **(ii)** $C_2H_5$ – | $R_2NH > R_3N > RNH_2 > NH_3$ |

**Illustration 2.** Correct basic order of the following different amine in chlorobenzene medium is -

(A) $CH_3 - CH_2 - NH_2$ (B) (C) (D)

**Solution.** (C > D > B > A)

## 1.2 Resonance Effect

The delocalisation of adjacent (parallel) p-orbital electron is called resonance. Through resonance the $e^-$ density in the molecule becomes uniform, due to uniformility of $e^-$ density the stability of molecule increases. Hence the phenomena of a resonance is a stabilising effect.

In resonance only parallel p-orbital $e^-$ are involved. To explain the property of actual molecule different lewis structure are drawn with the movement of p-orbital electrons.

This lewis structure are called resonating structure or canonical structure.

**Examples :**

**(i)**

**(ii)**

**(iii)** $CH_2 = CH - CH = \overset{\ominus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2 - CH = CH - \overset{\ominus}{C}H_2$

**(iv)** $\overset{\ominus}{C}H_2 = CH - \overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2 - CH = CH_2$

**(v)** $CH_2 = CH - \overset{\bullet}{C}H_2 \longleftrightarrow \overset{\bullet}{C}H_2 - CH = CH_2$

**(vi)** $:\ddot{\underset{\cdot\cdot}{C}}l - CH = CH_2 \longleftrightarrow \overset{\oplus}{C}l = CH - \overset{\ominus}{C}H_2$

Resonating structure are only hypothetical but they all contribute to a real structure which is called resonance hybrid. The resonance hybride is more stable than any resonating structure.

- **Condition for resonance :**

Molecule should be conjugated system

**Conjugated system :** Parallel p-orbitals are present in a planner system then system is known as conjugated system.

**E.g.**

**(i)** $CH_2 = CH - C \equiv CH$ (Show resonance)

**(ii)** $CH_2 = CH - CH_2 - CH = CH_2$ (does not show resonance)

**(iii)** (Show resonance)

**(iv)** (does not show resonance)

**(v)** $CH_2 = C = CH_2$ (does not show resonance)

- **Types of Conjugation:-**

**(i)** Conjugation between C = C and C = C

$CH_2 = CH - CH = CH_2$

**(ii)** Conjugation between +ve charge and C = C

$CH_2 = CH - \overset{\oplus}{C}H_2$

**(iii)** Conjugation between lone pair and C = C

$CH_2 = CH - \ddot{N}H_2$

**(iv)** Conjugation between odd electron and C = C

$CH_2 = CH - \dot{C}H_2$

**(v)** Conjugation between negative charge and C = C

$CH_2 = CH - CH = CH - \overset{\ominus}{C}H_2$

**(vi)** Conjugation between lone pair and vacant orbital

$CH_3-\overset{\oplus}{C}H-OCH_3 \longleftrightarrow CH_3-CH=\overset{\oplus}{O}CH_3$

- **Rule for writing resonating structure**

**(i)** In resonating structure only p-orbitals $e^-$ are shifted, σ bond $e^-$ are not involved in resonance, therefore the σ bond skeleton well remain same in two resonating structures.

**(ii)** The atoms are not moved

**(iii)** The no. of paired p $e^-$ are same and pair of unpaired p $e^-$ are same in two resonating structure.

**(iv)** High energy structure are rejected as resonating structure or their contribution to the resonance hybride is least.

**E.g.** Opposite charge on adjacent atoms and similar charge on adjacent atoms are cases of high energy. They are not accepted as resonating structures.

**E.g.**

**(i)** $CH_2 = CH - CH = CH_2 \longleftrightarrow$

They are not resonating structures as they have different atomic arrangement.

**(ii)** $CH_2 = CH - CH = CH_2 \longleftrightarrow CH_3 - CH = C = CH_2$

They are not resonating structures as they have different position of -H atom.

**(iii)** $CH_2 = CH\ \overset{\oplus}{N}H_3 \longleftrightarrow \overset{\oplus}{C}H_2 - CH = NH_3$

$10e^-$

They are not resonating structures as Nitrogen has 10 electrons in second structure.

**(iv)** $CH_2 = CH - CH = CH_2 \longleftrightarrow \dot{C}H_2 - CH = CH - \dot{C}H_2$

$2\pi$ electron and unpaired electron = 2

They are not resonating structures as they have different number of unpaired electrons.

**(v)** $CH_2 = CH - CH = CH_2 \longleftrightarrow$


## Illustrations

**Illustration 3.** Write resonating structure for each of the following molecules :

**(a)** $CH_3 - CH = CH - \overset{\overset{O}{\|}}{C} - CH_3$

**Solution.**

**(b)** $H_2\ddot{N}-CH=CH-C\equiv N$

**Solution.** $H_2\ddot{N}-CH=CH-C\equiv N \longleftrightarrow H_2\overset{\oplus}{N}=CH-CH=C=\overset{\ominus}{N}:$

**(c)**

**Solution.**

**(d)** $CH_3-O-CH=CH-\overset{\oplus}{C}H_2$

**Solution.** $CH_3-\ddot{O}-CH=CH-\overset{\oplus}{C}H_2 \longleftrightarrow CH_3-\overset{+}{O}=CH-CH=CH_2$

**(e)**

**Solution.**

**(f)** $CH_3-\overset{\oplus}{C}=\ddot{O}:$

**Solution.** $CH_3-\overset{\oplus}{C}=\ddot{O}: \longleftrightarrow CH_3-C\equiv\overset{+}{O}:$

**(g)**

**Solution.**

**(h)**

**Solution.**

**(i)**

**Solution.**

**(j)**

**Solution.**

**Illustration 4.** Draw resonating structure for following molecules

, $CH_2 = C = O$ , $N_3^{\ominus}$

**Solution** **(i)**

**(ii)**

**(iii)**

**Illustration 5.** Draw resonating structures of following species.

**(i)** , **(ii)** , **(iii)** , **(iv)** , **(v)** ,

**(vi)** **(vii)**

**Solution.** (i)

5-Resonating structures

(ii)

5-Resonating structures

(iii)

5-Resonating structures

( i v )

5-Resonating structures

(v)

5-Resonating structures

(vi)

5-Resonating structures

(vii)

5-Resonating structures

- **Characteristics of Resonance :**

  **(i)** In resonance only $e^-$ are transferred not atoms.

  **(ii)** The number of $e^-$ or number of unpaired or paired $e^-$ in all resonating structures should be same.

  **(iii)** It is permanent effect.

- **Resonance Hybrid**

$$\underset{1}{CH_2}=\underset{2}{CH}-\underset{3}{CH}=\underset{4}{CH_2} \longleftrightarrow \overset{\oplus}{\underset{1}{CH_2}}-\underset{2}{CH}=\underset{3}{CH}-\overset{\ominus}{\underset{4}{CH_2}} \longleftrightarrow \overset{\ominus}{\underset{1}{CH_2}}-\underset{2}{CH}=\underset{3}{CH}-\overset{\oplus}{\underset{4}{CH_2}}$$

I II III

In the structure I $C_1$—$C_2$ has double bond while in II and III $C_1$—$C_2$ has single bond, so $C_1$—$C_2$ shows bond length in between single and double bond similarly in structure I $C_2$—$C_3$ has single bond. While in structure II and III $C_2$—$C_3$ has double bond, so $C_2$—$C_3$ shows bond length in between single and double bond.

So hybrid resonating structure from all its resonating structures is :

$$\equiv \quad CH_2 \text{ ------ } CH \text{ ------ } CH \text{ ------ } CH_2 \qquad \text{Hybrid structure}$$

**Example :**

**(i)**

I (Resonating structure) II (Hybrid structure)

**(ii)**

(Resonating structure) (Hybrid structure)

- **Resonance energy**

Eenergy difference between most stable resonating structure and resonance hybrid is known as resonance energy.

- **Calculation of Resonance Energy**

The difference in the experimental and calculated energies (heat of hydrogenation) by which the compound is stable, is known as the resonance or delocalization energy. Higher the value of resonance energy, greater is the resonance stabilization.

**Resonance energy (R.E.) of Benzene :**

**The Resonance energy of benzene is calculated from the heat of hydrogenation as given below:**

but experimental value is 49.8 Kcal. so,

Resonance energy = Calculated value – Experimental value

= 85.8 – 49.8 = 36 Kcal.

- **Mesomeric effect or Resonance effect**

**(i)** Polarity developed in conjugate system by the complete transfer of non–bonding electron or π–bond electron due to the group or atom attach with conjugate system is known as mesomeric effect.

**(ii)** If transfer of pi-bond electron takes place from conjugate system to group then it is known as **negative mesomeric (–M)** effect.

**(iii)** For –M effect, group should have either be positive charge or should have vacant orbital.

**(iv)** Due to –M effect positive charge comes over conjugate system or due to –M effect electron density decrease in conjugate system, such type of conjugate system will be more reactive towards nucleophile or will be less reactive towards electrophile.

**(v)** **Group which shows –M effect are -**

$-NO_2$ > –CN > – CHO> –COR> –COOH> –COOR> $-CONH_2$

**(vi)** If transfer of non bonding electron takes place from group to conjugate system then it is known as **positive mesomeric (+M)** effect.

**(vii)** For +M effect, group should have either lone pair of electron or should have negative charge.

**(viii)** Due to + M effect negative charge comes over conjugate system or electron density increase on conjugate system such type of conjugate system will be more reactive towards electrophile or will be less reactive towards nucleophile.

**(ix)** **Group which shows + M effect are -**

$-\overset{\ominus}{O}$, $-\overset{\ominus}{N}H$, $-NR_2$ , $-NHR$, $-NH_2$ , $-OH$, $-OR$, $-SH$ $-SR$, $-F$, $-Cl$, $-NHCOR$ , $-O-COR$ etc.

- **Application of M- effect or Resonance effect**

**(A)** **Stability of carbocation :**

**(a)** Stability of carbocation is increased by resonance.

**(b)** Aromatic compound are more stable than non aromatic compound.

**Example :** Compare stability order of :-

(i) $CH_2=CH-\overset{\oplus}{C}H_2$ > $CH_3\rightarrow CH_2-\overset{\oplus}{C}H_2$ > $CH_2=CH\leftarrow CH-\overset{\oplus}{C}H_2$

stable by resonance  +I of Alkyl group  –I of Alkenyl group

(ii)

1°  2°  3°

(iii)

Resonance increases, stability increases

(iv)

(I)  (II)  (III)

stable by resonance  more resonance localized ⊕ve charge

stability order II > I > III

**(B)** **Stability of carbanion :**

(a) Stability of carbanion is increased by resonance.

**Example :** Compare stability order of :

(i) $CH_2=CH-\overset{\ominus}{C}H_2$ , $CH_2=\overset{\ominus}{C}H$ , $CH_3-\overset{\ominus}{C}H_2$

stable by resonance – ve charge on more EN atom

stability order I > II > III

(ii) , ,

(I) (II)

more resonance

so, stability order II > I.

(iii) $\overset{\ominus}{C}H_2-NO_2$ $\overset{\ominus}{C}H_2-CH_2-NO_2$ $CH_3-\overset{\ominus}{C}H-NO_2$

stable by resonance no resonance stable by resoncance, but +I of $CH_3$

so, stability order I > III > II

**(C) Stability of free radicals :**

(a) Stability of free radicals is increased by resonance.

**Example :** Compare stability order of :

(i) $CH_2=CH-\dot{C}H_2$ $CH_2=\dot{C}H$ $CH_2=CH-\dot{C}H-CH=CH_2$

less resonance no resonance more resonance

stability order III > I > II

(ii) , ,

resonance more resonance localized free radical

stability order II > I > III

**(D) Acidic strength :**

Acidic strength $\propto$ stability of conjugate base

$$\text{Acidic strength} \propto -M \propto -I \propto \frac{1}{+M} \propto \frac{1}{+I}$$

**Example :** Carboxylic acids are more acidic than phenols, why ?

**Solution.**

more stable conjugate base less stable conjugate base

so corresponding acid is more acidic

**Example :** Phenol is more acidic than alcohols why ?

**Solution.**

stable by resonance — no resonance.

So, it is more acidic.

**(E) Basic strength order :-**

If there is more resonance of lone pair or negative charge then it will be more stable, means less basicity.

$$\boxed{\text{Basic strength} \propto +M \propto +I \propto \frac{1}{-M} \propto \frac{1}{-I}}$$

**Example :** Give basic strength order :

(i)

l.P. is stabilized by resonance — no resonance of l.p. so maximum basic — l.p. is stabilized by resonance stabilized and +I of $CH_3$

basic order — II > III > I

(ii)

stable by resonance — localized l.p. on more EN

basic order — III > II > I

**Example :** Give basic strength order for :

(i)

diphenyl amine — benzyl amine

more resonance — no resonance

**Solution.** 3 > 2 > 1

**Example :** Aniline is less basic than alkyl amine, why ?

**Solution.** Due to delocalization of l.p. of nitrogen in aniline, aniline is less basic.

**Example :** Which is weakest base?

(i) $C_6H_5—CH_2—NH_2$ (ii) $C_6H_5—CH_2—NH—CH_3$

(iii) $O_2N—CH_2—NH_2$

(iv) $CH_3—NH—CHO$

**Solution.** (iv) due to resonance of l.p.

- **Rules for stability of resonating structure (R.S)**

**(i)** Non-polar R.S. is more stable than polar resonating structures.

**(ii)** In polar R.S. complete octet is more stable than incomplete octet.

**(iii)** R.S. in which positive charge on more EN is less stable.

**Example :** Arrange the following for stability order.

(i) $CH_2=CH-Cl$ — non-polar; $\overset{\ominus}{C}H_2-CH=\overset{\oplus}{Cl}$ — complete octet; $\overset{\ominus}{C}H_2-\overset{\oplus}{C}H-Cl$ — incomplete octet

stability order : 1 > 2 > 3

(ii)

non-polar > complete octet > incomplete octet

(iii) $R-\overset{\oplus}{C}=O$ incomplete octet (Acylium ion) < $R-C\equiv\overset{\oplus}{O}$ complete octet

(iv) $CH_2=CH-\overset{\ominus}{O}$ negative charge on more EN atom > $\overset{\ominus}{C}H_2-CH=O$ negative charge on less EN atom

## Illustrations

**Illustration 6.** Give stability order of :

**(i)**

**Solution.**

–M charge↑↑ | –I charge ↑ | +I charge ↓ | +M charge↓↓

So stability order IV > III > II > I

**(ii)**

**Solution.**

| –M | –I | +I | +M |
|---|---|---|---|
| charge↓↓ | charge ↓ | charge ↑ | charge↑↑ |

Stability order I > II > III > IV

**(iii)**

**Solution.**

–M and M = 0 –M and
more –I only –I less –I
charge is minimum
So stability order I > III > II > IV

**Illustration 7.** Give acidic strength order for :

–M –I +I +M

**Solution.** So acidic order is I > II > III > IV

**Illustration 8.** The mixture of ortho-nitrophenol and para-nitrophenol can be separated by steam distillation. Why and which can be distilled out ?

**Solution.** Ortho-nitrophenol is distilled out due to less B.P. of ortho-nitrophenol it is more volatile

**Illustration 9.** What is the increasing order of resonance stabilization of benzene, naphthalene and anthracene.

**Solution.** The values of resonance energy for benzene, naphthalene and anthracene are 36, 76 and 85 Kcal per mole respectively. It is clear from these values that the resonance stabilisation of naphthalene is more than that of benzene and less than that of anthracene. Thus, the increasing order of resonance stabilisation is as follows.

Benzene Naphthalene Anthracene

## BEGINNER'S BOX-1

### Electronic Effects

**1.** Which of the following orbital overlaps is involved in the formation of the carbon–carbon single bond in the molecule $HC \equiv C - CH = CH_2$?

(A) $sp^3$ - $sp^3$ (B) $sp^2$ - $sp^3$ (C) sp - $sp^2$ (D) $sp^3$ - sp

**2.** The inductive effect :

(A) implies the atom's and group's ability to cause bond polarization

(B) increases with increase of distance

(C) implies the transfer of lone pair of electrons from more electronegative atom to the lesser electronegative atom in a molecule

(D) implies the transfer of lone pair of electrons from lesser electronegative atom to the more electronegative atom in a molecule

**3.** Decreasing –I effect of given groups is -

(a) –CN (b) $-NO_2$ (c) $-NH_2$ (d) –F

(A) b > a > d > c (B) b > c > d > a (C) c > b > d > a (D) c > b > a > d

**4.** Which of the following has incorrect direction of Inductive effect?

(A)

(B)

(C)

(D) $CH_3 \leftarrow C(=O) \rightarrow CH_2 \rightarrow CH_3$

**5.** Which of the following statements is not true about the resonance contributing structures of a resonance hybrid?

(A) Contributing structures contribute to the resonance hybrid in proportion of their energies

(B) Equivalent contributing structures make the resonance very effective.

(C) Contributing structures represent hypothetical molecules having no real existence

(D) Contributing structures are less stable than the resonance hybrid

**6.** In which of the following delocalisation of $\pi$-electron is possible?

(A) $CH_2 = CH - CH_2 - CHO$

(B) $CH_2 = CH - CH = O$

(C) $CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3$

(D) $CH_2 = CH - CH_2 - CH = CH_2$

**7.** Which of the following is not a pair of resonating structures ?

(A) $H - C \equiv \overset{\oplus}{N}H$ ; $H - \overset{\oplus}{C} = \ddot{N}H$

(B) $CH_3CH = CHCH_3$ ; $CH_3CH_2CH = CH_2$

(C) $CH_3 - \underset{\underset{O^{\ominus}}{|}}{C} = CH - \underset{\underset{O}{\|}}{C} - CH_3$; $CH_3 - \underset{\underset{O}{\|}}{C} - \overset{\ominus}{C}H - \underset{\underset{O}{\|}}{C} - CH_3$

(D)

**8.** Which of the following resonating structure contributes equally to the resonance hybrid.

(A) $CH_3-\overset{\oplus}{C}(CH_3)-CH=CH-CH_3 \longleftrightarrow CH_3-C(CH_3)=CH-\overset{\oplus}{C}H-CH_3$

(B) $CH_3-C(=O)-NH_2 \longleftrightarrow CH_3-C(O^{\ominus})=\overset{\oplus}{N}H_2$

(C) $CH_3-C(=O)(O^{\ominus}) \longleftrightarrow CH_3-C(O^{\ominus})(=O)$

(D) $CH_2=CH-CH=O \longleftrightarrow \overset{\oplus}{C}H_2-CH=CH-O^{\ominus}$

**9.** The type of hybrid orbitals used by C and N in the formation of C–N bond in pyrrole
is :

(A) $sp^2$ and $sp^3$ (B) $sp^2$ and sp (C) $sp^2$ and $sp^2$ (D) $sp^2$ and s

**10.** Which of the following statements is NOT true ?

(A) Resonance forms must obey normal valency rules

(B) Resonance forms are in equilibrium

(C) The hybrid is more stable than the individual resonance forms

(D) Resonance forms differ only in the distribution of electrons

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## 1.3 Hyperconjugation Effect or H-effect

Complete transfer of $e^-$ of –C–H σ bond towards π bond or positive charge or free electron is called as H-effect (permanent effect). It is also called as non-bonded resonance and given by Nathen and Baker.

- **Conditions of H-effect**

**(i)** If there is one C–H σ bond and one positive charge are at alternate position then there will be H effect.

all are called as hyperconjugation structures.

If number of α – H are more then there will be more number of hyperconjugation structures, so more stable carbocation.

**(ii)** Carbon which is attached to $sp^2$ C is called as α–C and H which are attached to α-C are called as α-H.

If there is one –C–H σ bond and one free $e^-$ are at alternate position then there will be H-effect.

**(iii)** If there is one –C–H σ bond and π bond are at alternate position then there will be H-effect.

**Note :** If there is one –C–H σ bond and one negative charge at alternate position then there will be no H-effect.

(No H - effect)

no shifting of —C—H σ bond, because anion have complete octet. ($8e^-$)

- **Application of H-effect or h-effect**

**(A) Stability of carbocation :**

- If more hyperconjugation structures (more α-H) then more stable cation.
- Stability of carbocation ∝ No. of hyperconjugative structures ∝ No. of α H.

**Example :** Give stability order for :-

**(i)**

9 α-H  6 α-H  3 α-H  Zero α-H

Maximum stable

**(ii)**

**(B) Stability of carbon free radicals :**

- Stability of carbon free radical is explained by M and H-effect.
- More hyper conjugation structures (more α-H) more stable free radical.

**Example :** Give stability order for :-

3° 2° 1°

9 α-H 6 α-H 3 α-H Zero α-H

Maximum stable

Stability order I > II > III > IV

**(C) Stability of alkenes :** More hyperconjugation structures (more α-H) more stable alkene.

**(i)** $CH_3—CH=CH_2 >$ $CH_2=CH_2$

3 α-H Zero α-H

more stable

**(ii)** Stability order of alkenes will be

**Example :** Which of the following alkene is maximum stable?

(A) $R_2C=CR_2$ (B) $R—CH=CR_2$

(C) $R—CH=CH—R$ (D) $R—CH=CH_2$

**Solution.** (A) due to more substituted alkene.

**(D) Heat of hydrogenation :**

$R—CH=CH_2 + H_2 \longrightarrow R—CH_2—CH_3 + \Delta H$ (Heat of hydrogenation)

Heat evolved when any unsaturated hydrocarbon is hydrogenated is called heat of hydrogenation (ΔH)

If alkene is more reactive towards hydrogen then it will evolve more ΔH.

So, $\text{Heat of hydrogenation} \propto \dfrac{1}{\text{stability of alkene}} \propto \dfrac{1}{\text{number of } \alpha - H}$

## Illustrations

**Illustration 10.** Which of the following is maximum stable?

**(A)** Conjugated alkadiene ($CH_2=CH—CH=CH_2$)

**(B)** Isolated alkadiene ($CH_2=CH—CH_2—CH=CH_2$)

**(C)** Cumulated alkadiene ($CH_2=C=CH_2$)

**(D)** All are equal.

**Solution.** **(A)**

Due to resonance conjugated alkadiene is maximum stable. Isolated is more stable than cumulated alkadiene due to H-effect.

**Illustration 11.** Give order of electron density in benzene ring :

**Solution.** Electron density is $\propto$ no of $\alpha - H$

So, order is I > II > III > IV

### 1.4 Electromeric effect : (E Effect)

It is a temporary effect. The organic compounds having a multiple bond (a double or triple bond) show this effect in the presence of an attacking reagent only. It is defined as the complete transfer of a shared pair of -electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent. The effect is annulled as soon as the attacking reagent is removed from the domain of the reaction. It is represented by E and the shifting of the electrons is shown by a curved arrow ( ).

**Example.**

## 2.0 AROMATICITY

Compound which follow Huckel's rule is known as Aromatic compound.

### 2.1 Huckel's Rule

Cyclic, planar and completely conjugated compound which have $(4n+2)\pi$ electrons in conjugation is known as aromatic compound.

### 2.2 Antiaromatic Compound

Cyclic, planar and completely conjugated compound which have $(4n)\pi$ electrons in conjugation is known as anti-aromatic compound.

where n is = 0, 1, 2, 3.....

**Example.**

Determine whether the following compounds are Aromatic, Anti-aromatic or Non-aromatic.

**(i)** **(ii)** **(iii)** **(iv)** **(v)**

**(vi)** **(vii)** **(viii)** **(ix)** **(x)**

**Ans.** **(i)** Aromatic **(ii)** Anti-aromatic **(iii)** Non-aromatic **(iv)** Non-aromatic
**(v)** Aromatic **(vi)** Anti-aromatic **(vii)** Aromatic **(viii)** Aromatic
**(ix)** Aromatic **(x)** Aromatic

## 3.0 ATTACKING REAGENTS

The species which attack on a substrate molecule or intermediate and form a product is called as attacking reagent. These are of two types :

### 3.1 Electrophilic Reagent or Electrophiles

Electrophilic (electro + philic)

(electron + loving)

The reagent which attacks on the negative of the molecule or loves electrons are called electrophiles.

Electrophiles may be positively charged or electron deficient molecule (molecule with sextet or septet).

**(A) Positively charged electrophiles :**

$\overset{\oplus}{H}$, $\overset{\oplus}{N}O$, $\overset{\oplus}{N}O_2$, $\overset{\oplus}{X}$, $\overset{\oplus}{R}$, $C_6H_5\overset{\oplus}{N}_2$, $\overset{\oplus}{C}H_2—OH$, $CH_3—\overset{\oplus}{C}(=O)$

**(B) Neutral electrophiles :-** Which possess a electron dificiency.

(a) All Lewis acids as :

$BF_3$, $AlCl_3$, $ZnCl_2$, $BeCl_2$, $FeCl_3$, $SnCl_2$, $SnCl_4$.

(b) Neutral compounds in which electron dificient centre is present.

The star (*) indicates the atom that accept electrons.

(c) Free radicals, carbenes & nitrene acts as electrophiles.

### 3.2 Nucleophilic Reagent or Nucleophiles

Which attack on the electron dificient site of the substrate or loves nucleus.

Nucleophilic (Nucleo + philes)
↓
(Nucleus + loving)

Nucleophiles may be negatively charged ions or possess a lone pair of electron or donate an unshared electron pairs.

**(A)** Negatively charged nucleophiles.

$\overset{\ominus}{H}$, $\overset{\ominus}{OH}$, $\overset{\ominus}{OR}$, $\overset{\ominus}{CN}$, $\overset{\ominus}{X}$($\overset{\ominus}{I}$, $\overset{\ominus}{Br}$, $\overset{\ominus}{Cl}$, $\overset{\ominus}{F}$), $\overset{\ominus}{R}$, $R-COO^{\ominus}$, $\overset{\ominus}{NH_2}$, $\overset{\ominus}{CH_2}-COR$, $\overset{\ominus}{SH}$, $HSO_4^{\ominus}$, $\overset{\ominus}{NO_3}$, $\overset{\ominus}{RS}$, $\overset{\ominus}{CO_3}$, $CH_2=\overset{\ominus}{CH}$, $\overset{\ominus}{N}=\overset{\oplus}{N}=\overset{\ominus}{N}$.

**(B)** All Lewis base which contains lone pairs :

$H_2\ddot{O}$, $R-\ddot{O}H$, $R-\ddot{O}-R$, $\ddot{N}H_3$, $R-\ddot{N}H_2$, $R_3\ddot{N}$, $R\ddot{S}H$, $R-\ddot{S}-R$, $H_2\ddot{S}$

**(C)** $\overset{*}{R}-Mg-X$, $\overset{*}{R}-Li$, $LiAl\overset{*}{H}_4$, $CH_3-\overset{*}{CN}$, $NaB\overset{*}{H}_4$, $\overset{*}{R}_2Zn$, $\overset{*}{R}_2CuLi$, $\overset{*}{R}_2Cd$, $\overset{*}{Bu}_2Al\overset{*}{H}$

The star (*) indicates the atom which donates electrons to the substrate.

| S.No. | Electrophile | Nucleophile |
|---|---|---|
| 1 | Accepts the electron pair | Supplies the electron pair |
| 2 | Electron deficient | Electron rich |
| 3 | Attacks the points of high electron density | Attacks the point of low electron density |
| 4 | Lewis acid | Lewis base |
| 5 | Possess an empty orbital to receive the electron pair | Possess an electron pair which is loosely held and can be supplied easily |
| 6 | Usually positively charged species | Usually negatively charged species |
| 7 | Forms an extra bond with the nucleophile | Increases its covalency by one unit |

## BEGINNER'S BOX-2

### Electronic effects and Applications

**1.** The correct order of decreasing number of hyperconjugative hydrogen atom of the following compounds is -

(A) $CH_3CH{=}CH_2 > CH_3CH_2CH{=}CH_2 > (CH_3)_2\ CHCH{=}CH_2$
(B) $(CH_3)_2\ CHCH{=}CH_2 > CH_3CH{=}CH_2 > CH_3CH_2CH{=}CH_2$
(C) $(CH_3)_2\ CHCH{=}CH_2 > CH_3CH_2CH{=}CH_2 > CH_3CH{=}CH_2$
(D) $CH_3CH_2CH{=}CH_2 > CH_3CH{=}CH_2 > (CH_3)_2\ CHCH{=}CH_2$

**2.** Which of the following molecule has longest C=C bond length?

(A) $CH_2 = C = CH_2$ (B) $CH_3 — CH = CH_2$ (C) (D)

**3.** Which one of the following compounds maximum π electron density on aromatic ring?

(A) (B) (C) (D)

**4.** Which of the following statements is true about this molecule?

(A) $C_1$-$C_2$ and $C_3$-$C_4$ bonds are of same length.
(B) $C_1$-$C_2$ bond is shorter than $C_3$-$C_4$ bond.
(C) $C_1$-$C_2$ bond is longer than $C_3$-$C_4$ bond.
(D) $C_1$-$C_2$ and $C_2$-$C_3$ bonds are of same length.

**5.** Which has the most aromatic nature ?

(A) (B)

(C) (D) All having same aromatic character

**6.** Which is the most aromatic in character ?

(A) (B) (C) (D)

**7.** Rank the following alkenes in order of decreasing heats of hydrogenation (largest first):

(I) (II) (III) (IV)

(A) II > III > IV > I (B) II > IV > III > I (C) I > III > IV > II (D) I > IV > III > II

**8.** Which of the following molecules has all the effects : inductive, mesomeric and Baker Nathan effect?

(A) $C_2H_5Cl$ (B) $CH_3–CH=CH_2$

(C) $CH_2=CH–CH=CH_2$ (D) $CH_3–CH=CH–\underset{\underset{O}{\|}}{C}–CH_3$

**9.** C—C and C=C bond lengths are equal in :

(A) Benzene (B) 1,3 buta-di-ene (C) 1, 3 cyclohexa-di-ene (D) None

**10.** Which species is not aromatic?

(A)

(B)
(C)

(D)


## 4.0 REACTION INTERMEDIATES

In the study of organic chemistry follwing intermediates are more important :

**(i)** carbocation **(ii)** carbanion **(iii)** carbon free radical

**(iv)** carbene **(v)** Benzyne **(vi)** nitrene

### 4.1 Carbocation

Positively charged 'C' atom as reaction intermediate is called carbocation. Generally it contains only six electron in three bonds. It is electron deficent species act as electrophilic and lequid acid.

- **Structure and Hybridisation**

Classical carbocation (carbenium ion) are $sp^2$ hybridised and of planer structure. Unhybridised vaccant 'p'orbital lies below and above the plane.

- **Stability**

Carbocation are stabilised by :

**(i)** + I effect **(ii)** + M effect **(iii)** Hyper-conjugation

- **The generation of $-\overset{|}{\underset{|}{C}}^{\oplus}$ (carbonium ion)**

**(A) By the direct ionisation :** (In highly polar medium)

(i) $(CH_3)_3Cl \longrightarrow (CH_3)_3C^{\oplus} + Cl^{\ominus}$

(ii) $CH_2{=}CH{-}\overset{Cl}{\overset{|}{C}}H_2 \xrightarrow[\Delta]{-\overset{\ominus}{Cl}} CH_2{=}CH{-}\overset{\oplus}{C}H_2$

**(B) By the protonation of unsaturated compound :**

**(i)** $-CH{=}CH- \xrightarrow{H^{\oplus}} -\overset{\curvearrowright}{CH} \xrightarrow{H^{\oplus}} CH \longrightarrow CH^{\oplus}-CH_2-$

**(ii)** $>C{=}\ddot{\underset{\curvearrowleft}{O}}: \xrightarrow{H^{\oplus}} -\overset{\oplus}{C}-\overset{H}{\overset{|}{\ddot{O}}}:$

**(iii)** $-C{\equiv}\overset{\curvearrowright}{N}: \xrightarrow{H^{\oplus}} -\overset{\oplus}{C}{=}N{-}H$

**(C) By the protonation of lone pair of electron :**

**(i)** $R{-}CH_2{-}\ddot{\underset{\curvearrowleft}{O}}{-}H \xrightarrow{H^{\oplus}} R{-}CH_2{-}\overset{\oplus}{\underset{H}{\underset{|}{O}}}{-}H \xrightarrow{-H_2O} R{-}\overset{\oplus}{C}H_2$

**(ii)** $R{-}\overset{R}{\overset{|}{\underset{\curvearrowleft}{\ddot{O}}}}: \xrightarrow{H^{\oplus}} R{-}\overset{R}{\underset{\oplus}{\underset{|}{\ddot{O}}}}{-}H \longrightarrow \overset{\oplus}{R} + H{-}O{-}R$

**(iii)** $R{-}\overset{O}{\overset{\|}{C}}{-}\ddot{\underset{\curvearrowleft}{O}}{-}R \xrightarrow{H^{\oplus}} R{-}\overset{O}{\overset{\|}{C}}{-}\overset{\oplus}{\underset{H}{\underset{|}{O}}}{-}R \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{\overset{\oplus}{+}}H{-}\ddot{O}{-}R$

**(D) By electrophilic attack on alkyl halide or acyl halide :**

**(i)** $CH_3{-}CH_2{-}Cl \xrightarrow{AlCl_3} CH_3{-}CH_2{-}\overset{\oplus}{Cl}.....\overset{\ominus}{AlCl_3} \xrightarrow{-AlCl_4^{\ominus}} CH_3{-}\overset{\oplus}{C}H_2$

**(ii)** $R{-}\overset{O}{\overset{\|}{C}}{-}\overset{\ominus}{Cl} \xrightarrow{AlCl_3} R{-}C{-}\overset{\oplus}{Cl}.....\overset{\ominus}{AlCl_3} \xrightarrow{-AlCl_4^{\ominus}} R{-}\overset{\oplus}{C}{=}\ddot{O}: \longleftrightarrow R{-}C{\equiv}\overset{\oplus}{O}:$

**(E) By the decomposition of diazonium salt :**

**(i)** $CH_3{-}\overset{\curvearrowright}{N_2^{\oplus}} - Cl^{\ominus} \longrightarrow \overset{\oplus}{C}H_3 + N_2 + Cl^{\ominus}$

**(ii)**

- **Reaction of Carbocation (carbonium ion)**

**(A) Proton Loss :** To form a multiple bond.

**(i)**

**(B) Combination with Nucleophiles :**

**(i)**

**(ii)**

**(C) Addition to an alkene :**

**(i)** $^{+}CH_3 + CH_2 = CH_2 \rightarrow CH_3 - CH_2 - {}^{+}CH_2$

**(ii)**

**(D) Molecular Rearrangement :**

A carbocation would undergo a molecular rearrangement when it could produce a more stable carbocation e.g.

**(i) Hydride Shift :**

**(ii) Methyl Shift :**

**(iii) Aryl Shift :**

**(iv) Ring Expansion**

**(v) Ring Contraction**

**(E) Abstraction of hydride ion :**

4.2 Carbanion

A carbon intermediate which contain three bond pair and a negative charge on it, is called carbanion.

**Eg :** $CH_3^{\ominus}$, Methyl carbanion

$CH_3 - CH_2^{\ominus}$, Ethyl carbanion

$(CH_3)_2CH^{\ominus}$ Isopropyl carbanion

- **Structure and Hybridisation**

On the basis of the structure carbanion are of two types

**(a)** Carbanion ($sp^3$) hybridised (pyramidal)

**(b)** Planer carbanion ($sp^2$) hybridised (–ve charge is attached to π bonded system)

Unhybridised pure 'p' orbital

**Example :**

**(i)** $CH_2{=}CH-\overset{\ominus}{C}H_2$ ($sp^2$)

**(ii)**

**(iii)**

**(iv)** $\overset{\ominus}{C}H_2 -- \overset{O}{\overset{\|}{C}} - H$ ($sp^2$)

- **Stability of carbanion**

  Carbanions are stabilised by electron withdrawing effects as

  **(a)** –I effect

  **(b)** –M effect

  **(c)** Delocalisation of charge

  **(d)** Aromatization

- **Generation of Carbanion**

  **(A)** By Acid base reaction

**(i)**

**(ii)** $CH \equiv C-H \xrightarrow[-NH_3]{\ominus NH_2} CH \equiv \overset{\ominus}{C}$

**(iii)** $CH_3 - C \equiv C - H \xrightarrow[-NH_3]{\ominus NH_2} CH_3 - C \equiv C^{\ominus}$

**(B)** **In the form of organometallic compound :**

**(i)** $CH_3 - Cl \xrightarrow{Mg/ether} \overset{\delta-}{C}H_3\overset{\delta+}{M}gCl \longrightarrow \overset{\delta\ominus}{C}H_3\overset{\delta+}{M}gCl$

**(ii)** $2CH_3 - CH_2 - Cl \xrightarrow{Cd} (CH_3 - CH_2)_2Cd$

**(iii)** $2CH_3CH_2 - Br \xrightarrow{Zn} (CH_3 - CH_2)_2Zn + ZnBr_2$

**(iv)** $2CH_3 - CH_2 - I \xrightarrow[CuI]{Li} (CH_3 - CH_2)_2CuLi$ (Gilmann Reagent)

**(v)** $Br -- CH_2 -- \overset{O}{\overset{\|}{C}} -- O - C_2H_5 \xrightarrow[Et_2O]{Zn} Br\overset{\delta+}{Zn}\overset{\delta-}{C}H_2 -- \overset{O}{\overset{\|}{C}} -- O - C_2H_5$

- **Reactions of Carbanion**

**(A) Attachment of $H^+$ :** e.g. $^{\ominus}CH_3 + H^{\oplus} \rightarrow CH_4$ as

**(B) Loss of Leaving Group :**

In the system $\overset{\ominus}{C}-\overset{X}{\overset{|}{C}}$ carbanion losses leaving group to form a $\pi$ bond.

i.e.

**(C) Addition Reaction**

Carbanion gives Nucleophilic addition reaction :

**E.g.**

4.3 Carbon free Radical

Free radical is a species that contain an unparied electron in valance shell of one of its atom and if the atom is carbon atom the free radical is known as CARBON FREE RADICAL. It has three bond pairs and one unpaired electron i.e. $-\overset{\ominus}{\underset{|}{C}}-$ unpaired electron.

- **Structure and Hybridisation**

A free radical may considered as having pyramidal structure which are rapidly interconverting, $sp^3$ hybridised.

Planer structure ; $sp^2$ hybridised.

- **Generation of Free Radicals:**

**By Homolytic bond breaking**

**(i)** $Br-Br \xrightarrow{h\gamma} 2Br^{\circ}$

**(ii)** $R-\overset{O}{\overset{||}{C}}-O-O-\overset{O}{\overset{||}{C}}-R \xrightarrow{h\gamma} 2R-\overset{O}{\overset{||}{C}}-O^{\circ}$

**(iii)** $R-N=N-R \xrightarrow{\Delta} 2R^{\circ} + N_2$

- **Reaction of Free Radicals**

**(A) Recombination (coupling) :**

**(i)** $\dot{C}H_3 + \dot{C}H_2CH_2-CH_3 \longrightarrow CH_3CH_2CH_2-CH_3$

**(ii)** $CH_3-\dot{C}H_2 + \dot{C}H_2-CH_3 \longrightarrow CH_3-CH_2-CH_2-CH_3$

**(B) Disproportionation :**

**(i)** $\overset{H}{\overset{|}{C}}H_2 - \dot{C}H_2 + CH_3 - \dot{C}H_2 \longrightarrow CH_2 = CH_2 + CH_3 - CH_3$

**(ii)** $2CH_3 - \dot{C}H - CH_3 \rightarrow CH_3 - CH = CH_2 + CH_3 - CH_2 - CH_3$

**(C) Generation of another free radical**

$R^\circ + Br_2 \rightarrow R - Br + Br^\circ$

**(D) Reaction with unsaturated compound :**

**(i)** $CH_3^\bullet + CH_2 = CH_2 \rightarrow CH_3 - CH_2 - \dot{C}H_2$

**(ii)** $CH_3 - CH = CH_2 \xrightarrow{\dot{C}H_2} CH_3 - \dot{C}H - CH_2 - CH_3$

**(E) Polymerisation :**

$$\dot{C}H_3 + CH_2 = CH_2 \longrightarrow CH_3 - CH_2 - \dot{C}H_2 \xrightarrow{CH_2=CH_2} CH_3 - CH_2 - CH_2 - CH_2 - \dot{C}H_2$$

$$\xrightarrow{CH_2=CH_2} \dot{C}H_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3 \xrightarrow{CH_2=CH_2}$$

## 5.0 TYPES OF REACTIONS

In organic chemistry the following types of reaction are more important,

**(i)** Substitution reaction **(ii)** Elimination reaction

**(iii)** Addition reaction **(iv)** Rearrangement reaction

### 5.1 Substitution Reaction

**Electrophilic Substitution Reactions :**

In this reaction attacking reagent is Electrophile

- **Nucleophilic Substitution Reaction**

In this reaction attacking reagent is nucleophile

$OH^- + CH_3CH_2Cl \rightarrow CH_3CH_2OH + Cl^-$

### 5.2 Elimination Reactions

Elimination reactions, in which two groups are removed from a molecule, neither being replaced by another group, are the reverse of addition reactions. Usually they involve the loss of two substitutions from vicinal atoms resulting in the formation of a double or triple bond. Most commonly a proton is lost from one carbon whereas a nucleophile is lost from the adjacent carbon.

This type of elimination reaction is known β-elimination or 1, 2,-elimination reaction.

### 5.3 Addition Reaction

The reaction in which reagent adds to a multiple bonds to give less unsaturated or completely saturated product, are known as addition reactions. e.g.

**Example :**

**(i)** $CH_2 = CH_2 \xrightarrow{H_2} CH_3 - CH_3$

**(ii)** $CH_3 - CH = CH_2 \xrightarrow{HCl} CH_3 - \overset{Cl}{\overset{|}{CH}} - CH_3$

**(iii)** $CH_3 - CH = CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3 - CH_2 - \overset{Br}{\overset{|}{CH_2}}$

**(iv)** $CH_2 = CH_2 \xrightarrow[H^{\oplus}]{H-OH} \overset{H}{\overset{|}{CH_2}} - \overset{OH}{\overset{|}{CH_2}}$

**(v)** $CH_2 = CH_2 \xrightarrow[HOCl]{H_2O+Cl} \overset{Cl}{\overset{|}{CH_2}} — \overset{OH}{\overset{|}{CH_2}}$

### 5.4 Rearrangement Reaction

## BEGINNER'S BOX-3

## REACTION INTERMEDIATES, STABILITY ORDER, ACIDIC STRENGTH AND BASIC STRENGTH

**1.** Which of the following shows the correct order of decreasing acidity?

(A) $PhCO_2H > PhSO_3H > PhCH_2OH > PhOH$

(B) $PhSO_3H > PhOH > PhCH_2OH > PhCH_2OH$

(C) $PhCO_2H > PhOH > PhCH_2OH > PhSO_3H$

(D) $PhSO_3H > PhCO_2H > PhOH > PhCH_2OH$

**2.** Find the order of reactivity of labelled hydrogen with $NaNH_2$.

(A) 1 > 2 > 3 (B) 3 > 2 > 1 (C) 3 > 1 > 2 (D) 2 > 3 > 1

**3.** Which is maximum basic in nature ?

(A)
(B)
(C)
(D)

**4.** The basic strength order of following anion :

(A) $CH_3-\overset{\ominus}{C}H_2 > \overset{\ominus}{N}H_2 > CH_2=\overset{\ominus}{C}H > CH\equiv\overset{\ominus}{C} > H\overset{\ominus}{O} > \overset{\ominus}{F}$

(B) $\overset{\ominus}{N}H_2 > CH_3-\overset{\ominus}{C}H_2 > CH_2=\overset{\ominus}{C}H > CH\equiv\overset{\ominus}{C} > \overset{\ominus}{F} > H\overset{\ominus}{O}$

(C) $CH_3-\overset{\ominus}{C}H_2 > CH_2=\overset{\ominus}{C}H > \overset{\ominus}{N}H_2 > CH\equiv\overset{\ominus}{C} > H\overset{\ominus}{O} > \overset{\ominus}{F}$

(D) $\overset{\ominus}{F} > H\overset{\ominus}{O} > CH\equiv\overset{\ominus}{C} > CH_2=\overset{\ominus}{C}H > \overset{\ominus}{N}H_2 > CH_3-\overset{\ominus}{C}H_2$

**5.** Arrange stability of the given carbocations in decreasing order :

(I)
(II)
(III)
(IV)

(A) I > II > III > IV (B) III > II > I > IV (C) IV > I > II > III (D) II > III > I > IV

**6.** Which of the following carbocation is most stable ?

(A)
(B)
(C)
(D)

**7.** Rank the following radicals in order of Decreasing stability

(I) (II) (III) (IV)

(A) III > II > I > IV (B) III > II < I < IV (C) II > III > II > IV (D) III < II < I < IV

**8.** Which will give most stable cation upon strong heating?

(A) (B) $(Ph)_3C–Cl$ (C) (D)

**9.** Hybridisation of arrow headed 'C' is

(A) $sp^2\ sp^3$ (B) $sp^3\ sp^3$ (C) $sp^2\ sp^2$ (D) $sp^3\ sp^3d$

**10.** In which of the following case 'H' shift is more preferable than '$CH_3$' shift :

(A) (B) (C) (D) all

## 6.0 STRUCTURAL ISOMERISM

Compounds which have same molecular formula but have different structural formula are known as structural isomers.

| S.No. | Isomers | Characteristics | Conditions |
|---|---|---|---|
| 1 | Chain Isomers | They have different size of main chain or side chain | They have same nature of locant |
| 2 | Positional Isomers | They have different position of locant | They should have same size of main chain and side chain and same nature of locant |
| 3 | Functional Isomers | Different nature of locant | Chain and positional isomerism is not considered |
| 4 | Metamerism | Different nature of alkyl group along a polyvalent functional group | They should have same nature of functional group chain & positional isomer is ignored |
| 5 | Tautomerism | Different position of hydrogen atoms | The two functional isomers remains in dynamics equilibrium with each other |

### 6.1 Chain Isomerism

The compounds which have same molecular formula, same functional group, same position of functional group or multiple bond or substituent but different arrangement of carbon chain show chain isomerism.

**Examples**

**(i)** $CH_3-CH_2-CH_2-CH_3$ and $CH_3-CH(CH_3)-CH_3$

Butane(4C) — 2-Methyl propane (3C)

**(ii)** $CH_3-CH_2-CH=CH_2$ and $CH_2=C(CH_3)-CH_3$

1–Butene(4C) — 2-Methyl-1-propene(3C)

**(iii)** $CH_3-CH_2-CH_2-CH_2-OH$ and $CH_3-CH(CH_3)-CH_2-OH$

1-Butanol (4C) — 2-Methyl-1-propanol (3C)

**(iv)** $CH_3-CH_2-CH_2-CH_2-C(=O)-OH$ , $CH_3-CH(CH_3)-CH_2-C(=O)-OH$ , $CH_3-C(CH_3)_2-C(=O)-OH$

Pentanoic acid — 3-Methyl butanoic acid — 2,2-Dimethyl propanoic acid

### 6.2. Positional Isomerism

The compounds which have same molecular formula, same functional group, same parent carbon chain but different position of functional group or multiple bond or substituents, shows position isomerism.

**Examples**

**(i)** $CH_2=CH-CH_2-CH_3$ — But–1–ene

$CH_3-CH=CH-CH_3$ — But–2–ene

**(ii)** $CH_3-CH_2-CH_2-CH_2-OH$ — 1–Butanol

$CH_3-CH_2-CH(OH)-CH_3$ — 2–Butanol

**(iii)** $CH_3-CH_2-CH_2-CH_2-Cl$ — 1–Chlorobutane

$CH_3-CH_2-CH(Cl)-CH_3$ — 2–Chlorobutane

## Illustrations

**Illustration 12.** How many structural isomers are possible for molecular formula $C_4H_{10}$?

**Solution** $C_4H_{10}$ have two isomers **:** Both butane and isobutane are chain isomers.

Butane Isobutane

**Illustration 13.** How many structural isomers are possible for molecular formula $C_5H_{12}$?

**Solution** $C_5H_{12}$ have three isomers **:** All of three structures are chain isomers because only carbon chain (parent) is different.

Pentane 2–Methyl butane 2,2–Dimethylpropane

**Illustration 14.** How many structural isomers are possible for molecular formula $C_6H_{14}$?

**Solution** $C_6H_{14}$ has 5 isomers :

**(a)** $CH_3CH_2CH_2CH_2CH_2CH_3$

Hexane

**(b)**

2–Methyl pentane

**(c)**

3–Methyl pentane

**(d)**

2,3–Dimethyl butane

**(e)**

2,2–Dimethyl butane

a–b, b–d, a–c, c–d $\longrightarrow$ Chain Isomers

b–c, d–e $\longrightarrow$ Position Isomers

**Illustration 15.** How many structural isomers are possible for molecular formula $C_3H_6Cl_2$?

**Solution** $C_3H_6Cl_2$ has 4 isomers **:** Position of chlorine atom is different in all the structure, so these are position Isomers.

**(i)**
1,1–Dichloropropane

**(ii)**
1,3–Dichloropropane

**(iii)**
2,2–Dichloropropane

**(iv)**
1,2–Dichloropropane

**Illustration 16.** How many benzenoid isomers are possible for molecular formula $C_8H_{10}$?

**Solution** $C_8H_{10}$ has 4 aromotic isomers

**(o,m,p)**

## 6.3. Functional Isomerism

Compounds which have same molecular formula but different functional groups are known as functional isomers.

Following compounds show Functional isomerism, as they have same molecular formula and different functional group.

**(i)** Alcohol and ether $\longrightarrow$ $CH_3—CH_2—OH$ and $CH_3—O—CH_3$

**(ii)** Aldehydes and ketones $\longrightarrow$ $CH_3—CH_2—\underset{\underset{O}{\|}}{C}—H$ and $CH_3—\underset{\underset{O}{\|}}{C}—CH_3$

**(iii)** Acids and ester $\longrightarrow$ $CH_3—\underset{\underset{O}{\|}}{C}—OH$ and $H—\underset{\underset{O}{\|}}{C}—O—CH_3$

**(iv)** Cyanide and isocyanide $\longrightarrow$ $CH_3—CH_2—CH_2—CN$ and $CH_3—CH_2—CH_2—NC$

**(v)** Nitro and Nitrite $\longrightarrow$ $CH_3—CH_2—N(=O)—O$ and $CH_3—CH_2—O—N=O$

**(vi)** Keto and enol $\longrightarrow$ $CH_3—C(=O)—CH_3$ and $CH_2=C(OH)—CH_3$

**(vii)** Amide and Oxime $\longrightarrow$ $CH_3—C(=O)—NH_2$ and $CH_3—CH=NOH$

**(viii)** 1°, 2°, 3° amines

**(a)** $CH_3—CH_2—CH_2—NH_2$ **(b)** $CH_3—NH—CH_2—CH_3$ **(c)** $CH_3—N(CH_3)—CH_3$

**(ix)** Alcoholic and phenolic compounds :

and


**(x)** Alkyl halides do not show Functional isomerism.

## 6.4 Metamerism

Same molecular formula, same polyvalent Functional group but different alkyl or aryl groups attached to polyvalent Functional group.

Polyvalent Functional group [More than one free valency] are :

$—O—$ , $—S—$, $—C(=O)—O—$, $—C(=O)—NH—$, $—NH—$, $—N(—)—$,

,


**Examples**

**(i)** $CH_3—O—CH_2—CH_2—CH_3$ ; $CH_3–CH_2–O–CH_2–CH_3$

Both are metamers.

**(ii)** $CH_3—CH_2—NH—CH_2—CH_3$ $CH_3—NH—CH_2—CH_2—CH_3$

N–Ethyl ethanamine N–Methyl propanamine

They are only metamers.

## BEGINNER'S BOX-4

### Structural Isomerism

**1.** The compounds $C_2H_5OC_2H_5$ and $CH_3OCH_2CH_2CH_3$ are

(A) chain isomers (B) geometrical isomers

(C) metamers (D) conformational isomers

**2.** The number of primary, secondary and tertiary amines possible with the molecular formula $C_3H_9N$ respectively.

(A) 1, 2, 2 (B) 1, 2, 1 (C) 2, 1, 1 (D) 3, 0, 1

**3.** Which of the following has **incorrect** relation?

(A)

&

identical

(B)

&

positional

(C)

&

positional

(D)

&

homologues

**4.** How many structural formula are possible when one of the hydrogen is replaced by a chlorine atom in anthracene?

(A) 3 (B) 7 (C) 4 (D) 6

**5.** How many structural isomers are possible for $C_5H_{10}$ (excluding stereoisomers)?

(A) 10 (B) 11 (C) 12 (D) 13

**6.** Which of the following is an isomer of diethyl ether?

(A) $(CH_3)_3$ COH (B) $CH_3CHO$ (C) $C_3H_7OH$ (D) $(C_2H_5)_2CHOH$

**7.** Total number of isomeric alcohols with formula $C_4H_{10}O$ are :

(A) 1 (B) 2 (C) 3 (D) 4

**8.** An alkane can show structural isomerism if it has ..... number of minimum carbon atoms -

(A) 1 (B) 2 (C) 3 (D) 4

**9.** How many chain isomers can be obtained form the alkane $C_4H_{10}$ is?

(A) 4 (B) 2 (C) 6 (D) 7

## 6.5. Tautomerism or Desmotropism

Tautomerism was introduced by "Laar". It's also called desmotropism.

- Desmotropism means bond turning. [Desmos = Bond ; Tropos = Turn]
- Tautomers are two structural isomers (having different functional groups) which exist in dynamic equilibrium with each other. The isomers change into each other by shifting of H-atom from one position to another position and simultaneously the position of π bond also changes.
- The tautomerism is also called **kryptomerism or allotropism or desmotropism or dynamic isomerism.**

**Example :**

keto ene + ol = enol

***Note :***

***(i)*** *Tautomers always exist in dynamic equilibrium.*

***(ii)*** *Number of electrons and lone pairs in both tautomers always remain the same.*

***(iii)*** *It is a chemical phenomenon which takes place only in liquids and gaseous phase only. It never takes place in solid state.*

***(iv)*** *The process can be catalyzed by the acid as well a bases.*

- **Condition for Tautomerism**

**(a)** **For carbonyl compounds :-** Carbonyl compounds having atleast one α–H show tautomerism

**(i)** 3 α H, show tautomerism.

**(ii)** 6 α H, show tautomerism

**(iii)** 1 α H, show tautomerism

**(iv)** No α H, No tautomerism

**(v)** No α H, No Tautomerism

**(vi)** 3 α H, shows tautomerism (Acetophenone)

**(vii)** No α H, No tautomerism (Benzophenone)

**(viii)** 2 α H, shows tautomerism

**(ix)** 4 α H, shows tautomerism

**(x)** α–H, attached $sp^2$ carbon does not take part in tautomerism

**(b)** **For nitro compounds :** Nitro compounds having atleast one α – H show tautomerism

Nitro form Aci nitro form

(acidic form so soluble in base)

***Note :*** *Nitro compounds with at least one α–H are soluble in NaOH.*

## Illustrations

**Illustration 17.** Which of the following show tautomerism?

(A) $CH_3CH_2—NO_2$ (B) $(CH_3)_2CH—NO_2$

(C) $(CH_3)_3C—NO_2$ (D) $Ph—CH_2—NO_2$

**Solution** (A), (B) and (D)

**Illustration 18.** Which of the following does not soluble in NaOH?

(A) $CH_3CH_2—NO_2$ (B) $(CH_3)_2CH—NO_2$

(C) $(CH_3)_3C—NO_2$ (D) $Ph—CH_2—NO_2$

**Solution.** Only (C)

**Illustration 19.** Which of the following show keto enol tautomerism?

(A)
(B)
(C)
(D)

**Solution** (A), (B) and (D)

- **Enol Content**

In case of monocarbonyl compounds, the compound mainly exists in Keto form (99%). The enol form is insignificant (less than 1%)

As stability of enol increases (due to increase in hyper-conjugation or resonance) % enol content increases.

The β-dicarbonyl (or 1, 3-dicarbonyl) compounds have significant enol contents due to resonance stabilization of enol form

keto form (≃ 25%) enol form (≃ 75%)

**(i)**

"keto" (≈ 99%) "enol" (≈ 1%)

**(ii)** Less stable or unstable

≈ 99% ≈ 1%

**(iii)**


"keto" (< 1%) "enol" (stable by resonance and aromatic nature) (> 99%)

**(iv)**


Aceto acetic ester (AAE)

- **In aqueous solution**

Keto from is stablised by intermolecular H–Bonding.

- **In liquid state**

Enol form is stabilised by intramolecular H–Bonding.

**(i)** Enol content $\propto$ number of >C=O group.

**(ii)** If number of >C=O groups are equal then proportional to number of $\alpha$–H.

- **Acetyl acetone : (On same pattern)**

## BEGINNER'S BOX-5

### Tautomerism

**1.** Arrange the following in correct order of enol content.

(a) $CH_3COOCH_3$

(b) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

(c) $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-H$

(d) $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$

**2.** Which have maximum stable enol form?

(A)

(B)

(C)

(D)

**3.** Arrange the following in correct order of enol content.

(I) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_2=\underset{\underset{OH}{|}}{C}-CH_3$

(II) $CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_2=\underset{\underset{OH}{|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3$

(III) $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\underset{\underset{OH}{|}}{C}=CH-\underset{\underset{O}{\|}}{C}-CH_3$

**4.** Keto - enol tautomerism is observed in :

(A) $C_6H_5-\overset{\overset{O}{\|}}{C}-H$

(B) $C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3$

(C) $C_6H_5-\overset{\overset{O}{\|}}{C}-C_6H_5$

(D) $C_6H_5-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-C_6H_5$

**5.**

'P' is

(A)

(B)

(C)

(D)

**6.** Which of the following can show tautomerism ?

(A)
(B)
(C)
(D)

**7.** Which of the following will have maximum enol content ?

(A)
(B)
(C)
(D)

**8.** Which of the following have enol content greater than keto content ?

(A)
(B)
(C)
(D) $CH_3CHO$

## 7.0 STEREOISOMERISM

Two or more than two compounds having same molecular formula, same structural formula but different arrangements of atoms or groups in space.

## 7.1 Conformational Isomerism

The different arrangement of atoms in space that result from the free rotation arround C—C bond axis are called conformations. The phenomenon is called conformational isomerism

**Some Important Terms :**

**(i)** **Dihedral or Torsional angle :** Angle between bonds of two adajecent atoms is knows as dihedral or Torsional angle.

**(ii)** **Staggered Conformation :** Conformations which have 60° or 180° dihedral angle are known as staggered conformations.

**(iii)** **Eclipsed Conformation** : Conformations which have 0° or 120° dihedral angle are known as staggered conformations.

**(iv)** **Skew Conformation :** All other conformations are known as Skew Conformations.

- **Conformers of ethane [$CH_3$—$CH_3$]**

(I) (II)

(Saw horse projection)

(III) (IV)

(Newman projection)

I = III (Eclipsed form) in this form distance between 2C–H bonds is minimum so maximum repulsion or minimum stable.

II = IV (Staggered form) in this form distance between 2C–H bonds is maximum so minimum repulsion so maximum stable.

There are infinite conformers between eclipsed and staggered forms which are called as skew forms

Stability order : Staggered > Skew > Eclipsed.

The variation of energy with rotation about the C–C bond in ethane has been shown in figure below :

Changes in energy during rotation about C–C bond in ethane

The difference in the energy of various conformers constitutes an energy barrier to rotation. The energy required to rotate the ethane molecule about carbon-carbon single bond is called **torsional energy**. But this energy barrier is not large enough to prevent the rotation. Even at ordinary temperature the molecules possess sufficient thermal and kinetic energy to overcome the energy barrier through molecular collisions. Thus, conformations keep on changing form one form to another very rapidly and cannot be isolated as separate conformers.

**Conformation of Butane** [$CH_3$—$CH_2$—$CH_2$—$CH_3$]

(I) (II) (III) (IV)

I (Fully eclipsed form) : In this form distance between 2 methyl groups is minimum so maximum repulsion or minimum stable.

IV (Anti or staggered) : In this form distance between 2 methyl groups is maximum so minimum repulsion or maximum stable.

**Stability order :** IV > II > III > I

**Dihedral angle :** Angle between two planes.

**(i)** Angle of rotation to get minimum stable to maximum stable form in butane is 180°.

**(ii)** Angle of rotation to get maximum stable to maximum stable form in butane is 360°.

**(iii)** The energy profile diagram for the conformation of butane is given below along with the difference of energy between various conformation of butane.

Energy changes that arises from rotation about the $C_2$–$C_3$ bond of butane.

- **Conformational analysis of cyclohexane**

**(A)** **Chair form :** Experimental evidences show that cyclohexane is non-planar. If we look to the models of the different conformations that are free of angle strain first there is chair conformation. If we sight along each of the carbon-carbon bonds in turn we see in every case perfectly staggered bonds.

Chair conformation

Chair conformation(all staggered bonds)

The conformation is thus free of all the strains, it lies at energy minimum and is therefore a conformational isomer. The chair form is the most stable conformation of cyclohexane.

**Axial and equatorial bonds in chair form of cyclohexane** :

Axial C–H bonds

Equatorial C–H bonds

Axial & equatorial bonds together

The 12 hydrogen atoms of chair conformation of cyclohexane can be divided into two groups. Six of the hydrogens, called axial hydrogens, hence their bonds parallel to a vertical axis that passes through the rings centre. These axial bonds are directed up & down on adjacent carbons. The second set of six hydrogens called equatorial hydrogens are located approximately along the equator of the molecule.

**(B) Boat form :** Another conformation which is known as boat conformation has exactly eclipsed conformations.

Boat conformation

Boat conformation
(all eclipsed bonds)

In boat form of cyclohexane 6 hydrogens are equatorial, 4 hydrogens are axial and two hydrogens are flagpoles. It is an unstable conformation of cyclohexane due to torsional strain among axial hydrogens and due to van der waals strain caused by crowding between the "flagpole" hydrogens.

- **Conformational inversion (Ring flipping) in cyclohexane**

Like alkanes cyclohexane too is conformationally mobile. Through a process known as ring inversion, Chair-chair interconversion, or more simple ring flipping one chair conformation is converted to another chair.

By ring flipping all axial bonds convert to equatorial and vice-versa. The activation energy for cyclohexane ring inversion is 45 kJ/mol. It is a very rapid process with a half-life of about $10^{-5}$ sec at 25°C.

- **Conformational analysis of monosubstituted cyclohexanes**

In ring inversion in methylcyclohexane the two chair conformations are not equivalent. In one chair the methyl group is axial ; in the other it is equatorial. At room temperature 95% of the methylcyclohexane exist in equatorial methyl group whereas only 5% of the molecule have an axial methyl group.

**1,3-diaxial repulsion** : A methyl group is less crowded when it is equatorial than when it is axial. The distance between the axial methyl groups at C-1 and two hydrogens at C-3 and C-5 is less than the sum of their vander waal radii which causes vander waal strain in the axial conformation this type of crowding is called 1,3-diaxial repulsions. When the methyl group is equatorial, it experience no significant crowding.

Vander waals strain between hydrogen of axial $CH_3$ and axial hydrogens at C-3 and C-5

No vander waals strain between hydrogen at C-1 and axial hydrogens at C–3 and C–5

**Difference between conformation and configuration**

| S.N. | Conformation | Configuration |
|---|---|---|
| 1. | It refers to different arrangement of atoms or groups relative to each other and raised due to free rotation round a sigma bond | It refers to different arrangement of atoms or groups in space about a central atom. |
| 2. | The energy difference between two conformers is lower | The energy difference between two configuration forms is large |
| 3. | Conformers are not isomers and they can not be separated from each other. | These are optical isomers and can be separated from each other. |
| 4. | These are easily inter converted to one another. | These are not easily inter converted to one another. |

## Illustrations

**Illustration 20.** Evaporation of an aqueous solution of ammonium cyanate gives urea. This reaction follows the class of-

(A) Polymerization (B) Isomerization

(C) Association (D) Dissociation

**Solution** **(B)**

$$NH_4CNO \xrightarrow{heat} H_2N\text{–}CO\text{–}NH_2$$

**Illustration 21.** The possible number of alkynes with the formula $C_5H_8$ is -

(A) 2 (B) 3 (C) 4 (D) 5

**Solution** **(B)**

**Illustration 22.** How many isomers of $C_5H_{11}OH$ will be primary alcohols?

(A) 2 (B) 3 (C) 4 (D) 5

**Solution** **(C)**

(i) $CH_3CH_2CH_2CH_2CH_2OH$

(ii)


(iii)


(iv)


**Illustration 23.** Number of isomeric forms of $C_7H_9N$ having benzene ring will be -

(A) 7 (B) 6 (C) 5 (D) 4

**Solution** **(C)**

(i)

o-, m-, p-
(ii)(iii) (iv)

(v)

## BEGINNER'S BOX-6

### Conformational Isomerism

**1.** Considering rotation about the C-3 – C-4 bond of 2-methylhexane:

(a) Draw the Newman projection of the most stable conformation.

(b) Draw the Newman projection of the least stable conformation.

**2.** Draw most stable conformation of following compound.

(i) 2–methyl butane (around $C_2$–$C_3$ bond)

(ii) Ethylene glycol (around C–C bond)

(iii) cis–1,2–dimethyl cyclohexane.

(iv) trans–1,2, dimethyl cyclohexane.

(v) cis–1,3–dichloro cyclohexane.

**3.** Match the following columns :

| **Column-I (Newmann Projection)** | **Column-II (Conformations)** |
|---|---|
| (A) | (P) Fully eclipsed |
| (B) | (Q) Partially eclipsed |
| (C) | (R) Gauche |
| (D) | (S) Anti |
| | (T) Least stable confermer |

## GOLDEN KEY POINTS

- **Some important $pK_a$ values**

**Phenol : 9.98/1.10 × $10^{-10}$ $pK_a/K_a$ value**

| | | o | m | p |
|---|---|---|---|---|
| (i) | Me | **10.28**/0.63 ×$10^{-10}$ | 10.08/0.98 × $10^{-10}$ | 10.14/0.67 × $10^{-10}$ |
| (ii) | $NO_2$ | **7.23**/600 × $10^{-10}$ | 8.40/50 × $10^{-10}$ | 7.15/690 × $10^{-10}$ |
| (iii) | F | **8.81**/15 × $10^{-10}$ | 9.28/5.2 × $10^{-10}$ | 9.95/1.1 × $10^{-10}$ |
| (iv) | Cl | **8.48**/77 × $10^{-10}$ | 9.02/16 × $10^{-10}$ | 9.38/6.3 × $10^{-10}$ |
| (v) | $CH_3$–O | **9.98**/1.05 × $10^{-10}$ | 9.65/2.24 × $10^{-10}$ | 10.21/0.62 × $10^{-10}$ |
| (vi) | OH | **9.48** | 9.44/3 × $10^{-10}$ | 9.96 |
| (vii) | $NH_2$ | **9.71**/2.0 × $10^{-10}$ | 8.16/68 × $10^{-10}$ | 10.30 |
| (viii) | Br | 41 × $10^{-10}$ | 14 × $10^{-10}$ | 5.6 × $10^{-10}$ |
| (ix) | I | 34 × $10^{-10}$ | 13 × $10^{-10}$ | 6.0 × $10^{-10}$ |
| (x) 2.4- dinitrophenol | | **4.00** | | |
| (xi) 2,4,6-trinitro phenol | | pKa = 0.71 | 10.50 × $10^{-2}$ | |

**10.60**

**7.22**

**10.17**

**8.25**

| | $pK_a$/Benzoic acid → 4.20 | | | |
|---|---|---|---|---|
| H | **4.20** | 4.20 | 4.20 | 4.20 |
| Me | – | 3.91 | 4.27 | 4.37 |
| $NO_2$ | – | 2.17 | 3.48 | 3.43 |
| F | – | 3.27 | 3.87 | 4.14 |
| Cl | – | 2.94 | 3.83 | 3.98 |
| Br | – | 2.85 | 3.81 | 4.00 |
| OMe | – | 4.09 | 4.09 | 4.47 |
| OH | – | 2.98 | 4.08 | 4.58 |
| $NH_2$ | – | 4.92 | 4.72 | 4.98 |
| –COOH | – | 2.98 | 3.46 | 3.56 |
| H–COOH | 3.77 | | | |
| $CH_3$–COOH | 4.76 | | | |
| $CH_3$–$CH_2$–COOH | 4.88 | | | |
| HOOC–COOH | 1.23 | | | |
| HOOC–$CH_2$–COOH | 2.83 | | | |
| HOOC–$(CH_2)_2$–COOH | 4.19 | | | |
| Maleic acid | 1.92 ($pKa^1$) | 6.23 ($pKa^2$) | | |
| Fumaric acid | 3.02 ($pKa^1$) | 4.38 ($pKa^2$) | | |
| CH≡C–COOH | 1.84 | | | |
| $CH_2$=CH–COOH | 4.25 | | | |
| F–$CH_2$–COOH | 2.57 | | | |
| Cl–$CH_2$–COOH | 2.86 | | | |
| Br–$CH_2$–COOH | 2.90 | | | |
| I–$CH_2$–COOH | 3.16 | | | |
| $O_2N$–$CH_2$–COOH | 1.68 | | | |
| $Me_3N^+$–$CH_2$–COOH | 1.83 | | | |
| N≡C–$CH_2$–COOH | 2.47 | | | |
| EtOCO$CH_2$COOH | 3.35 | | | |
| MeO–$CH_2$–COOH | 3.58 | | | |

**$pK_a/K_a$ value-Aniline → 4.62**

| | | | |
|---|---|---|---|
| Me– | 4.39 | 4.69 | 5.12 |
| Me–O | 4.49 | 4.20 | 5.29 |
| $NH_2$ | 4.47 | 4.20 | 6.08 |
| $NO_2$ | –0.29 | 2.50 | 1.02 |
| Cl | 2.64 | 3.34 | 3.91 |
| Br | 2.60 | 3.51 | 3.91 |
| OH | 4.72 | 4.17 | 5.30 |
| | 4.85 | | ~0.5 |
| | 5.06 | | shown some acidic nature |
| | 5.11 | | |
| | 6.56 | | 13.6 |
| $Ph_2NH$ | 0.9 | | |
| Ph–NH–AC | 0.4 | | 12.4 |
| | 3.69 | $(C_2H_5)_2NH$ | 10.93 |
| | | $Et_3N$ | 10.88 |
| | | $Et–NH_2$ | 10.67 |
| | 4.60 | $NH_3$ | 9.25 |
| | | $Me_3N$ | 9.80 |
| | | $Me_2N$ | 10.77 |
| | | $Me–NH_2$ | 10.64 |

| | | | |
|---|---|---|---|
| | 10.50 | $Bu_3N$ | 9.87 |
| | | $Bu_2NH$ | 11.28 |
| | | $BuNH_2$ | 10.61 |
| | 7.1 | | 5.23 |
| | –0.27 | | 11.22 |
| | 2.53 | | 4.94 |
| | 7.03 | | 5.2 |

- Hyperconjugation is a stablizing effect.
- Anti aromatic compounds are para magnetic.
- Anti aromatic compounds are have tendency of dimerization.
- Carbocation and carbon free radical are electron deficient.
- Carbanion are electron rich species.
- Carbocation and carbon free radical show electrophilic character.
- Carbocation shows lewis acidic charactor but carbon free radical does not show lewis acidic character.
- Parent carbon chain and functional group must be same in chain isomers.
- Polyvalent functional group must be present for metamerism.
- Conformations are non resolvable at room temperature.
- Chair form is most stable conformation of cyclohexane.

## SOME WORKED OUT EXAMPLES

**Illustration 1.**

If $CH_3-\underset{\underset{CH_3}{|}}{CH}-CHO$ gives up proton the most-stable carbanion would be

(A) $\overset{\ominus}{C}H_2(CH_3)CH-CHO$ (B) $(CH_3)(\overset{\ominus}{C}H_2)CH-CHO$ (C) $(CH_3)(CH_3)\overset{\ominus}{C}-CHO$ (D) All the above

**Ans. (C)**

**Solution.**

This carbanion shows resonance :

**Illustration 2.**

The most stable intermediate is :

(A) $BrCH_2CH_2\dot{C}H_2$ (B) $CH_3-\underset{\underset{Br}{|}}{CH}-\dot{C}H_2$

(C) $CH_3-\dot{C}H-CH_2Br$ (D) All are equally stable

**Ans. (C)**

**Illustration 3.**

The electron attracting species in the following is –

(A) –CN (B) $-NH_2$ (C) –NHR (D) –NHCOR

**Solution.**

The groups having double or triple bonds are electron attracting. Hence–CN is electron attracting and in rest of the species N–atom has lone pair of electrons.

**Ans. (A)**

**Illustration 4.**

Which carbanion is less stable than the other three?

(A) $\overset{\ominus}{C}H_2-NO_2$ (B) $\overset{\ominus}{C}H_2-CHO$ (C) $\overset{\ominus}{C}H_2-CH_3$ (D) $\overset{\ominus}{C}H_3$

**Ans. (C)**

**Solution.**

Due to + I effect of $CH_3$ group $\overset{\ominus}{C}H_2-CH_3$ is less stable.

**Illustration 5.**

Compound : on removal of proton gives a carbanion. The most stable carbanion should be

(A) (B) (C) (D) All the above

**Ans. (C)**

**Solution.**

In this case negatively charged carbon is present between two electron attracting groups. As such it is a stable carbanion.

**Illustration 6.**

$\overset{\oplus}{C}H_2-O-H \longrightarrow CH_2=\overset{\oplus}{O}-H$. The stability order of above structure is -

I II

(A) I > II (B) II > I (C) I = II (D) None of these

**Ans. (B)**

**Solution.**

In II$^{nd}$ structure carbon completes its octet. Hence it is more stable.

* * * * *

# ANSWER KEY

## BEGINNER'S BOX-1

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1.** | (C) | **2.** | (A) | **3.** | (A) | **4.** | (D) | **5.** | (A) | **6.** | (B) |
| **7.** | (B) | **8.** | (C) | **9.** | (C) | **10.** | (B) | | | | |

## BEGINNER'S BOX-2

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1.** | (A) | **2.** | (D) | **3.** | (B) | **4.** | (B) | **5.** | (A) | **6.** | (D) |
| **7.** | (D) | **8.** | (D) | **9.** | (A) | **10.** | (B) | | | | |

## BEGINNER'S BOX-3

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1.** | (D) | **2.** | (B) | **3.** | (B) | **4.** | (C) | **5.** | (B) | **6.** | (C) |
| **7.** | (A) | **8.** | (C) | **9.** | (C) | **10.** | (A) | | | | |

## BEGINNER'S BOX-4

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1.** | (C) | **2.** | (C) | **3.** | (B) | **4.** | (A) | **5.** | (A) | **6.** | (A) |
| **7.** | (D) | **8.** | (D) | **9.** | (B) | | | | | | |

## BEGINNER'S BOX-5

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **1.** | (c) > (d) > (b) > (a) | **2.** | (D) | **3.** | III > II > I | **4.** | (B) | **5.** | (B) |
| **6.** | (CD) | **7.** | (B) | **8.** | (AB) | | | | |

## BEGINNER'S BOX-6

**1.** (a)


(b)


**2.** (i)


(ii)


(iii)

(iv)

(v)


**3.** (A) - (PT), (B) - (Q), (C) - (S), (D) - (R)

## EXERCISE (S-1)

### SECTION - 1 : NUMERICAL ANSWER BASED QUESTIONS

**1.** Write the number of hyperconjugable hydrogen atoms of following species :

(a)

number of hyperconjugable hydrogen atoms is x

(b)

number of hyperconjugable hydrogen atoms is y

Give x + y.

**2.** Give number of aromatic compounds.

(1)
(2)
(3)
(4)
(5)

(6)
(7)
(8)
(9)
(10)

(11)
(12)

**3.** The number of primary alcohols possible with the formula $C_4H_{10}O$ is -

**4.** The total number of benzene derivatives having the molecular formula $C_7H_7Cl$ is -

**5.** The total number of cyclic compounds (neglecting stereoisomers) with the molecular formula $C_5H_{10}$ is -

**6.** The total number of benzene derivatives having the molecular formula $C_7H_8O$ is -

**7.** How many rings and/or π bonds are present in a hydrocarbon with the formula $C_6H_{10}$ ?

**8.** How many compounds among the following will release $CO_2$ gas with $NaHCO_3$

, EtOH, $CH_3SO_3H$

## SECTION - 2 : MATRIX - MATCH QUESTIONS

**9.** Match the column I with column II.

| **Column-I** | **Column-II** |
|---|---|
| (A) $—NO_2$ | (p) – m effect |
| (B) $—O^-$ | (q) + m effect |
| (C) $—O—CH_3$ | (r) + I effect |
| (D) $—C \equiv N$ | (s) – I effect |

**10.** Match the column I with column II.

| **Column-I** | **Column-II** |
|---|---|
| (A) | (p) Aromatic |
| (B) | (q) Non-aromatic |
| (C) | (r) Anti-aromatic |
| (D) | |

**11.** Match the column I with column II.

**Column-I (reaction)**

(A)


(B)


(C)


(D)


**Column-II (stereoisomers)**

(p) Homologues

(q) Functional isomers

(r) Metamer

(s) Chain isomers

## EXERCISE (O-1)

### SINGLE CHOICE CORRECT QUESTIONS

**1.** Which of the following has the most acidic hydrogen ?

(A) 3-hexanone (B) 2, 4-hexanedione

(C) 2, 5-hexanedione (D) 2, 3-hexanedione.

**2.** Consider following acid

(I) $ClCH_2COOH$, (II) $CH_3COOH$, (III) $CH_3CH_2COOH$

Correct order of their pH value.

(A) III < II < I (B) I < II < III (C) I < III < II (D) II < I < III

**3.** In following acid, the correct increasing order of acidic strength acid

I. HCOOH II. $CH_3COOH$ III. $C_6H_5COOH$

(A) I < II < III (B) II < I < III (C) III < II < I (D) II < III < I

**4.** (I)

(II)

(III)


Arrange following phenol in increasing order of $pk_a$ value

(A) I < II < III (B) III < I < II (C) III < II < I (D) I < III < II

**5.** Give the correct order of increasing acidity of the following compounds -

**(I)**

**(II)**

**(III)**

**(IV)**


(A) II < I < IV < III (B) IV < II < I < III (C) I < II < IV < III (D) IV < I < II < III

**6.** Among the following compounds, the strongest acid is :

(A) $HC \equiv CH$ (B) $C_6H_6$ (C) $C_2H_6$ (D) $CH_3OH$

**7.** Amongst the following compounds the strongest acid is :

(A)


(B)


(C)


(D)


**8.** $(CH_3)_3COH$ is less acidic than $(H_3C)_3SiOH$ because :

(A) Carbon is more electronegative than Si
(B) $(CH_3)_3SiO^{\ominus}$ is stabilized due to $p\pi$-$d\pi$
(C) Bigger size of silicon than carbon
(D) None of these

**9.** Which one of the hydrocarbon is the most acidic ?

(A)


(B)


(C)


(D)


**10.** Arrange pKa of the given compounds in decreasing order :

(1) Phenol (2) Ethyl alcohol (3) Formic acid (4) Benzoic acid

(A) 1 > 2 > 3 > 4 (B) 2 > 1 > 4 > 3 (C) 3 > 2. > 4 > 1 (D) 4 > 3. > 1 > 2

**11.** 1,3-cyclopentadiene has a $pK_a = 15$ whereas simple cycloalkanes have $pK_a > 50$ with respect to their conjugate bases . This is because :

(A) 1, 3-cyclopentadiene is aromatic.

(B) 1, 3-cyclopentadiene is anti-aromatic.

(C) 1, 3-cyclopentadine is non-aromatic.

(D) 1, 3-cyclopentadiene is non-aromatic with an aromatic conjugate base.

**12.** H–O–C≡N H–N=C=O

(Cyanic acid) (Isocyanic acid)

Loss of proton from these two acids produces :

(A) same anion (B) different anions (C) same cation (D) different cations

**13.** Use resonance arguments to rank the following in order of increasing acidic strength.

(A) $H_c < H_a < H_b$ (B) $H_b < H_a < H_c$ (C) $H_b < H_c < H_a$ (D) $H_c < H_b < H_a$

**14.** The most acidic 'H'

is :

(A) X (B) Y (C) Z (D) W

**15.** Which of the following shows the correct order of decreasing basicity in aqueous medium ?

(A) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$

(B) $(CH_3)_2NH > (CH_3)_3N > CH_3NH_2 > NH_3$

(C) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

(D) $(CH_3)_2NH > CH_3NH_2 > NH_3 > (CH_3)_3N$

**16.** Give the correct order of decreasing basicity of the following compounds ?

(I) $C_6H_5NH_2$ (II) $(C_6H_5)_2NH$ (III) $(C_6H_5)_3N$ (IV) $C_6H_{11}NH_2$

(A) I > II > III > IV (B) IV > III > II > I (C) IV > I > II > III (D) III > II > I > IV

**17.** Arrange the following in Decreasing order of their $pK_a$ value -

I. $CH_2{=}CHCH_2NH_2$, II. $CH_3CH_2CH_2NH_2$ , III. $CH{\equiv}CCH_2NH_2$

(A) I > II < III (B) II > I > III (C) III > II > I (D) II < III < I

**18.** (I)

(II)

(III)

(IV)


The correct order of decreasing basicity of the above compound is -

(A) I > II > III > IV (B) II > I > IV > III (C) III > IV > II > I (D) II > I > III > IV

**19.** The correct order of basicities of the following compounds is–

(a)

(b) $CH_3CH_2NH_2$ (c) $(CH_3)_2NH$ (d)


(A) b > a > c > d (B) a > c > b > d (C) c > a > b > d (D) a > b > c > d

**20.** In the following compounds–

(I)

(II)

(III)

(IV)


The order of basicity is -

(A) IV > I > III > II (B) III > I > IV > II (C) II > I > III > IV (D) I > III > II > IV

**21.** Select the order of basic strength.

(I) $R_4N^+OH^-$ (II) $R_3N$ (III) $R_2NH$ (IV) $RNH_2$

(if R = Me)

(A) (I) > (III) > (IV) > (II) (B) (IV) > (III) > (I) > (II)

(C) (II) > (IV) > (III) > (I) (D) (II) > (IV) > (I) > (III)

**22.** The species $CH_3\overset{+}{C}HCH_3$ is less stable than -

(A) $(CH_3)_3C^+$ (B) $CH_3CH_2\overset{+}{C}H_2$ (C) $CH_3\overset{+}{C}H_2$ (D) $CH_3^+$

**23.** Which allylic carbocation is the most stable carbocation?

(A) $CH_3—CH=CH—\overset{\oplus}{C}H_2$ (B) $CH_3—CH=CH—\overset{\oplus}{C}H_2$

(C) $C_6H_5—CH=CH—\overset{\oplus}{C}(CH_3)—CH_3$ (D) All have same stability

**24.** The most unstable carbocation is

(A) $CH_3\overset{\oplus}{C}H_2$ (B) $Cl – CH_2 – \overset{\oplus}{C}H_2$ (C) $\overset{\oplus}{C}H_2 – CHO$ (D) $\overset{\oplus}{C}H_2 – O – CH_3$

**25.** Nonplanar cation is :

(A) $\overset{\oplus}{N}H_4$ (B) $\overset{\oplus}{C}H_3$ (C) $CH_3\overset{\oplus}{C}O$ (D) $(CH_3)_3C^+SbF_6^-$

**26.** The stability order of following carbocation is :

(I)
(II)
(III)
(IV)

(A) I > II > IV > III (B) III > I > II > IV (C) IV > II > III > I (D) II > IV > III > I

**27.** Consider the following carbanions -

(a) $CH_3 – \overset{\ominus}{C}H_2$ (b) $CH_2 = \overset{\ominus}{C}H$ (c) $CH \equiv \overset{\ominus}{C}$

Correct order of stability of these carbanions in decreasing order is -

(A) a > b > c (B) b > a > c (C) c > b > a (D) c > a > b

**28.** Arrange the following carbanions in decreasing order of stability :

(I)
(II)
(III)
(IV)

(A) III > I > IV > I (B) III > II > I > IV (C) I > III > II > IV (D) III > I > II > IV

**29.** Most stable radical among following.

(A)
(B)
(C)
(D)

**30.** Arrange the following radicals in decreasing order of their stability.

(I) $\dot{C}H_3$
(II) $CH_3-\dot{C}H_2$
(III) $CH_3-\underset{\underset{CH_3}{|}}{\dot{C}H}$
(IV) $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\bullet$

(A) IV > I > III > II
(B) IV > III > II > I
(C) I > II > III > IV
(D) IV > III > I > II

**31.** Type of isomerism exists between :-

$CH_3—CH_2—CH_2—CN$ and $CH_3—\underset{\underset{CN}{|}}{CH}—CH_3$

(A) Position
(B) Chain
(C) Both the above
(D) None of these

**32.** Which of the following will lead to maximum enolisation?

(A) $CH_3COCH_3$
(B) $CH_3COCH_2CHO$
(C) $CH_3—\underset{\underset{O}{\|}}{C}—\underset{\underset{Br}{|}}{CH}—\underset{\underset{O}{\|}}{C}—CH_3$
(D)

**33.** Tautomerism is not exhibited by :-

(A) $\begin{matrix} H_3C \\ C_2H_5 \end{matrix}\!\!>C=N—OH$
(B) $(CH_3)_2CHNO_2$
(C)
(D) $(CH_3)_3CCHO$

**34.** Which of the following compounds does not exhibit tautomerism?

(A) $CH_3NO_2$
(B) $CH_3CH_2NO_2$
(C) $C_6H_5CH=CH–OH$
(D) $CH_3CH_2OH$

**35.** Increasing order of stability among the three main conformation (i.e. eclipse, anti, gauche) of ethylene glycol is:

(A) Eclipse, gauche, anti

(B) Gauche, eclipse, anti

(C) Eclipse, anti, gauche

(D) Anti, gauche, eclipse

**36.** Only two isomeric monochloro derivatives are possible for (excluding stereo)

(A) n-butane

(B) 2, 2-dimethylpentane

(C) benzene

(D) neopentane

**37.** Which of the following is not the correct relationship?

I

II

III

IV

(A) II & IV are not functional isomers

(B) I & II are functional isomer

(C) I & III are chain isomer

(D) I and IV are positional isomer

# EXERCISE (O-2)

## SECTION - 1 : MULTIPLE CHOICE CORRECT QUESTIONS

**1.** Which of the following substituents will increase the acidity of phenol -

(A) $-NO_2$ (B) $-CN$ (C) $-CHO$ (D) $-CH_3$

**2.**

Which is/are correct statements ?

(A) I is more basic than II (B) II is more basic than I and III

(C) III is more basic than II (D) all are aromatic bases

**3.** Select the correct option :

(A) carbonic acid is weaker acid than acetic acid

(B) the boiling points of acids are higher than corresponding alcohols

(C) chloroacetic acid is stronger acid than acetic acid

(D) phenol is more acidic than ethanol

**4.** Which reacts with $AgNO_3$ to give ppt.?

(A)


(B)


(C)


(D)


**5.** Which statement is true?

(A) $\ddot{N}H_2$ is stronger base than $\ddot{O}H$

(B) $PhNH_2$ is less basic than $NH_3$

(C) $CH_3–NH_2$ is weaker base than $N(CH_3)_3$ in (aq) medium

(D)

is weaker base than


**6.** In which of the pair of carbanion have first more stable than second.

(A) $\overset{\ominus}{C}F_3, \overset{\ominus}{C}Cl_3$ (B) $HC \equiv C^{\ominus}, H_2C = \overset{\ominus}{C}H$

(C)


(D) $(CH_3)_3C^{\ominus}, \overset{\ominus}{C}H_3$

**7.** Which of the following statements would be **incorrect** about this compound?

(A) All three C – N bond are of same length

(B) $C_1$ – N and $C_3$ – N bonds are of same length but shorter than $C_5$ – N bond

(C) $C_1$ – N and $C_5$ – N bonds are of same length but longer than $C_3$ – N bond

(D) $C_1$ – N and $C_3$ – N bond are of different length but both are longer than $C_5$ – N bond

**8.** Tautomerism is shown by :-

(A) HCN

(B)

(C)

(D) $CCl_3CHO$

**9.** Tautomerism is exhibited by :-

(A)

(B)

(C)

(D)

**10.** Which of the following statements are correct?

(A) $CH_3CH_2CH_2CH_2OH$ and $CH_3\overset{CH_3}{\overset{|}{C}}HCH_2OH$ represent chain isomerism

(B) $CH_3CH_2CH_2CH{=}CH_2$ and $CH_3CH_2CH = CHCH_3$ are examples of position isomerism

(C) $C_2H_5OCH_3$ and $CH_3CH_2CH_2OH$ represent functional-group isomerism

(D) $CH_3CH_2NH_2$ and $CH_3NHCH_3$ are examples of metamerism

**11.** Which of the following statements is/are not correct?

(A) Metamerism belongs to the category of structural isomerism

(B) Tautomeric structures are the resonating structures of a molecule

(C) Keto form is always more stable than the enol form

(D) Tautomers are not resonating structures of each other

## SECTION - 2 : COMPREHENSION BASED QUESTIONS
## (SINGLE CHOICE CORRECT QUESTION)

**Comprehension-1**

Carbocation is a group of atoms with positively charged carbon atom having six electrons in the valence shell after sharing. Carbocations are formed in the heterolysis of a bond and are planar species. Stability of carbocation is determined by inductive effect, hyperconjugation and resonance effect. Greater the number of contributing structures, more is the stability of a Carbocation. Electron releasing groups (+I effect) increases the stability of a carbocation whereas the electron withdrawing groups (–I effect) have an opposite effect.

**12.** Which of the following is most stable carbocation ?

(A) $\overset{+}{C}H_3$ (B) $CH_3-\overset{+}{C}H-CH_3$ (C) $CH_3-\overset{+}{C}H_2$ (D) $CH_3-\overset{+}{\underset{CH_3}{C}}-CH_3$

**13.** The most stable carbocation among the following :

(A) (B) (C) (D)

**14.** In which of the following cases, the carbocation (I) is less stable than the carbocation (II) ?

(A) $C_6H_5-\overset{+}{C}H_2$ (I), $CH_2=CH-\overset{+}{C}H_2$ (II) (B) (I), (II)

(C) $CH_2=\overset{+}{C}H$ (I), $CH_3-\overset{+}{C}H_2$ (II) (D) $H_3C-\overset{+}{C}H_2$ (I), $\underset{F}{CH_2}-\overset{\oplus}{C}H_2$ (II)

**15.** The most stable and the least stable carbocation among (I), $CH_2=CH-\overset{+}{C}H_2$ (II), $C_6H_5-\overset{+}{C}H_2$ (III) and $CH_3-\overset{+}{C}H-CH_3$ (IV) are respectively :

(A) II, I (B) III, IV (C) I, II (D) I, IV

**16.** Most stable carbocation is formed by the heterolysis of :

(A) $(CH_3)_3CBr$ (B) $(C_6H_5)_3CBr$ (C) $(C_6H_5)_2CHBr$ (D) $C_6H_5CH_2Br$

**Comprehension-2**

The most important condition for resonance to occur is that the involved atoms in resonating structure must be coplanar or nearly coplanar for maximum delocalisation. If this condition does not fulfil, involved orbitals cannot be parallel to each other and as a consequence delocalisation cannot occcur. Bulky groups present on adjacent atoms inhibit the orbitals. This phenomenon is known as steric inhibition of resonance. Steric inhibition of resonance has profound effect on

(i) Physical properties (ii) Acidity and basicity (iii) Reactivity of organic compounds

**17.** Which of the following is most acidic?

(A)


(B)


(C)


(D)


**18.** Consider the following two structures and choose the correct statements -

(I)

(II)

(A) carbon-nitrogen bond length in structure I is greater than that in structure II

(B) carbon-nitrogen bond length in structure I is less than in structure II

(C) carbon-nitorogen bond length in both structure is same

(D) It can not be compared

**19.** Arrange the following carbocation in the increasing order of stability :

(I)


(II)


(III)


(A) I < II < III (B) II < III < I (C) III < II < I (D) III < I < II

**Comprehension-3**

Different spatial arrangements of the atoms that result from rotation about a single bond are conformers. n-Butane has four conformers eclipsed, fully eclipsed, gauche and anti. The stability order of these conformers are as follows :

Anti > gauche > Partial eclipsed > Fully eclipsed

Although anti is more stable than gauche but in some cases gauche is more stable than anti.

**20.** Which one of the following is most stable conformer ?

(A)


(B)


(C)


(D)


**21.** Which one of the following is the most stable conformer ?

(A)


(B)


(C)


(D)


**22.** Number of possible conformations of n-butane is :

(A) 2 (B) 4 (C) 6 (D) infinite

## EXERCISE (JM)

**1.** Arrange the carbanions, $(CH_3)_3\bar{C}$, $\bar{C}Cl_3$, $(CH_3)_2\bar{C}H$, $C_6H_5\bar{C}H_2$, in order of their decreasing stability :- **[AIEEE-2009]**

(1) $\bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$
(2) $(CH_3)_3\bar{C} > (CH_3)_2\bar{C}H > C_6H_5\bar{C}H_2 > \bar{C}Cl_3$
(3) $C_6H_5\bar{C}H_2 > \bar{C}Cl_3 > (CH_3)_3\bar{C} > (CH_3)_2\bar{C}H$
(4) $(CH_3)_2\bar{C}H > \bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_3\bar{C}$

**2.** The correct order of increasing basicity of the given conjugate base ($R=CH_3$) is :- **[AIEEE-2010]**

(1) $RCO\bar{O} < HC \equiv \bar{C} < \bar{N}H_2 < \bar{R}$
(2) $RCO\bar{O} < HC \equiv \bar{C} < \bar{R} < \bar{N}H_2$
(3) $\bar{R} < HC \equiv \bar{C} < RCO\bar{O} < \bar{N}H_2$
(4) $RCO\bar{O} < \bar{N}H_2 < HC \equiv \bar{C} < \bar{R}$

**3.** Identify the compound that exhibits tautomerism :- **[AIEEE-2011]**

(1) 2-Pentanone (2) Phenol (3) 2-Butene (4) Lactic acid

**4.** The strongest acid amongst the following compounds is ? **[AIEEE-2011]**

(1) $CH_3CH_2CH(Cl)CO_2H$
(2) $ClCH_2CH_2CH_2COOH$
(3) $CH_3COOH$
(4) HCOOH

**5.** How many cyclic structures are possible for $C_4H_6$? **[AIEEE ONLINE-2012]**

(1) 3 (2) 5 (3) 4 (4) 6

**6.** Which of the following compounds are antiaromatic? **[AIEEE ONLINE-2012]**

(I)
(II)
(III)
(IV)
(V)
(VI)

(1) (III) and (VI) (2) (II) and (V) (3) (I) and (V) (4) (V) and (VI)

**7.** In the below mentioned compounds the decreasing order of reactivity towards electrophilic substitution is : **[AIEEE ONLINE-2012]**

(i) (ii) (iii) (iv)

(1) (iii) > (i) > (iv) > (ii)
(2) (iv) > (i) > (ii) > (iii)
(3) (ii) > (iii) > (i) > (iv)
(4) (i) > (ii) > (iii) > (iv)

**8.** Among the following the molecule with the lowest dipole moment is :- **[AIEEE ONLINE-2012]**

(1) $CHCl_3$ (2) $CH_2Cl_2$ (3) $CCl_4$ (4) $CH_3Cl$

**9.** Which of the following cannot be represented by resonance structures ? **[AIEEE ONLINE - 2012]**

(1) Dimethyl ether (2) Carboxylate anion (3) Toluene (4) Nitrate anion

**10.** The IUPAC name of the compound

is :- **[AIEEE ONLINE - 2012]**

(1) 1, 2-Epoxy propane
(2) Propylene oxide
(3) 1, 2–Oxo propane
(4) 1, 2–Propoxide

**11.** Which one of the following is most Stable ? **[JEE MAINS - ONLINE - 2013]**

(1)
(2)
(3)

(4)


**12.** The order of stability of the following carbocations:

is :- **[JEE(MAIN)-2013]**

(1) III > II > I (2) II > III > I (3) I > II > III (4) III > I > II

**13.** Arrange the following compounds in order of decreasing acidity : **[JEE(MAIN)-2013]**

(1) II > IV > I > III (2) I > II > III > IV

(3) III > I > II > IV (4) IV > III > I > II

**14.** In which of the following pairs A is more stable than B ? **[JEE MAINS - ONLINE - 2014]**

**A** **B**

(1) ,

(2) ,

(3) ,

(4) $Ph_3C\bullet$ , $(CH_3)_3C\bullet$

**15.** In allene ($C_3H_4$), the type(s) of hybridization of the carbon atoms is (are):

**[JEE MAINS - ONLINE - 2014]**

(1) only $sp^2$ (2) $sp^2$ and sp (3) sp and $sp^3$ (4) $sp^2$ and $sp^3$

**16.** The correct 1UPAC name of the following compound is: **[JEE MAINS - ONLINE - 2014]**

(1) 3, 4 - ethyl methylhexane (2) 3 - ethyl - 4 - methylhexane

(3) 4 - ethyl - 3 - methylhexane (4) 4 - methyl - 3 - ethylhexane

**17.** Considering the basic strength of amines in aqueous solution, which one has the smallest $pK_b$ value? **[JEE(MAIN)-2014]**

(1) $(CH_3)_2NH$ (2) $CH_3NH_2$ (3) $(CH_3)_3N$ (4) $C_6H_5NH_2$

**18.** For which of the following molecule significant $\mu \neq 0$ ? **[JEE(MAIN)-2014]**

(a)


(b)


(c)


(d)


(1) Only (a) (2) (a) and (b) (3) Only (c) (4) (c) and (d)

**19.** Arrange the following amines in the order of increasing basicity :-

**[JEE MAINS - ONLINE - 2015]**

(1) $CH_3NH_2$ <


(2)

< $CH_3NH_2$

(3)

< $CH_3 \cdot NH_2$

(4)

< $CH_3NH_2$

**20.** The number of structural isomers for $C_6H_{14}$ is: **[JEE MAINS - ONLINE - 2015]**

(1) 6 (2) 4 (3) 3 (4) 5

**21.** Which of the following molecules is least resonance stabilized? **[JEE(MAIN)-2017]**

(1)


(2)

(3)


(4)

**22.** The IUPAC name of the following compound is : **[JEE MAINS - ONLINE - 2017]**

(1) 1-Ethyl-2,2-dimethylcyclohexane (2) 2,2-Dimethyl-1-ethylcyclohexane

(3) 1,1-Dimethyl-1-2ethylcyclohexane (4) 2-Ethyl-1,1-dimethylcyclohexane

**23.** Among the following compounds, the increasing order of their basic strength is:-

**[JEE MAINS - ONLINE - 2017]**

(I)


(II)


(III)


(IV)


(1) (II) < (I) < (III) < (IV) (2) (I) < (II) < (IV) < (III)

(3) (II) < (I) < (IV) < (III) (4) (I) < (II) < (III) < (IV)

**24.** The increasing order fo basicity of the following compounds is **[JEE(MAIN)-2018]**

(a)


(b)


(c)


(d)


(1) (a) < (b) < (c) < (d) (2) (b) < (a) < (c) < (d)

(3) (b) < (a) < (d) < (c) (4) (d) < (b) < (a) < (c)

**25.** The increasing basicity order of the following compounds is :

**[JEE MAINS - ONLINE - 2019]**

(A) $CH_3CH_2NH_2$ (B) $CH_3CH_2\overset{CH_2CH_3}{\overset{|}{N}}H$ (C) $H_3C-\overset{CH_3}{\overset{|}{N}}-CH_3$ (D) $Ph-\overset{CH_3}{\overset{|}{N}}-H$

(1) (D)<(C)<(A)<(B) (2) (A)<(B)<(D)<(C) (3) (A)<(B)<(C)< (D) (4) (D)<(C)<(B)<(A)

**26.** Arrange the following amines in the decreasing order of basicity :

**[JEE MAINS - ONLINE - 2019]**

(I) (II) (III)

(1) I > II > III (2) III > II > I (3) I > III > II (4) III > I > II

**27.** Which amongst the following is the strongest acid ? **[JEE MAINS - ONLINE - 2019]**

(1) $CHI_3$ (2) $CHCl_3$ (3) $CHBr_3$ (4) $CH(CN)_3$

**28.** The increasing order of the pKa values of the following compounds is :

**[JEE MAINS - ONLINE - 2019]**

A B C D

(1) D < A < C < B (2) B < C < D < A (3) C < B < A < D (4) B < C < A < D

**29.** In the following compound, **[JEE MAINS - ONLINE - 2019]**

the favourable site/s for protonation is/are :-

(1) (b), (c) and (d) (2) (a) (3) (a) and (e) (4) (a) and (d)

**30.** Which compound(s) out of the following is/are not aromatic ?

**[JEE MAINS - ONLINE - 2019]**

(A) (B) (C) (D)

(1) C and D (2) B, C and D (3) A and C (4) B

**31.** The correct order for acid strength of compounds **[JEE MAINS - ONLINE - 2019]**

$CH{\equiv}CH$, $CH_3{-}C{\equiv}CH$ and $CH_2{=}CH_2$ is as follows :

(1) $CH \equiv CH > CH_2 = CH_2 > CH_3{-}C \equiv CH$

(2) $HC \equiv CH > CH_3 - C \equiv CH > CH_2 = CH_2$

(3) $CH_3{-}C \equiv CH > CH_2 = CH_2 > HC \equiv CH$

(4) $CH_3{-}C \equiv CH > CH \equiv CH > CH_2 = CH_2$

**32.** In the following compounds, the decreasing order of basic strength will be -

**[JEE MAINS - ONLINE - 2019]**

(1) $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

(2) $(C_2H_5)_2NH > NH_3 > C_2H_5NH_2$

(3) $NH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

(4) $C_2H_5NH_2 > NH_3 > (C_2H_5)_2NH$

**33.** Which of the following compounds will show the maximum enol content?

**[JEE MAINS - ONLINE - 2019]**

(1) $CH_3COCH_2COCH_3$

(2) $CH_3COCH_3$

(3) $CH_3COCH_2CONH_2$

(4) $CH_3COCH_2COOC_2H_5$

**34.** The increasing order of the $pK_b$ of the following compound is :

**[JEE MAINS - ONLINE - 2019]**

(A)

(B)

(C)

(D)

**Options :**

(1) (A) < (C) < (D) < (B)

(2) (B) < (D) < (A) < (C)

(3) (C) < (A) < (D) < (B)

(4) (B) < (D) < (C) < (A)

**35.** The correct order of stability for the following alkoxides is : **[JEE MAINS - ONLINE - 2020]**

(1) (C) > (B) > (A)

(2) (C) > (A) > (B)

(3) (B) > (C) > (A)

(4) (B) > (A) > (C)

## EXERCISE (JA)

**1.** The correct stability order for the following species is : **[IIT-2008]**

(I) (II) (III) (IV)

(A) II > IV > I > III (B) I > II > III > IV (C) II > I > IV > III (D) I > III > II > IV

**2.** Hyperconjugation involves overlap of the following orbitals **[IIT-2008]**

(A) σ–σ (B) σ–p (C) p – p (D) π – π

**3.** The correct acidity order of the following is : **[IIT-2009]**

(I) (II) (III) (IV)

(A) (III) > (IV) > (II) > (I) (B) (IV) > (III) > (I) > (II)

(C) (III) > (II) > (I) > (IV) (D) (II) > (III) > (IV) > (I)

**4.** The correct stability order of the following resonance structures is : **[IIT-2009]**

$H_2C{=}\overset{+}{N}{=}\overset{-}{N}$ (I) $H_2\overset{+}{C}{-}N{=}\overset{-}{N}$ (II) $H_2\overset{-}{C}{-}\overset{+}{N}{\equiv}N$ (III) $H_2\overset{-}{C}{-}N{=}\overset{+}{N}$ (IV)

(A) (I) > (II) > (IV) > (III) (B) (I) > (III) > (II) > (IV)

(C) (II) > (I) > (III) > (IV) (D) (III) > (I) > (IV) > (II)

**5.** The bond energy (in kcal $mol^{-1}$) of a C–C single bond is approximately : **[IIT-2010]**

(A) 1 (B) 10 (C) 100 (D) 1000

**6.** In the Newman projection for 2,2–dimethylbutane **[IIT-2010]**

**X** and **Y** can respectively be –

(A) H and H (B) H and $C_2H_5$ (C) $C_2H_5$ and H (D) $CH_3$ and $CH_3$

**7.** The total number of basic groups in the following form of lysine is : **[IIT-2010]**

**8.** Amongst the given option, the compound(s) in which all the atoms are in one plane in all the possible conformations (if any), is (are) - **[IIT-2011]**

(A)

(B)

(C) $H_2C = C = O$

(D) $H_2C = C = CH_2$

**9.** Among the following compounds, the most acidic is : **[IIT-2011]**

(A) p-nitrophenol

(B) p-hydroxybenzoic acid

(C) o-hydroxybenzoic acid

(D) p-toluic acid

**10.** The total number of contributing structures showing hyperconjugation (involving C-H bonds) for the following carbocation is : **[IIT-2011]**

**11.** Which of the following molecules, in pure form, is (are) unstable at room temperature ?

**[IIT-2012]**

(A)

(B)

(C)

(D)

**12.** The compound that does NOT liberate $CO_2$, on treatment with aqueous sodium bicarbonate solution, is - **[JEE ADVANCED 2013]**

(A) Benzoic acid

(B) Benzenesulphonic acid

(C) Salicylic acid

(D) Carbolic acid (phenol)

**13.** The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to

**[JEE ADVANCED 2013]**

(A) $\sigma \rightarrow p$ (empty) and $\sigma \rightarrow \pi^*$ electron delocalisations

(B) $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi$ electron delocalisations

(C) $\sigma \rightarrow p$ (filled) and $\sigma \rightarrow \pi$ electron delocalisations

(D) p (filled)$\rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ electron delocalisations

**14.** The number of resonance structures for N is

**[JEE ADVANCED 2015]**

**15.** The correct order of acidity for the following compound is– **[JEE ADVANCED 2016]**

(I) (II) (III) (IV)

(A) I > II > III > IV (B) III > I > II > IV (C) III > IV > II > I (D) I > III > IV > II

**16.** The IUPAC name(s) of the following compound is(are) **[JEE ADVANCED 2017]**

(A) 4–methylchlorobenzene (B) 4–chlorotoluene

(C) 1–chloro–4–methylbenzene (D) 1–methyl–4–chlorobenzene

**17.** Among the following, the number of aromatic compound(s) is **[JEE ADVANCED 2017]**

(i)
(ii)
(iii)
(iv)

(v)
(vi)
(vii)
(viii)

(ix)

**18.** The order of basicity among the following compounds is **[JEE ADVANCED 2017]**

(I)

(II)

(III)

(IV)


(A) II > I > IV > III (B) IV > II > III > I (C) I > IV > III > II (D) IV > I > II > III

**19.** The correct order of acid strength of the following carboxylic acids is -

**[JEE ADVANCED 2019]**

I

II

III

IV

(A) I > III > II > IV (B) III > II > I > IV (C) II > I > IV > III (D) I > II > III > IV

# ANSWER KEY

## EXERCISE (S-1)

### NUMERICAL ANSWER BASED QUESTIONS

**1.** (12) **2.** (7) **3.** (2) **4.** (4) **5.** (5) **6.** (5)

**7.** (2) **8.** (4)

### MATRIX MATCH QUESTIONS

**9.** (A) - (ps), (B) - (qr), (C) - (qs), (D) - (ps) **10.** (A) - (q), (B) - (p), (C) - (p), (D) - (r)

**11.** (A) - (p), (B) - (r), (C) - (q), (D) - (s)

## EXERCISE (O-1)

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | B | B | D | C | B | D | B | B | A | B | D | A | A | C | C |
| Que. | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Ans. | C | B | B | B | D | A | A | C | C | A | D | C | D | C | B |
| Que. | 31 | 32 | 33 | 34 | 35 | 36 | 37 | | | | | | | | |
| Ans. | B | D | D | D | C | A | D | | | | | | | | |

## EXERCISE (O-2)

### MULTIPLE CHOICE CORRECT QUESTIONS

**1.** (ABC) **2.** (BD) **3.** (ABCD) **4.** (BD) **5.** (ABD)

**6.** (BC) **7.** (ABD) **8.** (ABC) **9.** (ACD) **10.** (ABC)

**11.** (BC)

### COMPREHENSION BASED QUESTIONS

**12.** (D) **13.** (C) **14.** (C) **15.** (D) **16.** (B)

**17.** (B) **18.** (B) **19.** (B) **20.** (A) **21.** (C)

**22.** (D)

## EXERCISE (JM)

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | 1 | 1 | 1 | 1 | 2 | 4 | 4 | 3 | 1 | 1 | 3 | 4 | 3 | 4 | 2 |
| Que. | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Ans. | 2 | 1 | 4 | 2 | 4 | 1 | 4 | 3 | 3 | 1 | 4 | 4 | 4 | 1 | 2 |
| Que. | 31 | 32 | 33 | 34 | 35 | | | | | | | | | | |
| Ans. | 2 | 1 | 1 | 2 | 1 | | | | | | | | | | |

## EXERCISE (JA)

**1.** (D) **2.** (B) **3.** (A) **4.** (B) **5.** (C) **6.** (BD)
**7.** (2) **8.** (BC) **9.** (C) **10.** (6) **11.** (BC) **12.** (D)
**13.** (A) **14.** (9) **15.** (A) **16.** (BC) **17.** (5) **18.** (D)
**19.** (D)

CHAPTER 6

# AROMATIC COMPOUNDS

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# IMPORTANT NOTES

CHAPTER 6

# AROMATIC COMPOUNDS

## 1.0 AROMATIC CHARACTER : [THE HUCKEL 4n + 2 RULE]

The following three rules are useful in predicting whether a particular compound is aromatic or non–aromatic.

**(i)** Aromatic compounds are cyclic and planar.

**(ii)** Each atom in an aromatic ring is $sp^2$ hybridised.

**(iii)** The cyclic $\pi$ molecular orbital (formed by overlap of p-orbitals) must contain (4n + 2) $\pi$ electrons, i.e., 2, 6, 10, 14 ..... $\pi$ electrons. Where n = an integer 0, 1, 2, 3,.....

| Characteristics | Aromatic compounds (A) | Anti Aromatic compounds (B) | Non-Aromatic compounds (C) |
|---|---|---|---|
| E.g. | | | |
| 1. Structure | Cyclic, planarity all atoms of ring $sp^2$ hybridised | Cyclic, planarity all atoms of ring $sp^2$ hybridised | Cyclic or acyclic planar, $sp^2$ or $sp^3$ |
| 2. No. Of $\pi$ $e^-$s | $(4n+2)\pi e^-$ (Huckle's rule) | $(4n)\pi e^-$ | Any no. of $\pi e^-$ |
| 3. Stability | Have extra stability due to close conjugation Of $\pi$ $e^-$s | Unstable non-existent at room temperature | Normal stability like a conjugated system |
| 4. Characteristic Reaction | Electrophilic substitution Reaction | Dimerisation reaction to attain stability | Electrophilic addtion reaction like alkenes |

Examples of Aromatic Compounds : (Table )

| n | S-electrons = (4n + 2) | Aromatic compound / ions | Salts | Examples of salts |
|---|---|---|---|---|
| 0 | 2 | Cyclopropenyl cation | Cyclopropenium salts | Hydroxydiphenyl Cyclopropenyl bromide Cyclopropenyl hexachloroantimonate |
| 0 | 2 | Cyclobutenyl di-cation | Cyclobutenium salt | tetraphenylcylo-butenyl fluoroborate |
| 1 | 6 | Cyclopentadienyl anion | Cyclopentadienide salts | Potassium cyclopentadienide |
| 1 | 6 | Tropylium cation (Cycloheptatrienyl cation) | Tropylium salt | Troplyium Bromide |
| 2 | 10 | Napthalene , azulene | | |
| 3 | 14 | Anthracene Phenanthrene | | |
| 4 | 18 | [18] Annulene | | |

## 2.0 STRUCTURE OF BENZENE

Analysis and molecular-weight determinations show that the molecular formula of benzene is $C_6H_6$. It is to be expected that benzene would exhibit addition reactions. This is found to be so in practice, e.g.

**(i)** Benzene adds on halogen,the maximum number of halogen atoms being six.

**(ii)** Benzene may be catalytically hydrogenated to cyclohexane

**(iii)** Benzene forms a triozonide $C_6H_6(O_3)_3$.

**(iv)** Alkaline permanganate has no action on benzene in the cold, but on prolonged boiling benzene it is broken down into $CO_2$ and $H_2O$.

**(v)** In the absence of sunlight, benzene undergoes substitution when treated with halogen in presence of lewis acid to give only one mono substituted product.

**(vi)** Halogen acids do not add on to benzene.

**So we conclude that**

**(a)** Benzene contains three double bonds.

**(b)** All the six hydrogen atoms in benzene are equivalent consequently there is only one possible mono-substituted derivative and there are three possible disubstitution products of benzene.

## 3.0 PREPARATION OF ARENES

### 3.1 Benzene

- **By polymerisation (of Acetylene)**

$$3HC \equiv CH \xrightarrow{\text{Red hot iron tube}}$$

- **By decarboxylation (of Benzoic acid)**

- **By catalytic reforming of n-Hexane**

$$CH_3-(CH_2)_4-CH_3 \xrightarrow[-H_2]{\text{Pt, 873 K}}$$ cyclohexane $$\xrightarrow[-3H_2]{\text{Pt, 873 K}}$$

- **By reduction (of Benzene diazonium Chloride)**

- **From benzene sulphonic acid**

- **Zinc-dust distillation of phenol**

- **From phenyl magnesiumbromide**

3.2 Toluene

- **By Friedel-Crafts reaction**

Toluene

- **By Wurtz fitting reaction**

Bromobenzene Toluene

- **From Grignard reagents**

- **By catalytic reforming of n-Heptane**

Methylcyclohexane Toluene

## 4.0 COMPARISION OF AROMATIC COMPOUNDS WITH ALKENES

Benzene is not as reactive as alkenes, which react rapidly with bromine at room temperature to give addition products. For example, cyclohexene reacts to give trans-1, 2-dibromocyclohexane. This reaction is exothermic by about 29 kcal/mol (121 kJ/mol.)

$\Delta H° = -29$ kcal (– 121 kJ)

The analogous addition of bromine to benzene is endothermic because it requires the loss of aromatic stability. The addition is not seen under normal circumstances. The substitution of bromine for a hydrogen atom gives an aromatic product. The substitution is exothermic, but it requires a Lewis acid catalyst to convert bromine to a stronger electrophile.

$\Delta H° = +2$ kcal (+ 8kJ)

+ HBr $\Delta H° = -10.8$ kcal (– 45 kJ)

## 5. 0 ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS IN BENZENE RING

Like an alkene, benzene has clouds of pi electrons above and below its sigma bond framework. Although benzene's pi electrons are in a stable aromatic system still they are available to attack a strong electrophile to give a carbocation. This resonance-stabilized carbocation is called a **sigma complex** because the electrophile is joined to the benzene ring by a new sigma bond.

The sigma complex (also called an arenium ion) is not aromatic because the $sp^3$ hybrid carbon atom interrupts the ring of p orbitals. This loss of aromaticity contributes to the highly endothermic nature of thus first step. The sigma complex regains aromaticity either by a reversal of the first step (returning to the reactants) or by loss of the proton on the tetrahedral carbon atom, leading to the substitution product.

The overall reaction is the substitution of an electrophile $(\overset{\oplus}{E})$ for a proton $(\overset{\oplus}{H})$ on the aromatic ring: **electrophilic aromatic substitution**.

**Step 1 : Attack of an electrophile on bezene ring forms the sigma complex**

Resonance hybrid [σ – complex] Arrenium Ion

**Step 2 : Loss of a proton gives the substitution product.**

**Potential Energy Diagram :**

**Electrophilic substitution reaction of benzene :**

| Substrate | Reagent | Product | Name of reaction | Electrophile |
|---|---|---|---|---|
| (1) | $Cl_2$ / $AlCl_3$ | | Chlorination of benzene | $Cl^{\oplus}$ |
| (2) | $Br_2$ / $AlCl_3$ | | Bromination of benzene | $Br^{\oplus}$ |
| (3) | R – Cl / $AlCl_3$ | | Alkylation of benzene | $R^{\oplus}$ |
| (4) | $R-\overset{O}{\overset{\|\|}{C}}-Cl$ / $AlCl_3$ | | Alkanoylation of benzene | $R-\overset{\oplus}{C}=O$ |
| (5) | $C_6H_5COCl$ / $AlCl_3$ | | Benzoylation of benzene | $C_6H_5-\overset{\oplus}{C}=O$ |
| (6) | $HNO_3$ / $H_2SO_4$ | | Nitration of benzene | $NO_2^{\oplus}$ |
| (7) | $H_2SO_4 + SO_3$ | | Sulphonation of benzene | $SO_3$ |

## 5.1 Halogenation

- **Bromination of Benzene**

Bromination follows the general mechanism for electrophilic aromatic substitution. Bromine itself is not sufficiently electrophilic to react with benzene, but a strong Lewis acid such as $FeBr_3$ catalyzes the reaction.

**Step 1 :** Formation of a stronger electrophile.

**Step 2 :** Electrophilic attack and formation of the sigma complex.

**Step 3 :** Loss of a proton gives the products.

Formation of the sigma complex is rate determining and the transition state leading to it occupies the highest-energy point on the energy diagram. This step is strongly endothermic because it forms a non-aromatic carbocation. The second step is exothermic because aromaticity is regained and a molecule of HBr is evolved. The overall reaction is exothermic by 10.8 kcal/mol (45 kJ/mol.)

- **Chlorination of benzene**

Chlorination of benzene works much like bromination, except that aluminum chloride ($AlCl_3$) is most often used as the Lewis acid catalyst.

- **Iodination of benzene**

Iodination of benzene requires an acidic oxidizing agent such as nitric acid. Nitric acid is consumed in the reaction, so it is a reagent (an oxidant) rather than a catalyst.

**Ex.** Benzene on treating with $Br_2$ in the presence of halogen carrier gives a compound (A) which on monochlorination gives two isomeric compounds (B) and (C). Monobromination of (B) gives several isomeric products of molecular formula $C_6H_3ClBr_2$ while monobromination of (C) yields only two isomers (D) and (E). Compound (D) is identical with one of the compounds obtained from the bromination of (B), however (E) is totally different from any of the isomeric forms obtained from the monobromination of (B). Give the structures from (A) to (E) and also structures of four isomeric monobrominated products of (B). Support your answer with reasoning.

**Sol.** (A)

(B)

(C)

(D)

(E)


## 5.2 Nitration

Nitration is brought about by the action of concentrated nitric acid or a mixture of concentrated nitric acid and sulphuric acid often called nitrating mixture. $HNO_3$ alone is a weak nitrating agent where as the mixture is strong nitrating mixture when concentrated $HNO_3$ and concentrated $H_2SO_4$ are mixed to form the nitrating mixture, $NO_2^+$ (Nitronium ion) is produced as follows :

$$H\ddot{O}-NO_2 \xrightleftharpoons{H_2SO_4} H_2\overset{\oplus}{O}-NO_2 \xrightleftharpoons{H_2SO_4} H_3O^{\oplus} + HSO_4^{\ominus} + \overset{\oplus}{N}O_2$$

$$HNO_3 + 2H_2SO_4 \rightleftharpoons \underbrace{\overset{\oplus}{N}O_2 + H_3O^{\oplus} + 2HSO_4^{\ominus}}$$

Now, the $NO_2^+$ ion attacks the benzene nucleus and forms an intermediate cation (a benzenonium ion) which loses a proton to yield the nitro derivative.

## 5.3 Sulphonation

The electrophilic reagent, $SO_3$, attacks the benzene ring to form the intermediate carbocation.

$$2H_2SO_4 \rightleftharpoons SO_3 + H_3O^{\oplus} + HSO_4^{\ominus}$$

Sulphonation, like iodination, is **reversible** and is believed to take place in concentrated sulphuric acid via the following pathway,

## 5.4 Friedel Craft reaction

- **Alkylation**

The carbon atom of alkyl halides, $\overset{\delta+}{R}-\overset{\delta-}{X}$, is an electrophile. The presence of a Lewis acid catalyst is also required. Anhydrous aluminium chloride. $AlCl_3$, being a Lewis acid, accepts a lone pair of electrons from halogen (Chlorine atom) of R – $\ddot{\underset{..}{Cl}}$:. This makes R (alkyl) group to be sufficiently polar so as to act as an electrophile. The mechanism for Friedel Craft's reaction involves the following steps.

**(i)**


**(ii)**


**(iii)**

- **Nature of Lewis acid as catalyst**

The order of effectiveness of Lewis acid catalyst has been shown below:

$AlCl_3 > FeCl_3 > BF_3 > TiCl_3 > ZnCl_2 > SnCl_4$

**Example :**

**(i)**


(Toluene)

**(ii)**


(Cumene)

**(iii)**


(t-butyl benzene)

**(iv)**


**(v)**


**(vi)**


**(vii)**


**(viii)**


**(ix)**


***Note:*** *Pd – C is used for dehydrogenation and aromatisation*

**Ex.**


- **Acylation**

  Acylation of benzene is carried out with acid chlorides or anhydrides in presence of Lewis acids.

- **Mechanism**

**Step 1 :** Formation of an acylium ion.

**Step 2 :** Electrophilic attack.

**Step 3 :** Loss of a proton. Complexation of the product.

- **Reagents of Acylation**

**(a)**

**(b)**

**(c)**

**(d)**

**Example :**

**(i)**

Acetophenone (Phenyl methyl ketone)

**(ii)**


**(iii)**

(Benzophenone)

**(iv)**

(Succinic anhydride)

- **Limitation of Fridel Craft Reaction**

**Friedel craft reaction is not possible in presence of following functional groups :**

**(i)** **Groups with –m effect:-**

$G \equiv NO_2$, CN, COOH, COOR, $SO_3H$, $NR_3^{\oplus}$, CHO, COR.

**Experimental Observation :** Nitrobenzene is used in some Friedel craft reactions which indicates that it is unreactive towards Friedel craft reaction.

**Reason :** The $C^{\oplus}$ electrophile is highly reactive, so it gives many other reactions if the aromatic ring is less nucleophilic (deactivated).

**(ii) Groups with strong +m effect:-** ($-NH_2$, $-NHR$, $-NR_2$, $-OH$, $-OR$)

**Reason:-**

In presence of $OH/NH_2$ groups Friedel craft reaction is not possible because these groups make coordinate bond with Lewis acid ($AlX_3$) and the aromatic ring also becomes deactivated.

**Friedel craft reaction is Possible in :**

**Application :**

**Mono bromination of Aniline :**

- **Limitation of Friedel Craft Alkylation:-**

**(A) Polyalkylation:-**

**if R = Me, Et**

**(i)** In alkylation product has more activated ring. So further alkylation takes place. (If excess of reagent is present).

**(ii)** In order to stop the reaction at mono-alkylation stage, a large excess of aromatic reactant should be used.

**(B) Rearrangement of Alkyl cation :** Rearrangement is possible during Freidel Craft alkylation.

**Synthesis of n-Alkyl benzene :**

## Illustrations

**Illustration 1.** What would be the major product of a Friedel-Crafts alkylation reaction using the following alkyl halides ?

(a) $CH_3CH_2Cl$ (b) $CH_3CH_2CH_2Cl$ (c) $CH_3CH_2CH(Cl)CH_3$

(d) $(CH_3)_3CCH_2Cl$ (e) $(CH_3)_2CHCH_2Cl$ (f) $CH_2 = CHCH_2Cl$

**Solution.** (a) Ethylbenzene (b) Isopropylbenzene (c) sec-butylbenzene
(d) tert-pentylbenzene (e) tert-butylbenzene (f) 3-phenylpropene

**Illustration 2.**

**Solution.** (X) =

## 5.5 Gattermann Koch Formylation

**Mechanism**

## 5.6 Gattermann formylation

**Mechanism**

Deactivated benzene rings do not give formylation, i.e. - M groups must not be present.

## 6.0 ACTIVATING AND DEACTIVATING EFFECTS

### 6.1 Activating Groups or Electron Releasing Groups (ERG)

All groups having one or more lone pair of electrons are activating groups because they release electrons towards the nucleus increasing electron density and hence energy of the system. Reaction rate is increased due to low energy of activation. Examples :

$-\ddot{\underset{..}{O}}^{-}$, $-\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{N}R_2$, $-\ddot{\underset{..}{O}}H$, $-OR$, $-\ddot{N}HCOR$, $-R$, $-Ar$

All the groups which are electron donating $-\ddot{\underset{..}{O}}H$, $-\ddot{\underset{..}{O}}R$, $-\ddot{N}H_2$, $-NHR$, $-NR_2$ etc. are ortho–para directing and facilitate electrophilic substitution in the benzene ring.

**Ex.** Compare the activating effects of the following o, p-directors and explain your order

(a) $-\ddot{\underset{..}{O}}H$, $-\ddot{\underset{..}{O}}^{\ominus}$ , $-\ddot{\underset{..}{O}}C(=O)-CH_3$

(b) $-\ddot{N}H_2$ and $-\ddot{N}H-C(=O)-CH_3$

**Sol.** (a) The order of activation is $-O^{\ominus} > -OH > -OCOCH_3$. The $-O^{\ominus}$, with a full negative charge, is best able to donate electrons, there by giving the very stable uncharged intermediate

### 6.2 Deactivating Group or Electron Withdrawing Group (EWG) or Meta Directors

Such groups have tendency to withdraw π electrons from the benzene nucleus and thus decreasing its electron density are known as deactivating groups.

Due to decrease in electron density of the ring, the rate of electrophilic substitution is retarded.

These groups develop positive charge at ortho and para positions leaving the meta-positions as the point of relatively high electron density and hence the electrophilic substitution occurs at m–position, not at o–and p–positions.

**Examples :**

$-\overset{+}{N}R_3$, $-\overset{\oplus}{N}(=O)(\rightarrow O)$ , $-S(=O)-OH$, $-CH(=O)$, $-C(=O)-R$, $-C(=O)-OH$, $-C(=O)-OR$, $-C-NH_2$, $-\overset{+}{N}H_3$

decreasing meta directing strength

## 7.0 DIRECTIVE INFLUENCE OF SUBSTITUENTS IN BENZENE

The first substituent may occupy any position in benzene ring i.e. one and only one monosubstituted benzene is obtained. The next group may go to ortho, meta or para position, it is the group already present in the benzene nucleus that determines how readily the attack occurs and at which position, of the ring it occurs. In other words, the group attached to the ring not only affects the reactivity but also determines the position of substitution. This is called **directive influence** of substituents in bezene nucleus. The substituent group is able to activate or deactivate the ring due to a number of factors like inductive effect, electromeric effect, resonance effect and hyperconjugative effect.

**Classification of Substituent Groups**

**(i)** Activating and o/p directing groups

**Examples :** $O^-$,$NH_2$,NHR, $NR_2$, OH, OR, –NHAC, –OAC , Me > Et > $-C(C)_2$ > $-C(C)_3$

**(ii)** Deactivating and o,p–directing groups

**Examples :** F, Cl, Br, I, –N = O

**(iii)** Deactivating and m–directing groups

**Examples :** $NR_3^{\oplus}$ , $\overset{\oplus}{N}H_3$ , $CX_3$, $-NO_2$, $>CO$, –CN, –COOH, –COOR, $-SO_3H$, COCl

**Reason :**

**(i)** o,p directing groups increase electron density at ortho and para position while mata directing groups decrease electron density at ortho and para position.

**(ii) Stability of Arenium Ion :**

o, p directing groups stabilize arenium ion during ortho or para substitution.

meta directing groups decrease stability of arenium ion during ortho or para substitution.

## BEGINNER'S BOX-1

### Reactivity and Directive influence

**1. Give correct order of reactivity towards EAS.**

(i) (a) (b)

(c)


(ii) (a)

(b)

(iii) (a)

(b)


(iv) (a)

(b)

(v) (a)

(b)


(vi) (a)

(b)

(vii) (a)

(b)


(viii) (a)

(b)

**2.** Show most reactive position towards EAS for following compounds in normal conditions.

## 8.0 REACTIONS OF ALKYL BENZENES

**Oxidation of alkyl benzene :**

Alkyl group having no α-H atom will not be oxidized to –COOH. Any alkyl group containing at least one α-H atom will be oxidized to –COOH. The product of oxidation will be benzoic acid.

**Etard Reaction :**

**Ozonolysis :**

## Illustrations

**Illustration 3.** Gives the products of the following reactions :–

(a)


(b)


(c)


**Solution.** X = phenylcyclohexane

Y =


O - methyl anisole

p – methyl anisole

Z = 1 - isopropyl – 4 – (1, 1, 2 – trimethyl propyl) benzene

**Illustration 4.** Predict the products (if any) of the following reactions

(a) excess


isobutylchloride

(b)


toluene (excess) 1 – butanol

(c)


nitrobenzene (excess)

(d)


Benzene (excess)

**Solution.** X =


ter-butyl benzene

Y =


2-sec. butyltoluene

or


4-sec. butyltoluene

Z = No reaction


P = (1, 1, 2-trimethylpropyl) benzene

**Illustration 5.** Nitrobenzene and nitrosobenzene both are deactivated rings as compared to benzene but their directive effects are different. Nitrobenzene mainly gives m– substituted product while nitrosobenzene gives ortho-para substituted product ?

**Solution.**


(-m effect)

(-I > m effect)

–NO group stabilize arenium ion during ortho para substitution due to presence of lone pair at Nitrogen.

## BEGINNER'S BOX-2

### Reactions of Benzene and its derivatives

**1.**


(A)


(B)


(C)


(D)


**2.**


(A)


(B)


(C)


(D)


**3.**

$+ H_2$ (1 mol) $\xrightarrow{Pt}$

(A)


(B)


(C)


(D) none of these

**4.**

(A)

(B)

(C)

(D)

**5.** Which one of the following compounds will be most readily attacked by an electrophile ?

(A) Chlorobenzene (B) Benzene (C) Phenol (D) Toluene

**6.** Benzene reacts with acetyl chloride in presence of anhydrous aluminium chloride to form :

(A) acetophenone (B) phenyl acetate (C) chlorobenzene (D) benzoic acid

**7.** In Friedel-Crafts reaction the electrophilic reagent is :

(A) $AlCl_3$ (B) $R\overset{\oplus}{C}O$ (C) $R\overset{\oplus}{C}OCl$ (D) none of these

## GOLDEN KEY POINTS

- All meta directing groups are deactivating but opposite is not true.
- All activating groups are ortho para directing but opposite is not true.

## SOME WORKED OUT EXAMPLES

**Illustration 1.**

Compound A ($C_{10}H_6$) liberates 2 moles of $CH_4$ when treated with Methyl magnesium bromide. On heating with $KMnO_4$ solution, A produces Benzene dicarboxylic acid which on mononitration produces only one product and no other isomers. A can be :

(A)

(B)


(C)


(D)


**Ans. (B)**

**Solution.**

**Illustration 2.**

Two compounds X and Y having same molecular formula ($C_9H_{10}$) give following reactions.

x and y can respectively be

(A)

and


(B)

and


(C)

and


(D)

and


**Ans. (D)**

**Solution.**

**Illustration 3.**

Which of the following alcohols would you expect to form a carbocation most readily in sulphuric acid

(A)


(B)


(C)


(D)


**Ans. (B)**

**Solution.**

Stable carbocation (The central ring has also become aromatic and an aromatic tropylium cation is formed.) (Due to formation of more stable carbocation)

**Illustration 4.**

Which of the following will accept $H^+$ ion with fastest rate ?

(A)
(B)
(C)
(D)

**Ans. (B)**

**Solution.**

The lone pair at N is not delocalized in the ring.

N atom does not show + M effect in other options. l ps. of N atom can show + M effect showing they are least basic in nature.

**Illustration 5.**

Dipole moment of p-nitroaniline (z) when compared to nitrobenzene (x) and aniline (y) will be

(z) (x) (y)

(A) x < z < y (B) z > x > y (C) x < z < y (D) equal to zero

**Ans. (B)**

**Solution.**

z > x > y

z is Due to + M and – M and – M ; x is due to – M effect ; y is due to + M effect.

**Illustration 6.**

Amongst the given compound II is respectively isomeric with I, III & IV as

(I)
(II)

(III)
(IV)

(A) Tautomer, functional, geometrical (B) Metamers, tautomer, identical
(C) Functional, tautomer, identical (D) Functional, tautomers & geometrical

**Ans. (C)**

**Solution.** Functional ; tautomer ; identical.

**Illustration 7.**

The product(s) of the following reaction is/are

(A)


(B)


(C)


(D)


**Ans. (C)**

**Solution.**

* * * * *

# ANSWER KEY

## BEGINNER'S BOX-1

**1.** (i) b > c > a (ii) b > a (iii) a > b (iv) b > a (v) b > a
(vi) a > b (vii) b > a (viii) a > b

**2.** (i)

(ii)

(iii)

(iv)

(v)

## BEGINNER'S BOX-2

**1.** (A) **2.** (B) **3.** (A) **4.** (B) **5.** (C) **6.** (A) **7.** (B)

## EXERCISE (S-1)

### SECTION - 1 : NUMERICAL ANSWER BASED QUESTIONS

**1.** How many statements is/are incorrect ?

(i) All aromatic compounds are most stable than non–aromatic compounds.

(ii) All ortho–para directing groups are activating groups.

(iii) All activating groups are ortho–para directing groups.

(iv) Meta directing groups increases electron density at meta position.

**2.** How many $\pi$ electron are there in resonance in the following species :

**3.** The number of benzylic hydrogen atoms in ethylbenzene is:

**4.** Which position will be attacked most rapidly by the nitronium ion ($-NO_2^{\oplus}$) when given compound undergoes nitration with $HNO_3 + H_2SO_4$ (conc.)

**5.**

At which place nitration will mainly take place ?

**6.** When the following compound is nitrated (conc. $HNO_3$ + conc. $H_2SO_4$) which ring carbon atom is involved

**7.** In the given reaction

Double bond equivalent of (X) is :

## SECTION - 2 : MATRIX - MATCH QUESTIONS

**8. Match the column-**

**Column - I** **Column-II**

(A)


(p) Group attached with phenyl ring is + M.

(B)


(q) Rate of electrophilic aromatic substitution is less than benzene ring

(C)


(r) Group attached with phenyl ring will show (+H) (Hyperconjugation)

(s) Group attached with phenyl ring will show (–H) effect (Hyperconjugation)

**9.** Match the following Columns :

**Column-I** **Column-II**
**(Order of reactivity for EAS reactions)**

(A)


(I) (II) (III)

(p) I > II > III

(B)


(I) (II) (III)

(q) II > I > III

(C)


(I) (II) (III)

(r) III > II > I

(D)


(I) (II) (III)

(s) III > I > II

**10.** Match the following Columns :

| | **Column I** | | **Column II** |
|---|---|---|---|
| (A) | | (p) | Group attached to the benzene ring is +M effect showing group |
| (B) | | (q) | Group attached to the benzene ring is –M effect showing group |
| (C) | | (r) | Group attached to the benzene ring is + H showing group. |
| (D) | | (s) | Group attached to the benzene ring is –I effect showing group |

# EXERCISE (O-1)

## SINGLE CHOICE CORRECT QUESTIONS

**1.** For preparing monoalkyl benzene, acylation process is preferred than direct alkylation because

(A) In alkylation, a poisonous gas is evolved

(B) In alkylation, large amount of heat is evolved

(C) In alkylation, polyalkylated product is formed

(D) Alkylation is very costly

**2.** Benzene is a resonance hybrid mainly of two Kekule structures. Hence:

(A) Half of the molecules correspond to one structure, and half of the second structure

(B) At low temperatures benzene can be separated into two structures

(C) Two structures make equal contribution to resonance hybrid

(D) An individual benzene molecule changes back and forth between two structures

**3.** Major product of this reaction will be :

(A) o-xylene (B) p-xylene (C) both (D) m-xylene

**4.** Which of the following group is divalent:

(A) Benzoyl (B) Benzyl (C) Benzal (D) p-Tolyl

**5.** Which of the following is not an aromatic compound:

(A)


(B)

(C)


(D)


**6.**

hydrocarbon (X) major product X is:

(A)


(B)


(C)


(D)

**7.** $C_6H_6 + A \xrightarrow{AlCl_3} C_6H_5CONH_2$

A in the above reaction is:

(A) $NH_2CONH_2$ (B) $ClCONH_2$ (C) $CH_3CONH_2$ (D) $CH_2(Cl)CONH_2$

**8.** In the sulphonation, acetylation and formylation of benzene the group of effective electrophiles would be:

(A) $SO_3^+, CH_3 \equiv \overset{+}{O}, H\overset{+}{C}O$ (B) $SO_3, CH_3 - C \equiv \overset{+}{O}, H\overset{+}{C}O$

(C) $SO_3$, $CH_3CHO$, $CO + HCl$ (D) $HSO_3$, $CH_3CO$, $HCO$

**9.** p-Nitrotoluene on further nitration gives:

(A)


(B)


(C)


(D)


**10.** For the electrophilic substitution reaction involving nitration, which of the following sequence regarding the rate of reaction is true?

(A) $k_{C_6H_6} > k_{C_6D_6} > k_{C_6T_6}$ (B) $k_{C_6H_6} < k_{C_6D_6} < k_{C_6T_6}$

(C) $k_{C_6H_6} = k_{C_6D_6} = k_{C_6T_6}$ (D) $k_{C_6H_6} > k_{C_6D_6} < k_{C_6T_6}$

**11.** For the electrophilic substitution reaction involving sulphonation, which of the following sequence regarding the rate of reaction is true?

(A) $k_{C_6H_6} > k_{C_6D_6} > k_{C_6T_6}$ (B) $k_{C_6H_6} < k_{C_6D_6} < k_{C_6T_6}$

(C) $k_{C_6H_6} = k_{C_6D_6} = k_{C_6T_6}$ (D) $k_{C_6H_6} > k_{C_6D_6} < k_{C_6T_6}$

**12.** Which of the following carbocations is expected to be most stable?

(A)


(B)


(C)


(D)


**13.** Reaction of $SO_3$ is easier in:

(A) Benzene (B) Toluene (C) Nitrobenzene (D) chlorobenzene

**14.** Which order is correct for the decreasing reactivity to ring monobromination of the following compounds:

(I) $C_6H_5CH_3$ (II) $C_6H_5COOH$ (III) $C_6H_6$ (IV) $C_6H_5NO_2$

(A) I > II > III > IV (B) I > III > II > IV (C) II > III > IV > I (D) III > I > II > IV

**15.** The highest yield of m-product is possible by the electrophilic substitution of the following:

(A) $C_6H_5CH_3$ (B) $C_6H_5CH_2COOC_2H_5$

(C) $C_6H_5CH(COOC_2H_5)_2$ (D) $C_6H_5C(COOC_2H_5)_3$

**16.** In a reaction of $C_6H_5Y$, the major product (>60%) is m-isomer, so the group Y is:

(A) –COOH (B) –Cl (C) –OH (D) $–NH_2$

**17.** Which of the following will undergo sulphonation at fastest rate ?

(A) (B) (C) (D)

**18.** Which of the following is most reactive towards electrophilic aromatic substitution?

(A) m-Xylene (B) o-Xylene (C) Toluene (D) p-Xylene

**19.** Ring nitration of dimethyl benzene results in the formation of only one nitro dimethyl benzene. The dimethyl benzene is:

(A)


(B)


(C)


(D) None of these

**20.** An aromatic compound of molecular formula $C_6H_4Br_2$ was nitrated then three isomers of formula $C_6H_3Br_2NO_2$ were obtained. The original compound is:

(A) o-dibromobenzene (B) m-dibromobenzene (C) p-dibromobenzene (D) Both A & C

**21.** Which of the following is/are produced when a mixture of benzene vapour and oxygen is passed over $V_2O_5$ catalyst at 775 K?

(A) Oxalic acid (B) Glyoxal (C) Fumaric acid (D) Maleic anhydride

**22.** Methyl group attached to benzene can be oxidised to carboxylic group by reacting with:

(A) $Fe_2O_3$ (B) $AgNO_3$ (C) $KMnO_4$ (D) $CrO_3$

**23.** If the mixture of the following four aromatic compounds on oxidation by strong oxidising agent gives:

(A) Mixture of $C_6H_5CH_2OH + C_6H_5COOH$ (B) Mixture of $C_6H_5CHO + C_6H_5COOH$

(C) Only $C_6H_5COOH$ (D) None of the above

**24.** Etard reaction in the following is:

(A) Oxidation of toluene to benzaldehyde by chromylchloride

(B) Oxidation of toluene to benzaldehyde by alkaline $KMnO_4$

(C) Dry distillation of calcium benzoate

(D) Reaction of benzene with $Cl_2$ in the presence of UV light

**25.** $+ H_2 \xrightarrow[\text{high pressure}]{\text{Ni, high temp.}}$ (A). Which of the following can be isolated as the product of this reaction.

(A)

(B)

(C)

(D)

# EXERCISE (O-2)

## SECTION - 1 : MULTIPLE CHOICE CORRECT QUESTIONS

**1.** Benzene reacts with n-propyl chloride in the presence of anhydrous $AlCl_3$ to give predominantly:

(A) n-Propylbenzene (B) Isopropylbenzene

(C) 3-Propyl-1-chlorobenzene (D) Cumene

**2.** In which of the following reaction t-butylbenzene is formed:

(A) Benzene + iso-butyl chloride, $AlCl_3$ (B) Benzene + $(CH_3)_2C = CH_2 \xrightarrow{BF_3.HF}$

(C) Benzene + t-butyl alcohol $\xrightarrow{H_2SO_4}$ (D) Benzene + $(CH_3)_2$ C= $CH_2 \xrightarrow{AlCl_3}$

**3.** Which of the following can be used in Friedel Crafts reaction to generate electrophile?

(A)


(B) $CH_2$=CH–Cl (C) $CH_3CH_2Cl$ (D) $CH_2$=CH–$CH_2$–Cl

**4.** Electrophilic attack of $NO_2^{\oplus}$ at meta position is observed in:

(A)


(B)


(C)


(D)


**5.** Which of the following will undergo nitration faster than benzene?

(A)


(B)

(C)


(D)


**6.** Which of the following statements is incorrect for electrophilic substitution.

(A) Ortho-and para-directing groups increase electron density at ortho-and para-positions

(B) Meta-directing groups increase electron density at meta-position

(C) Meta-directing groups decrease electron density at meta-position

(D) Ortho-and para-directing groups decrease electron density at meta-position

**7.** Which of the following statements is/are not true?

(A) All ortho-para directing groups activates the ring

(B) All ortho-para directing groups except halogens activate the ring

(C) All meta-directing groups have $\pi$-bond on the atom directly attached to the ring

(D) All meta directing groups are deactivating.

**8.** False statement is / are :

(A) Although benzene contains three double bonds, normally it does not undergo addition reaction.

(B) m-chlorobromobenzene is an isomer of m-bromochlorobenzene.

(C) In benzene, carbon uses all the three p orbitals for hybridization.

(D) An electron donating substitutent in benzene orients the incoming electrophilic group to the meta position.

**9.** Benzoic acid may be prepared by the oxidation of:

(A)


(B)


(C)


(D)


**10.** Which of the following are classified as aromatic?

(A) 1, 2, 3-Triphenylcyclopropenium cation

(B) Cyclooctatetraenyl dianion

(C) Azulene

(D) [4] Annulene

## SECTION - 2 : COMPREHENSION BASED QUESTIONS
## (SINGLE CHOICE CORRECT QUESTION)

**Comprehension-1**

Observe the following table and conclude the answer by ticking the right choice.

| Compound | Products formed | | | Nitration rate (relative to benzene) |
|---|---|---|---|---|
| | o | m | p | |
| Ph – F | 13 | 0.6 | 86 | 0.18 |
| Ph – Cl | 35 | 0.9 | 64 | 0.064 |
| Ph – Br | 43 | 0.9 | 56 | 0.060 |
| Ph – I | 45 | 1.3 | 54 | 0.12 |

**11.** The faster reation of PhF relative to others are

(A) F is showing more + R effect with benzene ring

(B) F is showing less + R effect with benzene ring

(C) F is showing more – I effect

(D) F is showing less – I effect

**12.** The % ortho product of fluoro to iodo increases because

(A) Strong – I effect of F

(B) Strong + R effect of F

(C) Weak – R effect of I

(D) Strong + R effect of I

**Comprehension-2**

Compound A gives white precipitate with $AgNO_3$ and a highly stable cation. whereas compound B which is antiaromatic reacts with Na metal to give an aromatic compound.

**13.** Which of the following is A?

(A)


(B)


(C)


(D)


**14.** Which of the following is B?

(A)

(B)

(C)

(D)

**15.** Which of the following statement is not correct about compound A ?

(A) A is more soluble than bromocyclopropane in polar solvent.

(B) A is having even number of DBE

(C) In A, bromine is present at vinylic position

(D) A is more ionic than

## EXERCISE (JM)

**1.** The electrophile, $E^{\oplus}$ attacks the benzene ring to generate the intermediate σ-complex. Of the following, which σ–complex is of lowest energy ? **[AIEEE-2008]**

(1)


(2)


(3)


(4)


**2.** Ortho - Nitrophenol is less soluble in water than p - and m – Nitrophenols becuase :

(1) o – Nitrophenol is more volatile in steam than those of m – and p - isomers. **[AIEEE-2012]**

(2) o – Nitrophenol shows o- intramolecular H – bonding

(3) o – Nitrophenol shows Intermolecular H – bonding

(4) Melting point of o – Nitrophenol is lower than those of m – and p - isomers.

**3.** Which of the following compounds is not aromatic ? **[JEE MAINS - ONLINE - 2019]**

(1)

(2)


(3)

(4)


**4.** Polysubstitution is a major drawback in: **[JEE MAINS - ONLINE - 2019]**

(1) Reimer Tiemann reaction (2) Friedel Craft's acylation

(3) Friedel Craft's alkylation (4) Acetylation of aniline

**5.** The correct IUPAC name of the following compound is : **[JEE MAINS - ONLINE - 2019]**

(1) 5-chloro-4-methyl-1-nitrobenzene (2) 2-methyl-5-nitro-1-chlorobenzene

(3) 3-chloro-4-methyl-1-nitrobenzene (4) 2-chloro-1-methyl-4-nitrobenzene

**6.** The increasing order of reactivity of the following compounds towards aromatic electrophilic substitution reaction is : **[JEE MAINS - ONLINE - 2019]**

(1) D < B < A < C (2) A < B < C < D

(3) D < A < C < B (4) B < C < A < D

**7.** The increasing order of the reactivity of the following compounds towards electrophilic aromatic substitution reactions is :- **[JEE MAINS - ONLINE - 2019]**

(1) I < III < II (2) II < I < III (3) III < I < II (4) III < II < I

**8.** What will be the major product when m-cresol is reacted with propargyl bromide ($HC{\equiv}C{-}CH_2Br$) in present of $K_2CO_3$ in acetone **[JEE MAINS - ONLINE - 2019]**

(1)


(2)


(3)


(4)

## EXERCISE (JA)

**1.** **STATEMENT-1 :** Bromobenzene upon reaction with $Br_2$/Fe gives 1,4-dibromobenzene as the major product.

**STATEMENT-2 :** In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile. **[JEE-2008]**

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

**2.** The compounds P, Q and S **[JEE-2010]**

P Q S

were separately subjected to nitration using $HNO_3$ / $H_2SO_4$ mixture. The major product formed in each case respectively, is :

(A)

(B)

(C)

(D)

**3.** The carboxyl functional group (–COOH) is present in **[JEE-2012]**

(A) picric acid (B) barbituric acid (C) ascorbic acid (D) aspirin

**4.** Among the following, reaction(s) which gives(give) tert–butyl benzene as the major product is(are) **[JEE-2016]**

(A)


(B)


(C)


(D)

# ANSWER KEY

## EXERCISE (S-1)

### NUMERICAL ANSWER BASED QUESTIONS

**1.** (3) **2.** (6) **3.** (2) **4.** (6) **5.** (4)

**6.** (2) **7.** (6)

### MATRIX MATCH QUESTIONS

**8.** (A) - (q), (B) - (p), (C) - (r)

**9.** (A) - (s), (B) - (r), (C) - (q), (D) - (p)

**10.** (A) - (r), (B) - (ps), (C) - (qs), (D) - (pqrs)

## EXERCISE (O-1)

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | C | C | D | C | B | D | B | B | A | C | A | D | B | B | D |
| Que. | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | | | | | |
| Ans. | A | B | A | C | B | D | C | C | A | A | | | | | |

## EXERCISE (O-2)

### MULTIPLE CHOICE CORRECT QUESTIONS

**1.** (BD) **2.** (ABCD) **3.** (CD) **4.** (ABC) **5.** (ABD)

**6.** (BCD) **7.** (ABC) **8.** (BCD) **9.** (AB) **10.** (ABC)

### COMPREHENSION BASED QUESTIONS

**11.** (A) **12.** (A) **13.** (B) **14.** (A) **15.** (C)

## EXERCISE (JM)

**1.** (1) **2.** (2) **3.** (3) **4.** (3) **5.** (4)

**6.** (3) **7.** (3) **8.** (4)

## EXERCISE (JA)

**1.** (C) **2.** (C) **3.** (D) **4.** (BCD)