

XII - NEET CHEMISTRY

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NEET SYLLABUS

IONIC EQUILIBRIUM : ionization of acids and bases, strong and weak electrolytes, degree of ionization, ionization of polybasic acids, acid strength, concept of pH, Hydrolysis of salts (elementary idea), buffer solutions, Henderson equation, solubility product, common ion effect (with illustrative examples).

OBJECTIVES

After studying this unit, you will be able to :

- *Classify acids and bases as weak or strong in terms of their ionization constants;*
- *Explain the dependence of degree of ionization on concentration of the electrolyte and that of the common ion;*
- *Describe pH scale for representing hydrogen ion concentration;*
- *Explain ionisation of water and its dual role as acid and base;*
- *Describe ionic product (K_w) and pK_w for water;*
- *Appreciate use of buffer solutions;*
- *Calculate solubility product constant.*
- *Classify substances as acids or bases according to Arrhenius, Bronsted-Lowry and Lewis concepts;*

"If you're not part of the solution, you're part of the precipitate."

Henry J. Tillman

IONIC EQUILIBRIUM

4.0 INTRODUCTION

Formulae :

$$(i) \quad \ln x = \log_e x = 2.303 \log_{10} x = 2.303 \log x$$

$$(ii) \quad \log (x \times y) = \log x + \log y$$

$$(iii) \quad \log \left(\frac{x}{y} \right) = \log x - \log y$$

$$(iv) \quad \log x^y = y \log x$$

$$\begin{aligned} \text{Ex. (i)} \quad \log 6 &= \log (2 \times 3) \\ &= \log 2 + \log 3 \\ &= 0.3010 + 0.4771 = 0.7781 \end{aligned}$$

$$\begin{aligned} (ii) \quad \log 30 &= \log (3 \times 10) \\ &= \log 3 + \log 10 \\ &= \log 0.4771 + 1 = 1.4771 \end{aligned}$$

$$\begin{aligned} (iii) \quad \log 1000 &= \log 10^3 \\ &= 3 \log 10 = 3 \times 1 = 3 \end{aligned}$$

A. Some values of Log :

$$\log 1 = 0$$

$$\log 2 = 0.3010$$

$$\log 3 = 0.4771$$

$$\log 4 = 0.6020$$

$$\log 5 = 0.699$$

$$\log 6 = 0.7781$$

$$\log 7 = 0.8451$$

$$\log 8 = 0.9030$$

$$\log 9 = 0.9542$$

$$\log 10 = 1$$

$$\log 11 = 1.04$$

$$\log 100 = 2$$

$$\log 1000 = 3$$

Some terms which are used in ionic equilibrium : **Antilog :** $\text{Antilog } (x) = 10^x$

$$\text{Ex. Antilog } (2) = 10^2 = 100$$

$$\text{Antilog } (0.3010) = 10^{0.3010} = 2$$

$$\text{Antilog } [\log (2)] = \text{Antilog } (0.3010) = 2$$

pH - Scale : Given by – **Sorenson**

pH Scale is called Sorenson scale.

pH scale is a measuring scale used to measure strength of acid and base and its value is equal to $-\log[H^+]$

$$\text{i.e.} \quad \text{pH} = -\log[H^+] = \log \frac{1}{[H^+]}$$

$$\begin{aligned} \text{Ex.} \quad [H^+] &= 10^{-3} \\ \text{pH} &= -\log 10^{-3} = +3 \log 10 = 3 \end{aligned}$$

Conclusion :

If $\text{pH} = x$ then $[H^+] = 10^{-x}$ or Vice versa

i.e. If $[H^+] = 10^{-x}$ then $\text{pH} = x$

pOH → It is equal to $-\log [OH^-]$ i.e. $\text{pOH} = -\log [OH^-] = \log \frac{1}{[OH^-]}$

Ex. If $X = \frac{a}{b} \times 10^{-c}$, then find pX ?

$$\text{Sol.} \quad \text{pX} = -\log X = -\log \left(\frac{a}{b} \times 10^{-c} \right)$$

$$\text{pX} = - \left[\log \frac{a}{b} + \log 10^{-c} \right] = - [\log a - \log b - c]$$

$$\boxed{\text{pX} = c + \log b - \log a}$$

Strong Acid

Weak Acid

Neutral

Weak Base

Strong Base

pH → 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

$[H^+] \rightarrow 10^0 10^{-1} 10^{-2} 10^{-3} 10^{-4} 10^{-5} 10^{-6} 10^{-7} 10^{-8} 10^{-9} 10^{-10} 10^{-11} 10^{-12} 10^{-13} 10^{-14}$

$[OH^-] \rightarrow 10^{-14} 10^{-13} 10^{-12} 10^{-11} 10^{-10} 10^{-9} 10^{-8} 10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^0$

pOH → 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0

Strength of Acid increases

Strength of Base increases

(1) Non-Conductor - Those substances which do not show the flow of current or electricity.

Exception – Graphite is a non-metal but show conductivity due to motion of free electrons.

(a) Metallic conductor – Those conductor which show conductivity due to motion of free electrons.

(b) Ionic conductors –

(1) Strong electrolytes – Those ionic conductors which are **completely ionized in aqueous solution** are called as strong electrolytes.

For strong electrolyte the value of degree of ionisation is 100% i.e. $\alpha = 1$

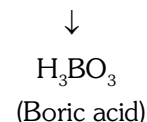
Ex. (a) Strong acid $\rightarrow$ H_2SO_4 , HCl , HNO_3 , HClO_4 , HBr , HI

(b) Strong base $\rightarrow$ KOH, NaOH, Ba(OH)₂, CsOH, RbOH

(c) All Salts $\rightarrow$ NaCl, KCl, CuSO₄.....

(2) **Weak electrolytes** – Those electrolytes which are **partially ionized in aqueous solution** are called as weak electrolytes. For weak electrolytes the value of α is less than one.

Ex. (a) Weak acids $\rightarrow$ HCN , CH_3COOH , HCOOH , H_2CO_3 , H_3PO_3 , H_3PO_2 , B(OH)_3 , etc.



(b) Weak bases $\rightarrow$ NH_4OH , $\text{Cu}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$ etc.

4.1 ARRHENIUS CONCEPT :

- (a) According to Arrhenius when an electrolyte dissolves in water it splits up into two oppositely charged particles i.e. cation and anion.
- (b) In an electrolytic solution (Aqueous solution of electrolyte), total +ve charge is equal to total -ve charge i.e. solution is electrically neutral.
 $\Rightarrow$ In an electrolytic solution number of +ve ions may or may not be equal to the number of negative ions.
- (c) Properties of an electrolytic solution are defined by its ions.
- Ex.** Blue colour of CuSO_4 aqueous solution is due to Cu^{+2} ion (dark blue colour)
- (d) When electric current is pass in aqueous solution of electrolyte then cation shows migration towards cathode where as anion shows migration towards anode.
- (e) When a weak electrolyte is dissolved in water an equilibrium is set up between unionized moles and ionized moles.

This condition of the reversible ionic reaction is known as ionic equilibrium. $\text{AB (Aq.)} \rightleftharpoons \text{A}^+(\text{Aq.}) + \text{B}^-(\text{Aq.})$

According to L.M.A.

$$\text{Ionisation constant } K = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]}$$

Illustrations

Illustration 1 If $[\text{H}^+] = \frac{5}{3} \times 10^{-4}$ then find pH ?

Solution $\text{pH} = -\log [\text{H}^+] = -\log \left(\frac{5}{3} \times 10^{-4} \right)$

$$\begin{aligned} &= - \left[\log \frac{5}{3} + \log 10^{-4} \right] = - [\log 5 - \log 3 - 4] \\ &= - [0.699 - 0.4771 - 4] = - [-3.778] = 3.778 \end{aligned}$$

Illustration 2 **Assertion :** H_2SO_4 is a strong acid.

Reason : H_2SO_4 undergoes almost completely ionised in aqueous solution.

(1) A

(2) B

(3) C

(4) D

Solution **Ans. (1)**

4.2 OSTWALD'S DILUTION LAW

$\Rightarrow$ Ostwald dilution law is applicable only for weak electrolytes.

Statement : According to Ostwald when solution of weak electrolyte is diluted then degree of ionisation of solution is increased, is called dilution law.

Let	$\text{AB (Aq.)} \rightleftharpoons \text{A}^+(\text{Aq.}) + \text{B}^-(\text{Aq.})$
Initial concentration	$\text{C} \qquad 0 \qquad 0$
Degree of ionisation (α)	$(\text{C} - \text{C}\alpha) \qquad (\text{C}\alpha) \qquad (\text{C}\alpha)$
According to L.M.A.	

$$\text{Ionisation constant } K = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]}; K = \frac{\text{C}\alpha \times \text{C}\alpha}{\text{C}(1-\alpha)} = \frac{\text{C}\alpha^2}{(1-\alpha)}$$

If $\alpha \ll 1$ then $1 - \alpha \simeq 1$

$$K = \text{C}\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K}{\text{C}}} \quad (K = \text{constant, At constant temperature})$$

$$\alpha \propto \frac{1}{\sqrt{\text{C}}} \quad (\text{C} \propto \frac{1}{V}) \quad \alpha \propto \sqrt{V}$$

volume $\equiv$ dilution $\alpha \propto \sqrt{\text{dilution}}$ by dilution law
 dilution $\uparrow$ $\alpha \uparrow$

At infinite dilution, $\alpha = 100\%$

Thus for weak electrolytes the degree of ionisation is directly proportional to square root of dilution or inversely proportional to square root of concentration. This law is known as Ostwald Dilution Law.

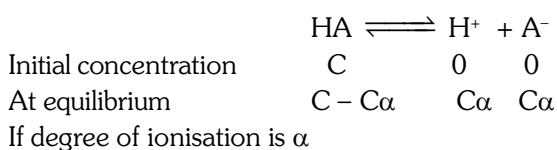
GOLDEN KEY POINTS

- At infinite dilution the value of α becomes equal to one.
- The value of concentration should be in terms of normality for calculation of pH.

Application of Ostwald's Dilution Law : $K = C\alpha^2$

(a) For mono basic weak acid (HA)

(i). Ionisation constant (K_a)



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{C\alpha \times C\alpha}{C - C\alpha}$$

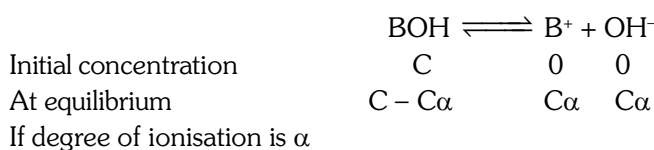
$$K_a = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

$$\because \alpha \ll \ll \ll 1 \quad \therefore (1-\alpha) \approx 1$$

$$\therefore K_a = C\alpha^2$$

(b) For mono acidic weak base (BOH)

Ionisation constant (K_b)



$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} = \frac{C\alpha \times C\alpha}{C - C\alpha}$$

$$K_b = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

$$\because \alpha \ll \ll \ll 1 \quad \therefore (1-\alpha) \approx 1$$

$$\therefore K_b = C\alpha^2$$

Where

$K_a \rightarrow$ Ionisation constant of weak acid
 $K_b \rightarrow$ Ionisation constant of weak base } Both K_a and K_b depends only on temperature

(ii). $[\text{H}^+]$ (Concentration of H^+)

$$[\text{H}^+] = C\alpha \quad \dots\dots(1)$$

$$K_a = C\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{C}} \quad \dots\dots(2)$$

$$\text{from Eq. (1) and (2) } [\text{H}^+] = C \times \frac{\sqrt{K_a}}{\sqrt{C}}$$

$$[\text{H}^+] = \sqrt{K_a \times C}$$

(iii). $\text{pH} = -\log [\text{H}^+]$

put the value of $[\text{H}^+]$

$$\text{pH} = -\log(\sqrt{K_a \times C}) = -\log(K_a \times C)^{1/2}$$

$$\text{pH} = -\frac{1}{2}[\log K_a + \log C]$$

$$\text{pH} = -\frac{1}{2}\log K_a - \frac{1}{2}\log C$$

$$\text{pH} = \frac{1}{2}\text{p}K_a - \frac{1}{2}\log C$$

$[\text{OH}^-]$ (Concentration of OH^-)

$$[\text{OH}^-] = C\alpha \quad \dots\dots(1)$$

$$K_b = C\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K_b}{C}} \quad \dots\dots(2)$$

$$\text{from Eq. (1) and (2) } [\text{OH}^-] = C \times \frac{\sqrt{K_b}}{\sqrt{C}}$$

$$[\text{OH}^-] = \sqrt{K_b \times C}$$

$\text{pOH} = -\log [\text{OH}^-]$

put the value of $[\text{OH}^-]$

$$\text{pOH} = -\log(\sqrt{K_b \times C}) = -\log(K_b \times C)^{1/2}$$

$$\text{pOH} = -\frac{1}{2}[\log K_b + \log C]$$

$$\text{pOH} = -\frac{1}{2}\log K_b - \frac{1}{2}\log C$$

$$\text{pOH} = \frac{1}{2}\text{p}K_b - \frac{1}{2}\log C$$

In summary :

1. $K_a = C\alpha^2$

2. $[H^+] = C\alpha = \sqrt{K_a \times C}$

3. $pH = -\log [H^+]$

or $pH = \frac{1}{2}pK_a - \frac{1}{2}\log C$

1. $K_b = C\alpha^2$

2. $[OH^-] = C\alpha = \sqrt{K_b \times C}$

3. $pOH = -\log [OH^-]$

or $pOH = \frac{1}{2}pK_b - \frac{1}{2}\log C$

Limitation of Ostwald Dilution Law :

It is not applicable for strong electrolytes.

Factors affecting the Value of Degree of ionisation :

(1) Temperature $\rightarrow$ On increasing temperature, ionization increases so α increases because dissociation is endothermic process.

(2) Dilution $\rightarrow \alpha \propto \sqrt{V}$ so on dilution, α increases.

(3) Nature of electrolytes

(i) Strong electrolytes

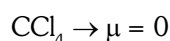
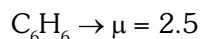
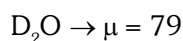
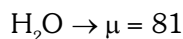
$$\alpha = 100\%$$

(ii) Weak electrolytes

$$\alpha < 100\%$$

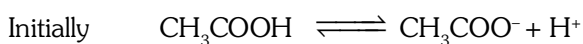
(4) Nature of solvent

If Dielectric constant μ of solvent increases then the value of α increases.

**Mixing of ions :**

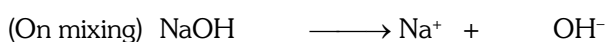
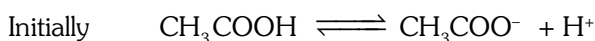
(a) Common ion effect	(b) Odd ion effect
When a strong electrolyte having a common ion, is mixed with weak electrolyte then the degree of ionisation (α) of weak electrolyte is decreased. This effect is called common ion effect.	When a strong electrolyte having a odd ion, is mixed with weak electrolyte then the degree of ionisation (α) of weak electrolyte is increased. This effect is called odd ion effect.

Common ion : On mixing CH_3COONa with CH_3COOH solution



(On mixing) $CH_3COONa \longrightarrow CH_3COO^- + Na^+$; $[CH_3COO^-]$ increases so $[H^+]$ decreases respectively.

Odd ion : On mixing, $NaOH$ with CH_3COOH solution



Due to odd ion effect $H^+ + OH^- \rightarrow \text{Water}$

Illustrations

Illustration 3 For which, dilution law is applicable :

- | | |
|---------------------------------------|--------------|
| (1) NaCl (SASB salt) | (2) HCl (SA) |
| (3) CH ₃ COONa (WASB salt) | (4) None |

Solution **Ans. (4)**

Illustration 4 Find out the value of α of 10^{-2} M HCN solution if $[H^+] = 10^{-3}$.

Solution $[H^+] = C\alpha$

$$10^{-3} = 10^{-2}\alpha \text{ or } \alpha = \frac{10^{-3}}{10^{-2}} = 10^{-1} \text{ or } \alpha = 0.1$$

$$\alpha = 10\%$$

Illustration 5 For 10 M CH₃COOH solution if $K_a = 10^{-5}$ then find out :

- | | | |
|--------------|--------------|----------|
| (i) α | (ii) $[H^+]$ | (iii) pH |
|--------------|--------------|----------|

Solution (i) α

$$(\text{Degree of ionisation}) :- K_a = C\alpha^2$$

$$10^{-5} = 10\alpha^2 \text{ or } \alpha^2 = \frac{10^{-5}}{10} = 10^{-6} \text{ or } \alpha = 10^{-3}$$

$$(ii) [H^+] = C\alpha = 10 \times 10^{-3} = 10^{-2}$$

$$(iii) \text{pH} = -\log [H^+] = -\log 10^{-2} = 2$$

Illustration 6 For 10^{-3} M H₂CO₃ if $\alpha = 10\%$ then find out the value of pH ?

Solution Normality = M $\times$ V.F. = $10^{-3} \times 2 = 2 \times 10^{-3}$

$$[H^+] = C\alpha = 2 \times 10^{-3} \times 0.1 = 2 \times 10^{-4}$$

$$\text{pH} = -\log [H^+] = -\log (2 \times 10^{-4}) = -\log 2 - \log 10^{-4} = -0.3010 + 4 = 3.7$$

Illustration 7 **Assertion :** NaCl + HCl does not experience common ion effect.

Reason : Both NaCl and HCl are strong electrolytes.

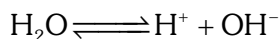
- | | | | |
|-------|-------|-------|-------|
| (1) A | (2) B | (3) C | (4) D |
|-------|-------|-------|-------|

Solution **Ans. (1)**

4.3 EXPLANATION OF WATER

- a. Nature of water is neutral. $[H^+] = [OH^-] [=10^{-7}\text{M (at } 25^\circ\text{C)}]$
i.e. at 25°C $\text{pH} = 7$ and $\text{pOH} = 7$
 $\therefore \text{pH} = \text{pOH}$
- b. No. of H₂O moles in 1 litre water = $\frac{1000}{18} = 55.5$ moles
- c. Molar concentration of H₂O = 55.5 mol L^{-1}
- d. Number of H₂O molecules in 1 litre water = $55.5 N_A$ (N_A = AVOGADRO'S NUMBER)
- e. Concentration of H⁺ and OH⁻ ions in 1 litre water
 $[H^+] = 10^{-7} \text{ mol L}^{-1}$ and $[OH^-] = 10^{-7} \text{ mol L}^{-1}$
- f. No. of H⁺ and OH⁻ ions in 1 litre water
No. of H⁺ ions = $10^{-7}N_A$ and No. of OH⁻ ions = $10^{-7}N_A$
- g. In water (Number of H₂O molecules : Number of H⁺ ions)
 $= 55.5 N_A : 10^{-7}N_A$
 $= 55.5 \times 10^7 : 1$
i.e. one H⁺ ion is obtained from $55.5 \times 10^7 \text{ H}_2\text{O}$ molecules

h. Degree of ionisation of water (α) :



According to Ostwald's dilution law

$$[\text{H}^+] = c \alpha$$

$$\alpha = \frac{10^{-7}}{55.5} = 1.8 \times 10^{-9}$$

$$\boxed{\alpha = 1.8 \times 10^{-7}\%}$$

Hence, water is a very weak electrolyte.

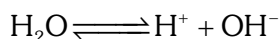
i. K (Ionisation constant of water) :



$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

$$K = \frac{10^{-7} \times 10^{-7}}{55.5} \quad \text{or} \quad \boxed{K = 1.8 \times 10^{-16}}$$

j. Ionic product of water K_w :



$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

$$K \times [\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$$

Since, dissociation takes place to a very small extent, $[\text{H}_2\text{O}]$ may be regarded as constant.

Thus, the product $K \cdot [\text{H}_2\text{O}]$ gives another constant which designated as K_w . So,

$$\boxed{K_w = [\text{H}^+][\text{OH}^-]}$$

$$\text{At } 25^\circ\text{C} - K_w = 10^{-7} \times 10^{-7} = 10^{-14}$$

$$K [\text{H}_2\text{O}] = K_w \Rightarrow \boxed{K_w > K} \quad (\text{always})$$

Various forms of K_w

(a) $K_w = [\text{H}^+][\text{OH}^-]$ for water $[\text{H}^+] = [\text{OH}^-]$

(b) $K_w = [\text{H}^+]^2$

(c) $K_w = [\text{OH}^-]^2$

(d) $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$

(e) $K_w = [\text{H}_3\text{O}^+]^2 \quad \{[\text{H}_3\text{O}^+] = [\text{H}^+]\}$
Hydronium ion Proton

• Relation in between pH and pOH :

$$K_w = [\text{H}^+][\text{OH}^-]$$

taking $-\log$ on both sides

$$-\log K_w = -\log [\text{H}^+] - \log [\text{OH}^-]$$

$$\boxed{\text{p}K_w = \text{pH} + \text{pOH}}$$

- Nature of water is neutral so,
[pH = pOH]

$$pK_w = pH + pOH$$

$$2pH = pK_w$$

$$pH = \frac{pK_w}{2}$$

$$pH = pOH = \frac{pK_w}{2}$$

$$pK_w = pOH + pOH$$

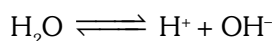
$$2 pOH = pK_w$$

$$pOH = \frac{pK_w}{2}$$

At 25°C, $K_w = 10^{-14}$ or $pK_w = 14$

$\therefore pH + pOH = 14$ or $pH = pOH = 7$

k. Effect of temperature :-



Ionization of water is endothermic process so, on increasing temperature α increases or $[H^+]$ and $[OH^-]$ increases or $[H^+][OH^-]$ increases i.e. K_w increases means pH decreases or pOH decreases.

$$T \uparrow = \alpha \uparrow = [H^+] [OH^-] \uparrow = K_w \uparrow \Rightarrow pK_w \downarrow$$

At 25°C, $K_w = 10^{-14}$

At 90°C, $K_w = 10^{-12}$

Parameters	At 25°C	At 90°C
K_w	10^{-14}	10^{-12}
pK_w	14	12
$pH = \frac{pK_w}{2} = pOH$	7	6
$[H^+] = [OH^-] = \sqrt{K_w}$	10^{-7}	10^{-6}
$pH + pOH = pK_w$	14	12

GOLDEN KEY POINTS

- On increasing temperature, both $[H^+]$ and $[OH^-]$ increases equally so water remains neutral but neutral pH changes from 7 to 6 at 90°C.

Illustrations

Illustration 8 Dissociation constant of water at 25°C is

$$(1) 10^{-14} \times (55.5)^{-1} \quad (2) 10^{-7} \times (18)^{-1} \quad (3) 10^{-14} \times (18)^{-1} \quad (4) 10^{-7} \times (55.4)^{-1}$$

Solution **Ans. (1)**

Illustration 9 What should be the number of H^+ ions in 1 mL of distilled water, if the number of H^+ ions in 1 L is 6.023×10^{16} ?

Solution Number of H^+ ions in 1 mL distilled water = $\frac{6.023 \times 10^{16}}{1000} = 6.023 \times 10^{13}$

BEGINNER'S BOX-1

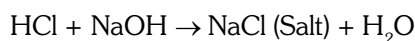
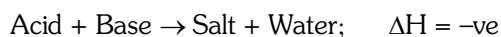
- The pH of a 0.005 M H_2SO_4 solution is—
(1) 3.3 (2) 5.0 (3) 2.0 (4) 4.0
- If pure water has $pK_w = 13.36$ at 50°C, the pH of pure water will be—
(1) 6.68 (2) 7.0 (3) 7.13 (4) 6.0

3. How many H^+ ions are present in 1 ml of a solution whose pH is 13 ?
 (1) 10^{-16} (2) 6.022×10^{13} (3) 6.022×10^7 (4) 6.022×10^{23}
4. The pH of solutions A, B, C and D are 9.5, 2.5, 3.5 and 5.5 respectively. The most acidic solution is—
 (1) D (2) C (3) A (4) B
5. Calculate the concentration of the formate ion present in 0.100 M formic acid ($HCOOH$) solution at equilibrium ($K_a = 1.7 \times 10^{-4}$).
 (1) 4.1×10^{-3} M (2) 3.1×10^{-3} M (3) 2.1×10^{-3} M (4) 5.1×10^{-3} M
6. Which of the following is the weakest acid ?
 (1) Phenol ($K_a = 1.3 \times 10^{-10}$) (2) Hydrocyanic acid ($K_a = 4.9 \times 10^{-10}$)
 (3) Acetic acid ($K_a = 1.8 \times 10^{-5}$) (4) Benzoic acid ($K_a = 6.5 \times 10^{-5}$)
7. The pH of 0.1 M monobasic acid is 4.50. The acidity constant (K_a) of the monobasic acid is—
 (1) 1.0×10^{-7} (2) 1.0×10^{-5} (3) 1.0×10^{-4} (4) 1.0×10^{-8}
8. Which of the following is the strongest base ?
 (1) $C_6H_5NH_2$ ($pK_b = 9.42$) (2) $C_6H_5NHCH_3$ ($pK_b = 9.15$)
 (3) $C_6H_5N(CH_3)_2$ ($pK_b = 8.94$) (4) $C_6H_5NHC_2H_5$ ($pK_b = 8.89$)
9. Value of dissociation constant of acetic acid is 10^{-6} , where as dissociation constant of formic acid is 10^{-5} . Which of the following will be the value of pK_a (acetic acid) - pK_a (formic acid)
 (1) 10 (2) +1 (3) 10^{-1} (4) -1
10. A solution has pOH equal to 13 at 298 K. The solution will be
 (1) highly acidic (2) highly basic (3) moderately basic (4) unpredictable
11. What would be $[H^+]$ of 0.006 M benzoic acid ($K = 6 \times 10^{-5}$)
 (1) 0.6×10^{-4} (2) 6×10^{-4} (3) 6×10^{-3} (4) 3.6×10^{-4}

4.4 SALTS, TYPES OF SALT AND CONJUGATE THEORY

(A) **SALT** : Salts are regarded as compounds made up of positive and negative ions. The positive part comes from a base while negative part from an acid. Salts are ionic compounds.

i.e. A compound formed by the combination of acid and base is known as salt.



(B) TYPES OF SALT

(a) **Normal/general salts** :- The salts formed by the loss of all possible protons. (replaceable hydrogen ions as H^+) are called normal salts. Such a salt does not contain either a replaceable hydrogen ion or a hydroxyl (OH^-) group.

Ex.: $NaCl$, $NaNO_3$, K_2SO_4 , $Ca_3(PO_4)_2$, Na_2HPO_3 , NaH_2PO_2 etc.

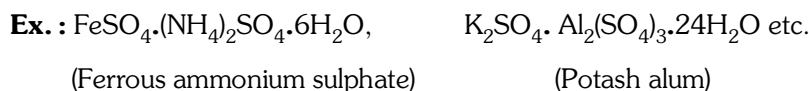
(b) **Acid salts** :- Salts formed by incomplete neutralisation of poly basic acids are called acid salts. Such salts still contain one or more replaceable hydrogen ions (H^+).

Ex.: $NaHCO_3$, $NaHSO_4$, NaH_2PO_4 , Na_2HPO_4 etc.

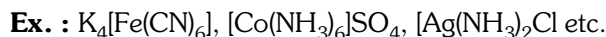
(c) **Basic salts** :- Salts are formed by incomplete neutralisation of poly acidic base are called basic salts. Such salts still contain one or more hydroxyl ion group.

Ex.: $Zn(OH)Cl$, $Mg(OH)Cl$, $Fe(OH)_2Cl$, $Bi(OH)_2Cl$ etc.

- (d) **Double salts** :- The addition compounds formed by the combination of two simple salts are termed double salts. Such salts are stable in solid state only i.e. when dissolved in water they break into simple ions.

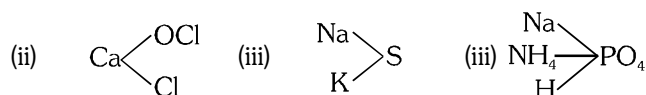
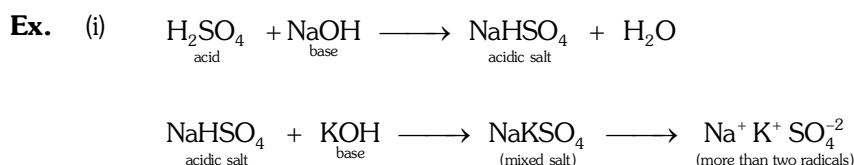


- (e) **Complex salts** :- These salts when dissolved in water give complex ions. Complex ions are stable in solid state as well as in solutions.



- (f) **Mixed salts** :- The salts which furnishes more than one type of cations or more than one type of anions when dissolved in water are called mixed salts.

These are formed by the neutralisation of more than one acids and bases.

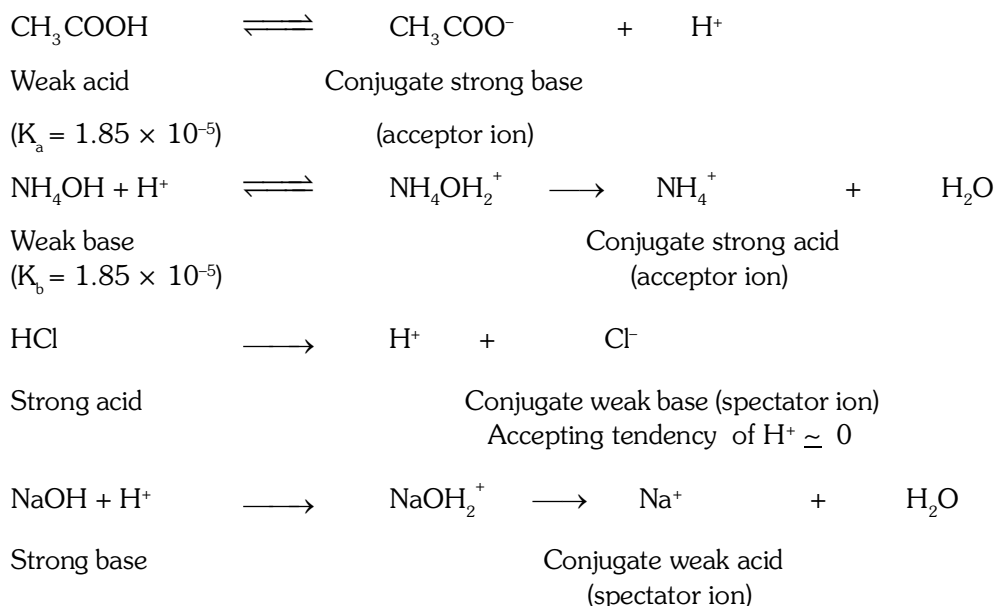


(a) Types of general salts :

- (i) SASB (ii) SAWB (iii) WASB (iv) WAWB

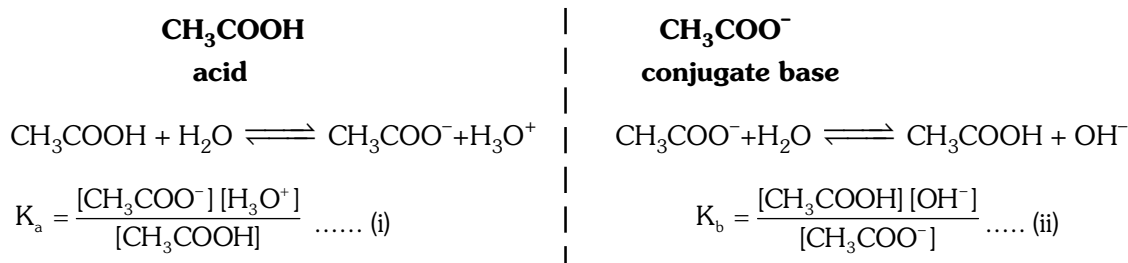
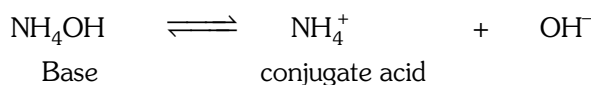
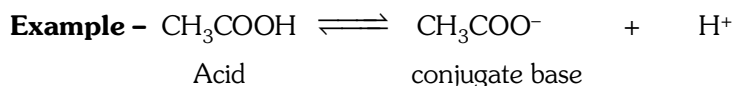
(C) Conjugate acid-base pair :

- (i) Conjugate acid-base pairs means difference between two species of only one H^+ ion.
(ii) When an acid loses a proton, the residual part of it has a tendency to regain a proton. Therefore it behaves as a base.



Note : Strong acids have weak conjugate bases while weak acids have strong conjugate bases. Similarly, strong bases have weak conjugate acids while weak bases have strong conjugate acids.

(D) Relation between conjugate acid-base pair :-



In both the reactions H_2O in excess quantity so active mass of H_2O is one.

Now multiply the equation (i) and (ii)

$$K_a \times K_b = [\text{H}^+][\text{OH}^-]$$

we know $[\text{H}^+] \times [\text{OH}^-] = K_w$ (Ionic product of water)

$$K_a \times K_b = K_w$$

Taking $-\log$ on both sides

$$pK_a + pK_b = pK_w$$

we know that for water at 25°C ,

$$K_w = 10^{-14} \text{ or } pK_w = 14$$

$$\text{So } K_a \times K_b = 10^{-14} \text{ or } pK_a + pK_b = 14$$

Above relation is applicable only for conjugate acid-base pairs.

Illustrations

Illustration 10 Which salt is not an example of acidic salt :-

(1) HCOONa

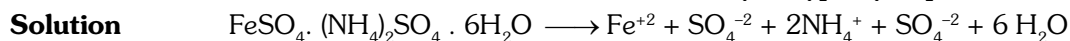
(2) NaH_2PO_2

(3) NaHS

(4) (1) and (2) both

Solution **Ans. (4)**

Illustration 11 Calculate the no. of ions in Mohr's salt $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$ or Ferrous Ammonium Sulphate



Total number of ions = 5

4.5. HYDROLYSIS OF SALTS

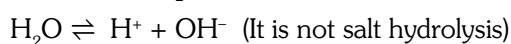
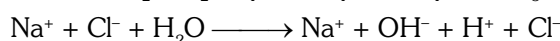
Salt hydrolysis is defined as the process in which water reacts with cation or anion or both of a salt to change the concentration of H^+ and OH^- ions of water.

Salt hydrolysis is reverse process of neutralization.



(A) Hydrolysis of strong acid and strong base [SA - SB] types of salt -

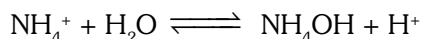
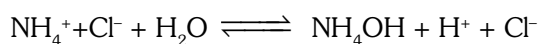
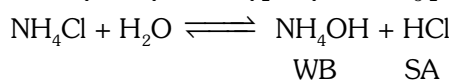
Ex. NaCl , BaCl_2 , Na_2SO_4 , KClO_4 , BaSO_4 , NaNO_3 , KBr , KCl etc.



- (i) Hydrolysis of salt of [SA - SB] is not possible as both cation and anion are not reactive.
- (ii) Aqueous solution of these type of salt is neutral in nature. ($\text{pH} = \text{pOH} = 7$)
- (iii) pH of the solution is 7.
- (iv) No effect on litmus paper.

(B) Hydrolysis of strong acid and weak base [SA - WB] types of salt -

Ex. $\text{CaSO}_4, \text{NH}_4\text{Cl}, (\text{NH}_4)_2\text{SO}_4, \text{Ca}(\text{NO}_3)_2, \text{ZnCl}_2, \text{CuCl}_2, \text{CaCl}_2, \text{AgCl}, \text{AgI}, \text{AgNO}_3$ etc



- (i) In this type of salt hydrolysis, cation reacts with H_2O therefore called as cationic hydrolysis. The cation of the salt which has come from weak base is reactive.
- (ii) Solution is acidic in nature as $[\text{H}^+]$ is increased.
- (iii) pH of the solution is less than 7.
- (iv) Solution turns blue litmus paper red.

K_h = Hydrolysis constant

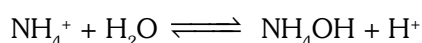
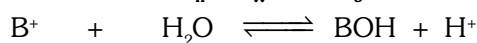
K_w = Ionic product of water

K_a = Ionisation constant of acid

K_b = Ionisation constant of base

h = Degree of hydrolysis

C = Concentration of salt (concentration of ions)

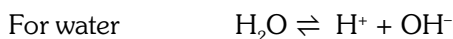
(a) Relation between K_h , K_w and K_b 

Hydrolysis constant $[K_h]$

$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \quad \dots\dots(1)$$



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \dots\dots(2)$$



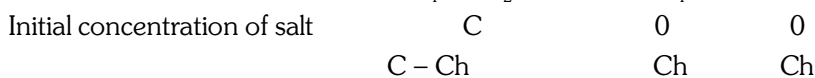
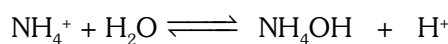
$$K_w = [\text{H}^+][\text{OH}^-] \quad \dots\dots(3)$$

Now multiplying Eq. (1) and (2) = Eq. (3)

$$\frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = [\text{H}^+][\text{OH}^-]$$

i.e. $K_h \times K_b = K_w$

$$K_h = \frac{K_w}{K_b} \quad \dots\dots(4)$$

(b) Degree of hydrolysis - Represented by h 

$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^2 h^2}{C(1 - h)} = \frac{Ch^2}{(1 - h)}$$

Since $h \ll 1$ then $(1 - h) \approx 1$

$$\therefore \boxed{K_h = Ch^2} \quad \dots\dots(5)$$

$$h^2 = \frac{K_h}{C} \quad \Rightarrow \quad h = \sqrt{\frac{K_h}{C}} \quad \dots\dots(6)$$

$$\therefore K_h = \frac{K_w}{K_b} \quad \Rightarrow \quad h = \sqrt{\frac{K_w}{K_b C}}$$

$$h = \sqrt{\frac{K_w}{K_b \times C}} \quad \dots\dots(7)$$

(c) pH of the solution : $\text{pH} = -\log [\text{H}^+]$

$$[\text{H}^+] = Ch = C \sqrt{\frac{K_w}{K_b \times C}} \quad \Rightarrow \quad [\text{H}^+] = \sqrt{\frac{K_w \times C}{K_b}} \quad \dots\dots(8)$$

taking $-\log$ on both sides

$$-\log [\text{H}^+] = -\log \sqrt{\frac{K_w \times C}{K_b}} \quad \Rightarrow \quad \text{pH} = -\log \left(\frac{K_w \times C}{K_b} \right)^{\frac{1}{2}}$$

$$\text{pH} = -\frac{1}{2} [\log K_w + \log C - \log K_b]$$

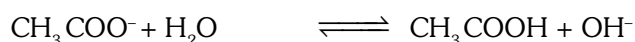
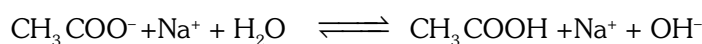
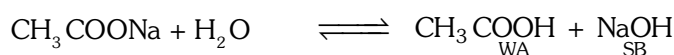
$$\text{pH} = -\frac{1}{2} \log K_w - \frac{1}{2} \log C - \frac{1}{2} (-\log K_b)$$

$$\text{pH} = \frac{1}{2} \text{p}K_w - \frac{1}{2} \log C - \frac{1}{2} \text{p}K_b$$

$$\boxed{\text{pH} = 7 - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log C} \quad \dots\dots(9)$$

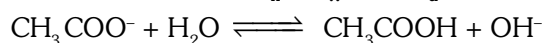
(C) Hydrolysis of weak acid and strong base [WA – SB] types of salt –

Ex. CH_3COONa , HCOONa , KCN , NaCN , K_2CO_3 , BaCO_3 , K_3PO_4 etc.



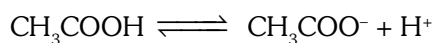
- (i) In this type of salt hydrolysis, anion reacts with water therefore called as anionic hydrolysis. The anion of the salt which has come from weak acid is reactive.
- (ii) Solution is basic in nature as $[\text{OH}^-]$ increases.
- (iii) pH of the solution is greater than 7.
- (iv) Solution turns red litmus paper blue.

(a) Relation between K_h , K_w and K_a



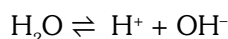
$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \quad \dots\dots(1)$$

For weak acid



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad \dots\dots(2)$$

For water



$$K_w = [\text{H}^+][\text{OH}^-] \quad \dots\dots\dots(3)$$

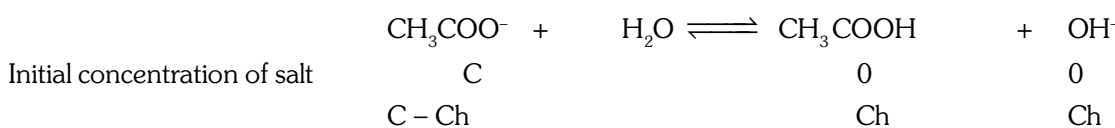
Now multiply eq. (1) $\times$ eq. (2) = eq. (3)

$$\frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \times \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = [\text{H}^+][\text{OH}^-]$$

$$K_h \times K_a = K_w$$

$$\boxed{K_h = \frac{K_w}{K_a}} \quad \dots\dots\dots(4)$$

(b) Degree of hydrolysis (h) :



$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^2 h^2}{C(1 - h)}$$

$$K_h = \frac{Ch^2}{(1 - h)}$$

Since $h \ll 1$ then $(1 - h) \approx 1$

$$\therefore \boxed{K_h = Ch^2} \quad \dots\dots\dots(5)$$

$$h^2 = \frac{K_h}{C} \quad \text{or} \quad h = \sqrt{\frac{K_h}{C}} \quad \dots\dots\dots(6)$$

$$\boxed{h = \sqrt{\frac{K_w}{K_a \times C}}} \quad \dots\dots\dots(7)$$

(c) pH of the solution

$$[\text{OH}^-] = Ch$$

$$[\text{OH}^-] = C \times \sqrt{\frac{K_w}{K_a \times C}} \quad \text{or} \quad [\text{OH}^-] = \sqrt{\frac{K_w \times C}{K_a}} \quad \dots\dots\dots(8)$$

taking $-\log$ on both sides

$$-\log [\text{OH}^-] = -\log \left(\frac{K_w \cdot C}{K_a} \right)^{1/2}$$

$$\text{pOH} = -\frac{1}{2} [\log K_w + \log C - \log K_a]$$

$$\text{pOH} = \frac{1}{2} \text{p}K_w - \frac{1}{2} \text{p}K_a - \frac{1}{2} \log C \quad \text{or} \quad \text{pOH} = 7 - \frac{1}{2} \text{p}K_a - \frac{1}{2} \log C$$

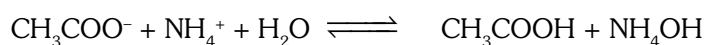
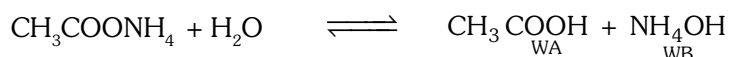
$$\therefore \text{pH} + \text{pOH} = 14$$

$$\text{pH} = 14 - \text{pOH}$$

$$\therefore \text{pH} = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C \quad \dots\dots\dots(9)$$

(D) Hydrolysis of weak acid and weak base (WA - WB) type of salt :

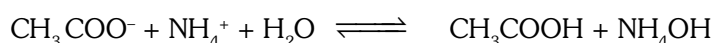
Ex. $\text{CH}_3\text{COONH}_4$, AgCN , NH_4CN , CaCO_3 , $[\text{NH}_4]_2\text{CO}_3$, ZnHPO_3 etc.



- (i) Maximum hydrolysis occurs of the salt of (WA – WB) as both the cation and anion are reactive.
- (ii) Solution is almost neutral but it may be acidic or basic depending upon the nature of acid base
- (iii) pH of the solution is near to 7.

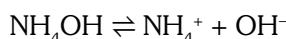
For WA - WB types of salt :

Terms	$K_a > K_b$	$K_b > K_a$	$K_a = K_b$
1. Hydrolysis	Cationic-anionic	Anionic-cationic	Neutral hydrolysis
2. Nature	Acidic	Basic	Neutral
3. pH	$\text{pH} < 7$	$\text{pH} > 7$	$\text{pH} = 7$

(a) Relation between K_h , K_w , K_a and K_b 

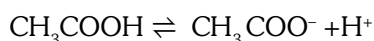
$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} \quad \text{.....(1)}$$

For weak base



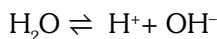
$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \text{.....(2)}$$

For weak acid



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad \text{.....(3)}$$

For water



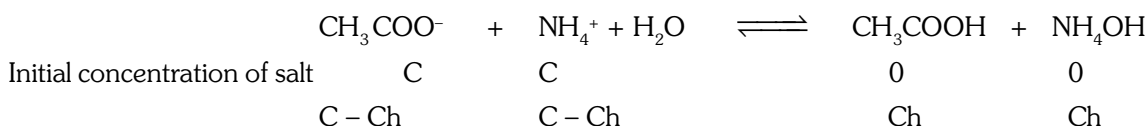
$$K_w = [\text{H}^+][\text{OH}^-] \quad \text{.....(4)}$$

Multiply Eq. (1) $\times$ Eq. (2) $\times$ Eq. (3) = Eq. (4)

$$\frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \times \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = [\text{H}^+][\text{OH}^-]$$

$$K_h \times K_b \times K_a = K_w$$

$$K_h = \frac{K_w}{K_a \times K_b} \quad \text{.....(5)}$$

(b) Degree of hydrolysis (h) –

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} = \frac{Ch \times Ch}{(C - Ch)(C - Ch)} = \frac{C^2 h^2}{C(1-h) \times C(1-h)}$$

Since $h \ll \ll \ll 1$ then $(1 - h) \approx 1$

$$\therefore \boxed{K_h = h^2} \quad \text{.....(6)}$$

$$\text{or } h^2 = \frac{K_w}{K_a \times K_b} \quad \text{or } \boxed{h = \sqrt{\frac{K_w}{K_a \times K_b}}} \quad \text{.....(7)}$$

(c) pH of the solution

from equation (3)

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$[\text{H}^+] = \frac{K_a \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{K_a \times Ch}{C - Ch} = \frac{K_a \times h}{1 - h}$$

Since $h \ll \ll \ll 1$ then $(1 - h) \approx 1$

$$[\text{H}^+] = K_a \times h \quad [\text{Now put the value of } h \text{ from eq. (5)}]$$

$$= K_a \times \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$\boxed{[\text{H}^+] = \sqrt{\frac{K_w \times K_a}{K_b}}} \quad \text{.....(8)}$$

$$\text{taking } -\log \text{ on both sides } -\log [\text{H}^+] = -\log \left(\frac{K_w \times K_a}{K_b} \right)^{\frac{1}{2}}$$

$$\text{pH} = -\frac{1}{2} [\log (K_w \times K_a) - \log K_b]$$

$$\text{pH} = -\frac{1}{2} [\log K_w + \log K_a - \log K_b]$$

$$\text{pH} = -\frac{1}{2} [\log K_w] - \frac{1}{2} [\log K_a] - \frac{1}{2} [-\log K_b]$$

$$\text{pH} = +\frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$$

$$\boxed{\text{pH} = 7 + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b} \quad \text{.....(9)}$$

GOLDEN KEY POINTS

- Degree of hydrolysis, pH of weak acid and weak base [WA – WB] type salts do not depend on the concentration of salt.

	SA SB salts	SA WB salts	WA SB salts	WA WB salts
1.	Neutral solution	Acidic solution	Basic solution	Almost neutral solution
2.	No hydrolysis	Cationic hydrolysis	Anionic hydrolysis	Hydrolysis by both cation and anion
3.	–	$K_h = \frac{K_w}{K_b}$	$K_h = \frac{K_w}{K_a}$	$K_h = \frac{K_w}{K_a \times K_b}$
4.	–	$h = \sqrt{\frac{K_w}{K_b \cdot C}}$	$h = \sqrt{\frac{K_w}{K_a \cdot C}}$	$h = \sqrt{\frac{K_w}{K_a \cdot K_b}}$
5.	–	$[H^+] = C \cdot h = \sqrt{\frac{K_w \cdot C}{K_b}}$	$[OH^-] = C \cdot h = \sqrt{\frac{K_w \cdot C}{K_a}}$	$[H^+] = K_a \cdot h = \sqrt{\frac{K_w \cdot K_a}{K_b}}$
6.	–	$pH = 7 - \frac{1}{2} pK_b - \frac{1}{2} \log C$	$pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C$	$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b$

Illustrations

Illustration 12 What is the pH of 1 M CH_3COONa solution? K_a of acetic acid = 1.8×10^{-5} , $K_w = 10^{-14} \text{ mol}^2 \text{ L}^{-2}$
 (1) 2.4 (2) 3.6 (3) 4.8 (4) 9.4

Solution **Ans. (4)**

Illustration 13 Calculate the degree of hydrolysis of a mixture containing 0.1N NH_4OH and 0.1N HCN
 If $K_a = 10^{-5}$ and $K_b = 10^{-5}$

Solution Salt is [WA – WB]

$$h = \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{10^{-14}}{10^{-5} \times 10^{-5}}} = \sqrt{10^{-14} \times 10^{+10}} = \sqrt{10^{-4}} = 10^{-2}$$

Illustration 14 **Assertion :** An aqueous solution of NH_4NO_3 is acidic in characters.

Reason : NH_4NO_3 in an aqueous solution undergoes anionic hydrolysis.

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

Solution **Ans. (3)**

BEGINNER'S BOX-2

- When sodium acetate (CH_3COONa) is added to aqueous solution of acetic acid (CH_3COOH), the–
 (1) the pH value becomes zero (2) pH value remains unchanged
 (3) pH value decreases (4) pH value increases
- Which of the following cations is not hydrolyzed in aqueous solution ?
 (i) Mg^{2+} (ii) Ca^{2+} (iii) Na^+ (iv) K^+
 (1) (i), (ii) (2) (iii), (iv) (3) (i), (ii), (iii), (iv) (4) (i), (ii), (iii)

3. Which of the anions is not hydrolysed in aqueous solution ?
 (i) Cl^- (ii) NO_3^- (iii) Br^- (iv) ClO_4^-
 (1) (i), (ii), (iii), (iv) (2) (ii), (iii), (iv) (3) (i), (ii), (iii) (4) (ii), (iv)
4. Which of the following salts does not undergo hydrolysis ?
 (1) KCN (2) KCl (3) NH_4NO_3 (4) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
5. Which of the following salts undergoes anionic hydrolysis ?
 (1) AlCl_3 (2) CuSO_4 (3) Na_2CO_3 (4) NH_4Cl
6. For cationic hydrolysis, pH is given by—
 (1) $\text{pH} = \frac{1}{2} \text{pK}_w + \frac{1}{2} \text{pK}_a + \frac{1}{2} \log C$ (2) $\text{pH} = \frac{1}{2} \text{pK}_w - \frac{1}{2} \text{pK}_b - \frac{1}{2} \log C$
 (3) $\text{pH} = \frac{1}{2} \text{pK}_w + \frac{1}{2} \text{pK}_a - \frac{1}{2} \text{pK}_b$ (4) $\text{pH} = \frac{1}{2} \text{pK}_w + \frac{1}{2} \text{pK}_b + \frac{1}{2} \log C$
7. Which of the following salts is neutral in water ?
 (1) KCl (2) NH_4NO_3 (3) NH_4CN (4) NH_4OH

4.6 SOLUBILITY AND SOLUBILITY PRODUCT (K_{sp})

(A) SOLUBILITY

- (a) Definition** At constant temperature the maximum number of moles of solute which can be dissolved in a solvent to obtain 1 litre of solution (i.e. saturated solution) is called solubility.

$$S(M) = \frac{\text{Number of moles of solute}}{\text{Volume of solution (L)}}$$

$$S = \frac{x}{M_w \times V_l} \text{ mol L}^{-1}$$

$$S_{g/\ell} = S_M \times \text{molar mass}$$

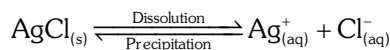
GOLDEN KEY POINTS

- Solubility does not depend on amount of substances and volume of solution where as depends on the following–
 - (i) Temperature
 - (ii) Presence of common ion
 - (iii) Nature of solvent (Molecular wt. of AgCl = 143.5)
(Molecular wt. of BaSO_4 = 233)
- Solubility can be expressed in terms of molarity.

(B) SOLUBILITY PRODUCT(K_{sp}) :

When a sparingly soluble salt such as AgCl is put into water, a very small amount of AgCl dissolves in water and most of the salt remains undissolved in its saturated solution.

- The salt AgCl is an electrolyte, its dissociation occurs in solution. Hence, the quantity of AgCl that dissolves in water dissociates into Ag^+ and Cl^- ions. Thus, in the saturated solution of AgCl an equilibrium exists between undissolved solid AgCl and its ions, Ag^+ and Cl^- ions.



according to law of mass action $K = \frac{[Ag^+].[Cl^-]}{[AgCl]}$

Since, the concentration of undissolved solid AgCl is constant. Thus, the product $K.[AgCl]$ gives another constant which is designated as K_{sp} .

$$\text{So, } K.[AgCl] = [Ag^+].[Cl^-] \quad \therefore \quad K_{sp} = [Ag^+] \cdot [Cl^-]$$

At constant temperature product of concentrations of ions in a saturated solution of substance is called solubility product of that substance. (Saturated solution is that solution in which solid solute and the ions in solution remain in equilibrium with each other.

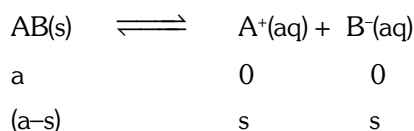
- **K_{sp} for $CaCl_2$** $CaCl_2(s) \rightleftharpoons Ca^{+2}(aq) + 2Cl^-(aq)$
Solubility product in terms of concentration of ions $K_{sp} = [Ca^{+2}] [Cl^-]^2$
- **K_{sp} for $AlCl_3$** $AlCl_3(s) \rightleftharpoons Al^{+3}(aq) + 3Cl^-(aq)$
Solubility product in terms of concentration of ions $K_{sp} = [Al^{+3}] [Cl^-]^3$
- **General form** $A_xB_y(s) \rightleftharpoons xA^{+y}(aq) + yB^{-x}(aq)$
 $K_{sp} = [A^{+y}]^x [B^{-x}]^y$

4.7 APPLICATION OF SOLUBILITY PRODUCT (K_{sp})

(A) To find out the solubility (S) :

(i) K_{sp} of AB (Mono-mono, di-di, tri-tri valency) type salt -

Ex. NaCl, $BaSO_4$, CH_3COONa , $CaCO_3$, NaCN, KCN, NH_4CN , NH_4Cl etc.

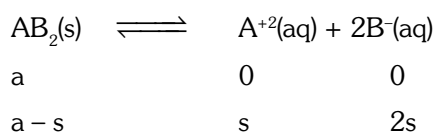


$$K_{sp} = [A^+] [B^-]$$

$$K_{sp} = s^2 \quad \text{or} \quad s = \sqrt{K_{sp}}$$

(ii) K_{sp} of AB_2 or A_2B (Mono-di or di-mono valency) type salt -

Ex. $CaCl_2$, $CaBr_2$, K_2S , $(NH_4)_2SO_4$, K_2SO_4 , K_2CO_3 etc.



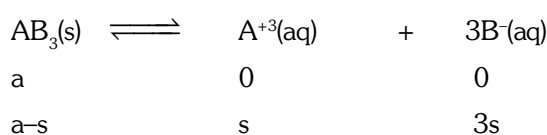
$$K_{sp} = [A^{+2}] [B^-]^2$$

$$K_{sp} = s \times (2s)^2 = s \times 4s^2 = 4s^3$$

$$s = \left(\frac{K_{sp}}{4} \right)^{\frac{1}{3}}$$

(iii) K_{sp} of AB_3 or A_3B (Mono-tri or tri-mono valency) type salt -

Ex. $FeCl_3$, $AlCl_3$, K_3PO_4 etc.

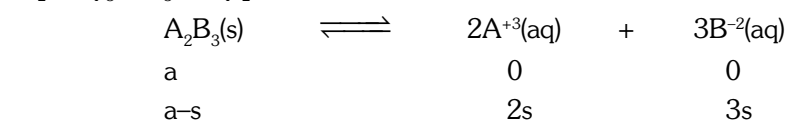


$$K_{sp} = [A^{+3}] [B^-]^3 = s \times (3s)^3 = 27s^4$$

$$s = \left(\frac{K_{sp}}{27} \right)^{\frac{1}{4}}$$

(iv) K_{sp} of A_2B_3 or A_3B_2 (Di-tri or tri-di valency) type salt

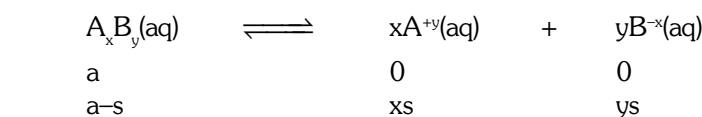
Ex. $Al_2(SO_4)_3$, $Ba_3(PO_4)_2$ etc.



$$K_{sp} = [A^{+3}]^2 [B^{-2}]^3 = 2s \times 2s \times 3s \times 3s \times 3s = 108s^5$$

$$s = \left(\frac{K_{sp}}{108} \right)^{1/5}$$

(v) General form :



$$K_{sp} = [A^{+y}]^x \cdot [B^{-x}]^y$$

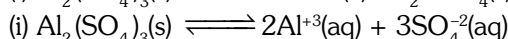
$$K_{sp} = (xs)^x \cdot (ys)^y \quad \boxed{K_{sp} = x^x \cdot y^y \cdot s^{(x+y)}}$$

Illustrations

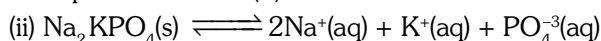
Illustration 15 What will be the solubility product of following in terms of solubility (mol L^{-1})

(i) $Al_2(SO_4)_3(s)$ (ii) $Na_2KPO_4(s)$ (iii) $NaKRbPO_4(s)$

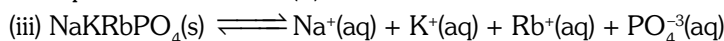
Solution



$$K_{sp} = 2^2 \times 3^3 \times (S)^{2+3} = 4 \times 27 \times S^5 = 108 S^5$$



$$K_{sp} = 2^2 \times 1^1 \times 1^1 (S)^{2+1+1} = 4S^4$$



$$K_{sp} = 1^1 \times 1^1 \times 1^1 \times 1^1 \times (S)^{1+1+1+1} = S^4$$

Illustration 16 If solubility product of the base $M(OH)_3$ is 2.7×10^{-11} , the concentration of OH^{-1} will be

(1) 3×10^{-3} (2) 3×10^{-4} (3) 10^{-3} (4) 10^{-11}

Solution

Ans. (1)

Illustration 17 **Assertion :** For a sparingly soluble salt, S is the maximum dissolved value of solute in a solution.

Reason : K_{sp} corresponds to the ionic product of the salt in a saturated solution.

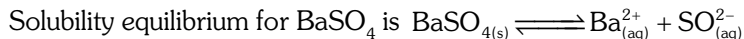
(1) A (2) B (3) C (4) D

Solution

Ans. (2)

Illustration 18 The solubility of $BaSO_4$ in water is $1.07 \times 10^{-5} \text{ mol dm}^{-3}$. Estimate its solubility product.

Solution



The solubility product is, $K_{sp} = [Ba^{2+}] [SO_4^{2-}]$

If S is the molar solubility of $BaSO_4$, then $K_{sp} = S^2$ because $x = 1 = y$.

Now, $S = 1.07 \times 10^{-5} \text{ M}$.

$$\text{Hence, } K_{sp} = (1.07 \times 10^{-5})^2 = 1.145 \times 10^{-10}$$

Illustration 19 The solubility product of $AgBr$ is 5.2×10^{-13} . Calculate its solubility in mol dm^{-3} and g dm^{-3} . (Molar mass of $AgBr$ = 187.8 g mol^{-1})

Solution



and $K_{sp} = [Ag^+] [Br^-] = S^2$ because $x = 1 = y$.

$$\text{The molar solubility } S \text{ of } AgBr \text{ is given by } S = \sqrt{K_{sp}} = \sqrt{5.2 \times 10^{-13}} = 7.2 \times 10^{-7} \text{ mol dm}^{-3}$$

The solubility in g dm^{-3} = molar solubility (mol dm^{-3}) $\times$ molar mass (g mol^{-1})

$$\text{Hence, solubility} = 7.2 \times 10^{-7} (\text{mol dm}^{-3}) \times 187.8 = 1.35 \times 10^{-4} \text{ g dm}^{-3}.$$

(B) Condition of precipitation /Ionic product (IP or Q_{sp}) :

- Ionic product (IP) of an electrolyte is defined in the same way as K_{sp} . The only difference is that ionic product expression contains the initial concentration of ions or the concentration at any time whereas the expression of K_{sp} contains only equilibrium concentration. Thus, for AgCl.
 $Q_{sp} = IP = [Ag^+]_i [Cl^-]_i$ and $K_{sp} = [Ag^+]_{eq} [Cl^-]_{eq}$
- Ionic product changes with concentration but K_{sp} does not. K_{sp} is applicable for saturated solution of the sparingly soluble electrolyte.
- To decide whether an ionic compound will precipitate, its K_{sp} is compared with the value of ionic product. The following three cases arise :
 - $Q_{sp} < K_{sp}$: The solution is unsaturated and precipitation will not occur.
 - $Q_{sp} = K_{sp}$: The solution is saturated and solubility equilibrium exists.
 - $Q_{sp} > K_{sp}$: The solution is supersaturated and hence precipitation of the compound will occur.

Thus, a salt is precipitated when its ionic product exceeds the solubility product of the salt.

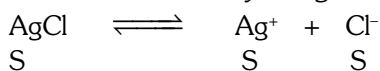
(C) Common ion effect on solubility :

Important point :- Solubility of substances always decreases in the presence of common ion. According to Le-Chatelier's principle on increasing common ion concentration equilibrium shifts in backward direction until the equilibrium is re-established so, the solubility of substances decreases but K_{sp} remains same because it is an equilibrium constant which depends only on temperature.

Illustrations

Illustration 20 Find out the solubility of AgCl in the presence of C molar NaCl solution ?

Solution.

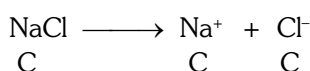


(Let solubility of AgCl is S mol L⁻¹)

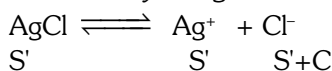
$$K_{sp} = [Ag^+] [Cl^-]$$

$$K_{sp} = S^2$$

In NaCl solution



Let solubility of AgCl in the presence of NaCl solution is S' mol L⁻¹.



According to L.M.A.

$$K_{sp} = [Ag^+] [Cl^-]$$

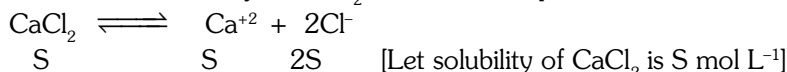
$$K_{sp} = S' (S' + C) = S'^2 + S'C \quad (\text{Neglecting the higher power terms of } S')$$

$$K_{sp} = S' C$$

$$S' = \frac{K_{sp}}{C}$$

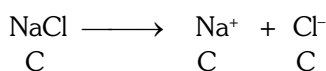
Illustration 21 Find out the solubility of CaCl₂ solution in the presence of C NaCl solution ?

Solution

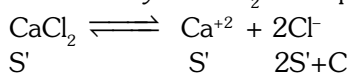


$$K_{sp} = [Ca^{+2}] [Cl^-]^2 = 4S^3$$

For NaCl solution



Let solubility of CaCl₂ in the presence of NaCl solution is S' mol L⁻¹.



According to L.M.A.

$$K_{sp} = [Ca^{+2}] [Cl^-]^2$$

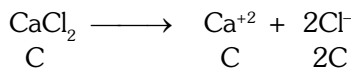
$$K_{sp} = S' (2S' + C)^2 = S' (4S'^2 + 4S'C + C^2)$$

$$K_{sp} = 4S'^3 + 4S'^2 C + S' C^2 \quad (\text{Neglecting the higher power terms of } S')$$

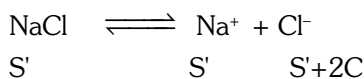
$$S' = \frac{K_{sp}}{C^2}$$

Illustration 22 Find out the solubility of NaCl in the presence of C CaCl₂ solution ?

Solution



Let solubility of NaCl in the presence of CaCl₂ solution is S' mol L⁻¹.



According to L.M.A.

$$K_{sp} = [\text{Na}^+] [\text{Cl}^-]$$

$$K_{sp} = \text{S}' (\text{S}' + 2\text{C}) = \text{S}'^2 + 2\text{S}'\text{C} \text{ (Neglecting the higher power terms of S')}$$

$$\boxed{\text{S}' = \frac{K_{sp}}{2\text{C}}}$$

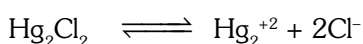
GOLDEN KEY POINTS

*● Group precipitation of Salt

Group	Radicals	Condition for precipitation (Group reagent)	Forms of precipitation
Zero	NH ₄ ⁺		
First	Pb ⁺² , Hg ⁺¹ , (Hg ₂ ⁺²), Ag ⁺	By mixing of dilute HCl	Chloride AgCl, Hg ₂ Cl ₂ , PbCl ₂
Second II(A)	Pb ⁺² , Cu ⁺² , Hg ⁺² , Cd ⁺² , Bi ⁺³	H ₂ S gas passed in	Sulphide
Second II(B)	As ⁺³ , Sb ⁺³ , Sn ⁺² , Sn ⁺⁴	the presence of acidic medium	PbS, HgS, CuS, CdS, SnS, SnS ₂ , As ₂ S ₃ , Sb ₂ S ₃ , Bi ₂ S ₃
Third	Al ⁺³ , Cr ⁺³ , Fe ⁺³	NH ₄ OH mixed in the presence of NH ₄ Cl	Hydroxide Al(OH) ₃ , Fe(OH) ₃ , Cr(OH) ₃
Fourth	Zn ⁺² , Ni ⁺² , Mn ⁺² , Co ⁺²	H ₂ S gas passed in presence of basic medium	Sulphide MnS, CoS, NiS, ZnS
Fifth	Ba ⁺² , Sr ⁺² , Ca ⁺²	(NH ₄) ₂ CO ₃ mixed in the presence of NH ₄ Cl	Corbonate BaCO ₃ , SrCO ₃ , CaCO ₃
Sixth	Na ⁺ , K ⁺ , Mg ⁺²	By mixing of Na ₂ HPO ₄	Hydrogen phosphate (MgHPO ₄)

● Hg⁺¹(us) → Unstable in aqueous solution.

[Stable in dimer form (Hg₂⁺²) ⇒ Hg₂Cl₂]



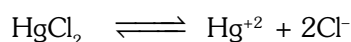
$$\text{S} \qquad \qquad \text{S} \qquad \qquad 2\text{S}$$

$$K_{sp} = [\text{Hg}_2^{+2}] [\text{Cl}^-]^2$$

$$= (\text{S}) (2\text{S})^2$$

$$\boxed{K_{sp} = 4\text{S}^3}$$

● Hg⁺²(ic) → HgCl₂ → stable in aqueous solution

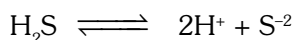


$$\text{S} \qquad \qquad \text{S} \qquad \qquad 2\text{S}$$

$$\boxed{K_{sp} = 4\text{S}^3}$$

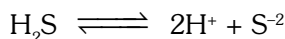
- For precipitation of II group, H_2S gas is passed in acidic medium to decrease S^{2-} concentration by common ion effect. So that ionic product of cations of group II and S^{2-} ions exceed the solubility product of their corresponding metal sulphides. Therefore only the cations of group II gets precipitated. But the sulphides of the cation of the other groups (III, IV & V) are not precipitated under these conditions because their solubility products are quite high.

When H_2S gas is directly passed through solution then IVth group is also precipitated with IInd group.



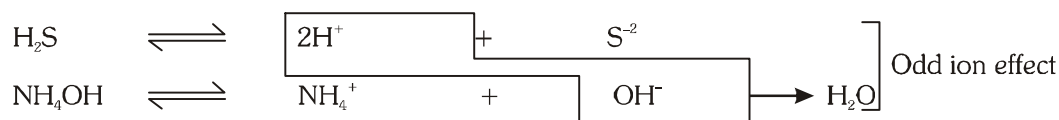
$$K_{sp_{II}} < K_{sp_{IV}} < [\text{radicals of II}^{\text{nd}} \text{ and IV group}] [\text{S}^{2-}]$$

When H_2S gas pass in acidic medium $[\text{H}^+]$ then only IInd group radicals are precipitated.



$$K_{sp_{II}} < [\text{radicals of II}^{\text{nd}} \text{ and IV group}] [\text{S}^{2-}] < K_{sp_{IV}}$$

- For precipitation of group III, NH_4OH is added in the presence of NH_4Cl to decrease the concentration of OH^- by common ion effect so that ionic product of cations of group III and hydroxides ions exceed the solubility product of their corresponding metal hydroxides and only group III cations will precipitated. On the other hand cations of group IV, V and VI, which require large concentration of OH^- due to their high solubility product, will not be precipitated.
- In IV group, H_2S gas is passed in basic medium to increase S^{2-} ion concentration by odd ion effect, so that the ionic product of cations of group IV and S^{2-} ions exceed the solubility product of their corresponding metal sulphide and hence gets precipitated.



So $[\text{S}^{2-}] \uparrow$

$$K_{sp_{IV}} < [\text{Radicals of group IV}] [\text{S}^{2-}]$$

(D) Precipitation of soap and salt (NaCl)

(i) Precipitation of NaCl (common salt) :

For the precipitation of NaCl, HCl gas passed in saturated solution of NaCl to increase the concentration of Cl^- ion by common ion, so ionic product of concentration of Na^+ and Cl^- ion becomes more than K_{sp} of NaCl and NaCl easily precipitated.



$$K_{sp} = [\text{Na}^+] [\text{Cl}^-]$$



due to common ion $K_{sp} < [\text{Na}^+] [\text{Cl}^-] \uparrow$

(ii) Precipitation of soap :

For precipitation of soap, NaCl mixed in saturated solution of soap to increase the concentration of Na^+ ion by common ion. So ionic product of concentration of Na^+ and stearate ions is more than K_{sp} of soap and soap is easily precipitated.

Ex. $\text{C}_{17}\text{H}_{35}\text{COONa}$ (Sodium stearate)



$$K_{sp} = [\text{C}_{17}\text{H}_{35}\text{COO}^-] [\text{Na}^+]$$



due to common ion $K_{sp} < [\text{C}_{17}\text{H}_{35}\text{COO}^-] [\text{Na}^+] \uparrow$

Illustrations

Illustration 23 Solubility products of $M(OH)_3$ and $M(OH)_2$ are 10^{-23} and 10^{-14} respectively. Which will be precipitated first on adding NH_4OH , if M^{+2} and M^{+3} both the ions are in solution ?

(1) M^{+2}

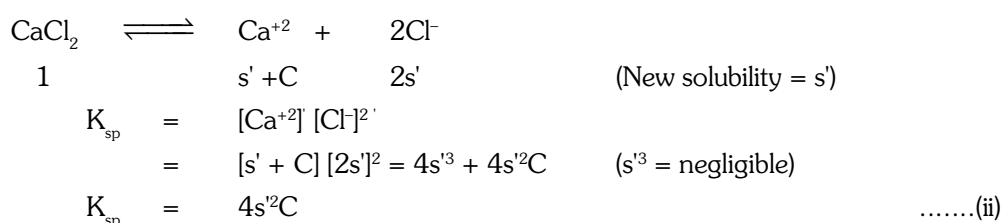
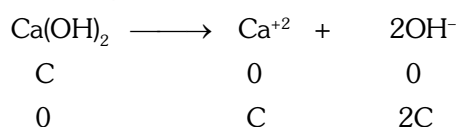
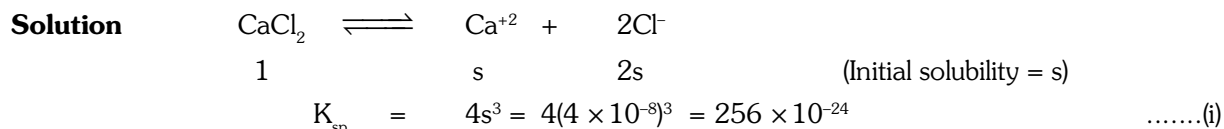
(2) M^{+3}

(3) Both M^{+2} and M^{+3} together

(4) Precipitation will not take place.

Solution **Ans. (2)**

Illustration 24 Solubility of $CaCl_2$ is 4×10^{-8} , then find out its K_{sp} and its new solubility in the presence of 10^{-2} M $Ca(OH)_2$.



$$\begin{aligned}
 \text{From equation (i) and (ii)} \quad s'^2 &= \frac{K_{sp}}{4C} = \frac{256 \times 10^{-24}}{4 \times 10^{-2}} = 64 \times 10^{-22} \\
 s' &= 8 \times 10^{-11} \text{ mol L}^{-1}
 \end{aligned}$$

4.8 FEW IMPORTANT POINTS

(A) Isohydric solution – If different-different solution has same pH are called isohydric solution.

Sp. point :- Isohydric conditions for two given weak acids HA_1 and HA_2 which has concentration C_1 and C_2 and ionisation constants are K_{a1} and K_{a2} respectively.

$$\text{Then } [H^+]_1 = \sqrt{K_{a1} C_1} \quad \text{and} \quad [H^+]_2 = \sqrt{K_{a2} C_2}$$

According to given condition for isohydric solution pH of different solution is same.

$$\text{Hence} \quad [H^+]_1 = [H^+]_2$$

$$\sqrt{K_{a1} C_1} = \sqrt{K_{a2} C_2}$$

$$\boxed{K_{a1} C_1 = K_{a2} C_2} \quad \text{or} \quad \text{If } n = 1 \text{ mole then} \quad \boxed{\frac{K_{a1}}{V_1} = \frac{K_{a2}}{V_2}} \quad \therefore \quad \boxed{C \propto \frac{1}{V}}$$

(B) Relative strength of Acids :- It indicates that how many times an acid is stronger than the other acid.

$$\text{We know} \quad \boxed{\text{Strength of acid} \propto [H^+]}$$

If there are two weak acids HA_1 and HA_2 which has concentration C_1 and C_2 , degree of ionisation α_1 and α_2 and ionisation constants K_{a1} and K_{a2} respectively then ratio of their strength of acids.

$$\text{We know} \quad [H^+] = C\alpha = \sqrt{K_a C}$$

$$\text{So} \quad \frac{\text{Strength of weak acid } HA_1}{\text{Strength of weak acid } HA_2} = \frac{[H^+]_1}{[H^+]_2} = \frac{C_1 \alpha_1}{C_2 \alpha_2} = \frac{\sqrt{K_{a1} C_1}}{\sqrt{K_{a2} C_2}}$$

If $C_1 = C_2$

$$\text{R.S.} = \frac{\text{Strength of weak acid HA}_1}{\text{Strength of weak acid HA}_2} = \sqrt{\frac{K_{a1}}{K_{a2}}} = \frac{\alpha_1}{\alpha_2}$$

Thus the relative strength of two acids of equimolar concentration can be compared by taking square root of the ratio of their ionisation constants.

Illustrations

Illustration 25 Which of the following solvents will undergo self-ionization ?

- (1) H_2O (2) NH_3 (3) HF (4) All of these

Solution **Ans. (4)**

Illustration 26 For two acids A and B, $\text{p}K_{a1} = 1.2$, $\text{p}K_{a2} = 2.8$ respectively in value, then which is true:-

- (1) A & B both are equally acidic
(2) A is stronger than B
(3) B is stronger than A
(4) None of these

Solution **Ans. (2)**

Illustration 27 pH values of two acids A and B are 4 and 5. The strengths of these two acids are related as :-

- (1) The strengths of the two acids cannot be compared.
(2) Acid B is 10 times stronger than acid A.
(3) Strength of acid A : Strength of acid B = 4 : 5
(4) Acid A is 10 times stronger than acid B.

Solution **Ans. (4)**

BEGINNER'S BOX-3

- The units of solubility product of silver chromate (Ag_2CrO_4) will be-
(1) $\text{mol}^2\text{L}^{-2}$ (2) $\text{mol}^3\text{L}^{-3}$ (3) mol L^{-1} (4) mol^{-1}L
- At a certain temperature, the solubility of the salt A_xB_y is S moles per liter. The general expression for its solubility product will be-
(1) $K_{sp} = x^y y^x S^{x+y}$ (2) $K_{sp} = (xy)^{x+y} S^{x+y}$ (3) $K_{sp} = (x^x y^y) S^{x+y}$ (4) $K_{sp} = x^x y^y S^{xy}$
- The molar solubility of silver sulphate is $1.5 \times 10^{-2} \text{ mol L}^{-1}$. The solubility product of the salt will be-
(1) 2.25×10^{-4} (2) 1.35×10^{-5} (3) 1.7×10^{-6} (4) 3.0×10^{-3}
- The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes of the following are mixed:
(1) $10^{-3} \text{ M Ca}^{2+} + 10^{-5} \text{ M F}^-$ (2) $10^{-5} \text{ M Ca}^{2+} + 10^{-3} \text{ M F}^-$
(3) $10^{-2} \text{ M Ca}^{2+} + 10^{-3} \text{ M F}^-$ (4) $10^{-4} \text{ M Ca}^{2+} + 10^{-4} \text{ M F}^-$
- If S_0 , S_1 , S_2 and S_3 are the solubilities of AgCl in water, 0.01 M CaCl_2 , 0.01 M NaCl and 0.5 M AgNO_3 solutions, respectively, then which of the following is true?
(1) $S_0 > S_2 > S_1 > S_3$ (2) $S_0 = S_2 = S_1 > S_3$
(3) $S_3 > S_1 > S_2 > S_0$ (4) $S_0 > S_2 > S_3 > S_1$
- Given $K_{sp}(\text{AgI}) = 8.5 \times 10^{-17}$. The solubility of AgI in 0.1 M KI solution is-
(1) 0.1 M (2) $8.5 \times 10^{-16} \text{ M}$
(3) $8.5 \times 10^{-17} \text{ M}$ (4) $8.5 \times 10^{-18} \text{ M}$

4.9 pH

1. INTRODUCTION

pH of some important substance :-

- | | | | |
|-------|---------------|---|------------|
| (i) | Blood | → | 7.4 |
| (ii) | Tear | → | 7.4 |
| (iii) | Gastric Juice | → | 1 to 3 |
| (iv) | Soft drink | → | 2 to 4 |
| (v) | Acidic rain | → | 6 |
| (vi) | Milk | → | 6.3 to 6.6 |
| (vii) | Water | → | 7 |

2. TYPES OF pH

- (i) pH of SA and SB. $[H^+] = C$, $[OH^-] = C$
- (ii) pH of WA and WB. $[H^+] = C\alpha$, $[OH^-] = C\alpha$
- (iii) pH of very dilute solution. (Consider H^+ & OH^- of H_2O also)
- (iv) pH of salt solution.
 - (a) SA SB Type Salt (always 7)
 - (b) SA WB Type Salt (< 7)
 - (c) WA SB Type Salt (> 7)
 - (d) WA WB Type Salt (Almost 7)

3. pH of mixture of acid and base.

- (a) pH of mixture of strong acids :
 $N_1V_1 + N_2V_2 + N_3V_3 + \dots = NV$
 $V = \text{Volume of final solution} = V_1 + V_2 + V_3 + \dots$
 $N = \text{Normality of final solution} = [H^+] \text{ in final solution.}$
- (b) pH of mixture of strong base :
 $N_1V_1 + N_2V_2 + N_3V_3 + \dots = NV$
 $V = \text{Volume of final solution} = V_1 + V_2 + V_3 + \dots$
 $N = \text{Normality of final solution} = [OH^-] \text{ in final solution.}$
- (c) pH of mixture of strong acids and strong bases :
For acid :
 $N_1V_1 + N_2V_2 + N_3V_3 + \dots = (NV)_{\text{Acid}}$
For base :
 $N_1V_1 + N_2V_2 + N_3V_3 + \dots = (NV)_{\text{Base}}$
 - (i) If $(NV)_{\text{Acid}} > (NV)_{\text{Base}}$ then solution is acidic.
 $NV = (NV)_{\text{Acid}} - (NV)_{\text{Base}}$ and
 $[H^+] = N$
 - (ii) If $(NV)_{\text{Base}} > (NV)_{\text{Acid}}$ then solution is basic.
 $NV = (NV)_{\text{Base}} - (NV)_{\text{Acid}}$ and
 $[OH^-] = N$
 - (iii) If, $(NV)_{\text{acid}} = (NV)_{\text{base}}$ then solution is neutral.
- (d) p^H of mixture of (WA + SB); when equivalent of WA $>$ SB]
pH of mixture of (SA + WB); When equivalent of WB $>$ SA]
 $\Downarrow$
gives rise to concept of buffer solution

4.10 BUFFER SOLUTION

- (A) **Definition** : A solution which resist the change in pH and pH does not change significantly on addition of small amount of strong acid or strong base is called buffer solution.
- (B) **Properties of buffer solution** :
- (i) The pH of buffer solution does not change appreciably upon the addition of small amount of either strong acid or strong base.
 - (ii) The pH of buffer solution does not depend on the volume of solution. Hence, solution can be diluted without change in pH.
 - (iii) The pH of buffer solution remains constant even if it is kept for a long time.
- (C) **Buffer solutions are used in**
- (a) Qualitative analysis of mixture
 - (b) Quantitative analysis of mixture
 - (c) Digestion of food
 - (d) Preservation of food and fruits.
 - (e) Agriculture and dairy product preservation.
 - (f) Industrial process such as manufacture of paper, dyes inks, paints, drugs etc.

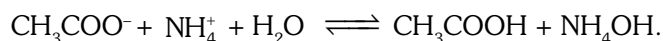
TYPES OF BUFFER SOLUTION

- (A). Simple buffer solution
- (B). Mixed buffer solution :- (i) Acidic buffer solution (ii) Basic buffer solution
- (A) **Simple buffer solution :-** Aqueous solution of weak acid-weak base (WA – WB) types of salt.

Ex. $\text{CH}_3\text{COONH}_4$, NH_4CN , AgCN etc.

$$\text{pH} = 7 + \frac{1}{2} \text{pK}_a - \frac{1}{2} \text{pK}_b$$

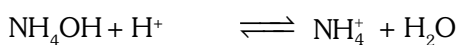
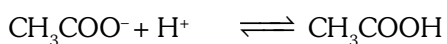
pH does not depend on concentration.



Buffer Action :

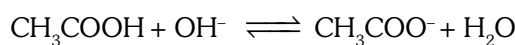
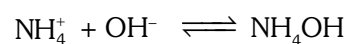
Case 1

When mixing of acid $[\text{H}^+]$



Case 2.

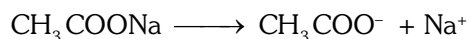
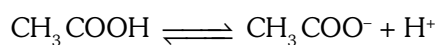
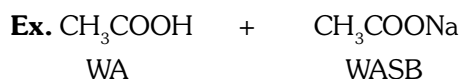
When mixing of base $[\text{OH}^-]$



(B) Mixed buffer solution :

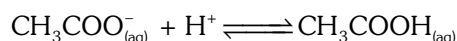
- (i) **Acidic buffer solution :-** The solution in which weak acid and its conjugate base are present.
OR

Aqueous solution of mixture of weak acid and salt of same weak acid with any strong base is called acidic buffer solution.

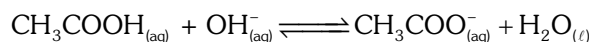


BUFFER ACTION :-

Case 1. If a small amount of acid is added to the buffer solution. The H^+ ions of the acid react with CH_3COO^- ions and produce CH_3COOH and most of the added H^+ ions are consumed so there is no appreciable change in pH.

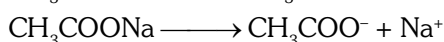
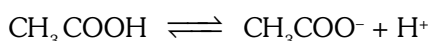
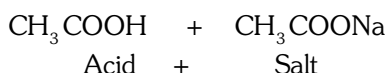


Case 2. If small amount of base is added to the buffer solution, the OH^- ions are consumed by CH_3COOH .



So, there is no appreciable change in pH.

(a) pH of acidic buffer solution :



$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$\text{or } [H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]} = \frac{K_a[\text{Acid}]}{[\text{Conjugate base}]}$$

taking $-\log$ on both sides

$$pH = pK_a - \log \frac{[\text{Acid}]}{[\text{Conjugate base}]} \quad \text{or} \quad pH = pK_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

Henderson's equation :

$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad \text{or} \quad \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

- $[\text{Conjugate base}]_{eq} \approx [\text{Salt}]$ because CH_3COO^- mainly comes from salt since dissociation of CH_3COOH in presence of CH_3COONa is appreciably decreased.
- $[\text{Acid}]_{aq} \approx$ initial concentration of acid since it is almost unionised in presence of salt due to common ion effect.

(b) pH range of acidic buffer solution : It depends on pK_a of acid and ratio of salt to acid concentrations.

$$[CH_3COOH] : [CH_3COONa] \Rightarrow pH = pK_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

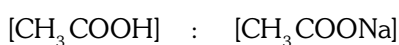
$$(i) \quad \text{If, } 1 : 10 \Rightarrow pH = pK_a + \log \frac{10}{1} = pK_a + 1$$

$$(ii) \quad \text{If, } 10 : 1 \Rightarrow pH = pK_a - 1$$

So pH range

$$pH = pK_a \pm 1$$

(c) Maximum buffer action condition of acidic buffer solution :



$$1 : 1 \Rightarrow pH = pK_a + \log \frac{1}{1}$$

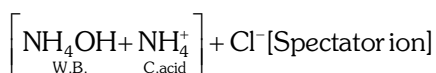
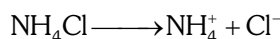
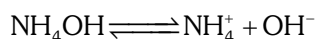
$$pH = pK_a$$

(ii) **Basic buffer solution :**

Definition : The solution in which weak base and its conjugate acid are present. OR

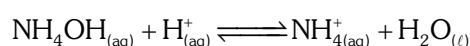
Aqueous solution of mixture of weak base and salt of same weak base with any strong acid is called basic buffer solution.

Ex. $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$



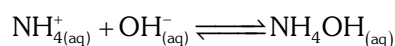
BUFFER ACTION :-

Case 1. If a small amount of the acid is added to the buffer solution, the H^+ ions are consumed by NH_4OH .



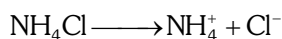
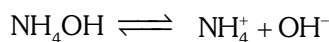
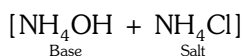
So there is no appreciable change in pH.

Case 2. If small amount of base is added to the buffer solution, the OH^- ions react with NH_4^+ ions to produce NH_4OH .



Hence most of the added OH^- ions are consumed. so there is no appreciable change in pH.

(a) **pOH of basic buffer solution :**



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \text{or} \quad [\text{OH}^-] = \frac{K_b [\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$$

taking $-\log$ on both sides $\text{pOH} = \text{p}K_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$

Henderson's equation :

$$\boxed{\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \text{ or } \frac{[\text{Conjugate acid}]}{[\text{Base}]}}$$

(b) **pOH range of basic buffer solution :** It depends on $\text{p}K_b$ of base and ratio of salt to base concentrations.

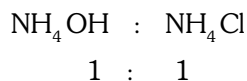
$$[\text{NH}_4\text{OH}] : [\text{NH}_4\text{Cl}] \Rightarrow \text{pOH} = \text{p}K_b + \log \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_4\text{OH}]}$$

(i) If, 1 : 10 $\Rightarrow \text{pOH} = \text{p}K_b + 1$

(ii) If, 10 : 1 $\Rightarrow \text{pOH} = \text{p}K_b - 1$

So, pOH range : $\boxed{\text{pOH} = \text{p}K_b \pm 1}$

(c) Maximum buffer action condition of basic buffer solution :



$$\boxed{\text{pOH} = \text{pK}_b}$$

3. BUFFER CAPACITY

Definition :-

- (i) It is defined as the number of moles of strong acid (or strong base) added to one litre of a buffer solution to change its pH by one unit.
- (ii) It measures the effectiveness of a buffer.
- (iii) Larger the value of buffer capacity more resistant is the solution to pH change.

$$\text{Buffer capacity} = \frac{\text{Number of moles of acid or base added per litre}}{\text{Change in pH of buffer solution}}$$

Illustrations

Illustration 28 When 2 moles of HCl is added to 1 L. of an acidic buffer solution, its pH changes from 3.9 to 3.4. Find its buffer capacity.

Solution $\text{B.C.} = \frac{2}{0.5} = 4$

BEGINNER'S BOX-4

1. A buffer solution is one which has—
(1) reserved acid (2) reserved base (3) constant pH (4) pH equal to 7
2. Which of the following solutions cannot act as a buffer system ?
(1) $\text{KH}_2\text{PO}_4/\text{H}_3\text{PO}_4$ (2) $\text{NaClO}_4/\text{HClO}_4$ (3) $\text{C}_5\text{H}_5\text{N}/\text{C}_5\text{H}_5\text{N}^+\text{HCl}^-$ (4) $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$
3. A buffer solution can not be prepared by mixing equimolar amounts of—
(1) B(OH)_3 and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (2) NH_3 and NH_4Cl
(3) HCl and NaCl (4) CH_3COOH and CH_3COONa
4. Which of the following salt solution will act as a buffer ?
(1) $\text{CH}_3\text{COONH}_4$ (aq.) (2) NH_4Cl (aq.) (3) CH_3COONa (aq.) (4) NaCl (aq.)
5. Which of the following combinations will make a buffer solutions ?
(i) CH_3COONa (2 mol) + HCl (1 mol) (ii) CH_3COOH (2 mol) + NaOH (1 mol)
(iii) CH_3COOH (1 mol) + CH_3COONa (1 mol)
(1) (iii) (2) (i), (ii) (3) (ii), (iii) (4) (i), (ii), (iii)
6. The pH of blood circulating in a human body is maintained around 7.4 by the action of the buffer system—
(1) $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ (2) $\text{NH}_4\text{Cl}/\text{NH}_3$
(3) $\text{H}_2\text{PO}_4^{2-}$ (4) $\text{H}_2\text{CO}_3/\text{HCO}_3^-$

4.11 INDICATOR

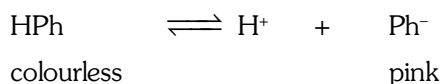
(A) **Definition :-** An indicator is a substance that undergoes change in its colour to show end point of an acid-base titration.

- Titration involves neutralization of an acid and base.

(B) **Types of indicators :**

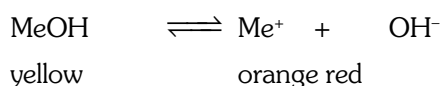
(a) **Acidic indicator (HIn)**

Ex. Phenolphthalein (HPh)



(b) **Basic indicator (InOH)**

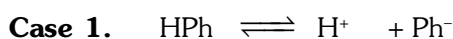
Ex. Methyl orange (MeOH)



OSTWALD THEORY OF INDICATORS

- According to this theory, all the indicators are weak organic acid or base.
- Every indicator has light colour in its unionised form and dark colour in ionised form.
- Every indicator has one colour in acidic medium and an altogether different colour in basic medium due to common ion effect and odd ion effect.

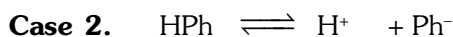
Ex. Acidic indicator [HPh]



In acidic medium $[\text{H}^+]$

$$[\text{HPh}] > [\text{Ph}^-]$$

Colourless due to common ion effect.

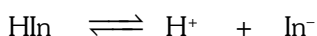


In basic medium $[\text{OH}^-]$

$$[\text{Ph}^-] > [\text{HPh}]$$

Pink colour due to odd ion effect.

(a) **pH of acidic indicator -**



$$K_a \text{ or } K_i = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

$$[\text{H}^+] = \frac{K_i [\text{HIn}]}{[\text{In}^-]}$$

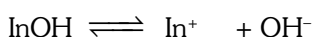
Taking - log on both sides

$$\text{pH} = \text{p}K_i - \log [\text{HIn}] + \log [\text{In}^-]$$

$$\text{pH} = \text{p}K_i + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

$$\text{pH} = \text{p}K_i + \log \frac{[\text{Ionised form}]}{[\text{Unionised form}]}$$

(b) **pOH of basic indicator -**



$$K_b \text{ or } K_i = \frac{[\text{In}^+][\text{OH}^-]}{[\text{InOH}]}$$

$$\text{pOH} = \text{p}K_i + \log \frac{[\text{Ionised form}]}{[\text{Unionised form}]}$$

(c) pH range of indicators :

Indicators show colour change for a certain pH range not at a definite pH which is called pH range of indicator.

(i) pH range of acidic indicator :

$$\begin{array}{ccc} [\text{HIn}] & : & [\text{In}^-] \\ 1 & : & 10 \\ 10 & : & 1 \end{array} \quad \boxed{\text{pH} = \text{pK}_1 \pm 1}$$

(ii) pOH range of basic indicator :

$$\begin{array}{ccc} [\text{InOH}] & : & [\text{In}^+] \\ 1 & : & 10 \\ 10 & : & 1 \end{array} \quad \boxed{\text{pOH} = \text{pK}_1 \pm 1}$$

(iii) Neutral condition for indicators (No working condition)

For acidic indicator

$$\begin{array}{ccc} [\text{HIn}] & : & [\text{In}^-] \\ 1 & : & 1 \end{array}$$

$$\boxed{\text{pH} = \text{pK}_1}$$

For basic indicators

$$\begin{array}{ccc} [\text{InOH}] & : & [\text{In}^+] \\ 1 & : & 1 \end{array}$$

$$\boxed{\text{pOH} = \text{pK}_1}$$

S.No.	Name of indicator	Colour in acidic medium	Colour in basic medium	Working pH range of indicators
1.	Methyl orange (MeOH)	Orange red	Yellow	3.1 to 4.5
2.	Methyl red	Red	Yellow	4.2 to 6.2
3.	Phenol red	Yellow	Red	6.2 to 8.2
4.	Phenolphthalein (HPh)	Colourless	Pink	8.2 to 10.2

3. ACID-BASE TITRATION

S.No.	Type of titration	pH range of titration	Suitable indicators
1.	SA/SB.	3 – 11	All indicators (MeOH, HPh etc.)
2.	SA/WB	3 – 7	Methyl orange (MeOH) and methyl red
3.	WA/SB	7 – 11	Phenolphthalein (HPh)

Important points of titration :

- Titration is always possible in two opposite solution. (i.e. one is acidic and other is basic).
- For any titration only that indicator is suitable if their working pH range is in pH range of titration.
- At the end point of titration equivalents of acids and bases are always same.
- At the equivalence point, nature of solution depends on the type of titration.

SA/SB	-	Neutral (pH = 7)
SA/WB	-	Acidic
WA/SB	-	Basic
WA/WB	-	Any one possible

4.12 ACID AND BASE

(1) INTRODUCTION

The earliest classification of substances into acids and bases was based upon the characteristic properties possessed by each one of them. For example,

Acid was defined as a substance whose aqueous solution possesses the following characteristic properties:

- (i) conducts electricity,
- (ii) reacts with active metals like zinc, magnesium etc. to give hydrogen,
- (iii) turns blue litmus red.
- (iv) has a sour taste.
- (v) whose acidic properties disappear on reaction with a base.

Base was defined as a substance whose aqueous solution possessed the following characteristic properties:

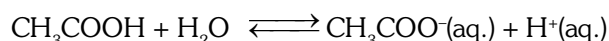
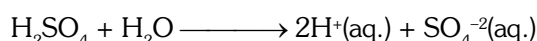
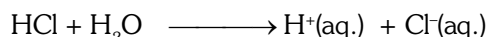
- (i) conducts electricity,
- (ii) reacts with active metals like zinc, magnesium etc. to give hydrogen,
- (iii) turns red litmus blue,
- (iv) has a bitter taste
- (v) whose basic properties are destroyed on reaction with an acid.

The above definitions of acids and bases are called operational definitions as they are based on certain operations (i.e. tests) to be performed on the substances. However, these have been replaced by conceptual definitions (put forward by Arrhenius, Bronsted-Lowry and Lewis) which go into the causes of the observed behavior, based upon structure and composition of the substances.

(2) Arrhenius Concept (1884)

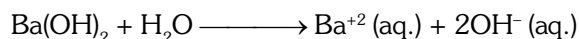
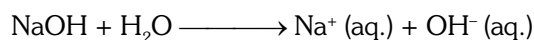
- (a) **Acid:-** According to this concept, those substances which produce free H^+ ions in aqueous solution are called acid.

Example $HCl, HNO_3, H_2SO_4, H_3PO_4, H_2CO_3, H_2S, CH_3COOH$ etc.



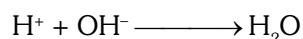
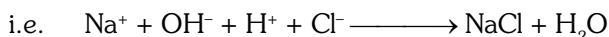
- (b) **Base :-** Those substances which produce free OH^- ions in aqueous solution are called base.

Example $NaOH, KOH, Cs(OH), Rb(OH), NH_4OH, Ba(OH)_2, Ca(OH)_2, Al(OH)_3$ etc.



- (c) **Nature of water :-** According to this concept nature of water is neutral and act as a solvent.

- (d) **Neutralisation Reaction :-** Those reactions in which acid and base react together to form water molecule are called neutralisation reactions.



- (e) **Strength of acids and bases :-** This concept explains the strength of acids and bases depending upon the basis of degree of ionisation.

Example For strong electrolytes $\alpha \simeq 100\%$

For weak electrolytes $\alpha < 100\%$

- (f) **Advantage :-** This concept explains the acids and bases practically. i.e. To find out the pH, ionisation constant, hydrolysis constants, heat of neutralisation etc.

(g) Disadvantage :-

It explains the behaviour of acids and bases only in aqueous (water) solvents.

Illustrations

Illustration 29 Gaseous hydrogen chloride is a very poor conductor of electricity but a solution of hydrogen chloride in water is a good conductor. This is due to the fact that :-

- (1) Water is a good conductor of electricity
- (2) Hydrogen chloride ionises in water
- (3) A gas cannot conduct electricity but a liquid can
- (4) HCl does not obey Ohm's law whereas the solution does

Solution (2)

Illustration 30 Which is acid in the following pairs according to Arrhenius concept ?

- (1) HCl(g) and HCl(aq) (2) $\text{CH}_3\text{COOH(l)}$ and $\text{CH}_3\text{COOH(aq)}$

Solution (1) HCl(aq.) (2) $\text{CH}_3\text{COOH(aq.)}$

(3) Bronsted-Lowry Concept (1923)

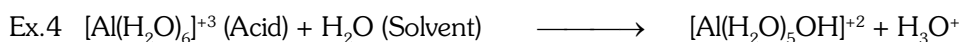
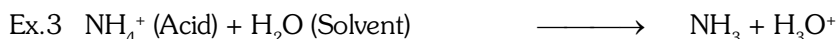
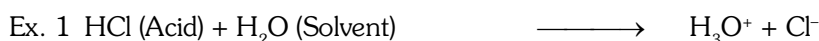
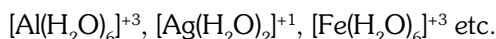
It is based upon the exchange of proton.

(a) Acid :- According to this concept those substances which have tendency to donate the proton (H^+) by any method in any solvent are called acids.

Example (i) Neutral molecules - HCl , HNO_3 , H_2SO_4 , H_2CO_3 , H_2S , CH_3COOH , H_3PO_3 etc.

(ii) Anions - HS^- , HCO_3^- , HSO_4^- , H_2PO_4^- , HPO_4^{2-} , H_2O etc.

(iii) Cations - NH_4^+ , H_3O^+ , PH_4^+ , $\text{CH}_3\text{COOH}_2^+$ etc.



(b) Base :- Those substances which have tendency to accept the proton by any method in any solvent are called the bases.

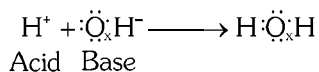
- (1) HS^- , HCO_3^- , HSO_4^- , H_2PO_4^- , HPO_4^{2-} , O^{2-} , SO_4^{2-} , CO_3^{2-} , Cl^- , Br^- , I^- , CN^- etc.
- (2) NH_3 , RNH_2 , R_2NH , R_3N , $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_5\text{H}_5\text{N}$, $\text{H}_2\text{N-NH}_2$ etc.

Example

- $$\begin{array}{lll} \text{(i)} & \text{HS}^- \text{ (Base)} + \text{H}_2\text{O (Solvent)} & \longrightarrow \text{H}_2\text{S} + \text{OH}^- \\ \text{(ii)} & \text{NH}_3 \text{ (Base)} + \text{H}_2\text{O (Solvent)} & \longrightarrow \text{NH}_4^+ + \text{OH}^- \\ \text{(iii)} & \text{CO}_3^{2-} \text{ (Base)} + \text{H}_2\text{O (Solvent)} & \longrightarrow \text{HCO}_3^- + \text{OH}^- \end{array}$$

(4) Lewis Concept (1939)

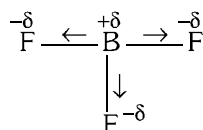
- (a) **Lewis Acid :-** According to this concept those species which have self tendency to accept the lone pair of electrons are called acids. i.e. Lewis acid is an electron pair acceptor (electrophilic).



Classification of Lewis Acids :-

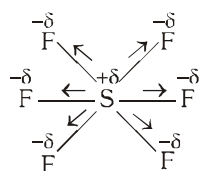
- (i) Compounds whose central atom have an incomplete octet (electron deficient)

Example BF_3 , BBr_3 , BCl_3 , BI_3 , $\text{B}(\text{CH}_3)_3$, $\text{B}(\text{OH})_3$, AlCl_3 , GeCl_3 etc.

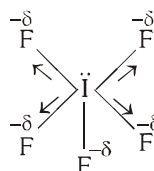


- (ii) Compounds whose central atom have vacant d-orbitals and can accept one or more pair of lone electrons.

Example SF_4 , SF_6 , SnCl_2 , SnCl_4 , PX_3 , PX_5 , GeX_4 , TeX_4 , IF_5 , IF_7 , etc.



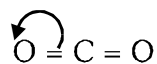
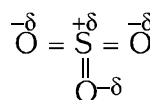
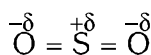
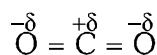
SF_6



IF_5

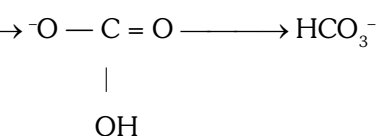
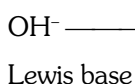
- (iii) Molecules with a multiple bond between atoms of different electronegativities.

Example CO_2 , SO_2 , SO_3 etc.



Lewis acid

+



Lewis acid

+



Lewis base

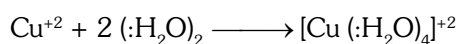


- (iv) **Cations :-**

Example Ag^+ , Na^+ , Li^+ , Al^{+3} , Be^{+2} , Mg^{+2} , I^+ , Cl^+ , H^+ etc.

False cations :- Example NH_4^+ , H_3O^+ , $\text{CH}_3\text{COOH}_2^+$, PH_4^+ etc.

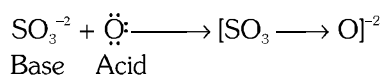
Example $\text{Ag}^+ + 2 : \text{NH}_3 \rightleftharpoons [\text{Ag} (: \text{NH}_3)_2]^+$



- (v) Elements which have six electrons in their outermost shell or valence shell.

O-Family (O, S, Se, Te)

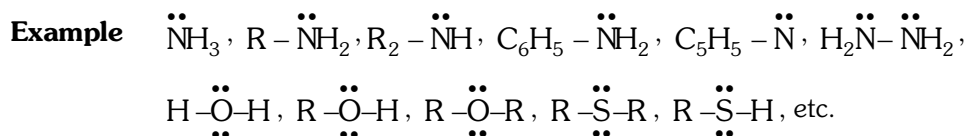
Po – Radioactive element



(b) Lewis Base :- Those species which have self tendency to donate the lone pair of electrons are called bases. i.e. a base is an electron pair (lone pair) donor (nucleophile).

Classification of Lewis Bases

(i) Those species whose central atom have lone pair of electrons and have self tendency to donate them –



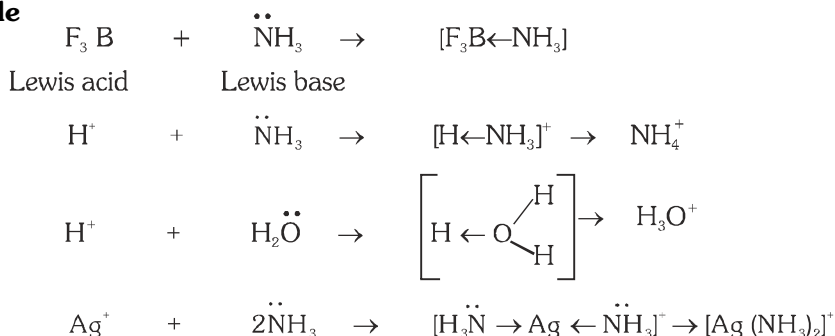
(ii) **Anions –**



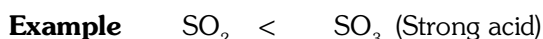
(c) Nature of water :- According to this concept nature of water is basic i.e. water is a base.

(d) Neutralisation Reaction :- According to this concept those reactions in which acid and base react together to form a co-ordinate bond between them are called neutralisation reactions.

Example



(e) Strength of acids and bases :- This concept explain the strength of acids and bases depending upon the basis of self tendency. To accept or donate the lone pair of electrons (e^-).

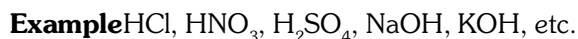


(f) Advantage :-

- This concept explains the acid and base without any solvent.
- This concept explains those acids and bases which are not explained by other concepts.

(g) Disadvantage :-

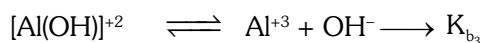
- This concept fails to explain the acid and base practically.
- According to this concept forming of co-ordinate bond in neutralisation reaction of acid and base is a slow process, whereas neutralisation reaction of acids and bases is actually fast process.
- This concept fails to explain the real acids and bases



- All the lewis bases are bronsted bases but all the lewis acids are not bronsted acids.
- All Arrhenius acids are Bronsted acids but it is not so for bases.

(6) POLYACIDIC BASE AND POLYBASIC ACIDS

(a) Polyacidic Base



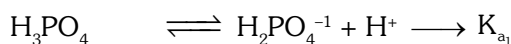
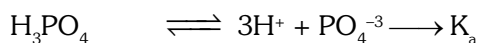
$$K_b = K_{b_1} \times K_{b_2} \times K_{b_3}$$

taking $-\log$ on both sides

$$\text{p}K_b = \text{p}K_{b_1} + \text{p}K_{b_2} + \text{p}K_{b_3}$$

$$\text{i.e. } \boxed{K_{b_1} > K_{b_2} > K_{b_3}} \Rightarrow \boxed{\text{p}K_{b_1} < \text{p}K_{b_2} < \text{p}K_{b_3}}$$

(b) Polybasic Acid



$$K_a = K_{a_1} \times K_{a_2} \times K_{a_3}$$

taking $-\log$ on both sides

$$\text{p}K_a = \text{p}K_{a_1} + \text{p}K_{a_2} + \text{p}K_{a_3}$$

$$\boxed{K_{a_1} > K_{a_2} > K_{a_3}} \Rightarrow \boxed{\text{p}K_{a_1} < \text{p}K_{a_2} < \text{p}K_{a_3}}$$

Illustrations

Illustration 33 In the dissociation, $\text{H}_2\text{A} \xrightleftharpoons{K_1} \text{H}^+ + \text{HA}^-$; $\text{HA}^- \xrightleftharpoons{K_2} \text{H}^+ + \text{A}^{2-}$

(1) K_1 is equal to K_2

(2) K_1 is smaller than K_2

(3) K_1 is greater than K_2

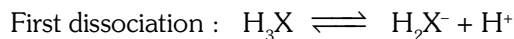
(4) K_1 is negligible

Solution.

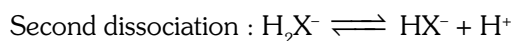
Ans. (3)

Illustration 34 Calculate the pH of 2.0×10^{-4} M H_3X Solution assuming first dissociation to be 100%, second to be 50% and third to be negligible :

Solution.



$$\therefore \text{H}^+ \text{ ion concentration} = 2 \times 10^{-4} \text{ M}$$



$$\text{H}^+ \text{ ion concentration} = C\alpha = 2 \times 10^{-4} \times 0.5$$

$\therefore$ Third dissociation is negligible

$$\therefore [\text{H}^+] = 2 \times 10^{-4} + 10^{-4} = 3 \times 10^{-4}$$

$$\text{pH} = 4 - \log 3 = 3.52$$

BEGINNER'S BOX-5

- Which of the following is a Bronsted acid ?
 (i) HCN (ii) H_2PO_4^- (iii) NH_4^+ (iv) HCl
 (1) (i), (iii) (2) (i), (ii), (iii), (iv) (3) (ii), (iii) (4) (i), (iii), (iv)
- Which of the following is a Bronsted base ?
 (i) NH_3 (ii) CH_3NH_2 (iii) HCO_3^- (iv) SO_4^{2-}
 (1) (i), (ii), (iii), (iv) (2) (i), (ii) (3) (i), (ii), (iii) (4) (i), (iii), (iv)
- The conjugate base of hydroxide ion is—
 (1) H_2O (2) H_3O^+ (3) O^{2-} (4) O_2
- The conjugate acid of amide ion (NH_2^-) is—
 (1) N_2H_4 (2) NH_2OH (3) NH_4^+ (4) NH_3
- Which of the following can act both as a Bronsted acid as well as a Bronsted base ?
 (1) H_2SO_4 (2) HCO_3^- (3) O^{2-} (4) NH_4^+
- Which of the following acid-base reactions cannot be explained by the Bronsted theory ?
 (1) $\text{CO}_2 + \text{CaO} \longrightarrow \text{CaCO}_3$ (2) $\text{BF}_3 + \text{NH}_3 \longrightarrow \text{BF}_3^+ \text{NH}_3^-$
 (3) $\text{Ni} + 4\text{CO} \longrightarrow \text{Ni}(\text{CO})_4$ (4) All of these
- Which of the following Bronsted acid has the weakest conjugate base ?
 (1) H_2O (2) HCN (3) HCOOH (4) HF

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	1	3	4	1	1	4	4	2	1
	Que.	11									
	Ans.	2									
BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	7			
	Ans.	4	2	1	2	3	2	1			
	Que.	1	2	3	4	5	6				
	Ans.	2	3	2	3	1	2				
BEGINNER'S BOX-3	Que.	1	2	3	4	5	6				
	Ans.	3	2	3	1	4	4				
	Que.	1	2	3	4	5	6				
	Ans.	2	1	3	4	2	4	4			
BEGINNER'S BOX-4	Que.	1	2	3	4	5	6				
	Ans.	2	1	3	4	2	4	4			
	Que.	1	2	3	4	5	6				
	Ans.	2	1	3	4	2	4	4			
BEGINNER'S BOX-5	Que.	1	2	3	4	5	6	7			
	Ans.	2	1	3	4	2	4	4			
	Que.	1	2	3	4	5	6				
	Ans.	2	1	3	4	2	4	4			

EXERCISE-I (Conceptual Questions)**INTRODUCTION**

- The formula weight of H_2SO_4 is 98. The weight of the acid in 400 mL of 0.1 M solution is:-
(1) 2.45 g (2) 3.92 g (3) 4.90 g (4) 9.8 g
- Normality of 2M sulphuric acid is:-
(1) 2 N (2) 4N (3) N/2 (4) N/4
- If $\text{pH} = 3.31$, then find out $[\text{H}^+]$ (Approxy)
(1) 3.39×10^{-4} (2) 5×10^{-4}
(3) 3.0×10^{-3} (4) None
- If $[\text{OH}^-] = 5.0 \times 10^{-5} \text{ M}$ then pH will be :-
(1) $5 - \log 5$ (2) $9 + \log 5$
(3) $\log 5 - 5$ (4) $\log 5 - 9$
- Basicity of H_3PO_3 and H_3PO_2 are respectively :-
(1) 1 and 2 (2) 2 and 3
(3) 3 and 2 (4) 2 and 1
- Find out pH of solution having 2×10^{-3} moles of OH^- ion's in 2 litre solution :-
(1) $\text{pH} = 3$ (2) $\text{pH} = 3 + \log 2$
(3) $\text{pH} = 3 - \log 2$ (4) $\text{pH} = 11$
- pH of tomato juice is 4.4. Then concentration of H_3O^+ will be :-
(1) 39×10^{-4} (2) 3.9×10^{-5}
(3) 3.9×10^{-4} (4) 3.9×10^5
- 8 g NaOH is dissolved in one litre of solution, the molarity of the solution is:-
(1) 0.2 M (2) 0.4 M (3) 0.02 M (4) 0.8 M
- The amount of acetic acid present in 100 mL of 0.1M solution is :-
(1) 0.30 g (2) 3.0 g (3) 0.60 g (4) None
- The number of milli equivalents of acid in 100 mL of 0.5N HCl solution is:-
(1) 50 (2) 100 (3) 25 (4) 200
- If the molar concentration of PbI_2 is $1.5 \times 10^{-3} \text{ mol L}^{-1}$, the concentration of iodide ions in g ion L^{-1} is:-
(1) 3.0×10^{-3} (2) 6.0×10^{-3}
(3) 0.3×10^{-3} (4) 0.6×10^{-6}

OSTWALD'S DILUTION LAW

- Order of dissociation of 0.1 N CH_3COOH is :- (Dissociation constant = 1×10^{-5})
(1) 10^{-5} (2) 10^{-4} (3) 10^{-3} (4) 10^{-2}

Build Up Your Understanding

- If α is the degree of dissociation of weak dibasic organic acid and y is the hydrogen ion concentration, what is the initial concentration of acid :-
(1) $\frac{\alpha(y)^{-1}}{2} \text{ M}$ (2) $y(\alpha)^{-1} \text{ M}$
(3) $\frac{y(\alpha)^{-1}}{2} \text{ M}$ (4) None of them
- The degree of dissociation of acetic acid is given by the expression $\alpha = 0.1 \times C^{-1}$ (where C = concentration of the acid) What is the pH of the solution :-
(1) 1 (2) 2 (3) 3 (4) 4
- Ostwald's dilution law is not applicable for strong electrolytes because:-
(1) Strong electrolytes are completely ionised
(2) Strong electrolytes are volatile
(3) Strong electrolytes are unstable
(4) Strong electrolytes often contain metal ions
- The degree of ionisation of a compound depends upon :
(1) Size of the solute molecules
(2) Nature of the solute molecules
(3) Nature of the container taken
(4) The amount of current passed
- Find out K_a for 10^{-2} M HCN acid, having pOH is 10 :-
(1) $K_a = 10^{-4}$ (2) $K_a = 10^{-2}$
(3) $K_a = 10^{-5}$ (4) None of them
- Which of the following will occur if a 1.0 M solution of a weak acid is diluted to 0.01 M at constant temperature:-
(1) Percentage ionisation will increase
(2) $[\text{H}^+]$ will decrease to 0.01M
(3) K_a will increase
(4) pH will decrease by 2 units
- The pH of 0.15 M solution of HOCl ($K_a = 9.6 \times 10^{-6}$) is:-
(1) 4.42 (2) 2.92 (3) 3.42 (4) None
- The extent of ionisation increases (weak electrolytes)
(1) With the increase in concentration of solute
(2) On decreasing the temp. of solution
(3) On addition of excess of water to the solution
(4) On stirring the solution vigorously

21. If K_a of $\text{HCN} = 4 \times 10^{-10}$, then the pH of 2.5×10^{-1} molar HCN (aq) is:-
 (1) 4.2 (2) 4.7 (3) 0.47 (4) 5.0

22. The molarity of nitrous acid at which its pH becomes 2. ($K_a = 4.5 \times 10^{-4}$) :-
 (1) 0.3333 (2) 0.4444
 (3) 0.6666 (4) 0.2222

23. Correct statement for HCN weak acid at 25°C temperature.:-

$$(1) \alpha = \frac{K_a}{[\text{H}^+]} \quad (2) \alpha = \frac{K_a \times [\text{OH}^-]}{K_w}$$

(3) (1) & (2) both (4) $K_b = C\alpha^2$

EXPLANATION OF WATER

24. Ionic product of water will increase, if :-

- (1) Dissociation the pressure
- (2) Add H^+
- (3) Add OH^-
- (4) Increase the temperature

25. For water at 25°C , 2×10^{-7} moles per litre is the correct answer for which one of the following

- (1) $[\text{H}^+] + [\text{OH}^-]$ (2) $[\text{H}^+]^2$
- (3) $[\text{OH}^-]^2$ (4) $[\text{H}^+] - [\text{OH}^-]$

26. At 25°C , the dissociation constant for pure water is given by :-

- (1) $(55.4 \times 10^{14})^{-1}$ (2) 1×10^{-14}
- (3) $\frac{1 \times 10^{-14}}{18}$ (4) None of these

27. Ionic product of water is equal to :-

- (1) Dissociation constant of water $\times [\text{H}_2\text{O}]$
- (2) Dissociation constant of water $\times [\text{H}^+]$
- (3) Product of $[\text{H}_2\text{O}]$ and $[\text{H}^+]$
- (4) Product of $[\text{OH}^-]^2$ and $[\text{H}^+]$

28. Addition of H^+ and OH^- ion's concentration at 90°C

- (1) 10^{-14} (2) 10^{-12}
- (3) 2×10^{-6} (4) 2×10^{-7}

29. At 90°C , pure water has $[\text{H}_3\text{O}^+] = 10^{-6.7} \text{ mol L}^{-1}$ what is the value of K_w at 90°C :-

- (1) 10^{-6} (2) 10^{-12}
- (3) 10^{-67} (4) $10^{-13.4}$

30. At 373 K, temp. the pH of pure H_2O can be:-

- (1) < 7 (2) > 7 (3) $= 7$ (4) $= 0$

31. The common ion effect is shown by which of the following sets of solutions :-

- (1) $\text{BaCl}_2 + \text{Ba}(\text{NO}_3)_2$ (2) $\text{NaCl} + \text{HCl}$
- (3) $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ (4) None

32. Basic strength of NH_4OH in presence of NH_4Cl

- (1) Increases
- (2) Remains unchanged
- (3) Decreases
- (4) Some times increases or sometimes decreases

33. Which of the following is a true statement :

- (1) The ionisation constant and ionic product of water are same.
- (2) Water is a strong electrolyte.
- (3) The value of ionic product of water is less than that of its ionisation constant.
- (4) At 298K, the number of H^+ ions in a litre of water is 6.023×10^{16} .

34. If it is known that H_2S is a weak acid and it is ionised into 2H^+ and S^{2-} . Then in this solution HCl is added so, pH becomes less, then what will happen :-

- (1) Decrease in S^{2-} ion concentration
- (2) Concentration of S^{2-} is not affected
- (3) Increase in S^{2-} ion concentration
- (4) It is not possible, to add HCl in solution

SALTS, TYPES OF SALT & CONJUGATE THEORY

35. Which of the following is not an acidic salt :-

- (1) NaHSO_4 (2) HCOONa
- (3) NaH_2PO_3 (4) None of them

36. Which is a basic salt :-

- (1) PbS (2) PbCO_3
- (3) PbSO_4 (4) $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$

37. The process of neutralisation invariably results in the production of :-

- (1) H^+ ions
- (2) OH^- ions
- (3) Both H^+ and OH^- ions
- (4) Molecules of water

38. Which of the following is an acid salt :-

- (1) Na_2S (2) Na_2SO_3
- (3) NaHSO_3 (4) Na_2SO_4

39. The mixed salt among the following is :-

- (1) $\begin{array}{c} \text{CH}(\text{OH})\text{COONa} \\ | \\ \text{CH}(\text{OH})\text{COONa} \end{array}$ (2) NaKSO_4
- (3) CaCl_2 (4) All

HYDROLYSIS OF SALTS

40. At 90°C, the pH of 0.1M NaCl aqueous solution is :-
 (1) < 7 (2) > 7 (3) 7 (4) 0.1
41. What will be the pH of 1.0 M ammonium formate solution, If $K_a = 1 \times 10^{-4}$ acid $K_b = 1 \times 10^{-5}$:-
 (1) 6.5 (2) 7.5 (3) 8.0 (4) 9.0
42. Which salt will not undergo hydrolysis :-
 (1) KCl (2) Na_2SO_4 (3) NaCl (4) All
43. Maximum efficiency of cationic hydrolysis will be shown by :-
 (1) Al^{+3} (2) Ga^{+3} (3) Tl^{+1} (4) Tl^{+3}
44. $\text{HCOO}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCOOH} + \text{OH}^-$ is related:-
 (1) $h = \sqrt{K_h}$ (2) $h = \sqrt{\frac{K_h}{C}}$
 (3) $h = \sqrt{\frac{K_h}{V}}$ (4) $K_h = \sqrt{hc}$
45. The pH of aqueous solution of sodium acetate is
 (1) 7 (2) Very low
 (3) > 7 (4) < 7
46. If pK_b for CN^- at 25°C is 4.7. The pH of 0.5M aqueous NaCN solution is :-
 (1) 12 (2) 10 (3) 11.5 (4) 11
47. The highest pH value is of :-
 (1) 0.1 M NaCl
 (2) 0.1 M NH_4Cl
 (3) 0.1 M CH_3COONa
 (4) 0.1 M $\text{CH}_3\text{COONH}_4$
48. pH of K_2S solution is:-
 (1) 7 (2) Less than 7
 (3) More than 7 (4) 0
49. For anionic hydrolysis, pH is given by:-
 (1) $\text{pH} = \frac{1}{2} \text{p}K_w - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log c$
 (2) $\text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$
 (3) $\text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log c$
 (4) None of above
50. A weak acid react with strong base, ionisation constant of weak acid is 10^{-4} . Find out equilibrium constant for this reaction :-
 (1) 10^{-10} (2) 10^{10} (3) 10^{-9} (4) 10^9

51. Hydroxyl ion concentration $[\text{OH}^-]$ in the case of sodium acetate can be expressed as (where K_a is dissociation constant of CH_3COOH and C is the concentration of sodium acetate):-

$$(1) [\text{OH}^-] = (\text{C}K_w \cdot K_a)^{1/2} \quad (2) [\text{OH}^-] = \text{C} \cdot K_w \sqrt{K_a}$$

$$(3) [\text{OH}^-] = \left(\frac{\text{C} \cdot K_w}{K_a} \right)^{1/2} \quad (4) [\text{OH}^-] = \text{C} \cdot K_a \cdot K_w$$

52. Consider :-
 (a) FeCl_3 in water - Basic
 (b) NH_4Cl in water - Acidic
 (c) Ammonium acetate in water - Acidic
 (d) Na_2CO_3 in water - Basic
 Which is/are not correctly matched:-
 (1) b and d (2) b only
 (3) a and c (4) d only
53. Which of the following salts undergoes hydrolysis in water:-
 (1) Na_3PO_4 (2) CH_3COONa
 (3) NaNO_3 (4) Both of (1) and (2)
54. A salt 'X' is dissolved in water of pH = 7. The resulting solution becomes alkaline in nature. The salt is made up of:-
 (1) A strong acid and strong base
 (2) A strong acid and weak base
 (3) A weak acid and weak base
 (4) A weak acid and strong base
55. K_a for cyano acetic acid is 3.5×10^{-3} . Then the degree of hydrolysis of 0.05 M. sodium cyano acetate solution will have the following value :-
 (1) 4.559×10^{-6} (2) 5.559×10^{-6}
 (3) 6.559×10^{-6} (4) 7.559×10^{-6}
56. Degree of Hydrolysis of $\frac{N}{100}$ solution of KCN is
 (Given $K_a = 1.4 \times 10^{-9}$)
 (1) 2.7×10^{-3} (2) 2.7×10^{-2}
 (3) 2.7×10^{-4} (4) 2.7×10^{-5}

SOLUBILITY & SOLUBILITY PRODUCT (K_{sp})

57. The solubility product of sparingly soluble univalent salt is defined as the product of ionic concentration in a:-
 (1) 1 M solution
 (2) Concentration solution
 (3) Very dilute solution
 (4) Saturated solution

- 77.** M_2SO_4 (M^+ is a monovalent metal ion) has a K_{sp} of 1.2×10^{-5} at 298 K. The maximum concentration of M^+ ion that could be attained in a saturated solution of this solid at 298 K is :-
 (1) 3.46×10^{-3} M (2) 2.89×10^{-2} M
 (3) 2.8×10^{-3} M (4) 7.0×10^{-3} M
- 78.** Which of the following has maximum solubility (K_{sp} value is given in brackets) :-
 (1) HgS (1.6×10^{-54}) (2) $PbSO_4$ (1.3×10^{-8})
 (3) ZnS (7.0×10^{-26}) (4) $AgCl$ (1.7×10^{-10})
- 79.** Maximum soluble is :- (K_{sp} is given)
 (1) CuS (8.5×10^{-36}) (2) CdS (3.6×10^{-28})
 (3) ZnS (1.2×10^{-28}) (4) MnS (1.4×10^{-10})
- 80.** In which of the following, the solubility of $AgCl$ will be maximum :-
 (1) 0.1 M $AgNO_3$ (2) Water
 (3) 0.1 M $NaCl$ (4) 0.1 M KCl
- 81.** The solubility product of three sparingly soluble salts are given below :
- | No. | Formula | Solubility product |
|-----|---------|-----------------------|
| 1 | PQ | 4.0×10^{-20} |
| 2 | PQ_2 | 3.2×10^{-14} |
| 3 | PQ_3 | 2.7×10^{-35} |
- The correct order of decreasing molar solubility is:-
 (1) 1, 2, 3 (2) 2, 1, 3 (3) 3, 2, 1 (4) 2, 3, 1
- 82.** The K_{sp} value for $Gd(OH)_3$ is 2.8×10^{-23} , the pH of $Gd(OH)_3$ in saturated solution :-
 (1) 6.08 (2) 5.08 (3) 8.47 (4) 4.08
- 83.** If the solubility product of $AgBrO_3$ and Ag_2SO_4 are 5.5×10^{-5} and 2×10^{-5} respectively, the relationship between the solubilities of these can be correctly represented as:-
 (1) $s_{AgBrO_3} > s_{Ag_2SO_4}$
 (2) $s_{AgBrO_3} = s_{Ag_2SO_4}$
 (3) $s_{AgBrO_3} < s_{Ag_2SO_4}$
 (4) Can't predict
- 84.** 0.5 M HCl solution has ions- Hg^{++} , Cd^{++} , Sr^{++} , Fe^{++} , Cu^{++} . To pass the H_2S gas in this solution, which are precipitated out :-
 (1) Cd^{+2} , Fe^{+2} , Sr^{+2} (2) Cd^{+2} , Hg^{+2} , Cu^{+2}
 (3) Hg^{+2} , Cu^{+2} , Fe^{+2} (4) Cu^{+2} , Sr^{+2} , Fe^{+2}
- 85.** Solubility product of $Mg(OH)_2$ is 1×10^{-11} . At what pH, precipitation of $Mg(OH)_2$ will begin from 0.1 M Mg^{2+} solution :-
 (1) 9 (2) 5 (3) 3 (4) 7
- 86.** A solution, containing 0.01 M Zn^{+2} and 0.01 M Cu^{2+} is saturated by passing H_2S gas. The S^{-2} concentration is 8.1×10^{-21} M, K_{sp} for ZnS and CuS are 3.0×10^{-22} and 8.0×10^{-36} respectively. Which of the following will occur in the solution:-
 (1) ZnS will precipitate
 (2) CuS will precipitate
 (3) Both ZnS and CuS will precipitate
 (4) Both Zn^{2+} and Cu^{2+} will remain in the solution
- 87.** Consider (i) $Zn(OH)_2$ (ii) $Cr(OH)_3$ (iii) $Mg(OH)_2$ (iv) $Al(OH)_3$ which hydroxide is precipitated by NH_4OH containing NH_4Cl :-
 (1) i, ii (2) ii, iv
 (3) Only iv (4) i, ii, iii and iv
- 88.** What will happen if the pH of the solution of 0.001 M $Mg(NO_3)_2$ solution is adjusted to pH = 9 ($K_{sp} Mg(OH)_2 = 8.9 \times 10^{-12}$)
 (1) ppt will take place
 (2) ppt will not take place
 (3) Solution will be saturated
 (4) None of these
- 89.** The solubility product constant K_{sp} of $Mg(OH)_2$ is 9.0×10^{-12} . If a solution is 0.010 M with respect to Mg^{2+} ion, what is the maximum hydroxide ion concentration which could be present without causing the precipitation of $Mg(OH)_2$:-
 (1) 1.5×10^{-7} M (2) 3.0×10^{-7} M
 (3) 1.5×10^{-5} M (4) 3.0×10^{-5} M
- 90.** When HCl gas is passed through a saturated solution of common salt, pure $NaCl$ is precipitated because:-
 (1) The impurities dissolve in HCl
 (2) HCl is slightly soluble in water
 (3) The ionic product $[Na^+] \times [Cl^-]$ exceeds the solubility product of $NaCl$
 (4) The solubility product of $NaCl$ is lowered by Cl^- from aq. HCl
- 91.** A solution is a mixture of 0.06 M KCl and 0.06 M KI . $AgNO_3$ solution is being added drop by drop till $AgCl$ starts precipitating ($K_{sp} AgCl = 1 \times 10^{-10}$ and $K_{sp} AgI = 4 \times 10^{-16}$). The concentration of Iodide ion at this stage will be nearly equal to :-
 (1) 4.0×10^{-5} M (2) 2.4×10^{-7} M
 (3) 2.0×10^{-8} M (4) 4×10^{-8} M
- 92.** Why only As^{3+} gets precipitated as As_2S_3 and not Zn^{2+} as ZnS when H_2S is passed through an acidic solution containing As^{3+} and Zn^{2+} :-
 (1) Enough As^{3+} are present in acidic medium
 (2) Zinc salt does not ionise in acidic medium
 (3) Solubility product of As_2S_3 is less than that of ZnS
 (4) Solubility product changes in presence of an acid

93. H_2S is passed through a solution of cations in HCl medium to precipitate cation of :-
 (1) II-A group of cation analysis
 (2) II - B group of cation analysis
 (3) IV group of cation analysis
 (4) Both II - A and II-B gps.
94. To have more sulphide ion concentration, H_2S should be passed through :-
 (1) 1 N HCl solution
 (2) 0.1 M HCl solution
 (3) A neutral solution such as water
 (4) An ammoniacal solution
95. The solubility product of hydroxides of Mg^{+2} , Zn^{+2} , and Fe^{+3} decreases as
 $K_{\text{sp}} \text{Mg}(\text{OH})_2 > K_{\text{sp}} \text{Zn}(\text{OH})_2 > K_{\text{sp}} \text{Fe}(\text{OH})_3$ The order of precipitation of hydroxides is:-
 (1) $\text{Fe}(\text{OH})_3$, $\text{Zn}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$
 (2) $\text{Mg}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$
 (3) $\text{Zn}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$
 (4) $\text{Zn}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$

FEW IMPORTANT POINTS

96. Two monobasic weak acids have the same concentration of H^+ ions. What is the relationship between dissociation constant and dilution:-
 (1) $K_{\text{a}_1} V_1 = K_{\text{a}_2} V_2$ (2) $K_{\text{a}_1} V_2 = K_{\text{a}_2} V_1$
 (3) $[K_{\text{a}_1} V_1]^{\frac{1}{2}} = K_{\text{a}_2} V_2$ (4) $K_{\text{a}_1} V_1 = [K_{\text{a}_2} V_2]^{\frac{1}{2}}$
97. What is the molar concentration of chloride ion in the solution obtained by mixing 300 mL of 3.0M NaCl and 200 mL of 4.0 M solution of BaCl_2 :-
 (1) 5.0 M (2) 1.8 M
 (3) 1.6 M (4) None of these
98. The pH of a 0.1 M formic acid 0.1% dissociated is equal to 4. What will be the pH of another weak monobasic acid (same concentration) which is 1% dissociated
 (1) 2 (2) 3 (3) 1 (4) 4

pH

99. pH of water is 7. When any substance Y is dissolved in water then pH becomes 13. Substance Y is a salt of :-
 (1) Strong acid and strong base
 (2) Weak acid and weak base
 (3) Strong acid and weak base
 (4) Weak acid and strong base

100. Minimum pH is shown by aqueous solution of :-
 (1) 0.1 M BaCl_2 (2) 0.1 M $\text{Ba}(\text{NO}_3)_2$
 (3) 0.1 M BeCl_2 (4) 0.1 M $\text{Ba}(\text{OH})_2$
101. Given :-
 (a) 0.005 M H_2SO_4 (b) 0.1 M Na_2SO_4
 (c) 10^{-2} M NaOH (d) 0.01 M HCl
 Choose the correct code having same pH :-
 (1) a, c, d (2) b, d (3) a, d (4) a, c
102. What is H^+ ion concentration of 5×10^{-3} M H_2CO_3 solution having a 10% dissociation:-
 (1) 10^{-3} (2) 10^{-2}
 (3) 10^{-1} (4) 5×10^{-2}
103. A metal hydroxide of molecular formula $\text{M}(\text{OH})_4$ is 50% ionised. Its 0.0025M solution will have the pH :-
 (1) 12 (2) 2 (3) 4 (4) 11.7
104. In the following solutions, the conc. of different acids are given, which mixture of the acid has highest pH :-
 (1) $\frac{M}{10} \text{H}_2\text{SO}_4$, $\frac{M}{20} \text{HNO}_3$, $\frac{M}{10} \text{HClO}_4$
 (2) $\frac{M}{20} \text{H}_2\text{SO}_4$, $\frac{M}{10} \text{HNO}_3$, $\frac{M}{20} \text{HClO}_4$
 (3) $\frac{M}{20} \text{H}_2\text{SO}_4$, $\frac{M}{10} \text{HNO}_3$, $\frac{M}{40} \text{HClO}_4$
 (4) $\frac{M}{20} \text{H}_2\text{SO}_4$, $\frac{M}{5} \text{HNO}_3$, $\frac{M}{5} \text{HClO}_4$
105. If 100 mL of pH = 3 and 400 mL of pH = 3 is mixed, what will be the pH of the mixture
 (1) 3.2 (2) 3.0 (3) 3.5 (4) 2.8
106. 10^{-6} M HCl is diluted to 100 times. Its pH is :-
 (1) 6.0 (2) 8.0 (3) 6.95 (4) 9.5
107. pH of 0.001M acetic acid would be :-
 (1) 2 (2) > 3 (3) 7 (4) 14
108. At 90°C , the pH of 0.001M KOH solution will be
 (1) 3 (2) 11 (3) 5 (4) 9
109. The pH of solution is increased from 3 to 6. Its H^+ ion concentration will be :-
 (1) Reduced to half
 (2) Doubled
 (3) Reduced by 1000 times
 (4) Increased by 1000 times
110. A solution has pOH equal to 13 at 298 K. The solution will be:-
 (1) Highly acidic (2) Highly basic
 (3) Moderately basic (4) Unpredictable

- 111.** The pH of the solution containing 10 mL of a 0.1M NaOH and 10 mL of 0.05M H_2SO_4 would be
(1) Zero (2) 1 (3) >7 (4) 7
- 112.** Which of the following statements are (is) correct
(a) The pH of 1.0×10^{-8} M solution of HCl is 8.
(b) The conjugate base of H_2PO_4^- is HPO_4^{2-} .
(c) Autoprotolysis constant of water increases with temperature.
(d) When a solution of a weak monoprotic acid is titrated against a strong base, at half neutralization point $\text{pH} = 1/2 \text{ pK}_a$
(1) a (2) a, b (3) a, b, d (4) b, c
- 113.** In a solution of $\text{pH} = 5$, more acid is added in order to reduce the $\text{pH} = 2$. The increase in hydrogen ion concentration is:-
(1) 100 times (2) 1000 times
(3) 3 times (4) 5 times
- 114.** The hydrogen ion concentration in a given solution is 6×10^{-4} M. Its pH will be :-
(1) 6 (2) 3.22 (3) 4 (4) 2.
- 115.** The pOH of beer is 10.0. The hydrogen ion concentration will be :-
(a) 10^{-10} (b) $\frac{K_w}{10^{-10}}$ (c) $\frac{K_w}{10^{-8}}$ (d) 10^{-4}
(1) a, d (2) b, c (3) a, b, c (4) None
- 116.** An aqueous solution whose $\text{pH} = 0$ is :-
(1) Basic (2) Acidic
(3) Neutral (4) Amphoteric
- 117.** The pH of the solution produced when an aqueous solution of strong acid pH 5 is mixed with equal volume of an aqueous solution of strong acid of pH 3 is :-
(1) 3.3 (2) 3.5 (3) 4.5 (4) 4.0
- 118.** Following five solution of KOH were prepare as-
First $\rightarrow$ 0.1 moles in 1 L
Second $\rightarrow$ 0.2 moles in 2 L
Third $\rightarrow$ 0.3 moles in 3 L
Fourth $\rightarrow$ 0.4 moles in 4 L
Fifth $\rightarrow$ 0.5 moles in 5 L
The pH of resultant solution is :-
(1) 2 (2) 1 (3) 13 (4) 7
- 119.** The pH of a 0.02 M ammonia solution which is 5% ionised will be :-
(1) 2 (2) 11 (3) 5 (4) 7
- 120.** For $\frac{N}{10}$ H_2SO_4 , pH value is :-
(1) 1 (2) 0.586 (3) 0.856 (4) None
- 121.** An aqueous solution of HCl is 10^{-9} M HCl. The pH of the solution should be:-
(1) 9 (2) Between 6 and 7
(3) 7 (4) Unpredictable
- 122.** H_2X is a dibasic acid which dissociates completely in water. Which one of the following is the molarity of an aqueous solution of this acid which has a pH of 1 :-
(1) 0.1 (2) 0.05 (3) 0.2 (4) 0.5
- 123.** How many moles of HCl must be removed from 1 litre of aqueous HCl solution to change its pH from 2 to 3 :-
(1) 1 (2) 0.02 (3) 0.009 (4) 0.01
- 124.** 8 g NaOH and 4.9 g H_2SO_4 are present in one litre of the solution. What is its pH
(1) 1 (2) 13 (3) 12 (4) 2
- 125.** Calculate pH of a solution whose 100 mL contains 0.2 g NaOH dissolved in it :-
(1) 10.699 (2) 11.699
(3) 12.699 (4) 13.699
- 126.** One litre solution contains 1M HOCl [$K_a = 10^{-8}$] and 1 M NaOH. What is the pH of the solution :-
(1) 8 (2) 11 (3) 5 (4) 2
- 127.** What is the quantity of NaOH present in 250 cc of the solution, so that it gives a $\text{pH} = 13$:-
(1) 10^{-13} g (2) 10^{-1} g (3) 1.0 g (4) 4.0 g
- 128.** 0.001 mol of the strong electrolyte $\text{M}(\text{OH})_2$ has been dissolved to make a 20 mL of its saturated solution. Its pH will be :- [$K_w = 1 \times 10^{-14}$]
(1) 13 (2) 3.3 (3) 11 (4) 9.8
- 129.** Choose the wrong statement :-
(1) For a neutral solution : $[\text{H}^+] = [\text{OH}^-] = \sqrt{K_w}$
(2) For an acidic solution : $[\text{H}^+] > \sqrt{K_w}$ and $[\text{OH}^-] < \sqrt{K_w}$
(3) For a basic solution : $[\text{H}^+] < \sqrt{K_w}$ and $[\text{OH}^-] > \sqrt{K_w}$
(4) For a neutral solution at all temperatures : $[\text{H}^+] = [\text{OH}^-] = 10^{-7}$ M
- 130.** The pH of 0.1 M solution of the following salts increases in order :-
(1) $\text{NaCl} < \text{NH}_4\text{Cl} < \text{NaCN} < \text{HCl}$
(2) $\text{NaCN} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{HCl}$
(3) $\text{HCl} < \text{NaCl} < \text{NaCN} < \text{NH}_4\text{Cl}$
(4) $\text{HCl} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{NaCN}$

BUFFER SOLUTIONS and INDICATOR

- 131.** In a buffer solution the ratio of concentration of NH_4Cl and NH_4OH is 1 : 1 when it changes in 2 : 1 what will be the value of pH of buffer :-
(1) Increase (2) Decrease
(3) No effect (4) N.O.T.
- 132.** To a 50 mL of 0.05M formic acid how much volume of 0.10M sodium formate must be added to get a buffer solution of pH = 4.0 ? (pK_a of the acid is 3.8)
(1) 50 mL (2) 4 mL (3) 39.6 mL (4) 100 mL
- 133.** In the volumetric estimation of HCl, if we make use of phenolphthalein as an indicator, which base is unsuitable for the titration :-
(1) NaOH (2) RbOH
(3) KOH (4) NH_4OH
- 134.** In a mixture of weak acid and its salt, the ratio of concentration of acid to salt is increased ten-fold. The pH of the solution :-
(1) Decreases by one (2) Increases by one-tenth
(3) Increases by one (4) Increases ten-fold
- 135.** pK_b for NH_4OH at certain temperature is 4.74. The pH of basic buffer containing equimolar concentration of NH_4OH and NH_4Cl will be:-
(1) 7.74 (2) 4.74 (3) 2.37 (4) 9.26
- 136.** What is the suitable indicator for titration of NaOH and oxalic acid:-
(1) Methyl orange (2) Methyl red
(3) Phenolphthalein (4) Starch solution
- 137.** Phenolphthalein does not act as an indicator for the titration between :-
(1) KOH and H_2SO_4
(2) NaOH and CH_3COOH
(3) Oxalic acid and KMnO_4
(4) $\text{Ba}(\text{OH})_2$ and HCl
- 138.** Which can act as buffer :-
(1) $\text{NH}_4\text{OH} + \text{NaOH}$
(2) $\text{HCOOH} + \text{CH}_3\text{COONa}$
(3) 40 mL 0.1 M NaCN + 20 mL of 0.1 M HCl
(4) None of them
- 139.** The buffer solution play an important role in :-
(1) Increasing the pH value
(2) Decreasing the pH value
(3) Keeping the pH constant
(4) Solution will be neutral
- 140.** K_a for HCN is 5×10^{-10} at 25°C . For maintaining a constant pH of 9, the volume of 5M KCN solution required to be added to 10mL of 2M HCN solution is-
(1) 4 mL (2) 7.95 mL
(3) 2 mL (4) 9.3 mL
- 141.** Buffering action of a mixture of CH_3COOH and CH_3COONa is maximum when the ratio of salt to acid is equal to -
(1) 1.0 (2) 100.0 (3) 10.0 (4) 0.1
- 142.** The pink colour of phenolphthalein in alkaline medium is due to -
(1) Negative ion (2) Positive ion
(3) OH^- ions (4) Neutral form
- 143.** Which indicator works in the pH range 8 – 9.8
(1) Phenolphthalein (2) Methyl orange
(3) Methyl red (4) Litmus
- 144.** A basic - buffer will obey the equation $\text{pOH} - \text{pK}_b = 1$ only under condition:-
(1) [Conjugate acid] : [base] = 1 : 10
(2) [Conjugate acid] = [base]
(3) [Conjugate acid] : [base] = 10 : 1
(4) N.O.T
- 145.** For weak acid strong base titration, the indicator used is :-
(1) Potassium di-chromate
(2) Methyl orange
(3) Litmus
(4) Phenolphthalein
- 146.** From the following in which titration methyl orange is a best indicator :-
(1) $\text{CH}_3\text{COOH} + \text{NaOH}$ (2) $\text{H}_2\text{C}_2\text{O}_4 + \text{NaOH}$
(3) $\text{HCl} + \text{NaOH}$ (4) $\text{CH}_3\text{COOH} + \text{NH}_4\text{OH}$
- 147.** The total number of different kind of buffers obtained during the titration of H_3PO_4 with NaOH are :-
(1) 3 (2) 1 (3) 2 (4) 0
- 148.** The H^+ ion concentration in 0.001 M acetic acid is $1.34 \times 10^{-4} \text{ g ion L}^{-1}$. The H^+ ion concentration of 0.164 g of CH_3COONa is added to a litre of 0.001 M CH_3COOH will be :-
(1) 9×10^{-6} (2) 18×10^{-6}
(3) 4.5×10^{-6} (4) 5×10^{-6}
- 149.** A certain acidic buffer solution contains equal concentration of X^- and HX . The K_b for X^- is 10^{-10} . The pH of the buffer is :-
(1) 4 (2) 7 (3) 10 (4) 14
- 150.** When 1.0 mL of dil. HCl acid is added to 100 mL of a buffer solution of pH 4.0. The pH of the solution
(1) Becomes 7 (2) Does not change
(3) Becomes 2 (4) Becomes 10
- 151.** The pH of blood is maintained by CO_2 and H_2CO_3 in the body and chemical constituents of blood. This phenomenon is called :-
(1) Colloidal (2) Buffer action
(3) Acidity (4) Salt balance

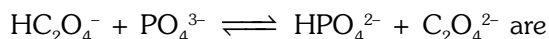
- 152.** Phenolphthalein is not a good indicator for titrating
 (1) NaOH against oxalic acid
 (2) NaOH against HCl
 (3) NaOH against H_2SO_4
 (4) Ferrous sulphate against KMnO_4
- 153.** Which of the following solutions does not act as buffer :-
 (1) $\text{H}_3\text{PO}_4 + \text{NaH}_2\text{PO}_4$
 (2) $\text{NaHCO}_3 + \text{H}_2\text{CO}_3$
 (3) $\text{NH}_4\text{Cl} + \text{HCl}$
 (4) $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
- 154.** 50 mL of 2N acetic acid mixed with 10 mL of 1N sodium acetate solution will have an approximate pH of ($K_a = 10^{-5}$) :-
 (1) 4 (2) 5 (3) 6 (4) 7
- 155.** On addition of NaOH to CH_3COOH solution, 60% of the acid is neutralised. If $\text{p}K_a$ of CH_3COOH is 4.7 then the pH of the resulting solution is :-
 (1) More than 4.7 but less than 5.0
 (2) Less than 4.7 but more than 4.0
 (3) More than 5.0
 (4) Remains unchanged
- 156.** 500 mL of 0.2 M acetic acid are added to 500 mL of 0.30 M sodium acetate solution. If the dissociation constant of acetic acid is 1.5×10^{-5} then pH of the resulting solution is:-
 (1) 5.0 (2) 9.0 (3) 3.0 (4) 4.0
- 157.** Half of the formic acid solution is neutralised on addition of a KOH solution to it. If $K_a(\text{HCOOH}) = 2 \times 10^{-4}$ then pH of the solution is : ($\log 2 = 0.3010$)
 (1) 3.6990 (2) 10.3010 (3) 3.85 (4) 4.3010
- 158.** A solution contains 0.2M NH_4OH and 0.2M NH_4Cl . If 1.0 mL of 0.001 M HCl is added to it. What will be the $[\text{OH}^-]$ of the resulting solution [$K_b = 2 \times 10^{-5}$] :-
 (1) 2×10^{-5} (2) 5×10^{-10}
 (3) 2×10^{-3} (4) None of these
- 159.** Henderson equation $\text{pH} - \text{p}K_a = 1$ will be applicable to an acidic buffer when :-
 (1) $[\text{Acid}] = [\text{Conjugate base}]$
 (2) $[\text{Acid}] \times 10 = [\text{Conjugate base}]$
 (3) $[\text{Acid}] = [\text{Conjugate base}] \times 10$
 (4) None of these
- 160.** 0.05 M ammonium hydroxide solution is dissolved in 0.001 M ammonium chloride solution. What will be the OH^- ion concentration of this solution: $K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$
 (1) 3.0×10^{-3} (2) 9.0×10^{-4}
 (3) 9.0×10^{-3} (4) 3.0×10^{-4}
- 161.** When 0.02 moles of NaOH are added to a litre of buffer solution, its pH changes from 5.75 to 5.80. What is its buffer capacity :-
 (1) 0.4 (2) 0.05 (3) - 0.05 (4) 2.5
- 162.** Calculate the pH of a buffer prepared by mixing 300 cc of 0.3 M NH_3 and 500 cc of 0.5 M NH_4Cl . K_b for $\text{NH}_3 = 1.8 \times 10^{-5}$:-
 (1) 8.1187 (2) 9.8117
 (3) 8.8117 (4) None of these
- 163.** What amount of sodium propanoate should be added to one litre of an aqueous solution containing 0.02 mole of propanoic acid ($K_a = 1.34 \times 10^{-5}$ at 25°C) to obtain a buffer solution of pH 4.75 :-
 (1) 4.52×10^{-2} M (2) 3.52×10^{-2} M
 (3) 2.52×10^{-2} M (4) 1.52×10^{-2} M
- 164.** What will be the pH of the solution, if 0.01 moles of HCl is dissolved in a buffer solution containing 0.02 moles of propanoic acid ($K_a = 1.34 \times 10^{-5}$) and 0.0152 moles of salt, at 25°C : $[\log(0.173) = -0.76]$
 (1) 3.11 (2) 4.11 (3) 5.11 (4) 6.11
- 165.** Calculate the pH of a buffer solution prepared by dissolving 30g of Na_2CO_3 in 500 mL of an aqueous solution containing 150 mL of 1M HCl. K_a for $\text{HCO}_3^- = 5.63 \times 10^{-11}$ $\left[\log\left(\frac{133}{150}\right) = -0.05 \right]$
 (1) 8.197 (2) 9.197
 (3) 10.197 (4) 11.197
- 166.** Calculate the ratio of pH of a solution containing 1 mole of $\text{CH}_3\text{COONa} + 1$ mole of HCl per litre and of other solution containing 1 mole $\text{CH}_3\text{COONa} + 1$ mole of acetic acid per litre :-
 (1) 1 : 1 (2) 2 : 1 (3) 1 : 2 (4) 2 : 3
- 167.** When 20 mL of $\frac{M}{20}$ NaOH are added to 10 mL of $\frac{M}{10}$ HCl, the resulting solution will:-
 (1) Turn blue litmus red
 (2) Turn phenolphthalein solution
 (3) Turn methyl orange red
 (4) Will have no effect on either red or blue litmus
- 168.** 10 mL of a solution contains 0.1 M $\text{NH}_4\text{Cl} + 0.01$ M NH_4OH . Which addition would not change the pH of solution :-
 (1) Adding 1 mL water
 (2) Adding 5 mL of 0.1 M NH_4Cl
 (3) Adding 5 mL of 0.1 M NH_4OH
 (4) Adding 10 mL of 0.1 M NH_4Cl

169. $\frac{N}{10}$ acetic acid was titrated with $\frac{N}{10}$ NaOH. When 25%, 50% and 75% of titration is over then the pH of the solution will be :- [$K_a = 10^{-5}$]
- (1) $5 + \log 1/3$, 5, $5 + \log 3$
 - (2) $5 + \log 3$, 4, $5 + \log 1/3$
 - (3) $5 - \log 1/3$, 5, $5 - \log 3$
 - (4) $5 - \log 1/3$, 4, $5 + \log 1/3$

ACID AND BASE

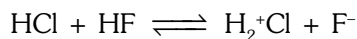
170. The conjugated acid of O^{2-} ion's is :-
 (1) O_2^+ (2) H^+ (3) H_3O^+ (4) OH^-
171. Ionization constant of AOH and BOH base are K_{b1} and K_{b2} . Their relation is $pK_{b1} < pK_{b2}$. Conjugate of following base, does not show maximum pH :
 (1) AOH (2) BOH
 (3) Both of them (4) NOT
172. Select the species which can function as - Lewis base, bronsted acid and bronsted base:-
 (a) H_2O (b) NH_4^+ (c) N^{3-}
 Correct code is :-
 (1) Only a (2) a, b (3) a, c (4) b, c
173. Which ion does not show acid behaviour :-
 (1) $[Al(H_2O)_6]^{+3}$ (2) $[Fe(H_2O)_6]^{+3}$
 (3) HPO_4^{-2} (4) ClO_3^-
174. An example of Lewis acid is:-
 (1) CaO (2) CH_3NH_2
 (3) SO_3 (4) None of these
175. In the reaction $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ water behaves as :-
 (1) Acid (2) Base
 (3) Neutral (4) Both acid & Base
176. Which acts as Lewis base in the reaction $BCl_3 + :PH_3 \rightarrow Cl_3B \leftarrow PH_3$
 (1) PH_3 (2) BCl_3
 (3) Both 1 & 2 (4) None
177. Which acts as Lewis acid in the reaction $SnCl_2 + 2Cl^- \longrightarrow [SnCl_4]^{2-}$
 (1) Cl^- (2) $SnCl_2$ (3) $SnCl_4$ (4) None
178. The conjugated base of $(CH_3)_2NH_2^+$ is :-
 (1) CH_3NH_2 (2) $(CH_3)_2N^+$
 (3) $(CH_3)_2N$ (4) $(CH_3)_2NH$
179. Which equilibrium can be described as Lewis acid base reaction but not Bronsted acid base reaction:-
 (1) $H_2O + CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$
 (2) $2NH_3 + H_2SO_4 \rightleftharpoons 2NH_4^+ + SO_4^{2-}$
 (3) $NH_3 + CH_3COOH \rightleftharpoons NH_4^+ + CH_3COO^-$
 (4) $Cu^{+2} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$
180. Conjugate base of hydrazoic acid is :-
 (1) HN_3^- (2) N_3^- (3) N^{3-} (4) N_2^-
181. NH_3 gas dissolves in water to give NH_4OH , in this reaction, water acts as :-
 (1) An acid (2) A base
 (3) A salt (4) A conjugate base
182. Conjugate acid of $Zn(OH)_2$ is :-
 (1) $Zn(OH)^+$ (2) $Zn(OH_3)^-$ (3) Zn^{2+} (4) None
183. When ammonia is added to water it decreases the concentration of which of the following ion
 (1) OH^- (2) H_3O^+ (3) NH_4^+ (4) None
184. The strongest acid among the following is -
 (1) $ClO_3(OH)$ (2) $ClO_2(OH)$
 (3) $SO(OH)_2$ (4) $SO_2(OH)_2$
185. Which of the following is not a Bronsted acid :-
 (1) $CH_3NH_4^+$ (2) CH_3COO^-
 (3) H_2O (4) HSO_4^-
186. Which of the following example behave as a Lewis acid BF_3 , $SnCl_2$, $SnCl_4$:-
 (1) Stanus chloride, stanic chloride
 (2) BF_3 , Stanus chloride
 (3) Only BF_3
 (4) BF_3 , stanus chloride, stanic chloride
187. In the reaction $HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$, the conjugate base of HNO_3 is :-
 (1) H_2O (2) H_3O^+
 (3) NO_3^- (4) H_3O^+ and NO_3^-
188. The conjugate base of the weak acid in the reaction $HBr + H_2O \rightleftharpoons H_3O^+ + Br^-$ is
 (1) HBr (2) H_2O (3) Br^- (4) H_3O^+
189. In the reaction, $AlCl_3 + Cl^- \rightarrow [AlCl_4]^-$, $AlCl_3$ acts as :-
 (1) Salt (2) Lewis base
 (3) Bronsted acid (4) Lewis acid
190. Mg^{2+} is ----- than Al^{3+} :-
 (1) Strong Lewis acid (2) Strong Lewis base
 (3) Weak Lewis acid (4) Weak Lewis base

191. The two Bronsted bases in the reaction



- (1) HC_2O_4^- and PO_4^{3-}
 (2) HPO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$
 (3) PO_4^{3-} and $\text{C}_2\text{O}_4^{2-}$
 (4) HC_2O_4^- and HPO_4^{2-}

192. The compound HCl behaves as ---- in the reaction,



- (1) Strong acid (2) Strong base
 (3) Weak acid (4) Weak base

193. Which of the following is not a lewis base:-

- (1) NH_3 (2) O^{2-} (3) H_2O (4) I^+

194. Which of the following is bronsted Lowry acid:-

- (1) SO_4^{2-} (2) H_3O^+ (3) OH^- (4) Cl^-

195. The conjugated base for bicarbonate ion is:-

- (1) CO_3^{2-} (2) HCO_3^-
 (3) CO_2 (4) H_2CO_3

196. Conjugated base of OH^- is :-

- (1) H_2O (2) H_3O^+ (3) H^+ (4) O^{2-}

197. HCl does not behave as acid in :-

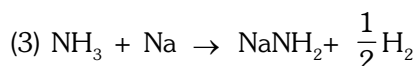
- (1) NH_3 (2) $\text{C}_2\text{H}_5\text{OH}$ (3) H_2O (4) C_6H_6

198. Which of the following is a base according to Lowry-Bronsted concept :-

- (1) I^- (2) H_3O^+ (3) HCl (4) NH_4^+

199. In which of the following reactions NH_3 acts as acid

- (1) $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$
 (2) $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$



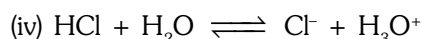
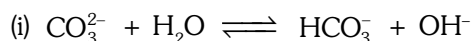
- (4) NH_3 cannot act as acid

200. According to Bronsted concept, the acids in the

following reaction $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ are :-

- (1) NH_3 and NH_4^+ (2) H_2O and OH^-
 (3) H_2O and NH_4^+ (4) NH_3 and OH^-

201. Consider the following reactions :-



Which of the pairs of reactions proves that water is amphoteric in character :-

- (1) (i) and (ii) (2) (ii) and (iii)
 (3) (iii) and (iv) (4) (i) and (iii)

202. CH_3COO^- ion is a :-

- (1) Weak conjugate base
 (2) Strong conjugate base
 (3) Weak conjugate acid
 (4) Strong conjugate acid

203. Which of the following is strongest conjugate base

- (1) ClO_4^- (2) HCO_3^- (3) F^- (4) HSO_4^-

204. Which of the following species can act as Lewis base :-

- (1) Cu^{2+} (2) AlCl_3 (3) NH_3 (4) BF_3

205. A compound having the formula $\text{NH}_2\text{CH}_2\text{COOH}$ may behave :-

- (1) Only as an acid
 (2) Only as a base
 (3) Both as an acid and base
 (4) Neither acid nor base

206. BF_3 is acid according to :-

- (1) Lewis
 (2) Arrhenius
 (3) Bronsted and Lowery
 (4) Madam Curie

207. Which of the following can act both as Bronsted acid and Bronsted base :-

- (1) Na_2CO_3 (2) O^{2-}
 (3) CO_3^{2-} (4) NH_3

208. The strongest conjugate base is :-

- (1) NO_3^- (2) Cl^-
 (3) SO_4^{2-} (4) CH_3COO^-

209. Aluminium chloride is :-

- (1) Bronsted Lowry acid (2) Arrhenius acid
 (3) Lewis acid (4) Lewis base

210. Water is a :-

- (1) Protogenic solvent (2) Protophilic solvent
 (3) Amphotropic solvent (4) Aprotic solvent

211. Ammonium ion is :-

- (1) A conjugate acid
 (2) A conjugate base
 (3) Neither an acid nor a basic
 (4) Both an acid and a base

212. Species which do not act both as Bronsted acid and base is :-

- (1) $(\text{HSO}_4^-)^{-1}$ (2) Na_2CO_3
 (3) NH_3 (4) OH^-

213. Which one of the following is strong Lewis base & Bronsted acid & bronsted base:-

- (1) NH_3 (2) PH_3 (3) CH_4 (4) BH_3

- 214.** Which of the following pair is Lewis acid & Lewis base & product of these is also Lewis base
 (1) BF_3 , NH_3 (2) SiCl_4 , 2Cl^-
 (3) $\text{CH}_3^\oplus$, $^\ominus\text{OC}_2\text{H}_5$ (4) None of these

- 215.** Which of the following is not a correct statement
 (1) Arrhenius theory of acids-bases is capable of explaining the acidic or basic nature of the substances in the solvents other than water
 (2) Arrhenius theory does not explain acidic nature of AlCl_3
 (3) The aqueous solution of Na_2CO_3 is alkaline although it does not contain OH^- ions
 (4) Aqueous solution of CO_2 is acidic although it does not contain H^+ ions

- 216.** For the reaction $\text{NH}_4^+ + \text{S}^{2-} \rightleftharpoons \text{NH}_3 + \text{HS}^-$, NH_3 and S^{2-} are a group of :-
 (1) Acids (2) Bases
 (3) Acid-base pair (4) None of these

- 217.** According to Lewis concept acid & base pair is-
 (1) HO^- , H^+ (2) Ag^+ , Cl^-
 (3) BF_3 , NH_3 (4) None of these

EXERCISE-I (Conceptual Questions)														ANSWER KEY	
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	2	2	2	4	4	2	1	3	1	1	4	3	1	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	2	4	1	2	3	4	4	3	4	1	1	1	3	4	1
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	3	3	4	1	2	4	4	3	2	1	1	4	1	2	3
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	3	3	3	3	2	3	3	4	4	4	2	4	4	3	2
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	4	3	1	3	3	3	4	3	4	1	4	2	2	3	4
Que.	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
Ans.	4	2	2	4	2	4	3	3	2	1	2	2	2	4	3
Que.	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105
Ans.	2	3	4	4	1	2	1	2	4	3	3	1	4	3	2
Que.	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120
Ans.	3	2	4	3	1	4	4	2	2	4	2	1	3	2	1
Que.	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135
Ans.	2	2	3	2	3	2	3	1	4	4	2	3	4	1	4
Que.	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150
Ans.	3	3	3	3	3	1	1	1	3	4	3	1	1	1	2
Que.	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165
Ans.	2	4	3	1	1	1	1	1	2	2	1	3	4	2	3
Que.	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180
Ans.	3	4	1	1	4	2	1	4	3	1	1	2	4	4	2
Que.	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195
Ans.	1	1	2	1	2	4	3	2	4	3	3	4	4	2	1
Que.	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210
Ans.	4	4	1	3	3	3	2	2	3	3	1	4	4	3	3
Que.	211	212	213	214	215	216	217								
Ans.	1	2	1	3	1	2	3								

EXERCISE-II (Previous Year Questions)**AIPMT 2006**

- Which of the following pairs constitutes a buffer :-
 (1) HNO_2 & NaNO_2 (2) NaOH & NaCl
 (3) HNO_3 & NH_4NO_3 (4) HCl & KCl
- The hydrogen ion concentration of a 10^{-8} M HCl aqueous solution at 298 K ($K_w = 10^{-14}$) is :-
 (1) 1.0×10^{-6} M (2) 1.0525×10^{-7} M
 (3) 9.525×10^{-8} M (4) 1.0×10^{-8} M

AIIMS 2006

- 40 mL of 0.1 M ammonia solution is mixed with 20 mL of 0.1 M HCl . What is the pH of the mixture (pK_b of ammonia solution is 4.74) :-
 (1) 4.74 (2) 2.26 (3) 9.26 (4) 5.00

AIPMT 2007

- Calculate the pOH of a solution at 25°C that contains 1×10^{-10} M of hydronium ions, i.e., H_3O^+
 (1) 7.000 (2) 4.000 (3) 9.000 (4) 1.000
- A weak acid HA has a K_a of 1.00×10^{-5} . If 0.100 moles of this acid is dissolved in one litre of water the percentage of acid dissociated at equilibrium is closed to :-
 (1) 99.0% (2) 1.00%
 (3) 99.9% (4) 0.100%

AIPMT 2008

- Equimolar solutions of the following were prepared in water separately. Which one of the solutions will record the highest pH?
 (1) BaCl_2 (2) MgCl_2 (3) CaCl_2 (4) SrCl_2
- Equal volumes of three acid solutions of pH 3, 4 and 5 are mixed in a vessel. What will be the H^+ ion concentration in the mixture ?
 (1) 3.7×10^{-4} M (2) 3.7×10^{-3} M
 (3) 1.11×10^{-3} M (4) 1.11×10^{-4} M

AIPMT 2009

- The ionization constant of ammonium hydroxide is 1.77×10^{-5} at 298 K. Hydrolysis constant of ammonium chloride is :-
 (1) 5.65×10^{-12} (2) 5.65×10^{-10}
 (3) 6.50×10^{-12} (4) 5.65×10^{-13}
- What is the $[\text{OH}^-]$ in the final solution prepared by mixing 20.0 mL of 0.050 M HCl with 30.0 mL of 0.10 M $\text{Ba}(\text{OH})_2$?
 (1) 0.12 M (2) 0.10 M
 (3) 0.40 M (4) 0.0050 M

AIPMT/NEET & AIIMS (2006-2018)

- The dissociation constants for acetic acid and HCN at 25°C are 1.5×10^{-5} and 4.5×10^{-10} , respectively. The equilibrium constant for the equilibrium
 $\text{CN}^- + \text{CH}_3\text{COOH} \rightleftharpoons \text{HCN} + \text{CH}_3\text{COO}^-$
 would be :-
 (1) 3.0×10^4 (2) 3.0×10^5
 (3) 3.0×10^{-5} (4) 3.0×10^{-4}

AIPMT 2010

- If pH of a saturated solution of $\text{Ba}(\text{OH})_2$ is 12, the value of its K_{sp} is :-
 (1) 5.00×10^{-7} M³ (2) 4.00×10^{-6} M³
 (3) 4.00×10^{-7} M³ (4) 5.00×10^{-6} M³
- In a buffer solution containing equal concentration of B^- and HB the K_b for B^- is 10^{-10} . The pH of buffer solution is :-
 (1) 4 (2) 10 (3) 7 (4) 6

AIIMS 2010

- The pH of blood from 7.26 to 7.42 is maintained by buffer :-
 (1) $\text{H}_2\text{CO}_3/\text{HCO}_3^-$
 (2) $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$
 (3) $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$
 (4) $\text{NH}_2-\text{CH}_2\text{COOH}/\text{NH}_2\text{CH}_2\text{COO}^-$
- K_{sp} of a salt $\text{Ni}(\text{OH})_2$ is 2×10^{-15} then molar solubility of $\text{Ni}(\text{OH})_2$ in 0.01 M NaOH is :-
 (1) 2×10^{-15} M (2) $2^{1/3} \times 10^{-5}$ M
 (3) 2×10^{-11} M (4) 10^{-7} M

AIPMT Mains 2011

- In qualitative analysis, the metals of Group I can be separated from other ions by precipitating them as chloride salts. A solution initially contains Ag^+ and Pb^{2+} at a concentration of 0.10 M. Aqueous HCl is added to this solution until the Cl^- concentration is 0.10 M. What will the concentrations of Ag^+ and Pb^{2+} be at equilibrium ?
 (K_{sp} for $\text{AgCl} = 1.8 \times 10^{-10}$, K_{sp} for $\text{PbCl}_2 = 1.7 \times 10^{-5}$)
 (1) $[\text{Ag}^+] = 1.8 \times 10^{-11}$ M ; $[\text{Pb}^{2+}] = 1.7 \times 10^{-4}$ M;
 (2) $[\text{Ag}^+] = 1.8 \times 10^{-7}$ M ; $[\text{Pb}^{2+}] = 1.7 \times 10^{-6}$ M;
 (3) $[\text{Ag}^+] = 1.8 \times 10^{-11}$ M ; $[\text{Pb}^{2+}] = 8.5 \times 10^{-5}$ M;
 (4) $[\text{Ag}^+] = 1.8 \times 10^{-9}$ M ; $[\text{Pb}^{2+}] = 1.7 \times 10^{-3}$ M;

16. A buffer solution is prepared in which the concentration of NH_3 is 0.30 M and the concentration of NH_4^+ is 0.20 M. If the equilibrium constant, K_b for NH_3 equals 1.8×10^{-5} , what is the pH of this solution ? ($\log 2.7 = 0.43$)
- (1) 9.08 (2) 9.43
(3) 11.72 (4) 8.73

AIIMS 2011

17. K_{sp} of a $\text{CaSO}_4 \cdot 5\text{H}_2\text{O}$ is 9×10^{-6} , Find the volume of CaSO_4 for 1gm (Mw = 136)
- (1) 2.45 litre (2) 5.1 litre
(3) 4.52 litre (4) 3.2 litre
18. 25ml, 0.2M Ca(OH)_2 is neutralised by 10ml of 1M HCl. Then pH of resulting solution is—
- (1) 1.37 (2) 9
(3) 12 (4) 7

AIPMT Mains 2012

19. Buffer solutions have constant acidity and alkalinity because:
- (1) they have large excess of H^+ or OH^- ions
(2) they have fixed value of pH
(3) these give unionised acid or base on reaction with added acid or alkali
(4) acids and alkalies in these solutions are shielded from attack by other ions
20. Equimolar solutions of the following substances were prepared separately. Which one of the these will record the highest pH value?
- (1) LiCl (2) BeCl_2
(3) BaCl_2 (4) AlCl_3

AIIMS 2012

21. Which will not be precipitated after addition of $(\text{NH}_4)_2\text{CO}_3$ in presence of NH_4Cl :-
- (1) Mg (2) Ba
(3) Ca (4) Sr

NEET UG 2013

22. Which is the strongest acid in the following ?
- (1) H_2SO_3 (2) H_2SO_4
(3) HClO_3 (4) HClO_4

AIIMS 2013

23. What will be the solubility product of AX_3 :-
- (1) $27 s^4$ (2) $4s^3$
(3) $36 s^4$ (4) $9s^3$

AIPMT 2014

24. Which of the following salts will give highest pH in water ?
- (1) KCl (2) NaCl
(3) Na_2CO_3 (4) CuSO_4

AIPMT 2015

25. The K_{sp} of Ag_2CrO_4 , AgCl , AgBr and AgI are respectively, 1.1×10^{-12} , 1.8×10^{-10} , 5.0×10^{-13} , 8.3×10^{-17} . Which one of the following salts will precipitate last if AgNO_3 solution is added to the solution containing equal moles of NaCl, NaBr, NaI and Na_2CrO_4 ?
- (1) AgCl (2) AgBr
(3) Ag_2CrO_4 (4) AgI

Re-AIPMT 2015

26. Which one of the following pairs of solution is not an acidic buffer ?
- (1) H_2CO_3 and Na_2CO_3
(2) H_3PO_4 and Na_3PO_4
(3) HClO_4 and NaClO_4
(4) CH_3COOH and CH_3COONa
27. What is the pH of the resulting solution when equal volumes of 0.1 M NaOH and 0.01 M HCl are mixed ?
- (1) 7.0 (2) 1.04
(3) 12.65 (4) 2.0

AIIMS 2015

28. What will be solubility of A_2X_3 if its solubility product (K_{sp}) is equal to 1.08×10^{-23}
- (1) $10^{-5} \text{ mol L}^{-1}$
(2) $3.7 \times 10^{-4} \text{ mol L}^{-1}$
(3) $1.2 \times 10^{-3} \text{ mol L}^{-1}$
(4) $7.5 \times 10^{-4} \text{ mol L}^{-1}$
29. pH of salt of weak acid with strong base at 25°C .
- (1) = 7
(2) > 7
(3) < 7
(4) None

NEET-I 2016

30. MY and NY₃, two nearly insoluble salts, have the same K_{sp} values of 6.2×10^{-13} at room temperature. Which statement would be **true** in regard to MY and NY₃?

- (1) The molar solubilities of MY and NY₃ in water are identical.
- (2) The molar solubility of MY in water is less than that of NY₃
- (3) The salts MY and NY₃ are more soluble in 0.5 M KY than in pure water.
- (4) The addition of the salt of KY to solution of MY and NY₃ will have no effect on their solubilities.

NEET-II 2016

31. The percentage of pyridine (C₅H₅N) that forms pyridinium ion (C₅H₅N⁺H) in a 0.10 M aqueous pyridine solution (K_b for C₅H₅N = 1.7×10^{-9}) is

- (1) 0.77% (2) 1.6%
- (3) 0.0060% (4) 0.013%

32. The solubility of AgCl(s) with solubility product 1.6×10^{-10} in 0.1 M NaCl solution would be

- (1) 1.6×10^{-11} M (2) zero
- (3) 1.26×10^{-5} M (4) 1.6×10^{-9} M

AIIMS 2016

33. Calculate the degree of ionization of 0.04 M HOCl solution having ionization constant 1.25×10^{-4} ?

- (1) 0.025 (2) 0.25 (3) 0.5 (4) 0.055

34. Calculate pH of a salt of weak monobasic acid and weak monoacidic base having concentration 0.1M at 25°C (Given :- pK_a = 4.8, pK_b = 5.2)

- (1) 7.2 (2) 6.8 (3) 9.6 (4) 7

35. The K_{sp} of salt AgCl at 25°C is 2.56×10^{-10} . Then how much volume of H₂O is required to dissolve 0.01 mole of salt.

- (1) 800 L (2) 400 L
- (3) 625 L (4) 50 L

36. Calculate pOH of 10^{-2} M monobasic acid if value of K_w at 90°C is 10^{-12} ?

- (1) 2 (2) 10
- (3) 12 (4) 7

37. K_{sp} of Sr(OH)₂ is x, then calculate value of [OH⁻] in saturated solution?

- (1) $\left(\frac{3x}{4}\right)^{1/3}$ (2) $2\left(\frac{x}{4}\right)^{1/3}$
- (3) $\left(\frac{x}{4}\right)^{1/3}$ (4) $\left(\frac{x}{3}\right)^{1/4}$

NEET(UG) 2017

38. Concentration of the Ag⁺ ions in a saturated solution of Ag₂C₂O₄ is 2.2×10^{-4} mol L⁻¹. Solubility product of Ag₂C₂O₄ is :-

- (1) 2.66×10^{-12} (2) 4.5×10^{-11}
- (3) 5.3×10^{-12} (4) 2.42×10^{-8}

AIIMS 2017

39. Calculate the ratio of solubility of AgCl in 0.1M AgNO₃ and in pure water.

Given : K_{sp} of AgCl = 1.8×10^{-10} :-

- (1) 1.34×10^{-5} M (2) 1.34×10^{-4} M
- (3) 2×10^{-8} M (4) 3×10^{-6} M

40. 200 ml of 0.005 M AgNO₃ reacts with 300 mL of 0.01 M KCl. If K_{sp} of AgCl is 1.8×10^{-10} . Then maximum conc. of Ag⁺ in mixture is :-

- (1) 2×10^{-8} (2) 4.5×10^{-8}
- (3) 4.8×10^{-5} (4) 1.34×10^{-5}

NEET(UG) 2018

41. Following solutions were prepared by mixing different volumes of NaOH and HCl of different concentrations :

a. $60\text{mL} \frac{M}{10} \text{HCl} + 40\text{mL} \frac{M}{10} \text{NaOH}$

b. $55\text{mL} \frac{M}{10} \text{HCl} + 45\text{mL} \frac{M}{10} \text{NaOH}$

c. $75\text{mL} \frac{M}{5} \text{HCl} + 25\text{mL} \frac{M}{5} \text{NaOH}$

d. $100\text{mL} \frac{M}{10} \text{HCl} + 100\text{mL} \frac{M}{10} \text{NaOH}$

pH of which one of them will be equal to 1 ?

- (1) b (2) a
- (3) d (4) c

42. The solubility of BaSO_4 in water $2.42 \times 10^{-3} \text{ g L}^{-1}$ at 298 K. The value of solubility product (K_{sp}) will be
(Given molar mass of $\text{BaSO}_4 = 233 \text{ g mol}^{-1}$)
- $1.08 \times 10^{-10} \text{ mol}^2 \text{ L}^{-2}$
 - $1.08 \times 10^{-12} \text{ mol}^2 \text{ L}^{-2}$
 - $1.08 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$
 - $1.08 \times 10^{-8} \text{ mol}^2 \text{ L}^{-2}$

AIIMS 2018

43. Mixture of ester and HCl is titrated with NaOH using phenolphthalein as an acidic indicator at end point pink color disappear after some time due to :-
- CH_3COOH is formed
 - Due to weak acidic nature of CH_3OH
 - Regeneration of HCl
 - Due to ionization of phenolphthalein
44. 50 ml of 0.1 M NH_3 solution and 10 mL of 0.1 M HCl mixed together then calculate pH of mixture. If $\text{p}K_b$ of NH_3 is 4.75 :-
- 8.86
 - 4.74
 - 9.86
 - 5.32

45. Which of following will have maximum pH :-
- Human saliva
 - Black coffee
 - Human blood
 - Gastric juice
46. Find concentration of $[\text{H}^+]$ after mixing of 15 mL, 0.1M H_2SO_4 and 15ml 0.1M NaOH :-
- 5×10^{-2}
 - 10^{-7}
 - 1×10^{-2}
 - 2×10^{-2}
47. Find the concentration of $[\text{H}^+]$ after mixing 20 mL, 0.1M CH_3COOH and 10 mL, 0.1 M NaOH. Given K_a for CH_3COOH 1.7×10^{-5} .
- 1.7×10^{-5}
 - 3.4×10^{-5}
 - 3.4×10^{-6}
 - 1.7×10^{-4}
48. Solubility of XB_2 is X mol/lit in water find out solubility of XB_2 in 10^{-3} M YB . Consider YB is completely soluble salt :-
- $4X^3 \times 10^{+6}$
 - $4X^3 \times 10^{-6}$
 - 10^{-3}
 - X^3
49. 0.02M of pyridium hydrochloride having $[\text{H}^+]$ is 5.55×10^{-6} what is ionisation constant of pyridine.
- 1.54×10^{-9}
 - 1.54×10^{-7}
 - 1.54×10^{-6}
 - 1.54×10^{-5}

EXERCISE-II (Previous Year Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	2	3	2	2	1	1	2	2	1	1	1	1	3	4
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	2	1	4	3	3	1	4	1	3	3	3	3	1	2	2
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	4	4	4	2	3	2	2	3	2	2	4	1	4	3	3
Que.	46	47	48	49											
Ans.	1	1	1	1											

EXERCISE-III (Analytical Questions)

- The concentration of $[H^+]$ and concentration of $[OH^-]$ of a 0.1 M aqueous solution of 2% ionised weak acid is [ionic product of water = 1×10^{-14}] :-
(1) 0.02×10^{-3} M and 5×10^{-11} M
(2) 1×10^{-3} M and 3×10^{-11} M
(3) 2×10^{-3} M and 5×10^{-12} M
(4) 3×10^{-2} M and 4×10^{-13} M
- The solubility of $BaSO_4$ in water, is $2.33 \times 10^{-3} \text{ gL}^{-1}$. Its solubility product will be (molecular weight of $BaSO_4 = 233$) :-
(1) 1×10^{-5} (2) 1×10^{-10}
(3) 1×10^{-15} (4) 1×10^{-20}
- What will be the H^+ ion concentration, when 4 g NaOH dissolved in 1000 mL of water:
(1) 10^{-1} (2) 10^{-13} (3) 10^{-4} (4) 10^{-10}
- When 10 mL of 0.1 M acetic acid ($pK_a=5.0$) is titrated against 10 mL of 0.1 M ammonia solution ($pK_b = 5.0$), the equivalence point occurs at pH:
(1) 5.0 (2) 6.0 (3) 7.0 (4) 9.0
- At 25°C , the dissociation constant of a base, BOH, is 1.0×10^{-12} . The concentration of hydroxyl ions in 0.01M aqueous solution of the base would be:
(1) $1.0 \times 10^{-6} \text{ mol L}^{-1}$ (2) $1.0 \times 10^{-7} \text{ mol L}^{-1}$
(3) $2.0 \times 10^{-6} \text{ mol L}^{-1}$ (4) $1.0 \times 10^{-5} \text{ mol L}^{-1}$
- The solubility product of $BaSO_4$ at 25°C is 1.0×10^{-9} . What would be the concentration of H_2SO_4 necessary to precipitate $BaSO_4$ from a solution of 0.01 M Ba^{+2} ions :-
(1) 10^{-9} (2) 10^{-8} (3) 10^{-7} (4) 10^{-6}
- pH of the solution of $HCOONH_4$ is 6.48 this can be explained by :-
(1) Hydrolysis of both cation and anion
(2) Hydrolysis of cation
(3) Hydrolysis of anion
(4) Hydrolysis of water
- The correct representation of solubility product of SnS_2 is :-
(1) $[Sn^{4+}][S^{2-}]^2$ (2) $[Sn^{4+}][S^{2-}]$
(3) $[Sn^{4+}][2S^{2-}]$ (4) $[Sn^{4+}][2S^{2-}]^2$
- A solution of $FeCl_3$ in water acts as acidic due to:-
(1) Acidic impurities
(2) Ionisation
(3) Hydrolysis of Fe^{3+}
(4) Dissociation

Check Your Understanding

- The pK_a of HNO_2 is 3.37. The pH of HNO_2 in its 0.01 mol L^{-1} aqueous solution will be :-
(1) 5.37 (2) 2.69 (3) 1.69 (4) 0.69
- When 0.01 M HCl is added in aqueous solution of acetic acid then :-
(1) $[CH_3COO^-]$ decreases
(2) $[CH_3COOH]$ decreases
(3) $[CH_3COO^-]$ increases
(4) NOT
- On passing H_2S gas through a solution of Cu^{+2} and Zn^{+2} ions, CuS is precipitated first because:-
(1) Solubility product of CuS is equal to the ionic product of ZnS ;
(2) Solubility product of CuS is equal to the solubility product of ZnS.
(3) Solubility product of CuS is lower than the solubility product of ZnS.
(4) Solubility product of CuS is greater than the solubility product of ZnS.
- Solubility of MX_2 - type electrolytes is $0.5 \times 10^{-4} \text{ mol L}^{-1}$ then find out K_{sp} of electrolytes:-
(1) 5×10^{-12} (2) 25×10^{-10}
(3) 1×10^{-13} (4) 5×10^{-13}
- A solution of $MgCl_2$ in water has pH :
(1) < 7 (2) > 7 (3) 7 (4) 14.2
- When H_2S gas is passed through the HCl containing aqueous solutions of $CuCl_2$, $HgCl_2$, $BiCl_3$ and $CoCl_2$, it does not precipitate out :
(1) CuS (2) HgS (3) Bi_2S_3 (4) CoS
- Mark the correct statement :
(1) I group basic radicals precipitate as chloride.
(2) IV group basic radicals precipitate as sulphides
(3) V group basic radicals precipitate as carbonates
(4) All the above statements are correct
- The role of NH_4Cl in group III for analysis of cations is :-
(1) that it acts as a catalyst.
(2) that it increases the solubility of hydroxides.
(3) that it lowers the OH^- concentration.
(4) that it causes the precipitation of cations as chlorides.
- K_{sp} of $Ca_3(PO_4)_2$ is :-
(1) $[Ca^{+2}][PO_4^{-3}]^2$ (2) $[Ca^{+2}]^3 [PO_4^{-3}]^2$
(3) $[Ca^{+2}]^2 [PO_4^{-3}]^3$ (4) $[Ca^{+2}] [PO_4^{-3}]$

- 19.** An acid HA has dissociated as following manner
 $HA \rightleftharpoons H^+ + A^-$
 It has concentration 1 M and pH = 5 then find out dissociation constant :-
 (1) 1×10^{-10} (2) 1×10^{-5}
 (3) 5×10^{-5} (4) 5
- 20.** Which of the following group of cations will be precipitated when passing of H_2S gas in the presence of acidic medium:-
 (1) Cu^{+2} , Cr^{+3} (2) Zn^{+2} , Co^{+2}
 (3) Cu^{+2} , Cd^{+2} (4) Al^{+3} , Cd^{+2}
- 21.** Solution of sodium carbonate is :-
 (1) Strongly acidic (2) Weakly basic
 (3) Strongly basic (4) Weakly acidic
- 22.** Aqueous solution of $Al_2(SO_4)_3$ is :-
 (1) Basic & acidic (2) Neutral
 (3) Basic (4) Acidic
- 23.** In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (Molecular mass = 283). The equilibrium which sets in is
 $AgIO_{3(s)} \rightleftharpoons Ag^+_{(aq)} + IO_{3(aq)}^-$ If the solubility product constant K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8} , what is the mass of $AgIO_3$ contained in 100 mL of its saturated solution :-
 (1) 2.83×10^{-3} g (2) 1.0×10^{-7} g
 (3) 1.0×10^{-4} g (4) 28.3×10^{-2} g
- 24.** If k_{sp} of CaF_2 in pure water is 1.70×10^{-10} , then find the solubility of CaF_2 in 0.10M NaF solution :-
 (1) 1.70×10^{-10} (2) 1.70×10^{-9}
 (3) 1.70×10^{-8} (4) 0.10 M
- 25.** The solubility product of $AgCl$ is 1×10^{-10} , then solubility of $AgCl$ is :-
 (1) 1×10^{-10} (2) 1×10^{-7}
 (3) 1×10^{-5} (4) 1×10^{-8}
- 26.** To precipitate Zn in form of ZnS , Why NH_4OH is first added in the solution before H_2S gas is passed through it :-
 (1) To convert Zn into Zn^{+2}
 (2) To reduce Zinc
 (3) To decrease the dissociation of H_2S
 (4) To increase the dissociation of H_2S
- 27.** K_a for CH_3COOH is 1.8×10^{-5} . Find out the percentage dissociation of 0.2M CH_3COOH in 0.1M HCl solution
 (1) 0.018 (2) 0.36 (3) 18 (4) 36
- 28.** The pK_a of a weak acid HA is 4.80. The pK_b of weak base BOH is 4.78. The pH of an aqueous solution of the corresponding salt BA will be :
 (1) 9.58 (2) 4.79 (3) 7.01 (4) 9.22
- 29.** 0.2M solution of $HCOOH$ is 3.2% ionised then find ionisation constant of acid :-
 (1) 4.2×10^{-4} (2) 4.2×10^{-5}
 (3) 2.1×10^{-4} (4) 2.1×10^{-5}
- 30.** Three reactions involving $H_2PO_4^-$ are given below :-
 (i) $H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO_4^-$
 (ii) $H_2PO_4^- + H_2O \rightarrow HPO_4^{2-} + H_3O^+$
 (iii) $H_2PO_4^- + OH^- \rightarrow H_3PO_4 + O^{2-}$
 In which of the above does $H_2PO_4^-$ act as an acid ?
 (1) (i) only (2) (ii) only
 (3) (i) and (ii) (4) (iii) only
- 31.** Given that for HA acid, $K_a = 10^{-6}$ and for MOH base $K_b = 10^{-6}$. The pH of 0.1 M MA salt solution will be :-
 (1) 5 (2) 7 (3) 9 (4) 2
- 32.** The K_{sp} for $Cr(OH)_3$ is 1.6×10^{-30} . The molar solubility of this compound in water is :-
 (1) $\sqrt[3]{1.6 \times 10^{-30}}$ (2) $\sqrt[4]{1.6 \times 10^{-30}}$
 (3) $\sqrt[4]{1.6 \times 10^{-30} / 27}$ (4) $1.6 \times 10^{-30} / 27$
- 33.** An acid HA ionises as
 $HA \rightleftharpoons H^+ + A^-$
 The pH of 1.0 M solution is 5. Its dissociation constant would be :-
 (1) 1×10^{-10} (2) 5
 (3) 5×10^{-8} (4) 1×10^{-5}
- 34.** The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant, K_a of this acid is :-
 (1) 1×10^{-7} (2) 3×10^{-7}
 (3) 1×10^{-3} (4) 1×10^{-5}
- 35.** How many litres of water must be added to 1 litre of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2 ?
 (1) 0.1 L (2) 0.9 L (3) 2.0 L (4) 9.0 L
- 36.** What volume of 0.1M H_2SO_4 is needed to completely neutralize 40 mL of 0.2M NaOH solution-
 (1) 10 mL (2) 40 mL (3) 20 mL (4) 80 mL

- 37.** If pH value of a solution is 3 and by adding water, it becomes 6, then the dilution is increased by :
 (1) 10 times (2) 100 times
 (3) 500 times (4) 1000 times
- 38.** The aqueous solution of which of the following salt will have the lowest pH
 (1) NaClO (2) NaClO₂
 (3) NaClO₃ (4) NaClO₄
- 39.** In the reaction $I_2 + I^- \rightarrow I_3^-$, the Lewis base is :
 (1) I⁻ (2) I₂
 (3) I₃⁻ (4) None of these
- 40.** In which of the following acid–base titration, pH is greater than 8 at equivalence point:-
 (1) Acetic acid versus ammonia
 (2) Acetic acid versus sodium hydroxide
 (3) Hydrochloric acid versus ammonia
 (4) Hydrochloric acid versus sodium hydroxide
- 41.** Which one of the following compounds is not a protonic acid :-
 (1) B(OH)₃ (2) PO(OH)₃
 (3) SO(OH)₂ (4) SO₂(OH)₂
- 42.** Which one of the following is NOT a buffer solution:-
 (1) 0.8M H₂S + 0.8M KHS
 (2) 2M C₆H₅NH₂ + 2M C₆H₅N⁺H₃Br
 (3) 3M H₂CO₃ + 3M KHCO₃
 (4) 0.05M KClO₄ + 0.05M HClO₄
- 43.** The rapid change of pH near the stoichiometric point of an acid–base titration is the basis of indicator detection. pH of the solution is related to ratio of the concentrations of the conjugate acid (HIn) and base (In⁻) forms of the indicator by the expression:-
 (1) $\log \frac{[HIn]}{[In^-]} = pK_{in} - pH$
 (2) $\log \frac{[HIn]}{[In^-]} = pH - pK_{in}$
 (3) $\log \frac{[In^-]}{[HIn]} = pH + pK_{in}$
 (4) $\log \frac{[In^-]}{[HIn]} = pK_{in} - pH$
- 44.** What is the pH of 0.01M glycine solution? For glycine, $K_{a1} = 4.5 \times 10^{-3}$ and $K_{a2} = 1.7 \times 10^{-10}$ at 298 K.
 (1) 3.0 (2) 10.0 (3) 6.1 (4) 7.2
- 45.** The correct order of acid strength is –
 (1) HClO₄ < HClO₃ < HClO₂ < HClO
 (2) HClO₂ < HClO₃ < HClO₄ < HClO
 (3) HClO₄ < HClO < HClO₂ < HClO₃
 (4) HClO < HClO₂ < HClO₃ < HClO₄
- 46.** Concentrations of NH₄Cl and NH₄OH in a buffer solution are in the ratio 1 : 10. If K_b for NH₄OH is 10^{-10} , then pH of the buffer is :-
 (1) 4 (2) 5 (3) 9 (4) 11
- 47.** 10 mL concentrated H₂SO₄ (18 molar) is diluted to 1 litre. Concentration of diluted acid is:-
 (1) 0.18N (2) 0.09N (3) 0.36N (4) 18N
- 48.** When HF is dissolved in formic acid, the equilibrium established is :-
 $HF + HCOOH \rightleftharpoons F^- + HCOOH_2^+$
 the true pair of conjugate acid base is as a [acid, conjugate acid] [Base, conjugate base]:-
 (1) (HF, HCOOH) and (HCOOH₂⁺, F⁻)
 (2) (HF, HCOOH₂⁺) and (HCOOH, F⁻)
 (3) (HCOOH₂⁺, HF) and (F⁻, HCOOH)
 (4) (HF, F⁻) and (HCOOH₂⁺, HCOOH)
- 49.** How many grams of dibasic acid (mol. wt. = 200) should be present in 100 mL the aqueous solution to give strength of (N/10) :-
 (1) 1g. (2) 2g. (3) 5g. (4) 10g.
- 50.** In a mixture of equimolar solutions of NaHCO₃ and NaOH the species present in solution shall be:-
 (1) Na₂CO₃ (2) NaHCO₃ + NaOH
 (3) NaOH (4) NaHCO₃ + Na₂CO₃
- 51.** An aqueous solution contains 10^{-4} [H⁺]. If it is diluted by mixing equal volume of water then the concentration of OH⁻ in mol dm⁻³ will be :-
 (1) 0.5×10^{-10} (2) 2×10^{-10}
 (3) 10^{-6} (4) 10^{-8}
- 52.** Which of the following is right for diprotic acid :
 (1) $K_{a2} > K_{a1}$ (2) $K_{a1} > K_{a2}$
 (3) $K_{a2} > \frac{1}{K_{a1}}$ (4) $K_{a2} = K_{a1}$

53. The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be:-
 (1) 5.0×10^{15} (2) 5.0×10^{-15}
 (3) 0.2×10^5 (4) 5.0×10^{-5}
54. The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is :-
 (1) 2.5 (2) 9.5 (3) 7.0 (4) 4.5
55. 50 mL solution of 0.1M CH_3COOH ($pK_a = 4.73$) is titrated with 0.1M NaOH solution, pH of solution when half of CH_3COOH is neutralized
 (1) 4.53 (2) 4.63 (3) 4.73 (4) 4.83
56. pK_a of Quinoline base is 4.88. What will be the pK_a of 0.01M solution of it
 (1) 4.88 (2) 0.01 (3) 9.12 (4) 14
57. The pH of an aqueous solution of a 1×10^{-7} M solution of HCl will be :-
 (1) 7 (2) slightly less than 7
 (3) slightly greater than 7 (4) 1
58. What will be the concentration of H^+ ions in 0.1M acetic acid and 0.1M sodium acetate solution, if the dissociation constant of acetic acid is 1.8×10^{-5} ?
 (1) 1.8×10^{-7} (2) 1.8×10^{-5}
 (3) 1.8×10^{-2} (4) 1.8×10^{-3}
59. Calculate the pH of 4×10^{-3} M, $Y(OH)_2$ solution assuming the first dissociation to be 100% second dissociation to be 50%:-
 (1) 11.78 (2) 9.9 (3) 2.5 (4) 2.22

EXERCISE-III (Analytical Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	2	2	3	2	4	1	1	3	2	1	3	4	1	4
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	4	3	2	1	3	2	4	1	3	3	4	1	3	3	2
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	2	3	1	4	4	2	4	4	1	2	1	4	1	3	4
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	
Ans.	2	3	2	1	1	2	2	2	2	3	1	2	2	1	

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

- Assertion :-** When small amount of acid or base is added to pure water, its pH undergoes a change.
Reason :- Addition of an acid or base increases the degree of ionisation of water.
 (1) A (2) B (3) C (4) D
- Assertion :-** Solubility of AgBr decreases in the presence of sodium bromide.
Reason :- Sodium bromide undergoes hydrolysis in water.
 (1) A (2) B (3) C (4) D
- Assertion :-** The pH of an aqueous solution of acetic acid remains unchanged on the addition of sodium acetate.
Reason :- The ionisation of acetic acid is suppressed by the addition of sodium acetate.
 (1) A (2) B (3) C (4) D
- Assertion :-** If HCl gas is passed through saturated NaCl solution, solid NaCl starts to precipitate.
Reason :- HCl decreases the solubility product of NaCl.
 (1) A (2) B (3) C (4) D
- Assertion :-** The aqueous solution of Na_3PO_4 is alkaline in nature.
Reason :- Na_3PO_4 in its aqueous solution undergoes anionic hydrolysis.
 (1) A (2) B (3) C (4) D
- Assertion :-** If $K_{sp} < \text{ionic product}$, precipitate is formed.
Reason :- Solubility product (K_{sp}) is the highest limit of ionic product of the electrolyte in saturated solutions.
 (1) A (2) B (3) C (4) D
- Assertion :-** To precipitate the cations of fourth group in qualitative analysis, medium is made alkaline before passing H_2S gas.
Reason :- This is done to suppress the ionisation of H_2S .
 (1) A (2) B (3) C (4) D
- Assertion :-** When an acid or a base is added to water at constant temperature the pH changes.
Reason :- This is due to change in ionic product of water.
 (1) A (2) B (3) C (4) D
- Assertion :** Addition of NH_4OH to an aqueous solution of BaCl_2 in the presence of NH_4Cl (excess) precipitates Ba(OH)_2 .
Reason : Ba(OH)_2 is insoluble in water.
 (1) A (2) B (3) C (4) D
- Assertion :-** Sb(III) is not precipitated as sulphide when in its alkaline solution H_2S is passed.
Reason :- The concentration of S^{2-} ion in alkaline medium is inadequate for precipitation.
 (1) A (2) B (3) C (4) D
- Assertion :-** For H_2SO_4 , K_{a1} value is much greater than K_{a2} .
Reason :- H_2SO_4 is a strong acid.
 (1) A (2) B (3) C (4) D
- Assertion :-** Solubility of salt of SB and WA changes when pH of the solution is changed.
Reason :- Solubility product (K_{sp}) depends on pH.
 (1) A (2) B (3) C (4) D
- Assertion :-** A mixture of a weak acid CH_3COOH and sodium acetate forms a buffer solution.
Reason :- A buffer solution reacts with small quantities of hydrogen or hydroxyl ions and keeps the pH almost same.
 (1) A (2) B (3) C (4) D
- Assertion :-** At 25°C the pH of 10^{-8} M HCl is 8.
Reason :- pH of acidic solution is always below 7 at 25°C .
 (1) A (2) B (3) C (4) D

15. **Assertion :-** In the acid base titration involving a strong base and a weak acid methyl orange can be used as an indicator.

Reason :- Methyl orange changes its colour in pH range 3 to 5.

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

16. **Assertion :-** pH of a buffer changes with temperature.

Reason :- Ionic product of water (K_w) changes with temperature.

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

17. **Assertion :-** H_3PO_3 is a dibasic compound.

Reason :- The two H-atom are directly attached to P.

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

18. **Assertion :** Boric acid behaves as a weak monobasic acid.

Reason : Boric acid contains hydrogen bonds in its structure.

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

19. **Assertion :** H_2O is amphoteric in nature.

Reason : H_2O can accept a proton to form H_3O^+ ion and can donate a proton to form OH^- ion.

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

20. **Assertion :** All Arrhenius acids are also Bronsted acids.

Reason : All Bronsted bases are also Lewis bases.

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

21. **Assertion :-** The buffer solution has a capacity to resist the change in pH value on addition of small amount of acid or base to it.

Reason :- pH value of buffer solution does not change on dilution or on keeping for long.

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

22. **Assertion :-** The species in the buffer must not react with each other.

Reason :- The pH of a buffer depends on the value of K_a of the weak acid and the relative concentration of that acid and its conjugate base.

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

23. **Assertion :-** Only a very small amount of indicator should be used.

Reason :- So that addition of the indicator does not effect the pH of the solution.

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

24. **Assertion :-** Solubility of sparingly soluble salt increases with increase in temperature.

Reason :- Enthalpy of solution is negative for all salts.

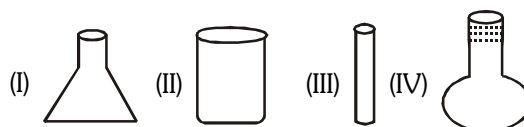
(1) A (2) B (3) C (4) D

25. **Assertion :-** HCl is titrated with NaOH using phenolphthalein as indicator, pink colour appears in solution when OH^- ion is present in excess in solution.

Reason :- At end point, both reacting species, neutralises each other.

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

26. **Assertion :-**



II is more suitable for titration.

Reason :- It is difficult to add titrant in first.

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

27. **Assertion :** In $NaHCO_3$ solution phenolphthalein is colorless.

Reason : Phenolphthalein is colorless in basic medium and pH of $NaHCO_3$ is less than 10.

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

28. **Assertion :-** Na_2SO_3 is alkaline towards litmus.

Reason :- H_2SO_3 is formed due to hydrolysis.

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

EXERCISE-IV (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	3	4	3	1	1	3	3	4	4	2	3	1	4	4
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28		
Ans.	2	3	2	1	3	2	2	1	3	2	4	4	2		

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NEET SYLLABUS

CHEMICAL KINETICS : Rate of a reaction (average and instantaneous), order and molecularity of a reaction; rate law and specific rate constant, integrated rate equations and half life (only for zero and first order reactions); concept of collision theory (elementary idea, no mathematical treatment). Activation energy, Arrhenious equation; factors affecting rate of reaction; concentration, temperature, catalyst.

OBJECTIVES

After studying this unit, we will be able to :

- *define the average and instantaneous rate of a reaction.*
- *write the rate of reaction in form of change in concentration of reactants or products.*
- *compare elementary and complex reactions.*
- *compare molecularity and order of a reaction.*
- *describe rate constant*
- *explain the dependence of rate of reaction on concentration, temperature and catalyst.*
- *derive integrated rate equations for zero, first and n^{th} order reactions.*
- *determine rate constants for various reactions.*
- *describe collision theory of reaction rates.*

"Kinetic research conducts to the knowledge of philosophical truth, and forms the mind to philosophical enlargement and accuracy of thought, more happily than almost any other investigation in which the human intellect can be employed"

Alexander Tilloch

CHEMICAL KINETICS

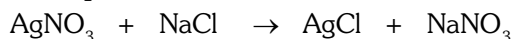
2.0 INTRODUCTION

Chemical Kinetics is the branch of physical chemistry which deals with the study of rate of reactions, the mechanism by which the reactions proceed and factors affecting rate of reaction.

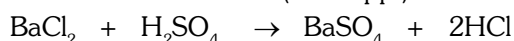
On the basis of rate, chemical reaction are broadly divided into three categories :-

(a) Very fast or instantaneous reactions : Generally these reactions involve ionic species and known as ionic reactions. These reactions take about 10^{-14} or 10^{-16} seconds for completion. So, it is almost impossible to determine the rate of these reactions.

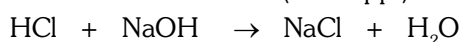
Examples :



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(white ppt)

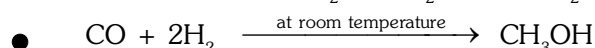


(b) Very slow reactions : These reactions proceed very slowly, may take days or months to show any measurable change at room temperature.

Examples :

- Rusting of iron.

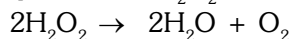
- Reaction between H_2 and O_2 to form H_2O at ordinary temperature in absence of catalyst.



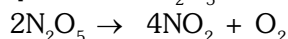
(c) Moderate or slow reactions : This type of reactions proceed with a measurable rates at normal temperature and we can measure the rate of these reactions easily. Mostly these reactions are molecular in nature.

Examples :

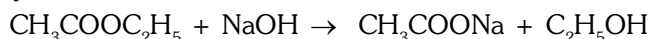
- Decomposition of H_2O_2



- Decomposition of N_2O_5

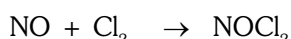


- Hydrolysis of ester



- Inversion of cane sugar in aqueous solution

- Reaction of NO with chlorine



2.1 RATE OF REACTION

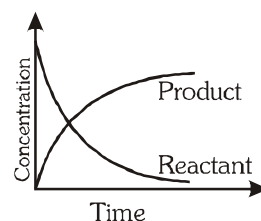
Rate of reaction is defined as the change in concentration or pressure of reactant or product per unit time. It is always a positive quantity.

$$\text{Rate of reaction} = \frac{\text{Change in concentration of reactant or product}}{\text{Time taken in change}} \quad \boxed{r = \pm \frac{\Delta C}{\Delta t}}$$

Where ΔC = change in concentration in a small interval Δt
[+] sign is used when we refer for product concentration.
[-] sign is used when we refer for reactant concentration.

For gaseous reactions $r = \pm \frac{\Delta P}{\Delta t}$ (unit of rate = pressure time⁻¹)

$$\text{and } r = \frac{1}{RT} \times \left[\pm \frac{\Delta P}{\Delta t} \right] \quad (\text{unit of rate} = \text{M time}^{-1})$$



Types of Rate of Reactions :-

(A) Average Rate of Reaction

The rate of reaction over a certain measurable period of time during the course of reaction is called average rate of reaction. It is denoted by $\bar{r}$.

For a reaction $A \longrightarrow B$

$$r_{\text{average}} = \bar{r} = \left(\frac{[A]_2 - [A]_1}{t_2 - t_1} \right) = - \frac{\Delta[A]}{\Delta t}$$

Where $[A]_1$ = Concentration of reactant A at time t_1 ,

$[A]_2$ = Concentration of reactant A at time t_2 .

(B) Instantaneous Rate of Reaction

The rate of reaction at any particular instant during the course of reaction is called instantaneous rate of reaction.

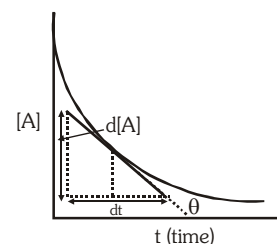
For a reaction $A \longrightarrow B$

Mathematically ; Instantaneous rate = $\lim_{\Delta t \rightarrow 0}$ (Average rate)

$$r_{\text{inst}} = \lim_{\Delta t \rightarrow 0} \left(- \frac{\Delta[A]}{\Delta t} \right) = \lim_{\Delta t \rightarrow 0} \left(\frac{\Delta[B]}{\Delta t} \right) \quad \text{or} \quad \boxed{r_{\text{inst}} = (-) \frac{d[A]}{dt} = (+) \frac{d[B]}{dt}}$$

Hence, Slope of the tangent at time t in plot of concentration with time gives instantaneous rate of reaction.

$$\text{Instantaneous rate of reaction} = \lim_{\Delta t \rightarrow 0} \left(\pm \frac{\Delta C}{\Delta t} \right) = \pm \frac{dC}{dt}$$



2.2 RATE OF REACTION IN THE FORM OF STOICHIOMETRY OF A CHEMICAL REACTION

Let us consider a reaction : $m_1A + m_2B \rightarrow n_1P + n_2Q$

Where, Rate of disappearance of A = $-\frac{d[A]}{dt}$

Rate of disappearance of B = $-\frac{d[B]}{dt}$

Rate of appearance of P = $\frac{d[P]}{dt}$

Rate of appearance of Q = $\frac{d[Q]}{dt}$

$$\boxed{\text{Rate of reaction} = \frac{1}{m_1} \left(- \frac{d[A]}{dt} \right) = \frac{1}{m_2} \left(- \frac{d[B]}{dt} \right) = \frac{1}{n_1} \frac{d[P]}{dt} = \frac{1}{n_2} \frac{d[Q]}{dt}}$$

- Rate of reaction is always positive; negative sign represents decrease in concentration of reactant.

Units of Rate of Reaction

Unit of rate of reaction = $\text{mol L}^{-1} \text{time}^{-1}$ i.e. ($\text{mol L}^{-1} \text{s}^{-1}$ or $\text{mol L}^{-1} \text{min}^{-1}$ or $\text{mol L}^{-1} \text{h}^{-1}$)

Illustrations

Illustration 1. For the reaction : $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$. If the concentration of NO_2 increases by $1.6 \times 10^{-2} \text{ M}$ in 4 s. Calculate the following -

- (i) rate of formation of NO₂
 (ii) rate of formation of O₂
 (iii) rate of disappearance of N₂O₅
 (iv) rate of reaction

Solution. (i) Rate of formation of NO_2 : $\frac{d[\text{NO}_2]}{dt} = \frac{1.6 \times 10^{-2}}{4} = 4.0 \times 10^{-3} \text{ M/s}$

- (ii) Rate of formation of O_2 : $\frac{d[O_2]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt} = \frac{1}{4} \times 4 \times 10^{-3} = 1.0 \times 10^{-3} \text{ M/s}$

- (iii) Rate of disappearance of N_2O_5 : $-\frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{1}{2} \times 4 \times 10^{-3} = 2.0 \times 10^{-3} \text{ M/s}$

- $$\text{(iv) Rate of reaction} = \frac{1}{2} \left(-\frac{d[\text{N}_2\text{O}_5]}{dt} \right) = \frac{1}{2} \times 2 \times 10^{-3} = 1.0 \times 10^{-3} \text{ M/s}$$

$$\text{or } \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{1}{4} \times 4 \times 10^{-3} = 1.0 \times 10^{-3} \text{ M/s}$$

$$\text{or } \frac{d[\text{O}_2]}{dt} = 1.0 \times 10^{-3} \text{ M/s}$$

Illustration 2. Express the rate of reaction for the following changes :

- (a) $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$
(b) $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$

Solution. (a) Rate of reaction $= \frac{1}{2} \left(-\frac{d[\text{HI}]}{dt} \right) = \frac{d[\text{H}_2]}{dt} = \frac{d[\text{I}_2]}{dt}$

- $$(b) \text{ Rate of reaction} = \frac{1}{2} \left(-\frac{d[\text{SO}_2]}{dt} \right) = \frac{-d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{SO}_3]}{dt}$$

BEGINNER'S BOX-1

1. The rate of a reaction is expressed as :

$$+\frac{1}{2}\frac{\Delta[C]}{\Delta t}=\frac{1}{3}\frac{\Delta[D]}{\Delta t}=\frac{1}{4}\left(-\frac{\Delta[A]}{\Delta t}\right)=\left(-\frac{\Delta[B]}{\Delta t}\right)$$

Then reaction is

- (1) $4A + B \rightarrow 2C + 3D$
(3) $A + B \rightarrow C + D$

- $$\begin{aligned} (2) \quad & \text{B} + 3\text{D} \rightarrow 4\text{A} + 2\text{C} \\ (4) \quad & \text{B} + \text{D} \rightarrow \text{A} + \text{C} \end{aligned}$$

2. In the reaction, $A + 2B \rightarrow 6C + 2D$ if the initial rate $(-)\frac{\Delta[A]}{\Delta t}$ at $t = 0$ is $2.6 \times 10^{-2} \text{ M s}^{-1}$, what will

be the value of $(-)\frac{\Delta[B]}{\Delta t}$ at $t = 0$?

- (1) $8.5 \times 10^{-2} \text{ M s}^{-1}$ (2) $2.6 \times 10^{-2} \text{ M s}^{-1}$ (3) $5.2 \times 10^{-2} \text{ M s}^{-1}$ (4) $7.5 \times 10^{-2} \text{ M s}^{-1}$

3. In the following reaction, how is the rate of appearance of the underlined product related to the rate of disappearance of the underlined reactant $\text{BrO}_3^-(\text{aq}) + 5\text{Br}^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\ell) + 3\text{H}_2\text{O}(\text{aq})$

(1) $(-)\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{\Delta[\text{Br}_2]}{\Delta t}$ (2) $(-)\frac{1}{3}\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{\Delta[\text{Br}_2]}{\Delta t}$ (3) $(-)\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{1}{3}\frac{\Delta[\text{Br}_2]}{\Delta t}$ (4) None of these

2.3 RATE LAW

The experimental expression of rate of reaction in terms of concentration of reactants is known as rate law. In this expression the rate of a reaction is proportional to the product of molar concentration of reactants with each term raised to the power or exponent that has to be found experimentally.

In a chemical reaction :- $aA + bB \longrightarrow \text{Product}$

The rate law is :- $\text{Rate} \propto [A]^x[B]^y$

The values of exponents x and y are found experimentally which may or may not be same as stoichiometric coefficients.

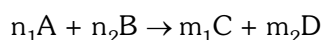
Above relationship can be written as :-

$$\text{Rate} = k[A]^x[B]^y$$

Where k is a proportionality constant known as rate constant.

Rate constant :

In a chemical reaction –



according to law of mass action

$$\text{Rate} = k[A]^{n_1}[B]^{n_2}$$

but according to rate law (experimental concept)

$$\text{Rate} = k[A]^x[B]^y$$

if $[A] = [B] = 1 \text{ mol/L}$

then, $\text{Rate} = k$

Rate of reaction at unit concentration of reactants is called as rate constant or specific reaction rate.

Rate constant does not depend on concentration of reactant but it depends on temperature and catalyst.

2.4 ORDER OF REACTION –

The sum of powers of concentration of reactants in rate law expression is known as order of reaction.

For the reaction $aA + bB \rightarrow \text{Product}$

Rate law is $\text{Rate} = k[A]^x[B]^y$

Here

$x = \text{order of reaction with respect to A}$

$y = \text{order of reaction with respect to B}$

$x + y = n \text{ (overall order of reaction)}$

- Order of reaction may be zero, positive, negative or fractional.
- Order of reaction is an experimental quantity.

Units of rate constant :

$$\text{Rate} = k[A]^n$$

$$k = \frac{r}{[A]^n} = \frac{\text{unit of rate}}{[\text{unit of concentration}]^n} = \frac{\frac{\text{mol}}{\text{L}} \times \text{time}^{-1}}{\left[\frac{\text{mol}}{\text{L}}\right]^n}$$

- Unit of $k = \left[\frac{\text{mol}}{\text{L}}\right]^{1-n} \times \text{time}^{-1}$
- For gaseous reaction unit of k may be $= (\text{atm})^{1-n} \times \text{time}^{-1}$

2.5 MECHANISM OF REACTION :

(a) Elementary reactions :

Those reactions which completes in single step and which have exponents in rate law equal to stoichiometric coefficients of the reactants.

If $A + B \longrightarrow \text{Products}$; is an elementary reaction
then rate law will be –

$$\text{Rate} = k[A][B]$$

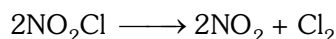
- Zero order reactions can never be elementary reactions.
- For elementary reactions fractional order is not possible.

(b) Complex reactions :

Those reactions which complete in multisteps. For these reactions a mechanism is proposed.

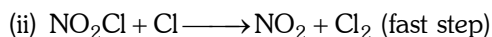
- For complex reactions the overall rate of reaction is controlled by the slowest step which is called as rate determining step (R.D.S.).
- In rate law expression rate of reaction depends on concentration of reactants of slowest step which must be free from intermediate.
- If R.D.S. contains intermediate, its value is solved using K_{eq} of fast step (assumed as reversible)

Example-1



Experimentally, the rate law is $\text{Rate} = k[\text{NO}_2\text{Cl}]$

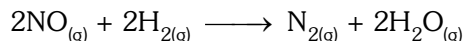
The mechanism of the reaction is given as –



So the rate law from slowest step $\text{Rate} = k[\text{NO}_2\text{Cl}]$

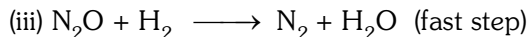
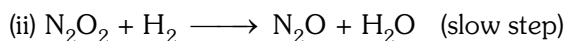
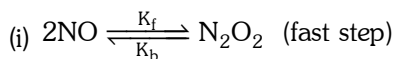
In this way the predicted rate law derived from two step mechanism agrees with experimental rate law.

Example-2



experimentally the rate law is, $\text{Rate} = k [\text{NO}]^2[\text{H}_2]$

The mechanism of the reaction is given as –



The Rate law from slowest step is :

$$\text{Rate} = k[\text{N}_2\text{O}_2][\text{H}_2]$$

The rate law expression should be free from intermediate species N_2O_2 .

From fast reversible step –

$$k_f[\text{NO}]^2 = k_b[\text{N}_2\text{O}_2]$$

$$\therefore [\text{N}_2\text{O}_2] = \frac{k_f}{k_b} [\text{NO}]^2$$

and rate law becomes

$$\text{Rate} = k \left(\frac{k_f}{k_b} \right) [\text{NO}]^2 [\text{H}_2]$$

therefore, $\text{Rate} = k'[\text{NO}]^2[\text{H}_2]$

This derived rate law agrees with experimental rate law.

2.6 MOLECULARITY

Total number of molecules, atoms or ions (reacting species) participating in an elementary reaction is called as molecularity of reaction.

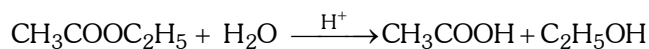
- Molecularity is a theoretical quantity.
- Molecularity can be an integer (1, 2 or 3) but it cannot be zero or negative or fractional.
- In elementary reaction molecularity is equal to its order.
- In complex reaction molecularity of each step of mechanism is defined separately.
- Total molecularity of complex reaction is meaningless.
- In complex reactions generally molecularity of slowest step is same as order of reaction which can be considered as molecularity of reaction. (Except when slowest step contain intermediate)
- Maximum value of molecularity or order is 3 because chances of effective collision of more than three molecules is very rare.

2.7 PSEUDO FIRST ORDER REACTION

A chemical reaction in which value of order of reaction is one but molecularity is more than one are known as pseudo unimolecular/pseudo first order reaction.

Example-1

Hydrolysis of ester in acidic medium.



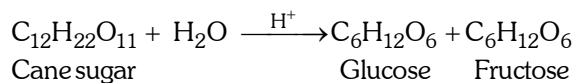
$$\text{Rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]$$

Water is in excess then its concentration remain constant during the reaction and $[\text{H}_2\text{O}]$ is taken as constant therefore,

$$\text{Rate} = k' [\text{CH}_3\text{COOC}_2\text{H}_5] \quad \text{where } k' = k [\text{H}_2\text{O}]$$

Example-2

Inversion of cane sugar.



$$\text{Rate} = k [\text{C}_{12}\text{H}_{22}\text{O}_{11}][\text{H}_2\text{O}]$$

Water is in excess then its concentration remain constant during the reaction and $[\text{H}_2\text{O}]$ is taken as constant therefore,

$$\text{Rate} = k' [\text{C}_{12}\text{H}_{22}\text{O}_{11}] \quad \text{where } k' = k [\text{H}_2\text{O}]$$

GOLDEN KEY POINTS

- Reactant taken in excess can't affect order of reaction.
- In certain complex reaction product is also considered in order calculation.
- Order of reaction is determined experimentally.

Illustrations

Illustration 3. Give the following data for the reaction : $A + B \rightarrow \text{Product}$.

Experiment No.	[A]	[B]	ROR ($\text{mol L}^{-1}\text{s}^{-1}$)
1	1	2	4
2	2	2	4
3	2	4	16

What is the rate law equation ?

Solution. We know that rate law is given by : $r = k[A]^x[B]^y$ (1)

put the values of experiment No. 1 and 2 in equation 1, we get

$$4 = k[1]^x[2]^y \quad \text{.....(2)}$$

$$\text{and } 4 = k[2]^x[2]^y \quad \text{.....(3)}$$

Now, Equation (2) is divided by (3), we get

$$1 = \left(\frac{1}{2}\right)^x \quad \text{i.e., } x = 0$$

Now, put the values of experiment no. 2 and 3 in equation (1), we get

$$4 = (2)^x (2)^y \quad \text{.....(4)}$$

$$16 = (2)^x (4)^y \quad \text{.....(5)}$$

Equation (4) is divided by (5), we get

$$\frac{1}{4} = \left(\frac{1}{2}\right)^y \quad \text{i.e., } y = 2$$

So, order of reaction with respect to 'A' is 0 and with respect to 'B' is 2 and the rate of reaction is $r = k[A]^0[B]^2 = k[B]^2$ i.e., order of reaction = 2

Illustration 4. The decomposition of dimethyl ether leads to the formation of CH_4 , H_2 and CO and the reaction rate is given by :

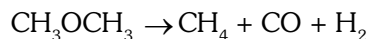
$$\text{Rate} = k[\text{CH}_3\text{OCH}_3]^{3/2}$$

The rate of reaction is followed by increase in pressure in a closed vessel and the rate can also be expressed in terms of the partial pressure of dimethyl ether i.e.,

$$\text{Rate} = k(P_{\text{CH}_3\text{OCH}_3})^{3/2}$$

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constant?

Solution.



$$\text{Rate} = k[\text{CH}_3\text{OCH}_3]^{3/2} = k(P_{\text{CH}_3\text{OCH}_3})^{3/2}$$

$$\text{Unit of rate} = \text{bar min}^{-1}$$

$$\text{Unit of } k = \frac{\text{Rate}}{(P_{\text{CH}_3\text{OCH}_3})^{3/2}} = \frac{\text{bar min}^{-1}}{\text{bar}^{3/2}} = \text{bar}^{-1/2} \text{ min}^{-1}$$

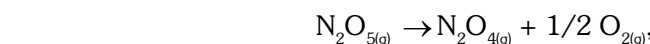
Illustration 5. For a reaction ; $3A \rightarrow \text{Products}$, it is found that the rate of reaction doubles if concentration of A is increased four times, calculate order of reaction.

Solution. Rate = $k[\text{Reactant}]^n$ if $[\text{Reactant}] = a$; rate = r_1
 $r_1 = k[a]^n$ if $[\text{Reactant}] = 4a$; rate = $2r_1$

$$2r_1 = k[4a]^n ; \frac{1}{2} = \left[\frac{1}{4}\right]^n \Rightarrow n = \frac{1}{2}$$

Illustration 6. For the decomposition, $N_2O_{5(g)} \rightarrow N_2O_{4(g)} + 1/2 O_{2(g)}$, the initial pressure of N_2O_5 is 114 mm and after 20 s the pressure of reaction mixture becomes 133 mm of Hg. Calculate the rate of reaction in terms of (a) change in atm s^{-1} and (b) change in molarity s^{-1} . Given that reaction is carried out at 127°C .

Solution.



Initial pressure P 0 0

Pressure at t = 20 s (P - P') P' P'/2

Given P = 114 mm

After 20 s, total pressure = (P - P') + P' + (P'/2) = 133 mm

$$\Rightarrow P'/2 = 19 \text{ mm} \quad P' = 38 \text{ mm}$$

Thus rate of reaction in terms of change in pressure = $38/20 = 1.9 \text{ mm s}^{-1}$

$$= \frac{1.9}{760} \text{ atm s}^{-1} = 2.5 \times 10^{-3} \text{ atm s}^{-1}$$

Also we have $PV = nRT$ or $\frac{n}{V} = C = \frac{P}{RT}$

$\therefore$ change in concentration in 20 second = $\Delta C = \frac{P'}{RT}$ (change in pressure)

$$= \frac{38}{760 \times 0.0821 \times 400} = 1.52 \times 10^{-3} \text{ M}$$

$\therefore$ rate of reaction in terms of change in concentration = $\frac{1.52 \times 10^{-3}}{20} = 7.61 \times 10^{-5} \text{ M s}^{-1}$

BEGINNER'S BOX-2

1. $A_2 + B_2 \rightarrow 2AB$; R.O.R. = $k[A_2]^a[B_2]^b$

$[A_2]$	$[B_2]$	Rate of reaction $[\text{Ms}^{-1}]$
0.2	0.2	0.04
0.1	0.4	0.04
0.2	0.4	0.08

order of reaction with respect to A_2 and B_2 are respectively :

(1) a = 1, b = 1 (2) a = 2, b = 0 (3) a = 2, b = 1 (4) None

2. For a reaction the initial rate is given as : $R_0 = k[A]_0^2[B]_0$ by what factor, the initial rate of reaction will increase if initial concentration of A is 1.5 times and B is tripled ?

(1) 4.5 (2) 2.25 (3) 6.75 (4) None of these

3. For $A_{(g)} + B_{(g)} \rightarrow C_{(g)}$; rate = $k[A]^{1/2}[B]^2$, if initial concentration of A and B are increased by factor of 4 and 2 respectively, then the initial rate is changed by the factor :-

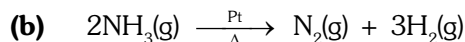
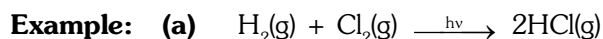
(1) 4 (2) 6 (3) 8 (4) None of these

2.8 STUDY OF DIFFERENT ORDER REACTIONS :

(A) Zero order reactions

Reactions in which rate of reaction remains independent of concentration of the reactant are said to be zero order reactions.

- Zero order reactions are relatively uncommon but they occur under special conditions. Some enzyme catalysed reactions and reactions which occur on metal surfaces are a few examples of zero order reactions.

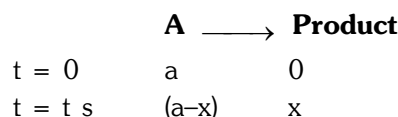


(c) Reaction between Acetone and Bromine.

(d) Dissociation of HI on gold surface.

(e) Adsorption of gases on metal surface :- At low P, rate of adsorption is proportional to surface area covered which is proportional to P or concentration of gas hence order is 1 whereas at high P, complete surface gets covered by gas & rate becomes independent of P & concentration hence order is 0.

Differential Rate Equation

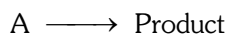


$$-\frac{d[A]}{dt} = k[A]^0$$

$$\frac{dx}{dt} = k[A]^0$$

Calculation of Rate Constant

Let us take the reaction



$$-\frac{d[A]}{dt} = k[A]^0 = k$$

$$-\int d[A] = \int k dt$$

$$-[A]_t = kt + C$$

$$\text{at } t = 0 \quad [A]_t = [A]_0$$

$$-[A]_0 = k \times 0 + C$$

$$C = -[A]_0$$

On substituting the value of C

$$-[A]_t = kt - [A]_0$$

$[A]_t = [A]_0 - kt$

 [Integrated rate equation]

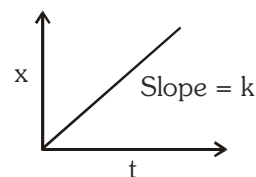
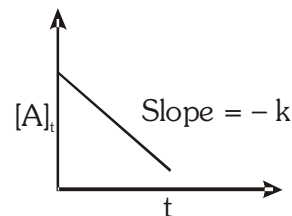
$$y = c - mx$$

$$[A]_0 - [A]_t = kt$$

$$k = \frac{[A]_0 - [A]_t}{t} = \frac{x}{t}$$

$x = kt$

x = Amount of reactant that will change in product.



- For zero order reaction, rate of reaction is equal to rate constant

Unit of rate constant

$k = \text{mol L}^{-1} \text{s}^{-1} = \text{unit of rate of reaction.}$

Half-life period – The time in which half of the initial amount of reactant is consumed.

$$\text{At } t = t_{1/2}, \quad [A]_t = \frac{[A]_0}{2}$$

$$\therefore k t_{1/2} = [A]_0 - \frac{[A]_0}{2} \quad \text{or} \quad t_{1/2} = \frac{[A]_0}{2k}$$

The half life period for a zero order reaction is directly proportional to the initial concentration of the reactants.

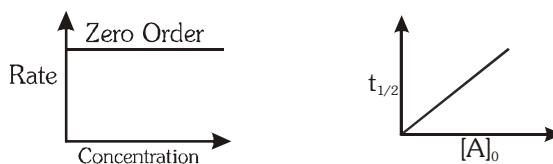
Time for completion of reaction

$$[A]_t = [A]_0 - kt$$

For completion $[A]_t = 0$

$$k = \frac{[A]_0}{t} \quad \boxed{t_{100\%} = \frac{[A]_0}{k}}$$

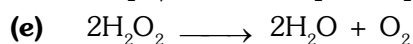
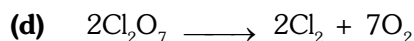
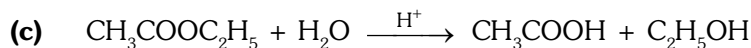
Graphical representation



(B) First order reactions

Reactions in which the rate of reaction is directly proportional to concentration of reactant.

Example :



Differential rate equation

	A	Product
$t = 0$	a	0
$t = t \text{ s}$	(a-x)	x

$$-\frac{d[A]}{dt} = k[A] \quad \boxed{\frac{dx}{dt} = k(a-x)}$$

Calculation of rate constant

$$-\int \frac{d[A]}{[A]} = k \int dt$$

$$-\ln[A]_t = kt + c \quad \dots\dots\dots(i)$$

At $t = 0$; $[A]_t = [A]_0 \therefore C = -\ln[A]_0$

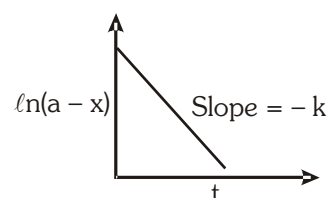
Putting the value of C in equation (i)

$$-\ln[A]_t = kt - \ln[A]_0$$

$$\boxed{\ln[A]_t = \ln[A]_0 - kt}$$

$$y = c - mx$$

$$\ln \frac{[A]_0}{[A]_t} = kt \quad \dots\dots\dots(ii) \quad \boxed{kt = \ln \left(\frac{a}{a-x} \right)}$$



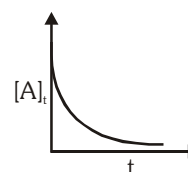
$$2.303 \log_{10} \frac{[A]_0}{[A]_t} = kt$$

$$\boxed{K = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}}$$

from equation(ii)

$$\frac{[A]_0}{[A]_t} = e^{kt}$$

$$\frac{[A]_t}{[A]_0} = e^{-kt} \Rightarrow \boxed{[A]_t = [A]_0 e^{-kt}} \text{ Wilhelmy equation}$$



Unit of rate constant $[k = \text{time}^{-1}]$

Half-life Period : The time in which half of the initial amount of reactant is consumed.

At $t = t_{1/2}$; $x = a/2$; $a-x = a/2$

$$t_{1/2} = \frac{1}{k} \ln \left(\frac{a}{a/2} \right) \quad \text{or} \quad t_{1/2} = \frac{\ln 2}{k} = \frac{2.303}{k} (\log 2) \quad \text{or} \quad \boxed{t_{1/2} = \frac{0.693}{k}}$$

Half-life period for first order reaction is independent of the initial concentration of reactant.

Time for 3/4th of the Reaction ($t_{3/4}$) : The time in which 3/4th of the initial amount of reactant is consumed.

At $t = t_{3/4}$; $x = 3a/4$; $a-x = a/4$

$$t_{3/4} = \frac{2.303}{k}(\log 4) = \frac{2.303}{k} \times 2 \log 2 = 2 \times t_{1/2}$$

$t_{3/4}$ for first order reaction is independent of the initial concentration of reactant.

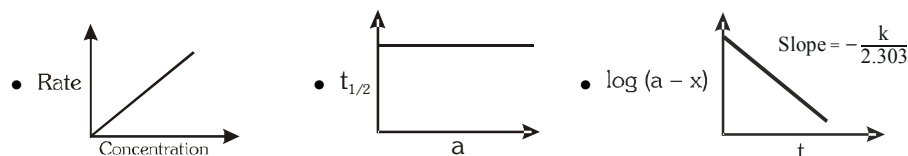
Interval Formula

$$k = \frac{2.303}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}$$

where x_1 and x_2 are the amount consumed at time t_1 and t_2 respectively.

Time required for the completion of definite fraction of the first order reaction is independent of the initial concentration of the reactant.

Graphical Representation



(C) GENERAL INTEGRATED RATE EQUATION (n^{th} order kinetics)

$$kt = \frac{1}{(n-1)} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right] \quad [n \neq 1]$$

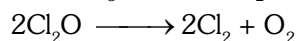
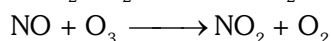
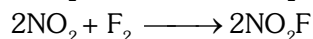
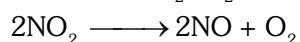
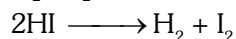
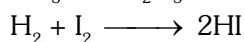
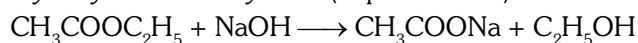
If $t = t_{1/2}$; $x = \frac{a}{2}$

Therefore $kt_{1/2} = \frac{1}{(n-1)} \left[\left(\frac{2}{a} \right)^{n-1} - \left(\frac{1}{a} \right)^{n-1} \right]$

$$kt_{1/2} = \frac{1}{(n-1)} \left[\frac{2^{n-1} - 1}{a^{n-1}} \right] \quad (n \neq 1) ; \quad t_{1/2} \propto \frac{1}{a^{n-1}}$$

(i) Second order reactions

Hydrolysis of ester by alkali (Saponification)

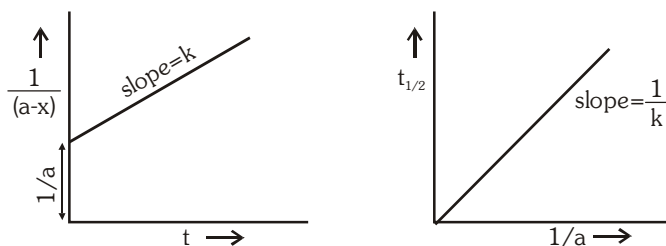


For second order : $n = 2$

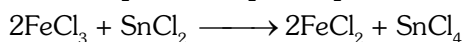
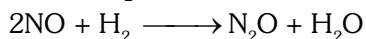
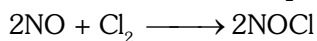
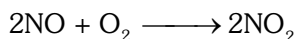
$$kt = \frac{1}{(2-1)} \left[\frac{1}{(a-x)} - \frac{1}{a} \right] = \frac{1}{(a-x)} - \frac{1}{a}$$

Half life

$$t_{1/2} = \frac{1}{ak}$$

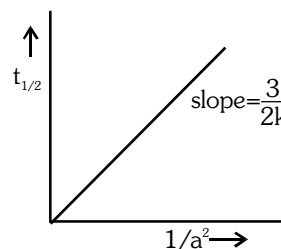
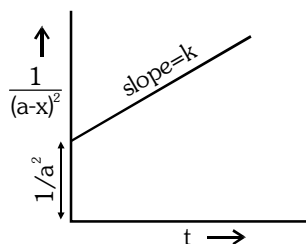


(ii) Third order reactions



for third order $n = 3$
$$kt = \frac{1}{(3-1)} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right] = \frac{1}{2} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$$

Half life
$$t_{1/2} = \frac{3}{2a^2k}$$



Examples of fractional order reaction

Reaction	Order
$\text{H}_2 + \text{Br}_2 \longrightarrow 2\text{HBr}$	1.5
$\text{CO} + \text{Cl}_2 \longrightarrow \text{COCl}_2$	2.5
$\text{COCl}_2 \longrightarrow \text{CO} + \text{Cl}_2$	1.5
$\text{CH}_3\text{CHO} \longrightarrow \text{CH}_4 + \text{CO}$	1.5
$\text{CHCl}_3 + \text{Cl}_2 \longrightarrow \text{CCl}_4 + \text{HCl}$	1.5

Illustrations

Illustration 7. 90% of a first order reaction was completed in 10 hours. When will 99.9% of the reaction complete ?

Solution.
$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}, \quad a = 100, \quad x = 90, \quad t = 10$$

So
$$k_1 = \frac{2.303}{10} \log \frac{100}{10} = 2.303 \times 10^{-1} \text{ hour}^{-1}$$

Now for 99.9% completion : $a = 100$ and $x = 99.9$

$$t = \frac{2.303}{k_1} \log \frac{100}{0.1} = \frac{2.303}{2.303 \times 10^{-1}} \times 3 = 30 \text{ hours}$$

Illustration 8. 20% of a first order reaction was completed in 5 min. When will 60% of the reaction complete ?

Solution. $t = 5 \text{ min}$, $a = 100$, $x_1 = 20$

$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x_1} \right) = \frac{2.303}{5} \log \frac{100}{80} = \frac{2.303}{5} \log \frac{5}{4} = \frac{2.303}{5} [\log 5 - \log 4]$$

$$k = \frac{2.303}{5} [0.6989 - 0.6020] = \frac{2.303}{5} [0.0969] = 0.0446$$

Now $x_2 = 60$

$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x_2} \right)$$

$$t = \frac{2.303}{0.0446} \log \frac{100}{40} = \frac{2.303}{0.0446} [\log 5 - \log 2] = \frac{2.303}{0.0446} \times 0.3979 = 20.55 \text{ min.}$$

Illustration 9. For the first order reaction, half life is 6 min. Calculate the rate constant of the reaction ?

Solution. $t_{1/2} = \frac{0.693}{k_1} \Rightarrow k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{6} = 0.1155 \text{ min}^{-1}$

Illustration 10. A first order reaction is 90% complete in 40 min. Calculate the Half life of the reaction.

Solution. $a = 100, x = 90$

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{40} \log \frac{100}{10} = \frac{2.303}{40} = 5.757 \times 10^{-2} \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k_1} = \frac{0.693}{5.757 \times 10^{-2}} = 12.03 \text{ min.}$$

Illustration 11. In a second order reaction both the reactants have equal initial concentration, the time taken for 60% completion of reaction is 3000 s. What will be the time taken for 20% of the reaction?

Solution. $k_2 = \frac{1}{t} \frac{x}{a(a-x)}, \quad \text{Let } a = 1,$

$$k_2 = \frac{1}{t} \frac{x}{a(1-x)} = \frac{1}{3000} \left(\frac{0.6}{1-0.6} \right) = \frac{1}{3000} \times \frac{0.6}{0.4} = \frac{1}{2000}$$

So time for the 20% completion is :

$$t = \frac{1}{k_2} \frac{x}{a(a-x)} = 2000 \times \frac{0.20}{0.80} = 500 \text{ s.}$$

Illustration 12. If the initial concentration of reactants are doubled then half life becomes half. Calculate order of the reaction ?

Solution. $\left(\frac{t_1}{2} \right)_1 = \left(\frac{a_2}{a_1} \right)^{n-1} \Rightarrow \left(\frac{t_1}{2} \right)_1 = \left(\frac{2a}{a} \right)^{n-1}$

$$2 = (2)^{n-1} \Rightarrow n - 1 = 1 \Rightarrow n = 2$$

so, the order of the reaction will be 2.

BEGINNER'S BOX-3

1. Which of the following expressions is correct for zero order and first order reactions respectively (where a is initial concentration) ?

(1) $t_{1/2} \propto a; t_{1/2} \propto \frac{1}{a}$ (2) $t_{1/2} \propto a; t_{1/2} \propto a^0$ (3) $t_{1/2} \propto a^0; t_{1/2} \propto a$ (4) $t_{1/2} \propto a; t_{1/2} \propto \frac{1}{a^2}$

2. For the zero order reaction, $A \rightarrow B + C$; initial concentration of A is 0.1 M. If $[A] = 0.08 \text{ M}$ after 10 minutes, then its half-life and completion time are respectively :

(1) 10 min; 20 min (2) $2 \times 10^{-3} \text{ min}; 4 \times 10^{-3} \text{ min}$
(3) 25 min, 50 min (4) 250 min, 500 min

3. For an elementary reaction, $X(g) \rightarrow Y(g) + Z(g)$ the half life period is 10 min. In what period of time the concentration of X will be reduced to 10% of original concentration?

(1) 20 min (2) 33 min (3) 15 min (4) 25 min

4. A first order reaction is 75% completed in 100 min. How long will it take for its 87.5% completion?

(1) 125 min (2) 150 min (3) 175 min (4) 200 min

5. The rate constant for a first order reaction which has half life 480 s is :-

(1) $1.44 \times 10^{-3} \text{ s}^{-1}$ (2) $1.44 \times \text{s}^{-1}$ (3) $0.72 \times 10^{-3} \text{ s}^{-1}$ (4) $2.88 \times 10^{-3} \text{ s}^{-1}$

2.9 COLLISION THEORY OF CHEMICAL REACTIONS

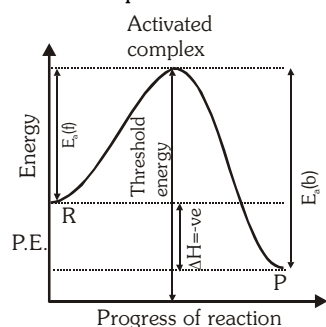
This theory was given by Max Trautz and William Lewis. According to it, for a reaction to occur there must be collisions in between reacting molecules. Total number of collisions per second in unit volume is called collision frequency (z). Generally its value is very high for gaseous reactions (10^{25} to 10^{28} collisions/sec-cm³). But only a small fraction of these collisions are capable to convert reactant into product. These collisions are called as effective collisions.

For effective collision following two conditions must be satisfied at a time :

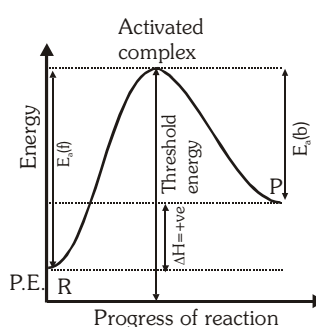
(a) Reacting molecules must possess a minimum amount of energy.

(b) Proper orientation of collision

- **Threshold energy** : The minimum energy which must be possessed by reacting molecules for a chemical reaction to occur.
- **Activation energy** : The minimum extra amount of energy required by reactant molecules for converting into products.



Exothermic reaction



Endothermic reaction

1. $E_a(f)$ = Activation energy for forward reaction
2. $E_a(b)$ = Activation energy for backward reaction

If not specified in questions then consider E_a for forward reaction.

$$\Delta H = E_{a(f)} - E_{a(b)} \quad ; \quad \Delta H = H_p - H_R$$

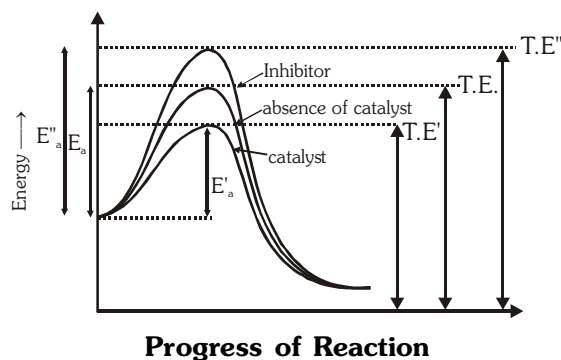
ACTIVATION ENERGY MAINLY DEPENDS UPON :

(i) **Nature of reactant** : For different reactants, number of bonds and bond energies are different, therefore activation energy will also be different.

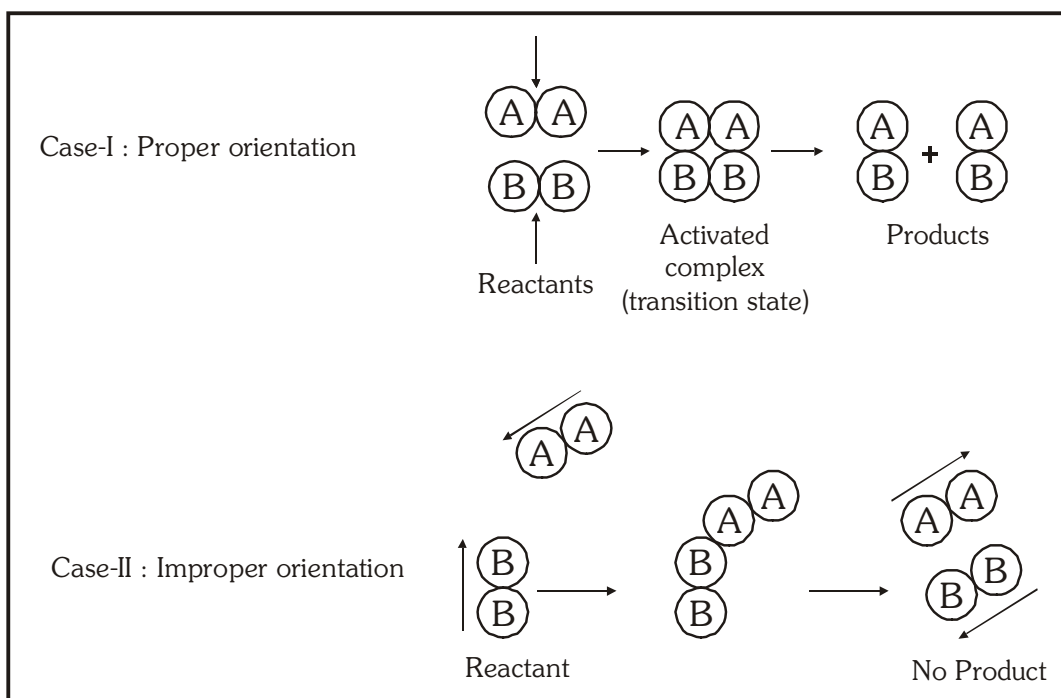
Reactions which have less E_a , take place at faster rate.

(ii) **Presence of catalyst** : Catalyst provide an alternative path of reaction mechanism for the reaction.

- In presence of catalyst threshold energy decreases, activation energy decreases and rate of reaction increases.
- In presence of negative catalyst (inhibitor) threshold energy increases, activation energy increases, rate of reaction decreases.



(b) Orientation :



• Limitations :

- This theory is mainly applicable for gaseous reactions and also for solutions in which reacting species are molecules.
- This theory is mainly applicable for simple bimolecular reactions but fails for complex reactions.
- It considers molecules to be hard sphere and ignore structural aspect of molecules.

GOLDEN KEY POINTS

- Activated complex is most unstable complex formed in the transition state with effective collision.
- On increasing temperature E_a for reaction does not decrease but number of active molecules which are crossing the energy barrier increases therefore rate of reaction increases.
- According to Arrhenius ; rate of reaction $\propto e^{-\frac{E_a}{RT}}$ E_a = Activation energy
 R = Gas constant
 T = Temperature (in K)

Illustrations

Illustration 13 The E_a for an exothermic reaction $A \rightarrow B$ is 80 kJ mol^{-1} . Heat of reaction is 20 kJ mol^{-1} . E_a for the reaction $B \rightarrow A$ will be ?

Solution $\Delta H = E_{a(f)} - E_{a(b)} \Rightarrow -20 = 80 - E_{a(b)}$
 $E_{a(b)} = 100 \text{ kJ mol}^{-1}$

Illustration 14 For the reaction $A + B \rightleftharpoons C + D$ the activation energy is 32 kJ mol^{-1} . For the reverse reaction the E_a is 58 kJ mol^{-1} . Determine (i) Nature of reaction (ii) ΔH

Solution $\Delta H = E_{a(f)} - E_{a(b)}$
 $\Delta H = 32 - 58$
 $\Delta H = -26 \text{ kJ mol}^{-1}$ (exothermic)

Illustration 15 For an endothermic reaction

- $E_a > \Delta H$
- $E_a < \Delta H$
- $E_a = \Delta H$
- any one of the above

Ans. (1)

Solution

Illustration 16 For an exothermic reaction

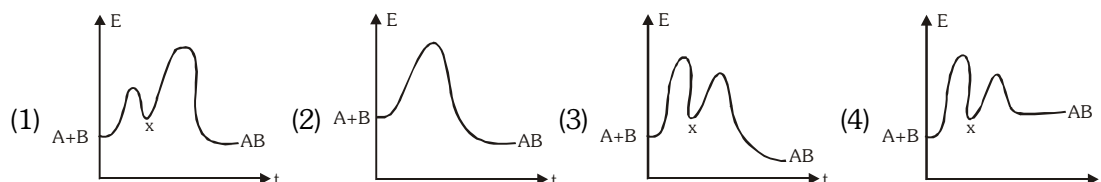
- (1) $E_a > \Delta H$ (2) $E_a < \Delta H$ (3) $E_a = \Delta H$ (4) any one of the above

Solution **Ans. (4)**

Illustration 17 An exothermic chemical reaction is occurring in two steps as follows

- (i) $A + B \rightarrow X$ (slow) (ii) $X \rightarrow AB$ (fast)

the process of reaction can be best described by



Solution **Ans. (3)**

2.10 FACTORS AFFECTING RATE OF REACTION :

1. Nature of reactant :

(a) Physical state of reactant :

increasing order of rate of reaction – Solid < liquid < gas

(Intermolecular attractive force decreases which provides more freedom for collisions)

(b) Physical size of particles (if reactant is solid) :

$$\text{Rate of reaction} \propto \frac{1}{\text{physical size}} \propto \text{surface area}$$

(c) **Chemical nature of reactant** : For different reacting species number of bonds broken and their bond energies are different. Therefore requirement of activation energy is also different. Now reactions having less value of activation energy will take place at faster rate.

2. Concentration of reactant : Rate of reaction $\propto$ concentration of reactant

3. **Pressure** : Effect of pressure on Rate of reaction is negligible when reactants are solid or liquid. But if reactants are in gaseous state then rate of reaction increases on increasing pressure because number of effective collisions increases.

4. **Temperature** : On increasing temperature rate of reaction increases whether the reaction is exothermic or endothermic. When temperature increases KE of molecules increases, number of activated molecules increases thus rate of reaction increases.

Relation between rate constant and Temperature :-

(a) Generally it is found that for every 10 °C rise in temperature Rate of reaction becomes 2 to 3 times.

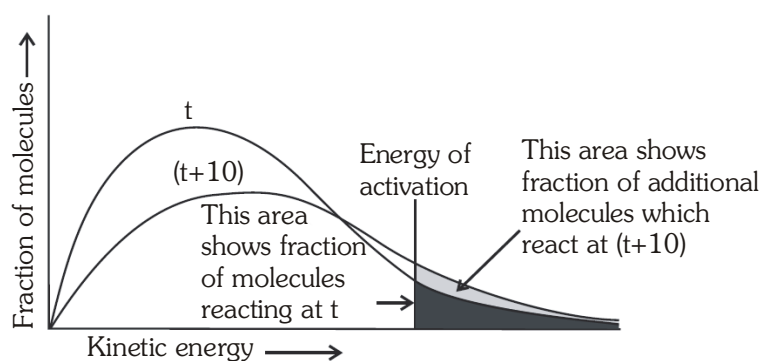
Temperature coefficient (μ) : It is defined as ratio of rate constant of a reaction at two different temperatures which will be differ by 10 °C.

$$\mu = \frac{k_{T+10}}{k_T} = 2 \text{ to } 3 ; \quad \frac{r_2}{r_1} = \frac{k_2}{k_1} = \mu^{\Delta T/10}$$

If temperature of reaction is not specified then consider 25 °C.

(If μ is not given consider it as minimum 2)

MAXWELL AND BOLTZMANN ENERGY DISTRIBUTION CURVE



(b) Arrhenius equation

$$k = Ae^{-E_a/RT} \quad \dots(1)$$

A = Arrhenius constant / pre-exponential factor / Frequency factor

E_a = Activation energy

R = gas constant

T = Temperature (Kelvin)

- k increases with increase in temperature

If $T \rightarrow \infty$; $k = A$

- $\frac{k}{A} = e^{-E_a/RT}$ = fraction of molecules having energy $\geq E_a$

$e^{-E_a/RT}$ = Boltzman factor

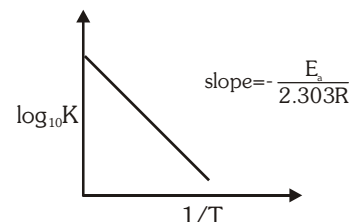
On taking logarithm for equation (1) on both sides.

$$\ln k = \ln A + \ln e^{-E_a/RT}$$

$$2.303 \log_{10} k = 2.303 \log_{10} A - \frac{E_a}{RT}$$

$$\boxed{\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}} \quad \dots(2)$$

$y = c - mx$



- E_a of reaction can be determined by measuring rate constant at two different temperatures
At temperature T_1 :

$$\log_{10} k_1 = \log_{10} A - \frac{E_a}{2.303RT_1} \quad \dots(3)$$

At temperature T_2 :

$$\log_{10} k_2 = \log_{10} A - \frac{E_a}{2.303RT_2} \quad \dots(4)$$

Equation (4) – Equation (3) gives -

$$\log k_2 - \log k_1 = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\boxed{\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)}$$

- From Arrhenius equation - $k = Ae^{-E_a/RT}$

$$\ln k = \ln A - \frac{E_a}{RT}$$

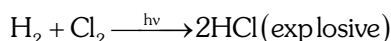
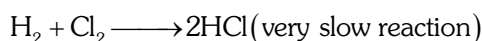
$$\frac{d}{dT}(\ln k) = \frac{d}{dT}(\ln A) + \frac{d}{dT}\left(-\frac{E_a}{RT}\right) = 0 - \frac{E_a}{R} \frac{d}{dT}(T^{-1}) = \frac{E_a}{R}(T^{-2})$$

$$\boxed{\frac{d}{dT} \ln k = \frac{E_a}{RT^2}} \text{ differential form of Arrhenius equation}$$

5. Presence of catalyst : In presence of catalyst E_a of reaction decreases and rate of reaction increases.

6. Exposure to radiation : Rate of some reactions also increases when reaction are carried out in the presence of radiation. (only for photochemical reaction)

e.g. formation of HCl



GOLDEN KEY POINTS

● PHOTO CHEMICAL REACTION

Reactions which occur in presence of light are photochemical reaction i.e., reaction which do not occur in dark.

Example : (i) $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$ (ii) Photo synthesis (iii) Vision

- In photochemical reaction, each molecule of the reacting substance absorbs one quantum (single photon) of radiation and is activated to form the product.
- For every reaction, a certain amount of energy is required.
- Higher the intensity of light greater will be the rate of reaction.
- For these reactions, the value of ΔG may be positive or negative.
- Temperature have no significant effect.

Mechanism : $Cl_2 + h\nu \longrightarrow Cl_2^*$ (activated molecule)

Primary step of reaction : $Cl_2^* \longrightarrow Cl + Cl$

Secondary step of reaction : $H_2 + Cl \longrightarrow HCl + H$

$Cl_2 + H \longrightarrow HCl + Cl$

Final step of reaction : $Cl + Cl \longrightarrow Cl_2$

● Quantum yield (or quantum efficiency) :

The quantum efficiency yield (ϕ) of a photochemical reaction may be expressed as

$$\phi = \frac{\text{Number of molecules reacted or product formed}}{\text{Number of photons absorbed}}$$

● Application of Photochemical Reaction

- | | | |
|--------------------|------------------------------|--|
| (i) In photography | (ii) In photo printing | (iii) In photosynthesis |
| (iv) In vision | (v) In electronic industries | (vi) In many polymerization reactions. |

Illustrations

Illustration 18 A reaction whose temperature is increased from 10 °C to 50 °C then increase in rate of reaction will be—

Solution. We know that on increasing temperature by 10°C the rate of reaction becomes 2 to 3 times.

Note : If the value of temperature coefficient is not given then we will take 2.

$$\begin{aligned} 10\text{ }^{\circ}\text{C} &\text{—} & 20\text{ }^{\circ}\text{C} &= 2 \text{ times} \\ 20\text{ }^{\circ}\text{C} &\text{—} & 30\text{ }^{\circ}\text{C} &= 2^2 \text{ times} \\ 30\text{ }^{\circ}\text{C} &\text{—} & 40\text{ }^{\circ}\text{C} &= 2^3 \text{ times} \\ 40\text{ }^{\circ}\text{C} &\text{—} & 50\text{ }^{\circ}\text{C} &= 2^4 \text{ times} \\ && &= 16 \text{ times} \end{aligned}$$

Illustration 19 For a reaction, temperature coefficient = 2, then calculate the activation energy (in kJ) of the reaction.

Solution. Let $T_1 = 25\text{ }^{\circ}\text{C}$, $T_2 = 35\text{ }^{\circ}\text{C}$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

Given : Temperature coefficient = $\frac{k_2}{k_1} = 2$

$$T_1 = 25 + 273 = 298\text{ K}, T_2 = 35 + 273 = 308\text{ K}, R = 8.314$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \times \left(\frac{10}{298 \times 308} \right)$$

$$E_a = 52.897\text{ kJ}$$

Illustration 20 An exothermic reaction $A \longrightarrow B$ has an activation energy of 17 kJ mol⁻¹ of A. The heat of the reaction is 40 kJ. Calculate the activation energy for the reverse reaction $B \longrightarrow A$.

Solution. For the reaction $A \longrightarrow B$.

Activation energy $E_a = 17\text{ kJ}$

$$\Delta H = -40\text{ kJ}$$

$$\Delta H = E_a(f) - E_a(b)$$

$$E_a(b) = 17 - (-40) = 57\text{ kJ}$$

Illustration 21 For first order gaseous reaction $\log k$ when plotted against $\frac{1}{T}$, gives a straight line with a slope of -8000. Calculate the activation energy of the reaction.

Solution. Arrhenius equation $k = Ae^{-E_a/RT}$

$$\log k = \log A - \frac{E_a}{2.303R} \times \frac{1}{T}$$

when curve is plotted between $\log k$ and $\frac{1}{T}$, a straight line is obtained. Slope of this line = $-\frac{E_a}{2.303R}$

$$\text{Then, } \frac{E_a}{2.303R} = 8000 \text{ or } E_a = 8000 \times 2.303 \times 1.987 = 36608\text{ Cal}$$

Illustration 22 If temperature of a reaction is increased from 10°C to 100°C then how many times rate of reaction will become?

Solution 2^9 times

Illustration 23 If temperature of a reaction is increased from t_1 to t_2 then rate of reaction becomes ?

Solution $(\mu)^{t_2-t_1/10} \Rightarrow (\mu)^{\Delta T/10}$ times ; $r_{\text{new}} = r_{\text{old}} \times (\mu)^{\Delta T/10}$

Illustration 24 A reaction is carried out at 10°C. If temperature is increased by 50°C then how many times rate of reaction will become?

Solution 32 times

BEGINNER'S BOX-4

1. For an endothermic reaction where ΔH represents the enthalpy of reaction in kJ mol^{-1} , the minimum value for the energy of activation will be
 (1) less than ΔH (2) more than ΔH
 (3) equal to ΔH (4) zero

2. The activation energy of the reaction, $A + B \rightarrow C + D + 38 \text{ kcal}$ is 20 kCal, what would be the activation energy of the reaction, $C + D \rightarrow A + B$
 (1) 20 kCal (2) - 20 kCal
 (3) 18 kCal (4) 58 kCal

3. $\frac{k_{35^\circ}}{k_{34^\circ}} > 1$, this means that
 (1) Rate increases with the rise in temperature (2) Rate decreases with rise in temperature
 (3) rate does not change with rise in temperature (4) None of the above

4. The plot of $\ln k$ versus $1/T$ is linear with slope of
 (1) $-\frac{E_a}{R}$ (2) $\frac{E_a}{R}$
 (3) $\frac{E_a}{2.303R}$ (4) $-\frac{E_a}{2.303R}$

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3							
	Ans.	1	3	3							
BEGINNER'S BOX-2	Que.	1	2	3							
	Ans.	1	3	3							
BEGINNER'S BOX-3	Que.	1	2	3	4	5					
	Ans.	2	3	2	2	1					
BEGINNER'S BOX-4	Que.	1	2	3	4						
	Ans.	2	4	1	1						

EXERCISE-I (Conceptual Questions)**RATE OF REACTION**

1. Consider the chemical reaction :
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$
 The rate of this reaction can be expressed in terms of concentration of $\text{N}_2(\text{g})$, $\text{H}_2(\text{g})$ or $\text{NH}_3(\text{g})$. Identify the correct relationship amongst the rate expressions.

$$(1) \text{Rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

$$(2) \text{Rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{3d[\text{H}_2]}{dt} = \frac{2d[\text{NH}_3]}{dt}$$

$$(3) \text{Rate} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

$$(4) \text{Rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{d[\text{H}_2]}{dt} = \frac{d[\text{NH}_3]}{dt}$$

2. In the formation of sulphur trioxide by the contact process $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$; the rate of reaction is expressed as

$$-\frac{d[\text{O}_2]}{dt} = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

The rate of disappearance of (SO_2) will be

- (1) $5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 (2) $-2.25 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 (3) $3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 (4) $50.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
3. In a catalytic reaction involving the formation of ammonia by Haber's process $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ the rate of appearance of NH_3 was measured as $2.5 \times 10^{-4} \text{ mole L}^{-1} \text{ s}^{-1}$. The rate of disappearance of H_2 will be –
- (1) $2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 (2) $1.25 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 (3) $3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 (4) $5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
4. Which of the following statement is correct for a reaction $\text{X} + 2\text{Y} \rightarrow \text{Product}$
- (1) The rate of disappearance of X = twice the rate of disappearance of Y.
 (2) The rate of disappearance of X = $\frac{1}{2}$ rate of appearance of products
 (3) The rate of appearance of products = $\frac{1}{2}$ the rate of disappearance of Y
 (4) The rate of appearance of products = $\frac{1}{2}$ the rate of disappearance of X

Build Up Your Understanding

5. For the reaction, $\text{N}_2\text{O}_5 \longrightarrow 2\text{NO}_2 + \frac{1}{2} \text{O}_2$

$$\text{Given } -\frac{d[\text{N}_2\text{O}_5]}{dt} = K_1[\text{N}_2\text{O}_5], \frac{d[\text{NO}_2]}{dt} = K_2[\text{N}_2\text{O}_5]$$

$$\frac{d[\text{O}_2]}{dt} = K_3[\text{N}_2\text{O}_5]$$

The relation between K_1 , K_2 and K_3 is –

- (1) $2K_1 = K_2 = 4K_3$ (2) $K_1 = K_2 = K_3$
 (3) $2K_1 = 4K_2 = K_3$ (4) None
6. Rate of formation of SO_3 according to the reaction $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ is $1.6 \times 10^{-3} \text{ kg min}^{-1}$. Hence rate at which SO_2 reacts is :-
- (1) $1.6 \times 10^{-3} \text{ kg min}^{-1}$
 (2) $8.0 \times 10^{-4} \text{ kg min}^{-1}$
 (3) $3.2 \times 10^{-3} \text{ kg min}^{-1}$
 (4) $1.28 \times 10^{-3} \text{ kg min}^{-1}$
7. For a general chemical change $2\text{A} + 3\text{B} \rightarrow \text{products}$, the rate of disappearance of A is r_1 and of B is r_2 . The rates r_1 and r_2 are related as :-
- (1) $3r_1 = 2r_2$ (2) $r_1 = r_2$
 (3) $2r_1 = 3r_2$ (4) $r_1^2 = 2r_2^2$
8. In a reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$ the rate of appearance of NH_3 is $2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$. The Rate of reaction & rate of disappearance of H_2 will be ($\text{In mol L}^{-1} \text{ sec}^{-1}$)
- (1) 3.75×10^{-4} , 1.25×10^{-4}
 (2) 1.25×10^{-4} , 2.5×10^{-4}
 (3) 1.25×10^{-4} , 3.75×10^{-4}
 (4) 5.0×10^{-4} , 3.75×10^{-4}
9. Which of the following statement is not correct for the reaction: $4\text{A} + \text{B} \rightarrow 2\text{C} + 2\text{D}$
- (1) The rate of disappearance of B is twice the rate of appearance of C
 (2) The rate of disappearance of B is one fourth the rate of disappearance of A
 (3) The rate of formation of D is one half the rate of consumption of A
 (4) The rate of formation of C and D are equal
10. For gaseous reaction, rate = $k[\text{A}][\text{B}]$. If volume of container is reduced to $\frac{1}{4}$ of initial, then the rate of the reaction will be..... times of initial:-

(1) $\frac{1}{8}$ (2) 8 (3) $\frac{1}{16}$ (4) 16

11. $2A_{(g)} + B_{(g)} \rightleftharpoons \text{Product}$ is an elementary reaction, If pressure is increased three times of the initial pressure, the velocity of forward reaction will be ----- of the previous velocity:-

- (1) 9 times (2) 27 times
(3) $\frac{1}{9}$ times (4) $\frac{1}{27}$ times

RATE LAW / ORDER / MOLECULARITY

12. The rate of certain hypothetical reaction
 $A + B + C \rightarrow \text{products}$ is given by

$$r = \frac{-d[A]}{dt} = k[A]^{\frac{1}{2}}[B]^{\frac{1}{3}}[C]^{\frac{1}{4}}$$

The order of the reaction –

- (1) 1 (2) $\frac{1}{2}$ (3) 2 (4) $\frac{13}{12}$

13. Which of the following rate law has an overall order of 0.5 for reaction involving substances x,y and z ?

- (1) Rate = $k(C_x)(C_y)(C_z)$
(2) Rate = $k(C_x)^{0.5}(C_y)^{0.5}(C_z)^{0.5}$
(3) Rate = $k(C_x)^{1.5}(C_y)^{-1}(C_z)^0$
(4) Rate = $k(C_x)(C_z)^0 / (C_y)^2$

14. A chemical reaction involves two reacting species. The rate of reaction is directly proportional to the concentration of one of them and inversely proportional to the concentration of the other. The order of reaction is –

- (1) 1 (2) 2
(3) Zero (4) Unpredictable

15. For the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$, the experimental data suggests, Rate = $k[H_2][Br_2]^{\frac{1}{2}}$. The order for this reaction is –

- (1) 2 (2) $1\frac{1}{2}$ (3) 1 (4) $2\frac{1}{2}$

16. Select the rate law that corresponds to the data shown for the following reaction $A + B \rightarrow C$

Exp.	[A]	[B]	Initial rate
1.	0.012	0.035	0.10
2.	0.024	0.070	1.6
3.	0.024	0.035	0.20
4.	0.012	0.070	0.80

- (1) Rate = $k[B]^3$ (2) Rate = $k[B]^4$
(3) Rate = $k[A][B]^3$ (4) Rate = $k[A]^2[B]^2$

17. In a certain gaseous reaction between X and Y, $X + 3Y \rightarrow XY_3$. The initial rates are reported as follows –

[X]	[Y]	Rate
0.1 M	0.1 M	0.002 Ms^{-1}
0.2 M	0.1 M	0.002 Ms^{-1}
0.3 M	0.2 M	0.008 Ms^{-1}
0.4 M	0.3 M	0.018 Ms^{-1}

The rate law is –

- (1) $r = k[X][Y]^3$ (2) $r = k[X]^q[Y]^2$
(3) $r = k[X][Y]$ (4) $r = [X]^q[Y]^3$

18. Select the law that corresponds to data shown for the following reaction $2A + B \rightarrow C + D$:-

Exp.	[A]	[B]	Initial rate ($\text{mol L}^{-1} \text{ min}^{-1}$)
1.	0.1	0.1	7.5×10^{-3}
2.	0.3	0.2	9.0×10^{-2}
3.	0.3	0.4	3.6×10^{-1}
4.	0.4	0.1	3.0×10^{-2}

- (1) Rate = $k[A]^2[B]$ (2) Rate = $k[A][B]^2$
(3) Rate = $k[A][B]^3$ (4) Rate = $k[A][B]$

19. For a hypothetical reaction ; $A + B \rightarrow C$ the following data were obtained in three different experiments :-

[A] (mol L^{-1})	[B] (mol L^{-1})	Rate of reaction ($\text{mol L}^{-1} \text{ min}^{-1}$)
0.01	0.01	1.0×10^{-4}
0.01	0.03	9.0×10^{-4}
0.03	0.03	2.70×10^{-3}

The rate law will be :-

- (1) $r = k[A]^2[B]$ (2) $r = k[A][B]^2$
(3) $r = k[A][B]$ (4) None of these

20. Calculate the order of the reaction w.r.t. A and B:

[A] (mol L^{-1})	[B] (mol L^{-1})	Rate
0.05	0.05	1.2×10^{-3}
0.10	0.05	2.4×10^{-3}
0.05	0.10	1.2×10^{-3}

- (1) 1 and 0 (2) 1 and 1
(3) 0 and 1 (4) None

21. For a chemical reaction $A + B \rightarrow \text{product}$, the order is one with respect to each A and B. Value of x and y from the given data is :-

Rate ($\text{mol L}^{-1}\text{s}^{-1}$)	[A]	[B]
0.10	0.20 M	0.05 M
0.40	x	0.05 M
0.80	0.40 M	y

- (1) 0.20, 0.80 (2) 0.80, 0.40
(3) 0.80, 0.20 (4) 0.40, 0.20
22. Time required to complete a half fraction of a reaction varies inversely to the concentration of reactant then the order of reaction is -
(1) Zero (2) 1
(3) 2 (4) 3
23. The rate law for the single step reaction $2A + B \rightarrow 2C$, is given by -
(1) Rate = $K[A][B]$ (2) Rate = $K[A]^2[B]$
(3) Rate = $K[2A][B]$ (4) Rate = $K[A]^2[B]^\circ$
24. For a reaction of the type $A + B \rightarrow \text{products}$, it is observed that doubling the concentration of A causes the reaction rate to be four times as great, but doubling the amount of B does not effect the rate. The rate equation is -
(1) Rate = $K [A][B]$
(2) Rate = $K [A]^2$
(3) Rate = $K[A]^2[B]$
(4) Rate = $K[A]^2[B]^2$
25. Point out incorrect statement.
(1) Rate law is an experimental value
(2) Law of mass action is a theoretical proposal
(3) Rate law is more informative than law of mass action for developing mechanism
(4) Rate law is always different from the expression of law of mass action.
26. For an elementary process $2X + Y \rightarrow Z + W$, the molecularity is -
(1) 2 (2) 1
(3) 3 (4) Unpredictable
27. For a reaction $A + B \rightarrow \text{products}$, the rate of the reaction was doubled when the concentration of A was doubled, the rate was again doubled when the concentration of A & B were doubled the order of the reaction with respect to A & B are:-
(1) 1, 1 (2) 2, 0
(3) 1, 0 (4) 0, 1

28. For the reaction $A + B \rightarrow \text{products}$, it is found that the order of A is 1 and the order of B is $\frac{1}{2}$.

When the concentration of both A and B are increased four times, the rate will increase by a factor of :-

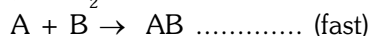
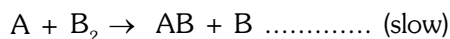
- (1) 16 (2) 8 (3) 6 (4) 4

29. The rate law for a reaction $A + B \rightarrow \text{product}$ is rate = $K[A]^1[B]^2$. Then which one of the following statement is false :-
(1) If [B] is held constant while [A] is doubled, the reaction will proceed twice as fast
(2) If [A] is held constant while [B] is reduced to one quarter, the rate will be halved
(3) If [A] and [B] are both doubled, the reaction will proceed 8 times as fast
(4) This is a third order reaction
30. For a chemical reaction $A \rightarrow B$, the rate of reaction doubles when the concentration of A is increased 8 times. The order of reaction w.r.t. A is :-
(1) 3 (2) $\frac{1}{2}$ (3) $\frac{1}{3}$ (4) Zero
31. The specific rate constant of a first order reaction depends on the :-
(1) Concentration of the reactant
(2) Concentration of the product
(3) Time
(4) Temperature

PSEUDO FIRST ORDER REACTION / MECHANISM OF REACTION

32. Following mechanism has been proposed for a reaction $2A + B \rightarrow D + E$
 $A + B \rightarrow C + D$ (slow)
 $A + C \rightarrow E$ (fast)
 The rate law expression for the reaction is -
 (1) $r = K[A]^2[B]$ (2) $r = K[A][B]$
 (3) $r = K[A]^2$ (4) $r = K[A][C]$
33. The chemical reaction $2O_3 \rightarrow 3O_2$ proceeds as follows
 $O_3 \rightleftharpoons O_2 + O$ (fast)
 $O + O_3 \rightarrow 2O_2$ (slow)
 The rate law expression should be -
 (1) $r = K[O_3]^2$ (2) $r = K[O_3]^2[O_2]^{-1}$
 (3) $r = K[O_3][O_2]$ (4) Unpredictable

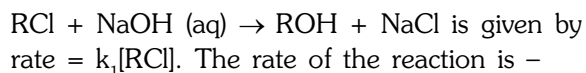
34. The hypothetical reaction $A_2 + B_2 \rightarrow 2AB$ follows the mechanism as given below –



The order of the over all reaction is –

- (1) 2 (2) 1 (3) $1\frac{1}{2}$ (4) Zero

35. The rate for the reaction



- (1) Doubled on doubling the concentration of NaOH
 (2) Halved on reducing the concentration of RCl to half
 (3) Decreased on increasing the temperature of reaction
 (4) Unaffected by increasing the temperature of the reaction

36. For reaction $NO_2 + CO \rightarrow CO_2 + NO$, the rate expression is, Rate = $k[NO_2]^2$

The number of molecules of CO involved in the slowest step will be –

- (1) 0 (2) 1
 (3) 2 (4) 3

37. The rate law of the reaction $A + 2B \rightarrow \text{product}$

is given by $\frac{d[P]}{dt} = K[A]^2[B]$. If A is taken in large

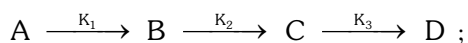
excess, the order of the reaction will be –

- (1) Zero (2) 1
 (3) 2 (4) 3

38. The acid hydrolysis of ester is –

- (1) Psuedo 1st order reaction
 (2) Bimolecular reaction
 (3) Pseudo unimolecular reaction
 (4) All

39. In the sequence of reaction



$K_3 > K_2 > K_1$, then the rate determining step of the reaction is :-

- (1) $A \rightarrow B$ (2) $C \rightarrow D$
 (3) $B \rightarrow C$ (4) $A \rightarrow D$

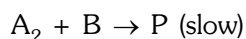
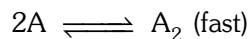
40. The reaction mechanism for the reaction $P \rightarrow R$ is as follows :-



the rate law for the main reaction ($P \rightarrow R$) is [where K_1 is an equilibrium constant]

- (1) $k_1[P][Q]$ (2) $k_1k_2[P]$
 (3) $k_1k_2[P]^2$ (4) $k_1k_2[a]$

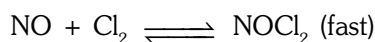
41. The reaction $2A + B \rightarrow P$, follows the mechanism



The order of the reaction is :-

- (1) 1.5 (2) 3 (3) 1 (4) 2

42. For the reaction $2NO + Cl_2 \rightarrow 2NOCl$ the following mechanism has been proposed



$NOCl_2 + NO \rightarrow 2NOCl$ (slow) the rate law for the reaction is :-

- (1) Rate = $K[NO]^2[Cl_2]$ (2) Rate = $K[NO][Cl_2]^2$
 (3) Rate = $K[NOCl_2]$ (4) Rate = $K[NOCl]^2$

ZERO / FIRST / nth ORDER REACTIONS

43. The rate constant is numerically the same for three reactions of first, second and third order respectively. Which one is true at a moment for rate of all three reactions if concentration of reactants is same and greater than 1 M.

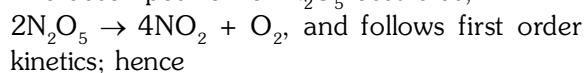
- (1) $r_1 = r_2 = r_3$ (2) $r_1 > r_2 > r_3$
 (3) $r_1 < r_2 < r_3$ (4) All

44. K for a zero order reaction is

$2 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$. If the concentration of the reactant after 25 s is 0.5 M, the initial concentration must have been.

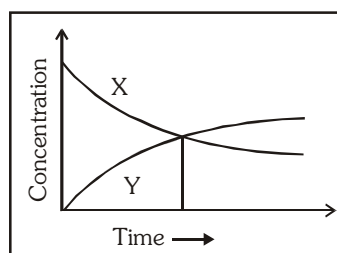
- (1) 0.5 M (2) 1.25 M
 (3) 12.5 M (4) 1.0 M

45. The decomposition of N_2O_5 occurs as,



- (1) The reaction is bimolecular
 (2) The reaction is unimolecular
 (3) $t_{1/2} \propto a^0$
 (4) $t_{1/2} \propto a^2$

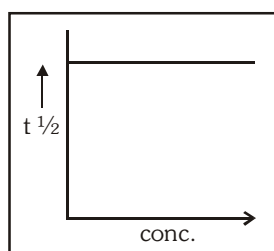
46. The accompanying figure depicts the change in concentration of species X and Y for the reaction $X \rightarrow Y$ as a function of time the point of intersection of the two curves represents.



- (1) $t_{1/2}$
 (2) $t_{3/4}$
 (3) $t_{2/3}$
 (4) Data are insufficient to predict

- 47.** If the first order reaction involves gaseous reactants and gaseous products the unit of its rate is –
 (1) atm. (2) atm - s
 (3) atm - s⁻¹ (4) atm² s²
- 48.** Plot of log(a - x) vs time t is straight line. This indicates that the reaction is of –
 (1) Second order (2) First order
 (3) Zero order (4) third order
- 49.** The rate constant of a first order reaction is $4 \times 10^{-3} \text{ s}^{-1}$. At a reactant concentration of 0.02 M, the rate of reaction would be –
 (1) $8 \times 10^{-5} \text{ M s}^{-1}$ (2) $4 \times 10^{-3} \text{ M s}^{-1}$
 (3) $2 \times 10^{-1} \text{ M s}^{-1}$ (4) $4 \times 10^{-1} \text{ M s}^{-1}$
- 50.** In a first order reaction the concentration of the reactant is decreased from 1.0 M to 0.25 M in 20 min. The rate constant of the reaction would be –
 (1) 10 min^{-1} (2) 6.931 min^{-1}
 (3) 0.6931 min^{-1} (4) 0.06931 min^{-1}
- 51.** In a first order reaction the $a/(a - x)$ was found to be 8 after 10 minute. The rate constant is
 (1) $\frac{(2.303 \times 3 \log 2)}{10}$ (2) $\frac{(2.303 \times 2 \log 3)}{10}$
 (3) $10 \times 2.303 \times 2 \log 3$ (4) $10 \times 2.303 \times 3 \log 2$
- 52.** 75 % of a first order reaction was found to complete in 32 min. When will 50 % of the same reaction complete –
 (1) 24 min (2) 16 min
 (3) 8 min (4) 4 min
- 53.** A first order reaction has a half life period of 69.3 s. At 0.10 mol L⁻¹ reactant concentration, the rate will be –
 (1) 10^{-4} M s^{-1} (2) 10^{-3} M s^{-1}
 (3) 10^{-1} M s^{-1} (4) $6.93 \times 10^{-1} \text{ M s}^{-1}$
- 54.** For a first order reaction $A \rightarrow$ products, the rate of reaction at $[A] = 0.2 \text{ M}$ is $1 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$. The half life period for the reaction is –
 (1) 832 min. (2) 440 s
 (3) 416 min. (4) 14 min.
- 55.** 99 % of a first order reaction was completed in 32 min. when will 99.9 % of the reaction complete ?
 (1) 50 min. (2) 46 min.
 (3) 49 min. (4) 48 min.
- 56.** The half life for the first order reaction $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$ is 24 hrs. at 30°C. Starting with 10 g of N_2O_5 how many grams of N_2O_5 will remain after a period of 96 hours ?
 (1) 1.25 g (2) 0.63 g
 (3) 1.77 g (4) 0.5 g
- 57.** What is the half life of a radioactive substance if 87.5% of any given amount of the substance disintegrate in 40 minutes ?
 (1) 160 min (2) 10 min
 (3) 20 min (4) 13 min 20 sec.
- 58.** For a given reaction of first order it takes 20 minute for the concentration to drop from 1 M to 0.6 M. The time required for the concentration to drop from 0.6 M to 0.36 M will be :
 (1) More than 20 min
 (2) Less than 20 min
 (3) Equal to 20 min
 (4) Infinity
- 59.** A first order reaction is carried out with an initial concentration of 10 mol per litre and 80% of the reactant changes into the product. Now if the same reaction is carried out with an initial concentration of 5 mol per litre for the same period the percentage of the reactant changing to the product is.
 (1) 40 (2) 80
 (3) 160 (4) Cannot be calculated
- 60.** In the following first order reactions,
 $A + \text{Reagent} \rightarrow \text{Product}$, $B + \text{Reagent} \rightarrow \text{Product}$
 Calculate the ratio of K_1 / K_2 , 50% of B has been reacted, when 94% of A has been reacted –
 (1) 4.06 (2) 0.246
 (3) 2.06 (4) 0.06
- 61.** The reaction $L \rightarrow M$ is started with 10 g/L. After 30 minute and 90 minute, 5 g/L and 1.25 g/L are left respectively. The order of reaction is
 (1) 0 (2) 2
 (3) 1 (4) 3
- 62.** The doubling the initial concentration of a reactant doubles $t_{1/2}$ of the reaction, then order of the reaction is –
 (1) 3 (2) 2
 (3) 1 (4) 0
- 63.** The half life period for catalytic decomposition of AB_3 at 50 mm is found to be 4 hrs and at 100 mm it is 2 hrs. The order of reaction is –
 (1) 3 (2) 1
 (3) 2 (4) 0

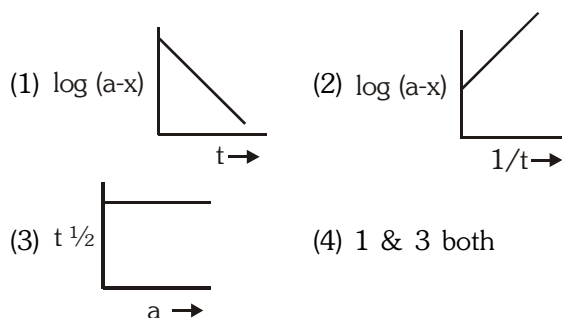
64. The rate constant for a reaction is $10.8 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$. The reaction obeys –
 (1) First order (2) Zero order
 (3) Second order (4) All are wrong
65. A substance 'A' decomposes in solution following the first order kinetics. Flask I contains 1 L of 1M solution of A and flask II contains 100 ml of 0.6 M solution. After 8 hr. the concentration of A in flask I becomes 0.25 M, what will be the time for concentration of A in flask II to become 0.3 M.
 (1) 0.4 hr.
 (2) 2.4 hr.
 (3) 4.0 hr.
 (4) Unpredictable as rate constant is not given
66. The rate constant (K) for the reaction $2A + B \rightarrow$ product, was found to be $2.5 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ after 15 s, $2.60 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ after 30 s and $2.55 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ after 50 s. The order of reaction is
 (1) 2 (2) 3 (3) Zero (4) 1
67. The rate constant for a second order reaction is $8 \times 10^{-5} \text{ M}^{-1} \text{ min}^{-1}$. How long will it take a 1M solution to be reduced to 0.5 M.
 (1) $8.665 \times 10^3 \text{ min}$ (2) $8 \times 10^{-3} \text{ min}$
 (3) $1.25 \times 10^4 \text{ min}$ (4) $4 \times 10^{-5} \text{ min}$
68. A graph between $t_{1/2}$ and concentration for n^{th} order reaction is a straight line. Reaction of this nature is completed 50% in 10 minutes when concentration is 2 mol L^{-1} . This is decomposed 50% in t minutes at 4 mol L^{-1} , n and t are respectively



- (1) 0, 20 min. (2) 1, 10 min.
 (3) 1, 20 min. (4) 0, 5 min.
69. In the first order reaction, 75% of the reactant disappeared in 1.388 h. Calculate the rate constant of the reaction :-
 (1) 1 s^{-1} (2) $2.8 \times 10^{-4} \text{ s}^{-1}$
 (3) $17.2 \times 10^{-3} \text{ s}^{-1}$ (4) $1.8 \times 10^{-3} \text{ s}^{-1}$

70. In the case of first order reaction, the ratio of time required for 99.9 % completion to 50 % completion is :-
 (1) 2 (2) 5 (3) 10 (4) None
71. From different sets of data of $t_{1/2}$ at different initial concentrations say 'a' for a given reaction, the $[t_{1/2} \times a]$ is found to be constant. The order of reaction is :-
 (1) 0 (2) 1 (3) 2 (4) 3
72. The reaction

$$2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$$
 is first order with respect to N_2O_5 . Which of the following graph would yield a straight line :-
 (1) $\log(P_{\text{N}_2\text{O}_5})$ v/s time with negative slope
 (2) $P_{\text{N}_2\text{O}_5}^{-1}$ v/s time
 (3) $P_{\text{N}_2\text{O}_5}$ v/s time
 (4) $\log(P_{\text{N}_2\text{O}_5})$ v/s time with positive slope
73. Which of the following statement is not correct for the reaction whose rate is $r = k$ (rate constant)
 (1) rate of reaction is independent of concentration of reactant
 (2) $t_{1/2}$ of reaction is not depends upon concentration of reactant
 (3) rate constant is independent of concentration of reactant
 (4) this is zero order reaction
74. Which of the following curves represents a 1st order reaction :-



75. The following data were obtained at a certain temperature for the decomposition of ammonia
- | p (mm) | 50 | 100 | 200 |
|-----------|------|------|------|
| $t_{1/2}$ | 3.64 | 1.82 | 0.91 |
- The order of the reaction is :-
 (1) 0 (2) 1
 (3) 2 (4) 3

76. A reaction is found to have the rate constant $\times s^{-1}$ by what factor the rate is increased if initial concentration of A is tripled

- (1) 3
- (2) 9
- (3) $\times$
- (4) Remains same

77. Which is incorrect :-

- (1) Half life of a first order reaction is independent of initial concentration
- (2) Rate of reaction is constant for first order reaction
- (3) Unit of K for second order reaction is $\text{mol}^{-1} \text{L s}^{-1}$
- (4) Half life of zero order is proportional to initial concentration

78. Hydrolysis of ester in alkaline medium is :-

- (1) First order reaction with molecularity one
- (2) Second order reaction with molecularity two
- (3) First order reaction with molecularity two
- (4) Second order reaction with molecularity one

79. The expression which gives $\frac{1}{4}$ th life of 1st order reaction is :-

- (1) $\frac{K}{2.303} \log \frac{4}{3}$
- (2) $\frac{2.303}{K} \log 3$
- (3) $\frac{2.303}{K} \log \frac{3}{4}$
- (4) $\frac{2.303}{K} \log \frac{4}{3}$

80. The rate constant of a zero order reaction is $0.2 \text{ mol dm}^{-3} \text{h}^{-1}$. If the concentration of the reactant after 30 minutes is 0.05 mol dm^{-3} . Then its initial concentration would be :-

- (1) 6.05 mol dm^{-3}
- (2) 0.15 mol dm^{-3}
- (3) 0.25 mol dm^{-3}
- (4) 4.00 mol dm^{-3}

81. A reaction is of first order. After 100 minutes 75 gm of the reactant A are decomposed when 100 gm are taken initially, calculate the time required when 150 gm of the reactant A are decomposed, the initial weight taken is 200 gm :-

- (1) 100 minutes
- (2) 200 minutes
- (3) 150 minutes
- (4) 175 minutes

82. For which of the following, the unit of rate and rate constant of the reaction are identical :-

- (1) First order reaction
- (2) Zero order reaction
- (3) Second order reaction
- (4) Fractional order of reaction

83. $2A \rightarrow \text{Product}$, follows the first order kinetics. If the half life period of the reaction at $[A]_{\text{initial}} = 0.2 \text{ mol L}^{-1}$ is 20 min. then the value of rate constant would be:-

- (1) 4 s^{-1}
- (2) 20 s^{-1}
- (3) $4 \text{ lit. mol}^{-1} \text{ min.}^{-1}$
- (4) 0.034 min^{-1}

84. Correct statement about first order reaction is:-

- (1) $t_{\text{completion}} = \text{finite}$
- (2) $t_{1/2} \propto \frac{1}{a}$
- (3) Unit of K is $\text{mole lit}^{-1} \text{ s}^{-1}$
- (4) $t_{1/2} \times K = \text{at constant temperature}$

COLLISION THEORY AND FACTORS AFFECTING RATE OF REACTION

85. According to collision theory of reaction rates –

- (1) Every collision between reactants leads to chemical reaction
- (2) Rate of reaction is proportional to velocity of molecules
- (3) All reactions which occur in gaseous phase are zero order reaction
- (4) Rate of reaction is directly proportional to collision frequency.

86. Activation energy of a reaction is –

- (1) The energy released during the reaction
- (2) The energy evolved when activated complex is formed
- (3) Minimum extra amount of energy needed to overcome the potential barrier of reaction
- (4) The energy needed to form one mole of the product

87. The minimum energy for molecules to enter into chemical reaction is called.

- (1) Kinetic energy
- (2) Potential energy
- (3) Threshold energy
- (4) Activation energy

88. The rate constant k_1 of a reaction is found to be double that of rate constant k_2 of another reaction. The relationship between corresponding activation energies of the two reactions at same temperature (E_1 & E_2) can be represented as

- (1) $E_1 > E_2$
- (2) $E_1 < E_2$
- (3) $E_1 = E_2$
- (4) $E_1 = 4E_2$

- 89.** At room temperature the reaction between NO and O_2 to give NO_2 is fast while that between CO and O_2 is slow it is due to –
 (1) CO is smaller in size than that of NO
 (2) CO is poisonous
 (3) The activation energy for the reaction $2NO + O_2 \rightarrow 2NO_2$ is less than $2CO + O_2 \rightarrow 2CO_2$
 (4) NO_2 is poisonous
- 90.** Chemical reaction occurs as a result of collision between reacting molecules. Therefore the reaction rate is given by
 (1) Total number of collisions occurring in a unit volume per second
 (2) Fraction of molecules which possess energy less than the threshold energy.
 (3) Total number of effective collisions
 (4) Temperature
- 91.** An endothermic reaction $A \rightarrow B$ have an activation energy 15 kCal/mol and the heat of the reaction is 5 k cal/mol. The activation energy of the reaction $B \rightarrow A$ is –
 (1) 20 kCal/mol (2) 15 kCal/mol
 (3) 10 kCal/mol (4) Zero
- 92.** A large increase in the rate of a reaction for a rise in temperature is due to –
 (1) Increase in the number of collisions
 (2) Increase in the number of activated molecules
 (3) Lowering of activation energy
 (4) Shortening of the mean free path
- 93.** Rate of which reactions increases with temperature
 (1) Of any reaction
 (2) Of exothermic reaction
 (3) Of endothermic reaction
 (4) Can't be predicted
- 94.** The rate of a chemical reaction doubles for every $10^\circ C$ rise in temperature. If the temp is increased by $60^\circ C$ the rate of reaction increases by :
 (1) 20 times (2) 32 times
 (3) 64 times (4) 128 times
- 95.** According to the arrhenius equation a straight line is to be obtained by plotting the logarithm of the rate constant of chemical reaction ($\log k$) against.
 (1) (T) (2) $\log T$
 (3) $\frac{1}{T}$ (4) $\log \frac{1}{T}$
- 96.** Which plot will give the value of activation energy.
 (1) k v/s T (2) $\frac{1}{k}$ v/s T
 (3) $\ln k$ v/s T (4) $\ln k$ v/s $\frac{1}{T}$
- 97.** Given that k is the rate constant for some order of any reaction at temp T then the value of $\lim_{T \rightarrow \infty} \log k$ _____.
 (1) $A/2.303$ (2) A
 (3) $2.303 A$ (4) $\log A$
- 98.** From the following data; the activation energy for the reaction (Cal/mol) $H_2 + I_2 \rightarrow 2HI$
- | T (in K) | $1/T$ (in K^{-1}) | $\log_{10} k$ |
|----------|----------------------|---------------|
| 769 | 1.3×10^{-3} | 2.9 |
| 667 | 1.5×10^{-3} | 1.1 |
- (1) 4×10^4 (2) 2×10^4
 (3) 8×10^4 (4) 3×10^4
- 99.** The rate constant, the activation energy and the arrhenius parameter of a chemical reaction at $25^\circ C$ are $3 \times 10^{-4} s^{-1}$; $104.4 kJ mol^{-1}$ and $6.0 \times 10^{14} s^{-1}$ respectively, the value of the rate constant as $T \rightarrow \infty$ is.
 (1) $2 \times 10^8 s^{-1}$ (2) $6 \times 10^{14} s^{-1}$
 (3) Infinity (4) $3.6 \times 10^{30} s^{-1}$
- 100.** For an endothermic reaction where ΔH represents the enthalpy of the reaction in kJ/mol ; the minimum value for the energy of activation will be
 (1) Less than ΔH (2) Zero
 (3) More than ΔH (4) Equal to ΔH
- 101.** The rate of reaction increases to 2.3 times when the temperature is raised from 300 K to 310 K. If K is the rate constant at 300 K then the rate constant at 310 K will be equal to –
 (1) $2k$ (2) k
 (3) $2.3k$ (4) $3k^2$
- 102.** If concentration of reactants is increased by 'x' then the k becomes –
 (1) $\ln \frac{k}{x}$ (2) $\frac{k}{x}$
 (3) $k + x$ (4) k

103. If the concentration units are reduced by n times then the value of rate constant of first order will

- (1) Increases by n times
- (2) Decreases by factor of n
- (3) Remain constant
- (4) Decrease $1/n$ times

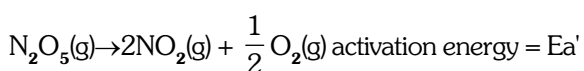
104. Which is used in the determination of reaction rates.

- (1) Reaction Temperature
- (2) Reaction Concentration
- (3) Specific rate constant
- (4) All of these

105. The rate constant of a first order reaction depends on the :-

- (1) Concentration of the reactant
- (2) Concentration of the product
- (3) Time
- (4) Temperature

106. For the decomposition of $N_2O_5(g)$ it is given that—
 $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ activation energy = E_a



then

- (1) $E_a = 2E_a'$
- (2) $E_a > E_a'$
- (3) $E_a < E_a'$
- (4) $E_a = E_a'$

107. For a reaction in which case the activation energies of forward and reverse reactions are equal :-

- (1) $\Delta H = 0$
- (2) $\Delta S = 0$
- (3) The order is zero
- (4) There is no catalyst

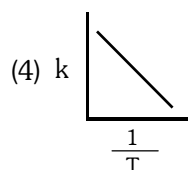
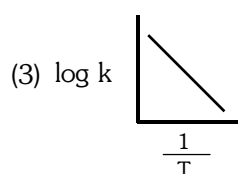
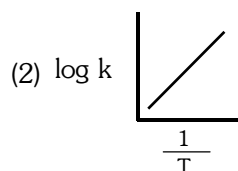
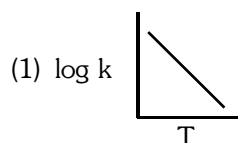
108. The energy of activation of a forward reaction is 50 kCal. The energy of activation of its backward reaction is:-

- (1) Equal to 50 kCal.
- (2) Greater than 50 kCal.
- (3) Less than 50 kCal.
- (4) Either greater or less than 50 kCal.

109. An exothermic reaction $X \rightarrow Y$ has an activation energy 30 kJ mol^{-1} . If energy change (ΔE) during the reaction is -20 kJ , then the activation energy for the reverse reaction is :-

- (1) 10 kJ
- (2) 20 kJ
- (3) 50 kJ
- (4) -30 kJ

110. Which of the following plot is in accordance with the arrhenius equation :-



111. The rate of reaction increases by the increase of temperature because :-

- (1) Collision is increased
- (2) Energy of products decreases
- (3) Fraction of molecules possessing energy $\geq E_T$ (Threshold energy) increases
- (4) Mechanism of a reaction is changed

112. For a certain gaseous reaction rise of temperature from 25°C to 35°C doubles the rate of reaction. What is the value of activation energy :-

(1) $\frac{10}{2.303R \times 298 \times 308}$

(2) $\frac{2.303 \times 10}{298 \times 308R}$

(3) $\frac{0.693R \times 10}{290 \times 308}$

(4) $\frac{0.693R \times 298 \times 308}{10}$

- 113.** The activation energy for the forward reaction $X \rightarrow Y$ is 60 kJ mol^{-1} and ΔH is -20 kJ mol^{-1} . The activation energy for the backward reaction $Y \rightarrow X$ is:-
 (1) 80 kJ mol^{-1} (2) 40 kJ mol^{-1}
 (3) 60 kJ mol^{-1} (4) 20 kJ mol^{-1}

- 114.** For producing the effective collisions, the colliding molecules must possess:-
 (1) A certain minimum amount of energy
 (2) Energy equal to or greater than threshold energy
 (3) Proper orientation
 (4) Threshold energy as well as proper orientation of collision

- 115.** The half life for a reaction is -----of temperature:-
 (1) Independent
 (2) Increased with increase
 (3) Decreased with increase
 (4) Increased or decreased with increase

- 116.** The activation energy for a chemical reaction depends upon :-
 (1) Temperature
 (2) Nature of reacting species
 (3) Concentration of the reacting species
 (4) Collision frequency

EXERCISE-I (Conceptual Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	1	3	3	1	4	1	3	1	4	2	4	3	3	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	3	2	2	2	1	3	3	2	2	4	3	3	2	2	3
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	4	2	2	3	2	1	2	4	1	3	2	1	3	4	3
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	1	3	2	1	4	1	2	2	4	4	2	4	3	2	1
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	3	4	3	2	3	1	3	2	2	3	3	1	2	4	3
Que.	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
Ans.	1	2	2	4	2	1	2	4	4	4	3	3	2	3	3
Que.	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105
Ans.	3	2	1	3	3	4	4	1	2	3	3	4	3	4	4
Que.	106	107	108	109	110	111	112	113	114	115	116				
Ans.	4	1	4	3	3	3	4	1	4	3	2				

EXERCISE-II (Previous Year Questions)**AIPMT/NEET & AIIMS (2006-2018)****AIPMT 2006**

1. For the reaction
 $2A + B \rightarrow 3C + D$
 Which of the following does not express the reaction rate ?
 (1) $-\frac{1}{3} \frac{d[C]}{dt}$ (2) $-\frac{d[B]}{dt}$ (3) $\frac{d[D]}{dt}$ (4) $-\frac{1}{2} \frac{d[A]}{dt}$
2. Consider the reaction
 $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
 The correct equality relationship between $\frac{d[NH_3]}{dt}$ and $-\frac{d[H_2]}{dt}$ is :
 (1) $\frac{d[NH_3]}{dt} = -\frac{1}{3} \frac{d[H_2]}{dt}$
 (2) $+\frac{d[NH_3]}{dt} = -\frac{2}{3} \frac{d[H_2]}{dt}$
 (3) $+\frac{d[NH_3]}{dt} = -\frac{3}{2} \frac{d[H_2]}{dt}$
 (4) $\frac{d[NH_3]}{dt} = -\frac{d[H_2]}{dt}$

AIPMT 2008

3. The rate constants k_1 and k_2 for two different reactions are $10^{16} e^{-2000/T}$ and $10^{15} e^{-1000/T}$, respectively.
 The temperature at which $k_1 = k_2$ is
 (1) $\frac{2000}{2.303}$ K (2) 2000 K
 (3) $\frac{1000}{2.303}$ K (4) 1000 K
4. The bromination of acetone that occurs in acid solution is represented by this equation
 $CH_3COCH_3(aq) + Br_2(aq) \rightarrow CH_3COCH_2Br(aq) + H^+(aq) + Br^-(aq)$
 The kinetic data were obtained for given reaction at different concentrations.
- | $[CH_3COCH_3]$ | $[Br_2]$ | $[H^+]$ | ROD of Br_2 , Ms^{-1} |
|----------------|----------|---------|---------------------------|
| 0.30 | 0.05 | 0.05 | 5.7×10^{-5} |
| 0.30 | 0.10 | 0.05 | 5.7×10^{-5} |
| 0.30 | 0.10 | 0.10 | 1.2×10^{-4} |
| 0.40 | 0.05 | 0.20 | 3.1×10^{-4} |
- Based on these data, the rate equation is :
 (1) Rate = $k[CH_3COCH_3][Br_2]$
 (2) Rate = $k[CH_3COCH_3][Br_2][H^+]^2$
 (3) Rate = $k[CH_3COCH_3][Br_2][H^+]$
 (4) Rate = $k[CH_3COCH_3][H^+]$

AIPMT 2009

5. For the reaction, $N_2 + 3H_2 \rightarrow 2NH_3$, if
 $\frac{d[NH_3]}{dt} = 2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$, the value of
 $-\frac{d[H_2]}{dt}$ would be :-
 (1) $1 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ (2) $3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 (3) $4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ (4) $6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
6. For the reaction $A + B \rightarrow \text{products}$, it is observed that :
 (a) on doubling the initial concentration of A only, the rate of reaction is also doubled and
 (b) on doubling the initial concentrations of both A and B, there is a change by a factor of 8 in the rate of the reaction.
 The rate of this reaction is given by :-
 (1) rate = $k[A][B]$ (2) rate = $k[A]^2[B]$
 (3) rate = $k[A][B]^2$ (4) rate = $k[A]^2[B]^2$
7. In the reaction
 $BrO_3^-(aq) + 5Br^-(aq) + 6H^+ \rightarrow 3Br_2(l) + 3H_2O(l)$
 The rate of appearance of bromine (Br_2) is related to rate of disappearance of bromide ions as following :-
 (1) $\frac{d[Br_2]}{dt} = \frac{3}{5} \frac{d[Br^-]}{dt}$
 (2) $\frac{d[Br_2]}{dt} = -\frac{3}{5} \frac{d[Br^-]}{dt}$
 (3) $\frac{d[Br_2]}{dt} = -\frac{5}{3} \frac{d[Br^-]}{dt}$
 (4) $\frac{d[Br_2]}{dt} = \frac{5}{3} \frac{d[Br^-]}{dt}$

8. Half life period of a first-order reaction is 1386 s. The specific rate constant of the reaction is :-
 (1) $5.0 \times 10^{-2} \text{ s}^{-1}$ (2) $5.0 \times 10^{-3} \text{ s}^{-1}$
 (3) $0.5 \times 10^{-2} \text{ s}^{-1}$ (4) $0.5 \times 10^{-3} \text{ s}^{-1}$

AIPMT 2010

9. The rate of the reaction
 $2NO + Cl_2 \rightarrow 2NOCl$ is given by the rate equation
 rate = $k[NO]^2[Cl_2]$
 the value of rate constant can be increased by :
 (1) Increasing the concentration of NO
 (2) Increasing the concentration of the Cl_2
 (3) Increasing the temperature
 (4) Doing all of these

10. For the reaction $\text{N}_2\text{O}_5(\text{g}) \longrightarrow 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$

the value of rate of disappearance of N_2O_5 is given as $6.25 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$. The rate of formation of NO_2 and O_2 is given respectively as :-

- (1) $1.25 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1}$ and $6.25 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$
- (2) $6.25 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$ and $6.25 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$
- (3) $1.25 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1}$ and $3.125 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$
- (4) $6.25 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$ and $3.125 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$

11. During the kinetic study of the reaction, $2\text{A} + \text{B} \rightarrow \text{C} + \text{D}$, following results were obtained:-

Ex. No.	[A](mol L ⁻¹)	[B](mol L ⁻¹)	Initial rate of formation of D(mol L ⁻¹ min ⁻¹)
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Based on the above data which one of the following is correct ?

- (1) rate = $k[\text{A}][\text{B}]^2$
- (2) rate = $k[\text{A}]^2[\text{B}]$
- (3) rate = $k[\text{A}][\text{B}]$
- (4) rate = $k[\text{A}]^2[\text{B}]^2$

12. For an endothermic reaction, energy of activation is E_a and enthalpy of reaction is ΔH (both of these in kJ/mol). Minimum value of E_a will be :-
- (1) Equal to zero
 - (2) Less than ΔH
 - (3) Equal to ΔH
 - (4) More than ΔH

AIIMS 2010

13. For a first order reaction, the value of rate constant for the reaction

$$\text{A}_{(\text{gas})} \longrightarrow 2\text{B}_{(\text{gas})} + \text{C}_{(\text{solid})}$$

- (1) $\frac{1}{t} \ln \left(\frac{P_0}{P_0 - P_t} \right)$
- (2) $\frac{1}{t} \ln \left(\frac{P_0}{2P_0 - P_t} \right)$
- (3) $\frac{1}{t} \ln \left(\frac{2P_0}{3P_0 - P_t} \right)$
- (4) $\frac{1}{t} \ln \left(\frac{P_0}{3P_0 - P_t} \right)$

AIPMT Pre. 2011

14. Which one of the following statements for the order of a reaction is incorrect ?
- (1) Order can be determined only experimentally
 - (2) Order is not influenced by stoichiometric coefficient of the reactants
 - (3) Order of reaction is sum of power to the concentration terms of reactants to express the rate of reaction
 - (4) Order of reaction is always whole number

AIPMT Mains 2011

15. The unit of rate constant for a zero order reaction is :-

- (1) s^{-1}
- (2) $\text{mol L}^{-1} \text{s}^{-1}$
- (3) $\text{L mol}^{-1} \text{s}^{-1}$
- (4) $\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$

16. The half life of a substance in a certain enzyme-catalysed first order reaction is 138 s. The time required for the concentration of the substance to fall from 1.28 mg L^{-1} to 0.04 mg L^{-1} :-

- (1) 276 s
- (2) 414 s
- (3) 552 s
- (4) 690 s

17. The rate of the reaction $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ can be written in three ways

$$\frac{-d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5]$$

$$\frac{d[\text{NO}_2]}{dt} = k' [\text{N}_2\text{O}_5]$$

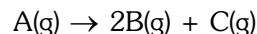
$$\frac{d[\text{O}_2]}{dt} = k'' [\text{N}_2\text{O}_5]$$

The relationship between k and k' and between k and k'' are :-

- (1) $k' = k$; $k'' = k$
- (2) $k' = 2k$; $k'' = k$
- (3) $k' = 2k$; $k'' = k/2$
- (4) $k' = 2k$; $k'' = 2k$

AIIMS 2011

18. For a first order gas phase reaction-



Let P_0 be initial pressure of A and P_t the total pressure at time 't'. Integrated rate equation is-

$$(1) \frac{2.303}{t} \log \left(\frac{P_0}{P_0 - P_t} \right) \quad (2) \frac{2.303}{t} \log \left(\frac{2P_0}{3P_0 - P_t} \right)$$

$$(3) \frac{2.303}{t} \log \left(\frac{P_0}{2P_0 - P_t} \right) \quad (4) \frac{2.303}{t} \log \left(\frac{2P_0}{2P_0 - P_t} \right)$$

AIPMT Pre. 2012

19. In a zero-order reaction for every 10° rise of temperature, the rate is doubled. If the temperature is increased from 10°C to 100°C , the rate of the reaction will become:

- (1) 64 times
- (2) 128 times
- (3) 256 times
- (4) 512 times

20. In a reaction $\text{A} + \text{B} \rightarrow \text{Product}$, rate is doubled when the concentration of B is doubled and rate increased by a factor of 8 when the concentrations of both the reactants (A and B) are doubled, rate law for the reaction can be written as:

- (1) Rate = $k[\text{A}][\text{B}]$
- (2) Rate = $k[\text{A}]^2[\text{B}]$
- (3) Rate = $k[\text{A}][\text{B}]^2$
- (4) Rate = $k[\text{A}]^2[\text{B}]^2$

AIPMT Mains 2012

21. Activation energy (E_a) and rate constants (k_1 and k_2) of a chemical reaction at two different temperatures (T_1 and T_2) are related by :

$$(1) \ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} + \frac{1}{T_1} \right) \quad (2) \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$(3) \ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4) \ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

AIIMS 2012

22. For a reaction $r = k(\text{CH}_3\text{COCH}_3)^{3/2}$ the unit of rate of reaction and rate constant respectively are :-

$$(1) \text{mol L}^{-1}\text{s}^{-1}, \text{mol}^{-\frac{1}{2}} \text{L}^{\frac{1}{2}}\text{s}^{-1}$$

$$(2) \text{mol}^{-1} \text{L}^{-1}\text{s}^{-1}, \text{mol}^{-\frac{1}{2}} \text{L}^{-\frac{1}{2}}\text{s}^{-1}$$

$$(3) \text{mol L}^{-1}\text{s}^{-1}, \text{mol}^{+\frac{1}{2}} \text{L}^{\frac{1}{2}}\text{s}^{-1}$$

$$(4) \text{mol Ls}, \text{mol}^{+\frac{1}{2}} \text{L}^{\frac{1}{2}}\text{s}$$

23. $t_{1/2}$ v/s $\frac{1}{a^2}$ is a straight line graph then determine

the order of reaction is :-

- (1) Zero order (2) First order
(3) Second order (4) Third order

NEET-UG 2013

24. A reaction having equal energies of activation for forward and reverse reactions has :-

- (1) $\Delta H = \Delta G = \Delta S = 0$ (2) $\Delta S = 0$
(3) $\Delta G = 0$ (4) $\Delta H = 0$

25. What is the activation energy of a reaction if its rate doubles when the temperature is raised from 20°C to 35°C ? ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)

- (1) 15.1 kJ mol^{-1} (2) 342 kJ mol^{-1}
(3) 269 kJ mol^{-1} (4) 34.7 kJ mol^{-1}

AIIMS 2013

26. Energy of activation of forward reaction for an endothermic process is 50 kJ and enthalpy change is 20 kJ then activation energy change for backward reaction will be :-

- (1) 30 kJ (2) 20 kJ
(3) 70 kJ (4) 50 kJ

AIIMS 2014

27. In 1st order reaction $A_{(g)} \longrightarrow 2B_{(g)} + C(s)$; if P_i is the initial pressure and P_f is the final pressure of mixture after time t then rate constant is :-

$$(1) k = \frac{2.303}{t} \log \left(\frac{2P_i}{3P_i - P_f} \right)$$

$$(2) k = \frac{2.303}{t} \log \left(\frac{P_i}{2P_i - P_f} \right)$$

$$(3) k = \frac{2.303}{t} \log \left(\frac{P_i}{P_i - 3P_f} \right)$$

$$(4) k = \frac{2.303}{t} \log \left(\frac{P_i}{P_i + P_f} \right)$$

28. If in a 1st order reaction 75% of reaction completes in 4 h. Then how much time is required to complete 87.5% of reaction ?

- (1) 32 h (2) 6 h (3) 8 h (4) 16 h

AIPMT 2015

29. The activation energy of a reaction can be determined from the slope of which of the following graphs ?

$$(1) \frac{\ln k}{T} \text{ v/s. } T \quad (2) \ln k \text{ v/s. } \frac{1}{T}$$

$$(3) \frac{T}{\ln k} \text{ v/s. } \frac{1}{T} \quad (4) \ln k \text{ v/s. } T$$

30. When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is :-

- (1) First
(2) Second
(3) More than zero but less than first
(4) Zero

Re-AIPMT 2015

31. The rate constant of the reaction $A \rightarrow B$ is $0.6 \times 10^{-3} \text{ M sec}^{-1}$. If the concentration of A is 5 M , then concentration of B after 20 min is :-

- (1) 0.36 M (2) 0.72 M
(3) 1.08 M (4) 3.60 M

AIIMS 2015

32. For a first order reaction rate constant is given as

$$\log k = 14 - \frac{1.2 \times 10^4}{T}, \text{ then what will be}$$

the value of temperature if its half life period is 6.93×10^{-3} min

- (1) 100 K (2) 1000 K
(3) 720 K (4) 327 K

33. For a reaction $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$;
Initial concentration of N_2O_5 is 7.2 mol L^{-1} and after 20 minute $[\text{NO}_2]$ is 2.4 mol L^{-1} , then what will be the rate of decomposition of N_2O_5 in $\text{mol L}^{-1} \text{ min}^{-1}$
(1) 0.06 (2) 0.03 (3) 1.3 (4) 2.4

34. For a reaction $\text{A} \rightarrow \text{B}$ half life period is 50 min. If reactant concentration is halved then half life period is 25 min. Calculate order of reaction ?
(1) 0 (2) 1 (3) 2 (4) 3

NEET-I 2016

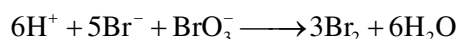
35. The rate of a first-order reaction is $0.04 \text{ mol L}^{-1} \text{ s}^{-1}$ at 10 s and $0.03 \text{ mol L}^{-1} \text{ s}^{-1}$ at 20 s after initiation of the reaction. The half-life period of the reaction is :
(1) 24.1 s (2) 34.1 s
(3) 44.1 s (4) 54.1 s
36. The addition of a catalyst during a chemical reaction alters which of the following quantities ?
(1) Entropy (2) Internal energy
(3) Enthalpy (4) Activation energy

NEET-II 2016

37. The decomposition of phosphine (PH_3) on tungsten at low pressure is a first-order reaction. It is because the
(1) rate is independent of the surface coverage
(2) rate of decomposition is very slow
(3) rate is proportional to the surface coverage
(4) rate is inversely proportional to the surface coverage

AIIMS 2016

38. For a reaction :-



If rate of consumption of BrO_3^- is $x \text{ mol L}^{-1} \text{ s}^{-1}$. Then calculate rate of formation of Br_2 :-

- (1) $\frac{x}{3}$ (2) $\frac{2x}{3}$ (3) $\frac{x}{4}$ (4) $3x$

39. On increasing temperature from 200K to 220K, rate of reaction A increases by 3 times and rate of reaction B increases by 9 times then correct relationship between activation energy of A and B is :-

- (1) $E_A = 3E_B$ (2) $3E_A = E_B$
(3) $E_B = 2E_A$ (4) $E_A = 2E_B$

40. The slope of $\frac{-E_a}{2.303R}$ is obtained by the plot of:-

- (1) $\log k$ v/s $\log A$
(2) $\log k$ v/s T
(3) $\log k$ v/s $\frac{1}{T}$
(4) k v/s $\frac{1}{T}$

41. For a first order reaction rate constant is $1 \times 10^{-5} \text{ s}^{-1}$ having $E_a = 1800 \text{ kJ/mol}$. Then value of $\ln A$ at $T = 600\text{K}$ is :-

- (1) 151.7 (2) 349.3
(3) 24.7 (4) 11.34

42. Half life of a radioactive decay of C^{14} is 5730 years. How much time it will take so that 25% of C^{14} was found in sample?

- (1) 5730 years (2) 11460 years
(3) 22920 years (4) 930 years

NEET(UG) 2017

43. Mechanism of a hypothetical reaction



- (i) $\text{X}_2 \rightleftharpoons \text{X} + \text{X}(\text{fast})$
(ii) $\text{X} + \text{Y}_2 \rightarrow \text{XY} + \text{Y}(\text{slow})$
(iii) $\text{X} + \text{Y} \rightarrow \text{XY}(\text{fast})$

The overall order of the reaction will be :

- (1) 2 (2) 0
(3) 1.5 (4) 1

44. A first order reaction has a specific reaction rate of 10^{-2} s^{-1} . How much time will it take for 20 g of the reactant to reduce to 5 g ?

- (1) 138.6 s (2) 346.5 s
(3) 693.0 s (4) 238.6 s

AIIMS 2017

45. For a first order gaseous reaction $A \rightarrow 2B + C$, if initial pressure is P_0 and total final pressure of mixture becomes P_t after time t . The rate constant is :-

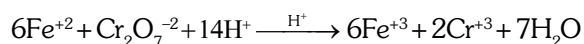
(1) $k = \frac{2.303}{t} \log \frac{2P_0}{P_0 - P_t}$

(2) $k = \frac{2.303}{t} \log \frac{2P_0}{3P_0 - P_t}$

(3) $k = \frac{2.303}{t} \log \frac{2P_0}{P_0 + P_t}$

(4) $k = \frac{2.303}{t} \log \frac{2P_0}{2P_0 + P_t}$

46. When Fe^{+2} reacts with $Cr_2O_7^{2-}$ in acidic medium then Fe^{+3} and Cr^{+3} are formed. If rate of disappearance of $Cr_2O_7^{2-}$ is x then the rate of appearance of Fe^{+3} will be :-



- (1) $x/6$ (2) $3x$ (3) $6x$ (4) $x/3$

47. For a first order reaction : $2A(g) \rightarrow 2B(g) + C(g)$, the initial pressure is P_0 and after time t , total pressure of reaction mixture becomes P_t . The rate constant is :-

(1) $k = \frac{2.303}{t} \log \frac{P_0}{P_0 - P_t}$

(2) $k = \frac{1}{t} \ln \frac{P_0}{3P_0 - 2P_t}$

(3) $k = \frac{1}{t} \ln \frac{P_0}{2P_0 - P_t}$

(4) $k = \frac{1}{t} \ln \frac{2P_0}{3P_0 - P_t}$

48. In the reaction $2A \rightarrow B$, the concentration of A decreases from 0.8 M to 0.4 M in 10 min . The rate of appearance of B is :-

- (1) 0.02 M min^{-1} (2) 0.04 M min^{-1}
(3) 0.08 M min^{-1} (4) 0.2 M min^{-1}

NEET(UG) 2018

49. The correct difference between first- and second-order reaction is that

- (1) the rate of a first-order reaction does not depend on reactant concentration; the rate of a second-order reaction does depend on reactant concentrations.
(2) the half-life of a first-order reaction does not depend on $[A]_0$; the half-life of a second-order reaction does depend on $[A]_0$
(3) a first-order reaction can be catalyzed; a second-order reaction cannot be catalyzed.
(4) the rate of a first-order reaction does depend on reactant concentrations; the rate of a second-order reaction does not depend on reactant concentrations

50. When initial concentration of the reactant is doubled, the half-life period of a zero order reaction

- (1) is halved (2) is doubled
(3) is tripled (4) remains unchanged

AIIMS 2018

51. For a unimolecular reaction $A \rightarrow B$ has rate constant K_1 and for another unimolecular reaction $C \rightarrow D$ has rate constant K_2 . If half life of first reaction is half of half life of second reaction then find $E_{a1} - E_{a2}$ will be :-

- (1) $-RT \ln 2$ (2) $RT \ln 2$

- (3) $\frac{RT}{\ln 2}$ (4) $\frac{1}{RT \ln 2}$

52. For zero order reaction relation between $t_{1/2}$ and $t_{1/4}$ is :-

- (1) $t_{1/2} = 2 t_{1/4}$ (2) $t_{1/2} = 1.5 t_{1/4}$

- (3) $t_{1/2} = \frac{1}{2} t_{1/4}$ (4) $t_{1/2} = \frac{1}{3} t_{1/4}$

53. For two zero order reaction having same rate at certain temperature; If $E_{a1} - E_{a2} = 2RT$

Then find $\ln \left(\frac{A_1}{A_2} \right)$:-

- (1) $+2$ (2) -2 (3) $\frac{2}{\ln 2}$ (4) $2 \ln 2$

54. For a first order reaction $t_{80\%}$ is 60 min. Calculate $t_{1/2}$:-

- (1) 25.7 min (2) 25 min
(3) 20 min (4) 257 min

55. The rate of first order reaction are 0.4 M min^{-1} and 0.04 M min^{-1} at 10 min and 30 min respectively. Then half life of reaction is :-

- (1) 6 min (2) 4 min
(3) 8 min (4) 13 min

56. Two different reactions at 300 K having same pre-exponential factor. The activation energy of first reaction is more than that of second reaction by

5.75 kJ. Then find $\frac{K_2}{K_1}$:-

- (1) 1000 (2) 10,000
(3) 10 (4) 1

57. For a reaction, activation energy is 83 kJ calculate

ratio of $\ln \frac{K_{37^\circ\text{C}}}{K_{27^\circ\text{C}}}$ for above gaseous reaction :-

- (1) 1 (2) 2
(3) 3 (4) 4

58. For a 1st order reaction what will be the time required to reach concentration from 1.28 M to 0.04 M if $t_{1/2}$ is 138 s :-

- (1) 690 s (2) 138 s
(3) 69 s (4) 27.6 s

EXERCISE-II (Previous Year Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	2	3	4	2	3	2	4	3	3	1	4	2	4	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	4	3	2	4	2	2,4	1	4	4	4	1	2	2	2	1
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	2	2	1	1	1	4	3	4	3	3	2	2	3	1	2
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58		
Ans.	3	2	1	2	2	1	1	1	1	1	3	1	1		

EXERCISE-III (Analytical Questions)

Check Your Understanding

- For the reaction

$$A + 2B \rightarrow \text{Product},$$
the differential rate equation is :-
 (1) $-\frac{1}{2} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B]^2$
 (2) $\frac{1}{2} \frac{d[A]}{dt} = \frac{d[B]}{dt} = k[A][B]^2$
 (3) $-\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = k[A][B]^2$
 (4) $\frac{dA}{dt} = \frac{1}{2} \frac{d[B]}{dt} = k[A][B]^2$
- The rate of reaction between two reactants A and B decreases by a factor of 4, if the concentration of reactant B is doubled. The order of the reaction with respect to reactant B is :
 (1) -1 (2) -2 (3) 1 (4) 2
- For the non-stoichiometric reaction $2A + B \rightarrow C + D$, the following kinetic data were obtained in three different experiments, measured at 298 K.

Initial Conc. (A)	Initial Conc. (B)	Initial rate of formation of C (mol L ⁻¹ s ⁻¹)
0.1M	0.1M	1.2×10^{-3}
0.1M	0.2M	1.2×10^{-3}
0.2M	0.1M	2.4×10^{-3}

 (1) $\frac{dc}{dt} = k[A][B]^2$ (2) $\frac{dc}{dt} = k[A]$
 (3) $\frac{dc}{dt} = k[A][B]$ (4) $\frac{dc}{dt} = k[A]^2[B]$
- The following mechanism has been proposed for the reaction of NO with Br₂ to form NOBr :

$$\text{NO(g)} + \text{Br}_2\text{(g)} \rightleftharpoons \text{NOBr}_2\text{(g)}$$

$$\text{NOBr}_2\text{(g)} + \text{NO(g)} \rightarrow 2\text{NOBr(g)}$$
 If the second step is the rate determining step, the order of the reaction with respect to NO(g) is :
 (1) 2 (2) 1 (3) 0 (4) 3
- Higher order (>3) reactions are rare due to :-
 (1) shifting of equilibrium towards reactants due to elastic collision
 (2) loss of active species on collision
 (3) low probability of simultaneous collision of all the reacting species
 (4) increase in entropy and activation energy as more molecules are involved.

- For a first order reaction :-
 (1) The degree of dissociation is equal to $(1 - e^{-kt})$
 (2) The pre-exponential factor in the arrhenius equation has the dimension of time⁻¹
 (3) A plot of reciprocal of concentration of the reaction v/s time gives a straight line
 (4) 1 & 2 both
- Azo isopropane decomposes according to the equation :-

$$(\text{CH}_3)_2\text{CHN} = \text{NCH}(\text{CH}_3)_2 \text{ (g)} \xrightarrow{250-290^\circ\text{C}} \text{N}_2\text{(g)} + \text{C}_6\text{H}_{14}\text{(g)}$$
 It is found to be a first order reaction. If initial pressure is P_o and pressure of the mixture at time t is P_t then rate constant k would be :-
 (1) $k = \frac{2.303}{t} \log \frac{P_o}{2P_o - P_t}$
 (2) $k = \frac{2.303}{t} \log \frac{P_o - P_t}{P_o}$
 (3) $k = \frac{2.303}{t} \log \frac{P_o}{P_o - P_t}$
 (4) $k = \frac{2.303}{t} \log \frac{2P_o}{2P_o - P_t}$
- A reagent undergoes 90% decomposition in 366 min. According to first order reaction, its half life is :-
 (1) $366 \times 100 \left(\frac{\ln 2}{90} \right)$ (2) $366 \left(\frac{\ln 2}{\ln 10} \right)$
 (3) $\frac{1}{366}$ (4) 183
- Which of the following statement is false :-
 (1) A fast reaction has a large rate constant and short half life
 (2) For a first order reaction, successive half lives are equal
 (3) For a first order reaction, the half life is independent of concentration
 (4) The half life of a reaction is half the time required for the reaction to go for completion
- The reaction

$$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$$
 is :-
 (1) Bimolecular reaction (2) II order reaction
 (3) Both (1) & (2) (4) None
- Correct expression for the first order reaction is:-
 (1) $C_t = C_0 e^{k_1 t}$ (2) $C_t e^{k_1 t} = C_0$
 (3) $\ln \frac{C_0}{C_t} = -k_1 t$ (4) $\ln \frac{C_t}{C_0} = k_1 t$

12. The rate of first order reaction is $1.5 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$ at 0.5 M concentration of the reactant. The half life of the reaction is
 (1) 7.53 min (2) 0.383 min
 (3) 23.1 min (4) 8.73 min
13. In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 min. The time taken for the concentration to change from 0.1 M to 0.025 M is
 (1) 7.5 min (2) 15 min
 (3) 30 min (4) 60 min
14. The rate equation for the reaction $2A + B \rightarrow C$ is found to be : rate = $k[A][B]$. The correct statement for this reaction is that the
 (1) rate of formation of C is twice the rate of disappearance of A.
 (2) Half life is a constant
 (3) unit of k must be s^{-1}
 (4) value of k is independent of the initial concentrations of A and B
15. The half-life of a radio isotope is four hours. If the initial mass of the isotope was 200 g, the mass remaining after 24 h undecayed is :
 (1) 3.125 g (2) 2.084 g
 (3) 1.042 g (4) 4.167 g
16. For a first order reaction $A \rightarrow B$ the reaction rate at reactant concentration of 0.01 M is found to be $2.0 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$. The half life period of the reaction is :
 (1) 220 s (2) 30 s (3) 300 s (4) 347 s
17. For reaction $aA \rightarrow xP$. When [A] is 2.2 mM, the rate was found to be 2.4 mM s^{-1} . On reducing concentration of A to half, the rate changes to 0.6 mM s^{-1} . The order of reaction with respect to A is :
 (1) 1.5 (2) 2.0 (3) 2.5 (4) 3.0
18. The $t_{1/2}$ of a reaction is halved as the initial concentration of the reactant is doubled. What is the order of reaction ?
 (1) 1 (2) 0 (3) 2 (4) 3
19. The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C , the rate of the reaction increases by about :-
 (1) 32 times (2) 64 times
 (3) 10 times (4) 24 times

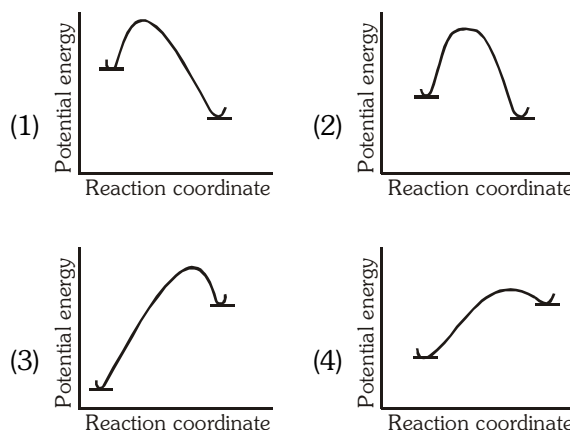
20. For a first order reaction, $(A) \rightarrow \text{products}$, the concentration of A changes from 0.1 M to 0.025 M in 40 min. The rate of reaction when the concentration of A is 0.01 M is :-
 (1) $1.73 \times 10^{-4} \text{ M/min}$ (2) $1.73 \times 10^{-5} \text{ M/min}$
 (3) $3.47 \times 10^{-4} \text{ M/min}$ (4) $3.47 \times 10^{-5} \text{ M/min}$

21. Arrhenius equation may be written as :-

$$(1) \frac{d}{dT} (\ln k) = - \frac{E_a}{RT} \quad (2) \frac{d}{dT} (\ln k) = - \frac{E_a}{RT^2}$$

$$(3) \frac{d}{dT} (\ln k) = + \frac{E_a}{RT^2} \quad (4) \frac{d}{dT} (\ln k) = \frac{E_a}{RT}$$

22. An endothermic reaction with high activation energy for the forward reaction is given by the diagram :



23. A reactant (A) forms two products :



If $E_{a2} = 2 E_{a1}$, then k_1 and k_2 are related as :-

$$(1) k_1 = 2k_2 e^{E_{a2}/RT} \quad (2) k_2 = k_1 e^{E_{a1}/RT}$$

$$(3) k_2 = k_1 e^{E_{a2}/RT} \quad (4) k_1 = k_2 e^{E_{a1}/RT}$$

24. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be

($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ and $\log 2 = 0.301$)

$$(1) 53.6 \text{ kJ mol}^{-1} \quad (2) 48.6 \text{ kJ mol}^{-1}$$

$$(3) 58.5 \text{ kJ mol}^{-1} \quad (4) 60.5 \text{ kJ mol}^{-1}$$

EXERCISE-III (Analytical Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	2	2	1	3	4	1	2	4	3	2	3	3	4	1
Que.	16	17	18	19	20	21	22	23	24						
Ans.	4	2	3	1	3	3	3	4	1						

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

1. **Assertion** : The rate of the reaction is the rate of change of concentration of a reactant or a product.
Reason : Rate of reaction remains constant during the complete reaction.
 (1) A (2) B (3) C (4) D
2. **Assertion** : The molecularity of a reaction is a whole number other than zero, but generally less than 3.
Reason : The order of a reaction is always whole number
 (1) A (2) B (3) C (4) D
3. **Assertion** : Formation of HI is a bimolecular reaction.
Reason : Two molecules of reactants are involved in this reaction.
 (1) A (2) B (3) C (4) D
4. **Assertion** : If in a zero order reaction, the concentration of the reactant is doubled, the half-life period is also doubled.
Reason : For a zero order reaction, the rate of reaction is independent of initial concentration.
 (1) A (2) B (3) C (4) D
5. **Assertion :-** In a first order reaction the rate constant double on doubling the initial concentration of the reaction.
Reason :- The rate constant varies directly with the concentration of the reactants in a first order reaction.
 (1) A (2) B (3) C (4) D
6. **Assertion :-** Rate of reaction double when concentration of reactant is double if it is a first order reaction.
Reason :- Rate constant also double.
 (1) A (2) B (3) C (4) D
7. **Assertion** : For a first order reaction $t_{1/2}$ is independent of the initial concentration of reactants.
Reason : For a first order reaction $t_{1/2}$ is twice the $t_{3/4}$.
 (1) A (2) B (3) C (4) D
8. **Assertion** : Acid catalysed of ethyl acetate is a first order reaction.
Reason : Water does not take part in the reaction.
 (1) A (2) B (3) C (4) D
9. **Assertion** : Half life period is always independent of initial concentration.
Reason : Half life period is directly proportional to rate concentration.
 (1) A (2) B (3) C (4) D
10. **Assertion** : In a reversible endothermic reaction activation energy of the forward reaction is higher than that of the backward reaction.
Reason : The threshold energy of the forward reaction is more than that of the backward reaction.
 (1) A (2) B (3) C (4) D
11. **Assertion** : The reaction having low value of activation energy are generally fast.
Reason : Temperature coefficient for reaction having low activation energy is large.
 (1) A (2) B (3) C (4) D
12. **Assertion :-** Two different reaction can never have same rate of reaction
Reason :- Rate of reaction always depends only on frequency of collision and Arrhenious factor
 (1) A (2) B (3) C (4) D
13. **Assertion :-** Rate constant of reaction depends on concentration of reactant.
Reason :- On changing concentration, rate of reaction always increases.
 (1) A (2) B (3) C (4) D

14. Assertion :- On increasing the temperature by 10°C , rate constant almost doubles.

Reason : On increasing temperature by 10°C , collision frequency doubles.

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

15. Assertion :- On increasing temperature rate of reaction always increases.

Reason :- For any reaction equilibrium always shifts in forward direction on increasing temperature.

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

16. Assertion : Catalyst increases rate of reversible reaction.

Reason : It increase the E_a for forward reaction but decreases the activation energy for backward reaction.

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

EXERCISE-IV (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	3	1	2	4	3	3	3	4	3	3	4	4	3	3
Que.	16														
Ans.	3														

IMPORTANT NOTES

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NEET SYLLABUS

Electrochemistry : Conductance in electrolytic solutions, specific and molar conductivity variation of conductivity with concentration, Kohlrausch's Law, Galvanic cells, Redox reactions, EMF of a cell, standard electrode potential, Relation between Gibbs energy change and EMF of a cell, electrolysis and electrolytic cells, Laws of electrolysis (elementary idea), dry cell, lead accumulator, fuel cells, corrosion.

OBJECTIVES

After studying this unit, we will be able to :

- describe an electrochemical cell and differentiate between galvanic and electrolytic cells;
- apply Nernst equation for calculating the emf of galvanic cell and define standard potential of the cell;
- derive relation between standard potential of the cell, Gibbs energy of cell reaction and its equilibrium constant;
- define resistivity (ρ), conductivity (κ) and molar conductivity (Λ_m) of ionic solutions;
- differentiate between ionic (electrolytic) and electronic conductivity;
- describe the methods for measurement of conductivity of electrolytic solutions and calculation of their molar conductivity;
- justify the variation of conductivity and molar conductivity of solutions with change in their concentration and define Λ_m^∞ (molar conductivity at zero concentration or infinite dilution);
- enunciate Kohlrausch law and learn its applications;
- understand quantitative aspects of electrolysis;
- describe the construction of some primary and secondary batteries and fuel cells;
- explain corrosion as an electrochemical process.

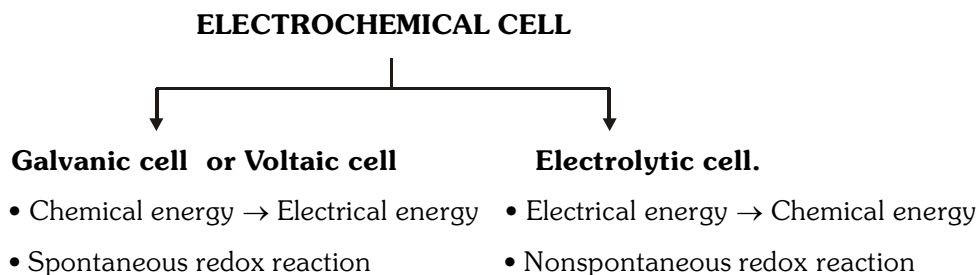
In arranging the bodies in order of their electrical nature, there is formed an electro-chemical system which, in my opinion is more fit than any other to give an idea of Chemistry.

Jons Jacob Berzelius

ELECTROCHEMISTRY

4.0 INTRODUCTION

Electrochemistry is the branch of physical chemistry which deals with the study of interconversion of chemical energy and electrical energy



4.1 CONDUCTORS

Substances which allow electric current to flow through them are called conductors.

Examples - Metals, Aqueous solution of acids, bases and salts, fused salts and impure water etc.

Conductors are of two types - (i) Metallic conductors or electronic conductors
(ii) Electrolytic conductors or ionic conductors

(i) Metallic conductors : The conductors which conduct electric current by the movement of electrons without undergoing any chemical change are known as metallic conductors.

Metals - Cu, Ag, Fe, Al etc, non metals - graphite

(ii) Electrolytic conductors : Those substances which conduct the electric current through ions in aqueous solution or in molten state are called electrolytic conductors.

- **Strong electrolyte :** Electrolytes which are completely ionized in aqueous solution are called strong electrolytes.

Ex. : Salts, strong acids and strong bases.

- **Weak electrolyte :-** Electrolytes which are not completely ionized in aqueous solution are called weak electrolytes.

Ex. : CH_3COOH , HCN , NH_3 , amine, etc.

Difference between metallic and electrolytic conductor

Metallic conductor	Electrolytic conductor
(i) Charge carriers are free electrons.	Charges carriers are free ions.
(ii) Flow of electricity takes place without any chemical change.	Flow of electricity takes place by chemical changes at electrodes.
(iii) No transfer of matter takes place.	Transfer of matter takes place in the form of ions.
(iv) Resistance is due to vibration of Kernels.	Resistance is due to inter ionic attraction and viscosity of medium.
(v) The resistance increases with the increase in temperature.	The resistance decreases with the increase in temperature.
(vi) Faraday's laws of electrolysis are not followed.	Faraday's laws of electrolysis are followed.

4.2 ELECTROLYTIC CONDUCTANCE

- (a) **Resistance (R)** :- Metallic and electrolytic conductors obey ohm's law according to which the resistance of a conductor is the ratio of the applied potential difference (V) to the current (I) flowing .

$$R = \frac{V}{I}$$

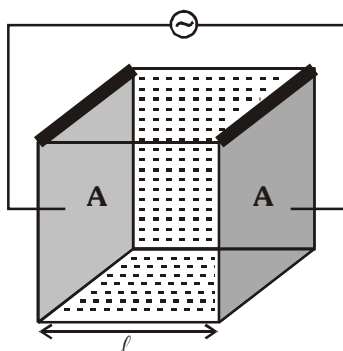
R is expressed in ohms.

- (b) **Conductance (G)** :- It is the property by virtue of which it favours flow of current. The conductance of a conductor is equal to reciprocal of resistance $G = \frac{1}{R}$

unit of G is **mho** or **ohm⁻¹** or **Siemens (S)**.

- (c) **Specific resistance/Resistivity (ρ)** :- The resistance (R) of a conductor is directly proportional to its length (ℓ) and inversely proportional to its area of cross section (A).

$$R \propto \frac{\ell}{A} \quad ; \quad R = \rho \frac{\ell}{A}$$



$$R = \rho \cdot \frac{\ell}{A} \quad ; \quad \rho = R \cdot \frac{A}{\ell}$$

If $\ell = 1 \text{ cm}$, $A = 1 \text{ cm}^2$, therefore $\rho = R$

$$\therefore V = A \times \ell = 1 \text{ cm}^3$$

Therefore resistance offered by 1 cm^3 electrolytic solution is known as resistivity.

Unit of $\rho \rightarrow \text{ohm cm}$

- (d) **Specific conductance/ Conductivity (κ)** :-

It is defined as the reciprocal of specific resistance, $\kappa = \frac{1}{\rho}$

$$R = \rho \frac{\ell}{A}$$

$$\frac{1}{\rho} = \frac{1}{R} \cdot \frac{\ell}{A}$$

$$\kappa = G \times G^*$$

Specific conductance = Conductance $\times$ Cell constant

Hence specific conductivity of a solution is defined as the conductance offered by 1 cm^3 of electrolytic solution. Unit of κ is $\text{ohm}^{-1} \text{ cm}^{-1}$

Cell constant :

$$G^* = \frac{\ell}{A} \quad ; \text{ Its unit is } \text{cm}^{-1}$$

- (e) **Molar conductivity or Molar conductance** :- (Λ_m , λ_m or μ) : It is defined as the conductance of all the ions produced by one mole of electrolyte present in the given volume of solution.

$$\Lambda_m = \kappa \times V$$

V = Volume of solution containing 1 mol of electrolyte.

If concentration of solution is M - mol per litre then

$$\Lambda_m = \frac{\kappa \times 1000}{M} \quad \text{Unit} \rightarrow \text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

- (f) **Equivalent conductivity or Equivalent conductance** (Λ_{eq} or λ_{eq}) :- It is defined as the conductance of all the ions produced by one gram equivalent of the electrolyte in the given volume of solution.

$$\therefore \Lambda_{eq} = \kappa \times V$$

V = Volume of solution containing 1 g-eq of electrolyte.

If concentration of solution is N - gram equivalent per litre then

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N} \quad \text{Unit} \rightarrow \text{ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

● **Relation between Λ_{eq} and Λ_m**

$$\Lambda_m = \frac{\kappa \times 1000}{M} \quad \text{and} \quad \Lambda_{eq} = \frac{\kappa \times 1000}{N}$$

We know that

Normality = Valency Factor $\times$ Molarity . So

$$\Lambda_{eq} = \frac{\Lambda_m}{V.F.}$$

Illustrations

- Illustration 1.** The resistance of a 1N solution of salt is 50 Ω . Calculate the equivalent conductance of the solution, if the two platinum electrodes in solution are 2.1 cm apart and each having an area of 4.2 cm².

Solution.

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \left(\frac{\ell}{A} \right) = \frac{1}{50} \times \frac{2.1}{4.2} = \frac{1}{100} \quad \text{and} \quad \Lambda_{eq} = \frac{\kappa \times 1000}{N} = \frac{1}{100} \times \frac{1000}{1} = 10 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

- Illustration 2.** Which of the following have maximum molar conductivity.

- (i) 0.08 M solution and its specific conductivity is $2 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$.
(ii) 0.1 M solution and its resistivity is 50 $\Omega \text{ cm}$.

Solution.

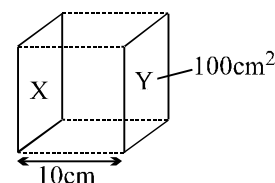
$$(i) \quad \Lambda_m = \frac{\kappa \times 1000}{M} = 2 \times 10^{-2} \times \frac{1000}{0.08} = 250 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$(ii) \quad \Lambda_m = \frac{\kappa \times 1000}{M}, \quad \therefore \kappa = \frac{1}{\rho}, \quad \therefore \Lambda_m = \frac{1}{50} \times \frac{1000}{0.1} = 200 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

So, the molar conductivity of 0.08 M solution will be greater than 0.1 M solution

- Illustration 3.** The conductance of a salt solution (AB) measured by two parallel electrodes of area 100 cm² separated by 10 cm was found to be 0.0001 Ω^{-1} . If volume enclosed between two electrodes contain 0.5 mol of salt. What is the molar conductivity ($\text{Scm}^2 \text{ mol}^{-1}$) of salt at same concentration.

- (A) 0.01 (B) 0.02 (C) 2×10^{-5} (D) none of these



Solution

$$G^* = \frac{\ell}{a} = \frac{10}{100} = 0.1; \quad G = 0.0001 \text{ S}; \quad V = 100 \times 10 = 1000 \text{ cm}^3 = 1 \text{ litre}$$

$$\kappa = G G^* = 0.1 \times 0.0001 = 10^{-5}$$

$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{(0.1 \times 0.0001) \times 1000}{0.5} = 0.02 \text{ S cm}^2 \text{ mol}^{-1}$$

4.3 FACTORS AFFECTING ELECTROLYTIC CONDUCTANCE

- (a) **Inter ionic attraction :-** If inter ionic attraction between ions of solute is more, then the conductance will be less.
- (b) **Polarity of solvent :-** If solvent has high-dielectric constant then the ionization and conductance will be higher.
- (c) **Viscosity of medium :-** On increasing the viscosity of medium, the conductance decreases.
- (d) **Temperature :-** As the temperature of electrolytic solution is increased, the conductance increases because K.E. of the ions increases and all types of attraction forces decrease and the viscosity of medium decreases.
- (e) **Hydrated size :** Due to hydration of ions conductance decreases.
- (f) **Dilution :-**
- (i) On increasing the dilution conductance (G) increases.
For strong electrolyte on dilution interionic force of attraction decreases therefore conductance increases.
For weak electrolyte with dilution degree of dissociation (α) increases therefore conductance increases.
 - (ii) On dilution specific conductance decreases because on dilution number of ions in 1 ml solution decreases.
 - (iii) On dilution equivalent and molar conductance increases because with dilution normality or molarity decreases

DETERMINATION OF MOLAR CONDUCTANCE OF ELECTROLYTES AT INFINITE DILUTION

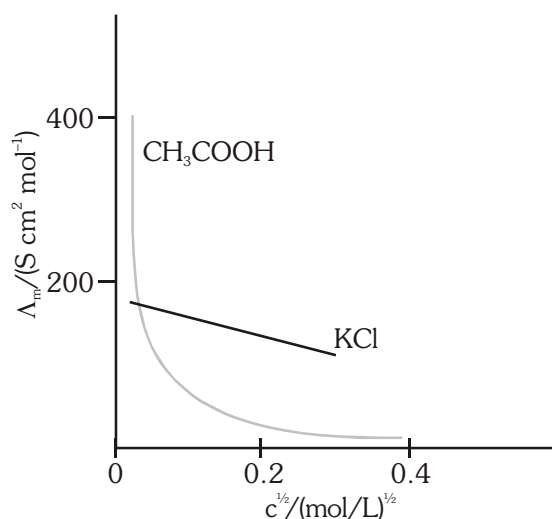
Debye Huckel Onsager equation –

$$\Lambda_m = \Lambda_m^\infty - b\sqrt{C} \quad [\text{only for strong electrolyte}]$$

where Λ_m = molar conductance at concentration C ,

Λ_m^∞ = molar conductance at ∞ dilution,

b = constant and its value is same for a particular type of electrolyte.



If a graph is plotted between Λ_m vs $\sqrt{C}$ a straight line is obtained for strong electrolyte. On extrapolation this line touches Λ_m axis. Therefore Λ_m^∞ for strong electrolyte can be found out from intercept. For weak electrolyte the slope of curve is not constant so it can not be extrapolated to obtain Λ_m^∞ .

4.4 KOHLRAUSCH'S LAW OF INDEPENDENT MIGRATION OF IONS

At infinite dilution when dissociation of electrolyte is complete; each ion makes a definite contribution towards equivalent conductivity of any electrolyte irrespective of the nature of other ion associated with it.

This law states that the equivalent conductivity of any electrolyte at infinite dilution (Λ_{eq}^{∞}) is the sum of equivalent ionic conductivities of the cation and anion given by the electrolytes at infinite dilution.

$$\Lambda_{eq}^{\infty} = \lambda_c^{\infty} + \lambda_a^{\infty}$$

Where λ_c^{∞} = equivalent conductance of cation at infinite dilution.

λ_a^{∞} = equivalent conductance of anion at infinite dilution.

For $A_x B_y \rightarrow xA^{y+} + yB^{x-}$

In terms of molar conductances of cation and anion

$$\Lambda_{eq}^{\infty} = \frac{1}{y} \lambda_{m(c)}^{\infty} + \frac{1}{x} \lambda_{m(a)}^{\infty}$$

Where $\lambda_{m(c)}^{\infty}$ = Limiting molar conductance of cation .

$\lambda_{m(a)}^{\infty}$ = Limiting molar conductance of anion .

y = charge on cation

x = charge on anion

$$\Lambda_m^{\infty} = x\lambda_{m(c)}^{\infty} + y\lambda_{m(a)}^{\infty}$$

Where x = Stoichiometric coefficient of cation

y = Stoichiometric coefficient of anion

Illustrations

Illustration 4. Calculate Λ_m^{∞} of oxalic acid, given that

$$\Lambda_{eq}^{\infty} \text{Na}_2\text{C}_2\text{O}_4 = 400 \Omega^{-1} \text{cm}^2 \text{eq}^{-1}$$

$$\Lambda_m^{\infty} \text{H}_2\text{SO}_4 = 700 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

$$\Lambda_{eq}^{\infty} \text{Na}_2\text{SO}_4 = 450 \Omega^{-1} \text{cm}^2 \text{eq}^{-1}$$

Solution $\Lambda_m^{\infty} \text{H}_2\text{C}_2\text{O}_4 = 700 + 800 - 900 = 600 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$

4.5 APPLICATIONS OF KOHLRAUSCH'S LAW :

(a) To calculate conductance of weak electrolyte.

(b) To calculate degree of dissociation :

$$\text{Degree of dissociation } \alpha = \frac{\Lambda_{eq}}{\Lambda_{eq}^{\infty}} = \frac{\text{equivalent conductance at a given concentration}}{\text{equivalent conductance at infinite dilution}}$$

$$\text{or } \alpha = \frac{\Lambda_m}{\Lambda_m^{\infty}} = \frac{\text{molar conductance at a given concentration}}{\text{molar conductance at infinite dilution}}$$

(c) To calculate dissociation constant of weak electrolyte

$$K_a = \frac{C\alpha^2}{(1-\alpha)}$$

If $\alpha \leq 5\%$ then $K_a = C\alpha^2$

Saturated solution of sparingly soluble salt can be considered as infinitely dilute solution.

M = Solubility (S).

$$\Lambda_m(\text{saturated}) = \Lambda_m^\infty = \frac{\kappa \times 1000}{\text{Solubility}}; S = \frac{\kappa \times 1000}{\Lambda_m^\infty}$$

- **Ionic conductance (λ) and mobility of ions (u)**

for a cation $\lambda_c \propto u_c$

or $\lambda_c = F u_c$ where $F = 96500 \text{ C}$

for an anion $\lambda_a \propto u_a$

or $\lambda_a = F u_a$

- **Transport number/Hittorf's number(t)**

The current flowing through an electrolytic solution is carried by ions (cation and anion). The fraction of total current carried by an ion is called its transport number.

$$\text{transport number of cation (t}_c\text{)} = \frac{\lambda_c}{\lambda_c + \lambda_a} = \frac{u_c}{u_c + u_a}$$

$$\text{transport number of anion (t}_a\text{)} = \frac{\lambda_a}{\lambda_c + \lambda_a} = \frac{u_a}{u_c + u_a}$$

and $t_c + t_a = 1$

if $u_c = u_a$ then $t_c = t_a = 0.5$

Illustrations

(3) $4.2 \text{ S cm}^2 \text{ mol}^{-1}$ (4) $42 \text{ S cm}^2 \text{ mol}^{-1}$

Solution $[\text{Salt}] = \frac{0.015}{2} \text{ M}; \wedge_{\text{m}} = \frac{6.3 \times 10^{-4} \times 1000}{0.015/2} = 84 \text{ S cm}^2 \text{ mol}^{-1}$

(3) $1.52 \times 10^{-3} \text{ S m}^{-1}$ (4) None

Solution

$$K_a = \frac{c\alpha^2}{1-\alpha} \Rightarrow 1.6 \times 10^{-5} = \frac{0.01 \times \alpha^2}{1-\alpha}$$

$$\alpha = \sqrt{\frac{1.6 \times 10^{-5}}{0.01}} = \sqrt{1.6 \times 10^{-3}} = 0.04 ; \quad \alpha = \frac{\wedge_m}{\wedge_m^\infty} ; \quad \wedge_m = 0.04 \times 380 \times 10^{-4}$$

$$\Lambda_m = \frac{\kappa \times 10^{-3}}{M}$$

$$\kappa = \frac{0.04 \times 380 \times 10^{-4} \times 0.01}{10^{-3}} = 1.52 \times 10^{-2} \text{ Sm}^{-1}$$

Illustration 7.

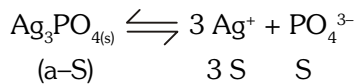
The conductivity of a saturated solution of Ag_3PO_4 is $9 \times 10^{-6} \text{ S m}^{-1}$ and its equivalent conductivity is $1.50 \times 10^{-4} \text{ S m}^2 \text{ eq}^{-1}$. The K_{sp} of Ag_3PO_4 is

- (1) 4.32×10^{-18} (2) 1.8×10^{-9} (3) 8.64×10^{-13} (4) None of these

Solution

$$\Lambda_{\text{eq}} = \kappa \times \frac{1000}{N}; \quad 1.50 \times 10^{-4} \times 10^4 = 9 \times 10^{-6} \times 10^{-2} \times \frac{1000}{N}; \quad N = 6 \times 10^{-5}$$

$$S = M = \frac{N}{n_f} = \frac{6 \times 10^{-5}}{3} = 2 \times 10^{-5} \text{ mol L}^{-1}$$



$$K_{sp} = (3S)^3 \cdot S = 27.S^4$$

$$= 27 \times (2 \times 10^{-5})^4 = 4.32 \times 10^{-18}$$

BEGINNER'S BOX-1

1. The resistance of 1 N solution of CH_3COOH is $250\ \Omega$, when measured in a cell of cell constant $1.15\ \text{cm}^{-1}$. The equivalent conductance will be

- (1) $4.6 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$ (2) $9.2 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$
(3) $18.4 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$ (4) $0.023 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$

- 2.** The specific conductivity of N/10 KCl solution at 20°C is $0.012 \Omega^{-1} \text{ cm}^{-1}$ and the resistance of the cell containing this solution at 20°C is 56Ω . The cell constant is

- (1) 4.616 cm^{-1} (2) 0.672 cm^{-1} (3) 2.173 cm^{-1} (4) 3.324 cm^{-1}

- 3.** Molar conductances of BaCl_2 , H_2SO_4 and HCl at infinite dilutions are x_1 , x_2 and x_3 , respectively. Equivalent conductance of BaSO_4 at infinite dilution will be :

- $$(1) \frac{[x_1 + x_2 - x_3]}{2} \qquad (2) \frac{[x_1 - x_2 - x_3]}{2}$$

- $$(3) \ 2(x_1 + x_2 - 2x_3) \qquad (4) \ \frac{[x_1 + x_2 - 2x_3]}{2}$$

4. The ionization constant of a weak electrolyte is 25×10^{-6} while the equivalent conductance of its 0.01 M solution is $19.6 \text{ S cm}^2 \text{ eq}^{-1}$. The equivalent conductance of the electrolyte at infinite dilution (in $\text{S cm}^2 \text{ eq}^{-1}$) will be

- (1) 39.2 (2) 78.4 (3) 392 (4) 196

5. Which has maximum conductivity :

- (1) $[\text{Cr}(\text{NH}_3)_3 \text{Cl}_3]$ (2) $[\text{Cr}(\text{NH}_3)_4 \text{Cl}_2]\text{Cl}$ (3) $[\text{Cr}(\text{NH}_3)_5 \text{Cl}]\text{Cl}_2$ (4) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$

4.6 ELECTRODE POTENTIAL :

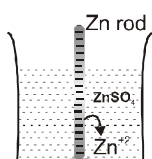
- The potential developed between metal electrode and its ions in solution is known as electrode potential.
- The potential developed between metal electrodes and the solution of its ions at 1 M concentration at 1 bar pressure and 298 K is known as **standard electrode potential**.
- There are two types of electrode potential :-

(a) Oxidation Potential (O.P.)

- The electrode potential for oxidation half reaction



- Tendency to get oxidised.
- **Greater the O.P. greater will be the tendency to get oxidised.**

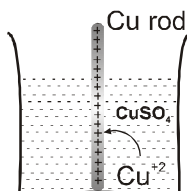


(b) Reduction Potential (R.P.)

- The electrode potential for reduction half reaction



- Tendency to get reduced.
- **Greater the R.P. greater will be the tendency to get reduced.**



- Electrode potential depends upon :
 - Concentration of the solution.
 - Nature of the metal.
 - Pressure temperature conditions.

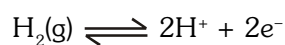
4.7 REFERENCE ELECTRODE :

- The potential of a single electrode cannot be determined but the potential difference between two electrodes can be accurately measured using a reference electrode.
- An electrode is chosen as a reference with respect to which all other electrodes are valued.
- There are two types of reference electrodes

(a) **Primary reference electrode : Standard hydrogen electrode (SHE)**

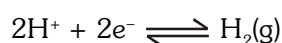
Representation : $\text{Pt}, \text{H}_2(\text{g}) \mid \text{H}^+ (1\text{M})$

When acts as anode

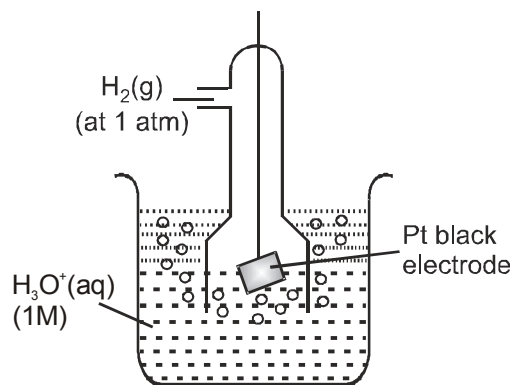


$$E^0_{\text{H}_2(\text{g})/\text{H}^+(\text{aq})} = \text{SOP}$$

When acts as cathode



$$E^0_{\text{H}^+/\text{H}_2(\text{g})} = \text{SRP}$$



- For SHE electrode potential is arbitrarily assumed to be zero at all temperature.

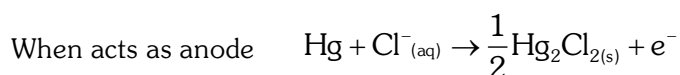
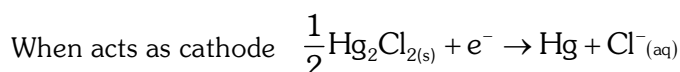
$$\text{SOP} = -\text{SRP} = 0 \text{ for SHE.}$$

- To calculate standard potential of any other electrode a cell is coupled with standard hydrogen electrode (SHE) and its potential is measured that gives the value of electrode potential of that electrode.

(b) **Secondary reference electrode :**

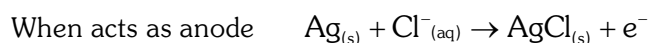
(i) **Calomel electrode (Hg_2Cl_2) -**

Representation : $\text{Pt} \mid \text{Hg}-\text{Hg}_2\text{Cl}_{2(\text{s})} \mid \text{KCl}_{(\text{aq})}$



(ii) **Silver-silver chloride electrode -**

Representation : $\text{Pt} \mid \text{Ag}-\text{AgCl}_{(\text{s})} \mid \text{KCl}_{(\text{aq})}$



4.8 CELL POTENTIAL (E^0_{cell}) :

$$E^0_{\text{cell}} = \text{SRP of cathode} - \text{SRP of anode}$$

$$E^0_{\text{cell}} = \text{SRP of cathode} + \text{SOP of anode}$$

$$E^0_{\text{cell}} = \text{SOP of anode} - \text{SOP of cathode}$$

4.9 ELECTROCHEMICAL SERIES

Arrangement of different elements on the basis of their SRP values is known as electrochemical series or activity series.

Electrode	Reaction	SRP (at 298 K)
Li	$\text{Li}^+ + e^- \rightarrow \text{Li(s)}$	- 3.05 V
K	$\text{K}^+ + e^- \rightarrow \text{K (s)}$	- 2.93 V
Ba	$\text{Ba}^{+2} + 2e^- \rightarrow \text{Ba}$	- 2.91 V
Ca	$\text{Ca}^{+2} + 2e^- \rightarrow \text{Ca(s)}$	- 2.87 V
Na	$\text{Na}^+ + e^- \rightarrow \text{Na(s)}$	- 2.71 V
Mg	$\text{Mg}^{+2} + 2e^- \rightarrow \text{Mg(s)}$	- 2.36 V
Al	$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	- 1.66 V
Mn	$\text{Mn}^{+2} + 2e^- \rightarrow \text{Mn}$	- 1.18 V
H ₂ O	$\text{H}_2\text{O(l)} + e^- \rightarrow \frac{1}{2}\text{H}_2 + \text{OH}^-$	- 0.828 V
Zn	$\text{Zn}^{+2} + 2e^- \rightarrow \text{Zn(s)}$	- 0.76 V
Cr	$\text{Cr}^{+3} + 3e^- \rightarrow \text{Cr(s)}$	- 0.74 V
Fe	$\text{Fe}^{+2} + 2e^- \rightarrow \text{Fe}$	- 0.44 V
Cd	$\text{Cd}^{+2} + 2e^- \rightarrow \text{Cd(s)}$	- 0.40 V
Co	$\text{Co}^{+2} + 2e^- \rightarrow \text{Co}$	- 0.28 V
Ni	$\text{Ni}^{+2} + 2e^- \rightarrow \text{Ni(s)}$	- 0.25 V
Sn	$\text{Sn}^{+2} + 2e^- \rightarrow \text{Sn(s)}$	- 0.14 V
Pb	$\text{Pb}^{+2} + 2e^- \rightarrow \text{Pb(s)}$	- 0.13 V
H ₂	$2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{(g)}$	0.00 V
Cu	$\text{Cu}^{+2} + 2e^- \rightarrow \text{Cu(s)}$	0.34 V
I ₂	$\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$	0.54 V
Fe	$\text{Fe}^{+3} + e^- \rightarrow \text{Fe}^{+2}$	0.77 V
Hg	$\text{Hg}_2^{+2} + 2e^- \rightarrow \text{Hg(l)}$	0.79 V
Ag	$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	0.80 V
Hg	$\text{Hg}^{+2} + 2e^- \rightarrow \text{Hg(l)}$	0.85 V
Br ₂	$\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-$	1.09 V
Pt	$\text{Pt}^{+2} + 2e^- \rightarrow \text{Pt}$	1.20 V
O ₂	$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O(l)}$	1.23 V
Cl ₂	$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	1.36 V
Au	$\text{Au}^{+3} + 3e^- \rightarrow \text{Au(s)}$	1.40 V
F ₂	$\text{F}_2 + 2e^- \rightarrow 2\text{F}^-$	2.87 V

Increasing strength of reducing agent

Increasing strength of oxidising agent

4.10 APPLICATIONS OF ELECTROCHEMICAL SERIES

(i) Oxidising and reducing power –

$$\text{Oxidising power} \propto \text{SRP} \propto \frac{1}{\text{SOP}}$$

$$\text{Reducing power} \propto \text{SOP} \propto \frac{1}{\text{SRP}}$$

(ii) **Reactivity of metals –**

$$\text{Reactivity of metal} \propto \text{SOP} \propto \frac{1}{\text{SRP}}$$

- In ECS reactivity of metal decreases from top to bottom.
- Li is most reactive metal.

(iii) **Reactivity of non-metals –**

$$\text{Reactivity of non-metal} \propto \text{SRP} \propto \frac{1}{\text{SOP}}$$

- In ECS reactivity of non-metal increases from top to bottom.
- F_2 is most reactive non-metal.

(iv) **Displacement reactions in solution –**

More reactive metal / non-metal displaces less reactive metal / non-metal in their solution.

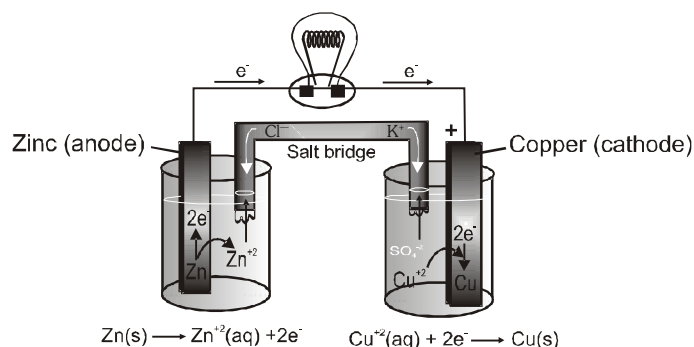
- $\text{Cu} + 2\text{AgNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{Ag}$
 $\text{Ag} + \text{Cu}(\text{NO}_3)_2 \rightarrow \text{No reaction}$
- $2\text{KI} + \text{Cl}_2 \rightarrow 2\text{KCl} + \text{I}_2$
 $\text{I}_2 + 2\text{KCl} \rightarrow \text{No reaction}$

(v) **Metal above hydrogen displaces H_2 from dilute acid solution.**

- $\text{Zn} + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{ZnSO}_4 + \text{H}_2(\text{g})$
 $\text{Cu} + \text{H}_2\text{SO}_4(\text{dilute}) \rightarrow \text{No reaction}$

4.11 GALVANIC CELL :

- It has two **half-cells**, each having a beaker containing a metal strip that dips in its aqueous salt solution.
- The metal strips are called **electrodes** and are connected by a conducting wire.
- Two solutions are connected by a **salt bridge**.
- The oxidation and reduction half reactions occur at separate electrodes and electric current flows through the wire.



Salt Bridge and its functions :

Salt bridge is inverted U-tube containing solution of inert electrolyte with agar-agar or gelatin to convert into semi solid form.

Ions of inert electrolyte do not involve in any chemical change.

The electrolyte in salt bridge should be such that speed of it's cation is nearly equal to speed of it's anion.

Ex. KCl , KNO_3 , NH_4NO_3

If Ag^+ , Hg_2^{+2} , Pb^{+2} , Tl^+ ions are present in a cell then KCl is not used because there can be formation of precipitate of AgCl , Hg_2Cl_2 , PbCl_2 or TlCl .

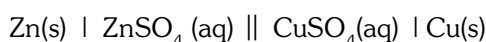
Functions

- It connects the solution of two half cell to complete the circuit.
- It maintains the electrical neutrality of the solution in order to give continuous flow or generation of current.
- If the salt bridge is removed then voltage drops to zero.
- It prevents the liquid-liquid junction potential. The potential difference which arises between two solutions when they brought in contact with each other.

Cell Representation :

We require two half cells to produce an electrochemical cell, which can be represented by following few rules;

- The anode half-cell is always written on the left followed on the right by cathode half cell.
- The separation of two phases (state of matter) is shown by a vertical line.
- The various materials present in the same phase are shown together using commas.
- The salt bridge is represented by a double slash ($\parallel$).
- The significant features of the substance like pressure of a gas, concentration of ions etc. are indicated in brackets immediately after writing the substance.



4.12 NERNST EQUATION :

It gives relation between electrode potential/ EMF of cell and concentration of electrolytic solution.

Walther Nernst derived a relation between free energy change (ΔG) and Reaction quotient (Q).

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \dots(1)$$

where ΔG and ΔG° are free energy change and standard free energy change; 'Q' is reaction quotient.

$$\therefore -\Delta G = nFE \quad \text{and} \quad -\Delta G^\circ = nFE^\circ$$

Thus from Eq. (1), $-nFE = -nFE^\circ + RT \ln Q$

$$E = E^\circ - \frac{2.303 RT}{nF} \log Q$$

Where - E° = standard electrode potential,

R = gas constant,

T = temperature (in K)

F = Faraday (96500 coulomb mol^{-1}),

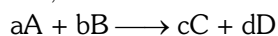
n = number of moles of e^- gained lost or transferred in balanced equation.

At 25°C, above equation may be written as

$$E = E^\circ - \frac{0.0591}{n} \log Q$$

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$

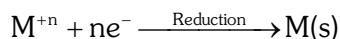
In general, for a redox cell reaction involving the transference of n electrons



$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{or} \quad E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

4.13 APPLICATIONS OF NERNST EQUATION

(i) Calculation of electrode potential (E_{RP} or E_{OP}) -

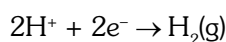


$$E_{RP} = E_{RP}^0 - \frac{0.0591}{n} \log \frac{[M]}{[M^{+n}]}$$

$$E_{RP} = E_{RP}^0 - \frac{0.0591}{n} \log \frac{1}{[M^{+n}]}$$

If $[M^{+n}]$ increases, then E_{RP} increases

(ii) Calculation of electrode potential and pH of hydrogen electrode -



$$E_{RP} = E_{RP}^0 - \frac{0.0591}{2} \log \frac{P_{H_2}}{[H^{+}]^2}$$

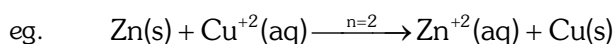
$$\therefore E_{RP}^0 = 0; \quad E_{RP} = E_{RP}^0 - \frac{0.0591}{2} \log \frac{1}{[H^{+}]^2} \quad [P_{H_2} \text{ is taken } 1 \text{ atm}]$$

$$E_{RP} = 0.0591 \log [H^{+}]$$

$$E_{RP} = -0.0591 \text{ pH}$$

$$E_{OP} = +0.0591 \text{ pH}$$

(iii) Calculation of EMF of cell (E_{cell}) -



$$E_{cell} = E_{cell}^0 - \frac{0.0591}{2} \log \frac{[Zn^{+2}]}{[Cu^{+2}]}$$

If $[Cu^{+2}]$ increases, then E_{cell} increases

If $[Zn^{+2}]$ increases, then E_{cell} decreases

(iv) Prediction and feasibility of a cell reaction -

For a feasible cell reaction

$$\Delta G = -ve \quad (\Delta G = -nFE_{cell})$$

$$E_{cell} = +ve$$

(v) Calculation of equilibrium constant (K_{eq}) and ΔG° -

From Nernst equation -

$$E_{cell} = E_{cell}^0 - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$

$$\text{At equilibrium, } E_{cell} = 0 \quad \text{and} \quad \frac{[P]}{[R]} = K_{eq}$$

$$E_{\text{cell}}^0 = \frac{0.0591}{n} \log K_{\text{eq}}$$

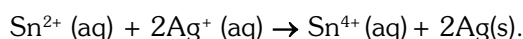
$$E_{\text{cell}}^0 = \frac{2.303RT}{nF} \log K_{\text{eq}}$$

$$n F E_{\text{cell}}^0 = 2.303 RT \log K_{\text{eq}}$$

$$\Delta G^\circ = -2.303RT \log K_{\text{eq}}$$

Illustrations

Illustration 8. Write cell representation for the following redox reaction,



Solution The cell consists of a platinum wire anode dipped in Sn^{2+} solution and a silver cathode dipped in Ag^+ solution therefore $\text{Pt}(\text{s}) | \text{Sn}^{2+}(\text{aq}), \text{Sn}^{4+}(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag}(\text{s})$.

Illustration 9. Calculate the EMF of a Daniel cell when the concentration of ZnSO_4 and CuSO_4 are 0.001 M and 0.1 M respectively. The standard EMF of the cell is 1.1 V.

Solution $\text{Zn}(\text{s}) + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu}$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 1.1 - \frac{0.0591}{2} \log \frac{10^{-3}}{10^{-1}} = 1.159 \text{ V}$$

Illustration 10. Calculate E^0 and E for the cell $\text{Sn} | \text{Sn}^{2+} (1\text{M}) || \text{Pb}^{2+} (10^{-3}\text{M}) | \text{Pb}$, $E^0 (\text{Sn}^{2+} | \text{Sn}) = -0.14\text{V}$, $E^0 (\text{Pb}^{2+} | \text{Pb}) = -0.13 \text{ V}$. Is cell representation correct?

Solution $E_{\text{cell}}^0 = E_{\text{Pb}^{2+}/\text{Pb}}^0 - E_{\text{Sn}^{2+}/\text{Sn}}^0 = -0.13 - (-0.14) = +0.01 \text{ V}$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} = +0.01 - \frac{0.0591}{2} \log \left[\frac{1}{10^{-3}} \right] = -0.078 \text{ V cell with not work}$$

Illustration 11. Calculate the equilibrium constant for the reaction $\text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+}$,

[Given : $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 = 1.44 \text{ V}$; $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.68 \text{ V}$]

$$\text{Take } \frac{2.303 RT}{F} = 0.06 \text{ at } 25^\circ\text{C}, \log 4.68 = 0.67$$

Solution $\text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+}$

$$E^0 = 1.44 - 0.68 = 0.76\text{V} = \frac{0.06}{1} \log K_{\text{C}}; K_{\text{C}} = 4.64 \times 10^{12}$$

Illustration 12. The 0.1 M copper sulphate solution in which copper electrode is dipped at 25°C . Calculate the electrode potential of copper electrode [Given $E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.34\text{V}$]

Solution. $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$

$$E_{\text{red}} = E_{\text{red}}^0 - \frac{0.059}{n} \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$\text{Here } n = 2 \text{ so } E = 0.34 - \frac{0.059}{2} \log 10$$

$$E = 0.34 - 0.03 = 0.31 \text{ V}$$

Illustration 13. Calculate the EMF of the cell $\text{Cr} \mid \text{Cr}^{+3} (0.1\text{M}) \parallel \text{Fe}^{+2} (0.01\text{M}) \mid \text{Fe}$

(Given $E^\circ_{\text{Cr}^{+3}/\text{Cr}} = -0.75\text{V}$, $E^\circ_{\text{Fe}^{+2}/\text{Fe}} = -0.45\text{V}$)

Solution.

Half cell reactions are –

At Anode $[\text{Cr} \rightarrow \text{Cr}^{+3} + 3e^-] \times 2$

At Cathode $[\text{Fe}^{+2} + 2e^- \rightarrow \text{Fe}] \times 3$

Cell reaction $2\text{Cr} + 3\text{Fe}^{+2} \rightarrow 2\text{Cr}^{+3} + 3\text{Fe}$

$E^\circ_{\text{cell}} = \text{Oxidation potential} + \text{Reduction potential} = 0.75 + (-0.45) = 0.30\text{V}$

$$E_{\text{cell}} = E^\circ - \frac{0.059}{n} \log \frac{[\text{Product}]}{[\text{Reactant}]} = 0.30 - \frac{0.059}{6} \log \frac{[\text{Cr}^{+3}]^2}{[\text{Fe}^{+2}]^3} = 0.30 - \frac{0.059}{6} \log \frac{[0.1]^2}{[0.01]^3}$$

$$= 0.30 + \frac{0.24}{6} = 0.34\text{V}$$

Illustration 14. For the cell $\text{Pt(s)} \mid \text{H}_2(0.4\text{ atm}) \mid \text{H}^+(\text{pH}=1) \parallel \text{H}^+(\text{pH} = 2) \mid \text{H}_2(0.1\text{ atm}) \mid \text{Pt}$
The measured potential at 25°C is

(1) -0.1V (2) -0.5V (3) -0.041V (4) -0.030V

Solution

Anode reaction : $\text{H}_2(0.4\text{ atm}) \rightarrow 2\text{H}^+(10^{-1}\text{M}) + 2e^-$

Cathode reaction : $2\text{H}^+(10^{-2}\text{M}) + 2e^- \rightarrow \text{H}_2(0.1\text{ atm})$

Cell reaction $\text{H}_2(0.4\text{ atm}) + 2\text{H}^+(10^{-2}\text{M}) \rightarrow 2\text{H}^+(10^{-1}\text{M}) + \text{H}_2(0.1\text{ atm})$

$$E = 0 - \frac{0.059}{2} \log \frac{(10^{-1})^2(0.1)}{(0.4)(10^{-4})} = -0.041\text{V}$$

Illustration 15. If $E^\circ_{\text{Au}^+/\text{Au}}$ is 1.69V & $E^\circ_{\text{Au}^{3+}/\text{Au}}$ is 1.40V , then $E^\circ_{\text{Au}^{3+}/\text{Au}^+}$ will be

(1) 0.19V (2) 2.945V (3) 1.255V (4) none

Solution

$\text{Au}^+ + e^- \longrightarrow \text{Au(s)}$ $E^\circ = 1.69\text{V}$... (1); ΔG_1°

$\text{Au}^{3+} + 3e^- \longrightarrow \text{Au(s)}$ $E^\circ = 1.40\text{V}$... (2); ΔG_2°

From (2) – (1)

$\text{Au}^{3+} + 2e^- \longrightarrow \text{Au}^+$... (3); ΔG_3°

$$\Delta G_3^\circ = \Delta G_2^\circ - \Delta G_1^\circ$$

$$-2 \times F \times E^\circ = -3 \times F \times 1.40 + 1 \times 1.69 \times F$$

$$E^\circ = 1.255\text{V}$$

GOLDEN KEY POINTS

- The value of electrode potential does not depend on stoichiometry of half reactions as it is an intensive property.
- Gibb's free energy is extensive property.
- In electrolytic cell, cathode is negative terminal whereas in Galvanic cell cathode is positive terminal.
- Cell reaction is spontaneous, if
 $\Delta G = -ve$ or $E_{\text{cell}} = +ve$
- Cell reaction will be in equilibrium, if
e.g. $\Delta G = 0$ or $-nFE_{\text{cell}} = 0$ or $E_{\text{cell}} = 0$

● **Work done by a cell :**

- (i) Let 'n' faraday charge be taken out of a cell of EMF 'E'; then work done by the cell will be calculated as:
 $\text{Work} = \text{Charge} \times \text{Potential} = nF \times E$
- (ii) Work done by cell = Decrease in free energy
 so $-\Delta G = nFE$ or $W_{\text{max}} = + nFE^\circ$, where E° is standard EMF of the cell.

BEGINNER'S BOX-2

1. Calculate E°_{cell} for the following cell

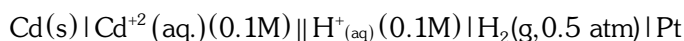


- (1) 0.04 V (2) - 1.56 V (3) 1.56 V (4) 0.84 V

2. Standard EMF of a galvanic cell involving $2e^-$ transfer is found to be 0.591 V at 25°C. Calculate equilibrium constant for the cell reaction

- (1) 20^{10} (2) 10^{20} (3) 10^{200} (4) 200^{10}

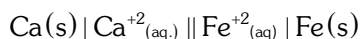
3. Calculate cell potential at 298 K for the following galvanic cell



$$E^\circ_{\text{Cd}^{+2}/\text{Cd}} = -0.40\text{V}$$

- (1) 0.38 (2) - 0.38 (3) 0.36 (4) - 0.36

4. Calculate E°_{cell} of the following galvanic cell at 298 K ;



$$E^\circ_{\text{Ca}^{+2}/\text{Ca}} = -2.87\text{V}; E^\circ_{\text{Fe}/\text{Fe}^{+2}} = 0.41\text{V}$$

- (1) 2.46 V (2) - 2.46 V (3) 3.28 V (4) - 3.28 V

5. Given $E^\circ_{\text{Ag}^{+}/\text{Ag}} = 0.80\text{V}$, $E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.37\text{V}$, $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}$, $E^\circ_{\text{Hg}^{2+}/\text{Hg}} = 0.79\text{V}$.

Which of the following statement is correct

- (1) AgNO_3 can be stored in copper vessel
 (2) $\text{Mg}(\text{NO}_3)_2$ can not be stored in copper vessel
 (3) CuCl_2 can be stored in silver vessel
 (4) HgCl_2 can be stored in copper vessel

6. $1/2 \text{H}_2(\text{s}) + \text{AgCl(s)} \longrightarrow \text{H}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq}) + \text{Ag(s)}$ occurs in the galvanic cell :

- (1) $\text{Ag(g)} | \text{AgCl(s)} | \text{KCl(sol)} || \text{AgNO}_3(\text{sol}) | \text{Ag(s)}$
 (2) $\text{Pt(s)} | \text{H}_2(\text{g}) | \text{HCl(sol)} || \text{AgNO}_3(\text{sol}) | \text{Ag(s)}$
 (3) $\text{Pt(s)} | \text{H}_2(\text{g}) | \text{HCl(sol)} || \text{Cl}^{-}(\text{aq}) | \text{AgCl(sol)} | \text{Ag(s)}$
 (4) $\text{Pt(s)} | \text{H}_2(\text{g}) | \text{KCl(sol)} || \text{AgCl(sol)} | \text{Ag(s)}$

4.14 SOME SPECIAL CELLS

(A) CONCENTRATION CELLS

A concentration cell is a form of galvanic cell that has two equivalent half cells of the same material having difference only in concentrations. For such cells anode and cathode are same so $E^\circ_{\text{cell}} = 0$.

eg. $\text{Pt}, \text{H}_2(\text{g}) (P_1 \text{ atm}) | \text{H}^{+} (C_1) || \text{H}^{+} (C_2) | \text{H}_2(\text{g}) (P_2 \text{ atm}), \text{Pt}$

Anode Reaction : $\text{H}_2(\text{P}_1) \longrightarrow 2\text{H}^+(\text{C}_1) + 2\text{e}^-$

Cathode Reaction : $2\text{H}^+(\text{C}_2) + 2\text{e}^- \longrightarrow \text{H}_2(\text{P}_2)$

Cell Reaction : $\text{H}_2(\text{P}_1) + 2\text{H}^+(\text{C}_2) \longrightarrow 2\text{H}^+(\text{C}_1) + \text{H}_2(\text{P}_2)$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{P}]}{[\text{R}]}$$

$$\text{So, } E_{\text{cell}} = 0 - \frac{0.0591}{2} \log \left[\frac{\text{C}_1}{\text{C}_2} \right]^2 \frac{\text{P}_2}{\text{P}_1}$$

Case 1 : If $\text{P}_1 = \text{P}_2 = 1 \text{ atm}$; $E_{\text{cell}} = -\frac{0.059}{2} \log \left[\frac{\text{C}_1}{\text{C}_2} \right]^2$

$$E_{\text{cell}} = -0.0591 \log \left[\frac{\text{C}_1}{\text{C}_2} \right]$$

If $\text{C}_2 > \text{C}_1$ then $E_{\text{cell}} > 0$ and cell will be spontaneous.

Case 2 : If $\text{C}_1 = \text{C}_2$ $E_{\text{cell}} = -\frac{0.0591}{2} \log \left[\frac{\text{P}_2}{\text{P}_1} \right]$

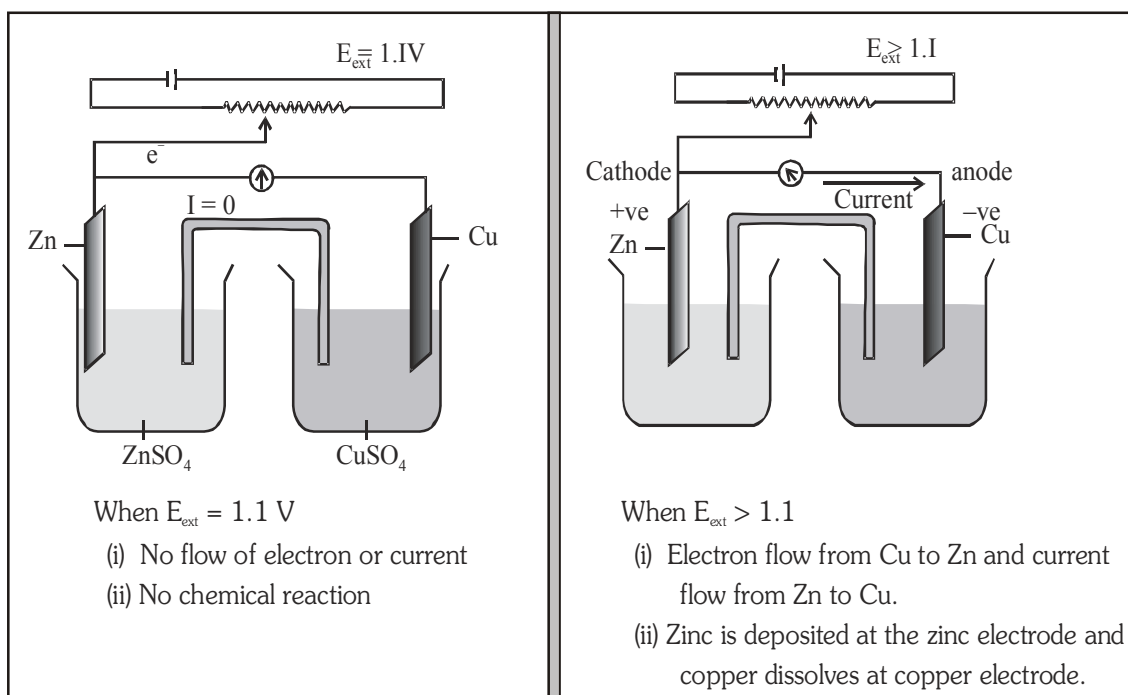
$$\text{P}_1 \neq \text{P}_2$$

If $\text{P}_1 > \text{P}_2$ then $E_{\text{cell}} > 0$ and cell will be spontaneous.

(B) REVERSIBLE CELLS :

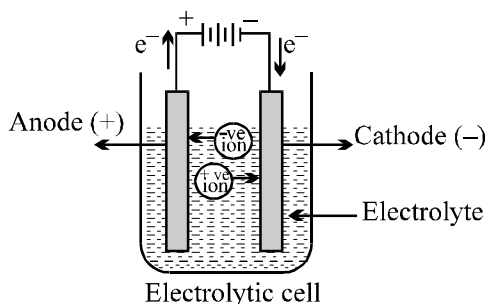
Those cell's in which chemical reactions are reversed by applying external emf in opposite directions known as reversible cells. A daniel cell is said to be reversible if it follows two conditions :

- (i) When $E_{\text{ext}} > 1.1 \text{ V}$ (emf of daniel cell) : cell reactions reversed
 - (ii) When $E_{\text{ext}} = 1.1 \text{ V}$ (emf of daniel cell) ; equilibrium will be established.
- In general secondary cells are reversible in nature.



4.15 ELECTROLYSIS

The process of chemical decomposition of an electrolyte by the passage of electricity is called electrolysis or electrolytic dissociation. It is carried out in **electrolytic cell** where electrical energy is converted into chemical energy. For electrolysis two suitable electrodes are immersed in the solution of an electrolyte. When an electric potential is applied between the electrodes, the positive ions move towards the cathode and negative ions move towards the anode. The gain of electrons (decrease in oxidation number) means reduction takes place at the cathode and loss of electrons (increase in oxidation number) means oxidation takes place at anode.



There are two aspects of electrolysis :

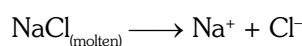
(A) Qualitative aspects of electrolysis :-

In qualitative aspect products formed at electrode are identified. At electrode product formation depends up on the following :

- (i) Nature of electrolyte
- (ii) Nature of electrodes : The metal strip at which current enters is called **anode**; anode is positively charged in electrolytic cell. On the other hand, the electrode at which current leaves is called **cathode**. Cathode is negatively charged. There are two types of electrodes
 - (a) Attackable : The attackable electrodes participate in the electrode reaction. They are made up of reactive metals like Zn, Cu, Ag etc in their respective solutions. In such electrodes, atom of the metal gets oxidised into the corresponding cation, which is passed into the solution. Thus, such anode gets dissolved and their mass decreases.
 - If electrode is active at cathode, metal goes on depositing and at anode metal is dissolved. The process is called electroplating.
 - (b) Non - attackable : Non-attackable electrodes do not participate in the electrode reaction as they are made up of unreactive elements like Pt, graphite etc. Such electrodes do not dissolve and their mass remain same.
 - Among the two cations, that cation is discharged at the cathode which has higher reduction potential. Among the two anions, that anion will be discharged at the anode which has lower reduction potential or higher oxidation potential.
 - The discharge of NO_3^- , PO_4^{3-} and SO_4^{2-} ions at anode does not commonly take place from aqueous solution.
- (iii) Concentration of electrolytic solution.

Examples of electrolysis :

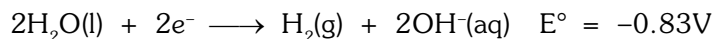
(a) Electrolysis of Molten Sodium Chloride



(b) Electrolysis of Sodium Chloride Solution

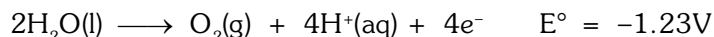
On electrolysis of aqueous solution of NaCl, the possible species involved in half-reactions are Na^+ , Cl^- and H_2O .

The possible cathode half-reactions are



Under the standard conditions, H_2O is to be reduced in preference to Na^+ and Hydrogen is evolved at the cathode.

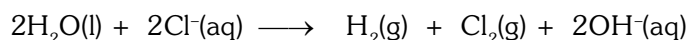
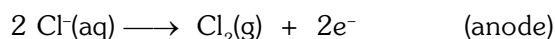
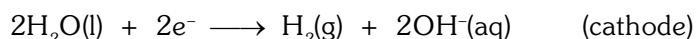
The possible anode half-reactions are



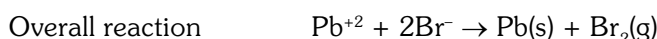
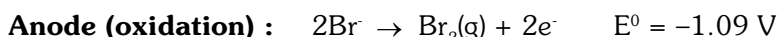
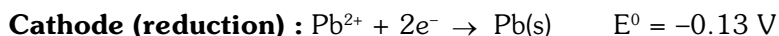
Under the standard-state conditions, H_2O is to be oxidized in preference to Cl^- . But since electrode potentials, depend on concentrations it turns out that when the solution is concentrated enough in Cl^- , Cl_2 is the product; but in dilute solution, O_2 is the product.

Starting with very dilute NaCl solutions, the oxidation potential of Cl^- is very negative, so H_2O is oxidised in preference to Cl^- . But as the NaCl concentration increase, the oxidation potential of Cl^- increases until eventually Cl^- is oxidized in preference to H_2O . The product changes from O_2 to Cl_2 .

The half-reactions and cell reaction for the electrolysis of aqueous sodium chloride to chlorine and hydroxide ion are as follows:

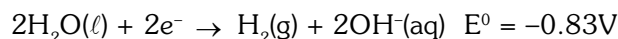
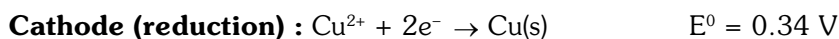


Because the electrolysis started with sodium chloride, the cation in the electrolyte solution is Na^+ . On evaporation of the electrolyte solution, sodium hydroxide NaOH is obtained.

(c) Electrolysis of Molten lead bromide using inert (pt/graphite) electrodes.

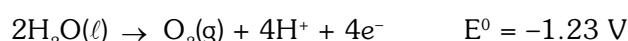
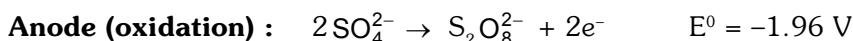
$$E_{\text{cell}} = -0.13 - 1.09 = -1.22\text{ V}$$

$$E_{\text{ext}} > 1.22\text{ V}$$

(d) Electrolysis of aq CuSO_4 using inert (pt/graphite) electrode

At cathode reduction of $\text{Cu}^{2+}(\text{aq})$ will be preferred over reduction of water as its standard reduction potential is more, than that of water.

Thus reaction at cathode : $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$

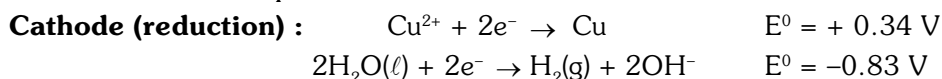


At anode oxidation of water is preferred over oxidation of sulphate ion as its standard oxidation potential is more, than that of sulphate ion.

Thus reaction at anode : $2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^-$

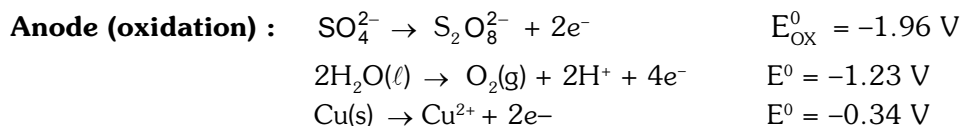
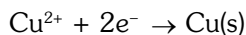
After electrolysis solution will become acidic ($\text{pH} < 7$)

(e) Electrolysis of aq. CuSO₄ using Cu electrode.



At cathode reduction of Cu²⁺ (aq) will be preferred over reduction of water as its standard reduction potential is more, than that of water.

Thus reaction at cathode :



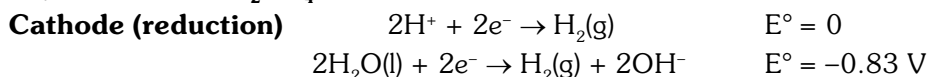
At anode oxidation of copper solid is preferred over oxidation of water and sulphate ion, as its standard oxidation potential is more than that of water and sulphate ion.

Thus reaction at anode :

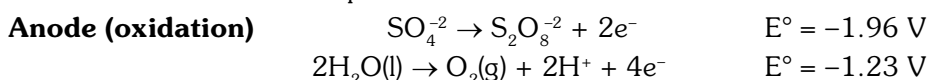


It is an example of electrolytic refining and there will be no change in the pH and concentration of electrolyte.

(f) Electrolysis of dilute H₂SO₄ :

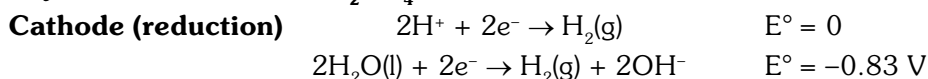


due to less availability of H⁺ ions, it will not participate in formation of H₂ gas therefore reduction of water will take place.

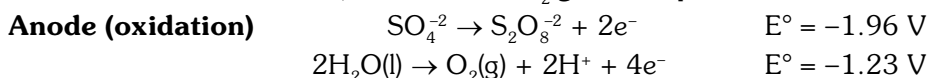


oxidation of water is preferred over oxidation of sulphate ion as its standard oxidation potential is more, than that of sulphate ion.

(g) Electrolysis of concentrated H₂SO₄



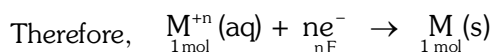
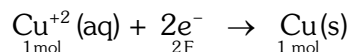
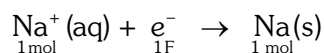
due to reduction of H⁺ ions, formation of H₂ gas takes place.



due to oxidation of SO₄²⁻ ions, formation of persulphate ion (S₂O₈²⁻) takes place.

(B) QUANTITATIVE ASPECTS OF ELECTROLYSIS

1 mole electron = N_A electron = 96500 coulomb = 1 Faraday



nF charge discharges = 1 mol of M⁺ⁿ ion

∴ 1 F charge discharges = $\frac{1}{n}$ mol of M⁺ⁿ ion

$$= \frac{1}{n} \times n = 1 \text{ g equivalent of M}^{+n} \text{ ion}$$

Hence 1 mole e⁻ = 1 F = 1 g equivalent

FARADAY'S LAWS OF ELECTROLYSIS

(a) First law of electrolysis :

Amount of substance deposited or liberated at an electrode is directly proportional to amount of charge passed through the solution.

$$W \propto Q$$

W = amount of substance deposited, Q = charge in coulomb

$$W = ZQ$$

Z = electrochemical equivalent

when $Q = 1$ coulomb, then $W = Z$

Thus, amount of substance deposited or liberated by 1 coulomb charge is called **electrochemical equivalent**.

Let I ampere current is passed till ' t ' seconds .

Then, $Q = It$ $\therefore W = ZIt$

1 Faraday = 96500 coulomb = Charge on one mole electrons

One faraday is the charge required to liberate or deposit one gram equivalent of a substance at corresponding electrode.

Let ' E ' is equivalent weight then ' E ' gram will be liberated by 96500 coulomb.

$\therefore$ 1 Coulomb will liberate $\frac{E}{96500}$ gram ;

By definition, $Z = \frac{E}{96500}$ $\therefore W = \frac{EIt}{96500}$ $\frac{W}{E} = \frac{It}{96500}$ = number of g eq = number of faraday

(b) Second law of electrolysis :

When same amount of charge is passed through different electrolyte solutions connected in series then weight of substances deposited or liberated at electrodes are in ratio of their respective equivalent weights.

$$\text{i.e. } \frac{W_1}{W_2} = \frac{E_1}{E_2}$$

GOLDEN KEY POINTS

PRODUCTS OF ELECTROLYSIS OF SOME ELECTROLYTES

S. No.	Electrolyte	Electrode	Product obtained at anode	Product obtained at cathode
(i)	Aqueous NaCl	Pt or Graphite	Cl_2	H_2
(ii)	Fused NaCl	Pt or Graphite	Cl_2	Na
(iii)	Aqueous NaOH	Pt or Graphite	O_2	H_2
(iv)	Fused NaOH	Pt or Graphite	O_2	Na
(v)	Aqueous CuSO_4	Pt or Graphite	O_2	Cu
(vi)	Aqueous CuSO_4	Copper	Cu oxidises to Cu^{+2} Ions	Cu
(vii)	Aqueous CuCl_2	Copper	Cu oxidises to Cu^{+2} ions	Cu
(viii)	Aqueous HCl	Pt or Graphite	Cl_2	H_2
(ix)	Dilute H_2SO_4	Pt or Graphite	O_2	H_2
(x)	Conc. H_2SO_4	Pt or Graphite	$\text{S}_2\text{O}_8^{2-}$	H_2
(xi)	Aqueous AgNO_3	Pt of Graphite	O_2	Ag
(xii)	Dilute NaCl	Pt or Graphite	O_2	H_2

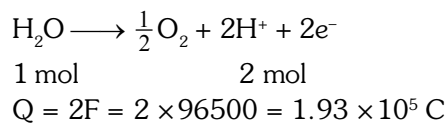
- For electrolysis $\Delta G = +ve$, So it is non-spontaneous process.
- In electrolytic cell D.C. current is used.

Illustrations

Illustration 16 How much electric charge is required to oxidise :

- (a) 1 mol of H_2O to O_2 (b) 1 mol of FeO to Fe_2O_3 ?

Solution (a) The oxidation reaction is :



- (b) The oxidation reaction is $\text{FeO} + \frac{1}{2}\text{H}_2\text{O} \longrightarrow \frac{1}{2}\text{Fe}_2\text{O}_3 + \text{H}^+ + \text{e}^-$

$$Q = F = 96500 \text{ C}$$

Illustration 17 One mole of electron passes through each of the solution of AgNO_3 , CuSO_4 and AlCl_3 when Ag, Cu and Al are deposited at cathode. The molar ratio of Ag, Cu and Al deposited are

- (1) 1 : 1 : 1 (2) 6 : 3 : 2 (3) 6 : 3 : 1 (4) 1 : 3 : 6

Solution Deposited equivalent will be same

$$1 \text{ eq. Ag} = 1 \text{ mol Ag}$$

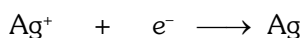
$$1 \text{ eq. Cu} = \frac{1}{2} \text{ mol Cu}$$

$$1 \text{ eq. Al} = \frac{1}{3} \text{ mol Al}$$

$$\Rightarrow \text{ratio} \quad 1 : \frac{1}{2} : \frac{1}{3} \Rightarrow 6 : 3 : 2$$

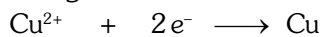
Illustration 18 Exactly 0.4 F electric charge is passed through three electrolytic cells connected in a series. First cell containing AgNO_3 , second cell containing CuSO_4 and third cell containing FeCl_3 solution. How many grams of each metal will be deposited assuming only cathodic reaction in each cell.

Solution The cathodic reaction in the cell are respectively,



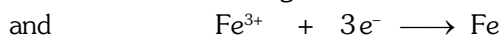
$$1 \text{ mol} \quad 1 \text{ mol}$$

$$108 \text{ g} \quad 1 \text{ F}$$



$$1 \text{ mol} \quad 1 \text{ mol}$$

$$63.5 \text{ g} \quad 2 \text{ F}$$



$$1 \text{ mol} \quad 1 \text{ mol}$$

$$56 \text{ g} \quad 3 \text{ F}$$

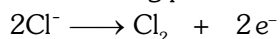
Hence, $\text{Ag deposited} = 108 \times 0.4 = 43.2 \text{ g}$

$$\text{Cu deposited} = \frac{63.5}{2} \times 0.4 = 12.7 \text{ g}$$

and $\text{Fe deposited} = \frac{56}{3} \times 0.4 = 7.47 \text{ g}$

Illustration 19 An electric current of 100 A is passed through a molten liquid of sodium chloride for 5 hours. Calculate the volume of chlorine gas liberated at the electrode at NTP.

Solution The reaction taking place at anode is



$$71.0 \text{ g} \quad 71.0 \text{ g} \quad 2 \times 96500 \text{ C}$$

$$= 1 \text{ mol}$$

$$Q = i \times t = 100 \times 5 \times 60 \times 60 \text{ C}$$

The amount of chlorine liberated by passing $100 \times 5 \times 60 \times 60 \text{ C}$ of electric charge.

$$= \frac{1}{2 \times 96500} \times 100 \times 5 \times 60 \times 60 = 9.3264 \text{ mole}$$

$$\text{Volume of } \text{Cl}_2 \text{ liberated at NTP} = 9.3264 \times 22.4 = 208.91 \text{ L}$$

Illustration 20 How long a current of 2 A has to be passed through a solution of AgNO_3 to coat a metal surface of 80 cm^2 with $5 \mu\text{m}$ thick layer? Density of silver = 10.8 g/cm^3 .

Solution

$$d = \frac{M}{V} \Rightarrow 10.8 = \frac{M}{80 \times 5 \times 10^{-4}} \Rightarrow M = 10.8 \times 400 \times 10^{-4}$$

$$W = \frac{E \times I \times t}{96500} \Rightarrow 10.8 \times 400 \times 10^{-4} = \frac{108 \times 2 \times t}{96500} \Rightarrow t = 193 \text{ s}$$

BEGINNER'S BOX-3

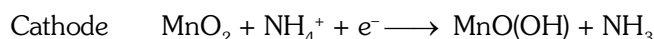
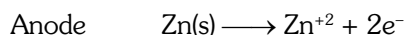
- 1 L of 1 M CuSO_4 solution is electrolysed. After passing 2 F charge, the molarity of CuSO_4 will be
(1) M/2 (2) M/4 (3) M (4) zero
- Same quantity of current is passed through molten NaCl and molten Al_2O_3 . If 4.6 g of Na was deposited in one cell, the mass of Al deposited in other cell is :-
(1) 0.9 g (2) 1.8 g (3) 2.7 g (4) 3.6 g
- A certain current liberates 0.5 g of hydrogen in 2 hr. How many grams of copper can be deposited by the same current flowing for the same time in a copper sulphate solution?
(1) 12.7 g (2) 15.9 g (3) 31.8 g (4) 63.5 g
- A quantity of electric charge that brings about the deposition of 4.5 g Al from Al^{+3} at the cathode will also produce the following volume (STP) of $\text{H}_2(\text{g})$ from H^+ at the cathode
(1) 44.8 L (2) 22.4 L (3) 11.2 L (4) 5.6 L
- A current of 9.65 A is passed through the aqueous solution of NaCl using suitable electrodes for 1000 s. The amount of NaOH formed during electrolysis is
(1) 2.0 g (2) 4.0 g (3) 6.0 g (4) 8.0 g
- If 0.224 L of H_2 gas is formed at the cathode, the volume of O_2 gas formed at the anode under identical conditions, is
(1) 0.224 L (2) 0.448 L (3) 0.112 L (4) 1.12 L

4.16 COMMERCIAL VOLTAIC CELLS

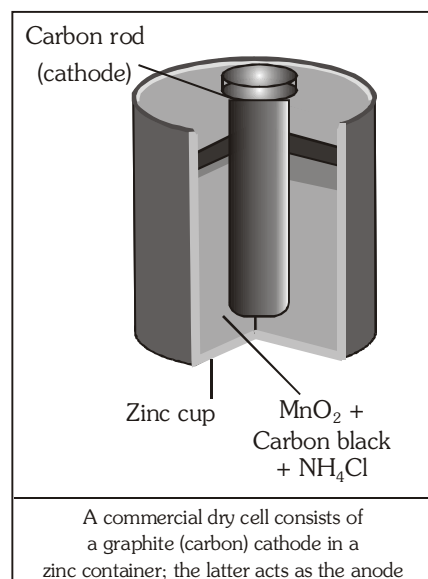
Batteries can be classified as primary and secondary. Primary batteries can not be returned to their original state by recharging, so when the reactants are consumed, the battery is "dead" and must be discarded. Secondary batteries are often called storage batteries or rechargeable batteries. The reactions in these batteries can be reversed; thus, the batteries can be recharged.

(A) Primary cells : Dry cells and mercury cells

The most familiar type of battery is the dry cell which is a compact of Leclanche cell known after its discoverer Leclanche (fig.). In this cell, the anode consists of a zinc container and the cathode is a graphite rod surrounded by powdered MnO_2 and carbon. The space between the electrodes is filled with a moist paste of NH_4Cl and ZnCl_2 . The electrode reactions are complex, but they can be written approximately as follows.



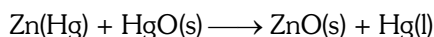
In the cathode reaction, manganese is reduced from the 4+ oxidation state to the 3+ state. Ammonia is not liberated as a gas but combines with Zn^{2+} to form $\text{Zn}(\text{NH}_3)_4^{2+}$ ion. Dry cells do not have an indefinite life as acidic NH_4Cl corrodes the zinc container even when not in use. **Dry cells have a potential of approximately 1.25 to 1.5V.**



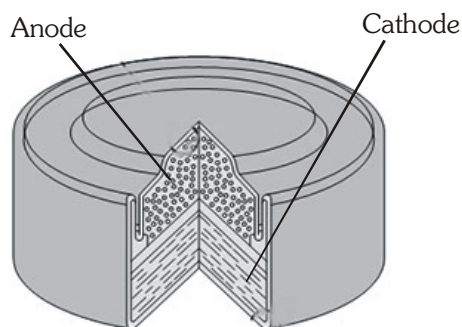
Mercury cell, suitable for low current devices like hearing aids, watches, etc. consists of zinc – mercury amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO. The electrode reactions for the cell are given below :



The overall reaction is represented by



The cell potential is **approximately 1.35 V** and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.



(B) SECONDARY OR RECHARGEABLE BATTERIES

The most important secondary cell is the lead storage battery. It consists of a **lead anode** and a grid of lead packed with **lead dioxide as cathode**. A solution of sulphuric acid (38 percent by mass or having density 1.30 gm cm^{-3}) is used as an electrolyte.

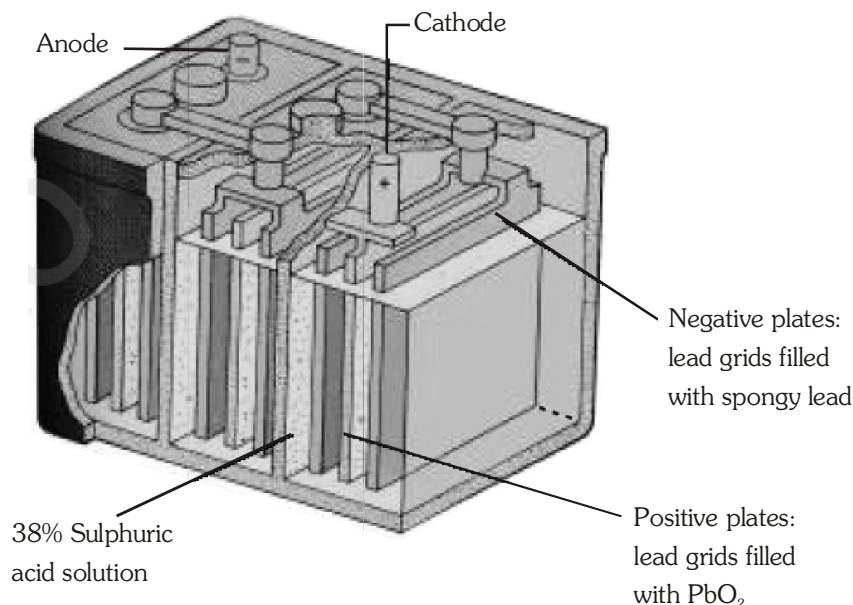
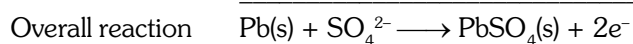


Fig : The Lead storage battery

When the cell discharges, it operates as a voltaic cell. The lead is oxidised to Pb^{+2} ion and lead plates acquire a negative charge.

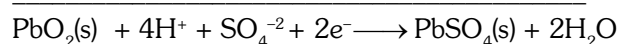
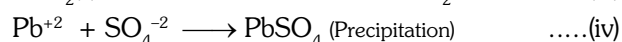
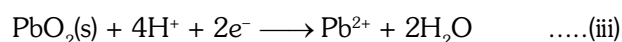


Pb^{+2} ions combine with sulphate ions of solution to form insoluble PbSO_4

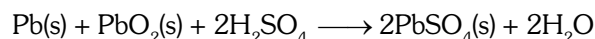
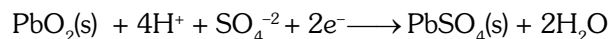
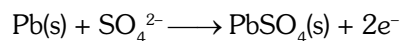


The electrons given by Pb are used at cathode (PbO_2 electrode)

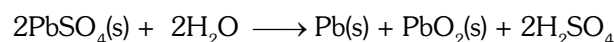
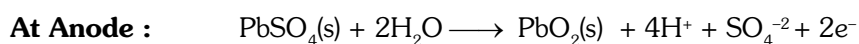
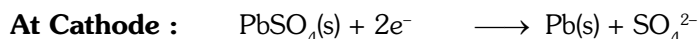
At Cathode :



Therefore the overall cell reaction during discharging



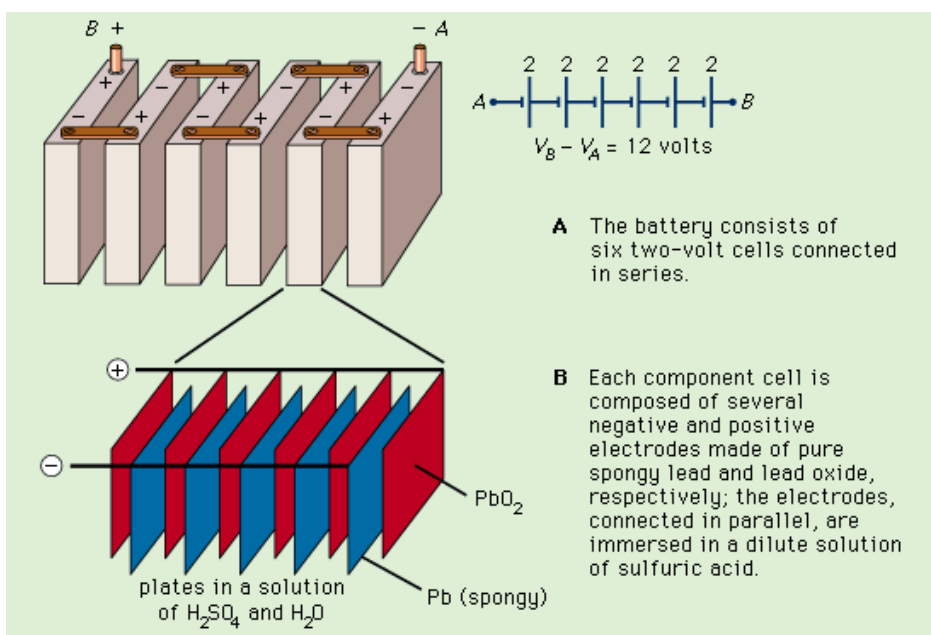
When a potential slightly greater than the potential of battery is applied, the battery can be recharged. During recharging the cell is operated like an **electrolytic cell** i.e. now electrical energy is supplied to it from an external source. The electrode reactions are reverse of those that occur during discharge :



It is clear that H_2SO_4 is used up during the discharge & produced during recharging reaction of cell.

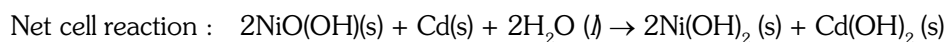
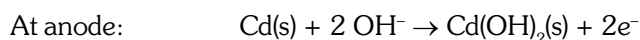
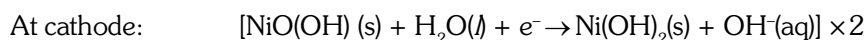
The discharging process of the storage cell is based on the principles of electrochemical cell, whereas the charging process is based upon the principles of electrolytic cells.

- n factor for H_2SO_4 during charging and discharging is equal to one.



(C) Nickel - Cadmium ("Ni - Cd") batteries :

They are used in variety of cordless appliances such as telephones, video camcorders, and cordless power tools, are lightweight and rechargeable. The chemistry of the cell utilizes the oxidation of cadmium and the reduction of nickel (III) oxide under basic conditions.

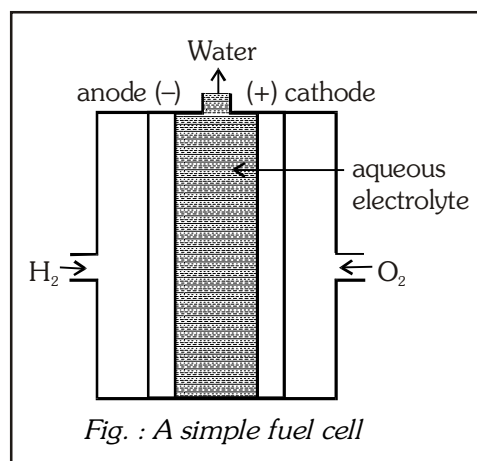


As the active masses of all reaction components are independent of their amount. The cell delivers constant EMF throughout.

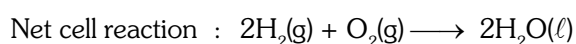
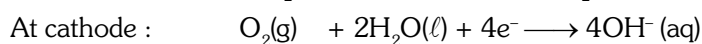
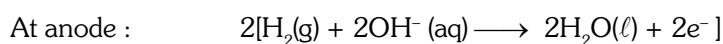
(D) Fuel Cells

It is possible to make batteries in which the reactants are fed continuously to the electrodes. Electrical cells that are designated to convert the free energy from the combustion of fuels such as hydrogen, carbon monoxide or methane directly into electrical energy are called **fuel cells**.

One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water (fig.). This cell has been used for electric power in the Appollo space programme. The water vapours produced were condensed and added to the drinking water supply for the astronauts.



In the cell shown in figure hydrogen and oxygen are bubbled through a porous carbon electrode into concentrated aqueous sodium hydroxide. Catalysts are incorporated in the electrode. The electrode reactions are :



This cell runs continuously as long as the reactants are supplied. Since fuel cells convert the energy of a fuel directly to electricity, they are potentially more efficient than the conventional method of generating electricity on a large scale by burning hydrogen, carbon fuels or by using nuclear reactor. Although **theoretically we expect 100 percent efficiency in fuel cells, so far an efficiency of only 60-70 per cent has been attained**. Since fuel cells are efficient and free from pollution, efforts are being made to produce better commercially practical fuel cells.

$$\text{Efficiency of a Fuel Cell : } \eta = \frac{(\Delta G)}{(\Delta H)} \times 100$$

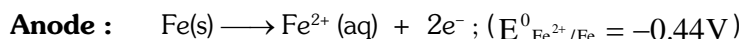
Main features of different cells.

	Name of the cell/Battery	Anode	Cathode	Electrolyte
(i)	Dry cell	Zinc	Graphite surrounded by MnO_2 & C.	$\text{NH}_4\text{Cl} + \text{ZnCl}_2$ (touching anode)
(ii)	Mercury cell	Zinc/Mercury Amalgum	Paste of HgO and carbon	Paste of KOH and ZnO
(iii)	Lead storage battery	Lead	Lead dioxide	H_2SO_4 (38%)
(iv)	Ni-Cd cell	Cadmium	Nickel dioxide	KOH sol.
(v)	H_2 - O_2 fuel cell	Porous carbon containing catalysts (H_2 passed)	Porous carbon containing catalysts (O_2 passed)	Conc. aq. NaOH sol.

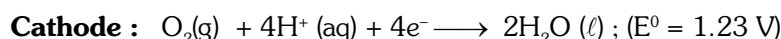
4.17 CORROSION

Corrosion is basically an electrochemical phenomenon. The rusting of iron, the tarnishing of silver, development of a green coating on copper and bronze are some of the examples of corrosion. Corrosion causes enormous damage to building, bridges, ships and to many other articles made of iron.

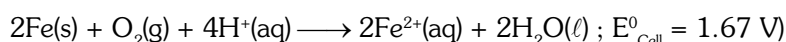
In corrosion, a metal is oxidised by loss of electrons to oxygen and forms metal oxide. Corrosion of iron (which is commonly known as rusting) occurs in presence of water and oxygen (air). Although the chemistry of corrosion is complex but it is understood that at one spot of an iron object oxidation occurs and that spot behaves as an anode.



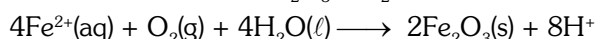
Electrons released at anode move through the metal and go to another spot on the metal and reduce the oxygen in presence of H^+ ions (which is believed to be available from H_2CO_3 formed due to dissolution of CO_2 in water). This spot works as a cathode :



Here Fe^{2+} ions move through water on the surface of the iron object. (If water present is saline, it will help more in carrying the current in the miniature cell thus formed and will enhance corrosion). The overall reaction of the miniature cell is the sum of the cathode and anode reactions as follows :



The Fe^{2+} ions are further oxidised by atmospheric oxygen to Fe^{3+} (as Fe_2O_3) and comes out as rust in the form of a hydrated iron (III) oxide expressed as $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.



H^+ ions produced in the above reaction help further in rusting.

Impurities present in iron also enhance rusting by setting a number of miniature cells. Very pure iron does not rust quickly.

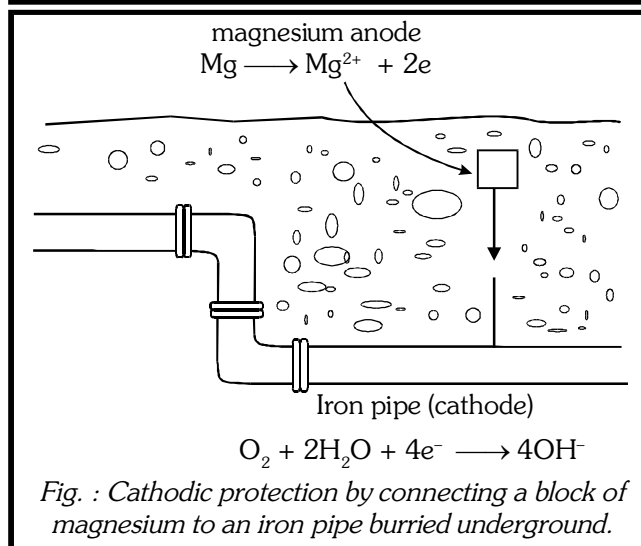
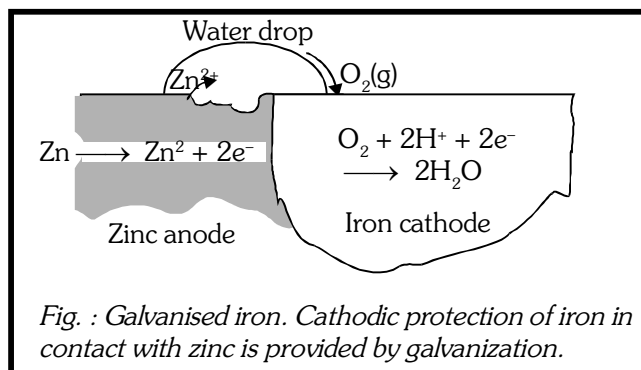
4.18 PREVENTION FROM CORROSION

Corrosion of a metal is prevented by applying protective coating (such as grease, paint, bisphenol or metal coatings) on metal surface. In case of iron this coating is done in two ways : (i) electrolysis (Cr, Ni and Cd coating) (ii) dipping iron objects in a molten metal (Zn and Sn coating). Use of zinc coating to protect iron is called Galvanisation. In galvanising iron, zinc being more reactive than iron serves as an anode and is oxidised



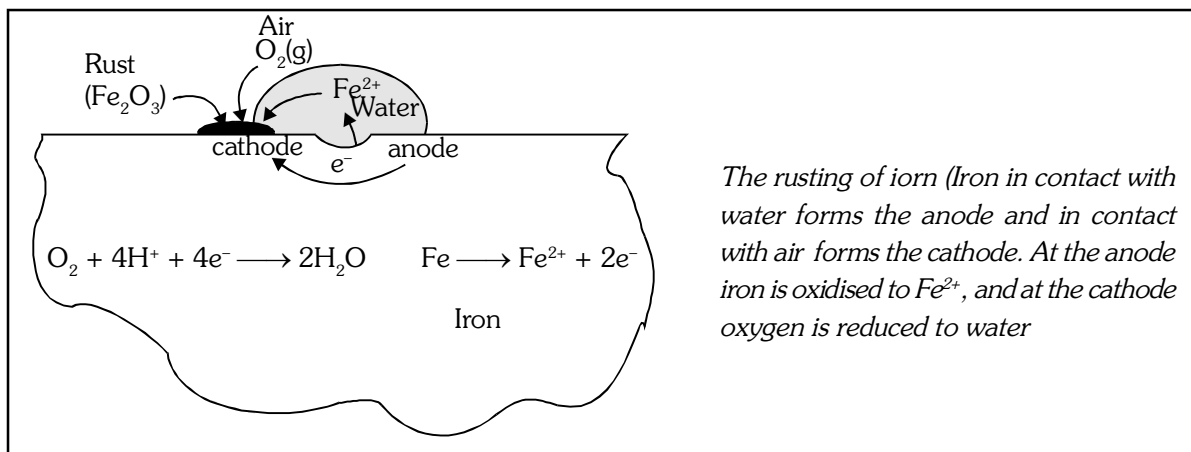
Here it is important to note that iron does not rust even after zinc coating is broken which is not true in case of tin coating over iron

($E^0_{\text{Sn}^{2+}/\text{Sn}} = -0.14\text{V}$). Now if the coating is broken, iron is exposed and iron being more active than both copper and tin, is corroded. Here iron corrodes more rapidly than it does in the absence of tin. But tin protects copper in the same way as zinc protects iron ($E^0_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}$).



Instead of coating more reactive metal on iron, the use of such metals is made as sacrificial anode. This method of preventing iron from corrosion is called CATHODIC PROTECTION.

In this method, a plate of reactive metal (Zn or Mg) is buried beside the iron pipe or tank and connected to it by wires. Here iron becomes **cathode** and more reactive metal becomes **anode**. The reactive metal anode is sacrificed to protect the iron. Since these reactive metal plates are oxidised quickly, they are replaced from time to time which is easy to do.



ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5					
	Ans.	1	2	4	3	4					
BEGINNER'S BOX-2	Que.	1	2	3	4	5	6				
	Ans.	3	2	1	1	3	3				
BEGINNER'S BOX-3	Que.	1	2	3	4	5	6				
	Ans.	4	2	2	4	2	3				

EXERCISE-I (Conceptual Questions)**Build Up Your Understanding****ELECTROLYTIC CONDUCTANCE**

- Strong electrolytes are those which :
(1) dissolve readily in water
(2) conduct electricity
(3) dissociate into ions even at high concentration
(4) dissociate into ions at high dilution.
- Molten sodium chloride conducts electricity due to the presence of :
(1) free electrons
(2) free ions
(3) free molecules
(4) free atoms of Na and Cl
- Electrolytic conduction is due to the movement of :
(1) molecules (2) atoms
(3) ions (4) electrons
- Which of the following solutions of KCl has the lowest value of equivalent conductance ?
(1) 1 M (2) 0.1 M
(3) .01 M (4) .001 M
- In the equation $\Lambda = \text{sp. cond.} \times V$, If V is the volume in cc containing 1 equivalent of the electrolyte then V for a $\frac{N}{10}$ solution will be :
(1) 10 c.c. (2) 100 c.c.
(3) 1000 c.c. (4) 10,000 c.c.
- If the specific resistance of a solution of concentration C g eq L^{-1} is R , then its equivalent conductance is :
(1) $\frac{100R}{C}$ (2) $\frac{RC}{1000}$
(3) $\frac{1000}{RC}$ (4) $\frac{C}{1000R}$
- The specific conductances in $\text{ohm}^{-1} \text{cm}^{-1}$ of four electrolytes P, Q, R and S are given in brackets :
P (5.0×10^{-5}) Q (7.0×10^{-8})
R (1.0×10^{-10}) S (9.2×10^{-3})
The one that offers highest resistance to the passage of electric current is
(1) P (2) S
(3) R (4) Q
- The specific conductance of a salt of 0.01 M concentration is $1.061 \times 10^{-4} \text{ S cm}^{-1}$. Molar conductance of the same solution will be :
(1) 1.061×10^{-4} (2) 1.061
(3) 10.61 (4) 106.1

- Which of the following solutions of NaCl will have the highest specific conductance ?
(1) 0.001 N (2) 0.1 N
(3) 0.01 N (4) 1.0 N
- The value of molar conductivity of HCl is greater than that of NaCl at a particular temperature because :
(1) Molecular mass of HCl is less than that of NaCl.
(2) Velocity of H^+ ions is more than that of Na^+ ions
(3) HCl is strongly acidic
(4) Ionisation of HCl is larger than that of NaCl
- Which statement is not correct :—
(1) Conductance of an electrolytic solution increases with dilution
(2) Conductance of an electrolytic solution decreases with dilution
(3) Specific conductance of an electrolytic solution decreases with dilution
(4) Equivalent conductance of an electrolytic solution increases with dilution.
- The resistance of 0.01 N solution of an electrolyte was found to be 210 ohm at 298 K using a conductivity cell of cell constant 0.66 cm^{-1} . The equivalent conductance of solution is :—
(1) $314.28 \text{ mho cm}^2 \text{ eq}^{-1}$
(2) $3.14 \text{ mho cm}^2 \text{ eq}^{-1}$
(3) $314.28 \text{ mho}^{-1} \text{ cm}^2 \text{ eq}^{-1}$
(4) $3.14 \text{ mho}^{-1} \text{ cm}^2 \text{ eq}^{-1}$
- Electrolytic conduction differs from metallic conduction from the fact that in the former
(1) The resistance increases with increasing temperature
(2) The resistance decreases with increasing temperature
(3) The resistance remains constant with increasing temperature
(4) The resistance is independent of the length of the conductor
- The specific conductance of a 0.01 M solution of KCl is $0.0014 \text{ ohm}^{-1} \text{cm}^{-1}$ at 25°C . Its equivalent conductance ($\text{cm}^2 \text{ ohm}^{-1} \text{eq}^{-1}$) is :—
(1) 140 (2) 14
(3) 1.4 (4) 0.14

15. Which one of the following is wrong :-
 (1) Specific conductance increases on dilution.
 (2) Specific conductance decreases on dilution.
 (3) Equivalent conductance increases on dilution.
 (4) Molar conductance increases on dilution.

KOHLRAUSCH LAW

16. At infinite dilution, the equivalent conductances of CH_3COONa , HCl and CH_3COOH are 91, 426 and 391 $\text{mho cm}^2 \text{eq}^{-1}$ respectively at 25 °C. The eq. conductance of NaCl at infinite dilution will be :
 (1) 126 (2) 209
 (3) 391 (4) 908
17. The equivalent conductivity of 0.1 N CH_3COOH at 25 °C is 80 and at infinite dilution it is 400. The degree of dissociation of CH_3COOH is :
 (1) 1 (2) 0.2
 (3) 0.1 (4) 0.5
18. The limiting molar conductivities Λ^0 for NaCl , KBr and KCl are 126, 152 and 150 $\text{S cm}^2 \text{mol}^{-1}$ respectively. The Λ^0 for NaBr is :
 (1) 278 $\text{S cm}^2 \text{mol}^{-1}$ (2) 176 $\text{S cm}^2 \text{mol}^{-1}$
 (3) 128 $\text{S cm}^2 \text{mol}^{-1}$ (4) 302 $\text{S cm}^2 \text{mol}^{-1}$
19. For HCl solution at 25 °C, equivalent conductance at infinite dilution, is 425 $\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$. The specific conductance of a solution of HCl is 3.825 $\text{ohm}^{-1} \text{cm}^{-1}$. If the degree of dissociation is 90%. The normality of the solution is :-
 (1) 0.90 N (2) 1.0 N
 (3) 10 N (4) 1.2 N
20. The molar conductivities Λ_{NaOAc}^0 and Λ_{HCl}^0 at infinite dilution in water at 25°C are 91.0 and 426.2 $\text{S cm}^2 \text{mol}^{-1}$ respectively. To calculate Λ_{HOAc}^0 the additional value required is :
 (1) Λ_{NaCl}^0 (2) $\Lambda_{\text{H}_2\text{O}}^0$
 (3) Λ_{KCl}^0 (4) Λ_{NaOH}^0
21. The molar conductance at infinite dilution of AgNO_3 , AgCl and NaCl are 116.5, 121.6 and 110.3 $\text{S cm}^2 \text{mol}^{-1}$ respectively. The molar conductance of NaNO_3 is :
 (1) 111.4 $\text{S cm}^2 \text{mol}^{-1}$ (2) 105.2 $\text{S cm}^2 \text{mol}^{-1}$
 (3) 130.6 $\text{S cm}^2 \text{mol}^{-1}$ (4) 150.2 $\text{S cm}^2 \text{mol}^{-1}$
22. The conductivity of a saturated solution of BaSO_4 is $3.06 \times 10^{-6} \text{ohm}^{-1} \text{cm}^{-1}$ and its molar conductance is 1.53 $\text{ohm}^{-1} \text{cm}^{-1} \text{mol}^{-1}$. The K_{sp} of BaSO_4 will be
 (1) 4×10^{-12} (2) 2.5×10^{-9}
 (3) 2.5×10^{-13} (4) 4×10^{-6}

GALVANIC CELL

23. In the galvanic cell
 $\text{Cu(s)} \mid \text{Cu}^{2+} (1 \text{ M}) \parallel \text{Ag}^+ (1 \text{ M}) \mid \text{Ag(s)}$
 the electrons will travel in the external circuit :
 (1) from Ag to Cu
 (2) from Cu to Ag
 (3) electrons do not travel in the external circuit
 (4) in any direction
24. The passage of electricity in the Daniell cell when Zn and Cu electrodes are connected is :
 (1) from Cu to Zn in the cell
 (2) from Cu to Zn out side the cell
 (3) from Zn to Cu outside the cell
 (4) in any direction in the cell
25. The equation representing the process by which standard reduction potential of zinc can be defined is
 (1) $\text{Zn}^{2+} (\text{s}) + 2\text{e}^- \longrightarrow \text{Zn} (\text{s})$
 (2) $\text{Zn} (\text{g}) \longrightarrow \text{Zn}^{2+} (\text{g}) + 2\text{e}^-$
 (3) $\text{Zn}^{2+} (\text{g}) + 2\text{e}^- \longrightarrow \text{Zn} (\text{s})$
 (4) $\text{Zn}^{2+} (\text{aq.}) + 2\text{e}^- \longrightarrow \text{Zn} (\text{s})$
26. A standard hydrogen electrode has zero electrode potential because :
 (1) Hydrogen is easiest to oxidize.
 (2) This electrode potential is assumed to be zero.
 (3) Hydrogen atom has only one electron.
 (4) Hydrogen is the lightest element.
27. Which is not true for a standard hydrogen electrode ?
 (1) The hydrogen ion concentration is 1 M.
 (2) Temperature is 25°C.
 (3) Pressure of hydrogen is 1 bar.
 (4) It contains a metallic conductor which does not adsorb hydrogen.
28. E° for the half cell
 $\text{Zn}^{2+} \mid \text{Zn}$ is -0.76 V. E.m.f. of the cell
 $\text{Zn} \mid \text{Zn}^{2+} (1\text{M}) \parallel 2\text{H}^+ (1\text{M}) \mid \text{H}_2 (1 \text{ atm})$ is :
 (1) -0.76 V (2) +0.76 V
 (3) -0.38 V (4) + 0.38 V
29. The chemical reaction,
 $2\text{AgCl(s)} + \text{H}_2(\text{g}) \longrightarrow 2\text{HCl(aq)} + 2\text{Ag(s)}$
 taking place in a galvanic cell is represented by the notation.
 (1) $\text{Pt(s)} \mid \text{H}_2(\text{g}).1\text{bar} \mid 1\text{MKCl(aq)} \mid \text{AgCl(s)} \mid \text{Ag(s)}$.
 (2) $\text{Pt(s)} \mid \text{H}_2(\text{g}).1\text{bar} \mid 1\text{MHCl(aq)} \mid 1\text{M Ag(aq)} \mid \text{Ag(s)}$.
 (3) $\text{Pt(s)} \mid \text{H}_2(\text{g}).1\text{bar} \mid 1\text{MHCl(aq)} \mid \text{AgCl(s)} \mid \text{Ag(s)}$.
 (4) $\text{Pt(s)} \mid \text{H}_2(\text{g}).1\text{bar} \mid 1\text{MHCl(aq)} \mid \text{Ag(s)} \mid \text{AgCl(s)}$.

30. $\text{Cu(s)} \mid \text{Cu}^{2+}(1 \text{ M}) \parallel \text{Zn}^{2+}(1 \text{ M}) \mid \text{Zn(s)}$
A cell represented above should have emf.
(1) Positive
(2) Negative
(3) Zero
(4) Cannot be predicted

31. Given electrode potentials :
 $\text{Fe}^{3+} + e \longrightarrow \text{Fe}^{2+}$; $E^\circ = 0.771 \text{ V}$
 $\text{I}_2 + 2e \longrightarrow 2\text{I}^-$; $E^\circ = 0.536 \text{ V}$
 E° cell for the cell reaction
 $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$ is -
 (1) $(2 \times 0.771 - 0.536) = 1.006 \text{ V}$
 (2) $(0.771 - 0.5 \times 0.536) = 0.503 \text{ V}$
 (3) $0.771 - 0.536 = 0.235 \text{ V}$
 (4) $0.536 - 0.771 = -0.235 \text{ V}$

32. Which of the following is not an anodic reaction—
 (1) $\text{Ag}^+ \rightarrow \text{Ag} - e^-$
 (2) $\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$
 (3) $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$
 (4) $4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4e^-$

33. Which of the following statements is correct :—
 (1) Oxidation occur at anode in both galvanic and electrolytic cell.
 (2) Reduction occurs at anode in both galvanic and electrolytic cell,
 (3) Reduction occur at anode in electrolytic cell where as oxidation occur at cathode in galvanic cell,
 (4) Oxidation occur at anode in electrolytic cell where as reduction occur at anode in a galvanic cell,

34. Other things being equal, the life of a Daniell cell may be increased by :—
 (1) Keeping low temperature
 (2) Using large copper electrode
 (3) Decreasing concentration of copper ions
 (4) Using large zinc electrodes

ELECTROCHEMICAL SERIES

35. Zn can not displace following ions from their aqueous solution :
 (1) Ag^+ (2) Cu^{2+}
 (3) Fe^{2+} (4) Na^+
36. The standard reduction potentials at 25°C for the following half reactions are given against each :
 $\text{Zn}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Zn(s)}$, -0.762 V
 $\text{Cr}^{3+}(\text{aq}) + 3e^- \rightleftharpoons \text{Cr(s)}$, -0.740 V
 $2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2(\text{g})$, 0.00 V
 $\text{Fe}^{3+} + 2e^- \rightleftharpoons \text{Fe}^{2+}$, 0.77 V
 Which is the strongest reducing agent ?
 (1) Zn (2) Cr
 (3) $\text{H}_2(\text{g})$ (4) $\text{Fe}^{2+}(\text{aq})$

37. Red hot carbon will remove oxygen from the oxide XO and YO but not from ZO. Y will remove oxygen from XO. Use this evidence to deduce the order of activity of the three metals X, Y and Z putting the most active first.

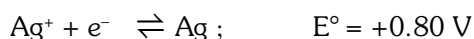
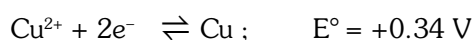
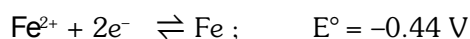
- (1) XYZ (2) ZYX
 (3) YXZ (4) ZXY

38. Adding powdered Pb and Fe to a solution containing 1.0 M in each of Pb^{2+} and Fe^{2+} ions, would result into the formation of :—
 (1) More of Fe and Pb^{2+} ions
 (2) More of Fe^{2+} and Pb^{2+} ions
 (3) More of Pb and Fe^{2+} ions
 (4) More of Fe and Pb

39. If a spoon of copper metal is placed in a solution of ferrous sulphate :
 (1) Cu will precipitate out
 (2) Iron will precipitate
 (3) Cu and Fe will precipitate
 (4) No reaction will take place

40. Which one will liberate Br_2 from KBr ?
 (1) HI (2) I_2
 (3) Cl_2 (4) SO_2

41. Using the standard electrode potential values given below, decide which of the statements, I, II, III and IV are correct. Choose the right answer from (1), (2), (3) and (4).



- I. Copper can displace iron from FeSO_4 solution.
 II. Iron can displace copper from CuSO_4 solution.
 III. Silver can displace copper from CuSO_4 solution.
 IV. Iron can displace silver from AgNO_3 solution.

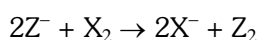
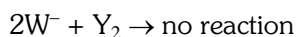
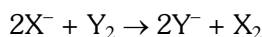
- (1) I and II (2) II and III
 (3) II and IV (4) I and IV

42. The standard electrode potential value of the elements A, B and C are 0.68 , -2.50 and 0.50 V respectively. The order of their reducing power is :
 (1) $A > B > C$ (2) $A > C > B$
 (3) $C > B > A$ (4) $B > C > A$

43. The oxidation potential of Zn, Cu, Ag, H₂ and Ni are 0.76 V, -0.34 V, -0.80 V, 0 V, 0.55 V respectively. Which of the following reaction will provide maximum voltage ?

- (1) $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Cu} + \text{Zn}^{2+}$
- (2) $\text{Zn} + 2\text{Ag}^+ \longrightarrow 2\text{Ag} + \text{Zn}^{2+}$
- (3) $\text{H}_2 + \text{Cu}^{2+} \longrightarrow 2\text{H}^+ + \text{Cu}$
- (4) $\text{H}_2 + \text{Ni}^{2+} \longrightarrow 2\text{H}^+ + \text{Ni}$

44. The following facts are available :-



Which of the following statements is correct :-

- (1) $E^\circ_{\text{W}^-/\text{W}_2} > E^\circ_{\text{Y}^-/\text{Y}_2} > E^\circ_{\text{X}^-/\text{X}_2} > E^\circ_{\text{Z}^-/\text{Z}_2}$
- (2) $E^\circ_{\text{W}^-/\text{W}_2} < E^\circ_{\text{Y}^-/\text{Y}_2} < E^\circ_{\text{X}^-/\text{X}_2} < E^\circ_{\text{Z}^-/\text{Z}_2}$
- (3) $E^\circ_{\text{W}^-/\text{W}_2} < E^\circ_{\text{Y}^-/\text{Y}_2} > E^\circ_{\text{X}^-/\text{X}_2} > E^\circ_{\text{Z}^-/\text{Z}_2}$
- (4) $E^\circ_{\text{W}^-/\text{W}_2} > E^\circ_{\text{Y}^-/\text{Y}_2} < E^\circ_{\text{X}^-/\text{X}_2} < E^\circ_{\text{Z}^-/\text{Z}_2}$

45. The standard reduction potential at 25 °C of Li⁺ / Li, Ba²⁺ / Ba, Na⁺ / Na and Mg²⁺ / Mg are -3.05 V, -2.73 V, -2.71 V and -2.37 V respectively. Which one of the following is the strongest oxidising agent ?

- (1) Na⁺
- (2) Li⁺
- (3) Ba²⁺
- (4) Mg²⁺

46. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y⁻ and 1 M Z⁻ at 25 °C. If the reduction potential of Z > Y > X then :

- (1) Y will oxidise X and not Z
- (2) Y will oxidise Z and not X
- (3) Y will oxidise both X and Z
- (4) Y will reduce both X and Z

47. The standard electrode potential of Zn, Ag and Cu are -0.76 V, 0.80 V and 0.34 V respectively, then :

- (1) Ag can oxidise Zn and Cu
- (2) Ag can reduce Zn²⁺ and Cu²⁺
- (3) Zn can reduce Ag⁺ and Cu²⁺
- (4) Cu can oxidise Zn and Ag

48. Each of the three metals x, y and z were put in turn into aqueous solution of the other two. x + salt of y (or z) → y (or z) + salt of x

Which one of the following observation is incorrect?

- (1) y + salt of x → no action observed
- (2) y + salt of z → z + salt of y
- (3) z + salt of x → x + salt of z
- (4) z + salt of y → no action observed

49. A standard reduction electrode potentials of four elements are

$$\text{A} = -0.250 \text{ V}, \quad \text{B} = -0.140 \text{ V}$$

$$\text{C} = -0.126 \text{ V}, \quad \text{D} = -0.402 \text{ V}$$

The element that displaces A from its compounds aqueous solution is :-

- (1) B
- (2) C
- (3) D
- (4) None of the above

50. The following four colourless salt solutions are placed in separate test tubes and a strip of Cu is placed in each solution which finally turns blue :-

- (1) Zn(NO₃)₂
- (2) Mg(NO₃)₂
- (3) KNO₃
- (4) AgNO₃

51. Which of the following displacement does not occur

- (1) $\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2 \uparrow$
- (2) $\text{Fe} + 2\text{Ag}^+ \rightarrow \text{Fe}^{2+} + 2\text{Ag} \downarrow$
- (3) $\text{Cu} + \text{Fe}^{2+} \rightarrow \text{Cu}^{2+} + \text{Fe} \downarrow$
- (4) $\text{Zn} + \text{Pb}^{2+} \rightarrow \text{Zn}^{2+} + \text{Pb} \downarrow$

NERNST EQUATION

52. $E^\circ(\text{Ni}^{2+}/\text{Ni}) = -0.25 \text{ V}$

$$E^\circ(\text{Au}^{3+}/\text{Au}) = 1.50 \text{ V}$$

The emf of the voltaic cell.

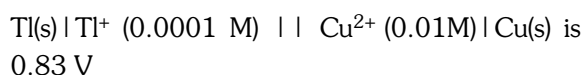


- (1) 1.25 V
- (2) -1.75 V
- (3) 1.75 V
- (4) 4.0 V

53. The emf of the cell in which the following reaction $\text{Zn(s)} + \text{Ni}^{2+} (a = 0.1) \rightleftharpoons \text{Zn}^{2+} (a = 1.0) + \text{Ni(s)}$ occurs, is found to be 0.5105 V at 298 K. The standard e.m.f. of the cell is :-

- (1) -0.5105 V
- (2) 0.5400 V
- (3) 0.4810 V
- (4) 0.5696 V

54. The emf of the cell



The emf of this cell will be increased by :-

- (1) Increasing the concentration of Cu²⁺ ions
- (2) Decreasing the concentration of Ti⁺
- (3) Increasing the concentration of both
- (4) (1) & (2) both

55. The potential of hydrogen electrode

$$(\text{P}_{\text{H}_2} = 1 \text{ atm}; \text{C}_{\text{H}^+} = 0.1 \text{ M}) \text{ at } 25^\circ\text{C} \text{ will be -}$$

- (1) 0.00 V
- (2) -0.059 V
- (3) 0.118 V
- (4) 0.059 V

- 56.** Which of the following represents the potential of silver wire dipped into 0.1 M AgNO_3 solution at 25°C ?
 (1) E°_{red} (2) $(E^\circ_{\text{red}} + 0.059)$
 (3) $(E^\circ_{\text{ox}} - 0.059)$ (4) $(E^\circ_{\text{red}} - 0.059)$
- 57.** The potential of a hydrogen electrode at $\text{pH} = 1$ is
 (1) 0.059 V (2) 0.00 V
 (3) -0.059 V (4) 0.59 V
- 58.** Consider the reaction
 $\text{Cl}_2(\text{g}) + 2\text{Br}^-(\text{aq}) \longrightarrow 2\text{Cl}^-(\text{aq}) + \text{Br}_2$
 The emf of the cell when
 $[\text{Cl}^-] = [\text{Br}_2] = [\text{Br}^-] = 0.01\text{ M}$ and Cl_2 gas at 1 atm pressure will be (E° for the above reaction is = 0.29 V)
 (1) 0.54 V (2) 0.35 V
 (3) 0.24 V (4) -0.29 V
- 59.** The standard emf for the cell reaction
 $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$ is 1.10 V at 25°C .
 The emf for the cell reaction when 0.1 M Cu^{2+} and 0.1 M Zn^{2+} solution are used at 25°C is :
 (1) 1.10 V (2) 0.110 V
 (3) -1.10 V (4) -0.110 V
- 60.** E° for $\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$ is 2.8 V,
 E° for $\frac{1}{2}\text{F}_2 + \text{e}^- \rightarrow \text{F}^-$ is ?
 (1) 2.8 V (2) 1.4 V (3) -2.8 V (4) -1.4 V
- 61.** ΔG° of the cell reaction
 $\text{AgCl}(\text{s}) + \frac{1}{2}\text{H}_2(\text{g}) \rightarrow \text{Ag}(\text{s}) + \text{H}^+ + \text{Cl}^-$ is -21.52 kJ
 ΔG° of $2\text{AgCl}(\text{s}) + \text{H}_2(\text{g}) \rightarrow 2\text{Ag}(\text{s}) + 2\text{H}^+ + 2\text{Cl}^-$ is :
 (1) -21.52 kJ (2) -10.76 kJ
 (3) -43.04 kJ (4) 43.04 kJ
- 62.** How much will the potential of $\text{Zn} / \text{Zn}^{2+}$ change if the solution of Zn^{2+} is diluted 10 times
 (1) increases by 0.03 V
 (2) decreases by 0.03 V
 (3) increases by 0.059 V
 (4) decreases by 0.059 V
- 63.** How much will the potential of a hydrogen electrode change when its solution initially at $\text{pH} = 0$ is neutralised to $\text{pH} = 7$?
 (1) increases by 0.059 V
 (2) decreases by 0.059 V
 (3) increases by 0.41 V
 (4) decreases by 0.41 V
- 64.** Which of the following will increase the voltage of the cell with following cell reaction
 $\text{Sn}_{(\text{s})} + 2\text{Ag}^+_{(\text{aq})} \rightarrow \text{Sn}^{2+}_{(\text{aq})} + 2\text{Ag}_{(\text{s})}$
 (1) Increase in the size of silver rod
 (2) Increase in the concentration of Sn^{2+} ions
 (3) Increase in the concentration of Ag^+ ions
 (4) Decrease in the concentration of Ag^+ ions
- 65.** E° for the reaction $\text{Fe} + \text{Zn}^{2+} \rightarrow \text{Zn} + \text{Fe}^{2+}$ is -0.35 V. The given cell reaction is :
 (1) feasible (2) not feasible
 (3) in equilibrium (4) can't say anything
- 66.** For a reaction - $\text{A}(\text{s}) + 2\text{B}^+ \rightarrow \text{A}^{2+} + 2\text{B}(\text{s})$
 K_c has been found to be 10^{12} . The E°_{cell} is:
 (1) 0.354 V (2) 0.708 V
 (3) 0.0098 V (4) 1.36 V
- 67.** The standard electrode potential (E°) for OCl^-/Cl^- and $\text{Cl}^- / \frac{1}{2}\text{Cl}_2$ respectively are 0.94 V and -1.36 V. The E° value of $\text{OCl}^- / \frac{1}{2}\text{Cl}_2$ will be :
 (1) -2.20 V (2) -0.42 V
 (3) 0.52 V (4) 1.04 V
- 68.** The standard reduction potentials of Cu^{2+}/Cu and $\text{Cu}^{2+}/\text{Cu}^+$ are 0.337 V and 0.153 V respectively. The standard electrode potential of Cu^+/Cu half cell is :
 (1) 0.184 V (2) 0.827 V
 (3) 0.521 V (4) 0.490 V
- 69.** The hydrogen electrode is dipped in a solution of $\text{pH} = 3$ at 25°C . The potential of the cell would be :
 (1) 0.177 V (2) - 0.177 V
 (3) 0.087 V (4) 0.059 V
- 70.** What is the potential of the cell containing two hydrogen electrodes as represented below
 $\text{Pt}; \text{H}_2(\text{g}) | \text{H}^+(10^{-8}\text{M}) || \text{H}^+(0.001\text{M}) | \text{H}_2(\text{g}); \text{Pt}$;
 (1) - 0.295 V (2) - 0.0591 V
 (3) 0.295 V (4) 0.0591 V
- 71.** Consider the cell $\text{Cu}/\text{Cu}^{2+} || \text{Ag}^+/\text{Ag}$. If the concentration of Cu^{2+} and Ag^+ ions becomes ten times then the emf of the cell will :-
 (1) Becomes 10 times
 (2) Remains same
 (3) Increases by 0.0295 V
 (4) Decreases by 0.0295 V

- 72.** The emf of the cell
 $\text{Ni} | \text{Ni}^{+2} (1.0 \text{ M}) || \text{Au}^{+3} (0.1 \text{ M}) | \text{Au}$
 $[E^\circ \text{ for } \text{Ni}^{+2}/\text{Ni} = -0.25 \text{ V}, E^\circ \text{ for } \text{Au}^{+3}/\text{Au} = 1.50 \text{ V}]$
 is given as:-
 (1) 1.25 V (2) -1.75 V
 (3) 1.75 V (4) 1.73 V

ELECTROLYSIS

- 73.** When an electric current is passed through acidified water, 112 mL of hydrogen gas at STP collects at the cathode in 965 s. The current passed, in ampere is :
 (1) 1.0 (2) 0.5
 (3) 0.1 (4) 2.0
- 74.** Two electrolytic cells one containing acidified ferrous chloride and another acidified ferric chloride are connected in series. The ratio of iron deposited at cathodes in the two cells when electricity is passed through the cells will be :
 (1) 3 : 1 (2) 2 : 1 (3) 1 : 1 (4) 3 : 2
- 75.** A current of 9.65 A flowing for 10 minute deposits 3.0 g of a metal. The equivalent weight of the metal is :
 (1) 10 (2) 30 (3) 50 (4) 96.5
- 76.** The same amount of electricity was passed through two separate electrolytic cells containing solutions of nickel nitrate $[\text{Ni}(\text{NO}_3)_2]$ and chromium nitrate $[\text{Cr}(\text{NO}_3)_3]$ respectively. If 0.3 g of nickel was deposited in the first cell, the amount of chromium deposited in the other cell is :-
 (at. wt. of Ni = 59, at. wt. of Cr = 52)
 (1) 0.1 g (2) 0.17 g
 (3) 0.3 g (4) 0.6 g
- 77.** How many coulombs of electricity are required for the oxidation of 1 mol of H_2O to O_2 ?
 (1) $9.65 \times 10^4 \text{ C}$ (2) $4.825 \times 10^5 \text{ C}$
 (3) $1.93 \times 10^5 \text{ C}$ (4) $1.93 \times 10^4 \text{ C}$
- 78.** When a quantity of electricity equal to that required to liberate 2.24 L of hydrogen at STP from 0.1 M aqueous H_2SO_4 is passed (At. mass of Cu = 63.5) then the mass of copper that will be deposited at cathode in electrolysis of 0.2 M solution of copper sulphate will be :
 (1) 1.59 g (2) 3.18 g
 (3) 6.35 g (4) 12.70 g
- 79.** 10800 C of electricity through the electrolyte deposited 2.977 g of metal with atomic mass 106.4 g mol⁻¹. The charge on the metal cation is -
 (1) +4 (2) +3 (3) +2 (4) +1
- 80.** On passing electricity through dilute H_2SO_4 solution the amount of substance liberated at the cathode and anode are in the ratio :
 (1) 1 : 8 (2) 8 : 1
 (3) 16 : 1 (4) 1 : 16
- 81.** During electrolysis of fused calcium hydride, the hydrogen is produced at :
 (1) Cathode
 (2) Anode
 (3) Hydrogen is not liberated at all
 (4) H_2 produced reacts with oxygen to form water
- 82.** A silver cup is plated with silver by passing 965 A current for one second, the mass of Ag deposited is :-(At. wt. of Ag = 107.87)
 (1) 9.89 g. (2) 107.87 g.
 (3) 1.0787 g. (4) 100.2 g.
- 83.** When electricity is passed through a solution of AlCl_3 , 13.5 g Al is deposited. The number of Faradays must be :-
 (1) 5.0 (2) 1.0 (3) 1.5 (4) 3.0
- 84.** A solution of sodium sulphate in water is electrolysed using inert electrodes. The product at the cathode and anode are respectively :-
 (1) H_2 , SO_2 (2) O_2 , H_2
 (3) O_2 , Na (4) H_2 , O_2
- 85.** One Faraday of electricity will liberate one mole of the metal from the solution of
 (1) Auric chloride (2) Silver nitrate
 (3) Calcium chloride (4) Copper sulphate
- 86.** When 96500 C of electricity are passed through barium chloride solution, the amount of barium deposited will be :-
 (1) 0.5 mol (2) 1.0 mol
 (3) 1.5 mol (4) 2.0 mol
- 87.** A factory produces 40 kg of calcium in two hours by electrolysis. How much aluminium can be produced by the same current in two hours :-
 (At wt. of Ca = 40, Al = 27)
 (1) 22 kg (2) 18 kg
 (3) 9 kg (4) 27 kg

88. What would be the ratio of moles each of Ag^+ , Cu^{+2} , Fe^{+3} ions would be deposited by passage of same quantity of electricity through solutions of their salts :-

(1) 1 : 1 : 1

(2) $1 : \frac{1}{2} : \frac{1}{3}$

(3) $\frac{1}{3} : \frac{1}{2} : 1$

(4) 1 : 2 : 3

89. Electrolysis of aq. CuSO_4 causes :-

(1) An increase in pH

(2) A decrease in pH

(3) Either decrease or increase

(4) None

90. The passage of current liberates H_2 at cathode and Cl_2 at anode the solution is :-

(1) CuSO_4 (aq)

(2) CuCl_2 (aq.)

(3) NaCl (aq.)

(4) Water

COMMERCIAL CELLS

91. When lead accumulator is charged it is :

(1) an electrolytic cell

(2) a galvanic cell

(3) a Daniel cell

(4) none of the above

92. When a lead storage battery is charged :

(1) PbO_2 dissolves

(2) The lead electrode becomes coated with lead sulphate

(3) Sulphuric acid is regenerated

(4) The amount of acid decreases

EXERCISE-I (Conceptual Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	2	3	1	4	3	3	3	4	2	2	1	2	1	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	1	2	3	3	1	2	4	2	2	4	2	4	2	3	2
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	3	1	1	4	4	1	2	3	4	3	3	4	2	2	4
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	1	3	3	3	4	3	3	2	4	2	4	3	2	1	1
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	3	1	4	3	2	1	3	3	2	3	3	4	1	4	3
Que.	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
Ans.	2	3	3	1	1	2	3	3	4	2	1	2	2	2	3
Que.	91	92													
Ans.	1	3													

EXERCISE-II (Previous Year Questions)**AIPMT/NEET & AIIMS (2006-2018)****AIPMT 2006**

1. If $E_{\text{Fe}^{+2}/\text{Fe}}^0 = -0.441\text{V}$ and $E_{\text{Fe}^{+3}/\text{Fe}^{+2}}^0 = 0.771\text{V}$ the standard EMF of the reaction $\text{Fe} + 2\text{Fe}^{+3} \rightarrow 3\text{Fe}^{+2}$ will be :
- (1) 0.330 V
 - (2) 1.653 V
 - (3) 1.212 V
 - (4) 0.111 V

2. A hypothetical electrochemical cell is shown



The emf measured is +0.20 V

The cell reaction is :

- (1) $\text{A}^+ + \text{B} \longrightarrow \text{A} + \text{B}^+$
- (2) $\text{A}^+ + \text{e}^- \longrightarrow \text{A}$, $\text{B}^+ + \text{e}^- \longrightarrow \text{B}$
- (3) The cell reaction cannot be predicted.
- (4) $\text{A} + \text{B}^+ \longrightarrow \text{A}^+ + \text{B}$

AIIMS 2006

3. The charge required for the reduction of 1 mol of MnO_4^- to MnO_2 is :
- (1) 1F
 - (2) 3F
 - (3) 5F
 - (4) 7F
4. The products formed when an aqueous solution of NaBr is electrolyzed in a cell having inert electrodes are :-
- (1) Na and Br_2
 - (2) Na and O_2
 - (3) H_2 , Br_2 and NaOH
 - (4) H_2 and O_2

AIPMT 2007

5. The equilibrium constant of the reaction : $\text{Cu(s)} + 2\text{Ag}^+(\text{aq.}) \longrightarrow \text{Cu}^{2+}(\text{aq.}) + 2\text{Ag(s)}$ $E^\circ = 0.46\text{V}$ at 298 K is :-
- (1) 2.0×10^{10}
 - (2) 4.0×10^{10}
 - (3) 4.0×10^{15}
 - (4) 2.4×10^{10}

AIPMT 2008

6. On the basis of the following E° values, the strongest oxidizing agent is :-
- $[\text{Fe}(\text{CN})_6]^{4-} \rightarrow [\text{Fe}(\text{CN})_6]^{3-} + \text{e}^-$, $E^\circ = -0.35\text{V}$
 $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$; $E^\circ = -0.77\text{V}$
- (1) Fe^{3+}
 - (2) $[\text{Fe}(\text{CN})_6]^{3-}$
 - (3) $[\text{Fe}(\text{CN})_6]^{4-}$
 - (4) Fe^{2+}

7. Kohlrausch's law states that at :-
- (1) Infinite dilution, each ion makes definite contribution to conductance of an electrolyte whatever be the nature of the other ion of the electrolyte.
 - (2) Infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte whatever be the nature of the other ion of the electrolyte.
 - (3) Finite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte whatever be the nature of the other ion of the electrolyte.
 - (4) Infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte depending on the nature of the other ion of electrolyte.

AIPMT 2009

8. Given :
- (i) $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$, $E^\circ = 0.337\text{V}$
 - (ii) $\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$, $E^\circ = 0.153\text{V}$
- Electrode potential, E° for the reaction, $\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$, will be :-
- (1) 0.38 V
 - (2) 0.52 V
 - (3) 0.90 V
 - (4) 0.30 V
9. The equivalent conductance of $\frac{M}{32}$ solution of a weak monobasic acid is $8.0\text{ mho cm}^2 \text{eq}^{-1}$ and at infinite dilution is $400\text{ mho cm}^2 \text{eq}^{-1}$. The dissociation constant of this acid is :-
- (1) 1.25×10^{-4}
 - (2) 1.25×10^{-5}
 - (3) 1.25×10^{-6}
 - (4) 6.25×10^{-4}
10. Al_2O_3 is reduced by electrolysis at low potential and high current. If $4.0 \times 10^4\text{A}$ of current is passed through molten Al_2O_3 for 6 hours, what mass of aluminium is produced ? (Assume 100% current efficiency, At. mass of Al = 27 g mol^{-1})
- (1) $1.3 \times 10^4\text{g}$
 - (2) $9.0 \times 10^3\text{g}$
 - (3) $8.1 \times 10^4\text{g}$
 - (4) $2.4 \times 10^5\text{g}$

AIPMT 2010

11. An increase in equivalent conductance of a strong electrolyte with dilution is mainly due to:-
- (1) Increase in number of ions.
 - (2) Increase in ionic mobility of ions.
 - (3) 100% ionisation of electrolyte at normal dilution.
 - (4) Increase in both i.e. number of ions and ionic mobility of ions.

12. Consider the following relations for emf of a electrochemical cell :
- emf of cell = (Oxidation potential of anode) – (Reduction potential of cathode)
 - emf of cell = (Oxidation potential of anode) + (Reduction potential of cathode)
 - emf of cell = (Reduction potential of anode) + (Reduction potential of cathode)
 - emf of cell = (Oxidation potential of anode) – (Oxidation potential of cathode)

Which of the above relations are correct :

- (a) and (b)
 - (c) and (d)
 - (b) and (d)
 - (c) and (a)
13. Which of the following expressions correctly represents the equivalent conductance at infinite dilution of $\text{Al}_2(\text{SO}_4)_3$. Given that $\Lambda^\circ_{\text{Al}^{3+}}$ and $\Lambda^\circ_{\text{SO}_4^{2-}}$ are the equivalent conductances at infinite dilution of the respective ions :-

- $\Lambda^\circ_{\text{Al}^{3+}} + \Lambda^\circ_{\text{SO}_4^{2-}}$
- $(\Lambda^\circ_{\text{Al}^{3+}} + \Lambda^\circ_{\text{SO}_4^{2-}}) \times 6$
- $\frac{1}{3} \Lambda^\circ_{\text{Al}^{3+}} + \frac{1}{2} \Lambda^\circ_{\text{SO}_4^{2-}}$
- $2\Lambda^\circ_{\text{Al}^{3+}} + 3\Lambda^\circ_{\text{SO}_4^{2-}}$

14. For the reduction of silver ions with copper metals, the standard cell potential was found to be +0.46 V at 25 °C. The value of standard Gibbs energy, ΔG° will be ($F = 96500 \text{ C mol}^{-1}$)
- 98.0 kJ
 - 89.0 kJ
 - 89.0 J
 - 44.5 kJ

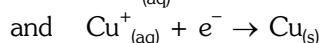
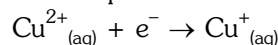
AIIMS 2010

15. Limiting molar conductance of H^+ and CH_3COO^- ions are $344 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and $40 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ respectively. Molar conductance of 0.008 M CH_3COOH is 48. What will be the value of K_a for CH_3COOH :-
- 1.4×10^{-5}
 - 1.2×10^{-5}
 - 1.4×10^{-4}
 - 1×10^{-5}
16. E value for the cell reaction $\text{Cu} | \text{Cu}^{2+} (0.001 \text{ M}) || \text{Cu}^{2+} (0.1 \text{ M}) | \text{Cu}$ is :-
- $-\frac{RT}{F} \ln(0.01)$
 - $-\frac{RT}{F} \ln(0.1)$
 - $+\frac{RT}{F} \ln(0.01)$
 - $+\frac{RT}{F} \ln(0.1)$

AIPMT Pre. 2011

17. Standard electrode potential of three metals X, Y and Z are -1.2 V, +0.5 V and -3.0 V respectively. The reducing power of these metals will be :-
- $Y > Z > X$
 - $Y > X > Z$
 - $Z > X > Y$
 - $X > Y > Z$

18. The electrode potentials for



are +0.15 V and +0.50 V respectively. The value of $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$ will be :-

- 0.500 V
- 0.325 V
- 0.650 V
- 0.150 V

19. Standard electrode potential for $\text{Sn}^{4+}/\text{Sn}^{2+}$ couple is +0.15 V and that for the Cr^{3+}/Cr couples is -0.74 V. These two couples in their standard state are connected to make a cell. The cell potential will be :-

- +1.19 V
- +0.89 V
- +0.18 V
- +1.83 V

20. If the E°_{cell} for a given reaction has a negative value, then which of the following gives the correct relationship for the values of ΔG° and K_{eq} ?

- $\Delta G^\circ > 0$; $K_{\text{eq}} > 1$
- $\Delta G^\circ < 0$; $K_{\text{eq}} > 1$
- $\Delta G^\circ < 0$; $K_{\text{eq}} < 1$
- $\Delta G^\circ > 0$; $K_{\text{eq}} < 1$

AIPMT Mains 2011

21. A solution contains Fe^{2+} , Fe^{3+} and I^- ions. This solution was treated with iodine at 35 °C. E° for $\text{Fe}^{3+} / \text{Fe}^{2+}$ is +0.77 V and E° for $\text{I}_2/2\text{I}^- = 0.536 \text{ V}$. The favourable redox reaction is :-
- Fe^{2+} will be oxidised to Fe^{3+}
 - I_2 will be reduced to I^-
 - There will be no redox reaction
 - I^- will be oxidised to I_2

AIPMT Pre. 2012

22. Limiting molar conductivity of NH_4OH

(i.e. $\Lambda^\circ_{\text{m}(\text{NH}_4\text{OH})}$) is equal to:-

- $\Lambda^\circ_{\text{m}(\text{NH}_4\text{OH})} + \Lambda^\circ_{\text{m}(\text{NH}_4\text{Cl})} - \Lambda^\circ_{\text{m}(\text{HCl})}$
- $\Lambda^\circ_{\text{m}(\text{NH}_4\text{Cl})} + \Lambda^\circ_{\text{m}(\text{NaOH})} - \Lambda^\circ_{\text{m}(\text{NaCl})}$
- $\Lambda^\circ_{\text{m}(\text{NH}_4\text{Cl})} + \Lambda^\circ_{\text{m}(\text{NaCl})} - \Lambda^\circ_{\text{m}(\text{NaOH})}$
- $\Lambda^\circ_{\text{m}(\text{NaOH})} + \Lambda^\circ_{\text{m}(\text{NaCl})} - \Lambda^\circ_{\text{m}(\text{NH}_4\text{Cl})}$

AIPMT Mains 2012

23. Molar conductivities (Λ_m°) at infinite dilution of NaCl, HCl and CH_3COONa are 126.4, 425.9 and $91.0 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. Λ_m° for CH_3COOH will be :-
 (1) $290.8 \text{ S cm}^2 \text{ mol}^{-1}$ (2) $390.5 \text{ S cm}^2 \text{ mol}^{-1}$
 (3) $425.5 \text{ S cm}^2 \text{ mol}^{-1}$ (4) $180.5 \text{ S cm}^2 \text{ mol}^{-1}$

AIIMS 2012

24. For $\text{Zn}^{2+} | \text{Zn} \text{ E}^\circ = -0.76 \text{ V}$ then EMF of this cell $\text{Zn} | \text{Zn}^{2+}(1\text{M}) || 2\text{H}^+(1\text{M}) | \text{H}_2(1 \text{ atm})$ will be :-
 (1) -0.76 V (2) 0.76 V
 (3) 0.38 V (4) -0.38 V

NEET-UG 2013

25. At 25°C molar conductance of 0.1 molar aqueous solution of ammonium hydroxide is $9.54 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and at infinite dilution its molar conductance is $238 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. The degree of ionisation of ammonium hydroxide at the same concentration and temperature is :-
 (1) 40.800% (2) 2.080%
 (3) 20.800% (4) 4.008%
26. A hydrogen gas electrode is made by dipping platinum wire in a solution of HCl of $\text{pH} = 10$ and by passing hydrogen gas around the platinum wire at 1 atm pressure. The oxidation potential of electrode would be ?
 (1) 1.18 V (2) 0.059 V
 (3) 0.59 V (4) 0.118 V

27. A button cell used in watches function as following
 $\text{Zn(s)} + \text{Ag}_2\text{O(s)} + \text{H}_2\text{O(l)} \rightleftharpoons 2\text{Ag(s)} + \text{Zn}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$
 If half cell potentials are
 $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn(s)}; \text{E}^\circ = -0.76 \text{ V}$
 $\text{Ag}_2\text{O(s)} + \text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow 2\text{Ag(s)} + 2\text{OH}^-(\text{aq}); \text{E}^\circ = 0.34 \text{ V}$
 The cell potential will be :-
 (1) 1.34 V (2) 1.10 V
 (3) 0.42 V (4) 0.84 V

AIIMS 2013

28. Electrode potential of hydrogen electrode is 18 mV then $[\text{H}^+]$ is :-
 (1) 0.2 (2) 1 (3) 2 (4) 5

AIPMT 2014

29. When $0.1 \text{ mol } \text{MnO}_4^{2-}$ is oxidised the quantity of electricity required to completely oxidise MnO_4^{2-} to MnO_4^- is :-
 (1) 96500 C (2) $2 \times 96500 \text{ C}$
 (3) 9650 C (4) 96.50 C
30. The weight of silver (at wt. = 108) displaced by a quantity of electricity which displaces 5600 mL of O_2 at STP will be :-
 (1) 5.4 g (2) 10.8 g
 (3) 54.0 g (4) 108.0 g

AIIMS 2014

31. Amount of charge is required to convert $17 \text{ g } \text{H}_2\text{O}_2$ into O_2 :-
 (1) 1F (2) 2F
 (3) 6F (4) None of these

AIPMT 2015

32. A device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy is known as :-
 (1) Electrolytic cell (2) Dynamo
 (3) Ni-Cd cell (4) Fuel Cell

AIIMS 2015

33. For the cell reaction
 $\text{Mg} + 2\text{Ag}^+(0.0001\text{M}) \rightarrow \text{Mg}^{2+}(0.01\text{M}) + 2\text{Ag}$
 $\text{E}_{\text{cell}}^\circ = 3.177 \text{ V}$ then what will be the value of E_{cell} for the above reaction ?
 (1) 2.5 (2) 3.0 (3) 3.2 (4) 3.8
34. If electrode potential of $0.01 \text{ M } \text{Cu}^{2+} / \text{Cu}$ is 0.32 V then what will be its $\text{E}_{\text{RP}}^\circ$ -
 (1) 0.18 V (2) 0.28 V
 (3) 0.74 V (4) 0.38 V

NEET-I 2016

35. The pressure of H_2 required to make the potential of H_2 -electrode zero in pure water at 298 K is :-
 (1) 10^{-14} atm (2) 10^{-12} atm
 (3) 10^{-10} atm (4) 10^{-4} atm

NEET-II 2016

36. The molar conductivity of a 0.5 mol/dm^3 solution of AgNO_3 with electrolytic conductivity of $5.76 \times 10^{-3} \text{ S cm}^{-1}$ at 298 K is
 (1) $0.086 \text{ S cm}^2/\text{mol}$ (2) $28.8 \text{ S cm}^2/\text{mol}$
 (3) $2.88 \text{ S cm}^2/\text{mol}$ (4) $11.52 \text{ S cm}^2/\text{mol}$

37. During the electrolysis of molten sodium chloride, the time required to produce 0.10 mol of chlorine gas using a current of 3 A is

- (1) 220 minutes (2) 330 minutes
(3) 55 minutes (4) 110 minutes

38. If the E_{cell}° for a given reaction has a negative value, which of the following gives the **correct** relationships for the values of ΔG° and K_{eq} ?

- (1) $\Delta G^{\circ} < 0$; $K_{\text{eq}} > 1$ (2) $\Delta G^{\circ} < 0$; $K_{\text{eq}} < 1$
(3) $\Delta G^{\circ} > 0$; $K_{\text{eq}} < 1$ (4) $\Delta G^{\circ} > 0$; $K_{\text{eq}} > 1$

39. The number of electrons delivered at the cathode during electrolysis by a current of 1 A in 60 s is (charge on electron = 1.60×10^{-19} C)

- (1) 3.75×10^{20} (2) 7.48×10^{23}
(3) 6×10^{23} (4) 6×10^{20}

AIIMS 2016

40. How many faraday charge is required for $\text{KMnO}_4/\text{Mn}^{2+}$:-

- (1) 3F (2) 2F (3) 5F (4) 1F

NEET(UG) 2017

41. In the electrochemical cell :-
 $\text{Zn} | \text{ZnSO}_4(0.01\text{M}) || \text{CuSO}_4(1.0\text{M}) | \text{Cu}$, the emf of this Daniel cell is E_1 . When the concentration of ZnSO_4 is changed to 1.0M and that of CuSO_4 changed to 0.01M, the emf changes to E_2 . Which one of the relationship is correct between E_1 and E_2 ?

(Given, $\frac{RT}{F} = 0.059$)

- (1) $E_1 < E_2$ (2) $E_1 > E_2$
(3) $E_2 = 0 \neq E_1$ (4) $E_1 = E_2$

AIIMS 2017

42. If limiting molar conductances of Ca^{+2} and Cl^- ions are 119 and $76.3 \text{ Scm}^2 \text{ mol}^{-1}$ respectively. The limiting molar conductivity of CaCl_2 is :-

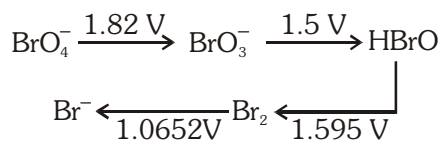
- (1) $347 \text{ S cm}^2 \text{ mol}^{-1}$ (2) $271.6 \text{ S cm}^2 \text{ mol}^{-1}$
(3) $42.7 \text{ S cm}^2 \text{ mol}^{-1}$ (4) $195.3 \text{ S cm}^2 \text{ mol}^{-1}$

EXERCISE-II (Previous Year Questions)

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	4	2	3	3	1	2	2	2	3	2	3	1	2	3
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	2	3	2	2	4	4	2	2	2	4	3	2	3	3	4
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	1	4	2	4	1	4	4	3	1	3	2	2	4	2	2
Que.	46	47													
Ans.	4	3													

NEET(UG) 2018

43. Consider the change in oxidation state of Bromine corresponding to different EMF values as shown in the diagram below:

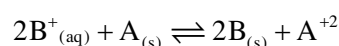


Then the species undergoing disproportionation is:-

- (1) BrO_3^- (2) BrO_4^-
(3) Br_2 (4) HBrO

AIIMS 2018

44. For given reaction



If K_{eq} of reaction is $10^{15.2}$

and $E^{\circ}(\text{A}^{+2}/\text{A}) = 0.34\text{V}$

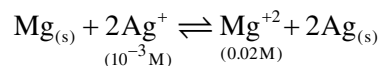
Then calculate $E^{\circ}(\text{B}^+/\text{B})$ will be :-

- (1) -0.80 (2) 0.80
(3) 1.27 (4) 1.60

45. For an electrolytic solution having concentration 0.1M and resistance is $1\text{K}\Omega$. If distance between electrode is 100 cm and area is 1 cm^2 then calculate λ_m in $\text{S cm}^2 \text{ mol}^{-1}$:-

- (1) 100 (2) 1000 (3) 500 (4) 50

46. What will be value of E_{cell} for reaction



Given E_{cell}° is 3.17 V

- (1) 2.67 (2) 2.13
(3) 3.27 (4) 3.041

47. 36 g H_2O is electrolysed by passing 3 ampere current. What will be time required for complete decomposition (in hour) :-

- (1) 17.87 hour (2) 15.84 hour
(3) 35.74 hour (4) 25.35 hour

ANSWER KEY

EXERCISE-III (Analytical Questions)

Check Your Understanding

- Specific conductance of 0.1 M Nitric acid is $6.3 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$. The molar conductance of the solution is :
 (1) $630 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
 (2) $315 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
 (3) $100 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
 (4) $6.300 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
 (5) $63.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
- The highest electrical conductivity of the following aqueous solution is of
 (1) 0.1 M fluoroacetic acid
 (2) 0.1 M difluoroacetic acid
 (3) 0.1 M acetic acid
 (4) 0.1 M chloroacetic acid
- Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100Ω . The conductivity of this solution is 1.29 S m^{-1} . Resistance of the same cell when filled with 0.02 M of the same solution is 520Ω . The molar conductivity of 0.02 M solution of the electrolyte will be.
 (1) $124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
 (2) $1240 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
 (3) $1.24 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
 (4) $12.4 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
- Resistance of 0.2 M solution of an electrolyte is 50Ω . The specific conductance of the solution is 1.4 S m^{-1} . The resistance of 0.5 M solution of the same electrolyte is 280Ω . The molar conductivity of 0.5 M solution of the electrolyte in $\text{S m}^2 \text{ mol}^{-1}$ is :
 (1) 5×10^3 (2) 5×10^2
 (3) 5×10^{-4} (4) 5×10^{-3}
- Resistance of 0.2 M solution of an electrolyte is 50Ω . The specific conductance of the solution is 1.3 S m^{-1} . If resistance of the 0.4 M solution of the same electrolyte is 260Ω then its molar conductivity is:-
 (1) $6250 \text{ S m}^2 \text{ mol}^{-1}$
 (2) $6.25 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
 (3) $625 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
 (4) $62.5 \text{ S m}^2 \text{ mol}^{-1}$
- The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_C and λ_∞ , respectively. The correct relationship between λ_C and λ_∞ is given by :
 (where the constant B is positive)
 (1) $\lambda_C = \lambda_\infty - (B) \sqrt{C}$ (2) $\lambda_C = \lambda_\infty + (B) \sqrt{C}$
 (3) $\lambda_C = \lambda_\infty + (B) C$ (4) $\lambda_C = \lambda_\infty - (B) C$

7.

Electrolyte	KCl	KNO ₃	HCl	NaOAc	NaCl
$\Lambda^\infty (\text{S cm}^2 \text{ mol}^{-1})$	149.9	145.0	426.2	91.0	126.5

- Calculate $\Lambda_{\text{HOAc}}^\infty$ using appropriate molar conductances of the electrolytes listed above at infinite dilution in H_2O at 25°C
 (1) 390.7 (2) 217.5 (3) 517.2 (4) 552.7
- Which of the following statements is TRUE for the electrochemical Daniel cell :
 (1) Electrons flow from copper electrode to zinc electrode.
 (2) Current flows from zinc electrode to copper electrode.
 (3) Cations move toward copper electrode.
 (4) Cations move toward zinc electrode.
 - Aluminium displaces hydrogen from dilute HCl whereas silver does not, the E.M.F. of a cell prepared by combining Al/Al^{3+} and Ag/Ag^+ is 2.46 V. The reduction potential of silver electrode is +0.80 V. The reduction potential of aluminium electrode is :
 (1) - 3.26 V (2) +1.66 V
 (3) -1.66 V (4) 3.26 V
 - Standard reduction electrode potential of three metals A, B and C are respectively + 0.5 V, - 3.0 V and -1.2 V. The reducing power of these metals are :
 (1) $C > B > A$ (2) $A > C > B$
 (3) $B > C > A$ (4) $A > B > C$
 - Consider the following E° values
 $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = +0.77 \text{ V}$
 $E_{\text{Sn}^{2+}/\text{Sn}}^\circ = -0.14 \text{ V}$
 Under standard conditions the potential for the reaction
 $\text{Sn(s)} + 2\text{Fe}^{3+}(\text{aq}) \longrightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{Sn}^{2+}(\text{aq})$ is
 (1) 0.91 V (2) 1.40 V
 (3) 1.68 V (4) 0.63 V
 - For the redox reaction :
 $\text{Zn(s)} + \text{Cu}^{2+} (0.1\text{M}) \rightarrow \text{Zn}^{2+} (1\text{M}) + \text{Cu(s)}$ taking place in a cell,
 E_{Cell}° is 1.10 V E_{Cell} for the cell will be
 $\left(2.303 \frac{RT}{F} = 0.0591 \right)$
 (1) 1.07 V (2) 0.82 V
 (3) 2.14 V (4) 1.80 V

- 13.** In a cell that utilises the reaction
 $\text{Zn(s)} + 2\text{H}^+(\text{aq.}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$ addition of H_2SO_4 to cathode compartment, will
 (1) increase the E_{cell} and shift equilibrium to the right
 (2) lower the E_{cell} and shift equilibrium to the right
 (3) lower the E_{cell} and shift equilibrium to the left
 (4) increase the E_{cell} and shift equilibrium to the left
- 14.** The e.m.f. of a Daniell cell at 298 K is E_1 .
 $\text{Zn} | \text{ZnSO}_4 | | \text{CuSO}_4 | \text{Cu}$
 (0.01M) (1.0M)
 When the concentration of ZnSO_4 is 1.0 M and that of CuSO_4 is 0.01 M, the e.m.f. changed to E_2 . What is the relationship between E_1 and E_2
 (1) $E_1 > E_2$ (2) $E_1 < E_2$
 (3) $E_1 = E_2$ (4) $E_2 = 0 \neq E_1$
- 15.** The reduction potential of hydrogen half-cell will be negative if :-
 (1) $p(\text{H}_2) = 2 \text{ atm}$ and $[\text{H}^+] = 1.0 \text{ M}$
 (2) $p(\text{H}_2) = 2 \text{ atm}$ and $[\text{H}^+] = 2.0 \text{ M}$
 (3) $p(\text{H}_2) = 1 \text{ atm}$ and $[\text{H}^+] = 2.0 \text{ M}$
 (4) $p(\text{H}_2) = 1 \text{ atm}$ and $[\text{H}^+] = 1.0 \text{ M}$
- 16.** For a cell reaction involving two-electron change, the standard e.m.f. of the cell is found to be 0.295 V at 25° C. The equilibrium constant of the reaction at 25 °C will be :
 (1) 10 (2) 1×10^{10}
 (3) 1×10^{-10} (4) 29.5×10^{-2}
- 17.** For a spontaneous reaction the ΔG , equilibrium constant (K) and E_{Cell}^0 will be respectively
 (1) -ve, < 1, -ve
 (2) -ve, > 1, -ve
 (3) -ve, > 1, +ve
 (4) +ve, > 1, -ve
- 18.** On the basis of the information available from the reaction $\frac{4}{3}\text{Al} + \text{O}_2 \rightarrow \frac{2}{3}\text{Al}_2\text{O}_3$,
 $\Delta G = -827 \text{ KJ mol}^{-1}$ of O_2 , the minimum e.m.f. required to carry out an electrolysis of Al_2O_3 is :-
 (F = 96500 C mol⁻¹)
 (1) 2.14 V (2) 4.28 V
 (3) 6.42 V (4) 8.56 V
- 19.** Given below are the half-cell reactions :-
 $\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}; E^\circ = -1.18 \text{ V}$
 $2(\text{Mn}^{3+} + \text{e}^- \rightarrow \text{Mn}^{2+}); E^\circ = +1.51 \text{ V}$
 The E° for $3\text{Mn}^{2+} \rightarrow \text{Mn} + 2\text{Mn}^{3+}$ will be :
 (1) -0.33 V; the reaction will not occur
 (2) -0.33 V; the reaction will occur
 (3) -2.69 V; the reaction will not occur
 (4) -2.69 V; the reaction will occur
- 20.** Given the data at 25°C,
 $\text{Ag} + \text{I}^- \rightarrow \text{AgI} + \text{e}^-; E^\circ = 0.152 \text{ V}$
 $\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-; E^\circ = -0.800 \text{ V}$
 What is the value of $\log K_{\text{sp}}$ for AgI ?
 $\left(2.303 \frac{RT}{F} = 0.059 \text{ V} \right)$
 (1) -8.12 (2) +8.612
 (3) -37.83 (4) -16.13
- 21.** The metal that cannot be obtained by electrolysis of an aqueous solution of its salts is:
 (1) Cu (2) Cr
 (3) Ag (4) Ca
- 22.** When during electrolysis of a solution of AgNO_3 9650 C of charge pass through the electroplating bath, the mass of silver deposited on the cathode will be :
 (1) 21.6 g (2) 108 g
 (3) 1.08 g (4) 10.8 g
- 23.** Aluminium oxide may be electrolysed at 1000 °C to furnish aluminium metal (At. Mass = 27 amu; 1 Faraday = 96500 C). The cathode reaction is $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$
 To prepare 5.12 kg of aluminium metal by this method would require.
 (1) $5.49 \times 10^4 \text{ C}$ of electric charge
 (2) $5.49 \times 10^1 \text{ C}$ of electric charge
 (3) $5.49 \times 10^7 \text{ C}$ of electric charge
 (4) $1.83 \times 10^7 \text{ C}$ of electric charge
- 24.** A current of 'i' A was passed for 't' s. through three cells P, Q and R connected in a series. These contain respectively silver nitrate, mercuric nitrate and mercurous nitrate. At the cathode of the cell P, 0.216 g of Ag was deposited. The weights of mercury deposited in the cathode of Q and R respectively are : (at. wt. of Hg = 200.59)
 (1) 0.4012 g and 0.8024 g
 (2) 0.4012 g and 0.2006 g
 (3) 0.2006 g and 0.4012 g
 (4) 0.1003 g and 0.2006 g

- 25.** A galvanic cell is set up from a zinc bar weighing 100 g and 1.0 L of 1.0 M CuSO_4 solution. How long would the cell will run if it is assumed to deliver a steady current of 1.0 A. (Atomic mass of Zn = 65)
- (1) 1.1 hr. (2) 46 hr.
(3) 53.6 hr. (4) 24.00 hr.
- 26.** The electrochemical equivalent of silver is 0.0011180 g. When an electric current of 0.5 A is passed through an aqueous silver nitrate solution for 200 s, the amount of silver deposited is :
- (1) 1.1180 g (2) 0.11180 g
(3) 5.590 g (4) 0.5590 g
- 27.** A current of 9.65 A is passed through an aqueous solution of NaCl using suitable electrodes for 1000 s. Given that 1 faraday equals 96500 C the amount of NaOH (mol wt. 40.00) formed on electrolysis is :
- (1) 2.0 g (2) 8.0 g
(3) 4.0 g (4) 1.0 g.
- 28.** An electric current is passed through silver voltameter connected to a water voltameter. The cathode of the silver voltameter weighed 0.108 g more at the end of the electrolysis. The volume of oxygen evolved at STP is :
- (1) 56 cm^3 (2) 550 cm^3
(3) 5.6 cm^3 (4) 11.2 cm^3
(5) 22.4 cm^3
- 29.** 4.5 g of aluminium (at. mass 27 amu) is deposited at cathode from Al^{3+} solution by a certain quantity of electric charge. The volume of hydrogen produced at STP from H^+ ions in solution by the same quantity of electric charge will be –
- (1) 44.8 L (2) 11.2 L
(3) 22.4 L (4) 5.6 L
- 30.** The thermodynamic efficiency of cell is given by -
- (1) $\frac{\Delta H}{\Delta G}$ (2) $\frac{nFE}{\Delta G}$
(3) $-\frac{nFE}{\Delta H}$ (4) Zero

EXERCISE-III (Analytical Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	2	1	3	2	1	1	3	3	3	1	1	1	1	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	2	3	1	3	4	4	4	3	3	3	2	3	3	4	3

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

- Assertion :-** Electrolysis of molten calcium hydride produces hydrogen gas at anode.
Reason :- Hydrogen in calcium hydride is present as H^- ion.
 (1) A (2) B (3) C (4) D
- Assertion :-** Molar conductance of 0.1 M NH_4OH solution is less than that of 0.001M NH_4OH solution.
Reason :- Dilution increases the degree of ionisation of NH_4OH .
 (1) A (2) B (3) C (4) D
- Assertion :-** Salt bridge is generally used in the electrochemical cells.
Reason :- The ions of the electrolyte used in the salt bridge should have nearly same transport number.
 (1) A (2) B (3) C (4) D
- Assertion :-** The electrode potential of SHE is zero.
Reason :- SHE is a standard reference electrode.
 (1) A (2) B (3) C (4) D
- Assertion :-** Copper sulphate solution cannot be stored in iron-vessel.
Reason :- Copper atoms are oxidised by iron ions.
 (1) A (2) B (3) C (4) D
- Assertion :-** Absolute value of E_{red}^0 of an electrode cannot be determined.
Reason :- Neither oxidation nor reduction can take place alone.
 (1) A (2) B (3) C (4) D
- Assertion :-** A dry cell became dead after long time even if it has not been used.
Reason :- The NH_4Cl slowly and gradually corrodes the zinc container.
 (1) A (2) B (3) C (4) D
- Assertion :-** The molar conductance of weak electrolytes is low as compared to that of strong electrolytes at moderate concentrations.
Reason :- Weak electrolytes at moderate concentration dissociates to a much greater extent as compared to strong electrolytes.
 (1) A (2) B (3) C (4) D
- Assertion :-** Galvanised iron does not rust.
Reason :- Zinc has a more negative electrode potential than iron.
 (1) A (2) B (3) C (4) D
- Assertion :-** Increase in the concentration of copper half cell in Daniel cell increases the emf of the cell.
Reason :- According to the nernst equation

$$\text{emf of Daniel cell} = E_{cell}^0 + \frac{0.059}{2} \log \frac{[Cu^{+2}]}{[Zn^{+2}]}$$
 (1) A (2) B (3) C (4) D
- Assertion :-** Sodium ions are discharged at the Hg electrode during electrolysis in preference to H^+ ions.
Reason :- The nature of electrode also affects the order of discharge of cations.
 (1) A (2) B (3) C (4) D
- Assertion :-** The cell constant of a cell depends upon the nature of the material of the electrodes.
Reason :- The observed conductance depends upon the nature of the electrolyte and the concentration of the solution.
 (1) A (2) B (3) C (4) D
- Assertion :-** At the end of electrolysis using platinum electrodes, an aqueous solution of copper sulphate turns colourless.
Reason :- Copper in $CuSO_4$ is converted to $Cu(OH)_2$ during the electrolysis.
 (1) A (2) B (3) C (4) D

- 14. Assertion :-** In electrolysis, the quantity of electricity needed for depositing 1 mol of silver is different from that required for 1 mol of copper.
Reason :- The atomic weight of silver and copper are different.
 (1) A (2) B (3) C (4) D
- 15. Assertion :-** pH of solution increases during electrolysis of aqueous solution of NaCl.
Reason :- Electrolysis is non-spontaneous process.
 (1) A (2) B (3) C (4) D
- 16. Assertion :-** A reaction is spontaneous if $E_{\text{cell}} = +ve$.
Reason :- For $E_{\text{cell}} = +ve$, (ΔG) is always $-ve$.
 (1) A (2) B (3) C (4) D
- 17. Assertion :-** Cu is stronger reducing agent than H_2 .
Reason :- E° of Cu^{+2}/Cu is negative.
 (1) A (2) B (3) C (4) D
- 18. Assertion :-** For cell reaction; at 298 K
 $Zn(s) + Cu^{+2}(1M) \rightleftharpoons Zn^{+2}(1M) + Cu(s)$
 $E_{\text{cell}}^0 = 0$.
Reason :- At standard condition ; cell potential is always zero.
 (1) A (2) B (3) C (4) D

- 19. Assertion :-** Molar conductivity of an electrolyte solution increases on dilution.
Reason :- Decrease in conductivity is overcome by increase in volume.
 (1) A (2) B (3) C (4) D
- 20. Assertion :-** In electrolytic refining, electrolytic cell consists of pure and impure Cu electrodes dipped in $CuSO_4(aq)$.
Reason :- Pure Cu is obtained at anode.
 (1) A (2) B (3) C (4) D
- 21. Assertion :-** Molar conductivity of CH_3COOH increases with dilution.
Reason :- The graph between λ_m v/s $(C)^{1/2}$ is a straight line for CH_3COOH .
 (1) A (2) B (3) C (4) D
- 22. Assertion :-** On electrolysis of aq. NaCl, Na is obtained.
Reason :- Na^+ is reduced at cathode.
 (1) A (2) B (3) C (4) D

EXERCISE-IV (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	1	2	2	3	1	1	3	1	1	1	4	3	2	2
Que.	16	17	18	19	20	21	22								
Ans.	1	4	4	1	3	3	4								

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NEET SYLLABUS

p-Block Elements : *General Introduction to p-Block Elements. General introduction, electronic configuration, occurrence, variation of properties, oxidation states, trends in chemical reactivity, anomalous properties of first element of the Groups 13 to 18 elements.*

OBJECTIVES

After studying this unit, you will be able to :

- *appreciate general trends in the chemistry of elements of groups 13 to 18;*
- *explain anomalous behaviour of boron and carbon;*
- *describe allotropic forms of carbon;*
- *learn the preparation, properties and uses of dinitrogen and phosphorus and some of their important compounds;*
- *describe the preparation, properties and uses of dioxygen and ozone and chemistry of some simple oxides;*
- *know allotropic forms of sulphur, chemistry of its important compounds and the structures of its oxoacids;*
- *describe the preparation, properties and uses of chlorine and hydrochloric acid;*
- *know the chemistry of interhalogens and structures of oxoacids of halogens;*
- *enumerate the uses of noble gases;*
- *appreciate the importance of these elements and their compounds in our day to day life.*

p-Block elements signify common man in society on whom all socio-economic rules are applicable.

Linus Pauling

p-BLOCK ELEMENTS

IMPORTANT CONCEPTS :

- | | |
|--|--------------------------------------|
| 1. Back bonding | 2. Dimerisation |
| 3. Inert pair effect | 4. Oxyacids |
| 5. Hydrolysis | 6. Allotropes |
| 7. Silicates and Silicones | 8. Drying agent and bleaching agents |
| 9. Reactions and compounds (Group 13-18) | |

1. BACK BONDING

It is formed between two covalently bonded adjacent atoms.

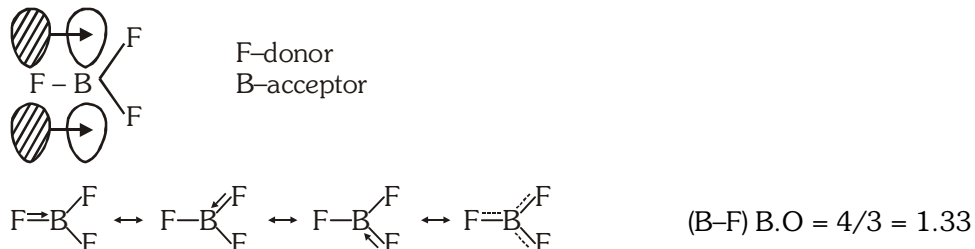
Conditions for back bonding :

- Both bonded atoms must belong to 2nd period or one bonded atom must belong to 2nd period and the other must belong to 3rd period.
- One bonded atom must possess vacant orbital and the other bonded atom must possess lone pair.

- As a result of back bonding between the bonded atoms, bond length decreases and bond energy increases.

Back bonding :

It is a partial sideways overlap in which there is a slight electron transference from electron rich atom to electron deficient atom. As a result the electron deficiency of the deficient atom gets slightly compensated.



Types of back bonding :

Based on type of orbital : (2 types)

- $p\pi-p\pi$ back bonding
- $p\pi-d\pi$ back bonding

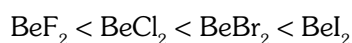
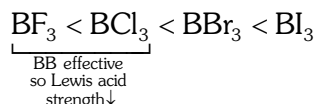
(1) $p\pi-p\pi$ back bonding :

Order of strength : $2p-2p > 2p-3p > 2p-4p \dots\dots$

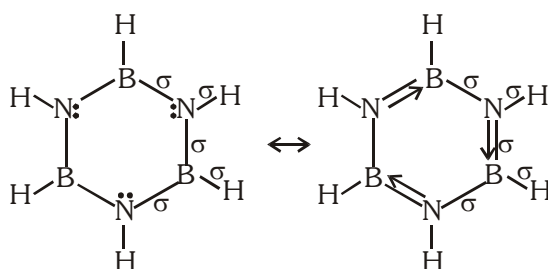
Size $\uparrow$ extent of B.B. $\downarrow$

It is used to explain following observations :-

- Abnormal bond length and bond energy of B-F bond in BF_3 .
- Lewis acidic order of **Boron** and **Beryllium** halides.

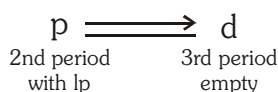


- (c) **Hybridisation :** If a lone pair participates in back bonding then it is not considered in hybridisation.
 Ex. $B_3N_3H_6$ (inorganic benzene or borazene or borazole)
- Hybridisation of B as well as N = sp^2



- Inorganic benzene is more reactive than organic benzene as in it the **bonds are polar**, although over all molecule is non polar.
- (d) If back bonding is present then tendency to form dimer or polymer decreases.
 Ex. BF_3 , BeF_2

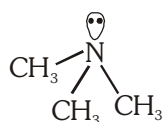
(2) $p\pi-d\pi$ back bonding :



it is used to explain following observations :

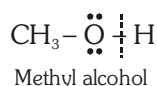
(a) Hybridisation

Ex. Trimethyl amine
 $(CH_3)_3N$



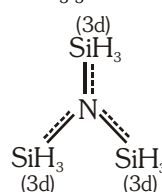
- sp^3 hybrid (N)
- trigonal pyramidal
- Lewis base (due to presence of lp)

(b) Acidic strength

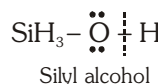


- No back bonding
- Less acidic

Trisilyl amine
 $(SiH_3)_3N$



- sp^2 hybrid (N)
- trigonal planar
- Not Lewis base
- Bond angle increases



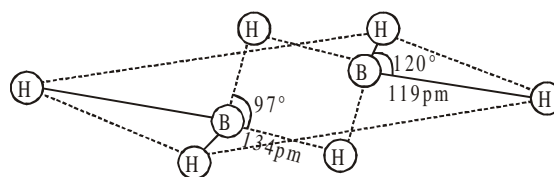
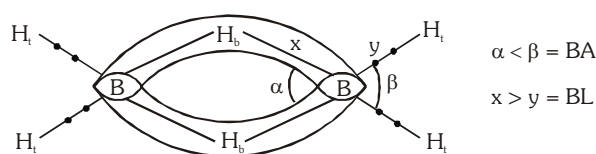
- Back bonding present in conjugate base
- More acidic

2. DIMERISATION / POLYMERISATION

Types of Dimerisation	
3C—2e	3C—4e
B ₂ H ₆	(BeCl ₂) ₂
(BeH ₂) ₂	(BeCl ₂) _n
(BeH ₂) _n	(AlCl ₃) ₂
Al ₂ (CH ₃) ₆	(ICl ₃) ₂
Ga ₂ (CH ₃) ₆	

(A) By banana Bond or by 3C—2e bond or by e⁻ deficient bond

(a) B₂H₆



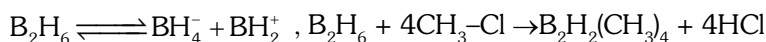
2C — 2e⁻ bonds = 4

3C — 2e⁻ bonds = 2

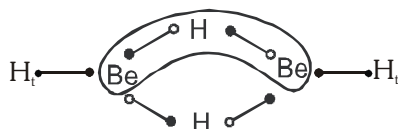
Hybridisation state = sp³

Electron deficient molecule (act as Lewis acid)

- All four terminal hydrogen and two boron atoms are present in same plane both bridging H are present in perpendicular plane.
- If substitution reaction takes place than only four terminal hydrogen atom will be substituted.



(b) (BeH₂)₂ (dimer of BeH₂ in vapour state)

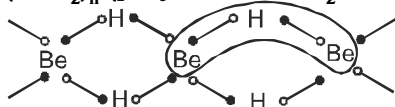


Hybridisation state = sp²

Planar

electron deficient molecule

(c) (BeH₂)_n (polymer of BeH₂ in solid state)



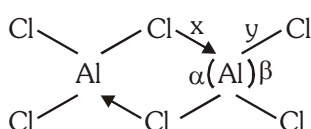
Hybridisation state = sp³

Non-planar

electron deficient molecule

(B) By-coordinate Bond / 3C—4e bond

(a) Al₂Cl₆ (dimer of AlCl₃ in liquid or solid state)



BA = $\alpha < \beta$

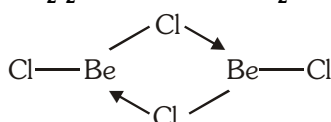
BL = $x > y$

Hybridisation state = sp³

Non-planar

octet complete

(b) (BeCl₂)₂ (dimer of BeCl₂ in vapour state)

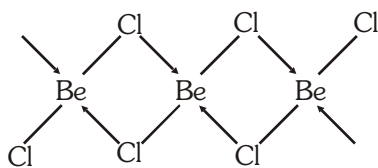


Hybridisation state = sp²

Planar

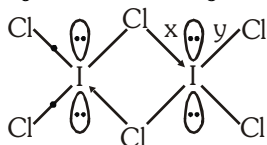
electron deficient molecule

(c) $(\text{BeCl}_2)_n$ (polymer of BeCl_2 in solid state)



Hybridisation state = sp^3
Non-planar
octet complete

(d) I_2Cl_6 (dimer of ICl_3)



Hybridisation state = sp^3d^2
Planar
super octet complete (12 electrons)

Note :

- (i) BCl_3 , BBr_3 & BI_3 do not form dimer due to smaller size of boron & large size of halogen (due to more steric repulsion)
- (ii) BF_3 cannot form dimer due to its back bonding.
- (iii) AlF_3 cannot form dimer due to its ionic nature.

BEGINNER'S BOX-1

1. In BF_3 :
 - (1) B-F bond has some double bond character and this bond is delocalised
 - (2) All the B-F bonds are single covalent in nature
 - (3) Bond energy and bond length of B-F bond indicate its single bond character
 - (4) All the bonds are ionic
2. Which of the following statements is incorrect in the context of the B-F bond in BF_3 :-
 - (1) All the three B-F bond lengths are equal and each of them is shorter than the sum of the covalent radii of boron and fluorine.
 - (2) The bond energy of the B-F bond is very high, higher than for any other single bond
 - (3) The unusual shortness and strength of the B-F bond may be explained by a $\pi\text{p}-\pi\text{p}$ interaction between boron and fluorine atoms.
 - (4) The unusual shortness and strength of the bonds may be explained by a $\pi\text{p}-\text{d}\pi$ interaction between the atoms of boron and fluorine.
3. In BF_3 , the B-F bond length is $1.30 \text{ \AA}$, when BF_3 is allowed to be treated with Me_3N , it forms an adduct, $[\text{Me}_3\text{N} \rightarrow \text{BF}_3]$. The bond length of B-F in the adduct is :
 - (1) Greater than $1.30 \text{ \AA}$
 - (2) Smaller than $1.30 \text{ \AA}$
 - (3) Equal to $1.30 \text{ \AA}$
 - (4) None of these
4. Which of the following structures correctly represents the boron trifluoride molecule :

(1)

(3)

(2)

(4)
5. Trisilylamine $[\ddot{\text{N}}(\text{SiH}_3)_3]$ has a
 - (1) Planar geometry
 - (2) Tetrahedral geometry
 - (3) Pyramidal geometry
 - (4) None of these

6. In which of the following molecule, vacant orbitals do not participate in bonding:-
 (1) B_2H_6 (2) Al_2Cl_6 (3) $[H_3N.BF_3]$ (4) Si_2H_6
7. Which of the following is not possible due to back bonding.
 (1) State of hybridisation may change (2) Bond order increases
 (3) Bond angle always increases (4) Lewis acidic strength decreases
8. In which of the following compounds B-F bond length is shortest?
 (1) BF_4^- (2) $BF_3 \leftarrow NH_3$ (3) BF_3 (4) $BF_3 \leftarrow N(CH_3)_3$
9. In diborane –
 (1) 2 bridged hydrogen and four terminal hydrogen are present
 (2) 3 bridged and three terminal hydrogen are present
 (3) 4 bridged hydrogen atoms are not in the same plane in diborane
 (4) 1 bridged hydrogen and 1 terminal hydrogen are present
10. Which of the following statements is correct in the context of diborane (B_2H_6)?
 (1) There are 12 valence electrons-three from each of the two boron atoms and six from the six hydrogen atoms
 (2) Two of the six hydrogen atoms form two bridges between two boron atoms
 (3) The two bridging hydrogen atoms are in a plane perpendicular to the rest of the molecule and prevent rotation between the two boron atoms
 (4) All of these

3. INERT PAIR EFFECT

	Group-13	Group-14	Group-15
(group oxidation state)	$\frac{ns^2np^1}{+3}$	$\frac{ns^2np^2}{+4}$	$\frac{ns^2np^3}{+5}$

- While moving down the group the stability of lower oxidation state (2 less than group oxidation state) progressively increases, for the last element of the group the stability of lower oxidation state becomes even greater than the group oxidation state. **This is called inert pair effect.**
- For the last element group oxidation state is highly oxidising in nature.

Group-13		Group-14		Group-15	
B	+3	C	+4	N	+5
Al	+3	Si	+4	P	+5

Ga	+3 > +1	Ge	+4 > +2	As	+5 > +3
In	+3 > +1	Sn	+4 > +2	Sb	+5 > +3
Tl	+3 < +1	Pb	+4 < +2	Bi	+5 < +3

Reason : As we move down the group there is presence of d & f-orbitals in inner shells which have poor shielding effect hence Z_{eff} increases. As a result the ns^2 electron pair becomes more and more tightly held to the nucleus and becomes reluctant to participate in bonding.

Examples :

- $PbCl_2$ is more stable than $PbCl_4$.
- $TlCl$ is more stable than $TlCl_3$.
- $GaCl_3$ is more stable than $TlCl_3$.
- $SnCl_4$ is more stable than $PbCl_4$.
- Thallium (III) iodide does not exist.
- PbI_4 does not exist.
- Only BiF_5 exists but $BiCl_5$ does not exist ?

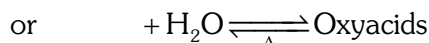


4. OXY ACID

General Formula of Oxy acid : $\text{H}_x\text{Z}_y\text{O}_z$ (Z = non metal)

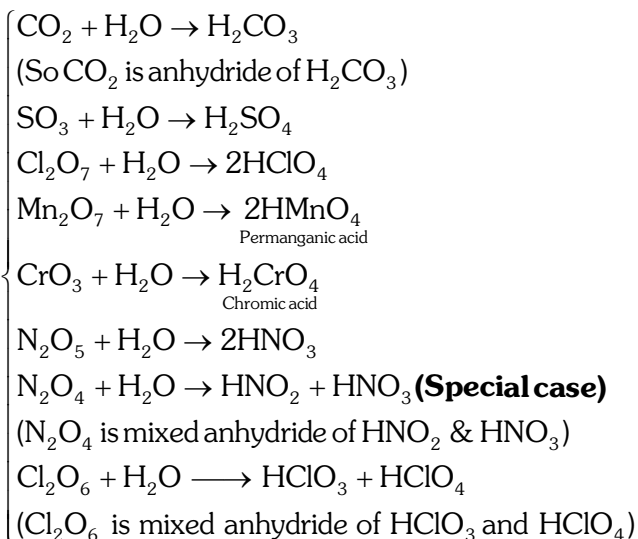
- Compounds which contain Z-OH bond are known as oxyacids.

- Acidic oxide



Non metallic oxide
 Anhydrides of oxyacids

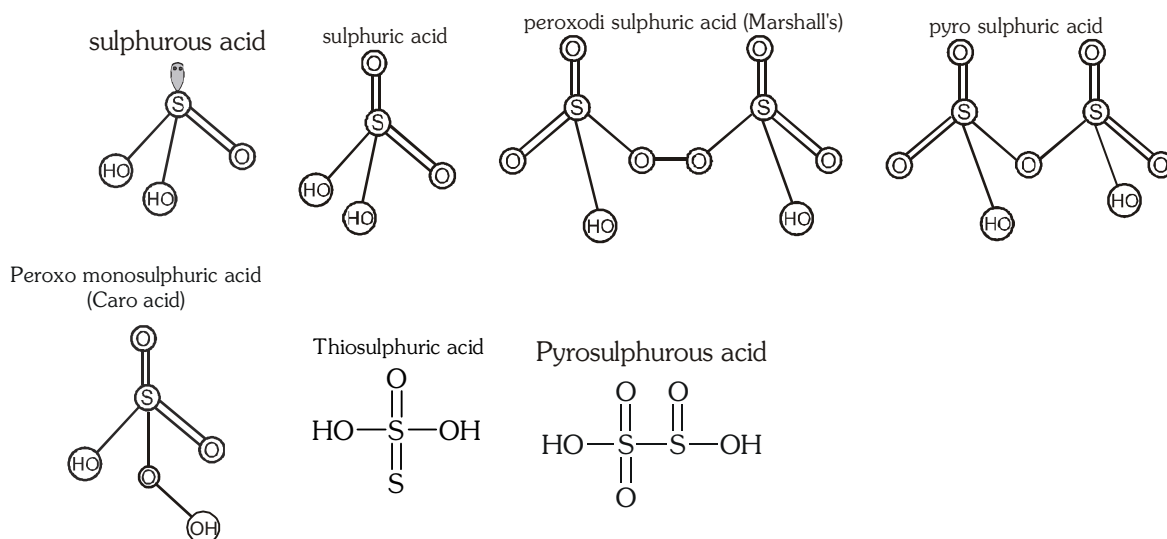
Anhydrides of their
 corresponding oxyacids



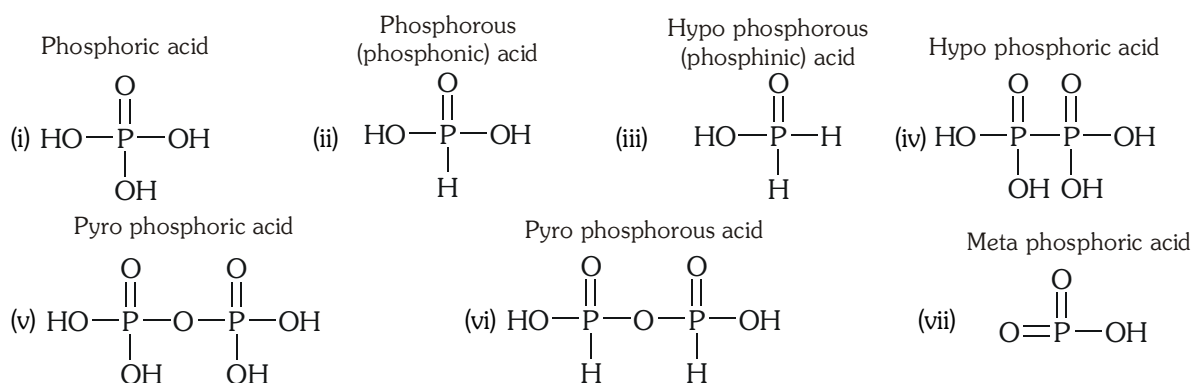
- Oxidation state of central atom does not change.

Pyro	Meta	Per oxy acid	Hypo	
↓	↓	↓	Ous acid	ic acid
2 mole oxy acid	1 mole oxy acid		↓ -O	↓ -O
↓ -H ₂ O	↓ -H ₂ O	Z—O—O—H	Hypo us acid	Hypo ic acid
pyro acid	meta acid			
Ex. $\text{H}_2\text{S}_2\text{O}_5$ $\text{H}_2\text{S}_2\text{O}_7$ $\text{H}_4\text{P}_2\text{O}_7$	Ex. HPO_3 HBO_2	Ex. H_2SO_5 $\text{H}_2\text{S}_2\text{O}_8$ HNO_4 $\text{CH}_3\text{CO}_3\text{H}$ $\text{C}_6\text{H}_5\text{CO}_3\text{H}$	Ex. HOX H_3PO_2	Ex. $\text{H}_4\text{P}_2\text{O}_6$

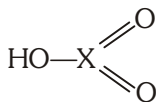
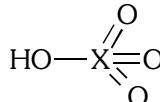
OXY ACIDS OF SULPHUR



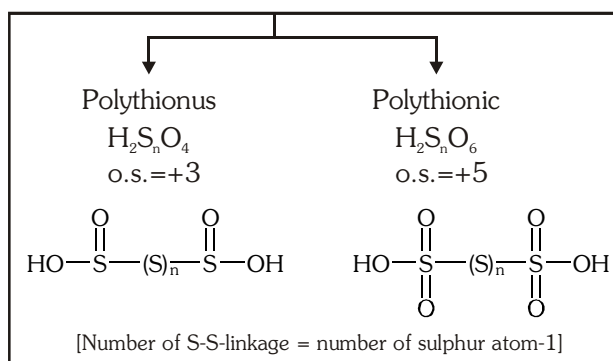
OXY ACID OF PHOSPHORUS

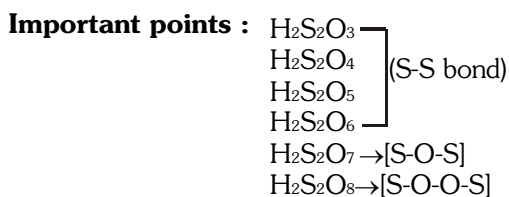


OXY ACIDS OF HALOGENS

Hypohalous	Halous	Halic	Per halic
HO—X	O=X—OH	HO—X 	HO—X 
+1 HOCl HOBr HOI	+3 HClO ₂ — —	+5 HClO ₃ HBrO ₃ HIO ₃	+7 HClO ₄ HBrO ₄ HIO ₄

OXY ACIDS CONTAINING S-S LINKAGE



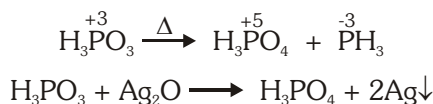


Trick for drawing structure of oxy compound

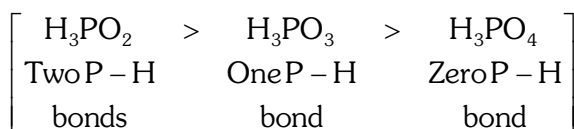
Oxy compounds	Group present
$\text{X}_2\text{O}_6^{-q}$	$[\text{X-X}]$
$\text{X}_2\text{O}_7^{-q}$	$[\text{X-O-X}]$
$\text{X}_2\text{O}_8^{-q}$	$[\text{X-O-O-X}]$

Some important points

- (1) Oxy acid of phosphorus having +1 & +3 oxidation state (having P-H bond) can act as reducing agent or give disproportionation reaction on heating.



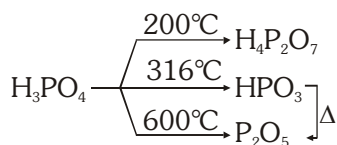
Order of reducing nature.



Note : Nitrogen compound having +1 & +3 oxidation state gives disproportion to reaction in acidic medium.



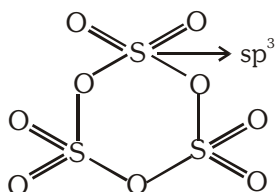
- (2) **Heating effect of phosphoric acid**



- (3) **Heating effect of boric acid**

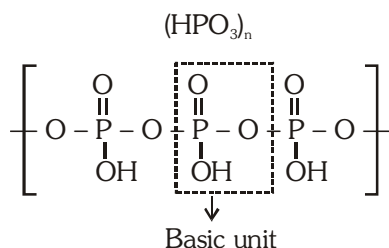
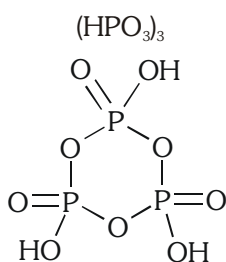


- (4) **SO_3 exists as a cyclic trimer (S_3O_9)**



6 S=O bonds
3 S-O-S bonds
 sp^3 hybrid 'S', Non planar

- (5) **Metaphosphoric acid exists as dimer, cyclic trimer or polymer**



(6) Acidic nature of oxy acids.

General concept :

$$\text{For same elements} \left(\begin{array}{l} \text{Acidic nature} \\ \text{of oxyacids} \end{array} \propto \begin{array}{l} \text{Oxidation number of} \\ \text{active element} \end{array} \right)$$

(Acidic nature of oxyacids $\propto$ EN of active element) for different elements

Exception :

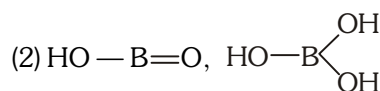
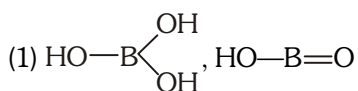
- for oxy acids of P**

$$\left(\text{Acidic nature} \propto \frac{1}{\text{Oxidation number}} \right)$$

Example : $\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_4$ (acidic order)

BEGINNER'S BOX-2

1. Structures of metaboric acid and orthoboric acid respectively are :



(3) Both the above

(4) None

2. Orthoboric acid –

(1) Donate proton to form H_2BO_3^-

(2) Accept proton of form H_4BO_3^+

(3) Donate OH^- to form H_2BO_2^+

(4) Accept OH^- to form $[\text{B}(\text{OH})_4]^-$

3. Pick out the incorrect statement :-

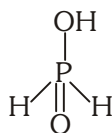
(1) Orthophosphorus acid can be obtained by reacting P_4O_6 with H_2O

(2) Orthophosphoric acid can be obtained by reacting P_4O_{10} with H_2O

(3) Pyrophosphoric acid can be obtained by heating Orthophosphorus acid

(4) Metaphosphoric acid is obtained by the dehydration of orthophosphoric acid at 316°C .

4. Hypophosphorus acid H_3PO_2 is –



(1) Tribasic acid

(2) Dibasic acid

(3) Monobasic acid

(4) Not acidic at all

5. The correct order of decreasing acid strength of oxy acids of group 15 elements is :

(1) $\text{HNO}_3 > \text{H}_3\text{SbO}_4 > \text{H}_3\text{AsO}_4 > \text{H}_3\text{PO}_4$

(2) $\text{H}_3\text{PO}_4 > \text{H}_3\text{AsO}_4 > \text{H}_3\text{SbO}_4 > \text{HNO}_3$

(3) $\text{HNO}_3 > \text{H}_3\text{PO}_4 > \text{H}_3\text{AsO}_4 > \text{H}_3\text{SbO}_4$

(4) $\text{HNO}_3 > \text{H}_3\text{AsO}_4 > \text{H}_3\text{PO}_4 > \text{H}_3\text{SbO}_4$

6. Which one of the following is a mixed anhydride :

(1) NO

(2) NO_2

(3) N_2O_3

(4) N_2O_5

7. Which of the following oxy acids of sulphur contains a sulphur-sulphur single bond :

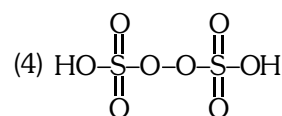
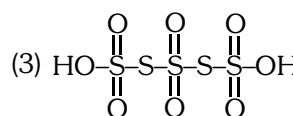
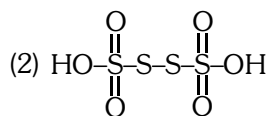
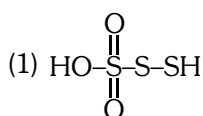
(1) $\text{H}_2\text{S}_2\text{O}_6$

(2) $\text{H}_2\text{S}_2\text{O}_7$

(3) $\text{H}_2\text{S}_2\text{O}_8$

(4) $\text{H}_2\text{S}_2\text{O}_3$

8. The structure of peroxodisulphuric acid is :



9. Number of S-S bond in $\text{H}_2\text{S}_n\text{O}_6$

(1) n

(2) $(n-1)$

(3) $(n-2)$

(4) $(n+1)$

10. Ga^+ acts as a reducing agent because –

(1) Ga^{3+} state is less stable than Ga^{+1}

(2) Ga^{3+} state is more stable than Ga^{+1}

(3) Ga^{3+} convert into Ga^{+1} reducing

(4) None of the above

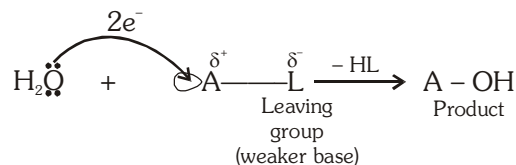
5. HYDROLYSIS

Chemical reaction of H_2O with a covalent compound.

Condition :

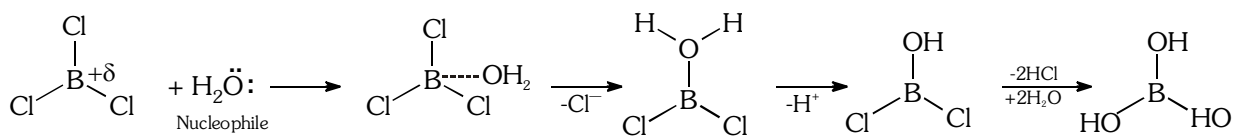
One atom must possess vacant orbital and positive charge.

Mechanism : (S_N^2 mechanism)



- Weaker base goes out and a stronger base substitutes it.

Example



- For hybridisation of transition state

Reactant $\longrightarrow$ Transition state

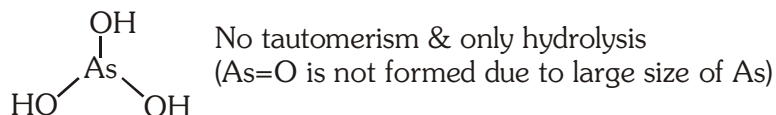
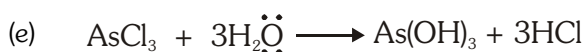
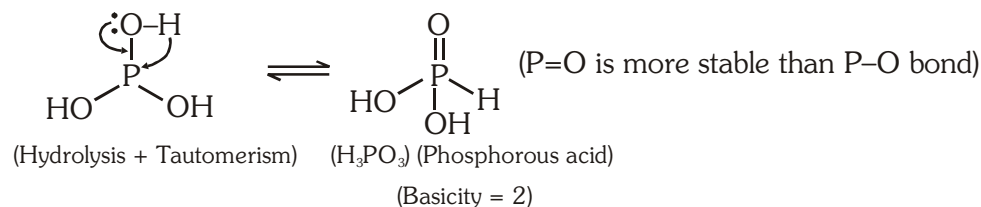
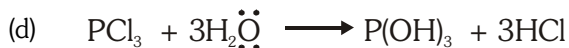
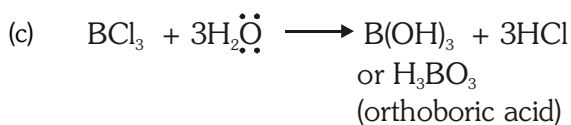
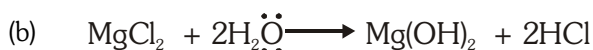
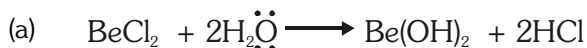
Ex. : $\text{sp} \longrightarrow \text{sp}^2$

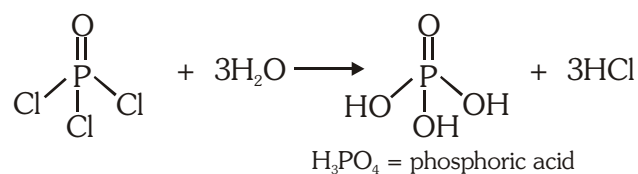
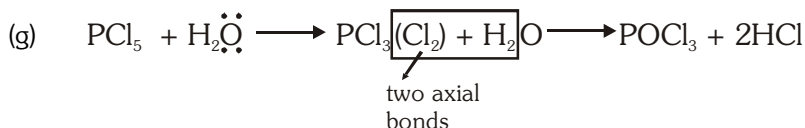
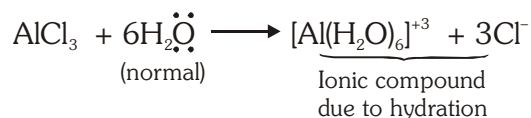
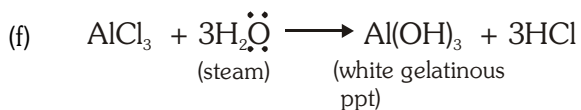
$\text{sp}^2 \longrightarrow \text{sp}^3$

$\text{sp}^3 \longrightarrow \text{sp}^3\text{d}$

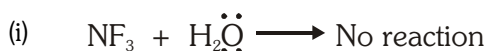
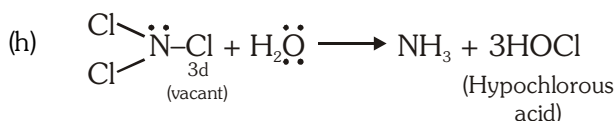
Important examples of hydrolysis

1. Hydrolysis of some important covalent molecules.

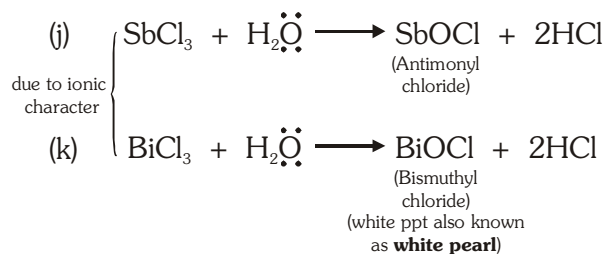




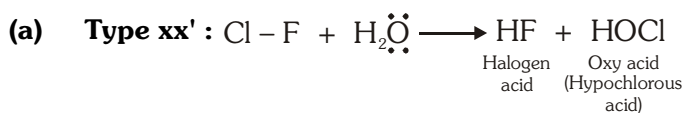
• **Hydrolysis is not a redox reaction**



• **Partial hydrolysis**

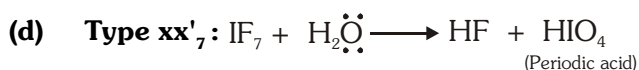
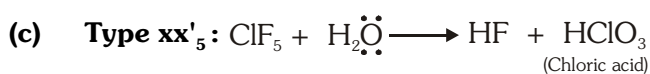
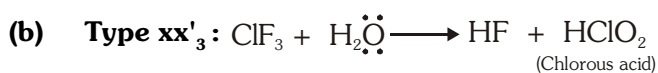


2. Hydrolysis of interhalogen compounds

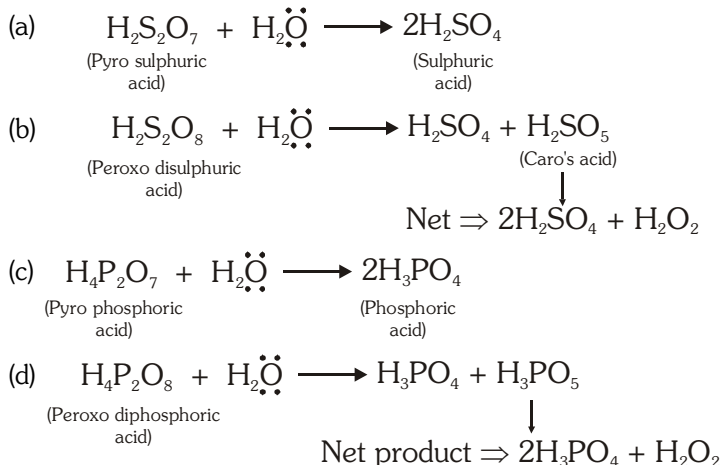


x = oxy acid (same oxidation number)

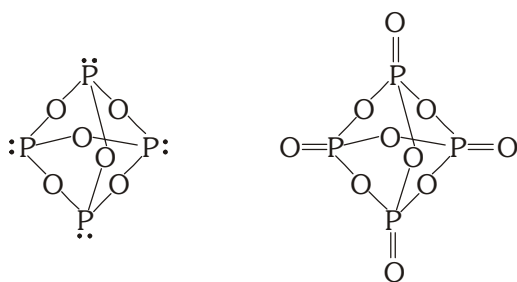
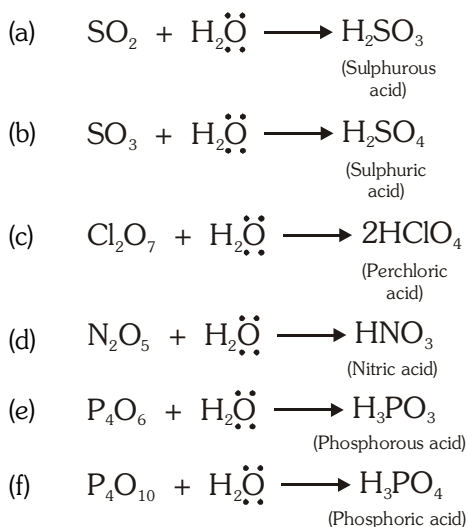
x' = Halogen acid



3. Hydrolysis of oxyacids



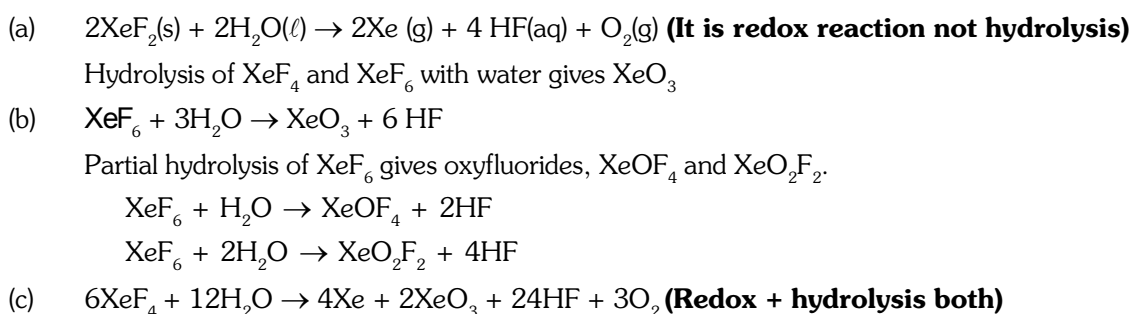
4. Hydrolysis of oxides (N, P, S, Cl)



P_4O_6
 $\rightarrow \text{sp}^3$ hybrid 'P'
 $\rightarrow 6 \text{ P-O-P bonds}$
 $\rightarrow \text{lp on 'P'} = 4$

P_4O_{10}
 $\rightarrow \text{sp}^3$ hybrid 'P'
 $\rightarrow 6 \text{ P-O-P bonds}$
 $\rightarrow 4 \text{ P=O bonds}$

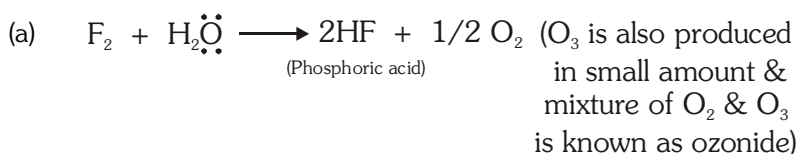
5. Hydrolysis of Xe-fluoride



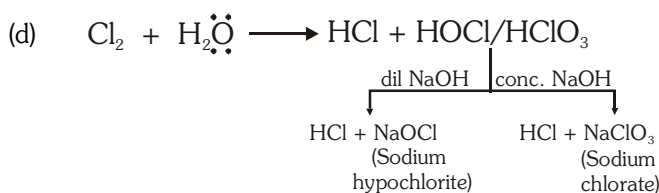
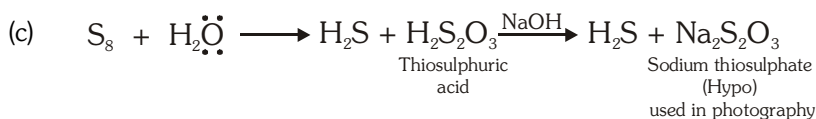
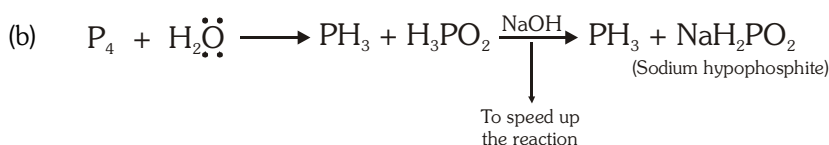
6. Hydrolysis of ionic compounds

- (a) Carbides (b) Nitrides (c) Phosphides

7. Hydrolysis of non-metals and halogen



- 'F₂' is the only non-metal that can oxidise H₂O as it is a powerful oxidising agent. Other halogens & non-metals undergo disproportionation with water in basic medium. (Redox reaction)



BEGINNER'S BOX-3

1. Which of the following statements is correct :

- (1) Aluminium carbide as well as beryllium carbide produce methane gas on treatment with water
- (2) On reacting with water, calcium carbide (CaC₂) produces acetylene while magnesium carbide (Mg₂C₃) gives propyne
- (3) Both of these
- (4) None of these

2. (a) $Al \xrightarrow[N_2]{\text{High temp.}} A$ (b) $Al \xrightarrow[C]{\text{High temp.}} B$

Product A and B on hydrolysis yields respectively.

- (1) Ammonia and acetylene
- (2) Ammonia and methane
- (3) Nitric oxide and acetylene
- (4) None

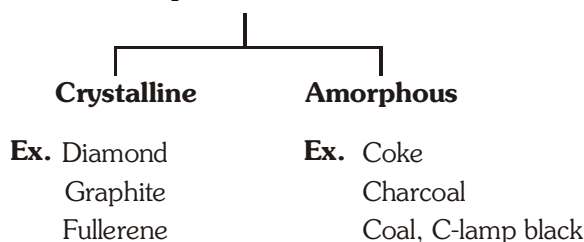
3. SbCl_3 and BiCl_3 on hydrolysis gives :
- (1) Sb^{+3} and Bi^{+3} (2) Sb(OH)_3 and Bi(OH)_3
 (3) SbOCl and BiOCl (4) None
4. The hydrolysis of PCl_3 , produces :
- (1) $\text{H}_3\text{PO}_3 + \text{HClO}$ (2) $\text{H}_3\text{PO}_3 + \text{HCl}$
 (3) $\text{H}_3\text{PO}_4 + \text{HCl}$ (4) $\text{PH}_3 + \text{HClO}$
5. The number of molecules of water needed to convert one molecule of P_2O_5 into orthophosphoric acid is :
- (1) 2 (2) 3 (3) 4 (4) 5
6. XeF_6 on partial hydrolysis produces :-
- (1) XeF_2 (2) XeOF_4 (3) XeF_4 (4) XeO_3
7. Which of the following halides does not hydrolysed?
- (1) PbCl_4 (2) SiCl_4 (3) CCl_4 (4) SnCl_4
8. which of the following is an uncommon hydrolysis product of XeF_2 and XeF_4 ?
- (1) Xe (2) XeO_3 (3) HF (4) O_2
9. Consider the following reactions :
- (i) $\text{PCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3 + 3\text{HCl}$
 (ii) $\text{SF}_4 + 3\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 + 4\text{HF}$
 (iii) $\text{BCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{BO}_3 + 3\text{HCl}$
 (iv) $\text{XeF}_6 + 3\text{H}_2\text{O} \rightarrow \text{XeO}_3 + 6\text{HF}$

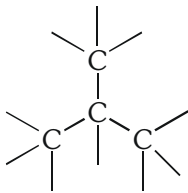
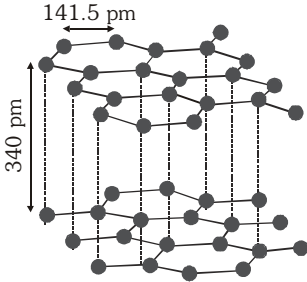
Then according to given information the incorrect statement is

- (1) During the (i) reaction the hybridisation of 15th group element does not change
 (2) During the (ii) reaction the hybridisation of 16th group element has been change
 (3) During the (iii) reaction the hybridisation of 13th group element does not change
 (4) During the (iv) reaction the hybridisation of 18th group element does not change
10. Select correct statement about hydrolysis of BCl_3 and NCl_3
- (1) NCl_3 is hydrolysed and gives HOCl but BCl_3 is not hydrolysed
 (2) Both NCl_3 and BCl_3 on hydrolysis gives HCl
 (3) NCl_3 on hydrolysis gives HOCl but BCl_3 gives HCl
 (4) Both NCl_3 and BCl_3 on hydrolysis gives HOCl

6. ALLOTROPES

(A) Allotropes of Carbon



DIAMOND	GRAPHITE
	
Each carbon bonded with four other carbon atom sp^3 hybridisation tetrahedral structure Insulator due to absence of free electrons Hard due to presence of strong sigma bond and 3D structure Density = 3.35 gm/cm^3 High melting point (giant molecule) Bond length (C—C) = $1.54 \text{ \AA}$	Each carbon bonded with three other carbon atom sp^2 hybridisation hexagonal layer structure Conductor due to presence of delocalised electrons Soft due to presence of weak van der Waals forces between two layers Density = 2.22 gm/cm^3 Low melting point Bond length (C—C) = $1.41 \text{ \AA}$

Special Point :

- (i) Thermodynamically graphite is more stable than diamond.
- (ii) Aqueous solution of graphite is known as **aquadag**.
- (iii) Graphite is also known as **plumbago (used in lead pencil)**
- (iv) Graphite use as a dry lubricants.
- (v) **Hardest allotrope** of carbon is diamond, **softest allotrope** is lamp black, **purest allotrope** is fullerene

Fullerene

- C-60 & C-70 are common fullerene.
- C-60 is also known as Buckminster fullerene (Bucky ball)

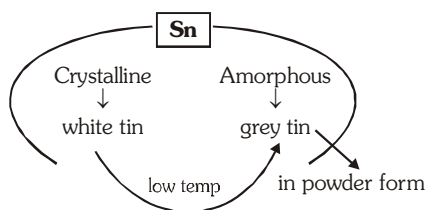
- There are 32 rings $\begin{matrix} 32 & \swarrow & 12 \text{ pentagonal} \\ & \searrow & 20 \text{ hexagonal} \end{matrix}$

- Each carbon atom bonded with 3 other carbon by sigma & double bond (resonance)
- sp^2 hybridisation & aromatic in nature

⚡ Dangling Bond

In diamond or graphite some surface carbon atom have free valency. These carbon atoms form new bonds with impurities. These new bonds are known as dangling bond.

(B) ALLOTROPE OF TIN



(C) ALLOTROPE OF PHOSPHOROUS

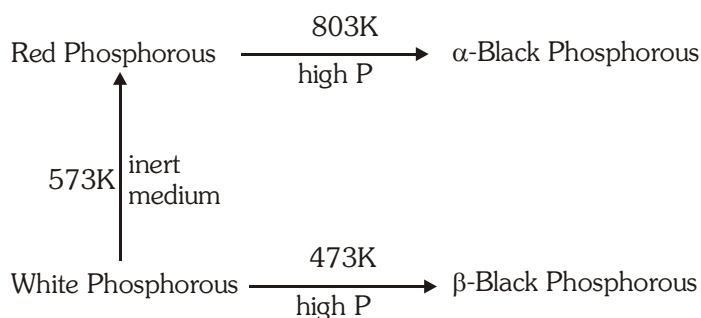
(a) white/yellow phosphorous

(b) Red phosphorous

(c) Black phosphorous

White phosphorous	Red Phosphorous
Waxy solid	Brittle powder
Poisonous	Non poisonous
Soluble in CS ₂ , Insoluble in water	Insoluble in water & CS ₂
Monomer of P ₄	Polymer of P ₄
Highly reactive due to bond angle strain	More stable than white phosphorous
It glows in dark due to slow oxidation (phosphorescence)	It does not glow in dark
It gives phosphene (PH ₃) on reaction with NaOH	It give hypo phosphoric acid when on reaction with NaOH

Order of stability or MP or density → white < red < black



(D) ALLOTROPE OF SULPHUR

S	
Crystalline	Amorphous
Rhombic sulphur (α-S) most stable form	Milk of sulphur Plastic sulphur (γ-S)
Monoclinic sulphur (β-S)	Colloidal sulphur
$\alpha\text{-S} \xrightleftharpoons[\text{<95}^\circ\text{,6}^\circ\text{C}]{\text{>95.6}^\circ\text{C}} \beta\text{-S}$	$\text{H}_2\text{S} + 2\text{HNO}_3 \xrightarrow{\text{Redox}} \text{S} + 2\text{NO}_2 + 2\text{H}_2\text{O}$ RA OA
95.6°C = transition Temp. both are soluble in CS ₂ but insoluble in water	

- II. (a) density of $\alpha S > \beta S$
 (b) Both are puckered crown shape having S_8 units
 (c) S_2 is paramagnetic sulphur which exist in vapour form at high temperature.
 (d) S_6 is chair form of S

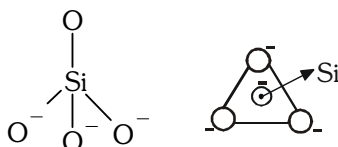
III. Effect of temperature :



7. (A) SILICATES

Basic / structural unit : SiO_4^{-4}

SiO_4^{-4} have a tendency of polymerisation



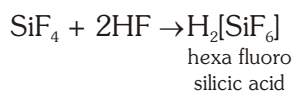
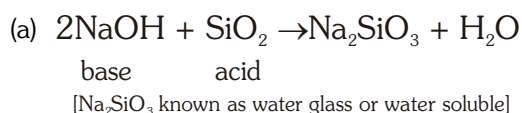
Silicate	No. of shared oxygen per unit	General formula	Structure	Example
Ortho silicate	0	SiO_4^{-4}		Zircon ZrSiO_4
Pyro silicate	1	$\text{Si}_2\text{O}_7^{-6}$		Hemi morphite $\text{Zn}_3\text{Si}_2\text{O}_7 \cdot \text{Zn}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$
Single chain silicate	2	$(\text{SiO}_3^{-2})_n$		$\text{LiAlSi}_2\text{O}_6$ Spodumene
Cyclic silicate	2	$(\text{SiO}_3^{-2})_n$		Beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$)
Sheet silicate	3	$(\text{Si}_2\text{O}_5^{-2})_n$		Talc $\text{Mg}_3(\text{OH})_2(\text{Si}_2\text{O}_5)_2$
3-D silicate	4	$(\text{SiO}_2)_n$		Silica (SiO_2)

(B) Sodium Zeolite $[\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8]/[\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}]$

- (i) It is a 3-D silicate
 (ii) It is used in
 (a) For softening of hard water
 (b) For cracking of hydrocarbon & isomerisation

Ex. ZSM-5 (Zeolite) is used to convert ethyl alcohol into petrol.

(C) SILICA : Generally silica is inert but it can react with NaOH & HF.



- This process is also known as **Etching of glass**.

(D) SILICONES

Silicones are organometallic polymer which contain R₂SiO as a basic unit.

Properties :

- Silicones are chemically inert due to presence of strong sigma bond.
- Silicones have water repelling nature due to presence of alkyl group.
- Silicones are insulator due to absence of free electrons.

Preparation :

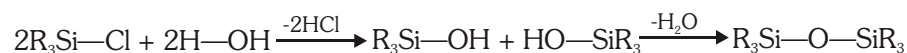
Alkyl chloro silane $\xrightarrow{\text{hydrolysis}}$ product $\xrightarrow{\text{condensation}}$ silicones

R₃SiCl : dimer (used to stop chain formation)

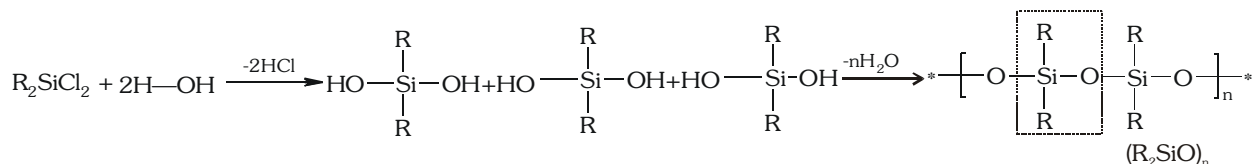
R₂SiCl₂ : linear polymer

RSiCl₃ : cross link polymer

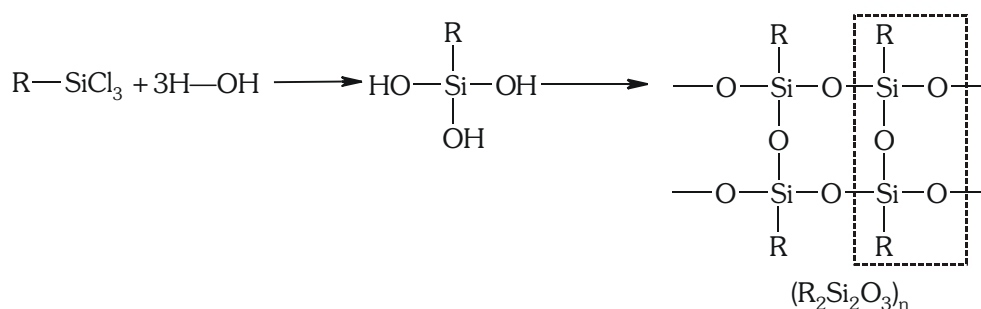
(a) Dimer silicone:



(b) Linear chain silicone



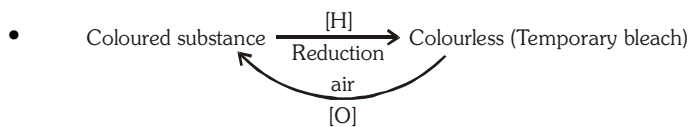
(c) Cross linked silicone



8. BLEACHING AGENTS AND DEHYDRATING AGENTS

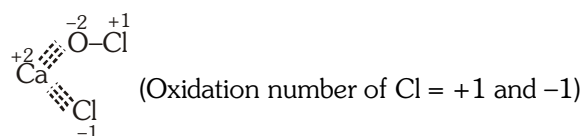
(A) BLEACHING AGENTS

- Bleaching can be done by oxidation or reduction.
- Coloured substance $\xrightarrow[\text{Oxidation}]{[\text{O}]}$ Colourless (Permanent bleach)



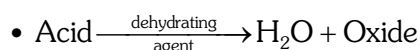
Examples :

- | By oxidation | By Reduction |
|--|-------------------------------|
| (1) O_3 (Dry bleach) | SO_2 (with moisture) |
| (2) H_2O_2 (with moisture) | |
| (3) Cl_2 (with moisture) | |
- **Bleaching powder** : Used in textile industries. Bleaches by oxidation.
 $\text{CaCl}_2 \cdot \text{Ca}(\text{OCl})_2 \cdot \text{Ca}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (average oxidation number of Cl = 0)
 or



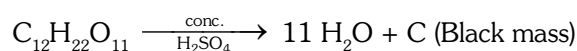
(B) DEHYDRATING AGENTS

Example : $[\text{P}_4\text{O}_{10}, (\text{Conc.}) \text{H}_2\text{SO}_4, \text{CaO} (\text{Quick lime}), \text{CaCl}_2 (\text{Anhydrous})]$



Example :

- $\text{HCOOH} \xrightarrow[\text{H}_2\text{SO}_4]{\text{conc.}} \text{H}_2\text{O} + \text{CO}$ (Lab preparation of CO)
- $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array} \xrightarrow[\text{H}_2\text{SO}_4]{\text{conc.}} \text{CO} + \text{CO}_2 + \text{H}_2\text{O}$ (Lab preparation of CO & CO_2)
- $\begin{array}{c} \text{COOH} \\ | \\ \text{CH}_2 \\ | \\ \text{COOH} \end{array} \xrightarrow[\text{H}_2\text{SO}_4]{\text{conc.}} 2\text{H}_2\text{O} + \text{O}=\text{C}=\text{C}=\text{C}=\text{O}$ (Carbon suboxide)
 (Malonic acid)
- $2\text{HClO}_4 \xrightarrow{\text{P}_4\text{O}_{10}} \text{H}_2\text{O} + \text{Cl}_2\text{O}_7$
- $2\text{HNO}_3 \xrightarrow{\text{P}_4\text{O}_{10}} \text{H}_2\text{O} + \text{N}_2\text{O}_5$
- Charring of sugar (dehydration) :



Some extra points :

- NH_3 can not be dried by conc. H_2SO_4 , P_4O_{10} and CaCl_2
- Alcohols, phenols can not be dried by metal hydrides.
- $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ can not be dried by heating alone.

BEGINNER'S BOX-4

1. Silicones have the general formula
 (1) SiO_4^{4-} (2) $\text{Si}_2\text{O}_7^{6-}$ (3) $(\text{R}_2\text{SiO})_n$ (4) $(\text{SiO}_3)_n^{2-}$
2. Glass or silica soluble in :
 (1) HClO_4 (2) HF (3) Aqua-regia (4) H_2SO_4
3. $\text{Si}_2\text{O}_7^{6-}$ anion is obtained when
 (1) no oxygen of a SiO_4^{4-} tetrahedron is shared with another SiO_4^{4-} tetrahedron
 (2) one oxygen of a SiO_4^{4-} tetrahedron is shared with another SiO_4^{4-} tetrahedron
 (3) two oxygen of a SiO_4^{4-} tetrahedron is shared with another SiO_4^{4-} tetrahedron
 (4) three or all four oxygen of a SiO_4^{4-} tetrahedron is shared with another SiO_4^{4-} tetrahedron
4. Consider the following route of reactions
 $\text{R}_2\text{SiCl}_2 + \text{Water} \rightarrow (\text{A}) \xrightarrow{\text{polymerisation}} (\text{B})$
 Compound(B) in above reaction is
 (1) Dimer silicone (2) Linear silicone
 (3) cross linked silicone (4) polymerisation of (A) does not occur
5. $(\text{Si}_2\text{O}_5)^{2n-}$ anion is obtained when
 (1) no oxygen of a SiO_4^{4-} tetrahedron is shared with another SiO_4^{4-} tetrahedron
 (2) one oxygen of a SiO_4^{4-} tetrahedron is shared with another SiO_4^{4-} tetrahedron
 (3) two oxygen of a SiO_4^{4-} tetrahedron is shared with another SiO_4^{4-} tetrahedron
 (4) three oxygen of a SiO_4^{4-} tetrahedron is shared with another SiO_4^{4-} tetrahedron
6. What is true about various allotropes of carbon ?
 (1) Diamond is the hardest and graphite is the softest
 (2) Diamond is the hardest and coke is the softest
 (3) Diamond is the hardest and lamp black is the softest
 (4) Coke is the hardest and diamond is the softest
7. Different layers in graphite are held together by :
 (1) Ionic bonding (2) Metallic bonding
 (3) Covalent bonding (4) Vander Waals forces
8. Bucky ball or buck minster fullerene is :
 (1) An allotrope of carbon
 (2) It is referred as C-60
 (3) It has sp^2 -hybridised nature and resembles with soccer ball
 (4) all of these
9. Which of the following statement is correct for allotrops of P :-
 (1) White P is soluble in CS_2 but red P is insoluble in CS_2
 (2) P-P-P bond angle is 60° in red P
 (3) On heating in air, white P change into red P
 (4) White P change in black P at ordinary temp.
10. Which of the following structural features of graphite best accounts for its use as a lubricant?
 (1) delocalized electrons
 (2) strong covalent bonds between carbon atoms
 (3) van der Waal's forces between layers
 (4) limited three covalency of carbon

BORON FAMILY (GROUP 13)

INTRODUCTION

The p-block elements are those elements of the periodic table in which the differentiating electron (or the last electron) enters the p-subshell of the last (outermost) shell. Since the maximum capacity of any atomic orbital is of two electrons with opposite spins (Pauli's principle), the maximum number of electrons that can be accommodated in any p-subshell is six. As a result, the p-block of the periodic table consists of six groups: 13 (III A), 14 (IV A), 15 (V A), 16 (VI A), 17 (VIIA) and 18 (zero group). On the basis of electronic configuration, the element He is to be excluded from the p-block as its last electron enters the s-subshell of the last shell.

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,

GENERAL CHARACTERISTICS

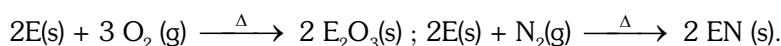
Physical properties :

- 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 members 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.

Chemical properties

Reactivity towards air

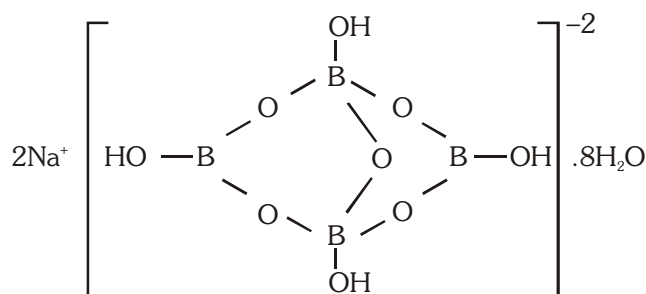
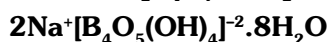
- Boron is unreactive in crystalline form.
- Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack.
- Amorphous boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at high temperature they form nitrides.



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.

COMPOUNDS OF BORON

(I) Borax ($Na_2B_4O_7 \cdot 10H_2O$)

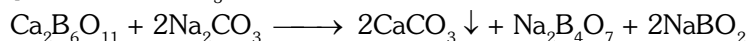


Important points :

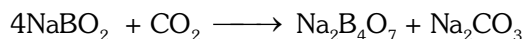
- B-O-B linkage = 5
- Total B-O bonds = 14
- Two Boron- sp^2 hybridised
- Two Boron- sp^3 hybridised

(i) From Colemanite.

When colemanite powder is heated with Na_2CO_3 solution, the following reaction occurs with the precipitation of CaCO_3 .

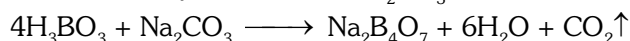


The filtrate is cooled when white crystals of borax are precipitated. The mother liquor on treatment with CO_2 converts NaBO_2 to $\text{Na}_2\text{B}_4\text{O}_7$ which precipitates out on crystallization.



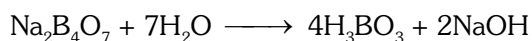
(ii) From orthoboric acid.

Borax is obtained by the action of Na_2CO_3 on orthoboric acid.



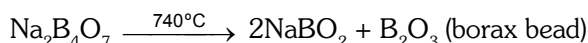
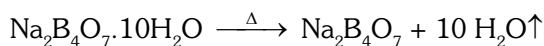
Properties :

- (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 .



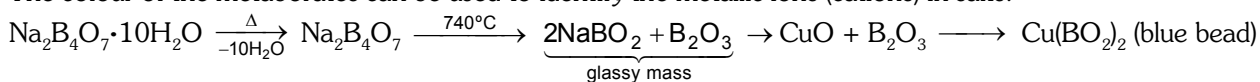
(iii) Action of heat.

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.



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.

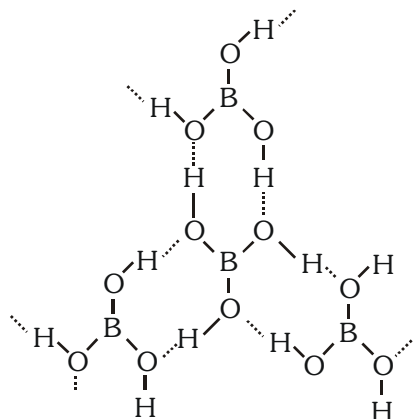


Uses : Borax is used

1. in borax bead test
2. in purifying gold
3. as flux during welding of metals and
4. in production of glass.

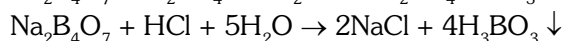
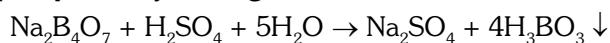
(II) ORTHO BORIC ACID [$\text{H}_3\text{BO}_3/\text{B}(\text{OH})_3$]

Orthoboric acid is greasy to touch less soluble in cold water but more soluble in hot water. In the solid state, the $\text{B}(\text{OH})_3$ units are hydrogen bonded together into two dimensional sheets with almost hexagonal symmetry.

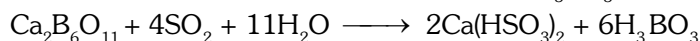


(A) Preparation :

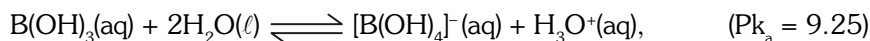
- (i) It is precipitated by treating a concentrated solution of borax with mineral acid.



- (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.

**(B) Properties:**

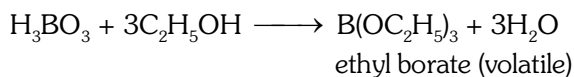
It is a weak monobasic acid soluble in water and in aqueous solution the boron atom completes its octet by accepting OH^- from water molecules:



It, therefore, functions as a Lewis acid and not as a proton donor like most acids.

(C) Test for Borate radical :

When boric acid is heated with ethyl alcohol, the evolved gas is burned forming a green edged flame.

**Uses :**

1. It is an antiseptic and its water solution is used as an eyewash.
2. It is also used in glass, enamel and pottery industry.

(III) DIBORANE (B_2H_6)

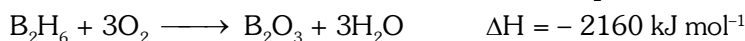
Binary compounds of boron with hydrogen are called boron hydrides or boranes.

Preparation :

- (i) $4\text{BF}_3 + 3\text{LiAlH}_4 \xrightarrow{\text{ether}} 2\text{B}_2\text{H}_6 + 3\text{LiF} + 3\text{AlF}_3$
- (ii) $2\text{NaBH}_4 + \text{I}_2 \xrightarrow{\text{ether}} \text{B}_2\text{H}_6 + 2\text{NaI} + \text{H}_2$
- (iii) $2\text{BF}_3 + 6\text{NaH} \xrightarrow{453\text{ K}} \text{B}_2\text{H}_6 + 6\text{NaF}$ (Industrial method)

Properties :

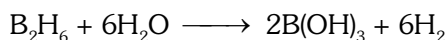
- (i) B_2H_6 is colourless gas and highly reactive (boiling point 183 K).
- (ii) It catches fire spontaneously in air and explodes with O_2 . Reaction with oxygen is extremely exothermic.



Mixtures of diborane with air or oxygen in flame 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.

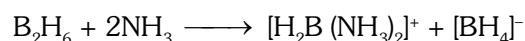
At red-heat the boranes decomposes to boron and hydrogen.

- (iii) Reaction with water is instantaneous.

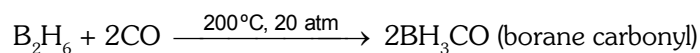
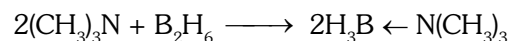


- (iv) The electron deficient 3c-2e B-H-B bridges are sites of nucleophilic attack.

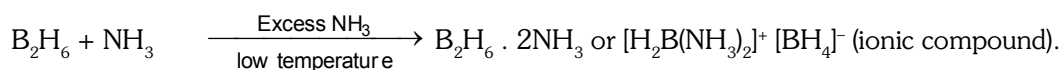
Small amines such as NH_3 , CH_3NH_2 and $(\text{CH}_3)_2\text{NH}$ give unsymmetrical cleavage of diborane.



Large amines such as $(\text{CH}_3)_3\text{N}$ and pyridine give symmetrical cleavage of diborane.



- (v) The reaction with ammonia depends on conditions.

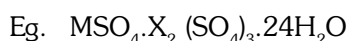


Borazole is much more reactive than benzene.

COMPOUNDS OF ALUMINIUM :

ALUM

- (a) Alums are double sulphates with their general formula $\text{M}_2\text{SO}_4 \cdot \text{M}'_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
where M = 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 - $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
 - (ii) Chrome alum - $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}$
 - (iii) Iron alum - $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
 - (iv) Ammonium alum - $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
- (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**.



M = divalent or Bivalent ion

X = Trivalent metal ion

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} .

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.

BEGINNER'S BOX-5

1. On the addition of mineral acid to an aqueous solution of borax, the compound formed is –

(1) Orthoboric acid	(2) Boron hydride
(3) Metaboric acid	(4) Pyroboric acid
2. Which of the following can be detected by the borax-bead test ?

(1) Ni^{2+}	(2) Co^{2+}	(3) Pb^{+2}	(4) Both (1) & (2)
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3. A mixture of boric acid with ethyl alcohol burns with green edged flame due to the formation of –

(1) Ethyl borax	(2) Ethyl borate
(3) Methyl borax	(4) Methyl borate
4. The hydrolysis of borax produces –

(1) An acidic medium	(2) A basic medium
(3) A neutral medium	(4) An acidic or an neutral medium
5. In alums, each metal ion is surrounded by–

(1) Two water molecules	(2) Four water molecules
(3) Six water molecules	(4) Eight water molecules
6. Which of the following is false statements :-

(1) Boranes are easily hydrolysed	(2) LiAlH_4 reduces BCl_3 to borane
(3) BH_3 is a Lewis acid	(4) All the B–H distances in diborane (B_2H_6) are equal
7. Inorganic graphite is :-

(1) $\text{B}_3\text{N}_3\text{H}_6$	(2) B_2H_6	(3) BN	(4) BF_3
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8. By which of the following reactions is borazine prepared ?

(1) $\text{B}_2\text{H}_6 + \text{NH}_3 \text{ (excess)} \xrightarrow{\text{low temperature}}$	(2) $\text{B}_2\text{H}_6 + \text{NH}_3 \text{ (excess)} \xrightarrow{\text{high temperature}}$
(3) $\text{B}_2\text{H}_6 + \text{NH}_3 \xrightarrow[\text{high temperature}]{\text{(ratio } 2\text{NH}_3 : 1\text{B}_2\text{H}_6)}$	(4) None of the above
9. When an inorganic compound (X) having 3c–2e as well as 2c–2e bonds reacts with ammonia gas at a certain temperature, gives a compound (Y), isostructural with benzene. Compound (X) with ammonia at a high temperature produces a substance (Z) :

(1) (X) is B_2H_6	(2) (Z) is known as inorganic graphite
(3) (Y) is $\text{B}_3\text{N}_3\text{H}_6$	(4) All of these
10. Which one of the following has the lowest m.p.?

(1) B	(2) Al	(3) Ga	(4) Tl
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CARBON FAMILY (GROUP 14)

PHYSICAL PROPERTIES

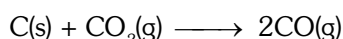
- All group 14 members are solids.
- Carbon and silicon are non-metals, germanium is metalloid whereas tin and lead are soft metals with low melting points.
- Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13 due to stronger metallic bonding.

COMPOUNDS OF CARBON

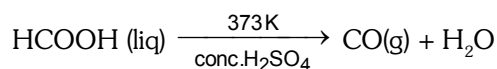
(A) Carbon Monoxide (CO)

(I) 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.



- (ii) In the laboratory it can be prepared by dehydrating methanoic acid with concentrated sulphuric acid.



(II) Physical Properties

- (i) Carbon monoxide is a colourless, odourless gas which burns in air with a blue flame, forming CO_2 .
- (ii) It is sparingly soluble in water and is a neutral oxide.
- (iii) 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.
- (iv) It acts as good reducing agents for all metal oxide.

(B) CARBON DIOXIDE (CO_2)

Preparation :

- (i) Complete combustion of carbon containing compounds.
- $$\text{CH}_4 + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$$
- (ii) In the laboratory it can be conveniently made by the action of dilute hydrochloric acid on marble chips :
- $$\text{CaCO}_3(\text{aq}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell)$$
- (iii) Industrially it is produced as a by-product during the manufacture of quicklime and in fermentation processes:
- $$\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g}) ; \quad \text{C}_6\text{H}_{12}\text{O}_6(\text{aq})\{\text{glucose}\} \longrightarrow 2\text{C}_2\text{H}_5\text{OH}(\text{aq}) + 2\text{CO}_2(\text{g})$$

Properties :

- (i) It is a colourless, odourless and heavy gas.
- (ii) Carbon dioxide is the acid anhydride of carbonic acid, which is a weak dibasic acid and ionises in two steps as follows :
- $$\text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$
- $$\text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{CO}_3^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$
- $\text{H}_2\text{CO}_3 / \text{HCO}_3^-$ 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.
- (iii) Carbon dioxide readily reacts with alkalis forming the carbonate and, if CO_2 is in excess, the hydrogen carbonate. This is the basis of the lime-water test for CO_2 gas.
- $$\text{Ca(OH)}_2(\text{aq}) + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{liq}) ; \quad \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{liq}) + \text{CO}_2(\text{g}) \rightarrow \text{Ca(HCO}_3)_2(\text{aq})$$
- The above reaction accounts for the formation of temporarily hard water.
- (iv) 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.

(C) Carbides :

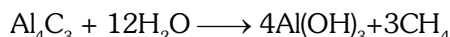
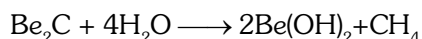
On the basis of type of bonding carbides are of three types :-

- (I) Salt like carbides (ionic carbides)
- (II) Covalent carbides (giant molecular carbides)
- (III) Interstitial carbides.

(I) Salt like carbides (ionic carbides) :

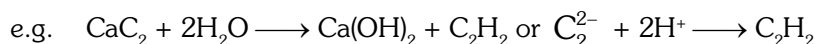
- (a) These are formed by strong electropositive elements of groups 1, 2 and 13
- (b) These are transparent crystalline substances and do not conduct electric current in the solid state.
- (c) These are easily hydrolysed by water or dilute acids to give aliphatic hydrocarbons,
 - (i) **Methanides (Methides)** – Methanides are the carbides which give methane on hydrolysis.

They contain C^{4-} ions.



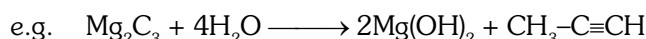
- (ii) **Acetylides** – These are the carbides which yield acetylene on hydrolysis.

They contain the ion C_2^{2-} .



- (iii) **Allylides** – These carbides give methylacetylene or allylene ($CH_3-C\equiv CH$) on hydrolysis.

They contain C_3^{4-} ions.



(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.

(III) Interstitial carbides.

Transition metals like Ti, Zr, Hf, V, Nb, Ta and Mo form these carbides. The metals retain their **close packed lattice** and carbons are incorporated in their interstitial spaces. These carbides are extremely 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.

GLASS

- (a) 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.
- (b) Being amorphous solid (not a true solid) it has no sharp melting and melts at high temperature.
- (c) Glass has no definite chemical formula, however it may be represented as :



where M = monovalent metals (eg : Na, K)

M' = bivalent metals Ca, Pb, Zn etc. x and y are integers.

- (d) $CaO + Na_2CO_3 + 6SiO_2 \xrightarrow{1700K} Na_2SiO_3 + CaSiO_3 + 4SiO_2 + CO_2$
Glass

Different Types of Glass

- (i) **Soda or Soft glass or Sodalime glass** : It is common glass. Contains Na & Ca metal carbonate. Used for formation of tube, window.
- (ii) **Potash or Hard glass** : It is a mixture of potassium and calcium silicates. It fuses with difficulty. 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 coefficient and thermal expansion, can with stand sudden change in temperature so used for making lab glass wares.

SOME GASEOUS FUELS

(a) Water gas or syn gas = $\text{CO} + \text{H}_2$

(b) Producer gas = $\text{CO} + \text{N}_2$

(c) Semi water gas = $\text{CO} + \text{N}_2 + \text{H}_2$

(d) Natural gas = CH_4

(e) Coal gas = $[\text{CO}_2 + \text{CO} + \text{H}_2 + \text{CH}_4]$

BEGINNER'S BOX-6

1. Carbon has no tendency to form complex compounds because of :

(1) Its small size

(2) The availability of vacant d-orbitals

(3) Non availability of vacant d-orbitals

(4) No tendency to form covalent bonds

2. Which of the following statement is false :

(1) Dry ice is solid CO_2

(2) CO_2 is weakly acidic

(3) CO_2 and SiO_2 are linear molecules

(4) CO_2 is a gas while SiO_2 is solid

3. CO is :

(1) Reductant

(2) Poisonous gas

(3) Neutral to litmus

(4) all

4. Which is/are true statements :

(1) Diamond is unaffected by conc. acids but graphite reacts with hot conc. HNO_3 forming mellitic acid, $\text{C}_6(\text{COOH})_6$

(2) CO is toxic because it forms a complex with haemoglobin in the blood

(3) In C_3O_2 , all carbons are sp hybridised

(4) All are true statements

NITROGEN FAMILY (GROUP 15)

Group 15 includes nitrogen phosphorus, arsenic, antimony and bismuth.

PHYSICAL PROPERTIES:

- Dinitrogen is a diatomic gas while all others are solids.
- Except nitrogen, all the elements show allotropy.
- As we go down the group, there is a shift from non-metallic to metallic through metalloidal character. Nitrogen and phosphorus are non-metal, arsenic and antimony are metalloid and bismuth is a typical metal.

CHEMICAL PROPERTIES

Oxidation States and trends in a chemical reactivity :

- The common oxidation states of these elements are -3 , $+3$ and $+5$. The tendency to exhibit -3 oxidation state decreases down the group, bismuth hardly forms any compound in -3 oxidation state.
- Nitrogen also exhibits $+1$, $+2$, $+4$ oxidation states when it reacts with oxygen. Phosphorus also shows $+1$ and $+4$ oxidation states in some oxyacids.
- In the case of nitrogen, all oxidation states from $+1$ to $+4$ tend to disproportionate in acid solution.
For example, $3 \text{HNO}_2 \longrightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2 \text{NO}$
- Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into $+5$ and -3 both in alkali and acid. However $+3$ oxidation state in case of arsenic, antimony and bismuth become increasingly stable with respect to disproportionation.

Reactivity towards hydrogen :

- All the elements of Group 15 form hydrides of the type EH_3 where $\text{E}=\text{N}, \text{P}, \text{As}, \text{Sb}$ or Bi .
- The stability of hydrides decreases from NH_3 to BiH_3 . Consequently the reducing character of the hydrides increases. Ammonia is only a mild reducing agent while BiH_3 is the strongest reducing agent amongst all the hydrides. Due to weaker Bi-H bond.

Reactivity towards oxygen :

- All these elements form two types of oxides : E_2O_3 and E_2O_5 . The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth is predominantly basic.

Reactivity towards halogens :

- These elements react to form two series of halides : EX_3 and EX_5 .
- All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen, only NF_3 is known to be stable. Trihalides except BiF_3 are predominantly covalent in nature.

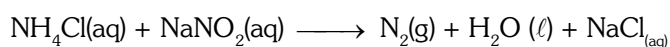
COMPOUND OF NITROGEN

1. NITROGEN GAS (N_2) :

Nitrogen is an important and essential constituent of proteins and amino acids. Nitrates and other nitrogen compounds are extensively used in fertilizers and explosive.

(a) Preparation :

(i) Laboratory method of preparation :

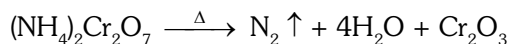


N_2 is collected by the downward displacement of water.

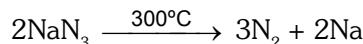
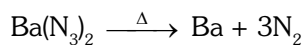
This reaction takes place in two steps as given below :



(ii) **By heating ammonium dichromate :**



(iii) **Very pure nitrogen can be obtained by heating sodium or barium azide.**



(iv) **Industrial methods of preparation :**

From liquified air by fractional distillation : The boiling point of N_2 is -196°C and that of oxygen is -183°C and hence they can be separated by fractional distillation of air.

(b) Properties :

- (i) N_2 is a colourless, odourless gas very less soluble in water. It is neither combustible nor a supporter of combustion.
- (ii) **Reaction with oxygen:** Dinitrogen combines with dioxygen only at very high temperature (at about 2000K) to form nitric oxide.

This reaction is endothermic. $\text{N}_2 + \text{O}_2 \longrightarrow 2\text{NO}$

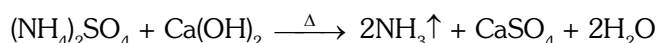
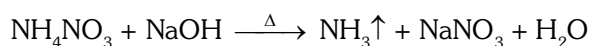
(c) Uses :

- (i) For providing an inert atmosphere during many industrial processes where presence of air or O_2 is to be avoided.
- (ii) For manufacture of NH_3 by the Haber's process.
- (iii) Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items & cryosurgery.

2. AMMONIA (NH_3)

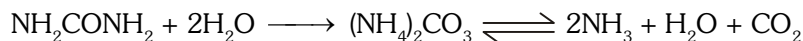
(a) Preparation :

- (i) By the action of any base or alkali on any ammonium salt :

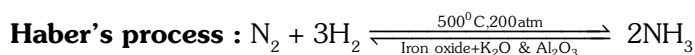


This is a general method and is used as a test for ammonium salts.

Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.



(ii) Industrial methods of preparation :

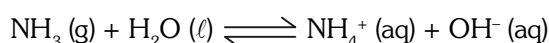


In accordance with Le Chatelier's principle, high pressure would favour the formation of ammonia. The optimum conditions for the production of ammonia are a pressure of 200×10^5 Pa (about 200 atm), a temperature of ~ 700 K and the use of a catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium.

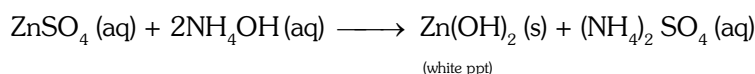
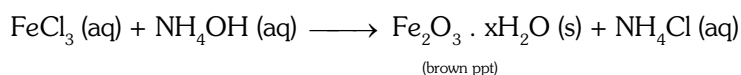
(b) Physical properties : Ammonia is a colourless gas with a pungent odour.

(c) Chemical properties :

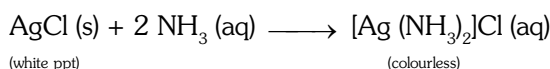
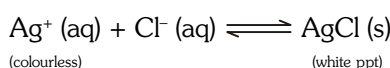
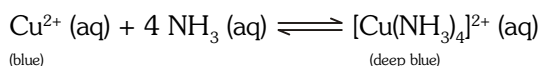
- (i) Its aqueous solution is weakly basic due to the formation of OH^- ions.



- (ii) It forms ammonium salts with acids, e.g., NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$ etc. As a weak base, it precipitates the hydroxides of many metals from their salt solutions. For example,



- (iii) The presence of lone pair of electrons on the nitrogen atoms of the ammonia molecule makes it a Lewis base. It donates the electrons pair and forms linkage with metal ions and the formation of such complex compounds finds applications in detection of metal ions such as Cu^{2+} , Ag^+

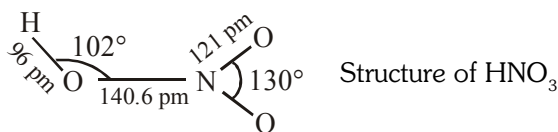


3. OXIDES OF NITROGEN :

Nitrogen forms a number of oxides, N_2O , NO , N_2O_3 , NO_2 or N_2O_4 and N_2O_5 . All these oxides of nitrogen exhibit $\text{p}\pi\text{-p}\pi$ multiple bonding between nitrogen and oxygen.

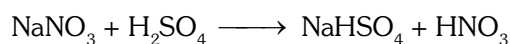
Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	N_2O	+ 1	$\text{NH}_4\text{NO}_3 \xrightarrow{\text{Heat}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$	colourless gas, neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+ 2	$2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + 2\text{NO}$	colourless gas, neutral
Dinitrogen trioxide [Nitrogen(III) oxide]	N_2O_3	+ 3	$2\text{NO} + \text{N}_2\text{O}_4 \xrightarrow{250\text{ K}} 2\text{N}_2\text{O}_3$	blue solid, acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO_2	+ 4	$2\text{Pb}(\text{NO}_3)_2 \xrightarrow{673\text{ K}} 4\text{NO}_2 + 2\text{PbO} + \text{O}_2$	brown gas, acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N_2O_4	+ 4	$2\text{NO}_2 \xrightleftharpoons[\text{Heat}]{\text{cool}} \text{N}_2\text{O}_4$	colourless solid / liquid, acidic
Dinitrogen pentoxide [Nitrogen(V) oxide]	N_2O_5	+ 5	$4\text{HNO}_3 + \text{P}_4\text{O}_{10} \longrightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$	colourless solid, acidic

4. NITRIC ACID (HNO_3)



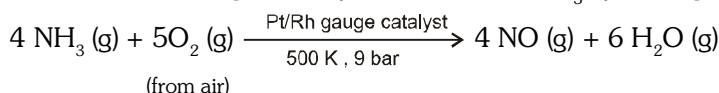
(a) Preparation :

In the laboratory, nitric acid is prepared by heating KNO_3 or NaNO_3 and concentrated H_2SO_4 in a glass retort.

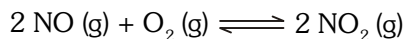


On a large scale it is prepared mainly by **Ostwald's process**.

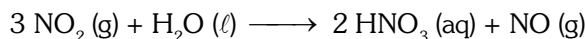
This method is based upon catalytic oxidation of NH_3 by atmospheric oxygen.



Nitric oxide thus formed combines with oxygen giving NO_2 .



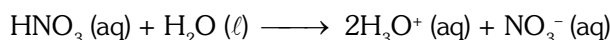
Nitrogen dioxide so formed, dissolves in water to give HNO_3 .



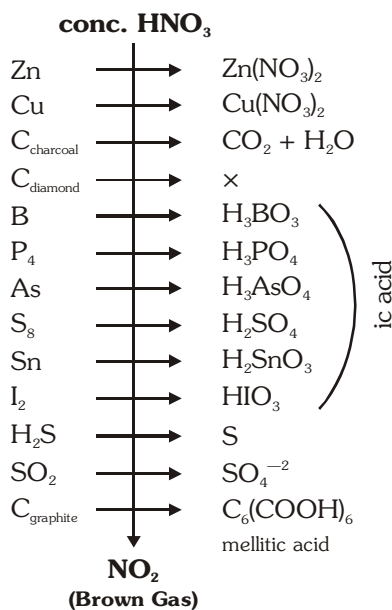
NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4 .

(b) Physical properties :

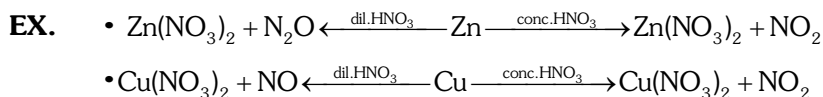
- (i) It is a colourless liquid. Freezing point is 231.4 K and boiling point is 355.6 K. Laboratory grade nitric acid contains ~ 68% of the HNO_3 by mass and has a specific gravity of 1.504.
- (ii) In the gaseous state, HNO_3 exists as a planar molecule.
- (iii) In aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.



- (iv) Concentrate nitric acid is a strong oxidising agent and attacks most metals except Au & Pt. The product of oxidation depend upon the concentration of the acid, temperature and nature of metal.
- (v) Concentrate HNO_3 also oxidises non-metals and their compounds.

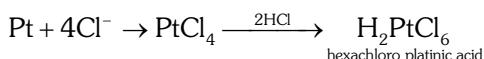
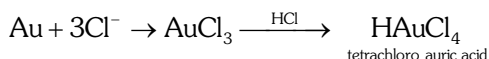


Types of Metal	conc. HNO_3	dil. HNO_3	very dil. HNO_3
negative SRP metal	Metal nitrate + NO_2	Metal nitrate + N_2O	Metal nitrate + $\text{NH}_4\text{NO}_3/(\text{NH}_3)$
positive SRP metal & Pb	Metal nitrate + NO_2	Metal nitrate + NO	×
Metalloids, Non-metals & Sn	ic-acid + NO_2	×	×



SOME EXCEPTIONAL POINTS

- **Mg and Mn form H_2 gas on reaction with very dilute HNO_3**
- **Be, Al, Fe, Cr do not react with conc. HNO_3 due to formation of protective oxide layer.**
- **Au and Pt (Noble metals) do not react with conc. HNO_3**
- **Sn reacts with conc. HNO_3 and forms H_2SnO_3 (metastannic acid)**
- **Au and Pt react only with aqua regia (3 part of conc. HCl and 1 part of conc. HNO_3)**



conc. HNO_3 + skin $\rightarrow$ yellow spot (protein $\rightarrow$ xanthoprotein)

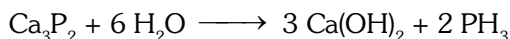
- **The major use of nitric acid is in the manufacture of ammonium nitrate for fertilizers and other nitrates for use in explosives and pyrotechnics. It is also used for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds. Other major uses are in the pickling of stainless steel, etching of metals and as an oxidiser in rocket fuels.**

COMPOUNDS OF PHOSPHORUS :

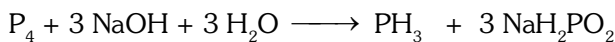
1. Phosphine (PH_3) :

(a) Preparation :

- (i) Phosphine is prepared by the reaction of calcium phosphide with water.

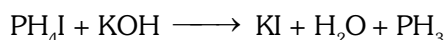


- (ii) In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO_2 .



(sodium hypophosphite)

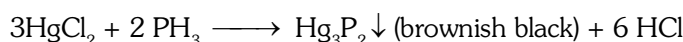
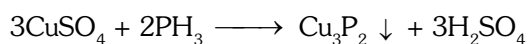
- (iii) When pure, it is non inflammable but becomes inflammable owing to the presence of P_2H_4 or P_4 vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH_4I) which on treating with KOH gives off phosphine.



(b) Properties :

- (i) It is a colourless gas with rotten fish smell and is highly poisonous. It is slightly soluble in water. The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2 .

- (ii) When absorbed in copper sulphate or mercuric chloride, the corresponding phosphides are obtained.



- (iii) Phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids



- **Uses :** The spontaneous combustion of phosphine is technically used in **Holme's signals**. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.
- It is also used in the production of smoke screens. Calcium phosphide reacts with water producing phosphine which burns in air to give clouds of phosphorus pentaoxide and that acts as smoke screens.

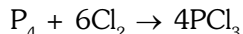
2. PHOSPHOROUS HALIDES

Phosphorous forms two types of halides, PX_3 ($X = F, Cl, Br, I$) and PX_5 ($X = F, Cl, Br$).

Phosphorous Trichloride (PCl_3)

(a) Method of preparation

- (i) It is obtained by passing dry chlorine over heated white phosphorus.

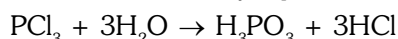


- (ii) It is also obtained by the action of thionyl chloride with white phosphorus.

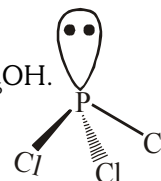
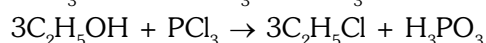
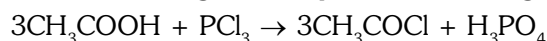


(b) Properties

- (i) It is a colourless oily liquid and hydrolyses in the presence of moisture.



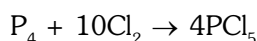
- (ii) It reacts with organic compounds containing $-OH$ group such as CH_3COOH , C_2H_5OH .



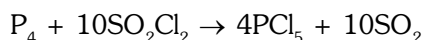
PHOSPHORUS PENTACHLORIDE (PCl_5)

(a) Method of preparation

- (i) Phosphorus pentachloride is prepared by the reaction of white phosphorus with excess of dry chlorine.

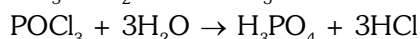
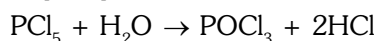


- (ii) It can also be prepared by the action of SO_2Cl_2 on phosphorus.

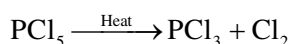


(b) Properties

- (i) PCl_5 is a yellowish white powder and in moist air, it hydrolyses to $POCl_3$ and finally gets converted to phosphoric acid.



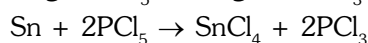
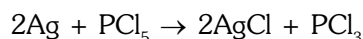
- (ii) When heated, it sublimes but decomposes on stronger heating.



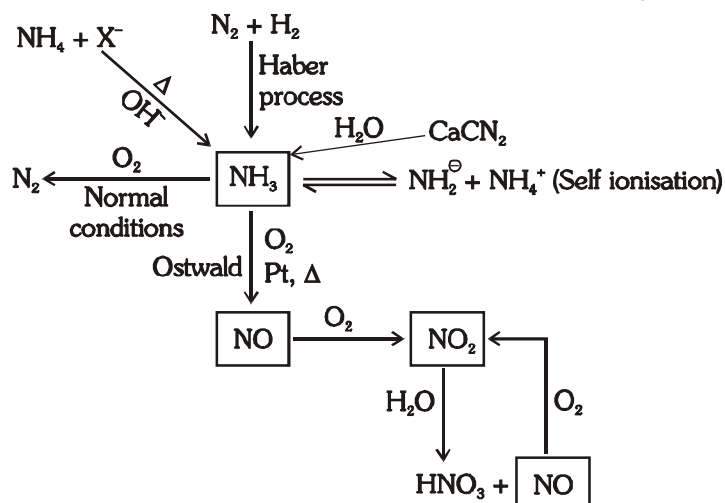
- (iii) It reacts with organic compounds containing $-OH$ group converting them to chloro derivatives.



- (iv) Finally divided metals on heating with PCl_5 give corresponding chlorides.



- (v) It is used in the synthesis of some organic compounds, e.g., C_2H_5Cl , CH_3COCl .



NCERT QUESTIONS (REASONING)

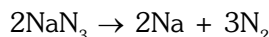
Q.1 Why BiH_3 is the strongest reducing agent amongst all the hydrides of Group 15 elements ?

Ans. In hydrides of nitrogen family on moving down the group M–H bond length increases so bond strength decreases hence tendency to release hydrogen increases and reducing nature increases.

Increasing order of reducing nature is $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{BiH}_3$

Q.2 Write the reaction of thermal decomposition of sodium azide.

Ans. Thermal decomposition of sodium azide gives dinitrogen gas.



Q.3 Why N_2 is less reactive at room temperature?

Ans. N_2 is less reactive at room temperature because of the high bond enthalpy of $\text{N}\equiv\text{N}$ bond.

Q.4 Why does $\text{R}_3\text{P}=\text{O}$ exist but $\text{R}_3\text{N}=\text{O}$ does not (R = alkyl group)?

Ans. Due to presence of vacant d orbital phosphorous can form five covalent bond, while nitrogen restricts its covalency to four due to absence of vacant d orbitals.

Q.5 Why does nitrogen show catenation properties less than phosphorus?

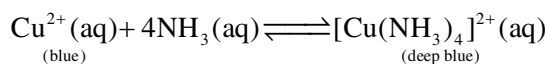
Ans. N–N bond is weaker than the single P–P bond due to high interelectronic repulsion of non-bonding electrons as a result the catenation tendency is weaker in nitrogen.

Q.6 Mention the conditions required to maximise the yield of ammonia.

Ans. In accordance with Le Chatelier's principle, high pressure would favour the formation of ammonia. The optimum conditions for the production of ammonia are a pressure of 200×10^5 Pa (about 200 atm), a temperature of ~ 700 K and the use of a catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium.

Q.7 How does ammonia react with a solution of Cu^{2+} ?

Ans. The presence of a lone pair of electrons on the nitrogen atom of the ammonia molecule makes it a Lewis base. It donates the electron pair and forms linkage with metal ions and the formation of such complex compounds finds applications in detection of Cu^{2+} .



Q.8 Illustrate how copper metal can give different products on reaction with HNO_3 .

Ans. $3\text{Cu} + 8\text{HNO}_3(\text{dilute}) \rightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$

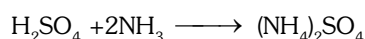
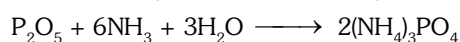


Q.9 Why is nitrogen di-oxide paramagnetic in gaseous state but the solid obtained on cooling it is diamagnetic.

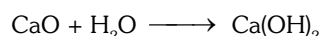
Ans. NO_2 contains odd number of electrons in its valence shell. On cooling it forms dimer and converted to stable N_2O_4 which is a colourless solid and diamagnetic in nature.

Q.10 Why NH_3 gas cannot be dried by passing over P_2O_5 , CaCl_2 and H_2SO_4 ?

Ans. $\text{CaCl}_2 + 8\text{NH}_3 \longrightarrow \text{CaCl}_2 \cdot 8\text{NH}_3$



So it is dried by passing over quick lime (CaO).

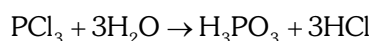


Q.11 Why inert atmosphere of CO_2 is taken in the formation of PH_3 by the reaction of white phosphorous with conc. NaOH solution.

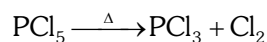
Ans. To decrease the partial pressure of O_2 in atmosphere.

Q.12 Why does PCl_3 fumes in moisture?

Ans. PCl_3 hydrolyses in the presence of moisture giving fumes of HCl

**Q.13 What happens when PCl_5 is heated?**

Ans. When heated, it sublimes but decomposes on stronger heating

**Q.14 Can PCl_5 act as an oxidising as well as reducing agent? Justify.**

Ans. It can act as an oxidising as well as reducing agent due to oxidising nature of P(V) and reducing nature of Cl⁻

BEGINNER'S BOX-7

- Which of the following halide of nitrogen is stable?
 (1) NF_3 (2) NCl_3 (3) NBr_3 (4) NI_3
- The nitrogen oxide(s) that does not contain N-N bond(s) is
 (1) N_2O (2) N_2O_3 (3) N_2O_4 (4) N_2O_5
- What is false about N_2O_5 ?
 (1) It is anhydride of HNO_3 (2) It is a powerful oxidizing agent
 (3) Solid N_2O_5 is called nitronium nitrate (4) Structure of N_2O_5 contains no $[\text{N} \rightarrow \text{O}]$ bond
- Conc. HNO_3 is yellow coloured liquid due to –
 (1) Dissolution of NO in conc. HNO_3 (2) Dissolution of NO_2 in conc. HNO_3
 (3) Dissolution of N_2O in conc. HNO_3 (4) Dissolution of N_2O_3 in conc. HNO_3
- Which of the following process is not involved in Ostwald's process for the manufacture of HNO_3 ?
 (1) $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \xrightarrow[500\text{K}, 9\text{bar}]{\text{Pt}} 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
 (2) $2\text{NO}(\text{g}) + \text{O}_2 \rightleftharpoons 2\text{NO}_2(\text{g})$
 (3) $3\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{HNO}_3(\text{aq}) + \text{NO}(\text{g})$
 (4) None
- Which of the following salts give NH_3 in alkaline medium?
 (1) $(\text{NH}_4)_2\text{CO}_3$ (2) $(\text{NH}_4)_2\text{SO}_4$ (3) NH_4Cl (4) All of the above
- Which of the following reaction is suitable for obtaining very pure nitrogen?
 (1) $\text{NH}_4\text{Cl}(\text{aq}) + \text{NaNO}_2(\text{aq}) \longrightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + \text{NaCl}(\text{aq})$
 (2) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \text{N}_2 + 4\text{H}_2\text{O} + \text{Cr}_2\text{O}_3$
 (3) $\text{Ba}(\text{N}_3)_2 \xrightarrow{\Delta} \text{Ba} + 3\text{N}_2$
 (4) All of the above
- In warfare smoke screens are prepared from
 (1) CaC_2 (2) PH_3 (3) P_2O_5 (4) COCl_2
- White phosphorous on reaction with NaOH gives PH_3 as one of the products. This is a
 (1) dimerisation reaction (2) disproportionation reaction
 (3) condensation reaction (4) precipitation reaction
- Which of the following is not correctly matched?
 (1) $\text{P}_4\text{O}_{10} + \text{H}_2\text{O} \longrightarrow$ reactants involved in formation of H_3PO_4
 (2) $\text{CaC}_2 + \text{H}_2\text{O} \longrightarrow \text{C}_2\text{H}_2 + \text{Ca}(\text{OH})_2$;
 $\text{Ca}_3\text{P}_2 + \text{H}_2\text{O} \longrightarrow \text{PH}_3 + \text{Ca}(\text{OH})_2$ reactions involved in Holmes signal
 (3) $\text{PH}_3 + \text{HI} \longrightarrow \text{PH}_4\text{I} \xrightarrow{\text{KOH}} \text{KI} + \text{H}_2\text{O} + \text{PH}_3$; purification of PH_3
 (4) $\text{PH}_3 + \text{HI} \longrightarrow \text{PH}_4\text{I}$; shows Lewis acidic nature of PH_3

OXYGEN FAMILY (GROUP 16)

INTRODUCTION

Oxygen, sulphur, selenium, tellurium and polonium constitute group 16 of the periodic table. This is sometimes known as group of chalcogens (ore forming elements) because a large number of metals ores are oxides or sulphides.

Physical Properties :

- Oxygen and sulphur are non-metal, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 13.8 days).
- The melting and boiling points increase with an increase in atomic number down the group. The larger difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exist as diatomic molecules (O_2) whereas sulphur exists as polyatomic molecule (S_8).

CATENATION

Tendency for catenation decreases down the group. This property is prominently displayed by sulphur (S_8). The S—S bond is important in biological system and is found in some proteins and enzymes such as cysteine.

Chemical Properties

Oxidation states and trends in chemical reactivity :

The elements of group 16 exhibit a number of oxidation states. The stability of -2 oxidation state decreases down the group. Except oxygen other elements of the group exhibit + 2, + 4, + 6 oxidation states but + 4 and + 6 are more common. Sulphur, selenium and tellurium usually show + 4 oxidation in their compounds with oxygen and +6 oxidation state with fluorine. The stability of +6 oxidation state decreases down the group and stability of + 4 oxidation state increases (inert pair effect). Bonding in + 4 and + 6 oxidation states are primarily covalent.

(i) Reactivity with hydrogen :

All the elements of group 16 form hydrides of the type H_2E ($E = O, S, Se, Te, Po$).

(ii) Reactivity with oxygen :

All these elements form oxides of the EO_2 and EO_3 types where $E = S, Se, Te$ or Po . Ozone (O_3) and sulphur dioxide (SO_2) are gases while selenium dioxide (SeO_2) is solid. Reducing property of dioxide decreases from SO_2 to TeO_2 ; SO_2 is reducing while TeO_2 is an oxidising agent. Besides EO_2 type sulphur, selenium and tellurium also form EO_3 type oxides (SO_3, SeO_3, TeO_3). Both types of oxides are acidic in nature.

(iii) Reactivity toward the halogens :

Elements of group 16 form a larger number of halides of the type EX_6 , EX_4 and EX_2 where E is an element of the group -16 and X is an halogen. The stabilities of the halides decrease in the order $F > Cl > Br > I$. Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. They have octahedral structure. Sulphur hexafluoride SF_6 is exceptionally stable for steric reasons.

Amongst tetrafluorides, SF_4 is a gas, SeF_4 liquid and TeF_4 a solid

All elements except selenium form dichlorides and dibromides. The well known monohalides are dimeric in nature, Examples are $S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2$ and Se_2Br_2 . These dimeric halides undergo disproportionation

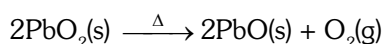
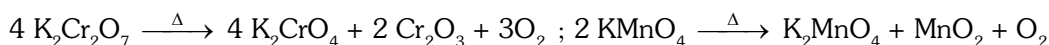
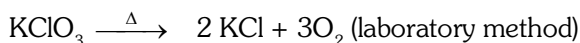
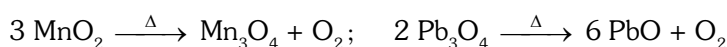
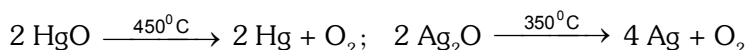
as given $2Se_2Cl_2 \longrightarrow SeCl_4 + 3Se$.

COMPOUNDS OF OXYGEN

1. DIOXYGEN (O_2)

(a) Preparation of DiOxygen (O_2) :

By thermal decomposition of oxides of metals.

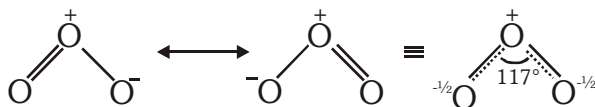


Properties:

- Dioxygen is a colourless and odourless gas.
- Oxygen atom has three stable isotopes: ^{16}O , ^{17}O and ^{18}O . Molecular oxygen.
- O_2 is paramagnetic (by MOT)
- Dioxygen directly reacts with nearly all metals and non-metals except some metals (e.g., Au, Pt) and some noble gases.

2. OZONE (O_3) :

Preparation : It is prepared by passing silent electric discharge through pure and dry oxygen.



Mixture obtained contains 5-10% ozone by volume and this mixture is called ozonised oxygen.

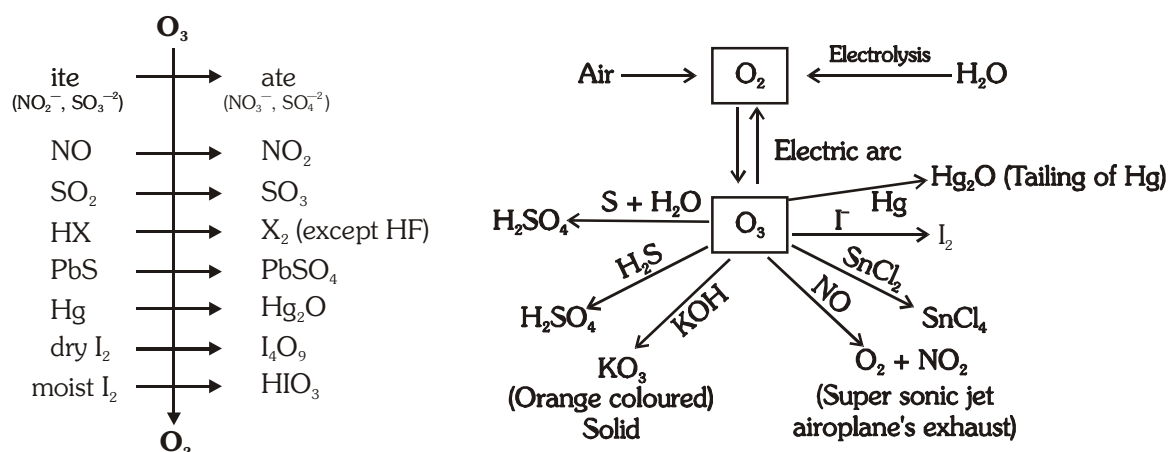
Since the formation of ozone from oxygen is an endothermic process, it is necessary to use a silent electrical discharge in its preparation to prevent its decomposition. If concentrations of ozone greater than 10 per cent are required, a battery of ozonisers can be used, and pure ozone (b.p. 385 K) can be condensed in a vessel surrounded by liquid oxygen.

Properties :

- Pure ozone is a pale blue gas, dark blue liquid and violet-black solid.
- Ozone is thermodynamically unstable with respect to oxygen since its decomposition into oxygen results in the liberation of heat (ΔH is negative) and an increase in entropy (ΔS is positive). These two effects reinforce each other, resulting in large negative Gibbs energy change (ΔG) for its conversion into oxygen. Therefore, high concentrations of ozone can be dangerously explosive.

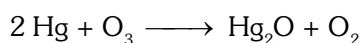
Oxidising behaviour of ozone :

Due to the ease with which it liberates atoms of nascent oxygen ($\text{O}_3 \rightarrow \text{O}_2 + \text{O}$), it acts as a powerful oxidising agent. For example, it oxidises lead sulphide to lead sulphate and iodide ions to iodine.

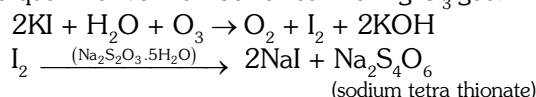


Tests for Ozone

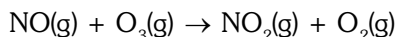
Tailing of mercury : Pure mercury is a mobile liquid but when brought in contact with O_3 its mobility decreases and it starts sticking to glass surface forming a type of tail due to the dissolution of Hg_2O (mercury sub-oxide) in Hg.



Estimation of Ozone : When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating O_3 gas.



Depletion of ozone layer : Experiments have shown that nitrogen oxides (particularly nitric oxide) combine very rapidly with ozone and there is, thus, the possibility that nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.

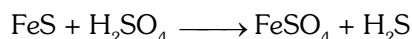


Another threat to this ozone layer is probably posed by the use of freons which are used in aerosol sprays and as refrigerants.

COMPOUNDS OF SULPHUR :

1. Hydrogen Sulphide (H_2S)

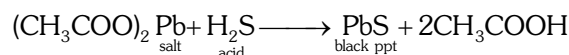
Preparation :



It is prepared in kipp's apparatus

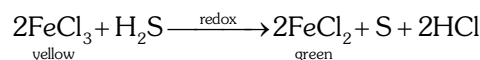
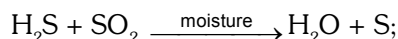
Properties :

- (i) Colourless gas with rotten egg smell .
- (ii) Moderately soluble in water but solubility decreases with increasing temperature.
- (iii) It gives black ppt with lead acetate



Reducing behaviour :

Acts as a strong reducing agent as it decomposes evolving hydrogen.



2. SO_2 (Sulphur Dioxide)

Preparation :

- (i) $S + O_2$ or air $\xrightarrow{\text{Burn}} SO_2$
- (ii) By reaction of metal sulphites with dilute HCl (Laboratory method)

$$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + SO_2 + H_2O$$

Similarly bisulphites also give SO_2 with dilute HCl

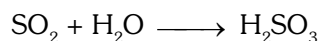
$$NaHSO_3 + HCl \longrightarrow NaCl + SO_2 + H_2O$$
- (iii) By heating sulphides (metal sulphide ores) in excess of air.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

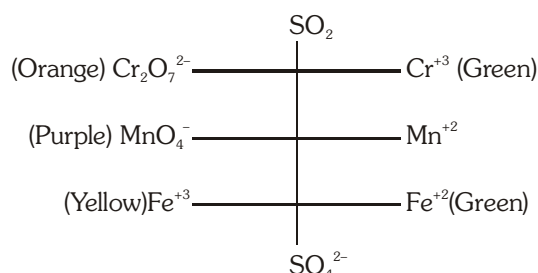
By this method SO_2 is obtained in large scale

Properties :

- (i) Colourless gas with pungent smell.
- (ii) It is heavier than air and is highly soluble in water.
- (iii) Acidic Nature : Acidic oxide and thus dissolve in water forming sulphurous acid.

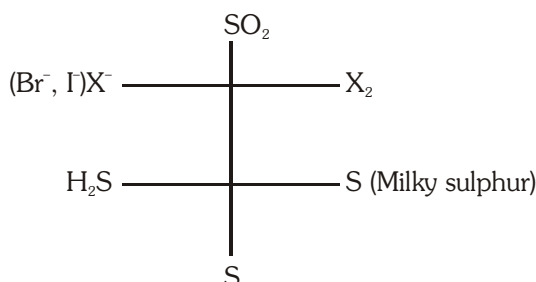


Reducing nature :



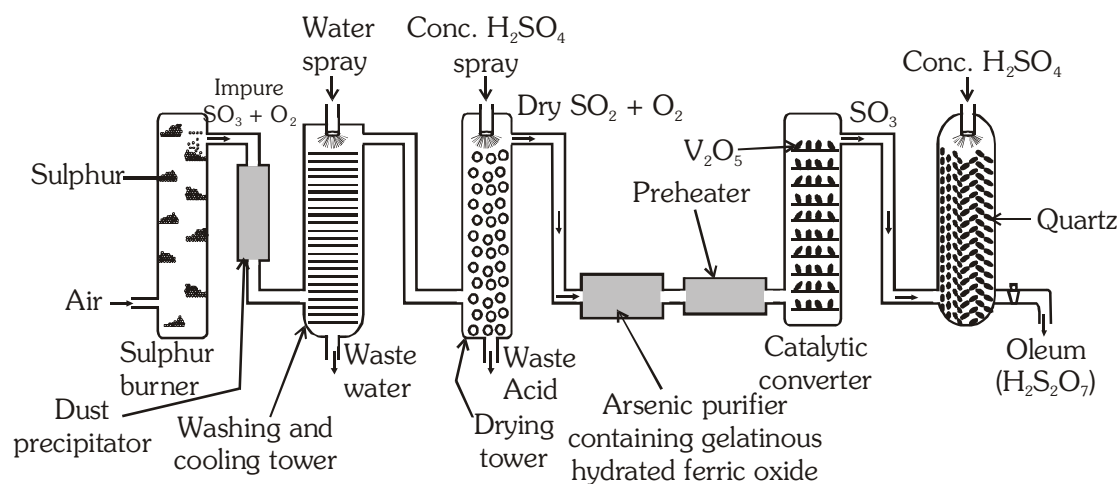
The above reactions are not given by CO_2 , so they are used to distinguish between SO_2 and CO_2

Oxidising nature : Acts as oxidising agent with strong reducing agent



3. SULPHURIC ACID (H_2SO_4) :

Manufacture by contacts process :



Flow diagram for the manufacture of sulphuric acid

Sulphuric acid is one of the most important industrial chemicals worldwide.

Sulphuric acid is manufactured by the contact process which involves three steps :

- burning of sulphur or sulphide ores in air to generate SO_2
- Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5), and
- Absorption of SO_3 in H_2SO_4 to give Oleum ($\text{H}_2\text{S}_2\text{O}_7$)

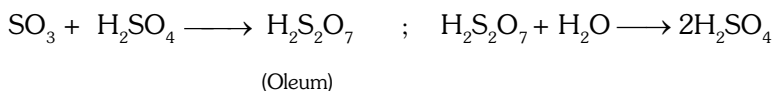
The SO_2 produced is purified by removing dust and other impurities such as arsenic compounds.

The key step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 in the presence of V_2O_5 (catalyst).



The reaction is exothermic reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low otherwise rate of reaction will become slow.

Dilution of oleum with water gives H_2SO_4 of the desired concentration. In the industry two steps are carried out simultaneously to make the process a continuous one and also to reduce the cost.

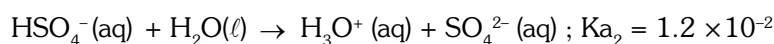
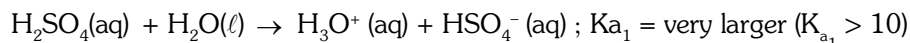


The sulphuric acid obtained by Contact process is 96-98% pure.

Properties : Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K. The acid freezes at 283 K and boils at 611 K. It dissolves in water with the evolution of a larger quantity of heat.

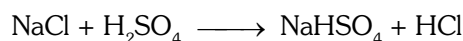
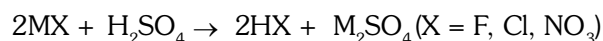
The chemical reaction of sulphuric acid are as a result of the following characteristics : (a) low volatility (b) strong acidic character (c) strong affinity for water and (d) ability to act as an oxidising agent in aqueous solution,

- (i) Sulphuric acid ionises in two steps.

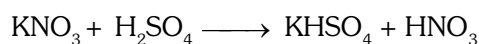


The larger value of K_{a1} ($K_{a1} > 10$) means that H_2SO_4 is largely dissociated into H^+ and HSO_4^- . Greater the value of dissociation constant (K_a) the stronger is the acid.

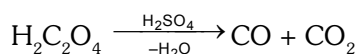
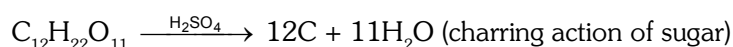
- (ii) **The acid forms two series of salts :** Normal sulphates (such as sodium sulphate and copper sulphate and acid sulphate (e.g., sodium hydrogen sulphate)
- (iii) Sulphuric acid, because of its low volatility can be used to manufacture more volatile acid from their corresponding salts.



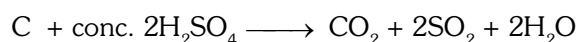
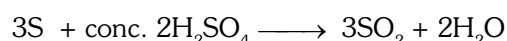
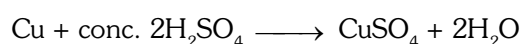
(M = Metal)



- (iv) Concentrated sulphuric acid is a strong dehydrating agent. Many wet gases can be dried by passing them through sulphuric acid, provided the gases do not react with the acid. Sulphuric acid removes water from organic compound; it is evident by its charring action on carbohydrates.



- (v) Hot concentrated sulphuric acid is moderately strong oxidising agent. In this respect it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to SO_2 .



NCERT QUESTIONS (REASONING)

Q.1 H_2S is less acidic than H_2Te . Why?

Ans. Due to the decrease in bond (E–H) dissociation enthalpy down the group, acidic character increases.

Q.2 Why is H_2O a liquid and H_2S a gas?

Ans. Hydrogen bonds are present between H_2O molecules while between H_2S molecules, vander Waal's forces are present.

Q.3 Why is dioxygen a gas but sulphur a solid?

Ans. Oxygen exist as a O_2 molecule while sulphur exist as a S_8 molecule due to more molecular mass sulphur is solid.

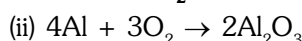
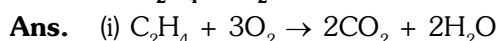
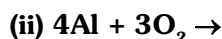
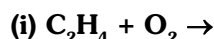
Q.4 Knowing the electron gain enthalpy values for $\text{O} \rightarrow \text{O}^-$ and $\text{O} \rightarrow \text{O}^{2-}$ as -141 and 702 kJ mol^{-1} respectively, how can you account for the formation of a large number of oxides having O^{2-} species and not O^- ?

Ans. Consider lattice energy factor in the formation of compounds.

Q.5 Which of the following does not react with oxygen directly? Zn, Ti, Pt, Fe

Ans. Pt is a noble metal which does not react directly with oxygen.

Q.6 Complete the following reactions:



Q.7 How is O_3 estimated quantitatively?

Ans. When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating O_3 gas.

Q.8 What happens when sulphur dioxide is passed through an aqueous solution of Fe(III) salt?



Q.9 How is the presence of SO_2 detected?

Ans. It has colourless gas with pungent smell and decolourise acidified KMnO_4 solution.

Q.10 Write the conditions to maximise the yield of H_2SO_4 by Contact process.

Ans. The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low otherwise rate of reaction will become slow.

Q.11 Why is $K_{a2} \ll K_{a1}$ for H_2SO_4 in water?

Ans. It is difficult to remove H^+ ion from HSO_4^- ion.

BEGINNER'S BOX-8

- Which of the following is not oxidised by O_3 ?
 (1) KI (2) FeSO_4 (3) KMnO_4 (4) K_2MnO_4
- In which of the following reaction conc. H_2SO_4 is not used as an oxidising agent?
 (1) $\text{Cu} + 2\text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$ (2) $2\text{HI} + \text{H}_2\text{SO}_4 \longrightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$
 (3) $\text{CaF}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + 2\text{HF}$ (4) None
- Hot conc. H_2SO_4 acts as strong oxidising agent which of the following element is oxidised by conc. H_2SO_4 into two gaseous products?
 (1) Cu (2) S (3) C (4) Zn
- HCOOH reacts with conc. H_2SO_4 to produce
 (1) CO (2) CO_2 (3) NO (4) NO_2

HALOGEN FAMILY (GROUP-17)

(A) PHYSICAL PROPERTIES

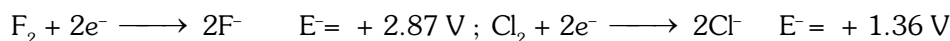
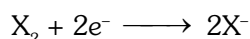
- (i) Fluorine and chlorine are gases, bromine is a liquid whereas iodine is a solid.
- (ii) Their melting and boiling points steadily increase with atomic number.
- (iii) All halogens are coloured. This is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level. By absorbing different quanta of radiation, they display different colours.
For example, F_2 , has yellow, Cl_2 , greenish yellow, Br_2 , red and I_2 , violet colour.
- (iv) Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water. But are soluble in organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.
- (v) Except the smaller enthalpy of dissociation of F_2 compared to that of Cl_2 . **The X-X bond disassociation enthalpies from chlorine onwards show the expected trend : $Cl - Cl > Br - Br > F - F > I - I$. The reason for the smaller enthalpy of dissociation of F_2 is the relatively larger electrons-electrons repulsion among the lone pairs in F_2 molecule where they are much closer to each other than in case of Cl_2 .**

(B) CHEMICAL PROPERTIES

(i) Oxidation states and trends in chemical reactivity

- All the halogens exhibit -1 oxidation state. However, chlorine, bromine and iodine exhibit +1, +3, +5 and +7 oxidation states also. The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms e.g., in interhalogens, oxides and oxoacids.
- The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only -1 oxidation state.
- All the halogens are highly reactive. They react with metals and non-metals to form halides. The reactivity of the halogens decreases down the group.

Standard Reduction Potential (SRP)



More the value of the SRP, more powerful is the oxidising agent.

Hence the order of oxidising power is $F_2 > Cl_2 > Br_2 > I_2$

Order of reducing behaviour is $I^- > Br^- > Cl^- > F^-$

(ii) Halogen oxides :

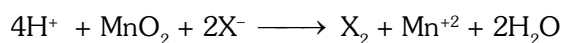
- Fluorine forms two oxides OF_2 and O_2F_2 . However, only OF_2 is the thermally stable at 298 K. These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents.
- O_2F_2 oxidises plutonium to PuF_6 and the reaction is used in removing plutonium as PuF_6 from spent nuclear fuel.
- Chlorine, bromine and iodine form oxides in which the oxidation states of these halogens vary from +1 to +7. A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens, $I > Cl > Br$. The higher oxides of halogens tend to be more stable than the lower ones. This is called middle row anomaly.
- Chlorine oxides, Cl_2O , ClO_2 , Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment.
- The bromine oxides, Br_2O , BrO_2 , BrO_3 are the least stable halogen oxides and exist only at low temperature. They are very powerful oxidising agents.
- The iodine oxides, I_2O_4 , I_2O_5 , I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

COMPOUNDS OF HALOGEN

1. CHLORINE GAS (Cl₂)

(a) Preparation :

- (i) By heating chloride with concentrated H₂SO₄ in presence of MnO₂.

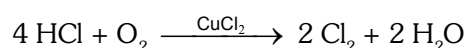


Bromides and iodides also liberate Br₂ and I₂ respectively with concentrated H₂SO₄ and MnO₂.

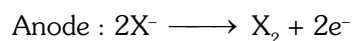
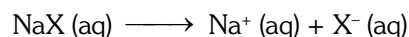
- (ii) • $\text{CaOCl}_2 + 2\text{HCl} \longrightarrow \text{CaCl}_2 + \text{Cl}_2 + \text{H}_2\text{O}$
• $2\text{KMnO}_4 + 16\text{HCl} \rightarrow 2\text{KCl} + 2\text{MnCl}_2 + 5\text{Cl}_2 + 8\text{H}_2\text{O}$
• $\text{PbO}_2 + 4\text{HCl} \rightarrow \text{PbCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$

(iii) Manufacture of chlorine :

- **Deacon's process :** By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of CuCl₂ (catalyst) at 723 K.



- **Electrolytic process :** Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is liberated at anode. It is obtained as a by-product in many chemical industries e.g.; in manufacturing of sodium hydroxide.

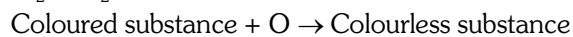
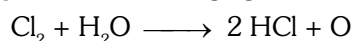


(b) Properties :

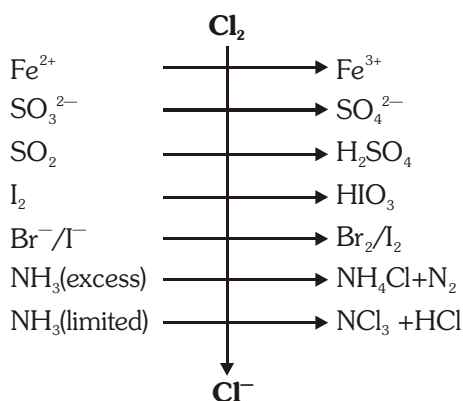
- (i) It is a greenish-yellow gas with pungent and suffocating odour. It is about 2–5 times heavier than air. It can be liquefied into greenish-yellow liquid which boils at 239 K. It is soluble in water.

- (ii) **Oxidising & bleaching properties :** Chlorine dissolves in water giving HCl and HOCl. Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

It is a powerful bleaching agent ; bleaching action is due to oxidation.



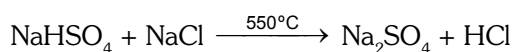
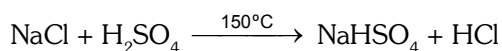
It bleaches vegetable or organic matter in the presence of moisture. Bleaching effect of chlorine is permanent.



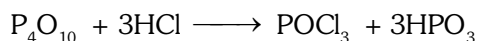
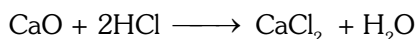
2. HALOGEN ACIDS (HCl)

(a) Preparation :

- (i) **By heating a halide with concentrated acid :**



- Above method is called as salt cake method as it involves the formation of NaHSO_4 (salt cake).
- HCl cannot be dried over P_2O_5 (P_4O_{10}) or quick lime since they react with gas chemically.



- HCl is, hence dried by passing through concentrated H_2SO_4 .

(b) Properties :

- This is colourless, pungent smelling gas with acidic taste.
- This is neither combustible nor supporter of combustion.
- When perfectly dry, HX have no action on litmus, but in presence of moisture, they turn blue litmus red, showing acidic nature. Among HX , HI is the strongest and HF is the weakest acid.

3. Pseudo halogens and pseudo halides : Some inorganic compounds consisting of two or more atoms of which at least one is N have been found to behave like halogens & they are known as pseudo halogen solids,

Pseudo halogens	Pseudo halides
(i) $(\text{CN})_2$ cyanogen	(i) $(\text{CN})^-$ cyanide ion
(ii) $(\text{SCN})_2$ thiocyanogen	(ii) $(\text{SCN})^-$ thiocyanate ion
(iii) $(\text{SeCN})_2$ selenocyanogen	(iii) $(\text{SeCN})^-$ selenocyanate ion
(iv) $(\text{SCSN}_3)_2$ azidocarbendisulphide	(iv) $(\text{OCN})^-$ cyanate ion
	(v) $(\text{NCN})^{2-}$ cyanamide ion
	(vi) $(\text{N}_3)^-$ azide ion etc.

4. INTERHALOGEN COMPOUNDS :

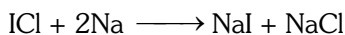
We know that halogen atoms have different electronegativity. Due to this difference in electronegativity the halogen atoms combine with each other and give rise to the formation of binary covalent compounds, which are called interhalogen compounds. These are of four types.

AB	AB_3	AB_5	AB_7^*
ClF	ClF_3	ClF_5	IF_7
BrF	BrF_3	BrF_5	
ICl	ICl_3	IF_5	
IF	IF_3		

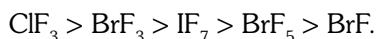
* Where A - halogen of smaller size and A is more electro positive than B.

(a) Properties :

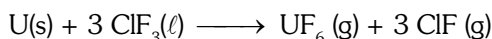
- These compounds may be gases, liquids or solids.
Gases : ClF , BrF , ClF_3 , IF_7 ; Liquids : BrF_3 , BrF_5 ; Solids : ICl , IBr , IF_3 , ICl_3 .
- Interhalogens containing fluorine are generally colourless but inter halogens consisting of heavier halogens are coloured. The intensity of colour increases with increase in the molecular weight of the compounds.
- All interhalogens are covalent molecules and are diamagnetic in nature since all the valence electrons present as bonding or non-bonding electrons are paired.
- Interhalogen compounds are more reactive than the parent halogens but less reactive than F_2 .



The order of reactivity of some interhalogens is as follows :



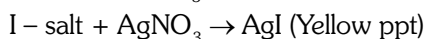
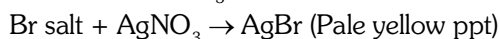
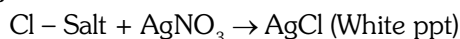
- (v) These compounds can be used as non aqueous solvents. Interhalogen compounds are very useful fluorinating agents. ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U .



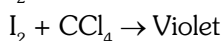
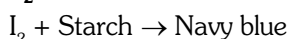
TEST OF HALOGENS

1. F^- = **Itching of glass**

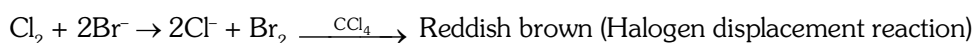
2. **AgNO_3 test** (Cl^- , Br^- , I^-)



3. **Test of I_2**



4. **Layer test (Br^- , I^-)**



(Note : In case of I^- violet colour is obtained.)

5. **Chromyl chloride test** (Test of Cl^-) : see d-block

NCERT QUESTIONS (REASONING)

Q.1 Covalent radius of fluorine is 64 pm but the bond length is not equal to 128 pm and that is 143 pm and bond energy is found to be comparable to I_2 .

Ans. This may be attributed to $\ell.p - \ell.p$ repulsions due to small size of F atom.

Q.2 Electron affinity of chlorine is more than F. In spite of this F_2 is the better oxidising agent. Why?

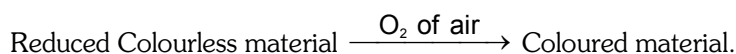
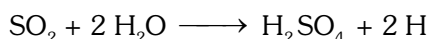
Ans. SRP of F_2 is much higher than that of Cl_2 on account of smaller bond dissociation energy and high hydration energy of F^- ion.

Q.3 Layer test of Br^- is successful with Cl_2 but not with I_2 . Explain?

Ans. Br^- is oxidised by Cl_2 but not by I_2

Q.4 What is the difference between bleaching action of SO_2 and Cl_2

Ans. The bleaching action of SO_2 is temporary because it takes place through reduction.



The bleaching action of Cl_2 is permanent because it takes place through oxidation

Q.5 (a) When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. why?

(b) Chlorine water turns blue litmus red but solution becomes colourless after sometime.

Ans. (a) It forms H_2 gas. $\text{Fe} + 2 \text{HCl} \longrightarrow \text{FeCl}_2 + \text{H}_2$.

Liberation of hydrogen prevents the formation of ferric chloride.

(b) Blue litmus change into red due to acidic nature ($\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl}$) but it is bleaching agent, therefore, it decolourises the red litmus.

ZERO GROUP (GROUP-18)

INTRODUCTION

Group 18 consists of six elements: helium, neon, argon, krypton, xenon and radon. All these are gases and chemically unreactive. They form very few compounds. Because of this they are termed noble gases.

(A) PHYSICAL PROPERTIES

- (i) All the noble gases are mono-atomic.
- (ii) They are colourless, and tasteless. They are sparingly soluble in water.
- (iii) They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces.
- (iv) Helium has the lowest boiling point (4.2K) of any known substance. It has a unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

(B) CHEMICAL PROPERTIES

In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

- (i) The noble gases except helium ($1s^2$) have completely filled $ns^2 np^6$ electronic configuration in their valence shell.
- (ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

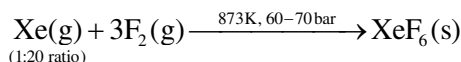
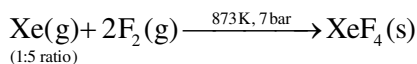
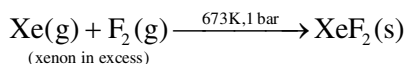
Neil Bartlett, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as $O_2^+ [PtF_6]^-$. He, then realised that the first ionisation enthalpy of molecular oxygen (1175 kJ mol^{-1}) was almost identical with that xenon (1170 kJ mol^{-1}). He made efforts to prepare same type of compound with $Xe^+ [PtF_6]^-$ by mixing PtF_6 and Xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.

The compounds of krypton are fewer. Only the difluoride (KrF_2) has been studied in detail. Compounds of radon have not been isolated but only identified (e.g., RnF_2) by radiotracer technique. No true compounds of Ar, Ne or He are yet known.

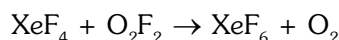
COMPOUNDS OF XENON

Xenon-fluorine compounds

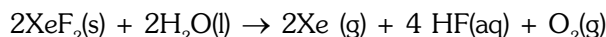
Xenon forms three binary fluorides, XeF_2 , XeF_4 and XeF_6 by the direct reaction of elements under appropriate experimental conditions.



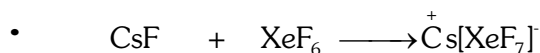
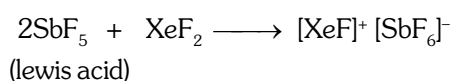
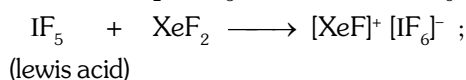
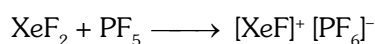
XeF_6 can also be prepared by the interaction of XeF_4 and O_2F_2 at 143K.



XeF_2 , XeF_4 and XeF_6 are colourless crystalline solids and sublime readily at 298 K. They are powerful fluorinating agents. They are readily hydrolysed even by traces of water. For example, XeF_2 is hydrolysed to give Xe, HF and O_2 .



Formation of addition compounds : XeF_2 reacts with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.



[With s-block fluorides and alkyl fluorides it is F^- acceptor with others it is F^- donor]

USES OF INERT GASES :

- (1) He is non-inflammable and light gas, so it is used in filling balloons for meteorological observations.
- (2) He is used in gas cooled nuclear reactors.
- (3) Liquid He is used as cryogenic agent.
- (4) He is used to produce powerful superconducting magnets.
- (5) Ne is used in discharge tubes.
- (6) Ar is used as inert atmosphere in metallurgical process.
- (7) Xenon and Krypton are used in light bulbs designed for special purposes.

IMPORTANT ORDER :

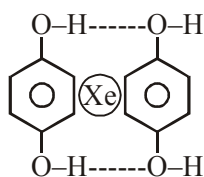
- | | |
|---|--------------------------|
| (1) $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$ | Atomic radius |
| (2) $\text{He} > \text{Ne} > \text{Ar} > \text{Kr} > \text{Xe}$ | Ionisation energy |
| (3) $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe} < \text{Rn}$ | Density |
| (4) $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe} < \text{Rn}$ | mpt. bpt |

[Atomic mass / size / polarisability / London force] $\uparrow$

- (5) $\text{He} < \text{Ne} < \text{Ar} < \text{Xe} < \text{Rn}$ **[solubility in water because of dipole-induced dipole attraction]**

Clathrate Compounds : Larger inert gas atoms are trapped into cavity or crystal structure of some organic compounds and form clathrate compounds. For eg xenon diquinoxaline.

- Force of attraction between noble gas and organic compound is **dipole-induced dipole** attraction.



He, Ne do not form clathrate compounds due to smaller size

BEGINNER'S BOX-9

- Which is correct

(1) $\text{NaCl} \xrightarrow{\text{conc. H}_2\text{SO}_4} \text{yellow green gas}$	(2) $\text{NaBr} \xrightarrow{\text{conc. H}_2\text{SO}_4} \text{red brown vapour}$
(3) $\text{NaF} + \text{Cl}_2 \longrightarrow \text{NaCl} + \text{F}_2$	(4) All
- “Middle row anomaly” is related with

(1) stability of transition metal oxides	(2) stability of alkali metal oxides
(3) stability of halogen oxides	(4) stability of alkaline earth metal oxides
- True statement about I^- will be

(1) weak base	(2) strong nucleophile
(3) strong reducing agent	(4) all

4. Of the following statements :
- (a) Cl_2 gas is dried by using conc. H_2SO_4
 (b) Fluorine have highest oxidising power
 (c) Oxidising power of halogens follow the order $\text{I}_2 > \text{Br}_2 > \text{Cl}_2$
 (d) HI is the strongest acid among HI, HBr, HCl
- (1) a, b and d are correct (2) a, c are correct (3) b, c are correct (4) c, d are correct
5. Chromyl chloride test is performed for the confirmation of the presence of the following in mixture:
- (1) SO_4^{2-} (2) Cr^{+++} (3) Cl^- (4) Cr^{+++} and Cl^-
6. The ion that cannot undergo disproportionation is
- (1) ClO_4^- (2) ClO_3^- (3) ClO_2^- (4) ClO^-
7. A greenish yellow gas reacts with an alkali metal hydroxide to form a halate which can be used in fire works and safety matches. The gas and halate respectively are :
- (1) Br_2 , KBrO_3 (2) Cl_2 , KClO_3 (3) I_2 , NaIO_3 (4) Cl_2 , NaClO
8. In the clathrates of xenon with water, the nature of bonding between xenon and water molecule is :
- (1) covalent (2) hydrogen bonding (3) co-ordinate (4) dipole-induced dipole interaction
9. XeF_2 reacts with PF_5 to give :
- (1) XeF_6 (2) $[\text{XeF}]^+ [\text{PF}_6]^-$ (3) XeF_4 (4) $[\text{PF}_4]^+ [\text{XeF}_3]^-$
10. The first compound of noble gases prepared by Neil-Bartlett was :-
- (1) $\text{Xe}^+ [\text{PtF}_6]^-$ (2) XeF_4 (3) XeF_6 (4) XeOF_4

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	1	4	1	1	1	4	3	3	1	4
BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	2	4	3	3	3	2	1	4	2	2
BEGINNER'S BOX-3	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	2	3	2	2	2	3	2	4	3
BEGINNER'S BOX-4	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	2	2	2	4	3	4	4	1	3
BEGINNER'S BOX-5	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	1	4	2	2	3	4	3	3	4	3
BEGINNER'S BOX-6	Que.	1	2	3	4						
	Ans.	3	3	4	4						
BEGINNER'S BOX-7	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	1	4	4	2	4	4	3	2	2	4
BEGINNER'S BOX-8	Que.	1	2	3	4						
	Ans.	3	3	3	1						
BEGINNER'S BOX-9	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	2	3	4	1	3	1	2	4	2	1

EXERCISE-I (Conceptual Questions)**Build Up Your Understanding****IMPORTANT CONCEPTS**

- "Hybridisation of central atom does not always change due to back bonding". This statement is valid for which of the following compounds?
 (i) CCl_3^- (ii) CCl_2
 (iii) CF_2 (iv) $\text{N}(\text{SiH}_3)_3$
 (1) (i), (ii) (2) (i), (iii)
 (3) (ii), (iii) (4) All
- The geometry with respect to the central atom of the following molecules are $\text{N}(\text{SiH}_3)_3$, Me_3N , $(\text{SiH}_3)_3\text{P}$
 (1) planar, pyramidal, planar
 (2) planar, pyramidal, pyramidal
 (3) pyramidal, pyramidal, pyramidal
 (4) pyramidal, planar, pyramidal
- In which of the following compounds, observed bond angle is found to be greater than expected, but not due to back bonding
 (1) $\text{N}(\text{SiH}_3)_3$ (2) $\text{O}(\text{CH}_3)_2$
 (3) $\text{O}(\text{SiH}_3)_2$ (4) All of these
- According to following reactions,

$$\text{CHF}_3 \xrightarrow{K\alpha} \text{CF}_3^- + \text{H}^+$$

$$\text{CHCl}_3 \xrightarrow{K'\alpha} \text{CCl}_3^- + \text{H}^+$$
 correct statement(s) is :
 (1) $K_\alpha > K'_\alpha$
 (2) CHF_3 act as a stronger bronsted acid than CHCl_3
 (3) CCl_3^- is more stable than CF_3^-
 (4) None of these
- The product formed in the reaction,
 $\text{BCl}_3 + \text{H}_2\text{O} \longrightarrow \text{Product is -}$
 (1) $\text{H}_3\text{BO}_3 + \text{HCl}$ (2) $\text{B}_2\text{O}_3 + \text{HOCl}$
 (3) $\text{B}_2\text{H}_6 + \text{HCl}$ (4) No reaction
- Which of the following statements is incorrect in relation to the structure of diborane
 (1) All the terminal B-H bond length are equal
 (2) The terminal B-H bond is a 2-centre 3-electron bond
 (3) The terminal B-H bond is a 2-centre 2-electron bond
 (4) The bridge  is a 3-centre 2-electron bond
- The type of hybridization of boron in diborane is -
 (1) sp (2) sp^2
 (3) sp^3 (4) sp^3d^2

- Which is less hydrolysed :
 (1) PCl_3 (2) NCl_3
 (3) AsCl_3 (4) SbCl_3
- Which of the following halids cannot be hydrolysed?
 (i) TeF_6 (ii) SF_6 (iii) NCl_3 (iv) NF_3
 Choose the correct code
 (1) iii and iv (2) i, ii and iii
 (3) i, ii and iv (4) ii and iv
- Which of the following is an uncommon hydrolysis product of XeF_2 and XeF_4 ?
 (1) Xe (2) XeO_3 (3) HF (4) O_2
- In which of the following dimer empty atomic orbital of central atom of monomer does not involve in hybridisation?
 (1) Ga_2H_6 (2) Al_2Br_6 (3) Be_2H_4 (4) Cl_2O_6
- Which of the following molecule is having complete octet
 (1) $\text{BeCl}_2(\text{dimer})$ (2) $\text{BeH}_2(\text{dimer})$
 (3) $\text{BeH}_2(\text{s})$ (4) $\text{BeCl}_2(\text{s})$
- Which one of the following oxy acid of fluorine exists ?
 (1) HOF (2) HFO_3
 (3) HFO_4 (4) HFO_2
- Which of the following statements is correct
 (1) All form HOXO_3 type oxy acid
 (2) Only chlorine and bromine form oxyacids
 (3) All halogens form oxyacids
 (4) Only iodine forms oxyacid
- Consider the oxy acids HClO_n series, here value of n is 1 to 4. Then incorrect statement regarding these oxy acids is
 (1) acidic character of oxy acids increases with increasing value of n .
 (2) oxidising power of oxy acids increases with decreasing value of n .
 (3) thermal stability of oxy acids decreases with increasing value of n .
 (4) Cl-O bond order decreases with decreasing value of n .
- $2\text{P} \xrightarrow{-\text{H}_2\text{O}} \text{Q} \xrightarrow{-[\text{O}]} \text{R}$
 If P is parent phosphoric acid then according to given information the incorrect statement is
 (1) Q is pyro form and R is hypo form of given present oxy acid P
 (2) Number of H-atoms present in each given oxy acid is equal to its basicity
 (3) In P, Q, R oxy acids, oxidation state of central atom remains same
 (4) All given oxy acids have $p\pi-d\pi$ bond(s) in their structure

17. Silicate having one monovalent corner oxygen atom in each tetrahedron unit is
 (1) sheet silicate (2) cyclic silicate
 (3) single chain silicate (4) double chain silicate
18. The silicate anion in the mineral kinoite is a chain of three SiO_4^{4-} tetrahedra, that share corners with adjacent tetrahedra. The charge of the silicate anion is
 (1) -4 (2) -8
 (3) -6 (4) -2
19. Which of the following is an organo silicon polymer?
 (1) silica (2) silicon
 (3) silicon carbide (4) silicic acid
20. Which reacts rapidly with oxygen in the air at ordinary temperature :
 (1) White P (2) Red P
 (3) N_2 (4) C
21. Red and yellow phosphorus are :
 (1) Allotropes (2) Isobars
 (3) Isomers (4) Isotopes
22. Phosphorus is kept in :
 (1) Kerosene oil (2) Alcohol
 (3) Water (4) Ammonia
23. Graphite conducts electricity because of the –
 (1) Highly polarized nature of π -electrons.
 (2) Highly delocalized nature of π -electrons
 (3) Highly localized nature of π -electrons
 (4) None of these

BORON AND CARBON FAMILY

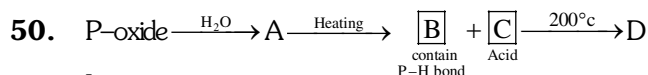
24. Melting point is higher for –
 (1) B (2) Al (3) Ga (4) In
25. Alane is chemically –
 (1) AlH_3 (2) $(\text{AlH}_3)_n$ (3) LiAlH_4 (4) None
26. Aluminium is not acted upon by pure water as –
 (1) Impurities in water are essential for the reaction to occur
 (2) It is light metal
 (3) It is protected by a film of aluminium oxide
 (4) It is not a reactive metal
27. The borax bead test is based upon the formation of
 (1) Boron oxide (2) Boric acid
 (3) Meta borates (4) Elemental boron
28. Boric acid polymerizes due to –
 (1) The presence of hydrogen bonds
 (2) Its acidic nature
 (3) Its geometry
 (4) Its monobasic nature

29. Alum is found to contain hydrated monovalent cation $[\text{M}(\text{H}_2\text{O})_6]^+$, trivalent cation $[\text{M}'(\text{H}_2\text{O})_6]^{+3}$ and SO_4^{2-} in the ratio of :
 (1) 1 : 1 : 1 (2) 1 : 1 : 2
 (3) 1 : 2 : 2 (4) 1 : 2 : 3
30. Borax $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ is actually :-
 (1) $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$
 (2) $\text{Na}_2[\text{B}_4\text{O}_4(\text{OH})_6] \cdot 7\text{H}_2\text{O}$
 (3) $\text{Na}_2[\text{B}_4\text{O}_3(\text{OH})_8] \cdot 6\text{H}_2\text{O}$
 (4) $\text{Na}_2[\text{B}_4\text{O}_2(\text{OH})_{10}] \cdot 5\text{H}_2\text{O}$
31. Diborane is a Lewis acid forming addition compound $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ with NH_3 , a Lewis base. This
 (1) Is ionic and exists as $[\text{BH}_2(\text{NH}_3)_2]^+$ and $[\text{BH}_4]^-$ ions
 (2) On heating, is converted into borazine, $\text{B}_3\text{N}_3\text{H}_6$
 (3) Both are correct
 (4) None is correct
32. Which alum is a double salt made up of two salts :
 (1) Salt of a (SA + WB) + Salt of a (WA + WB)
 (2) Salt of a (SA + SB) + Salt of a (SA + WB)
 (3) Salt of a (SA + SB) + Salt of a (WA + WB)
 (4) Salt of a (SA + WB) + Salt of a (WA + WB)
33. From B_2H_6 all the following can be prepared except :
 (1) H_3BO_3 (2) $\text{B}_2(\text{CH}_3)_4\text{H}_2$
 (3) $\text{B}_2(\text{CH}_3)_6$ (4) NaBH_4
34. Borax on heating with cobalt oxide forms a blue bead of
 (1) $\text{Co}(\text{BO}_2)_2$ (2) CoBO_2
 (3) $\text{Co}_3(\text{BO}_3)_2$ (4) $\text{Na}_3\text{Co}(\text{BO}_3)_2$
35. The hydrides of group 14 elements are :
 (1) Ionic (2) Oxidising
 (3) Covalent (4) None of these
36. Which gas is responsible for green house effect :
 (1) CO_2 (2) SO_2 (3) CO (4) SO_3
37. Artificial gem used for cutting glass is :
 (1) Graphite (2) Diamond
 (3) SiC (4) CaCN_2

NITROGEN FAMILY

38. Nitrogen reacts with calcium carbide to give –
 (1) Calcium nitride (2) Calcium cyanide
 (3) Calcium cyanamide (4) Calcium nitrate
39. P_2O_5 is used extensively as a :
 (1) Dehydrating agent (2) Catalytic agent
 (3) Reducing agent (4) Preservative
40. PH_3 produces smoky rings when it comes in contact with air. This is because :
 (1) It is inflammable
 (2) It combines with water vapours
 (3) It combines with nitrogen
 (4) It contains impurity of P_2H_4

41. Which of the following is the correct statement for PH_3
- (1) It is less basic than NH_3
 - (2) It is less poisonous than NH_3
 - (3) Bond angle of $\text{PH}_3 > \text{NH}_3$
 - (4) It does not show reducing properties
42. Ammonia reacts with excess of chlorine to form:
- (1) N_2 and NH_4Cl
 - (2) NCl_3 and HCl
 - (3) NH_4Cl and NCl_3
 - (4) N_2 and HCl
43. Concentrated nitric acid reacts with iodine to give:-
- (1) HI
 - (2) HOI
 - (3) HOIO_2
 - (4) HOIO_3
44. Each of the following is true of white and red phosphorus except that they
- (1) Are both soluble in CS_2
 - (2) Can be oxidised by heating in air
 - (3) Consist of the same kind of atoms
 - (4) Can be converted into one another
45. A gas which is used as anaesthetic in dental surgery is :
- (1) N_2
 - (2) CO
 - (3) N_2O
 - (4) NH_3
46. The wrong statement about NH_3 is :
- (1) It is oxidised with oxygen at 700°C in the presence of platinum
 - (2) It gives reddish brown ppt with nessler's reagent
 - (3) It can be dried by P_2O_5 , H_2SO_4 and CaCl_2
 - (4) It gives white fumes with HCl
47. On heating, ammonium dichromate and barium azide separately, we get :-
- (1) N_2 with ammonium dichromate and NO with barium azide
 - (2) N_2O with ammonium dichromate and NO_2 with barium azide
 - (3) N_2O with ammonium dichromate and NO with barium azide
 - (4) N_2 in both cases
48. Which one of the following acid possesses oxidising, reducing and complex forming properties?
- (1) HNO_3
 - (2) HCl
 - (3) H_2SO_4
 - (4) HNO_2
49. NO_2 is formed when
- (1) Cu reacts with conc. HNO_3
 - (2) Zn reacts with conc. HNO_3
 - (3) $\text{Pb}(\text{NO}_3)_2$ is heated
 - (4) All



Incorrect statement is :-

- (1) Gas B is PH_3
 - (2) D is pyrophosphoric acid
 - (3) A is H_3PO_3
 - (4) D on strong heating gives P_2O_3
51. Which of the following does not produce NO_2 gas with conc. HNO_3 ?
- (1) Cu
 - (2) I_2
 - (3) Ag
 - (4) Au

OXYGEN FAMILY

52. SO_2 can acts as -
- (1) Reducing agent
 - (2) Oxidising agent
 - (3) Bleaching agent
 - (4) All
53. Which reaction cannot be used for the preparation of the halogen acid-
- (1) $2\text{KBr} + \text{H}_2\text{SO}_4 \xrightarrow{\text{Conc.}} \text{K}_2\text{SO}_4 + 2\text{HBr}$
 - (2) $\text{NaCl} + \text{H}_2\text{SO}_4 \xrightarrow{\text{conc.}} \text{NaHSO}_4 + \text{HCl}$
 - (3) $\text{NaHSO}_4 + \text{NaCl} \xrightarrow{\text{conc.}} \text{Na}_2\text{SO}_4 + \text{HCl}$
 - (4) $\text{CaF}_2 + \text{H}_2\text{SO}_4 \xrightarrow{\text{conc.}} \text{CaSO}_4 + 2\text{HF}$
54. Ozone acts as
- (1) Oxidising agent
 - (2) reducing agent
 - (3) bleaching agent
 - (4) all
55. A black sulphide when treated with ozone becomes white. The white compound is :
- (1) ZnSO_4
 - (2) CaSO_4
 - (3) BaSO_4
 - (4) PbSO_4
56. H_2S gas changes a filter paper dipped in lead acetate solution into :
- (1) Black
 - (2) Red
 - (3) Green
 - (4) Yellow
57. The number of S-S bonds in sulphur trioxide trimer (S_3O_9) is :
- (1) Three
 - (2) Two
 - (3) One
 - (4) Zero
58. Dry bleaching is done by :
- (1) Cl_2
 - (2) SO_2
 - (3) O_3
 - (4) None
59. Compounds A and B are treated with dilute HCl separately. The gases liberated are Y and Z respectively Y turns acidified dichromate paper green while Z turns lead acetate paper black. So A and B compounds are respectively :-
- (1) Na_2SO_3 , Na_2S
 - (2) NaCl , Na_2CO_3
 - (3) Na_2S , Na_2SO_3
 - (4) Na_2SO_3 , K_2SO_4

60. When KBr is treated with conc. H_2SO_4 reddish brown gas is evolved. The gas is :
 (1) Br_2 (2) HOBr (3) NO_2 (4) H_2O_2
61. One gas bleaches the colour of the flowers by reduction while the other by oxidation. The gases are :
 (1) CO and CO_2 (2) H_2S and Br_2
 (3) SO_2 and Cl_2 (4) NH_3 and SO_3
62. On addition of conc. H_2SO_4 to a chloride salt, colourless fumes are evolved but in case of iodide salt, violet fumes come out. This is because:-
 (1) H_2SO_4 reduces HI to I_2
 (2) HI is of violet colour
 (3) HI gets oxidised to I_2
 (4) HI changes to HIO_3
63. Which of the following is responsible for turning starch-iodide paper blue when it is brought in contact with O_3 ?
 (1) Liberation of iodine
 (2) Liberation of oxygen
 (3) Formation of alkali
 (4) Reaction of ozone with litmus paper.
64. Which one of the following property is not correct for ozone ?
 (1) It oxidises lead sulphide
 (2) It oxidises potassium iodide
 (3) It oxidises mercury
 (4) It cannot act as bleaching agent in dry state.
65. By which of the following SO_2 is formed ?
 (1) Reaction of dilute H_2SO_4 with O_2 .
 (2) Heating $\text{Fe}_2(\text{SO}_4)_3$.
 (3) Reaction of concentrated H_2SO_4 with Cu .
 (4) None.
66. Pick out the statement/s that is/are wrong :-
 (1) Oxygen is paramagnetic in all the three states of matter
 (2) Ozone is diamagnetic
 (3) Ozone is a linear molecule
 (4) The O-O bonds in ozone have considerable double bond character
67. **Column-I** **Column-II**
 (A) Caro's acid (p) - S - S - bond
 (B) Polythionic acid (q) - S = S bond
 (C) Pyrosulphuric acid (r) - S - O - S - bond
 (D) Thiosulphuric acid (s) - S - O - O - bond
 (1) A-p, B-q, C-r, D-s (2) A-p, B-q, C-s, D-r
 (3) A-s, B-p, C-r, D-q (4) A-q, B-s, C-r, D-p

HALOGEN FAMILY AND INERT GASES

68. Select the correct statement (s) from the following-
 (1) Fluorine displaces other halogens from the corresponding halides
 (2) Fluorine reacts slowly with halogens
 (3) Fluorine does not decompose water
 (4) Except fluorine, other halogens directly combine with carbon
69. Which of the following is a false statement
 (1) Halogens are oxidizing agent
 (2) Halogens show only (-1) oxidation state
 (3) HF molecules form intermolecular H-bonds
 (4) Fluorine is highly reactive
70. The halide which does not give a precipitate with AgNO_3 is-
 (1) F^- (2) Cl^- (3) Br^- (4) I^-
71. Volatile nature of halogen is because :
 (1) Halogen molecules are bonded by strong forces
 (2) Halogen molecules are bonded by electrostatic forces
 (3) The forces existing between the discrete molecule are only weak vander Waals force.
 (4) Halogen molecules are more reactive
72. Iodine gas turns starch iodide paper :
 (1) Blue (2) Red
 (3) Colourless (4) Yellow
73. BrF_5 is a :
 (1) Interhalogen compound
 (2) Pseudohalogen compound
 (3) Both the above
 (4) None of the above
74. Which of the following statements is not correct when a mixture of NaCl and $\text{K}_2\text{Cr}_2\text{O}_7$ is gently warmed with conc. H_2SO_4 :
 (1) A deep red vapour is evolved
 (2) The vapour when passed into NaOH solution gives a yellow solution of Na_2CrO_4
 (3) Chlorine gas is evolved
 (4) Chromyl chloride is formed
75. Which of the following does not decolourise iodine?
 (1) Na_2SO_3 (2) $\text{Na}_2\text{S}_2\text{O}_3$
 (3) NaCl (4) NaOH
76. Which one of the following halogen liberates oxygen on reacting with H_2O
 (1) I_2 (2) Cl_2 (3) Br_2 (4) F_2
77. Which of the following gases can be dried by concentrated H_2SO_4 ?
 (1) HCl (2) HBr
 (3) HI (4) H_2S

- 78.** Helium is added to oxygen used by deep sea divers because :

 - (1) It is less soluble in blood than nitrogen under high pressure
 - (2) It is lighter than nitrogen
 - (3) It is readily miscible with oxygen
 - (4) It is less poisonous than nitrogen

79. Which of the following is not correct :

 - (1) XeO_3 has four σ and four π bonds
 - (2) The hybridization of Xe in XeF_4 is sp^3d^2
 - (3) Among noble gases, the occurrence of argon is highest in air
 - (4) Liquid helium is used as cryogenic liquid

80. XeF_2 reacts with SbF_5 to form :

 - (1) $[\text{XeF}]^+ [\text{SbF}_6]^-$
 - (2) $[\text{XeF}_3]^+ [\text{SbF}_4]^-$
 - (3) $\text{Xe}^- [\text{PtF}_6]^+$
 - (4) XeF_4

81. Which factor is most responsible for the increase in boiling points of noble gases from He to Xe?

 - (1) decrease in I.E.
 - (2) Monoatomic nature
 - (3) decrease in polarisability
 - (4) increase in polarisability

82. The compound that cannot be formed by xenon is

 - (1) XeO_3
 - (2) XeF_4
 - (3) XeCl_4
 - (4) XeO_2F_2

83. XeF_6 dissolves in anhydrous HF to give a good conducting solution which contains

 - (1) H^+ and XeF_7^- ion
 - (2) HF_2^- and XeF_5^+ ions
 - (3) HXeF_6^+ and F^- ions
 - (4) none of these

84. SbF_5 reacts with XeF_4 to form an adduct. The shapes of cation and anion in the adduct are respectively

 - (1) square planar, trigonal bipyramidal
 - (2) T-shaped, octahedral
 - (3) square pyramidal, octahedral
 - (4) square planar, octahedral

85. Which of the following noble gas does not form clathrate compound?

 - (1) Kr
 - (2) Ne
 - (3) Xe
 - (4) Ar

86. An inorganic salt when heated with concentrated H_2SO_4 evolves a colourless pungent smelling gas but with concentrated H_2SO_4 and MnO_2 evolves a coloured pungent smelling gas which bleaches moist litmus paper. The coloured gas is :-

 - (1) NO_2
 - (2) Cl_2
 - (3) Br_2
 - (4) I_2

87. Identify the incorrect statement (Structure is including the location of lone pair of electrons) :-

 - (1) XeO_2F_2 has 7 bonded electron pairs and one valence shell lone pair of electron. Its structure is square pyramidal with one pi bond.
 - (2) XeO_2F_2 has 6 bonded electron pairs and one valence shell lone pair of electrons. Its structure is trigonal bipyramidal with two pi bonds.
 - (3) XeF_6 has 6 bonded electron pairs and one valence shell lone pair of electrons. Its structure is pentagonal bipyramidal.
 - (4) XeF_2 has 5 electron pairs (bonded and valence shell lone pairs both) and its structure is trigonal bipyramidal.

EXERCISE-I (Conceptual Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	2	2	3	1	2	3	4	4	2	4	4	1	3	3
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	3	1	2	2	1	1	3	2	1	2	3	3	1	2	1
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	3	2	3	1	3	1	3	3	1	4	1	2	3	1	3
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	3	4	4	4	4	4	4	1	4	4	1	4	3	1	1
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	3	3	1	4	3	3	3	1	2	1	3	1	1	3	3
Que.	76	77	78	79	80	81	82	83	84	85	86	87			
Ans.	4	1	1	1	1	4	3	2	2	2	2	1			

EXERCISE-II (Previous Year Questions)**AIPMT 2006**

1. Which of the following is **not** a correct statement?
- (1) Multiple bonds are always shorter than corresponding single bonds
 - (2) The electron-deficient molecules can act as Lewis acids
 - (3) The canonical structures have no real existence
 - (4) Every AB_5 molecule does in fact have square pyramid structure.

AIIMS 2006

2. The colour imparted by Co(II) compounds to glass is –
- (1) Green
 - (2) Deep-Blue
 - (3) Yellow
 - (4) Red
3. Tincture of iodine is –
- (1) Aqueous solution of I_2
 - (2) Solution of I_2 in aqueous KI
 - (3) Alcoholic solution of KI with I_2
 - (4) Aqueous solution of KI
4. Which two of the following salts are used for preparing iodized salt–
- (i) KIO_3
 - (ii) KI
 - (iii) I_2
 - (iv) HI
- (1) (i) and (ii)
 - (2) (i) and (iii)
 - (3) (ii) and (iv)
 - (4) (iii) and (iv)
5. Borax is used as cleansing agent because on dissolving in water it gives.
- (1) Alkaline solution
 - (2) Acidic solution
 - (3) Bleaching solution
 - (4) Colloidal solution

AIPMT 2007

6. Which one of the following anions is present in the chain structure of silicates :
- (1) SiO_4^{4-}
 - (2) $Si_2O_7^{6-}$
 - (3) $(Si_2O_5^{2-})_n$
 - (4) $(SiO_3^{2-})_n$

AIPMT 2009

7. The straight chain polymer is formed by :-
- (1) Hydrolysis of $(CH_3)_2SiCl_2$ followed by condensation polymerisation
 - (2) Hydrolysis of $(CH_3)_3SiCl$ followed by condensation polymerisation
 - (3) Hydrolysis of CH_3SiCl_3 followed by condensation polymerisation
 - (4) Hydrolysis of $(CH_3)_4Si$ by addition polymerisation

AIPMT Pre. 2010

8. Which one of the following molecular hydrides acts as a Lewis acid ?
- (1) CH_4
 - (2) NH_3
 - (3) H_2O
 - (4) B_2H_6

AIPMT/NEET & AIIMS (2006-2018)

9. Oxidation states of P in $H_4P_2O_5$, $H_4P_2O_6$, $H_4P_2O_7$, are respectively :-
- (1) +3, +4, +5
 - (2) +3, +5, +4
 - (3) +5, +3, +4
 - (4) +5, +4, +3
10. How many bridging oxygen atoms are present in P_4O_{10} :-
- (1) 4
 - (2) 2
 - (3) 5
 - (4) 6

AIIMS 2010

11. The product obtained when one mole of diborane reacts with two mole of NH_3 at high temperature
- (1) $B_2H_6 \cdot 2NH_3$
 - (2) $B_3N_3H_6$
 - (3) $(BN)_x$
 - (4) $[BH_2(NH_3)_2]^+ [BH_4]^-$

AIPMT Pre. 2011

12. Name the type of the structure of silicate in which one oxygen atom of $[SiO_4]^{4-}$ is shared ?
- (1) Linear chain silicate
 - (2) Sheet silicate
 - (3) Pyrosilicate
 - (4) Three dimensional

AIPMT Mains 2010

13. Which of the following oxide is amphoteric :-
- (1) CO_2
 - (2) SnO_2
 - (3) CaO
 - (4) SiO_2

AIIMS 2011

14. The wrong statement about fullerene is–
- (1) It has 5-membered carbon ring
 - (2) It has 6-membered carbon ring
 - (3) It has sp^2 hybridization
 - (4) It has no. of 5-membered ring more than 6-membered ring

15. First compound for Xe synthesized was–
- (1) $[XeF^+][XePtF_5]^-$
 - (2) $[XeO_2]$
 - (3) $Xe[PtF_6]$
 - (4) $O_2[XeF_6]$

16. Iodine oxidises sodium borohydride to gives:
- (1) B_2H_6
 - (2) Sodium hydride
 - (3) HI
 - (4) I_3^-

AIPMT Pre. 2012

17. Which of the following statements is not valid for oxyacids of phosphorus?
- (1) All oxyacids contain tetrahedral four coordinated phosphorus
 - (2) All oxyacids contain atleast one $P=O$ unit and one $P-OH$ group
 - (3) Orthophosphoric acid is used in the manufacture of triple superphosphate
 - (4) Hypophosphorous acid is a diprotic acid

18. Sulphur trioxide can be obtained by which of the following reaction:

- (1) $S + H_2SO_4 \xrightarrow{\Delta}$
 (2) $H_2SO_4 + PCl_5 \xrightarrow{\Delta}$
 (3) $CaSO_4 + C \xrightarrow{\Delta}$
 (4) $Fe_2(SO_4)_3 \xrightarrow{\Delta}$

AIIMS 2012

19. How many P = O bond present in $(HPO_3)_3$?
 (1) 0 (2) 3 (3) 6 (4) 9

20. N-N bond length minimum in :-
 (1) N_2O (2) N_2O_3 (3) N_2O_4 (4) N_2O_5

21. $S_2O_8^{2-}$ have :-
 (1) S-S bond
 (2) S-O bridge
 (3) O-O bridge
 (4) All S-O bond length same

NEET-UG 2013

22. The basic structural unit of silicates is :-
 (1) SiO_4^{2-} (2) SiO^- (3) SiO_4^{4-} (4) SiO_3^{2-}

23. Which of these is not a monomer for a high molecular mass silicone polymer ?
 (1) $PhSiCl_3$ (2) $MeSiCl_3$
 (3) Me_2SiCl_2 (4) Me_3SiCl

24. Which of the following does not give oxygen on heating ?
 (1) $(NH_4)_2Cr_2O_7$ (2) $KClO_3$
 (3) $Zn(ClO_3)_2$ (4) $K_2Cr_2O_7$

25. Roasting of sulphides gives the gas X as a by product. This is colourless gas with choking smell of burnt sulphur and causes great damage to respiratory organs as a result of acid rain. Its aqueous solution is acidic, acts as reducing agent and its acid has never been isolated. The gas X is :-
 (1) SO_3 (2) H_2S (3) SO_2 (4) CO_2

AIIMS 2013

26. Bleaching powder does not contain :-
 (1) $CaCl_2$ (2) $Ca(OH)_2$
 (3) $Ca(OC)_2$ (4) $Ca(ClO)_2$

AIIMS 2014

27. sp^2 carbon is not present in :-
 (1) Fullerene (2) Graphite
 (3) Carbonic acid (4) Dry ice

28. Which of the following halogen form only one oxyacids (HOX)

- (1) F (2) Br (3) I (4) Cl

29. Rhombic sulphur is not soluble in :-
 (1) CS_2 (2) Benzene (3) Water (4) Ether

30. Which compound is used for enrichment of U_{235} concentration in nuclear reactions ?
 (1) ClF_3 (2) IF_7
 (3) U_3O_8 (4) $XePtO_4$

AIPMT 2015

31. Nitrogen dioxide and sulphur dioxide have some properties in common. Which property is shown by one of these compounds, but not by the other?
 (1) is a reducing agent
 (2) is soluble in water
 (3) is used as a food-preservative
 (4) forms 'acid-rain'

Re-AIPMT 2015

32. Strong reducing behaviour of H_3PO_2 is due to :
 (1) High oxidation state of phosphorus
 (2) Presence of two -OH groups and one P-H bond
 (3) Presence of one -OH group and two P-H bonds
 (4) High electron gain enthalpy of phosphorus

33. Which of the statements given below is incorrect?
 (1) ONF is isoelectronic with O_2N^-
 (2) OF_2 is an oxide of fluorine
 (3) Cl_2O_7 is an anhydride of perchloric acid
 (4) O_3 molecule is bent

34. The stability of +1 oxidation state among Al, Ga, In and Tl increases in the sequence :
 (1) $Tl < In < Ga < Al$
 (2) $In < Tl < Ga < Al$
 (3) $Ga < In < Al < Tl$
 (4) $Al < Ga < In < Tl$

AIIMS 2015

35. Which of the following statement is correct about solid state of boric acid.
 (1) H-bond is present
 (2) dissolves in water to yield H^+
 (3) shape of B is tetrahedral
 (4) None of these

36. Which of the following allotrope of phosphorous has tetrahedral discrete unit?

- (1) Red black P
- (2) White P
- (3) Red P
- (4) Red, black & white P

37. Chain growth can be controlled by

- (1) R_2SiCl_2
- (2) R_3SiCl
- (3) $RSiCl_3$
- (4) $R_4Si/SiCl_4$

38. Lowest oxidation state of phosphorous is in

- (1) H_3PO_2
- (2) H_3PO_4
- (3) $H_4P_2O_7$
- (4) H_3PO_3

39. Which one of the following element can shown +7 oxidation state with fluorine

- (1) I
- (2) Mn
- (3) F
- (4) Br

40. S-S linkage absent in

- (1) $H_2S_2O_7$
- (2) $H_2S_2O_3$
- (3) $H_2S_2O_5$
- (4) $H_2S_2O_6$

41. Which of the following gives B_2H_6 on reaction with $NaBH_4$

- (1) $LiAlH_4$
- (2) $NaOH$
- (3) I_2
- (4) None

NEET-I 2016

42. Among the following, the correct order of acidity is

- (1) $HClO_3 < HClO_4 < HClO_2 < HClO$
- (2) $HClO < HClO_2 < HClO_3 < HClO_4$
- (3) $HClO_2 < HClO < HClO_3 < HClO_4$
- (4) $HClO_4 < HClO_2 < HClO < HClO_3$

43. When copper is heated with conc. HNO_3 it produces

- (1) $Cu(NO_3)_2$ and NO_2
- (2) $Cu(NO_3)_2$ and NO
- (3) $Cu(NO_3)_2$, NO and NO_2
- (4) $Cu(NO_3)_2$ and N_2O

44. Which is the **correct** statement for the given acids?

- (1) Phosphinic acid is a diprotic acid while phosphonic acid is a monoprotic acid
- (2) Phosphinic acid is a monoprotic acid while phosphonic acid is a diprotic acid
- (3) Both are triprotic acids
- (4) Both are diprotic acids

NEET-II 2016

45. Boric acid is an acid because its molecule

- (1) accepts OH^- from water releasing proton
- (2) combines with proton from water molecule
- (3) contains replaceable H^+ ion
- (4) gives up a proton

46. AlF_3 is soluble in HF only in presence of KF . It is due to the formation of

- (1) AlH_3
- (2) $K[AlF_3H]$
- (3) $K_3[AlF_3H_3]$
- (4) $K_3[AlF_6]$

AIIMS 2016

47. At $1000^\circ C$ air is passed on coal then which product will be form :-

- (1) producer gas
- (2) water gas
- (3) CH_4
- (4) none of these

48. Which one of the following statement is not true regarding B_2H_6 :-

- (1) It react with NaH to form $NaBH_4$
- (2) It is non inflammable gas
- (3) It contain four equal B-H bonds
- (4) It react with lewis base to form always adduct

49. Which of the following is correct :-

- (1) N_2O is a coloured gas
- (2) CO is an acidic oxide
- (3) CO_2 is not absorbed in $CsOH$
- (4) N_2O is a neutral oxide

50. Which of the following has least tendency in +3 oxidation state to show disproportionation reaction.

- (1) N
- (2) P
- (3) Bi
- (4) Sb

NEET(UG) 2017

51. In which pair of ions both the species contain S-S bond?

- (1) $S_4O_6^{2-}$, $S_2O_3^{2-}$
- (2) $S_2O_7^{2-}$, $S_2O_8^{2-}$
- (3) $S_4O_6^{2-}$, $S_2O_7^{2-}$
- (4) $S_2O_7^{2-}$, $S_2O_3^{2-}$

52. It is because of inability of ns^2 electrons of the valence shell to participate in bonding that:-

- (1) Sn^{2+} is oxidising while Pb^{4+} is reducing
- (2) Sn^{2+} and Pb^{2+} are both oxidising and reducing
- (3) Sn^{4+} is reducing while Pb^{4+} is oxidising
- (4) Sn^{2+} is reducing while Pb^{4+} is oxidising

AIIMS 2017

53. Which of the following statement is incorrect about silicones ?
 (1) R_2SiCl_2 & $RSiCl_3$ are monomers of silicones
 (2) Silicones are hydrophobic
 (3) R_3SiCl is used to close polymeric chain
 (4) Polymers of $(R_3SiO)_2$
54. Boric acid in water produces ?
 (1) $H_2BO_3^-$ (2) BO_3^{3-}
 (3) $(H_4BO_4)^-$ (4) $[B(OH)]^-$
55. Which of the following is not completely soluble in conc. HNO_3 .
 (1) S_8 (2) I_2
 (3) Al (4) Zn
56. Which of the following pair of compounds gives white fumes, on exposing to moist air
 (1) $AlCl_3$ & $NiCl_2$ (2) $AlCl_3$ & $CrCl_3$
 (3) $TiCl_4$ & $SiCl_4$ (4) $SiCl_4$ & $SnCl_4$
57. Which of the following covalent hydride having highest lewis acidic character ?
 (1) $Al(CH_3)_3$ (2) $NaBH_4$
 (3) B_2H_6 (4) AsH_3
58. The structure of graphite belongs to :-
 (1) Monoclinic (2) Triclinic
 (3) Hexagonal (4) Rhombohedral

NEET(UG) 2018

59. Which of the following statements is **not** true for halogens ?
 (1) All form monobasic oxyacids.
 (2) All are oxidizing agents.
 (3) All but fluorine show positive oxidation states.
 (4) Chlorine has the highest electron-gain enthalpy.
60. The correct order of N-compounds in its decreasing order of oxidation states is
 (1) HNO_3 , NO, N_2 , NH_4Cl
 (2) HNO_3 , NO, NH_4Cl , N_2
 (3) HNO_3 , NH_4Cl , NO, N_2
 (4) NH_4Cl , N_2 , NO, HNO_3

AIIMS 2018

61. Halides of which of the following element always have only one lone pair on central atom :-
 (1) Xe (2) Cl
 (3) Se (4) N
62. Which of the following statement is not correct :-
 (1) Black phosphorus is more stable than white & red phosphorus
 (2) Red phosphorus is highly toxic
 (3) White phosphorus is highly soluble in CS_2
 (4) Red phosphorus converts in black on heating
63. The best compound which convert nitrite in N_2 is:-
 (1) Urea
 (2) Thiourea
 (3) Sulphamic acid
 (4) Ammonium chloride
64. Which pair not shows same shape :-
 (1) I_3^{-1} , $BeCl_2$ (2) BF_3 , ClO_3^{-1}
 (3) SO_2 , H_2O (4) XeF_4 , BrF_4^-
65. Which one is wrong :-
 (1) Pyroxene is a linear silicate
 (2) Zeolite is a 2 dimensional double strand silicate
 (3) Beryl is a cyclic silicate
 (4) Pyrex is a man-made silicate
66. When cyanogen gas is passed through strong alkali then product formed is ?
 (1) OCN^- (2) N_2
 (3) NCN^- (4) NH_2CH
67. Which of the following insoluble in dil HCl :-
 (1) $SnCl_2$ (2) $PbCl_2$
 (3) $CdCl_2$ (4) $BiOCl$
68. Which gas will diffuse fastest in Rubber
 (1) Xenon (2) Fluorine
 (3) Oxygen (4) Helium
69. Which will give Blue colour with SO_2
 (1) I_2 + Cellulose (2) Iodate + Starch
 (3) $CuSO_4$ + KI (4) I_2 solution
70. Which of the following will not convert N_2H_4 into N_2
 (1) Oxygen (2) $CuSO_4$
 (3) Ozone (4) Zn + HCl

71. Which change will not take place when NaCl and MnO_2 is placed in conc. H_2SO_4

- (1) Oxidation state of sulphur will change
- (2) Cl^- will be oxidised to Cl_2
- (3) Greenish-yellow coloured vapour will be of Cl_2
- (4) Oxidation state of Mn^{+4} is change to Mn^{+2}

72. Which is incorrect?

- (1) ΔG_f of Br_2 is maximum in halogen.
- (2) Bond dissociation energy of Br_2 is more than F_2 .
- (3) Hydration energy of F^- is more than I^-
- (4) I_2 is more soluble in water than Br_2

EXERCISE-II (Previous Year Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	2	3	1	1	4	1	4	1	4	2	3	2	4	3
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	1	4	4	2	1	3	3	4	1	3	4	4	1	3	1
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	3	3	2	4	1	2	2	1	1	1	3	2	1	2	1
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	4	1	2	4	3	1	4	4	3	3	4	3	3	1	1
Que.	61	62	63	64	65	66	67	68	69	70	71	72			
Ans.	4	2	3	2	2	1	2	4	2	4	1	1			

EXERCISE-III (Analytical Questions)**Check Your Understanding**

1. One mole of magnesium nitride on the reaction with an excess of water gives
(1) Two moles of ammonia (2) One mole of nitric acid
(3) One mole of ammonia
(4) Two moles of nitric acid
2. Which of the following oxides of nitrogen is solid :-
(1) NO_2 (2) N_2O
(3) NO (4) N_2O_5
3. Which has no S-S-bond.
(1) $\text{S}_2\text{O}_4^{-2}$ (2) $\text{S}_2\text{O}_5^{-2}$
(3) $\text{S}_2\text{O}_3^{-2}$ (4) $\text{S}_2\text{O}_7^{-2}$
4. The products obtained on heating LiNO_3 will be:-
(1) $\text{LiNO}_2 + \text{O}_2$
(2) $\text{Li}_2\text{O} + \text{NO}_2 + \text{O}_2$
(3) $\text{Li}_3\text{N} + \text{O}_2$
(4) $\text{Li}_2\text{O} + \text{NO} + \text{O}_2$
5. Which of the following on thermal-decomposition yields a basic as well as an acidic oxide ?
(1) NH_4NO_3 (2) NaNO_3
(3) KClO_3 (4) CaCO_3
6. An example of a cyclic silicate is :-
(1) Beryl (2) Zeolite
(3) Talc (4) Zircon
7. Which one of the following reacts with glass ?
(1) H_2SO_4 (2) HF
(3) HNO_3 (4) $\text{K}_2\text{Cr}_2\text{O}_7$
8. When I_2 is passed through KCl , KF , KBr solutions :
(1) Cl_2 and Br_2 are evolved
(2) Cl_2 is evolved
(3) Cl_2 , Br_2 , F_2 are evolved
(4) None of these
9. Ammonia can be dried by
(1) Conc. H_2SO_4 (2) P_4O_{10}
(3) CaO (4) Anhydrous CaCl_2
10. Which of the following product is not formed by the reaction of PH_4I and KOH :-
(1) KI (2) PH_3
(3) H_2O (4) P_2O_3
11. Out of the following which does not liberate N_2 gas on heating :-
(1) $\text{NaNO}_2 + \text{NH}_4\text{Cl}$ (2) $\text{Ba}(\text{N}_3)_2$
(3) $\text{O}_3 + \text{NO}$ (4) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
12. Which of the following is incorrect ?
(1) O_2 is weaker oxidant than O_3
(2) O_2 has small bond length than O_3
(3) Both O_2 and O_3 are paramagnetic
(4) O_3 is angular in shape
13. Which of the following statements regarding sulphur is incorrect ?
(1) At 600°C the gas mainly consists of S_2 molecules
(2) The oxidation state of sulphur is never less than +4 in its compounds
(3) S_2 molecule is paramagnetic
(4) The vapour at 200°C consists mostly of S_8 rings
14. The correct order of acidic strength is :
(1) $\text{Cl}_2\text{O}_7 > \text{SO}_3 > \text{P}_4\text{O}_{10}$
(2) $\text{CO}_2 > \text{N}_2\text{O}_5 > \text{SO}_3$
(3) $\text{Na}_2\text{O} > \text{MgO} > \text{Al}_2\text{O}_3$
(4) $\text{K}_2\text{O} > \text{CaO} > \text{MgO}$
15. Which of the following statements is correct ?
(1) BCl_3 and AlCl_3 are both Lewis acids and BCl_3 is stronger than AlCl_3
(2) BCl_3 and AlCl_3 both Lewis acids and AlCl_3 is stronger than BCl_3
(3) BCl_3 and AlCl_3 are both equally strong Lewis acids
(4) Both BCl_3 and AlCl_3 are not Lewis acids.
16. Which of the following statements about H_3BO_3 is not correct
(1) It is a strong tribasic acid
(2) It is prepared by acidifying an aqueous solution of borax
(3) It has a layer structure in which planar H_3BO_3 units are joined by hydrogen bonds
(4) It does not act as proton donor but acts as a Lewis acid by accepting hydroxyl ion
17. Which of the following property is not related with PH_3
(1) It is a colorless gas having rotten fish smell
(2) it is non poisonous
(3) it is slightly soluble in water
(4) it is a weak Lewis base

18. Which of the following is a mixed anhydride

- (1) P_4O_{10} (2) SO_3
(3) Cl_2O_6 (4) SO_2

19. In which of the following phosphorous atoms are at the corner of tetrahedron.

- (1) P_4 (2) P_4O_6
(3) P_4O_{10} (4) All of these

20. In which of the following option product gas X and Y (other than water vapour) are same ?

- (1) $Mg_2C_3 + H_2O \rightarrow X$; $Al_4C_3 + H_2O \rightarrow Y$
(2) $NH_4NO_3 \xrightarrow{\Delta} X$; $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} Y$
(3) $NH_4Cl \xrightarrow{\Delta} X$; $UREA \xrightarrow{H_2O} Y$
(4) $Zn + \text{dil. } HNO_3 \rightarrow X$; $Ag + \text{dil. } HNO_3 \rightarrow Y$

21. When con. H_2SO_4 is added to charcoal :

- (1) There is no reaction
(2) Water gas is formed
(3) SO_2 and CO_2 are evolved
(4) CO and SO_2 are evolved

22. Which of the following statements are correct for SO_2 gas?

- (1) It acts as bleaching agent in moist conditions.
(2) It's molecule has linear geometry.
(3) It's dilute solution is used as lubricant
(4) It can be prepared by the reaction of dilute H_2SO_4 with metal sulphide

23. Iodine is placed between two liquids C_6H_6 and water then :

- (1) It dissolves more in C_6H_6
(2) It dissolves more in water
(3) It dissolves equally in both
(4) Does not dissolve in both

24. Chromyl chloride vapours are dissolved in water and acetic acid and barium acetate solution is added, then :-

- (1) The solution will remain colourless
(2) The solution will become dark green
(3) A yellow solution will be obtained
(4) A yellow precipitate will be obtained

25. The correct order of sulphur-oxygen bond length is :-

- (1) $SOF_2 > SOCl_2 > SOBr_2$
(2) $SOCl_2 > SOBr_2 > SOF_2$
(3) $SOF_2 = SOCl_2 = SOBr_2$
(4) $SOBr_2 > SOCl_2 > SOF_2$

26. Which is/are wrong about P_4O_{10} molecule :-

- (1) Each 'P' atom can be considered to be sp^3 hybridised
(2) There are six P-O-P bonds in the molecule
(3) There are two types of P-O bond lengths
(4) P-O-P angle is 180°

27. Which of the following order(s) is/are incorrect ?

- (1) $H_3PO_4 > H_3PO_3 > H_3PO_2$ (reducing character)
(2) $N_2O < NO < N_2O_3 < N_2O_5$ (oxidation state on nitrogen atom)
(3) $NH_3 > PH_3 > AsH_3 > SbH_3$ (basicity)
(4) $HClO < HClO_2 < HClO_3 < HClO_4$ (Acidic nature)

28. Which of the following is correct :-

- (1) H_3BO_3 can be considered to be a lewis acid
(2) The correct order of lewis acid strength order is $BF_3 > BCl_3 > BBr_3$
(3) One mole borax in aqueous solution will require one mole HCl for titration
(4) B_2H_6 can be methylated completely to give $B_2(CH_3)_6$

EXERCISE-III (Analytical Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	4	4	2	4	1	2	4	3	4	3	3	2	1	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28		
Ans.	1	2	3	4	3	3	1	1	4	4	4	1	1		

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

- Assertion** : CCl_4 is not hydrolysed by water
Reason : Carbon in CCl_4 is sp^3 hybridised
 (1) A (2) B (3) C (4) D
- Assertion** : Between SiCl_4 and CCl_4 only SiCl_4 reacts with water.
Reason : SiCl_4 is ionic and CCl_4 is covalent.
 (1) A (2) B (3) C (4) D
- Assertion** : PbI_4 is a stable compound.
Reason : Iodine stabilizes higher oxidation state.
 (1) A (2) B (3) C (4) D
- Assertion** : The atoms in a covalent molecule are said to share electrons, yet some covalent molecules are polar.
Reason : In polar covalent molecules, the shared electrons spend more time on the average near one of the atoms due to high EN.
 (1) A (2) B (3) C (4) D
- Assertion** : Nitrogen is unreactive at room temperature but becomes reactive at elevated temperature (on heating or in the presence of catalysts).
Reason : In nitrogen molecule, there is extensive delocalization of electrons.
 (1) A (2) B (3) C (4) D
- Assertion** :- H_3PO_2 can act as strong reducing agent and gives disproportionation reaction on heating.
Reason :- Due to presence of one $-\text{OH}$ group and two $\text{P}-\text{H}$ group, H_3PO_2 is a monobasic bronsted acid.
 (1) A (2) B (3) C (4) D
- Assertion** :- NO_2 is paramagnetic in gaseous state but become diamagnetic solid on cooling.
Reason :- In gaseous state, NO_2 exists as monomer odd electron species but on cooling it dimerise to N_2O_4 .
 (1) A (2) B (3) C (4) D
- Assertion** :- For drying H_2 , conc. H_2SO_4 cannot be used.
Reason :- conc. H_2SO_4 on absorbing H_2O form moist H_2 along with large amount of heat which burn H_2 .
 (1) A (2) B (3) C (4) D
- Assertion** :- NH_3 can be dried by quick lime.
Reason :- Quick lime is also basic in nature and no reaction take place with NH_3 .
 (1) A (2) B (3) C (4) D
- Assertion** :- $\text{Cl}_2 + \text{H}_2\text{O}$ reaction is a disproportionation reaction and HOCl is formed.
Reason :- Increase in pH will increase the yield of HOCl .
 (1) A (2) B (3) C (4) D
- Assertion** :- NO_2 and ClO_2 both being odd electron molecule dimerise.
Reason :- On dimerisation, NO_2 is converted to stable N_2O_4 molecule with even number of electrons.
 (1) A (2) B (3) C (4) D
- Assertion** :- All inter halogens are diamagnetic.
Reason :- AB type of interhalogen undergoes hydrolysis giving a halide ion derived from the smaller halogen and a hypohalite ion derived from the larger halogen.
 (1) A (2) B (3) C (4) D

- 13. Assertion :-** Anhyd. calcium chloride cannot be used to dry NH_3 .
Reason :- Anhyd. CaCl_2 forms an adduct $\text{CaCl}_2 \cdot 8\text{NH}_3$ with NH_3 .
 (1) A (2) B (3) C (4) D
- 14. Assertion :-** Surface of diamond is generally impure.
Reason :- It has dangling bonds.
 (1) A (2) B (3) C (4) D
- 15. Assertion :-** SiCl_4 is more hydrolysed than SiF_4 .
Reason :- -I effect of $\text{F} > \text{Cl}$.
 (1) A (2) B (3) C (4) D
- 16. Assertion :-** The solubility of I_2 increases in water in presence of KI .
Reason :- I_2 forms ionic polyhalide with KI .
 (1) A (2) B (3) C (4) D
- 17. Assertion :-** H_3PO_2 is monoprotic acid.
Reason :- It has H-bonding in solid state.
 (1) A (2) B (3) C (4) D
- 18. Assertion :-** O_3 is a good oxidising agent.
Reason :- O_3 very rapidly gives dioxygen.
 (1) A (2) B (3) C (4) D
- 19. Assertion :-** Sulphur is soluble in CS_2 .
Reason :- Sulphur exists in S_8 form.
 (1) A (2) B (3) C (4) D
- 20. Assertion :-** P_4O_{10} dehydrates HNO_3 .
Reason :- In P_4O_{10} oxidation state of P is +5.
 (1) A (2) B (3) C (4) D
- 21. Assertion :-** Peroxy disulphuric acid & oleum have same oxidation state.
Reason :- In oleum oxygen bridges two sulphur atoms.
 (1) A (2) B (3) C (4) D
- 22. Assertion :-** $3\text{O}_{2(g)} \longrightarrow 2\text{O}_{3(g)}$ the reaction occurs in presence of silent electric discharge.
Reason :- because at 298 K, $\Delta S = +ve$.
 (1) A (2) B (3) C (4) D
- 23. Assertion :-** Conc. H_2SO_4 on addition to HCOOH liberates CO .
Reason :- Hot conc. H_2SO_4 is a moderate oxidising agent.
 (1) A (2) B (3) C (4) D
- 24. Assertion :-** Salts of H_3PO_3 and H_3PO_4 used as fertilizers.
Reason :- Formed H_3PO_3 increases solubility of water in soil on addition of phosphate fertilizers.
 (1) A (2) B (3) C (4) D
- 25. Assertion :-** Pb_3O_4 reacts with HNO_3 forms PbO_2 .
Reason :- Pb^{+4} is most stable.
 (1) A (2) B (3) C (4) D
- 26. Assertion :-** SO_2 mixed with H_2SO_4 to make oleum.
Reason :- SO_2 in presence of water forms H_2SO_4 in air.
 (1) A (2) B (3) C (4) D
- 27. Assertion :-** Cl_2 is oxidised by hot & conc. NaOH .
Reason :- It is favoured by formation of NaClO_3 .
 (1) A (2) B (3) C (4) D
- 28. Assertion :-** XeF_4 is a good fluorinating agent.
Reason :- XeF_4 sublimes at 298 K.
 (1) A (2) B (3) C (4) D
- 29. Assertion :-** $\text{Ba}(\text{N}_3)_2$ give highly pure N_2 .
Reason :- Atomic weight of Ba is very high.
 (1) A (2) B (3) C (4) D
- 30. Assertion :-** As temp. increases intensity of brown colour of NO_2 decreases.
Reason :- Formation of NO_2 is an endothermic process.
 (1) A (2) B (3) C (4) D
- 31. Assertion :-** Black phosphorus is oxidised easily in air.
Reason :- Black phosphorus consists of polymer tetrahedral units of P_4 .
 (1) A (2) B (3) C (4) D
- 32. Assertion :-** Fluorine oxidises H_2O to O_2 but Cl_2 does not.
Reason :- Electronegativity of fluorine is greater than oxygen but EN of chlorine is lesser than oxygen.
 (1) A (2) B (3) C (4) D
- 33. Assertion :-** SO_2 (at room temp.) and SeO_2 (at higher temp. vapour condition) have same shape.
Reason :- Covalent radius of Se is somewhat larger than sulphur.
 (1) A (2) B (3) C (4) D

34. **Assertion :-** I_2O_5 oxidises CO
Reason :- Oxidation Number of Iodine is +5 in I_2O_5 .
 (1) A (2) B (3) C (4) D
35. **Assertion :-** O_2F_2 is used for the purification of Plutonium from spent nuclear fuel.
Reason :- O_2F_2 convert Plutonium to PuF_6 .
 (1) A (2) B (3) C (4) D
36. **Assertion :-** NH_3 is easily desolved in alkaline HgI_4^{-2}
Reason :- Compound of Hg and I^- is used in detection of NH_3 .
 (1) A (2) B (3) C (4) D

37. **Assertion :-** Liquid N_2 is used as refrigerant.
Reason :- Because Liquid N_2 is not Harmful for environment and its is non reactive.
 (1) A (2) B (3) C (4) D
38. **Assertion :-** 1ppm of NaF is compulsory in drinking water.
Reason :- It helps in maintaining blood pressure.
 (1) A (2) B (3) C (4) D
39. **Assertion :-** Graphene is obtained from graphite
Reason :- Graphene and graphite both have layered structure.
 (1) A (2) B (3) C (4) D

EXERCISE-IV (Assertion & Reason)										ANSWER KEY					
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	3	4	1	3	2	1	1	1	2	4	2	1	1	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	1	2	2	2	2	2	3	2	1	3	4	2	2	2	4
Que.	31	32	33	34	35	36	37	38	39						
Ans.	4	2	2	2	1	1	1	1	3						

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NEET SYLLABUS

d and f Block Elements : General introduction, electronic configuration, characteristics of transition metals, general trends in properties of the first row transition metals- metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation. Preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$.

Lanthanoids - electronic configuration, oxidation states, chemical reactivity, and lanthanoid contraction and its consequences.

Actinoids: Electronic configuration, oxidation states and comparison with lanthanoids.

OBJECTIVES

After studying this unit, you will be able to :

- *learn the positions of the d- and f-block elements in the periodic table;*
- *know the electronic configurations of the transition (d-block) and the inner transition (f-block) elements;*
- *appreciate the relative stability of various oxidation states in terms of electrode potential values;*
- *describe the preparation, properties, structures and uses of some important compounds such as $K_2Cr_2O_7$ and $KMnO_4$;*
- *understand the general characteristics of the d- and f-block elements and the general horizontal and group trends in them;*
- *describe the properties of the f-block elements and give a comparative account of the lanthanoids and actinoids with respect to their electronic configurations, oxidation states and chemical behaviour.*

"d & f-block elements signify special people in society, on whom no social or economic rule is applicaton."

Mitch Album

d & f-BLOCK ELEMENTS

2.0 INTRODUCTION :

- (i) d-block elements are often called as 'transition elements' because their position in periodic table is between the s-block and p-block elements.
- (ii) Their properties are transitional between the highly reactive metallic elements of s-block (which form ionic compounds) and the elements of p-block (which are largely covalent).
- (iii) Typically the transition elements have an incompletely filled d-orbital. A transition element may be defined as the element whose atom in ground state or ion in one of common oxidation states, has partly filled d-sub shell i.e. having electrons between 1 to 9.
- (iv) Group 12 (the zinc group) elements have completely filled d-orbitals in the ground state as well as in their common oxidation states. Therefore, they are not regarded as transition elements.
- (v) The general electronic configuration of d-block elements is $(n-1) d^{1-10} ns^{1-2}$, where n is the outer most shell. However, palladium does not follow this general electronic configuration. It has electron configuration $[Kr]^{36} 4d^{10} 5s^0$ in order to have stability.
- (vi) Zn, Cd and Hg are involved in transition series but they are called non transition elements due to completely filled d-orbitals.

1st Series										
Z	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
21	22	23	24	25	26	27	28	29	30	
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

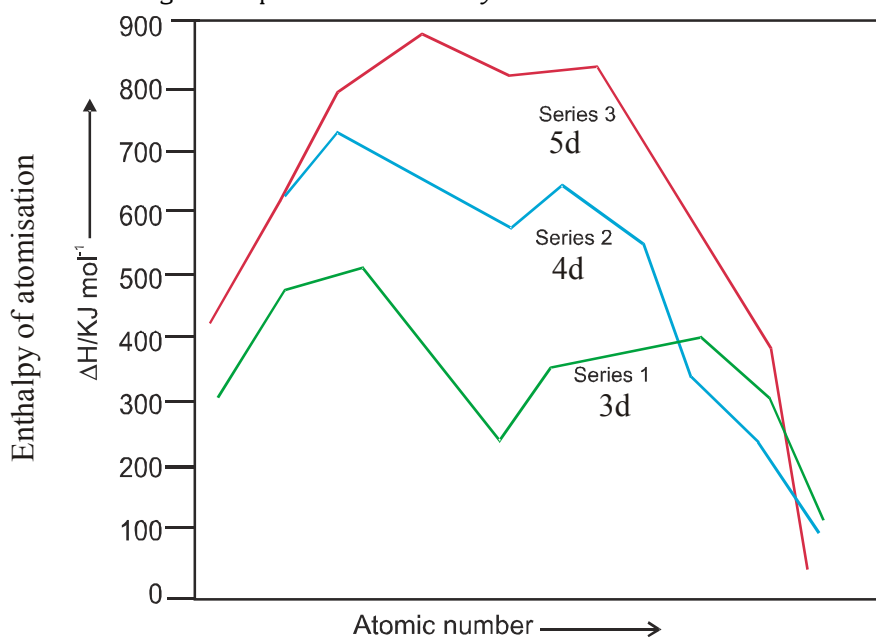
2nd Series										
Z	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
39	40	41	42	43	44	45	46	47	48	
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

3rd Series										
Z	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
57	72	73	74	75	76	77	78	79	80	
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

2.1 GENERAL TRENDS IN THE CHEMISTRY OF TRANSITION ELEMENTS.

(A) Metallic character :

- (i) In d-block elements the last but one (i.e. the penultimate) shell of electrons is expanding. Thus they have many physical and chemical properties in common.
- (ii) Nearly all the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre.
- (iii) Most transition elements have ccp/hcp type structures.
- (iv) The transition elements are very much hard and have low volatility, they have high enthalpy of atomisation.
- (v) Cr, Mo and W have maximum number of unpaired electrons and therefore, these are very hard metals and have maximum enthalpies of atomisation in their respective period.
- (vi) The metals with very high enthalpy of atomisation (i.e., very high boiling point) tend to be noble in their reactions.
- (vii) The metals of the 4d and 5d series have greater enthalpies of atomisation than the corresponding elements of the 3d and this is an important factor indicating for the occurrence of much more frequent metal-metal bonding in compounds of the heavy transition metals.

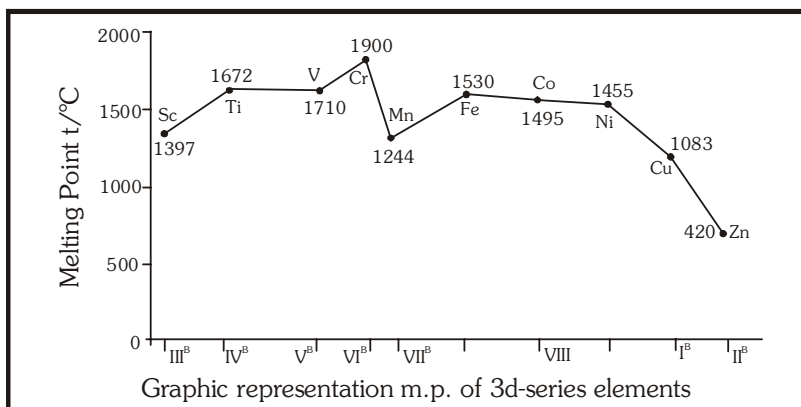


Graph showing Trends in enthalpies of atomisation of transition elements

(B) MELTING AND BOILING POINTS

- (i) Melting and boiling point of d-block > s-block
Reason : Stronger metallic bond formed present by unpaired d-electrons.
- (ii) In Zn, Cd, and Hg there is no unpaired electron present in d-orbital, hence due to absence of covalent bond melting and boiling point are very low in series. (Volatile metals Zn, Cd, Hg)
- (iii) In 3d series Sc to Cr melting and boiling point increases then Mn to Zn melting and boiling point decreases
- (iv) As the number of unpaired d-electron increases, the number of covalent bond and bond energy between the atoms is expected to increase up to Cr-Mo-W family where each of the d-orbital has only unpaired electron and the opportunity for covalent sharing is greatest.

- (v) Mn and Tc have comparatively low melting point, due to weak metallic bond because of stable Half filled (d^5) configuration and high IP.
- (vi) Lowest melting point Hg (-38°C) ; Highest melting point W ($\approx 3400^\circ\text{C}$)



Illustrations

Illustration 1 : Why do the transition elements have higher boiling & melting points ?

Solution Because of having larger number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence stronger bonding between atoms. Hence strong metallic bonds between the atoms of these elements attribute to their high melting and boiling points.

(C) DENSITY :

- (i) The atomic volumes of the transition elements are low compared with the elements of group 1 and 2. This is because the increased effective nuclear charge. In addition, the extra electrons added occupy inner orbitals. Consequently the densities of the transition metals are high.
- (ii) Across a period from left to right atomic volumes decrease and atomic masses increase. Hence the densities also increase across a period.

$$\text{Sc} \leq \text{Ti} \leq \text{V} \leq \text{Cr} \leq \text{Mn} \leq \text{Fe} \leq \text{Co} \leq \text{Ni} \approx \text{Cu} > \text{Zn}$$

(zinc is an exception, having large atomic volume and hence has lower density)

- (iii) $3d < 4d < 5d$ Series

- (iv) Maximum density : $\text{Ir} \geq \text{Os}$

(D) Ionisation energies or Ionisation enthalpies :

- (i) The first ionisation energy of Zn, Cd, and Hg are very high because of their fully filled $(n-1) d^{10} ns^2$ configuration.
- (ii) Order of second ionisation energy : $\text{Sc} < \text{Ti} < \text{V} < \text{Mn} < \text{Cr}$

(E) Oxidation states :

- (i) The transition metals exhibit a large number of oxidation states. With the exception of a few elements, most of these show variable oxidation states. These different oxidation states are related to the electronic configuration of their atoms.
- (ii) The existence of the transition elements in different oxidation states means that their atoms can lose different number of electrons. This is due to the participation of inner $(n-1)$ d-electrons in addition to outer ns-electrons because, the energies of the ns and $(n-1)$ d-sub-shells are nearly same.
- (iii) In general oxidation state of d-block element is given as minimum oxidation state = number of 's' electrons
maximum oxidation state = number of 's' electrons + unpaired 'd' electron

Different oxidation states of first transition series.

Element	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+3
Ti	$3d^2 4s^2$	+2, +3, +4
V	$3d^3 4s^2$	+2, +3, +4, +5
Cr	$3d^5 4s^1$	+2, +3, (+4), (+5), +6
Mn	$3d^5 4s^2$	+2, +3, +4, (+5), +6, +7
Fe	$3d^6 4s^2$	+2, +3, (+4), (+5), (+6)
Co	$3d^7 4s^2$	+2, +3, (+4)
Ni	$3d^8 4s^2$	+2, +3, +4
Cu	$3d^{10} 4s^1$	+1, +2
Zn	$3d^{10} 4s^2$	+2

• Oxidation states given in parenthesis are unstable.

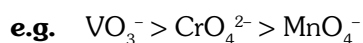
Higher oxidation state in d-block = +8 (Os, Ru)

Zero oxidation state for e.g. $[\text{Ni}(\text{CO})_4]$, $[\text{Fe}(\text{CO})_5]$

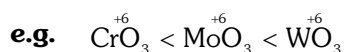
(iv) Relative stability of oxidation state :

$\text{Sc}^{+2} < \text{Sc}^{+3}$	inert gas stable configuration
$\text{Ti}^{+3} < \text{Ti}^{+4}$	
$\text{Mn}^{+6} < \text{Mn}^{+7}$	
$\text{V}^{+4} < \text{V}^{+5}$	
$\text{Mn}^{+3} < \text{Mn}^{+2}$	d^5 stable configuration
$\text{Cr}^{+2} < \text{Cr}^{+3}$	d^3 is more stable than d^4 in aq. solution
$\text{Ni}^{+2} > \text{Ni}^{+4}$	On the basis of sum of first four I.P's.
$\text{Pt}^{+2} < \text{Pt}^{+4}$	

(v) On moving in a period stability of higher oxidation state decreases

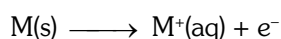


(vi) On moving down the group stability of higher oxidation state increases

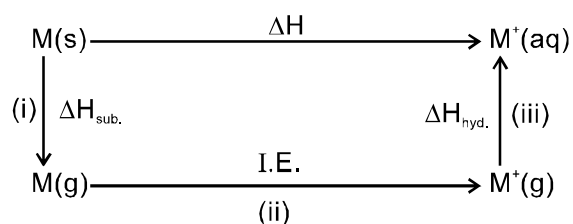


(F) ELECTRODE POTENTIALS :

In addition to ionisation enthalpy, the other factors such as enthalpy of sublimation, hydration enthalpy, ionisation enthalpy etc. determine the stability of a particular oxidation state in solution. This can be explained in terms of their electrode potential values. The oxidation potential of a metal involves the following process:



This process actually takes place in the following three steps as given in following flowchart :



The oxidation potential which gives the tendency of the overall change to occur, depends upon the net effect of these three steps. The overall energy change is $\Delta H = \Delta_{\text{sub}} H^\ominus + \Delta H + \Delta_{\text{hyd}} H$

If SOP is +ve $\rightarrow$ Means Oxidation easy

If SRP is +ve $\rightarrow$ Means reduction easy

Some important examples :

1. $E_{\text{M}^{+2}/\text{M}}^0 \Rightarrow$ +ve only for Cu among 3d elements because HE of Cu^{+2} is not enough to compensate for sublimation energy, IP_1 and IP_2 for Cu.

2. $E_{\text{M}^{+3}/\text{M}^{+2}}^0 \Rightarrow$

(a) $E_{\text{Cr}^{+3}/\text{Cr}^{+2}}^0 = -ve$

Reason : $t_2g^3 eg^0 \leftarrow d^3 > d^4$

(b) $E_{\text{Mn}^{+3}/\text{Mn}^{+2}}^0 = +ve \text{ (high)}$

Reason : $d^4 < d^5$

(c) $E_{\text{Fe}^{+3}/\text{Fe}^{+2}}^0 = \text{less +ve (learn)}$

Reason : $d^5 > d^6$

Note : The SRP of $E_{\text{Fe}^{+3}/\text{Fe}^{+2}}^0$ is less than expected because of extra stability of d^5 configuration of Fe^{+3} ion.

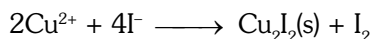
(G) TRENDS IN STABILITY OF HIGHER OXIDATION STATES

Standard electrode potential data provide valuable information about the stabilities of different oxidation states shown by an element. The highest oxidation states are shown generally among halides and oxides.

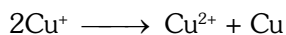
Halides of first transition series

- In metal halides.** The transition elements react with halogens at high temperatures to form transition metal halides. These reactions have very high heat of reaction. But once the reaction starts, the heat of reaction is sufficient to continue the reaction. The halogens react in the following decreasing order ; $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- In general, the elements of first transition series tend to exist in low oxidation states. Chromium to zinc form stable difluorides and the other chlorides are also known.
- Since fluorine is the most electronegative element, the transition metals show highest oxidation states with fluorine. The highest oxidation states are found in TiX_4 (tetrahalides, $\text{X} = \text{F}, \text{Cl}, \text{Br}$ and I), VF_5 and CrF_6 .

- (iv) The +7 oxidation state for Mn is not shown by simple halides. However, MnO_3F is known in which the oxidation state of Mn is +7.
- (v) The tendency of fluorine to stabilise the highest oxidation state is due to either higher lattice enthalpy as in case of CoF_3 or higher bond enthalpy due to higher covalent bonds e.g., VF_5 and CrF_6 .
- (vi) Fluorides are relatively unstable in their low oxidation states. For example, vanadium form only VX_2 ($\text{X} = \text{Cl}, \text{Br}$ or I) and copper can form CuX ($\text{X} = \text{Cl}, \text{I}$). All copper (II) halides are known except the iodide. This is because, Cu^{2+} oxidises I^- to I_2 .



It has been observed that many copper (I) compounds are unstable in aqueous solution and they undergo disproportionation to Cu(II) and Cu(0) as :



Copper in +2 oxidation state is more stable than in +1 oxidation state. This can be explained on the basis of much larger negative hydration enthalpy ($\Delta_{\text{hyd}}H^\ominus$) of Cu^{2+} (aq) than Cu^+ , which is much more than compensates for the large energy required to remove the second electron i.e., second ionisation enthalpy of copper.

(H) IN METAL OXIDES AND OXOCATIONS.

- (i) The ability of oxygen to stabilize the highest oxidation state is demonstrated in their oxides. The highest oxidation states in their oxides coincides with the group number. For example, the highest oxidation state of scandium of group 3 is +3 in its oxides, Sc_2O_3 whereas the highest oxidation state of manganese of group 7 is +7, in Mn_2O_7 .
- (ii) Besides the oxides, oxocation of the metals also stabilise higher oxidation states. For example, V^{V} as VO_2^+ , V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+} .
- (iii) It may be noted that the ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. For example, manganese forms highest fluoride as MnF_4 whereas the highest oxide is Mn_2O_7 . This is due to the fact that oxygen has great ability to form multiple bonds to metals.
- (iv) The transition elements in the +2 and +3 oxidation states mostly form ionic bonds whereas with higher oxidation states, the bonds are essentially covalent e.g., in MnO_4^- all bonds are covalent. As the oxidation number of a metal increases, the ionic character of their oxides decrease. For example, in case of Mn, Mn_2O_7 is a covalent. In these higher oxides the acidic character is predominant. Thus CrO_3 gives H_2CrO_4 and $\text{H}_2\text{Cr}_2\text{O}_7$ and Mn_2O_7 gives HMnO_4 . **V_2O_5 is, however amphoteric though mainly acidic and with alkalis as well as acids gives VO_4^{3-} and VO_2^+ respectively.**

In general

Oxidation state	Nature of oxide/Hydroxide (d-block)
+1, +2, +3	Basic
+4	Amphoteric
+5, +6, +7, +8	Acidic

Except Cr_2O_3 = Amphoteric

(I) **FORMATION OF COLOURED IONS** : See coordination compound

(J) MAGNETIC PROPERTIES

It is interesting to note that when the various substances are placed in a magnetic field, they do not behave in a similar way i.e., they show different behaviour which are known as magnetic behaviour.

These are classified as :

- (i) **Paramagnetic substances.** The substances which are attracted by magnetic field are called paramagnetic substances and this character arises due to the presence of unpaired electrons in the atomic orbitals.
- (ii) **Diamagnetic substances.** The substances which are repelled by magnetic field are called diamagnetic substances and this character arises due to the presence of paired electrons in the atomic orbitals. Most of the compounds of transition elements are paramagnetic in nature and are attracted by the magnetic field.
- The transition elements involve the partial filling of d-sub-shells. Most of the transition metal ions or their compounds have unpaired electrons in d-sub-shell (from configuration d^1 to d^9) and therefore, they give rise to paramagnetic character.
- (iii) The magnetic moment arise only from the spin of the electrons. This can be calculated from the relation $\mu = \sqrt{n(n+2)}$ B.M. n = Number of unpaired electrons

Table : Calculated and Observed Magnetic Moments (BM)

Ion	Configuration	Unpaired electron(s)	Magnetic moment	
			Calculated	Observed
Sc ³⁺	3d ⁰	0	0	0
Ti ³⁺	3d ¹	1	1.73	1.75
Ti ²⁺	3d ²	2	2.84	2.76
V ²⁺	3d ³	3	3.87	3.86
Cr ²⁺	3d ⁴	4	4.90	4.80
Mn ²⁺	3d ⁵	5	5.92	5.96
Fe ²⁺	3d ⁶	4	4.90	5.3 – 5.5
Co ²⁺	3d ⁷	3	3.87	4.4 – 5.2
Ni ²⁺	3d ⁸	2	2.84	2.9 – 3.4
Cu ²⁺	3d ⁹	1	1.73	1.8 – 2.2
Zn ²⁺	3d ¹⁰	0	0	

(K) **FORMATION OF COMPLEXES :** See coordination compound

(L) **FORMATION OF INTERSTITIAL COMPOUNDS**

Transition metals form interstitial compounds with elements such as hydrogen, boron, carbon and nitrogen. The small atoms of these non-metallic elements (H, B, C, N, etc.) get trapped in vacant spaces of the lattices of the transition metal atoms as shown below.

e.g. WC, Fe₃C, TiH_{1.30 – 1.80}

Properties :

- (1) They are generally non-stoichiometric compound.
- (2) Neither typical ionic nor covalent
- (3) Harder than pure metal
- (4) High melting point than pure metal
- (5) Malleability and ductility less than pure metal
- (6) Chemically inert

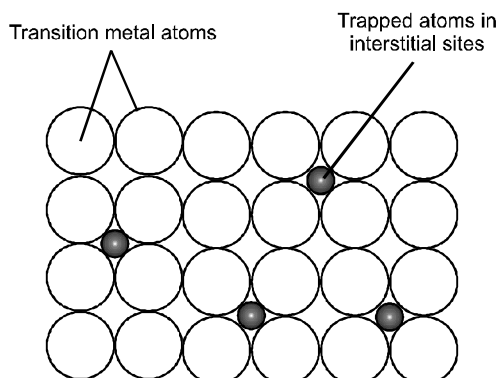


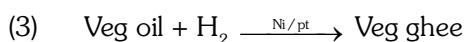
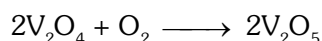
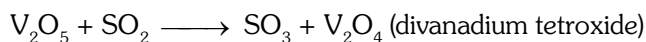
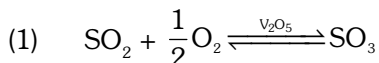
Figure showing formation of interstitial compounds

(M) CATALYTIC PROPERTIES

d-block metals or their compound act as catalyst in many reaction due to :

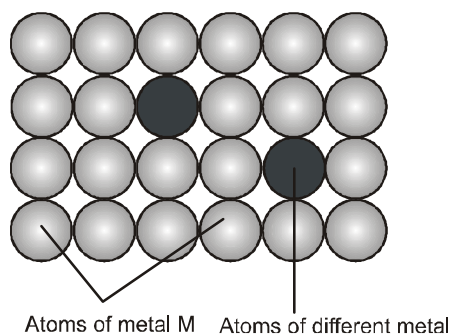
- (i) Possibility of variable oxidation state
- (ii) Presence of free valencies over metal surface (adsorption power)
- (iii) Presence of vacant d-orbital

e.g.



(N) ALLOY FORMATION :

Alloys are homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other metal. The alloys are generally formed by those atoms which have metallic radii within about 15% of each other. Transition metals form a large number of alloys. The transition metals are quite similar in size and therefore the atoms of one metal can substitute the atoms of other metal in its crystal lattice.



Alloy formation

Note : Fe, Co, Ni do not form amalgam with Hg (Due to large difference in size)

BEGINNER'S BOX-1

1. The general electronic configuration of d-block elements is $(n-1)d^{1-10} ns^{1-2}$. This generalisation has several exceptions mainly due to
 - (1) strong shielding of $(n-1)$ d-electrons
 - (2) very little energy difference between $(n-1)d$ and ns orbitals
 - (3) presence of unpaired electrons
 - (4) high energy difference between $(n-1)d$ and ns orbitals
2. Select group of transition elements
 - (1) Pb, Sc, V
 - (2) Pd, Cd, La
 - (3) Pd, La, Fe
 - (4) Zn, Pd, Bi
3. Which element is having lowest melting and boiling point :
 - (1) Ti
 - (2) Cu
 - (3) Zn
 - (4) Mn

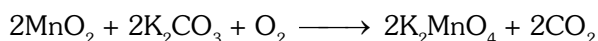
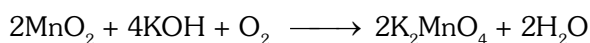
4. Density of which of the following element is highest
 (1) Pt (2) Hg (3) Mn (4) Cu
5. Not more than one oxidation state is shown by :
 (1) Mn (2) Cr (3) Fe (4) Sc
6. Consider the ions Fe^{2+} , Fe^{3+} , Cr^{2+} , Cr^{3+} , Mn^{2+} , Mn^{3+}
 (i) Strongest oxidising ion is
 (1) Fe^{2+} (2) Cr^{3+} (3) Mn^{3+} (4) Mn^{2+}
 (ii) Strongest reducing ion is
 (1) Fe^{2+} (2) Mn^{2+} (3) Cr^{2+} (4) Mn^{3+}
7. Which compound does exist
 (1) MnO_3F (2) $\text{K}_2[\text{CuI}_4]$ (3) MnF_7 (4) CrF_7
8. In the form of dichromate, Cr(VI) is a strong oxidising agent in acidic medium but Mo(VI) in MoO_3 and W(VI) in WO_3 are not because
 (1) Cr(VI) is more stable than Mo(VI) & W(VI)
 (2) Mo(VI) and W(VI) are less stable than Cr(VI)
 (3) H.O.S. of heavier members of group 6 of transition metals are more stable
 (4) L.O.S. of heavier members of group 6 of transition metals are more stable
9. By which of the following species, a transitional metal can brought in to its highest oxidation state
 (1) F_2 (2) Cl_2 (3) Br_2 (4) I_2

2.2 COMPOUNDS OF d-BLOCK ELEMENTS :

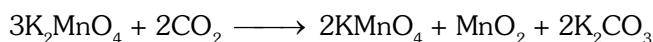
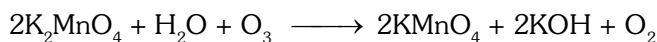
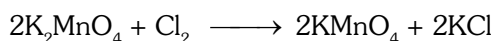
POTASSIUM PERMANGANATE (KMnO_4) :

(a) Preparation

This is the most important and well known salt of permanganic acid and is prepared from the pyrolusite ore. It is prepared by fusing pyrolusite ore either with KOH or K_2CO_3 in presence of atmospheric oxygen or any other oxidising agent such as KNO_3 . The fused mass turns green with the formation of potassium manganate, K_2MnO_4 .

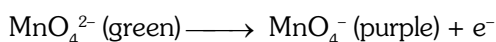


The fused mass is extracted with water and the solution is now treated with a current of chlorine or ozone or carbon dioxide to convert manganate into permanganate.

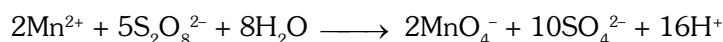


(disproportionate in acidic medium)

Commercially it is prepared by fusion of MnO_2 with KOH followed by electrolytic oxidation of manganate.



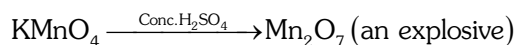
In the laboratory, a manganese(II) ion salt is oxidised by peroxodisulphate to permanganate



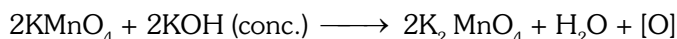
- (b) **Physical property :** It is purple coloured crystalline compound. It is moderately soluble in water at room temperature.

(c) Chemical property:

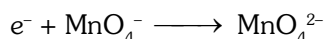
- **Effect of heating** $2\text{KMnO}_4 \xrightarrow{750\text{K}} \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$
- On treatment with concentrated H_2SO_4 (KMnO_4 is taken in excess), it forms manganese heptoxide via permanganyl sulphate which decomposes explosively on heating.



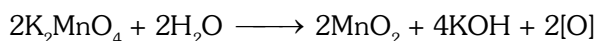
- Potassium permanganate is a powerful oxidising agent.
Potassium permanganate acts as an oxidising agent in alkaline, neutral or acidic solutions.
- In alkaline & neutral medium :
In strongly alkaline medium KMnO_4 is reduced to manganate.



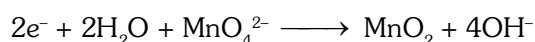
or



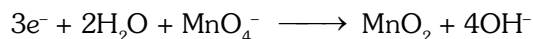
However if solution is dilute then K_2MnO_4 is converted into MnO_2 which appears as a brownish precipitate.



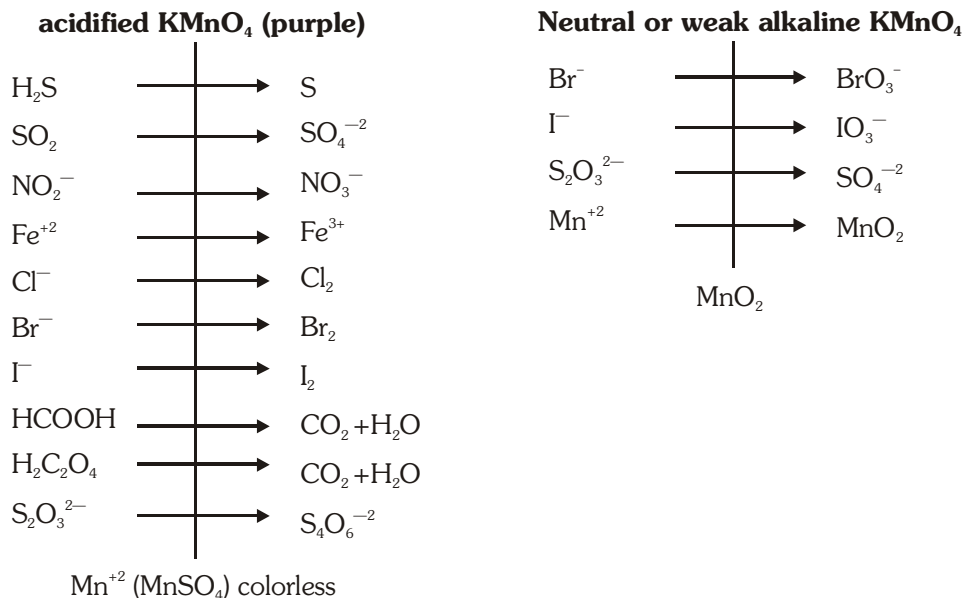
or



This type of behaviour is shown by KMnO_4 itself in neutral medium

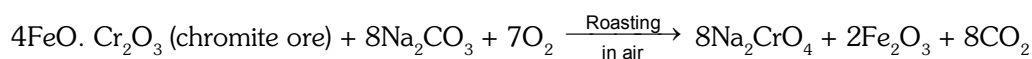


(d) Other reactions

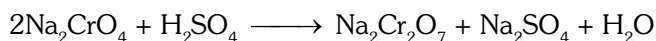


POTASSIUM DICHROMATE ($\text{K}_2\text{Cr}_2\text{O}_7$) :

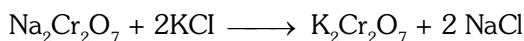
- (a) Preparation :** The chromite ore is roasted with sodium carbonate in presence of air in a reverberatory furnace



The roasted mass is extracted with water when Na_2CrO_4 goes into the solution leaving behind insoluble Fe_2O_3 . The solution is then treated with calculated amount of H_2SO_4 .



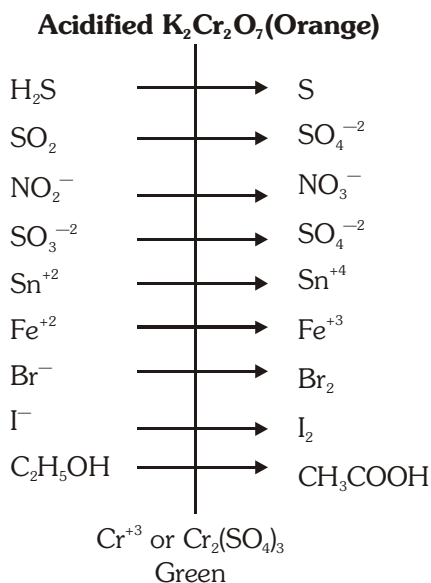
The solution is concentrated when less soluble Na_2SO_4 crystallises out. The solution is further concentrated when crystals of $\text{Na}_2\text{Cr}_2\text{O}_7$ are obtained. Hot saturated solution of $\text{Na}_2\text{Cr}_2\text{O}_7$ is then treated with KCl when orange red crystals of $\text{K}_2\text{Cr}_2\text{O}_7$ are obtained on crystallisation.



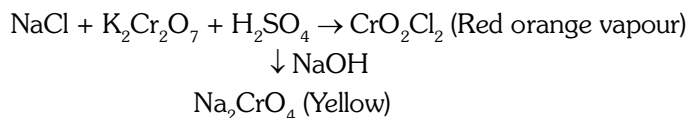
- $\text{K}_2\text{Cr}_2\text{O}_7$ is preferred over $\text{Na}_2\text{Cr}_2\text{O}_7$ as a primary standard in volumetric estimation because $\text{Na}_2\text{Cr}_2\text{O}_7$ is hygroscopic in nature but $\text{K}_2\text{Cr}_2\text{O}_7$ is not.
- $\text{CrO}_4^{2-} \xrightleftharpoons[\text{OH}^-]{\text{H}^+} \text{Cr}_2\text{O}_7^{2-}$
- Solubility of $\text{Na}_2\text{Cr}_2\text{O}_7$ is higher than $\text{K}_2\text{Cr}_2\text{O}_7$
- (b) **Physical property :** It is orange-red coloured crystalline compound. It is moderately soluble in cold water but freely soluble in hot water. It melts at 398°C .
- (c) **Chemical property :**
 - **Effect of heating :** On strongly heating, it decomposes with liberating oxygen.



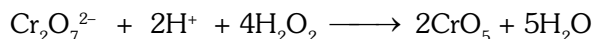
(d) **Other reactions**



1. **Chromyl chloride test :**



2. Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution reacts with H_2O_2 in an ethereal solution to give a deep blue solution due to the formation of CrO_5 .



Note : Reaction with $\text{C}_2\text{H}_5\text{OH}$ is used in drunken driver test.

f-BLOCK ELEMENTS

2.3 INNER TRANSITION ELEMENTS

The elements in which the additional electron enters in $(n - 2)f$ orbitals are called **inner transition elements** or **f-block elements**.

Position in The Periodic Table

The lanthanoids resemble with Yttrium in most of their properties. So it became necessary to accommodate all the fifteen elements together at one place. This has been done by placing the first element, lanthanum below yttrium and placing the remaining fourteen elements separately in the lower part of the periodic table.

Lanthanoid series (Z = 58 – 71) (Ce – Lu)

Actinide series (Z = 90 – 103) (Th – Lr)

2.4 LANTHANIDS (Rare Earths or Lanthanones)

- (i) Lanthanoids are reactive elements so do not found in free state in nature.
- (ii) Most important minerals for lighter Lanthanoids are – Monazite, cerites and orthite and for heavier lanthanoids – Gadolinite and Xenotime

(a) Electronic configuration

- (i) The general configuration of lanthanoids may be given as $[Xe] 4f^{1-14} 5s^2 5p^6 5d^{0-1} 6s^2$.

Atomic No.	Element	Symbol	Outer electronic configuration	
			Atomic	+3 ion
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^1$
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^2$
60.	Neodymium	Nd	$4f^4 6s^2$	$4f^3$
61.	Promethium	Pm	$4f^5 6s^2$	$4f^4$
62.	Samarium	Sm	$4f^6 6s^2$	$4f^5$
63.	Europium	Eu	$4f^7 6s^2$	$4f^6$
64.	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7$
65.	Terbium	Tb	$4f^9 6s^2$	$4f^8$
66.	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^9$
67.	Holmium	Ho	$4f^{11} 6s^2$	$4f^{10}$
68.	Erbium	Er	$4f^{12} 6s^2$	$4f^{11}$
69.	Thulium	Tm	$4f^{13} 6s^2$	$4f^{12}$
70.	Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{13}$
71.	Lutecium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14}$

- (ii) It is to be noted that filling of 4f orbitals in the atoms is not regular. A 5d electron appears in gadolinium (Z = 64) with an outer electronic configuration of $4f^7 5d^1 6s^2$ (and not $4f^8 6s^2$). This is because the 4f and 5d electrons are at about the same potential energy and that the atoms have a tendency to retain stable half filled configuration.
- (iii) On the other hand, the filling of f-orbitals is regular in tripositive ions.
- (iv) After losing outer electrons, the f-orbitals shrink in size and became more stable.
- (v) **Pm** is the only synthetic radioactive lanthanoid.

(b) Oxidation states

- (i) In lanthanoids +3 oxidation state is most common.
- (ii) **Except Ce, Tb, Nd, Dy, Pr** which also exhibit +4.
- (iii) **Sm, Eu, Tm, and Yb**, also exhibit +2 state.

(c) Magnetic Properties

- (i) In tripositive lanthanoid ions the number of unpaired electrons regularly increases from lanthanum to Gadolinium (0 to 7) and then continuously decreases upto lutecium (7 to 0).
- (ii) lanthanum and lutecium ions are diamagnetic, while all other tripositive lanthanoid ions are paramagnetic. (Exception – Neodymium is the most paramagnetic lanthanoid).
- (iii) Ce^{+4} and Yb^{+2} are also diamagnetic ions.

(d) Colour

- (i) The lanthanoid ions have unpaired electrons in their 4f orbitals. Thus these ions absorb visible region of light and undergo f–f transition and hence exhibit colour.
- (ii) The colour exhibited depends on the number of unpaired electrons in the 4f orbitals.
- (iii) The ions often with $4f^n$ configuration have similar colour to those ions having $4f^{14-n}$ configuration.
- (iv) Lanthanoid ions having $4f^0$, $4f^{14}$ are colourless.

(e) Lanthanoid Contraction

- (i) In the lanthanoid series with increasing atomic number, there is a progressive decrease in the size from lanthanum to lutecium or from La^{+3} to Lu^{+3} . This contraction in size is known as lanthanoid contraction.
- (ii) The general electronic configuration of these elements is $4f^{1-14}5s^2p^6d^{0-1}6s^2$. In these elements the added electron enters the deep seated f-orbitals and therefore experiences considerable pull by the nucleus.
- (iii) Due to very poor shielding effect of (n-2)f electrons, they exert very little screening effect on the outermost $6s^2$ electrons.

Hence with increasing atomic number, the enhanced nuclear charge leads to contraction in the size of atoms and ions.

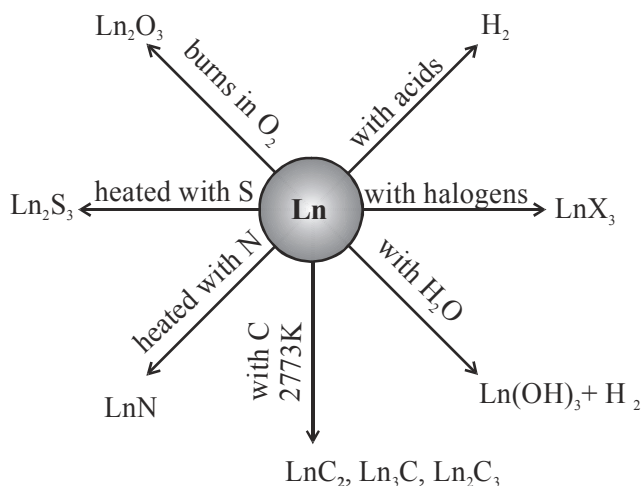
APPLICATIONS OF LANTHANOID CONTRACTION

- **Atomic size** : The ionic radii of Zr^{+4} is about 9% more than Ti^{+4} . Similar trend is not maintained on passing from the second to third transition series. The ionic radius of Hf^{+4} , instead of increasing (because of inclusion of one more electronic shell), decreases (or is virtually equal to Zr^{+4}) as a consequence of the lanthanoid contraction.

This explains the close similarities between the members of the second and third transition series than between the elements of the first and second series.

- **Basic nature of hydroxide** : The effect of lanthanoid contraction basic nature of hydroxide regularly decreases.
- **Similarity in properties of lanthanoid** : Due to small difference in size the chemical properties of lanthanoids are similar and their separation is difficult.

(e) Important reactions of Lanthanoids



Chemical reactions of the lanthanoids

Mish metal is an alloy of lanthanoids (Mainly cerium) and iron.

2.5 ACTINOIDS OR (5f - SERIES)

- The elements in which the extra electron enters 5f-orbitals of $(n - 2)$ th main shell are known as actinoids.
- The man-made eleven elements $\text{Np}_{93} - \text{Lr}_{103}$ are placed beyond uranium in the periodic table and are collectively called trans-uranium elements.
- Th, Pa and U first three actinoids are natural elements.

(a) Electronic Configuration

The general configuration of actinoids may be given as $[\text{Rn}] 5f^{1-14} 6d^{0,1,2} 7s^2$.

Atomic No.	Elements	Symbol	Outer Electronic Configuration	
			Atomic	+3 ion
90	Thorium	Th	$6d^2 7s^2$	$5f^1$
91	Proactinium	Pa	$5f^2 6d^1 7s^2$	$5f^2$
92	Uranium	U	$5f^3 6d^1 7s^2$	$5f^3$
93	Neptunium	Np	$5f^4 6d^1 7s^2$	$5f^4$
94	Plutonium	Pu	$5f^6 6d^0 7s^2$	$5f^5$
95	Americium	Am	$5f^6 6d^1 7s^2$	$5f^6$
96	Curium	Cm	$5f^7 6d^1 7s^2$	$5f^7$
97	Berkellium	Bk	$5f^9 6d^0 7s^2$	$5f^8$
98	Californium	Cf	$5f^{10} 6d^0 7s^2$	$5f^9$
99	Einsteinium	Es	$5f^{11} 6d^0 7s^2$	$5f^{10}$
100	Fermium	Fm	$5f^{12} 6d^0 7s^2$	$5f^{11}$
101	Mandeleevium	Md	$5f^{13} 6d^0 7s^2$	$5f^{12}$
102	Nobellium	No	$5f^{14} 6d^0 7s^2$	$5f^{13}$
103	Lowrencium	Lr	$5f^{14} 6d^1 7s^2$	$5f^{14}$

(b) Oxidation states

- In lanthanoids and actinoids +3 oxidation is the most common for both of the series of elements.
- This oxidation state becomes increasingly more stable as the atomic number increases in the actinide series.

- (iii) Highest oxidation states in the actinoids is +7 exhibited by Np_{93} & Pu_{94} , it is unstable.
- (iv) Highest stable oxidation state is +6 shown by U_{92} .

Other Properties

- **Physical appearance** : Actinides are silvery white metals. They get tarnished when exposed to the attack of alkalies.
- **Density** : All the actinoids except **thorium** and **americium** have high densities.
- **Colour** : Actinide ions are generally coloured. The colour of actinide ions depends upon the number of 5f-electrons. The ions containing no unpaired 5f-electrons (exactly full filled f-subshell) are colourless, as expected.
- **Ionisation energies** : Ionisation energies values of actinoids are low.
- **Electropositive character** : All the known actinide metals are **highly electropositive**. They resemble lanthanoid series in this respect.
- **Melting Boiling properties** : They have **high melting and boiling points**. They do not follow regular gradation of melting or boiling points with increase in atomic number.
- **Magnetic properties** : The actinide elements are paramagnetic due to the presence of unpaired electrons.
- **Radioactive nature** : All the actinoids are radioactive in nature.
- **Actinide contraction** : The size of atom/cation decrease regularly along the actinoids series. The steady decrease in ionic radii with increase in atomic number is referred to as **actinide contraction**. This is due to poor shielding of 5f-electrons.

Comparison of Lanthanides and Actinoids

Points of Resemblance :

- Both lanthanoids and actinoids show a dominant oxidation state of +3.
- Both are electropositive and act as strong reducing agents.
- Cations with unpaired electrons in both of them are paramagnetic.
- Most of the cations of lanthanoids and actinoids are coloured.
- Both of them show a steady decrease in their ionic radii along the series. Thus, lanthanoids show **lanthanoid contraction** and actinoids show **actinide contraction**.

POINTS OF DISTINCTION

Lanthanoids	Actinoids
1. Besides the most common oxidation state of +3 lanthanoids show +2 and +4 oxidation states in case of certain elements.	Besides the most common oxidation state of +3, actinoids show +4, +5 and +6 oxidation states in case of certain elements.
2. Lanthanoids have less tendency towards complex formation.	Actinoids have a stronger tendency towards complex formation.
3. Except promethium, they are non radioactive.	All the actinoids are radioactive.
4. Oxides and hydroxide of lanthanoids are less basic.	Oxides and hydroxides of actinoids are more basic

Some important uses of actinoids are as follows –

Thorium : Thorium is used in atomic reactors as fuel rods and in the treatment of cancer.

Uranium : Uranium is used as nuclear fuel. Its salts are used in glass industry (for imparting green colour). textile industry and also in medicines.

Plutonium : Plutonium is used as fuel for atomic reactors as well as in atomic bombs.

BEGINNER'S BOX-2

- KMnO_4 can be acidified by

(1) Dil. HCl (2) conc. H_2SO_4 (3) conc. HNO_3 (4) dil. H_2SO_4
- $\text{NaCl} \xrightarrow[\text{X}]{\text{conc. H}_2\text{SO}_4} \text{yellow green gas, X is}$

(1) $\text{K}_2\text{Cr}_2\text{O}_7$ (2) MnO_2 (3) KMnO_4 (4) both (2) & (3)
- $\text{X} \xrightarrow[\text{K}_2\text{Cr}_2\text{O}_7]{\text{conc. H}_2\text{SO}_4} \text{red brown vapours. X can be}$

(1) NaI (2) NaBr (3) Both (1) & (2) (4) None of these
- $\text{X} \xrightarrow[\text{black coloured ore}]{\text{KOH, air}} \text{Y} \xrightarrow[\text{dark green}]{\text{H}^+} \text{Z} + \text{X}$
an oxidising agent

True statement is

(1) X can't be MnO_2 (2) Y can be KMnO_4
 (3) Z can be K_2MnO_4 (4) step (1) is oxidation while step (ii) is disproportionation
- $\text{X} \xrightleftharpoons[\text{OH}^-]{\text{H}^+} \text{Y}; \text{Y} \xrightarrow{\text{SO}_2} \text{Z} + \text{SO}_4^{2-}$

X and Y are oxy anion of Cr than oxidation state of Cr in X, Y, Z will be respectively

(1) +3, +6, +6 (2) +6, +3, +6 (3) +6, +6, +6 (4) +6, +6, +3
- When KMnO_4 solution is added to oxalic acid, solution, the decolourisation is slow in beginning but become instantaneous after some time because

(1) CO_2 is a by product (2) Mn^{2+} acts as a catalyst
 (3) reaction is exothermic (4) MnO_4^- catalyzes the reaction
- The elements from cerium (At.No. 58) to lutetium (At.No. 71) in which 4f energy levels are filled up are called :

(1) lanthanides (2) rare earths (3) lanthanones (4) all the above
- Which of the following is a lanthanide :

(1) Ta (2) Rh (3) Th (4) Gd
- The element with the electronic configuraton $[\text{Xe}]^{54} 4f^{14} 5d^1 6s^2$ is a

(1) representative element (2) transition element
 (3) lanthanide (4) actinide
- Name the three lanthanides which show +2 oxidation state also :

(1) Sm, Tb, Gd (2) Sm, Eu, Yb (3) La, Gd, Lu (4) Yb, Pm, Sm

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7	8	9	
	Ans.	2	3	3	1	4	3,3	1	3	1	
BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	4	4	2	4	4	2	4	4	3	2

NCERT QUESTIONS (REASONING)

Q.1 Why do the transition elements have higher boiling & melting points ?

Ans. Because of having larger number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence stronger bonding between atoms. Hence strong metallic bonds between the atoms of these elements attribute to their high melting and boiling points.

Q.2 Give the main difference in oxidation states of transition elements & p-block elements.

Ans. (i) The variation of oxidation state in transition elements is in such a way that their oxidation state differ from each other by unity e.g. V^{+2} , V^{+3} , V^{+4} , V^{+5} . While in p block elements oxidation states normally differ by two due to inert pair effect.

(ii) Stability of higher oxidation state in transition elements increase down the group

e.g. Pt^{+4} is more stable than Pt^{+2}

While in p block elements lower oxidation state become increasingly stable down the group as result of inert pair effect.

Q.3 For the first series of transition metals the $E^\ominus$ values are

$E^\ominus$	V	Cr	Mn	Fe	Co	Ni	Cu
(M^{2+}/M)	-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

Explain the irregularity in the above values.

Ans. This is because of irregular variation of ionization energies ($IE_1 + IE_2$) and also the sublimation energies which are much less for manganese and vanadium

Q.4 Zinc does not show variable valency because of :

(A) complete 'd' sub-shell (B) inert pair effect (C) $4s^2$ sub-shell (D) none.

Ans. $Zn = [Ar]^{18} 3d^{10} 4s^2$. Zinc has completely filled d-sub-shell so removal of electron from completely filled 4d sub-shell would be quite difficult. Thus it does not show variable valency.

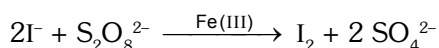
Q.5 Explain the blue colour of $CuSO_4 \cdot 5H_2O$.

Ans. Cu^{2+} ion ($3d^9$) absorbs red light from the visible region, for the promotion of 3d electrons, the ions reflect blue light and appear blue.

Q.6 How iron (III) catalyses the reaction between iodide & persulphate?

Ans. $2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$

$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$



EXERCISE-I (Conceptual Questions)**Build Up Your Understanding****d-BLOCK ELEMENTS**

- For a catalyst which condition is not essential :
 (1) Variable valency
 (2) High ionisation energy
 (3) Empty orbitals
 (4) Free valency on the surface
- To which of the following series the transition element from $Z = 39$ to $Z = 48$ belong :
 (1) 3d series (2) 4d series
 (3) 5d series (4) 6d series
- KMnO_4 on treatment with conc. H_2SO_4 forms a compound (X) which decomposes explosively on heating forming (Y). The (X) and (Y) are respectively
 (1) Mn_2O_7 , MnO_2 (2) Mn_2O , Mn_2O_3
 (3) MnSO_4 , Mn_2O_3 (4) Mn_2O_3 , MnO_2
- Which pair of ions is colourless :
 (1) Mn^{3+} , Co^{3+} (2) Fe^{3+} , Cr^{3+}
 (3) Zn^{2+} , Sc^{3+} (4) Ti^{2+} , Cu^{2+}
- $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (Ammonium dichromate) is used in fire works. The green coloured powder blown in air is :
 (1) Cr_2O_3 (2) CrO_2 (3) Cr_2O_4 (4) CrO_3
- $\text{Cr}_2\text{O}_7^{2-} \xrightleftharpoons[X]{X} 2\text{CrO}_4^{2-}$, X and Y are respectively
 (1) $X = \text{OH}^-$, $Y = \text{H}^+$ (2) $X = \text{H}^+$, $Y = \text{OH}^-$
 (3) $X = \text{OH}^-$, $Y = \text{H}_2\text{O}_2$ (4) $X = \text{H}_2\text{O}_2$, $Y = \text{OH}^-$
- During estimation of oxalic acid Vs KMnO_4 , self indicator is :
 (1) KMnO_4 (2) Oxalic acid
 (3) K_2SO_4 (4) MnSO_4
- The higher oxidation states of transition elements are found to be the combination with A and B, which are:
 (1) F, O (2) O, N
 (3) O, Cl (4) F, Cl
- Magnetic moment of x^{n+} is $\sqrt{24}$ B.M. Hence No. of unpaired electron and value of 'n' respectively. (Atomic number = 26)
 (1) 4, 3 (2) 3, 5
 (3) 4, 2 (4) 4, 1

- The product of oxidation of I^- with MnO_4^- in alkaline medium is :
 (1) IO_3^- (2) I_2 (3) IO^- (4) IO_4^-
- Copper becomes green when exposed to moist air for longer period.
 (1) Because of the formation of a layer of cupric oxide on the surface of copper
 (2) Because of the formation of a layer of basic carbonate of copper on the surface of copper
 (3) Because of the formation of a layer of cupric hydroxide on the surface of copper.
 (4) (1) and (3) both
- Which of the following oxide of chromium is amphoteric in nature
 (1) CrO (2) Cr_2O_3
 (3) CrO_3 (4) CrO_5
- Compared to Cu^{2+} having $3d^9$ configuration, Cu^+ having $3d^{10}$ configuration (aq. solution) :-
 (1) Is more stable
 (2) Is equally stable
 (3) Is less stable
 (4) Stability depends upon nature of copper salt
- Pick out the wrong statement :-
 (1) $\text{K}_2\text{Cr}_2\text{O}_7$ reduces ferric sulphate to ferrous sulphate
 (2) Iron do not form amalgam
 (3) Permanent magnet is made by an alloy called Alnico
 (4) In the Lathanides ionic radius decreases from La^{+3} to Lu^{+3}
- CrO_3 is red or orange in colour. The nature of oxide is :-
 (1) Acidic (2) Basic
 (3) Amphoteric (4) Neutral
- Cl_2 gas is obtained by various reactions but not by :
 (1) $\text{KMnO}_4 + \text{conc. HCl} \xrightarrow{\Delta}$
 (2) $\text{KCl} + \text{K}_2\text{Cr}_2\text{O}_7 + \text{conc. H}_2\text{SO}_4 \xrightarrow{\Delta}$
 (3) $\text{MnO}_2 + \text{conc. HCl} \xrightarrow{\Delta}$
 (4) $\text{KCl} + \text{F}_2 \xrightarrow{\Delta}$

17. Maximum magnetic moment is shown by :

- (1) d^5 (2) d^6
(3) d^7 (4) d^8

18. Disproportion can be shown by

- (1) MnO_4^{2-} in acidic medium
(2) Cu^+ in aqueous medium
(3) Cl_2 in alkaline medium
(4) All of these

19. The basic character of the transition metal monoxides follows the order :

(Atomic no. Ti = 22, V = 23, Cr = 24, Fe = 26)

- (1) $TiO > FeO > VO > CrO$
(2) $TiO > VO > CrO > FeO$
(3) $VO > CrO > TiO > FeO$
(4) $CrO > VO > FeO > TiO$

20. Which of the following reactions is used to estimate copper volumetrically ?

- (1) $2Cu^{2+} + 4F^- \longrightarrow Cu_2F_2 + F_2$
(2) $Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$
(3) $2Cu^{2+} + 2CNS^- + SO_2 + 2H_2O \longrightarrow Cu_2(CNS)_2 + H_2SO_4 + 2H^+$
(4) $2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$

21. Atomic size of gold is almost the same as that of silver. It is due to :

- (1) the same crystal structure of silver and gold
(2) almost the same electropositive character of the two metals
(3) transition metals contraction in a series
(4) the effect of lanthanide contraction

22. Which among the following statements is incorrect

- (1) In d-block elements oxidation state differ by unity.
(2) In p-block metals oxidation state differ by two units.
(3) In a group of p-block lower oxidation states are favoured by the heavier members.
(4) In a group of d-block higher oxidation states are favoured by the lighter member.

23. Which among the following order of oxidising character is correct—

- (1) $CrO_3 > MoO_3$ (2) $K_2Cr_2O_7 > KMnO_4$
(3) $Fe(CO)_5 > Mn(CO)_5$ (4) $V_2O_3 > V_2O_5$

24. Which of the following configurations of 3d series metals exhibits the largest number of oxidation states—

- (1) $[Ar] 3d^8 4s^2$ (2) $[Ar] 3d^{10} 4s^1$
(3) $[Ar] 3d^5 4s^2$ (4) $[Ar] 3d^7 4s^2$

25. Which of the following statement regarding interstitial compounds is incorrect—

- (1) They are chemically inert
(2) They are soft and nonconductive
(3) They retain metallic conductivity
(4) They have high melting point.

26. Which of the following pair of ions has same value of "spin-only" magnetic moment

- (1) Cu^+ , Cu^{2+} (2) Co^{3+} , Fe^{2+}
(3) Ti^{2+} , V^{2+} (4) Sc^{2+} , Zn^{+2}

f-BLOCK ELEMENTS

27. The elements from thorium (At.No. 90) to lawrencium (At.No. 103) in which 5f energy levels are filled up are called :

- (1) lanthanides (2) rare earths
(3) actinides (4) transuranics

28. Select the element in the following which does not show +4 oxidation state :

- (1) Ti (2) Zr
(3) La (4) Pt

29. With increase in atomic number the ionic radii of actinides :

- (1) contract slightly
(2) increase gradually
(3) show no change
(4) change irregularly

30. The general electronic configuration of lanthanide is :

- (1) $[Xe] 4f^{14} 5d^{0-1} 6s^2$
(2) $[Xe] 4f^{0-14} 5d^{1-2} 6s^1$
(3) $[Xe] 4f^{0-14} 5d^{0-1} 6s^{1-2}$
(4) None of these

- 31.** Cerium can show the oxidation state of +4 because
 (1) it resemble alkali metals
 (2) it has very low value of I.E.
 (3) of its tendency to attain noble gas configuration of xenon
 (4) of its tendency to attain $4f^7$ configuration
- 32.** In aqueous solution Eu^{+2} acts as :
 (1) an oxidising agent
 (2) reducing agent
 (3) can act as redox agent
 (4) None of these
- 33.** The maximum oxidation state shown by actinides is :
 (1) +6 (2) +7
 (3) +5 (4) +4
- 34.** The outer electronic configuration of gadolinium (At. No. 64) is :
 (1) $4f^7 5d^1 6s^2$ (2) $4f^8 5d^0 6s^2$
 (3) $4f^8 5d^1 6s^1$ (4) $4f^7 5d^0 6s^2$
- 35.** The most characteristic oxidation state of lanthanides is :
 (1) +2 (2) +3
 (3) +4 (4) none of these
- 36.** The common oxidation state of actinides is :
 (1) +4 (2) +3
 (3) +5 (4) +6
- 37.** Which of the following f - block elements, will change its group on emitting α -particle (alpha particle) :
 (1) $_{58}\text{Ce}$ (2) $_{70}\text{Lu}$
 (3) $_{90}\text{Th}$ (4) $_{92}\text{U}$
 Correct answer is :-
 (1) Only 1 and 3 (2) Only 2 and 4
 (3) All (4) None
- 38.** Which of the following pair have almost similar size
 (1) Ti_{22} and Zr_{40} (2) Nb_{41} and Ta_{73}
 (3) Y_{39} and La_{57} (4) Ca_{20} and Ir_{31}
- 39.** An increase in both atomic and ionic radii with atomic number occurs in any group of the periodic table. In accordance of this the ionic radii of Ti (IV) and Zr (IV) ions are $0.68 \text{ \AA}$ and $0.74 \text{ \AA}$ respectively but for Hf (IV) ion the ionic radius is $0.75 \text{ \AA}$, which is almost the same as that for Zr (IV) ion. This is due to :-
 (1) greater degree of covalency in compounds of Hf^{4+}
 (2) Lanthanide contraction
 (3) Difference in the co-ordination number of Zr^{+4} and Hf^{+4} in their compounds
 (4) Actinide contraction

EXERCISE-I (Conceptual Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	2	1	3	1	1	1	1	3	1	2	2	3	1	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	2	1	4	2	4	4	4	1	3	2	2	3	3	1	4
Que.	31	32	33	34	35	36	37	38	39						
Ans.	3	2	2	1	2	2	1	2	2						

EXERCISE-II (Previous Year Questions)**AIPMT/NEET & AIIMS (2006-2018)****AIPMT 2006**

- In which of the following pairs are both the ions coloured in aqueous solution ?
(At. no. : Sc = 21, Ti = 22, Ni = 28, Cu = 29, Co = 27)
(1) Ni^{2+} , Cu^+ (2) Ni^{2+} , Ti^{3+}
(3) Sc^{3+} , Ti^{3+} (4) Sc^{3+} , Co^{2+}
- More number of oxidation states are exhibited by the actinoids than by the lanthanoids. The main reason for this is
(1) more active nature of the actinoids
(2) more energy difference between 5f and 6d orbitals than that between 4f and 5d orbitals
(3) lesser energy difference between 5f and 6d orbitals than that between 4f and 5d orbitals
(4) greater metallic character of the lanthanoids than that of the corresponding actinoids

AIPMT 2007

- Which one of the following ions is the most stable in aqueous solution
(1) V^{3+} (2) Ti^{3+} (3) Mn^{3+} (4) Cr^{3+}
- Identify the incorrect statement among the following
(1) Lanthanoid contraction is the accumulation of successive shrinkages.
(2) As a result of lanthanoid contraction, the properties of 4d series of the transition elements have no similarities with the 5d series of elements.
(3) Shielding power of 4f electrons is quite weak.
(4) there is a decrease in the radii of the atoms or ions as one proceeds from La to Lu.

AIPMT 2008

- The correct order of decreasing second ionisation enthalpy of Ti (22), V (23), Cr (24) and Mn (25) is:-
(1) $\text{Mn} > \text{Cr} > \text{Ti} > \text{V}$ (2) $\text{Ti} > \text{V} > \text{Cr} > \text{Mn}$
(3) $\text{Cr} > \text{Mn} > \text{V} > \text{Ti}$ (4) $\text{V} > \text{Mn} > \text{Cr} > \text{Ti}$

AIPMT 2009

- Which one of the elements with the following outer orbital configurations may exhibit the largest number of oxidation states?
(1) $3d^2 4s^2$ (2) $3d^3 4s^2$ (3) $3d^5 4s^1$ (4) $3d^5 4s^2$

AIPMT 2010

- Which of the following oxidation states is the most common among the lanthanoids :-
(1) 2 (2) 5 (3) 3 (4) 4
- Which of the following pairs has the same size ?
(1) Zn^{2+} , Hf^{4+} (2) Fe^{2+} , Ni^{2+}
(3) Zr^{4+} , Ti^{4+} (4) Zr^{4+} , Hf^{4+}
- Which one of the following ions has electronic configuration $[\text{Ar}]3d^6$? (At. nos. Mn = 25, Fe = 26, Co = 27, Ni = 28)
(1) Co^{3+} (2) Ni^{3+} (3) Mn^{3+} (4) Fe^{3+}
- Which of the following ions will exhibit colour in aqueous solutions ?
(1) Sc^{3+} (z = 21) (2) La^{3+} (z = 57)
(3) Ti^{3+} (z = 22) (4) Lu^{3+} (z = 71)

AIIMS 2010

- Uranium can be obtained by the electrolysis of:-
(1) UF_6 (2) UF_4 (3) UCl_6 (4) UI_6

AIPMT Pre. 2011

- For the four successive transition elements (Cr, Mn, Fe and Co), the stability of +2 oxidation state in gaseous state will be there in which of the following order ?
(1) $\text{Mn} > \text{Fe} > \text{Cr} > \text{Co}$
(2) $\text{Fe} > \text{Mn} > \text{Co} > \text{Cr}$
(3) $\text{Co} > \text{Mn} > \text{Fe} > \text{Cr}$
(4) $\text{Cr} > \text{Mn} > \text{Co} > \text{Fe}$
(At. nos. Cr = 24, Mn = 25, Fe = 26, Co = 27)

AIIMS 2011

- When KMnO_4 reacts with Br_2 in weak alkaline medium gives bromate ion. Then oxidation state of Mn changes from +7 to:
(1) +6 (2) +4 (3) +3 (4) +2

AIPMT Pre. 2012

- Which of the statements is not true?
(1) $\text{K}_2\text{Cr}_2\text{O}_7$ solution in acidic medium is orange
(2) $\text{K}_2\text{Cr}_2\text{O}_7$ solution becomes yellow on increasing the pH beyond 7
(3) On passing H_2S through acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution, a milky colour is observed
(4) $\text{Na}_2\text{Cr}_2\text{O}_7$ is preferred over $\text{K}_2\text{Cr}_2\text{O}_7$ in volumetric analysis

AIPMT Mains 2012

15. Which one of the following does not correctly represent the correct order of the property indicated against it ?
(1) $Ti < V < Cr < Mn$: increasing melting points
(2) $Ti < V < Mn < Cr$: increasing 2nd ionization enthalpy
(3) $Ti < V < Cr < Mn$: increasing number of oxidation states
(4) $Ti^{3+} < V^{3+} < Cr^{3+} < Mn^{3+}$: increasing magnetic moment
16. The catalytic activity of transition metals and their compounds is ascribed mainly to :-
(1) their ability to adopt variable oxidation states
(2) their chemical reactivity
(3) their magnetic behaviour
(4) their unfilled d-orbitals

AIIMS 2012

17. Magnetic moment of Cr^{2+} is nearest to :-
(1) Fe^{2+} (2) Mn^{2+} (3) Co^{+2} (4) Ni^{2+}

AIIMS 2013

18. Which of the following element has lowest melting point :-
(1) Cr (2) Fe (3) Ni (4) Cu
19. Maximum no. of unpaired electrons are present in :-
(1) Gd^{+3} (2) Yb^{+2} (3) Tb^{+2} (4) Pm^{+3}
20. $K_2Cr_2O_7$ in acidic medium converts into :-
(1) Cr^{2+} (2) Cr^{3+} (3) Cr^{4+} (4) Cr^{+5}
21. Which of the following metal ion forms unstable complex with CN^- :-
(1) $Ag(I)$ (2) $Zn(II)$ (3) $Cu(II)$ (4) $Cr(II)$
22. Which of the following ion does not exist ?
(1) $[CuI_4]^{2-}$ (2) VO_4^{3-} (3) WO_4^{2-} (4) CrO_4^{2-}

AIPMT 2015

23. Magnetic moment 2.84 B.M. is given by :-
(At. no.), Ni = 28, Ti = 22, Cr = 24, Co = 27)
(1) Ti^{3+} (2) Cr^{2+} (3) Co^{2+} (4) Ni^{2+}
24. Which of the following processes does not involve oxidation of iron ?
(1) Decolourization of blue $CuSO_4$ solution by iron
(2) Formation of $Fe(CO)_5$ from Fe
(3) Liberation of H_2 from steam by iron at high temperature
(4) Rusting of iron sheets

25. Because of lanthanoid contraction, which of the following pairs of elements have nearly same atomic radii ? (Numbers in the parenthesis are atomic numbers).
(1) Zr (40) and Nb (41)
(2) Zr (40) and Hf (72)
(3) Zr (40) and Ta (73)
(4) Ti (22) and Zr (40)

AIIMS 2015

26. Highly unstable species is
(1) $Sc(II)$ (2) $Ti(II)$
(3) $Co(II)$ (4) $V(II)$
27. Which of the following is diamagnetic
(1) Aurum (2) Tungsten
(3) Palladium (4) Niobium

NEET-I 2016

28. Which one of the following statements is correct when SO_2 is passed through acidified $K_2Cr_2O_7$ solution ?
(1) The solution turns blue
(2) The solution is decolourized
(3) SO_2 is reduced
(4) Green $Cr_2(SO_4)_3$ is formed
29. The electronic configurations of Eu (Atomic No 63), Gd (Atomic No 64) and Tb (Atomic No. 65) are
(1) $[Xe]4f^76s^2$, $[Xe]4f^8 6s^2$ and $[Xe]4f^85d^16s^2$
(2) $[Xe]4f^75d^16s^2$, $[Xe]4f^7 5d^1 6s^2$ and $[Xe]4f^96s^2$
(3) $[Xe]4f^65d^16s^2$, $[Xe]4f^75d^16s^2$ and $[Xe]4f^85d^16s^2$
(4) $[Xe]4f^76s^2$, $[Xe]4f^75d^16s^2$ and $[Xe]4f^96s^2$

NEET-II 2016

30. Which one of the following statements related to lanthanons is **incorrect** ?
(1) All the lanthanons are much more reactive than aluminium
(2) $Ce(+4)$ solutions are widely used as oxidizing agent in volumetric analysis
(3) Europium shows +2 oxidation state.
(4) The basicity decreases as the ionic radius decreases from Pr to Lu.

AIIMS 2016

31. Which of the following is ferromagnetic :-
 (1) U (2) Co
 (3) Cr (4) Cu
32. Aquaregia convert :-
 (1) Pt to $[\text{PtCl}_4]^{-2}$ (2) Ag to AgCl
 (3) Pt to PtCl_2 (4) Au to $[\text{AuCl}_4]^{-}$
33. Which of the following can convert Cl^- into Cl_2 :-
 (1) KMnO_4 (2) H_2SO_3
 (3) $\text{Fe}_2(\text{SO}_4)_3$ (4) HIO_3
34. Which of the following Lanthanoid show yellow colour :-
 (1) La^{+3} (2) Yb^{+3}
 (3) Lu^{+3} (4) Ce^{+4}

NEET(UG) 2017

35. Name the gas that can readily decolourise acidified KMnO_4 solution :
 (1) SO_2 (2) NO_2 (3) P_2O_5 (4) CO_2
36. HgCl_2 and I_2 both when dissolved in water containing I^- ions the pair of species formed is :
 (1) HgI_2, I^- (2) $\text{HgI}_4^{2-}, \text{I}_3^-$
 (3) $\text{Hg}_2\text{I}_2, \text{I}^-$ (4) $\text{HgI}_2, \text{I}_3^-$
37. The reason for greater range of oxidation states in actinoids is attributed to :-
 (1) actinoid contraction
 (2) 5f, 6d and 7s levels having comparable energies
 (3) 4f and 5d levels being close in energies
 (4) the radioactive nature of actinoids

AIIMS 2017

38. Gadolinium is :-
 (1) Ferromagnetic
 (2) Anti ferromagnetic
 (3) Ferrimagnetic
 (4) Diamagnetic
39. Which of the following pair contains all diamagnetic ions.
 (1) Yb^{+2} & Lu^{+3} (2) Ce^{+4} & Pr^{+4}
 (3) Dy^{+3} & Lu^{+3} (4) Lu^{+3} & Gd^{+3}

40. Which of the following is incorrect about interstitial compound.

- (1) they have high melting points in comparison to pure metals.
 (2) they are very hard
 (3) they retain metallic conductivity
 (4) they are chemically very reactive

41. Which of the following does not decolourises acidic KMnO_4 solution.

- (1) KI & NaNO_2
 (2) NaNO_3 & $\text{Na}_2\text{C}_2\text{O}_4$
 (3) Na_2SO_4 & $\text{Na}_2\text{C}_2\text{O}_4$
 (4) I_2 & NaNO_3

42. Select the incorrect statement about iodide of Millon's base.

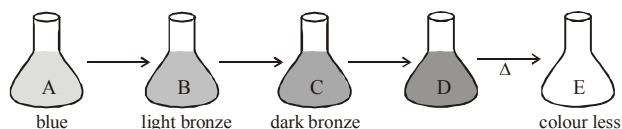
- (1) it is formed by the reaction $\text{K}_2[\text{HgI}_4] + \text{KOH} + \text{NH}_4^+$ solution

- (2) its formula $\left[\text{Hg} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{NH}_2 \diagup \end{array} \text{Hg} \right] \text{I}$

- (3) it is a brown ppt. but give test of complex cation I^- ions.

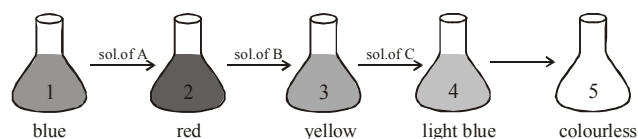
- (4) it is a Nesler's reagent of alkaines solution of $\text{K}_2[\text{HgI}_4]$

43. Which of the following will not be present in last flask during the iodometric titration of Cu^{+2}



- (1) starch (2) Cu_2I_2
 (3) I_2 (4) $\text{Na}_2\text{S}_2\text{O}_3$

44. In iodometric titration of Cu^{+2} .



Select the correct statement.

- (1) the colour of solution 2 is due to Iodine
 (2) the colour of solution 2 & solution 4 are due to the same ions.
 (3) solution 4 on strongly heating gives colourless solution 5.
 (4) None of these

NEET(UG) 2018

45. Which one of the following ions exhibits d-d transition and paramagnetism as well ?

- (1) CrO_4^{2-} (2) $\text{Cr}_2\text{O}_7^{2-}$
 (3) MnO_4^- (4) MnO_4^{2-}

46. Match the metal ions given in Column I with the spin magnetic moments of the ions given in Column II and assign the **correct** code :

Column I

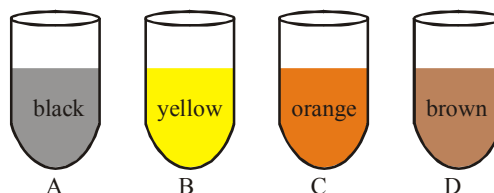
Column II

- | | |
|---------------------|----------------------|
| a. Co^{3+} | i. $\sqrt{8}$ B.M. |
| b. Cr^{3+} | ii. $\sqrt{35}$ B.M. |
| c. Fe^{3+} | iii. $\sqrt{3}$ B.M. |
| d. Ni^{2+} | iv. $\sqrt{24}$ B.M. |
| | v. $\sqrt{15}$ B.M. |

- | | a | b | c | d |
|-----|-----|----|-----|-----|
| (1) | iv | v | ii | i |
| (2) | i | ii | iii | iv |
| (3) | iv | i | ii | iii |
| (4) | iii | v | i | ii |

AIIMS 2018

47. Which of the following elements have least difference in E^0 value of M^{+2}/M :-
 (1) V & Mn (2) Mn & Fe
 (3) Fe & Co (4) Co & Ni
48. Violet color of glass is due to :-
 (1) K(I) (2) Mn(IV) (3) I_2 (4) Cr(III)
49. In which compound oxidation state not changed in acidic & basic medium :-
 (1) MnO_4^- (2) CrO_4^{2-}
 (3) FeO_4^{2-} (4) MnO_4^{2-}
50. Which can displace Al from Alum :-
 (1) Mn (2) Tl
 (3) Sc (4) In
51. Which shows least number of oxidation states ?
 (1) Mn (2) Th
 (3) Cr (4) Np
52. Spin only magnetic moment of a divalent metal ion having total 23 electrons :-
 (1) 5.9 (2) 5.2
 (3) 4.0 (4) 5.0
53. In salts of Co, Sb, Sn & Cd, H_2S was added. The colour of the precipitates obtained were as follows



Which set is correct for its colour of its sulphide:-

- | | |
|----------|----------|
| (1) A-Co | (2) B-Sb |
| (3) C-Sn | (4) D-Cd |
54. The colour of compound formed when KMnO_4 is fused with KOH :-
 (1) Green (2) Black
 (3) Brown (4) Pale Pink
55. In which of the following conversion Blue colour is appeared.
 (1) $\text{MnO}_4^- + \text{SO}_2 \longrightarrow$
 (2) $\text{Cr}_2\text{O}_7^{2-} + \text{KI} \longrightarrow$
 (3) $\text{K}_2\text{Cr}_2\text{O}_7 + \text{NaCl} + \text{conc. H}_2\text{SO}_4 \longrightarrow$
 (4) $\text{CuSO}_4 + \text{KI} + \text{Starch} \longrightarrow$
56. Which of the following pair is soluble in excess NH_4OH
 (1) $\text{Zn}(\text{OH})_2, \text{Pb}(\text{OH})_2$
 (2) $\text{Zn}(\text{OH})_2, \text{Sn}(\text{OH})_2$
 (3) $\text{Cd}(\text{OH})_2, \text{Zn}(\text{OH})_2$
 (4) $\text{Be}(\text{OH})_2, \text{Cd}(\text{OH})_2$

EXERCISE-II (Previous Year Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	3	4	2	3	4	3	4	1	3	2	1	2	4	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	1	1	4	1	2	3	1	4	2	2	1	3	4	4	1
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	2	4	1	4	1	2	2	1	1	4	4	4	3	3	4
Que.	46	47	48	49	50	51	52	53	54	55	56				
Ans.	1	1	2	2	3	2	1	1	1	4	3				

EXERCISE-III (Analytical Questions)

- The correct order of ionic radii of Y^{3+} , La^{3+} , Eu^{3+} and Lu^{3+} is
(1) $Lu^{3+} < Eu^{3+} < La^{3+} < Y^{3+}$
(2) $La^{3+} < Eu^{3+} < Lu^{3+} < Y^{3+}$
(3) $Y^{3+} < La^{3+} < Eu^{3+} < Lu^{3+}$
(4) $Y^{3+} < Lu^{3+} < Eu^{3+} < La^{3+}$
- Among the following series of transition metal ions, the one where all metal ions have $3d^2$ electronic configuration is :-
(1) Ti^{2+} , V^{3+} , Cr^{4+} , Mn^{5+}
(2) Ti^{2+} , V^{2+} , Cr^{3+} , Mn^{4+}
(3) Ti^{+} , V^{4+} , Cr^{6+} , Mn^{7+}
(4) Ti^{4+} , V^{3+} , Cr^{2+} , Mn^{3+}
- The aqueous solution containing which one of the following ions will be colourless :-
[Atomic n : Sc = 21, Fe = 26, Ti = 22, Mn = 25]
(1) Fe^{2+} (2) Mn^{2+}
(3) Ti^{3+} (4) Sc^{3+}
- The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is
(1) +4 (2) +6 (3) +2 (4) +3
- The lanthanide contraction is responsible for the fact that
(1) Zr and Y have about the same radius
(2) Zr and Nb have similar oxidation state
(3) Zr and Hf have about the same radius
(4) Zr and Zn have the same oxidation state
- Which one of the following nitrates will leave behind a metal on strong heating ?
(1) Copper nitrate (2) Manganese nitrate
(3) Silver nitrate (4) Ferric nitrate
- Excess of KI reacts with $CuSO_4$ solution and then $Na_2S_2O_3$ solution is added to it. Which of the statements is incorrect for this reaction :-
(1) $Na_2S_2O_3$ is oxidised
(2) CuI_2 is formed
(3) Cu_2I_2 is formed
(4) Evolved I_2 is reduced
- In which of the following oxidation state of Mn is six
(1) K_2MnO_4 (2) MnO_2
(3) $KMnO_4$ (4) MnO_4^{-1}
- Which has maximum magnetic moment :-
(1) Co^{+2} (2) Mn^{+3}
(3) Mn^{+2} (4) Cr^{+3}

Check Your Understanding

- Atomic number 21, shows the oxidation states
(1) +1 (2) +3 (3) -1 (4) +5
- Transition element makes complex compound due to -
(1) Presence of empty d-orbital
(2) large size
(3) Variable valency
(4) presence of $2e^-$
- Lanthanoid contraction is caused due to
(1) the same effective nuclear charge from Ce to Lu
(2) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge
(3) the appreciable shielding on outer electrons by 4f electrons from the nuclear charge
(4) the appreciable shielding on outer electrons by 5d electrons from the nuclear charge
- $KMnO_4$ is a strong oxidizing agent in acid medium. To provide acid medium H_2SO_4 is used instead of HCl. This is because
(1) H_2SO_4 is a stronger acid than HCl
(2) HCl is oxidized by $KMnO_4$ to Cl_2
(3) H_2SO_4 is a dibasic acid
(4) rate is faster in the presence of H_2SO_4
- When hydrogen peroxide is added to acidified potassium dichromate, a blue colour is produced due to formation of
(1) CrO_3 (2) Cr_2O_3
(3) CrO_5 (4) CrO_4^{2-}
- Identify the incorrect statement among the following
(1) 4f and 5f orbitals are equally shielded.
(2) d-Block elements show irregular and erratic chemical properties among themselves.
(3) La and Lu have partially filled d orbitals and no other partially filled orbitals.
(4) The chemistry of various lanthanoids is very similar.
- The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because
(1) due to less energy difference between 6d & 5f
(2) the 5f orbitals are more buried than the 4f orbitals
(3) there is a similarity between 4f and 5f orbitals in their angular part of the wave function
(4) the actinoids are more reactive than the lanthanoids.

17. In $\text{Cr}_2\text{O}_7^{-2} \longrightarrow \text{CrO}_4^{-2}$ reaction the change in oxidation number is :-
 (1) +3 (2) -3 (3) 2 (4) 0
18. Which of the following properties of Zr and Hf can be explained due to lanthanide contraction :-
 (1) Radius of Zr and Hf is same
 (2) Their EN is same
 (3) They are f-block elements
 (4) All
19. Similar sizes of second and third transition elements can be explained on the basis of :-
 (1) Inert-pair effect
 (2) Screening effect
 (3) Lanthanide contraction
 (4) Increasing effective nuclear charge
20. Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is **incorrect**?
 (1) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.
 (2) Ferrous oxide is more basic in nature than the ferric oxide.
 (3) Ferrous compounds are relatively more ionic than the corresponding ferric compounds.
 (4) Ferrous compounds are less volatile than the corresponding ferric compounds.
21. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest positive $E_{\text{M}^{3+}/\text{M}^{2+}}^0$ value ?
 (1) Cr(Z = 24) (2) Mn(Z = 25)
 (3) Fe (Z = 26) (4) Co(Z = 27)
22. Which of the following metal cation is reduced from its higher oxidation state (+2) to (+1) by both KI solution and excess of KCN solution ?
 (1) Zn^{2+} (2) Hg^{2+} (3) Cu^{2+} (4) None
23. A test tube containing a nitrate and another containing a bromide and MnO_2 are treated with concentrated H_2SO_4 . The reddish brown fumes evolved are passed through water. The water will be coloured by :-
 (1) The nitrate (2) The bromide
 (3) Both (4) None of the two
24. Cr^{2+} is reducing in nature because—
 (1) In Cr^{2+} , configuration changes from d^4 to d^3 to achieve half filled t_{2g} .
 (2) Cr^{2+} gain an electron to achieve d^5 configuration
 (3) Cr^{2+} give an electron to achieve d^5 configuration
 (4) In Cr^{2+} configuration changes from d^4 to d^3 to achieve half filled d-subshell.
25. Highest stable Mn fluoride is MnF_4 where as highest Mn oxide is Mn_2O_7 due to—
 (1) O atom is smaller the F.
 (2) Oxygen has ability to form multiple bonds
 (3) Mn^{7+} does not exist
 (4) F can not-stabilise higher oxidation states.
26. Which among the following order of oxidising power is correct—
 (1) $\text{CrO}_4^- < \text{MoO}_4^- < \text{WO}_4^-$
 (2) $\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$
 (3) $\text{CrO}_3 < \text{MnO}_2 < \text{Fe}_2\text{O}_3$
 (4) $\text{Pb}^{4+} < \text{Sn}^{4+} < \text{C}^{4+}$
27. Cu^+ ion is not stable in aqueous solution, due to—
 (1) d^{10} configuration
 (2) disproportionation
 (3) less charge
 (4) pseudo inert gas configuration

EXERCISE-III (Analytical Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	1	4	4	3	3	2	1	3	2	1	2	2	3	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27			
Ans.	1	4	1	3	1	4	3	2	1	2	2	2			

EXERCISE-IV (Assertion & Reason)**Target AIIMS****Directions for Assertion & Reason questions**

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
(B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
(C) If Assertion is True but the Reason is False.
(D) If both Assertion & Reason are false.

1. **Assertion** : 1st ionisation potential of mercury is greater than cadmium
Reason : Hg has stable electronic configuration ($5d^{10} 6s^2$)
(1) A (2) B (3) C (4) D
2. **Assertion** : Zr and Hf have about the same atomic radius.
Reason : Zr and Hf lies in the same group.
(1) A (2) B (3) C (4) D
3. **Assertion** : Zn, Cd, Hg are non-transition elements while Cu, Ag, Au are transition element
Reason : In Zn, Cd, Hg ($n - 1$)d orbitals are completely filled in their atomic state where as in Cu, Ag, Au they are incomplete.
(1) A (2) B (3) C (4) D
4. **Assertion** : Cu^+ is more stable than Cu^{+2}
Reason : ΔIP is greater than 16 eV
(1) A (2) B (3) C (4) D
5. **Assertion** : $KMnO_4$ is dark pink coloured compound
Reason : In the $KMnO_4$ charge transfer spectrum occurs.
(1) A (2) B (3) C (4) D
6. **Assertion** : Hg is the only metal which is liquid at $0^\circ C$.
Reason : It has very high IP and weak metallic bond
(1) A (2) B (3) C (4) D
7. **Assertion** : Valency of transition elements is variable
Reason : Energy of ns and $(n-1)d$ orbital is almost same.
(1) A (2) B (3) C (4) D
8. **Assertion** : Melting point of Mn less than that of Fe
Reason : Mn has less number of unpaired e^- than Fe in atomic state
(1) A (2) B (3) C (4) D
9. **Assertion** : Solution of Na_2CrO_4 in water is intensely coloured.
Reason : Ox. state of Cr in Na_2CrO_4 is +6.
(1) A (2) B (3) C (4) D
10. **Assertion** : Ce^{+4} acts as oxidising agent in aqueous medium
Reason : +4 is common oxidation state of lanthanides
(1) A (2) B (3) C (4) D
11. **Assertion** : Neptunium is transuranic element.
Reason : It is heavier than uranium
(1) A (2) B (3) C (4) D
12. **Assertion** : $La(OH)_3$ is more basic than $Lu(OH)_3$
Reason : Lanthanum is d-block element
(1) A (2) B (3) C (4) D
13. **Assertion** : Actinides show much higher range of oxidation states
Reason : Energy difference between 5f and 6d orbitals is large
(1) A (2) B (3) C (4) D
14. **Assertion** : All the lanthanide elements exhibits a common oxidation state of +3 in their compounds.
Reason : The atoms of the lanthanide elements contains three electron in their outermost shell.
(1) A (2) B (3) C (4) D

15. **Assertion:-** $K_2Cr_2O_7$ is used as a primary standard in volumetric analysis.
Reason:- It has a good solubility in water.
 (1) A (2) B (3) C (4) D
16. **Assertion:-** Change in colour of acidic solution of potassium dichromate by breath is used to test drunk drivers.
Reason:- Change in colour is due to the complexation of alcohol with potassium dichromate.
 (1) A (2) B (3) C (4) D
17. **Assertion:-** Eu^{2+} & Yb^{2+} are reducing agents for their ions.
Reason:- Both ions have stable half filled configuration.
 (1) A (2) B (3) C (4) D
18. **Assertion :-** MnO_2 is anti ferromagnetic in nature.
Reason :- In MnO_2 , equal number of domain are aligned with parallel and antiparallel spin.
 (1) A (2) B (3) C (4) D

19. **Assertion :-** La_2O_3 is basic nature.
Reason :- La in aqueous solution gives $La(OH)_3$
 (1) A (2) B (3) C (4) D
20. **Assertion :-** $FeCl_3$ does not affect iodometric titration of $CuSO_4$ Solution
Reason :- FeI_3 is formed.
 (1) A (2) B (3) C (4) D
21. **Assertion :-** Actinoids can posses +4 O.S. more easily then lanthanoid.
Reason :- 4f, 5d, 6s have almost same energy levels.
 (1) A (2) B (3) C (4) D
22. **Assertion :-** UF_6 is more covalent than UF_4 .
Reason :- Fluorine is smaller in size.
 (1) A (2) B (3) C (4) D

EXERCISE-IV (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	2	3	4	1	1	1	3	2	3	1	2	3	3	3
Que.	16	17	18	19	20	21	22								
Ans.	3	3	1	1	4	2	2								

COORDINATION COMPOUND

E

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NEET SYLLABUS

Coordination Compounds : Coordination compounds: Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds, isomerism (structural and stereo) bonding, Werner's theory VBT,CFT; importance of coordination compounds (in qualitative analysis, biological systems).

OBJECTIVES

After studying this unit, you will be able to :

- appreciate the postulates of Werner's theory of coordination compounds;
- know the meaning of the terms: coordination entity, central atom/ion, ligand, coordination number, coordination sphere, coordination polyhedron, oxidation number, homoleptic and heteroleptic;
- learn the rules of nomenclature of coordination compounds;
- write the formulas and names of mononuclear coordination compounds;
- define different types of isomerism in coordination compounds;
- understand the nature of bonding in coordination compounds in terms of the Valence Bond and Crystal Field theories;
- learn the stability of coordination compounds;
- appreciate the importance and applications of coordination compounds in our day to day life.

Every science consists in the coordination of facts, if the different observations were entirely isolated, there would be no science.

Auguste Comte

COORDINATION COMPOUND

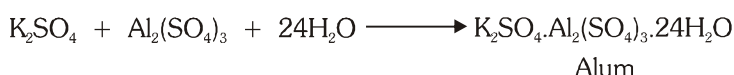
3.0 INTRODUCTION

- (a) The concept of coordination compounds arises from the complex formation tendency of transition elements.
- (b) These compounds play a vital role in our lives. Haemoglobin of blood and chlorophyll of plants are also coordination compounds of Fe, Mg respectively.

3.1 TYPE OF COMPOUNDS

Molecular or Addition Compounds

- (a) When two or more simple salts are chemically combined together in fixed proportion by weight the molecular or addition compounds are formed.
- (b) Some common examples are as follows.



- (c) Depending upon the behavior in an aqueous solution they are of two types
 - (i) Double salt or lattice compound
 - (ii) Coordination or complex compounds.

Double Salt or Lattice Compounds

The addition compounds which lose their identity in aq. solution and get completely ionised in water.

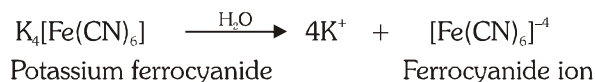
Ex. (i) $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (Potash Alum)

(ii) $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (Mohr's salt)

(iii) $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Carnallite)

Coordination or Complex Compounds

- (a) Those molecular or addition compounds which retain their identity in aq. solution or lose the identity of constituents are called complex salt.
- (b) Complexes retain their identity in aqueous solution. i.e., they do not dissociate into separate ion.



- (c) On the basis of type of ligands complex compounds are divided as follows :

(i) Homoleptic complexes :

Complex in which all the ligands are identical is called homoleptic complex.

Ex. $[\text{Co}(\text{NH}_3)_6]^{+2}$

(ii) Heteroleptic complexes :

Complex in which all the ligands are not identical is known as heteroleptic complex.

Ex. $[\text{Fe}(\text{en})_2\text{Cl}_2]^{+1}$

TERMINOLOGY

(a) Complex Ion

An aggregate of metal ion with anions, cation or neutral molecules is called as **complex ion**.

(b) Central Metal Ion

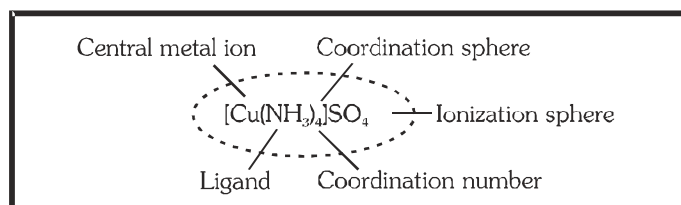
- (i) The metal ion which forms complex ion in combination with anions, cation or neutral molecules is called as **central metal ion**.
- (ii) Central metal ion acts as an electron pair acceptor and forms coordinate covalent bond.

(c) Coordination Number

The total number of coordinate covalent bonds formed by central metal ion with ligands is called as coordination number.

(d) Coordination Sphere - (Entity)

- (i) The central metal atom and the ligands directly attached to it are collectively termed as the coordination sphere.
- (ii) Coordination sphere is written inside square bracket, for example $[\text{Co}(\text{NH}_3)_6]^{3+}$
- (iii) The part outside the bracket is called **ionisation sphere**.
- (iv) The species present in the coordination sphere are non-ionisable.
- (v) The species present in the ionization sphere are ionisable.



(e) Oxidation State

It is a number which represents the electrical charge on the central metal atom of a complex ion.

Ex. the oxidation number of Fe, Co and Ni in $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $\text{Ni}(\text{CO})_4$ is +2, +3 and zero respectively.

(f) Charge On the Complex Ion

It is the algebraic sum of the total charge of the ligands and central metal ion.

(g) Ligands

- (i) The anions, cation or neutral molecules which combine with central metal ion to form complex ion are called as ligands.
- (ii) They act as electron pair donor (Lewis bases), but strong crystal field ligands like CO, CN^- etc can accept electron pair from the metal ion, because these ligands are π - acids.

(h) Naming of ligands

- (i) o-suffix is provided to the name of anionic ligands.
- (ii) ium-suffix is provided to the name of cationic ligands.

Classification of ligands :

On the basis of denticity :

1. **Monodentate ligands :** Which has only one donor site.

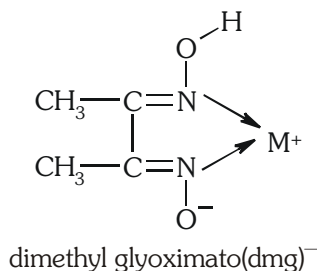
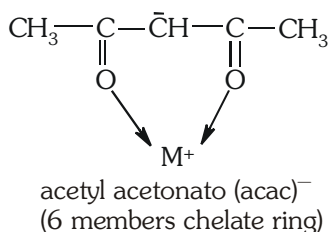
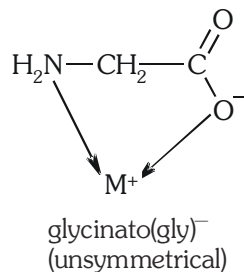
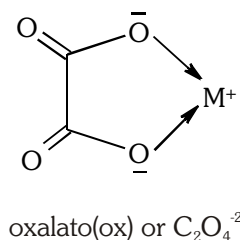
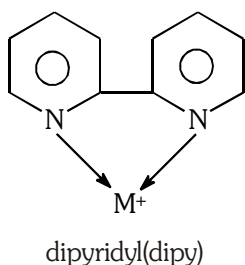
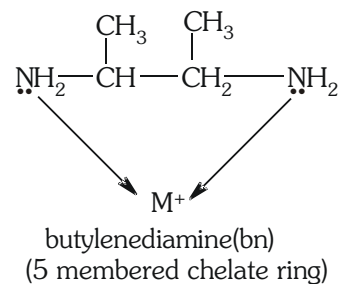
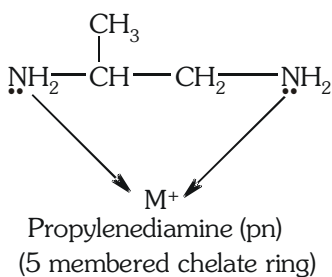
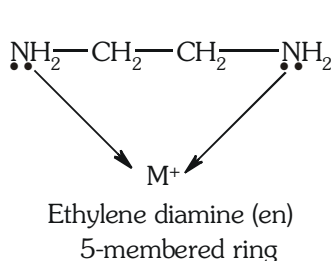
Neutral monodentate ligands	
NH_3	ammine
H_2O	aqua
NO	nitrosyl
PH_3	phosphine
PPh_3	triphenyl phosphine
O_2	dioxygen
N_2	dinitrogen
$\text{CH}_3\text{-OH}$	methyl alcohol
$\text{CH}_3\text{-NH}_2$	methyl amine
NH_2CONH_2	urea
NH_2NH_2	hydrazine
$\text{CH}_3\text{-O-CH}_3$	dimethyl ether
CO	carbonyl
CS	thiocarbonyl

Cationic monodentate ligands :

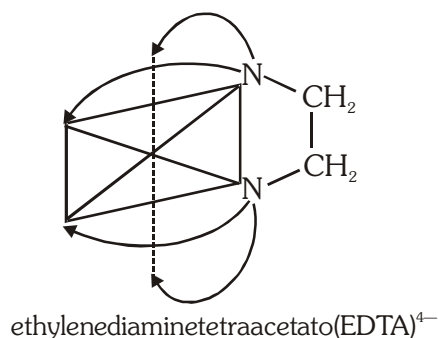
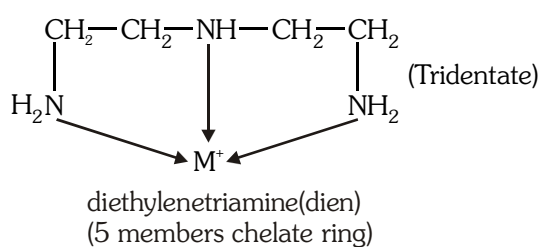
O_2^+	oxygenium
NO^+	nitrosylium or nitrosonium
NO_2^+	nitronium
$H_2N^+-NH_3$	hydrazinium

Anionic monodentate ligands :

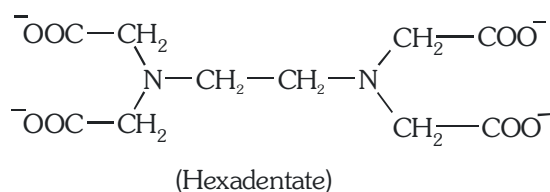
F^-	Fluorido / fluoro
Cl^-	Chlorido / chloro
Br^-	bromido / bromo
I^-	iodido / iodo
O^{2-}	oxido/oxo
S^{2-}	sulphido/sulpho
OH^-	hydroxido / hydroxo
CH_3O^-	methoxido / methoxo
O_2^-	superoxido / superoxo
O_2^{2-}	peroxido / peroxo
N^{3-}	nitrido
N_3^-	azido
$(NH_2)^-$	amido
NH^{2-}	imido
H^-	hydrido

2. Bidentate ligands : Ligands which has two donor sites (simultaneously)

3. Polydentate ligands



or



4. Ambidentate ligand : Ligands which have two different donor atoms but at the time of coordination can donate electron pair from any one donor atoms are called ambidentate ligand.

- (i) $\text{M} \leftarrow \bar{\text{C}} \equiv \text{N}$ cyanido (CN)
 $\text{M} \leftarrow \text{N} \equiv \bar{\text{C}}$ isocyanido(NC)
- (ii) $\text{M} \leftarrow \bar{\text{O}} - \text{C} \equiv \text{N}$ cyanato / cyanato-O
 $\text{M} \leftarrow \text{N} \equiv \text{C} - \bar{\text{O}}$ isocyanato / cyanato-N
- (iii) $\text{M} \leftarrow \bar{\text{S}} - \text{C} \equiv \text{N}$ Thiocyanato / Thiocyanato-S
 $\text{M} \leftarrow \text{N} \equiv \text{C} - \bar{\text{S}}$ Isothiocyanato/thiocyanato-N
- (iv) $\text{M} \leftarrow \bar{\text{O}} - \text{N} = \text{O}$ Nitrito / Nitrito-O
- $\text{M} \leftarrow \text{N} \begin{array}{l} \text{O} \\ \text{O}^- \end{array}$ Nitro / Nitrito-N

5. Flexidentate ligands : Ligands which can change their denticity.

SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, CO_3^{2-} , NO_3^- , CH_3COO^- etc are generally act as monodentate ligand but in some compound they can act as bidentate ligand

eg. (i) $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Cl}$ in this complex SO_4^{2-} act as a monodentate ligand.

(ii) $[\text{Co}(\text{en})_2(\text{SO}_4)]\text{Cl}$ in this complex SO_4^{2-} act as a bidentate ligand.

6. Chelating ligands : Bidentate or polydentate ligands which attach themselves with central metal ion in such a way that they form a ring, are known as chelating ligands.

No. of rings = denticity - 1

5 or 6 membered rings are more stable

- e.g. (i) $[\text{Pt}(\text{trien})]\text{SO}_4$ denticity = 4
 chelating rings = 3
- (ii) $\text{Na}_2[\text{Fe}(\text{OH})(\text{EDTA})]$
 denticity of EDTA = 5
 chelating rings = 4

On the basis of nature of bonding between central metal atom and ligand.

(i) Normal or classical ligands :

Ligand which only donate electron pair to central metal ion & form coordinate (σ) bond
e.g. OH^- , NH_2^- , Cl^- , N^{3-} , O^{2-} etc.

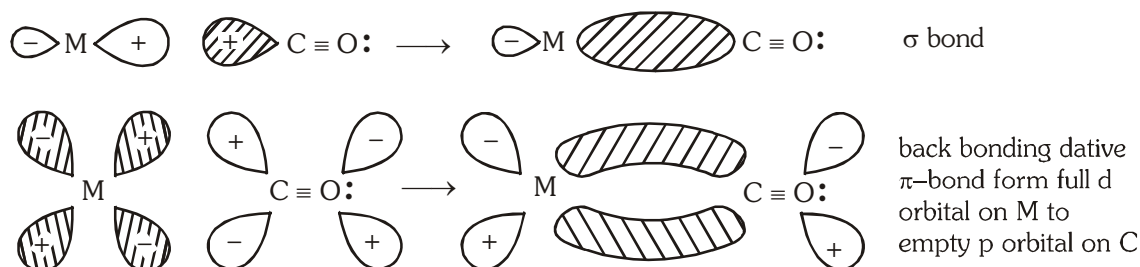
(ii) Non classical or π -acid or π -acceptor ligands :

Ligand which donate electron pair to central metal ion & form coordinate σ bond but simultaneously they accept electron pair from central metal ion through back bonding or synergic bonding.

CO , NO^+ , CN^- , R_3P , R_3As etc.

The electronic configuration of CO molecule shows that it has lone pair of electrons on carbon and oxygen atom each. Carbon atom can donate its electron pair of a transition metal atom (M), forming $\text{OC} \rightarrow \text{M}$ coordinate bond.

Since the metal atom in metal carbonyl is in zero oxidation state, the formation of $\text{M} \leftarrow \text{CO}$ σ bond accumulates a negative charge on the metal atom. The accumulation of negative charge on the metal atom can be counter balanced by transferring some negative charge from the metal atom to CO molecule (ligand). This transfer can be done by making a $\text{M} \rightarrow \text{CO}$ π bond by the overlap between an appropriate filled orbital on the metal atom and empty π_y^* or π_z^* molecular orbital on CO molecule. This type of bonding between M and CO is called **synergic bonding**.



[Schematic of orbital overlaps in metal carbonyls]

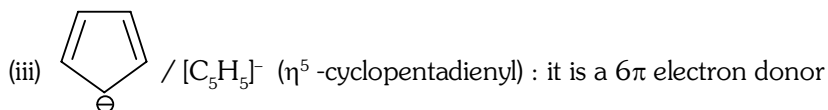
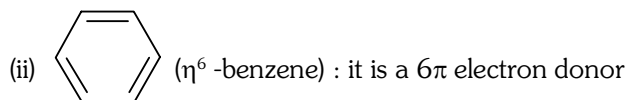
Conclusion of synergic bonding : due to synergic bonding

- (a) $\text{M}-\text{C}$ bond strength increases; $\text{M}-\text{C}$ bond length decreases; because double bond character increases
(b) $\text{C}-\text{O}$ bond strength decreases; $\text{C}-\text{O}$ bond length increases; because bond order of $\text{C}-\text{O}$ decreases, electron density in ABMO of CO increases.

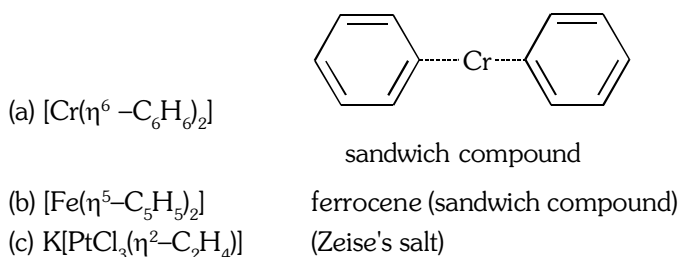
π -donor and π -acceptor ligands

ligands which donate π electron to central metal ion & also accept electron density from central metal ion through synergic bonding.

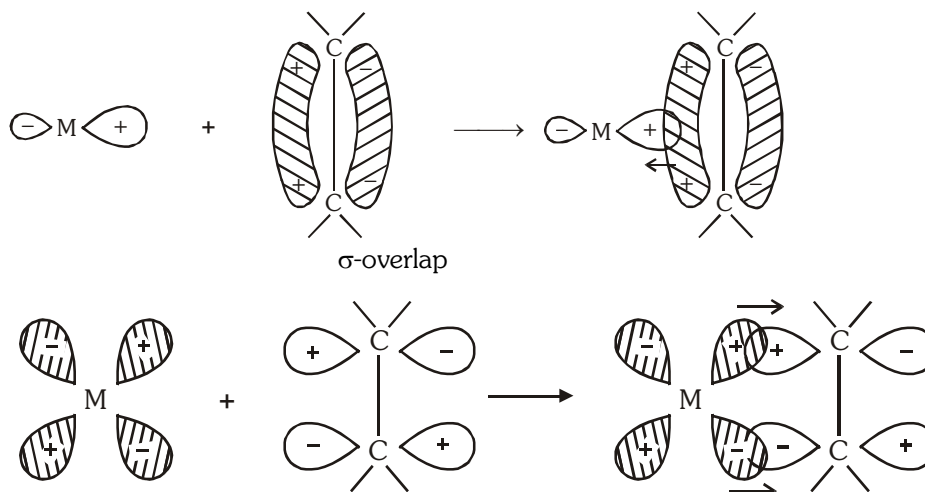
- (i) $\text{H}_2\text{C}=\text{CH}_2$ (η^2 - ethylene) : it is a 2π electron donor



for example



The bonding of alkenes to a transition metal to form complexes has two components. First, the π -electron density of the alkene overlaps with a σ -type vacant orbital of the metal atom. Second is the back bonding formed by the flow of electron density from a filled d-orbital on the metal into the vacant π^* -antibonding molecular orbital of the carbon atom as shown below:



BEGINNER'S BOX-1

- Which of the following is true about metal-EDTA complex (if it is a 3d metal)
 - (1) The ratio of moles of metal & EDTA in complex is 1:6
 - (2) The ratio of moles of metal & EDTA in complex is 6:1
 - (3) The ratio of moles of metal & EDTA in complex is 1:1
 - (4) 3d metal ion cannot bonded with EDTA
- CN^- is ambidentate ligand because
 - (1) it has multiple bonds
 - (2) carbon as a negative charge
 - (3) it form chelate
 - (4) both C & N can donate lone pair
- Highest C–O bond length will be in
 - (1) $[\text{Mn}(\text{CO})_6]^+$
 - (2) $[\text{Cr}(\text{CO})_6]$
 - (3) $[\text{V}(\text{CO})_6]^-$
 - (4) same in all
- The strongest –CO bond is present in
 - (1) $[\text{Cr}(\text{CO})_6]^+$
 - (2) $[\text{Fe}(\text{CO})_5]$
 - (3) $[\text{V}(\text{CO})_6]^-$
 - (4) all have equal strength
- Match the following

Ligand

- (A) ethylenediamine
- (B) hydrazene
- (C) dimethylglyoximate(dmg^-)
- (D) dien

Property

- (P) bidentate
- (Q) tridentate
- (R) form hydrazenium ion on protonation
- (S) can form dimer

[Ans. A $\rightarrow$ P, B $\rightarrow$ R, C $\rightarrow$ P, D $\rightarrow$ Q]

- Match the following

Complex

- (A) $[\text{Ni}(\text{dmg})_2]$
- (B) $[\text{Ca}(\text{EDTA})]^{2-}$
- (C) $[\text{Fe}(\text{en})_3]\text{Cl}_3$
- (D) $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$

Property

- (P) number of 5 member rings = 2
- (Q) number of 6 member rings = 2
- (R) coordination number of central metal ion = 2
- (S) coordination number of central metal ion = 6
- (T) intramolecular H-bonding

[Ans. A $\rightarrow$ P, Q, T; B $\rightarrow$ S; C $\rightarrow$ S; D $\rightarrow$ R]

7. The oxidation state of metal in Iron in $[\text{Fe}(\text{CN})_6]^{3-}$ is
 (1) -6 (2) +3 (3) -3 (4) +6
8. Coordination number of Co in $[\text{CoF}_6]^{3-}$ is
 (1) 4 (2) 5 (3) 6 (4) 8
9. The neutral ligand is
 (1) Chlorido (2) Hydroxido (3) Ammine (4) Oxalato
10. $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ serves as :
 (1) Monodentate ligand (2) Chelating ligand (3) Bridging ligand (4) Cationic ligand

3.2 IUPAC NOMENCLATURE OF COORDINATION COMPOUNDS

The present system of nomenclature derived from the suggestions of **Alfred Werner** and recommended by the Inorganic Nomenclature Committee of the I.U.P.A.C. The main rules of naming of complexes are -

- (a) Like simple salts, the positive part of the coordination compound is named first.

Ex. $\text{K}_4[\text{Fe}(\text{CN})_6]$ the naming of this complex starts with potassium.

- (b) Then after ligands of the coordination sphere are to be named.

- (c) The ligands can be neutral, anionic or cationic.

- (i) The neutral ligands are named as the molecule

Ex. $\text{C}_5\text{H}_5\text{N}$ (pyridine), $(\text{C}_6\text{H}_5)_3\text{P}$ (Triphenyl phosphine),

$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ (ethylene diamine)

The neutral ligands which are not named as the molecule are

CO (carbonyl), NO (nitrosyl), H_2O (Aqua), NH_3 (ammine)

- (ii) Anionic ligands ending with 'ide' are named by replacing the 'ide' with suffix 'O'.

Symbol	Name as ligand	Symbol	Name as ligand
Cl^-	Chloro/Chlorido	N^{3-}	Nitrido
Br^-	Bromo/Bromido	O_2^{2-}	Peroxo, O_2^- superoxo
CN^-	Cyano	O_2H^-	Perhydroxo
O^{2-}	Oxo	S^{2-}	Sulphido
OH^-	Hydroxo	NH_2^-	Amido
H^-	Hydrido	NH^{2-}	imido

Ligands whose names end in 'ite' or 'ate' become 'ito' i.e., by replacing the ending 'e' with 'o' as follows.

CO_3^{2-}	Carbonato	SO_3^{2-}	Sulphito
$\text{C}_2\text{O}_4^{2-}$	Oxalato (Ox) ²⁻	CH_3COO^-	Acetato
SO_4^{2-}	Sulphato	NO_2^-	(bonded through oxygen) nitrite
NO_3^-	Nitrato		(bonded through nitrogen) nitro
$\text{S}_2\text{O}_3^{2-}$	Thiosulphato		

→ $\begin{bmatrix} \text{Nitrito} - \text{N} \\ \text{Nitrito} - \text{O} \end{bmatrix}$

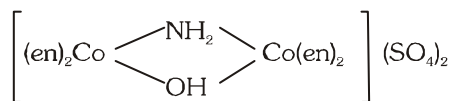
- (iii) Positive ligands naming ends in 'ium'

$\text{NH}_2-\text{NH}_3^+$ (Hydrazinium), NO_2^+ (nitronium); NO^+ (nitrosonium)

- (d) If ligands are present more than once, then their repetition is indicated by prefixes like di, tri, tetra etc. However, when the name of the ligand includes a number.

Ex. dipyridyl, ethylene diamine, then bis, tris, tetrakis are used in place of di, tri, tetra, etc.

- (e) In case of chelating ligands or ligands having di, tri, tetra, etc, in their name the prefixes bis, tris, tetrakis are used before ligands placed in paranthesis.



Bis(ethylenediamine) cobalt(III)-μ- amido-μ- hydroxobis(ethylenediamine) cobalt (III) sulphate

- (f) When more than one type of ligand is present in the complex, then the ligands are named in the alphabetical order.
- (g) After naming of ligands the central metal ion is to be named followed by its oxidation state in Roman numbers in brackets. (as per IUPAC)

If the complex is neutral or provides a cationic complex ion, then the central metal ion is to be named as it is.

If the complex provides anionic complex ion then the name of central metal ion ends in 'ate'

- (h) After the naming of central metal ion, anion which is in the outer sphere is to be named.

The naming of some of the complexes is done as follows – (as per IUPAC)

Complex Compounds	IUPAC Name
(i) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (anionic complex) so suffix ate is added with metal's name	Potassium hexacyanidoferrate (II)
(ii) $\text{K}_2[\text{Pt Cl}_6]$	Potassium hexachloridoplatinate (IV)
(iii) $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$ (Cationic complex) so metal is without any suffix	Hexamminecobalt (III) chloride
(iv) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2] \text{Cl}$	Tetraaquadichlorochromium (III) chloride
(v) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$	Diammine tetrachloroplatinum (IV)
(vi) $[\text{Co}(\text{NH}_3)_3 \text{Cl}_3]$ (Neutral complex) So no suffix is used with metal ion	Triamminetrichlorocobalt (III)
(vii) $\text{K}_3[\text{Co}(\text{NO}_2)_6]$	Potassium hexanitrocobaltate (III)
(viii) $\text{Na}_2[\text{Fe}(\text{CN})_5 \text{NO}]$	Sodium pentacyanonitrosoniumferrate (II)
(ix) $[\text{NiCl}_4]^{-2}$	Tetrachloronickelate (II) ion
(x) $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{+2}$	Pentamminechlororuthenium (III) ion
(xi) $[\text{Fe}(\text{en})_3]\text{Cl}_3$	Tris (ethylenediamine) iron (III) chloride
(xii) $[\text{Ni}(\text{Gly})_2]$	Bis (glycinato) nickel (II)

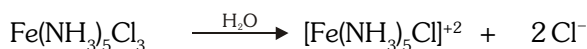
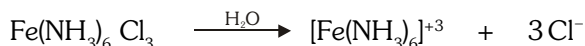
- (i) If coordination compound contains 2 coordination spheres then both spheres should have opposite charges. Name of cationic part written first following the name of anionic sphere according to the general IUPAC rule.

Ex. $[\text{Fe}(\text{NH}_3)_6]^{3+}[\text{Co}(\text{NO}_2)_6]^{2-}$ [Hexamine iron (II) hexanitro cobaltate(III)]

3.3 BONDING IN COORDINATION COMPOUNDS

(A) Werner's Theory

This was postulated by **Alfred Werner** in 1893. The postulates of Werner's theory of complexes are –



Every metal forming a complex exhibits two types of valencies - Primary valency and Secondary Valency. In the above complexes chlorine act as primary valency and NH_3 acts as secondary valency.

According to Werner central metal have 2 types of valencies :

Primary valencies	Secondary valencies
(i) Equal to oxidation state of CMA	(i) Equal to coordination number of CMA
(ii) Satisfied by anions	(ii) satisfied by ligands
(iii) Non directional	(iii) Directional
(iv) Ionisable	(iv) Non-ionisable
(v) not helpful geometry predictions	(v) helpful in geometry predictions

Shapes : According to Werner all secondary valencies has shapes arrangement according to coordination number

Experimental evidence of werner's theory

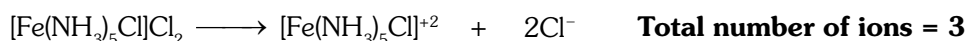
- (a) Precipitation of primary valencies on the addition of a suitable reagent.

Ex. $\text{Fe}(\text{NH}_3)_6 \text{Cl}_3$ forms 3 moles of AgCl in the form of precipitate on addition of AgNO_3 solution.

This indicates that the complex ionises as $\text{Fe}(\text{NH}_3)_6 \text{Cl}_3 \xrightarrow{\text{H}_2\text{O}} [\text{Fe}(\text{NH}_3)_6]^{+3} + 3 \text{Cl}^-$

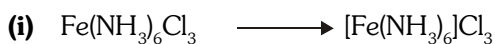
- (b) **Electrical conductance of complexes** : More the number of ions provided greater is the electrical conductance of the complex in aqueous medium. **Electrical conductivity $\propto$ no. of ions.**

Ex. The electrical conductance of aqueous $[\text{Fe}(\text{NH}_3)_6] \text{Cl}_3$ is greater than that of aqueous solution of $[\text{Fe}(\text{NH}_3)_5 \text{Cl}] \text{Cl}_2$.

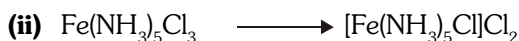
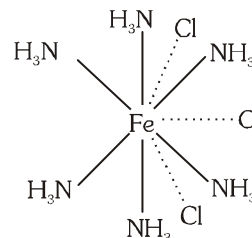


Complex	Modern formula	No. of Cl^- ions precipitated	Total number of ions
$\text{PtCl}_4 \cdot 6\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_6] \text{Cl}_4$	4	5
$\text{PtCl}_4 \cdot 5\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_5 \text{Cl}] \text{Cl}_3$	3	4
$\text{PtCl}_4 \cdot 4\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_4 \text{Cl}_2] \text{Cl}_2$	2	3
$\text{PtCl}_4 \cdot 3\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_3 \text{Cl}_3] \text{Cl}$	1	2
$\text{PtCl}_4 \cdot 2\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_2 \text{Cl}_4]$	0	0 (non-electrolyte)

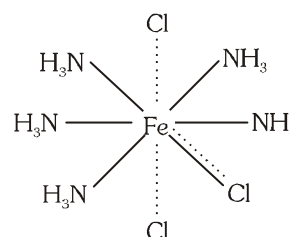
Werner's Representation of complexes

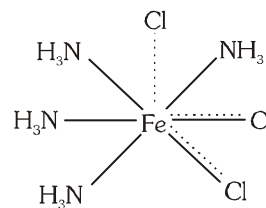
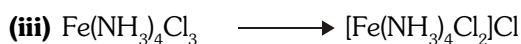


Dotted lines indicate primary valency and continuous lines indicate secondary valency of metal ion.



In this complex 'Cl' groups act as primary valencies and one of the 'Cl' acts as secondary valency also. Thus werner's representation of this complex –





In this complex 'Cl' groups act as primary valency and two of the 'Cl' group act as secondary valencies also. Thus
Werner's representation of this complex –

$$\text{E.A.N.} = (\text{No. of electron in the metal ion}) + (\text{No. of electrons gained from the ligands})$$

OR

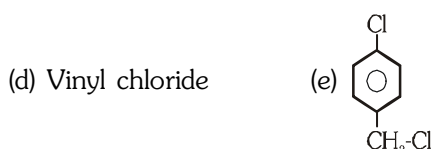
$$\text{Atomic number} - (\text{Oxidation state}) + (2 \times \text{Coordination number})$$

Example :

Complex	Metal (Oxidation State)	Atomic Number of Metal	Coordination number	Effective atomic number (E.A.N.)
$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$	+2	29	4	$(29 - 2) + (4 \times 2) = 35$
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	+3	27	6	$(27 - 3) + (6 \times 2) = 36$ [Kr]
$\text{K}_2[\text{HgI}_4]$	+2	80	4	$(80 - 2) + (4 \times 2) = 86$ [Rn]
$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$	+1	47	2	$(47 - 1) + (2 \times 2) = 50$

BEGINNER'S BOX-2

- The IUPAC name of $\text{Fe}(\text{CO})_5$ is
 (1) Pentacarbonyl ferrate (0) (2) Pentacarbonyl Ferrate (III)
 (3) Pentacarbonyl Iron (0) (4) Pentacarbonyl Iron (II)
- The compound $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ is called
 (1) Sodium pentacyanonitrosonium ferrate (II) (2) Sodium nitroprusside
 (3) Sodium nitrosoferrocyanide (4) 1 & 2 both
- $\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$ is actually :
 (1) $[\text{Fe}(\text{H}_2\text{O})_4]\text{Cl}_3$ (2) $[\text{Fe}(\text{H}_2\text{O})_3\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (3) $[\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ (4) $[\text{Fe}(\text{H}_2\text{O})_3\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$
- Which of the following compound does not give test of sulphate ion in aqueous solution
 (1) $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (2) $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$
 (3) $[\text{CoSO}_4(\text{NH}_3)_5]\text{Br}$ (4) $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
- Which of the following compound is expected to yield a white precipitate with AgNO_3 solution :-
 (a) $\text{PtCl}_4 \cdot 4\text{NH}_3$ (b) $\text{CoCl}_3 \cdot 3\text{NH}_3$ (c) Impure chloroform



(f) Carnallite

(1) a, c, f, e

(2) a, d, e

(3) a, b, c, f

(4) a, b, e, f

6. Which of the following is most likely formula of platinum complex, if $\frac{1}{4}$ of total chlorine of the compound is precipitated by adding AgNO_3 to its aqueous solution
 (1) $\text{PtCl}_4 \cdot 6\text{H}_2\text{O}$ (2) $\text{PtCl}_4 \cdot 5\text{H}_2\text{O}$ (3) $\text{PtCl}_2 \cdot 2\text{H}_2\text{O}$ (4) $\text{PtCl}_4 \cdot 3\text{H}_2\text{O}$
7. The Effective atomic number of Cr in $\text{Cr}(\text{CO})_6$ is
 (1) 36 (2) 38 (3) 28 (4) 54
8. According to the rule of effective atomic number, central atom acquires :
 (1) Inert gas configuration (2) Duplet
 (3) Pseudo inert electronic configuration (4) Quartet
9. The Effective atomic number of iron in $\text{K}_4[\text{Fe}(\text{CN})_6]$ is :
 (1) 35 (2) 34 (3) 36 (4) 38
10. The formula of the complex tris (ethylene diamine) cobalt (III) sulphate is
 (1) $[\text{Co}(\text{en})_2]\text{SO}_4$ (2) $[\text{Co}(\text{en})_3]\text{SO}_4$ (3) $[\text{Co}(\text{en})_3]\text{SO}_4$ (4) $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$

(B) VALENCE BOND THEORY

This theory was mainly developed by **Linus Pauling**. The main features of this theory are -

- Every metal ion when it forms a complex compound undergoes formation of coordinate covalent bond.
- During this bond formation, the metal ion acts as electron pair acceptor. For this the metal ion provides vacant orbitals.
- The number of vacant orbitals provided is equal to the coordination number of metal ion.

Ex. In the formation of $[\text{Fe}(\text{NH}_3)_6]^{3+}$, Fe^{+3} ion provides six vacant orbitals.

In $[\text{Cu}(\text{NH}_3)_4]^{2+}$, Cu^{+2} ion provides four vacant orbitals.

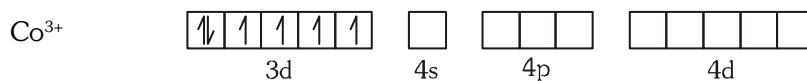
- The metal provides vacant orbitals only after the process of hybridisation, thus vacant hybrid orbitals are provided by the metal ion.
- The vacant hybrid orbitals of metal ion get overlapped by orbitals of ligands containing lone pair of electrons.
- The number of such overlappings is equal to the coordination number of metal ion.
- The empty 'd' orbitals involved in hybridisation may be inner (n-1)d or outer "nd" orbitals.
- These complexes are called as **Inner orbital complexes** and **outer orbital complexes** respectively. It is applicable for coordination number = 6 (complexes).
- If inner 'd' orbitals are involved in hybridisation, then it is through the pairing of unpaired electrons in the (n-1)d orbitals of metal ion.
- Then such type of complexes will be **diamagnetic** or **less paramagnetic** and will be called as **Low spin complexes**.
- Generally outer orbital complexes have **paramagnetic** nature and they are called as **High spin complexes**.

Applications of valence bond Theory

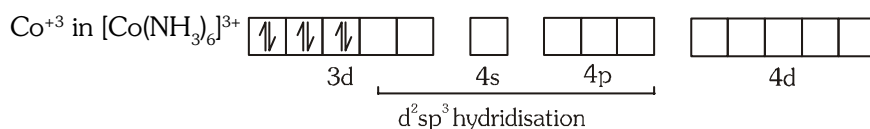
(a) To 6-coordinated complexes :



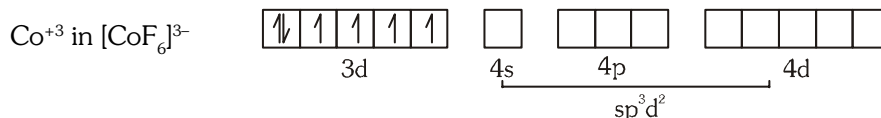
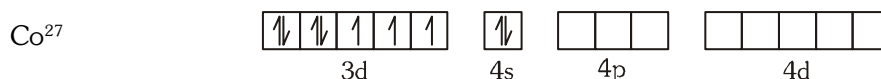
e^- configuration of $_{27}\text{Co} = [\text{Ar}] 3d^7 4s^2$ So, $\text{Co}^{+3} = [\text{Ar}] 3d^6$



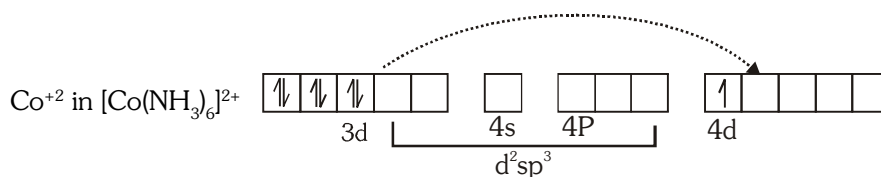
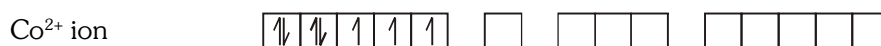
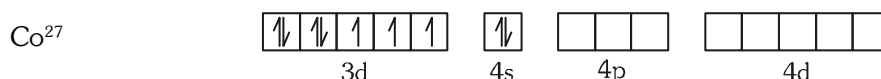
Due to presence strong ligand electrons get paired up so metal ion provides vacant '3d' orbitals for hybridisation.



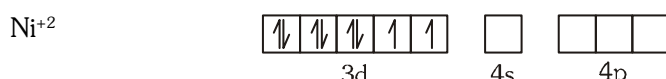
- This is a **diamagnetic complex**.
- As inner 'd' orbitals are involved in hybridisation, hence it is an **inner orbital complex**.
- It is a **low spin complex**.



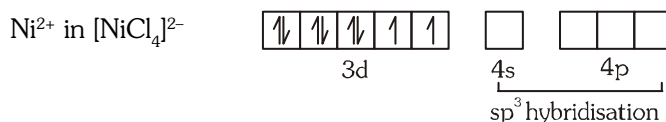
- This is a **paramagnetic complex** and **high spin** complex.
- The outer 'd' orbitals are involved in hybridisation, hence it is an **outer orbital complex**.



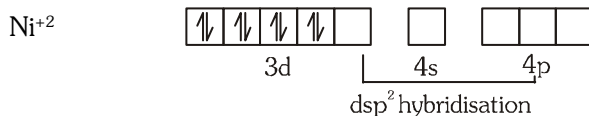
(b) 4-coordinated complexes :



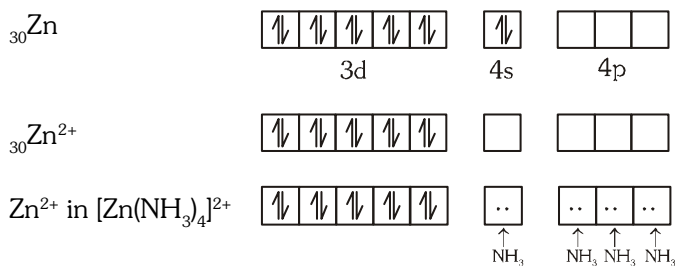
- The unpaired electrons remain as such because Cl^- is a weak ligand as it is a **paramagnetic complex**.



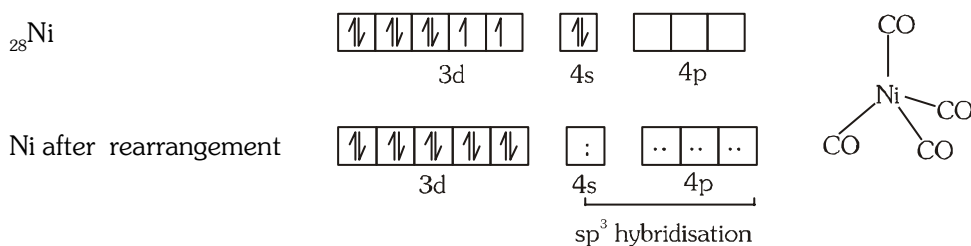
- $[\text{NiCl}_4]^{2-}$ has **tetrahedral geometry**.
- It is a **high spin complex**.



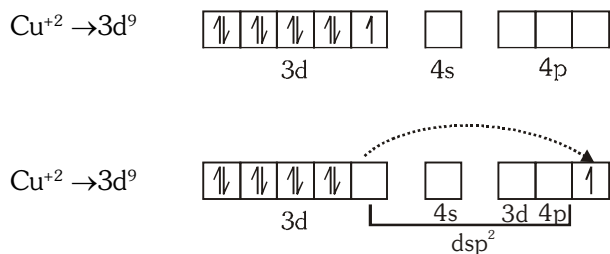
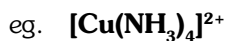
- CN^- is **strong field ligand**. Thus the complex has **square planar geometry**.
- The unpaired electrons in '3d' orbitals of Ni^{2+} get paired up, So $[\text{Ni}(\text{CN})_4]^{2-}$ is **diamagnetic** in nature.
- This Ni^{2+} complex is an **inner orbital complex** and a **low spin complex**.



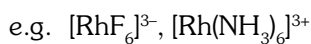
- Because the complex is formed by sp^3 hybridisation, hence it is **tetrahedral**
- Since all electrons are paired, hence it is **diamagnetic**

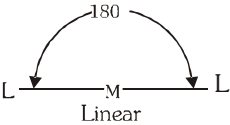
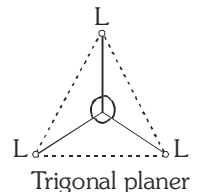
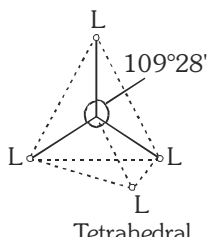
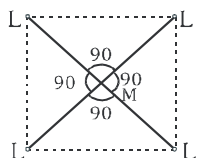
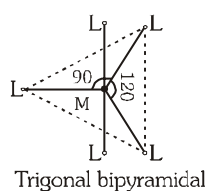
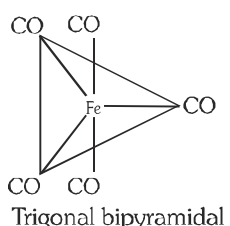
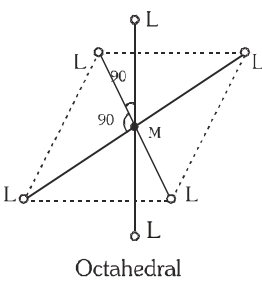


- CO is a strong ligand. So it is **low spin complex**.
- The empty one 4s and three 4p orbitals mix to form four new sp^3 hybridised orbitals.
- Each orbital accepts one electron pair from carbon monoxide molecule forming $[Ni(CO)_4]$
- It is **diamagnetic** in nature, the shape of nickel tetra carbonyl is **tetrahedral** as shown above.



Note : In case, if metal belongs to 4d & 5d series all ligand will act as a strong field ligand.



Coordination Number	Hybridised orbital	Geometrical shape of the Complex	Examples of Complex
2	sp	 Linear	$[\text{Ag}(\text{NH}_3)_2]^+$ $[\text{Ag}(\text{CN})_2]^-$
3	sp^2	 Trigonal planar	$[\text{HgI}_3]^-$
4	sp^3	 Tetrahedral	$[\text{CuCl}_4]^{2-}$ $[\text{ZnCl}_4]^{2-}$ $[\text{FeCl}_4]^-$ $[\text{Ni}(\text{CO})_4]$ $[\text{Zn}(\text{NH}_3)_4]^{+2}$
4	dsp^2 ($d_{x^2-y^2}$ orbital)	 Square planar	$[\text{PdCl}_4]^{2-}$ $[\text{Ni}(\text{CN})_4]^{2-}$ $[\text{Pt}(\text{NH}_3)_4]^{+2}$ $[\text{Cu}(\text{NH}_3)_4]^{+2}$ $[\text{PtCl}_4]^{2-}$
5	sp^3d	 Trigonal bipyramidal	$[\text{CuCl}_5]^{3-}$
5	dsp^3	 Trigonal bipyramidal	$[\text{Fe}(\text{CO})_5]$
6	d^2sp^3 When d-orbitals are (n - 1)d-orbitals (Inner orbital complexes) or sp^3d^2 When d-orbitals are nd orbitals (Outer orbital complexes) In both cases d-orbitals are d_{z^2} and $d_{x^2-y^2}$ orbitals	 Octahedral	$[\text{Cr}(\text{NH}_3)_6]^{+3}$ $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$ $[\text{Fe}(\text{CN})_6]^{3-}$ $[\text{Co}(\text{NH}_3)_6]^{+3}$ $[\text{PtCl}_6]^{2-}, [\text{CoF}_6]^{3-}$

BEGINNER'S BOX-3

1. Complex ion square planar geometry :-
 (1) $[\text{Ni}(\text{CN})_4]^{2-}$ (2) $[\text{Cu}(\text{CN})_4]^{-2}$ (3) $[\text{Cu}(\text{NH}_3)_4]^{+2}$ (4) All
2. Which is low spin complex ?
 (1) $[\text{Fe}(\text{CN})_6]^{3-}$ (2) $[\text{Co}(\text{NO}_2)_6]^{3-}$ (3) $[\text{Mn}(\text{CN})_6]^{3-}$ (4) All
3. For the complex $[\text{Fe}(\text{CO})_x]$ what is wrong :-
 (1) It is σ - π bonded organometallic compound (2) In the complex value of $x = 6$
 (3) In the complex CO is π -acid ligand (4) It is trigonal bipyramidal shape
4. In the complex ion ML_6^{n+} , M^{n+} has five d-electrons and L is weak field ligand. According to crystal field theory, the magnetic properties of the complex ion corresponds to how many unpaired electrons
 (1) 0 (2) 5 (3) 2 (4) 3
5. Among $[\text{Ni}(\text{CO})_4]$, $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{Cl})_4]^{2-}$:
 (1) $[\text{Ni}(\text{CO})_4]$ and $[\text{NiCl}_4]^{2-}$ are diamagnetic and $[\text{Ni}(\text{CN})_4]^{2-}$ is paramagnetic
 (2) $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic and $[\text{Ni}(\text{CO})_4]$ is paramagnetic
 (3) $[\text{Ni}(\text{CO})_4]$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic and $[\text{NiCl}_4]^{2-}$ is paramagnetic
 (4) $[\text{Ni}(\text{CO})_4]$ is diamagnetic and $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are paramagnetic
6. Which is correct geometry in the case of $[\text{NiCl}_4]^{2-}$ complex ?
 (1) Tetrahedral (2) Octahedral (3) Square planar (4) Pyramidal
7. For $\text{K}_3[\text{CoF}_6]$, incorrect statement is :
 (1) It is high spin complex (2) Its magnetic moment is $\sqrt{24}$ BM
 (3) Primary valency of Co is six (4) Hybridisation state of CoF_6^{3-} is sp^3d^2
8. Which of the following compound is square planar and does not have any unpaired electron:
 (a) $[\text{Cu}(\text{NH}_3)_4]^{+2}$ (b) XeF_4 (c) $[\text{Ni}(\text{CO})_4]$ (d) $[\text{NiCl}_4]^{-2}$ (e) $[\text{Ni}(\text{CN})_4]^{-2}$ (f) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 (1) a, e, f (2) a, b, c (3) b, e (4) b, c, f
9. Which of the following complex does not have chelation
 (1) $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$ (2) $[\text{Pt}(\text{en})_2]\text{Cl}_2$ (3) $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ (4) $\text{K}_2[\text{Ni}(\text{EDTA})]$
10. Match list - I with list - II and choose the correct answer from the code given below

List - I (complex)

- (A) $[\text{Ni}(\text{CN})_4]^{-2}$
 (B) $[\text{Pt}(\text{NH}_3)_6]^{+4}$
 (C) $[\text{Ag}(\text{NH}_3)_2]^+$
 (D) $[\text{Zn}(\text{NH}_3)_4]^{+2}$

A B

- (1) b a
 (2) a b
 (3) c d
 (4) b c

List - II (geometry)

- (a) Octahedral
 (b) Squareplanar
 (c) Tetrahedral
 (d) Linear

C D

- d c
 c d
 b a
 d a

(C) Crystal field theory

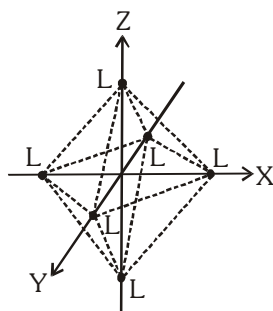
Crystal Field Theory : This is a model of electronic structure of transition-metal complexes that considers how the energies of the d-orbitals of a metal ion are affected by the electric field of the ligand. According to this theory.

- The ligands in a transition-metal complex are treated as point charges.
- A ligand anion becomes simply a point of negative charge. A neutral molecule, with its electron pair that it donates to the metal atom, is replaced by a negative charge, representing the negative end of the molecular dipole.
- In the electric field of these negative charges, the five d orbitals of the metal atom no longer have exactly same energy. Splitting of five degenerate d-orbitals of the metal ion into sets of orbitals having different energies is called crystal field splitting.
- The extent of splitting of metal d-orbitals depends upon the nature and number of ligands surrounding it and the charge on the central metal ion.
- The extent of splitting of metal d-orbitals determines the magnetic and spectroscopic properties of the complexes.

SPLITTING IN OCTAHEDRAL COMPLEXES

In an octahedral complex, the co-ordination number is 6. The metal ion is at the centre and the ligands occupy the six corners of the octahedron as shown in figure.

We know that two orbitals, $d_{x^2-y^2}$ and d_{z^2} are oriented along the axis while the remaining three orbitals, viz., d_{xy} , d_{yz} and d_{zx} are oriented in between the axis.

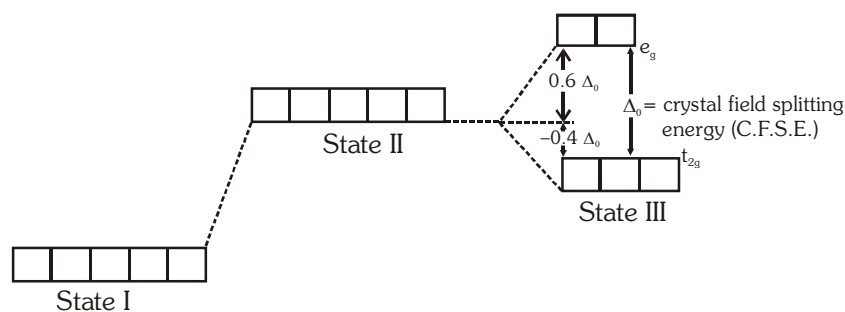


The two orbitals $d_{x^2-y^2}$ and d_{z^2} are designated as e_g orbitals while the three orbitals d_{xy} , d_{yz} and d_{zx} are designated as t_{2g} orbitals. As the six ligands approach the central ion along the axis, e_g orbitals, is repelled more by the ligand than in the t_{2g} orbitals.

In other words, the energy of the d_{z^2} and $d_{x^2-y^2}$ orbitals increases

much more than the energy of the d_{xy} , d_{yz} and d_{zx} orbitals.

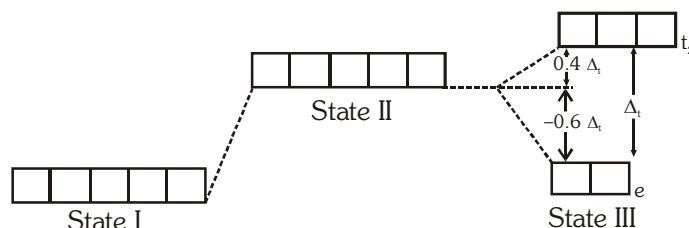
Thus, in octahedral complexes, the five d-orbitals split up into two sets : one set consisting of two orbitals ($d_{x^2-y^2}$ and d_{z^2}) of higher energy (e_g orbitals) and the other set consisting of three orbitals (d_{xy} , d_{yz} and d_{zx}) of lower energy (t_{2g} orbitals).



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Tetrahedral arrangement of four ligands

Thus, the d orbitals are also splitted into two groups but in a reverse order. The three orbitals, d_{xy} , d_{yz} and d_{xz} , designated as t_2 orbitals, now have higher energy than the two orbitals $d_{x^2-y^2}$ and d_{z^2} designated as eg-orbitals.



(i) For octahedral $\text{CFSE} = \left[-0.4(n_{t_{2g}}) + 0.6(n_{e_g}) \right] \Delta_0 + \text{Pairing energy (P.E.)}$

$$n_{eg} = \text{number of electron in eg orbitals}$$
$$\Delta_0 = \text{crystal field **splitting** energy}$$

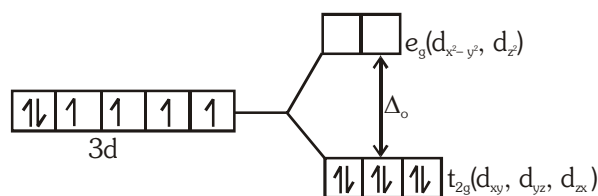
(ii) For tetrahedral $\text{CFSE} = [-0.6(n_e) + 0.4(n_{t_2})] \Delta_t + \text{Pairing energy (P.E.)}$

$$n_e = \text{number of electron in } e \text{ orbitals}$$
$$\Delta_{+} = \text{crystal field **splitting** energy}$$

Explain the formation of $\text{Na}_4[\text{Fe}(\text{CN})_6]$ and $\text{Na}_4[\text{FeF}_6]$? Show which is low spin and which is high spin complex and also calculate the Crystal field stabilisation energy (CFSE) ?

In given compounds CN^- is strong field ligands and F^- is weak field ligand and in both compounds ions is in +2 oxidation state d^6 configuration.

So in $\text{Na}_4[\text{Fe}(\text{CN})_6]$



3d

$e_g(d_{x^2-y^2}, d_{z^2})$

Δ_o

$t_{2g}(d_{xy}, d_{yz}, d_{zx})$

In presence

In presence
of ligand

For octahedral CFSE = $\left[-0.4(n_{t_{2g}}) + 0.6(n_{e_g})\right] \Delta_o + P.E.$

where $n_{t_{2g}}$ = number of electron in t_{2g} orbitals

n_{e_g} = number of electron in e_g orbitals

$Na_4[Fe(CN)_6]$ CFSE = $-2.4 \Delta_o + 3P$. $[n_{t_{2g}} = 6, n_{e_g} = 0]$

$Na_4[Fe(F)_6]$ CFSE = $-0.4 \Delta_o + P$ $[n_{t_{2g}} = 4, n_{e_g} = 2]$

where P = pairing energy to pair up electron.

Factors affecting Δ

factor affecting splitting

- | | |
|---|--|
| (i) Strength of ligand | [C.F.S.E. is more in case of S.F.L. as compared to W.F.L.] |
| (ii) Oxidation state of central metal ion | [C.F.S.E. $\propto$ oxidation state] |
| (iii) Transition series (d-series) | [C.F.S.E. , $5d > 4d > 3d$] |
| (iv) Geometry (number of ligands). | $[\Delta_{sq} > \Delta_o > \Delta_t]$ |

$$\Delta_{sp} = \frac{4}{3} \Delta_o \quad ; \quad \Delta_t = \frac{4}{9} \Delta_o \quad ; \quad [\Delta_{sp} = 1.3 \Delta_o]$$

Factors affecting strength of ligands

Strength of ligand depends upon :

- | | | | |
|-------------------------|--------------------------|----------------------------|--------------------|
| (i) good σ donor | (ii) good π acceptor | (iii) high negative charge | (iv) Small in size |
|-------------------------|--------------------------|----------------------------|--------------------|

Spectro-chemical series for ligands

Series which shows the relative strength of ligands

I(weakest) < Br < SCN⁻ < Cl⁻ < S²⁻ > NO₃⁻ < F⁻ < OH⁻ < C₂O₄²⁻ < H₂O < NCS⁻ < edta⁴⁻ < NH₃ < en < NO₂⁻ < CN⁻ < CO(strongest)

APPLICATION OF CRYSTAL FIELD THEORY

Applications of C.F.T are

- To predict the geometry that the compound is either inner orbital or outer orbital complex.
- To calculate the magnitude of paramagnetism.
- To show the colour property.

Que.

Give the magnetism in following configuration

- | | |
|---|---|
| (i) d ⁴ high spin octahedral | (ii) d ⁴ low spin octahedral |
| (iii) d ⁵ high spin octahedral | (iv) d ⁵ tetrahedral |
| (v) d ⁶ tetrahedral | (vi) d ⁸ low spin octahedral |
| (vii) d ⁷ tetrahedral | (viii) d ⁷ high spin octahedral. |

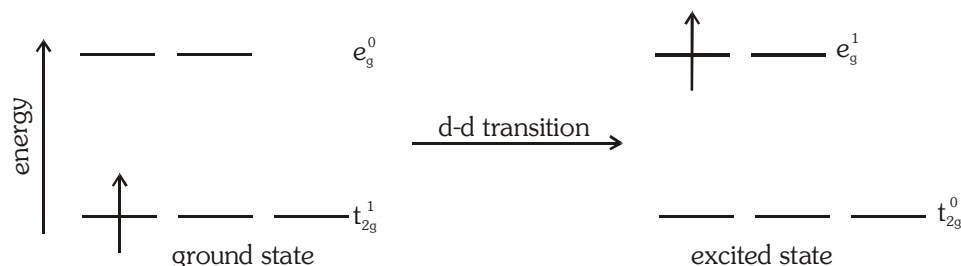
Solution

- | | |
|-------------------------------|--------------------------------|
| (i) four unpaired electron | (ii) two unpaired electron |
| (iii) five unpaired electron | (iv) five unpaired electron |
| (v) four unpaired electron | (vi) two unpaired electron |
| (vii) three unpaired electron | (viii) three unpaired electron |

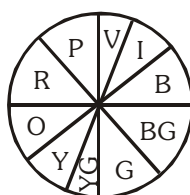
(II)

COLOUR PROPERTY :

Reason for colour in complexes is due to d-d-transition



Complementary colour wheel



For example complementary colour of red is blue green.

Example. $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$ is violet in colour explain using CFT.

Solution In $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ d-orbitals of Ti^{3+} lost their degeneracy in the presence of octahedral ligand field and produce t_{2g}^1 & e_g^0 . orbital of different energy complex absorbed visible light for excitation of electron from t_{2g}^0 to e_g^1 (d-d transition) and show complimentary violet colour.

Example. How the complex compounds show the colour?

Solution When d-electrons absorb energy from visible region they will get excited. Absorbed energy is related to a particular wavelength.

$$E(\Delta)_{\text{absorbed}} = \frac{hc}{\lambda_{\text{absorbed}}}$$

when electrons fall into lower energy level it will show colour whose wavelength (λ) is the complimentary of absorbed wavelength ($\lambda_{\text{absorbed}}$).

Example. Why violet coloured $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$ becomes colourless when heated ?

Solution When $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$ is heated water molecules are removed and in the absence of ligand crystal field splitting does not occur and hence the substance is colourless.

Example. $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ are of different colours in dilute solutions. Why ?

Solution It is due to difference in power of ligands.

Example. What will be the correct order for the wavelengths of absorption in the visible region for the following : $[\text{Ni}(\text{NO}_2)_6]^{4-}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$?

Solution $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} > [\text{Ni}(\text{NH}_3)_6]^{2+} > [\text{Ni}(\text{NO}_2)_6]^{4-}$

GOLDEN KEY POINTS

- Red colour of ruby is due to presence of small amount of Cr^{+3} in atmosphere of Al_2O_3
- Green colour of emerald is due to presence of Cr^{+3} in atmosphere of $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ [beryl]
- Complex become colourless in absence of ligand field because in absence of ligand d-d-transition does not occur.
- $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ become colourless on heating due to removal of water molecules.
- Anhydrous CuSO_4 is colourless but hydrated CuSO_4 is blue due to moisture.
- Halogens are coloured due to the HOMO-LUMO transition.
- KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, CrO_2Cl_2 are coloured due to charge transfer spectra.

3.4 STABILITY OF CO-ORDINATION COMPOUNDS IN SOLUTION

According to thermodynamic stability, the reaction between a metal ion and the ligands may be considered as a Lewis acid base reaction in solution. If the equilibrium constant is high then the complex obtained is thermodynamically stable in solution. The reaction can be written as follows : $M + nL \rightleftharpoons [ML_n]$

The stability constant K , of the complex $[ML_n]$ is given by the relation, $K = \frac{[ML_n]}{[M][L]^n}$. The greater the value of K , more stable is the complex.

The strength of a complex ion also depends upon –

- Higher charge of the central metal ion.
- Greater base strength of the ligand.
- Ring formation (chelation) in structure of complexes.

BEGINNER'S BOX-4

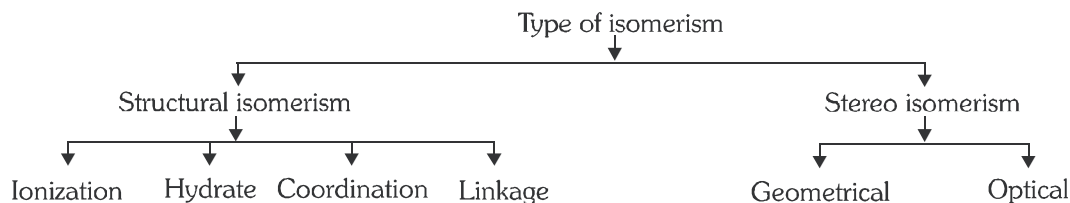
- Consider the following statements
 S_1 : $[Cr(NH_3)_6]^{3+}$ is a inner orbital complex with crystal field stabilization energy equal to $-1.2 \Delta_o$
 S_2 : The complex formed by joining the CN^- ligands to Fe^{3+} ion has theoretical value of 'spin only' magnetic moment equal to 1.73 B.M.
 S_3 : $Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5NOS]$,
 In reactant and product the oxidation states of iron are same and arrange in the order of true/false.
 (1) T T F (2) T T F (3) T T T (4) F F F
- For the $t_{2g}^6 e_g^2$ system, the value of magnetic moment (μ) is :
 (1) 2.83 B.M. (2) 1.73 B.M. (3) 3.87 B.M. (4) 4.92 B.M.
- Which of the following compound is not coloured :-
 (1) $Na_2[CuCl_4]$ (2) $Fe_4[Fe(CN)_6]_3$ (3) $Na_2[CdCl_4]$ (4) Na_2CrO_4
- The stability constants of the complexes formed by a metal ion M^{2+} with NH_3 , CN^- , H_2O are of the order of 10^{15} , 10^{27} , 10^{11} respectively. Then :-
 (1) NH_3 is the strongest ligand
 (2) CN^- is the strongest ligand
 (3) These values cannot predict the strength of the ligand
 (4) All the ligands are equally strong
- The value for crystal field stabilisation energy is zero for
 (1) $K_2[MnF_6]$ (2) $K_3[Fe(CN)_6]$ (3) $K_3[FeF_6]$ (4) $K_4[Fe(CN)_6]$
- Match the following

Complexes	Property
(i) $(CoCl_6)^{3-}$	(a) No. of electrons in $t_{2g} = 5$
(ii) $[Co(ox)_3]^{3-}$	(b) No. of electrons in $e_g = 0$
(iii) $[Co(H_2O)_6]^{2+}$	(c) No. of electrons in $t_{2g} = 6$
(iv) $[Fe(CN)_6]^{4-}$	(d) No. of electrons in $e_g = 2$

[Ans. i-d, ii-b, iii-a, d iv-c]
- Which order is correct
 (1) $[NiCl_6]^{4-} > [NiCl_4]^{2-}$ splitting energy Δ_o
 (2) $[Cr(en)_3]Cl_3 > [Cr(H_2O)_6]Cl_3$ crystal field stabilisation energy
 (3) $[Co(CN)_6]^{4-} > [Co(CN)_6]^{3-}$ reducing behaviour
 (4) All of these
- Which is inner d-complex
 (1) $[Co(H_2O)_6]^{3+}$ (2) $[RhF_6]^{3-}$ (3) $[IrF_6]^{3-}$ (4) All
- Which stability order is incorrect
 (1) $[Fe(C_2O_4)_3]^{3-} > [Fe(H_2O)_6]^{3+}$ (2) $[Fe(EDTA)]^{2-} > [Fe(en)_3]^{3+}$
 (3) $[Ni(en)_2]^{2+} > [Ni(dmg)_2]$ (4) $[Fe(CN)_6]^{3-} > [Fe(CN)_6]^{4-}$
- The complex exhibit lowest energy absorption bond is
 (1) $[NiCl_4]^{2-}$ (2) $[Ni(CO)_4]$ (3) $[Ni(CN)_4]^{2-}$ (4) $[Ni(H_2O)_6]^{2+}$

3.5 ISOMERISM IN COMPLEXES

- (a) Compounds which have the same molecular formula, but differ in their properties due to the difference in structure are called as **Isomers**.
- (b) Isomerism is commonly considered, to be the characteristic of only organic compounds, it is also found although less frequently among inorganic substances.
- (c) **Classification of isomerism :**



- **Structural Isomerism**

It arises due to the difference in the type of chemical linkages and distribution of ligands within and outside the coordination sphere.

- **Ionisation Isomers**

The type of isomerism which is due to the exchange of groups or ion between the coordinating sphere and the ionisation sphere.

Ex. (a) $\text{Co}(\text{NH}_3)_4 \text{Br}_2 \text{SO}_4$ can represent

(i) $[\text{Co}(\text{NH}_3)_4 \text{Br}_2] \text{SO}_4$ (red violet)

(ii) $[\text{Co}(\text{NH}_3)_4 \text{SO}_4] \text{Br}_2$ (red).

These complexes give sulphate ion and bromide ion respectively

(b) $[\text{Pt}(\text{NH}_3)_4 \text{Cl}_2] \text{Br}_2$ and $[\text{Pt}(\text{NH}_3)_4 \text{Br}_2] \text{Cl}_2$

(c) $[\text{Co}(\text{NH}_3)_4 (\text{NO}_3)_2] \text{SO}_4$ and $[\text{Co}(\text{NH}_3)_4 \text{SO}_4] (\text{NO}_3)_2$

- **Hydrate Isomers**

This type of isomerism is due to presence of different number of water molecules inside a coordination sphere.

Ex. (a) $\text{Cr}(\text{H}_2\text{O})_6 \text{Cl}_3$ has three possible structures

(i) $[\text{Cr}(\text{H}_2\text{O})_6] \text{Cl}_3$ violet

(ii) $[\text{Cr}(\text{H}_2\text{O})_5 \text{Cl}] \text{Cl}_2 \cdot \text{H}_2\text{O}$ green

(iii) $[\text{Cr}(\text{H}_2\text{O})_4 \text{Cl}_2] \text{Cl} \cdot 2\text{H}_2\text{O}$ dark green.

These complexes differ from one another with respect to the number of water molecules acting as ligands.

Other hydrate isomers are

(i) $[\text{Co}(\text{NH}_3)_4 \text{H}_2\text{O Cl}] \text{Cl}_2$

(ii) $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2] \text{Cl} \cdot \text{H}_2\text{O}$

- **Linkage or Salt Isomers**

(a) This type of isomerism arises due to presence of ambidentate ligands like NO_2^- , CN^- and SCN^-

(b) These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex.

(c) Such type of isomers are distinguished by infra red (I.R.) spectroscopy.

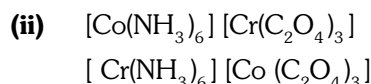
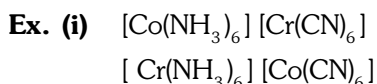
Ex. (i) $[\text{Co}(\text{NH}_3)_5 \text{NO}_2] \text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5 \text{ONO}] \text{Cl}_2$

(ii) In NO_2^- ligand, The coordinating sites are nitrogen (i.e., NO_2^- Nitro ligand) or through oxygen (i.e. ONO Nitrito ligand)

(iii) The nitro isomer is yellow and is stable to acids whereas nitrito isomer is red and is decomposed by acids.

- Coordination Isomers**

- This type of isomerism is exhibited when the complex has two complex ions in it - '**Cationic and Anionic**'.
- This type of isomerism is caused by the interchange of ligands between the two complex ions of the same complex.



- Stereo Isomerism**

- They have same molecular formula, same constitution, they differ only with respect to the spatial orientation of ligands in space around the metal ion.
- The two stereo isomers which are possible are - Geometrical and optical.

(A) Geometrical or cis - Trans Isomers

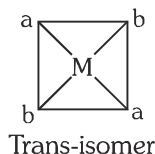
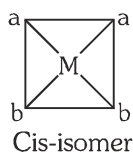
- The ligands occupy different positions around the central metal ion.
- When two identical ligands are coordinated to the metal ion from same side then it is **cis isomer**. (Latin, cis means same).
- If the two identical ligands are coordinated to the metal ion from opposite side then it is **Trans isomer** (in Latin, Trans means across).
- These geometrical isomers differ in physical as well as in chemical properties.
- Geometrical isomerism is most important in compounds with coordination numbers 4 and 6.
- 4-coordinated complexes with tetrahedral geometry do not exhibit cis- Trans isomerism, because relative position of ligands remain same for each other.
- It is exhibited by 4-coordinated complexes with square planar geometry.

Note : There are only 5 possible cases which shows geometrical isomerism in square planar complex.

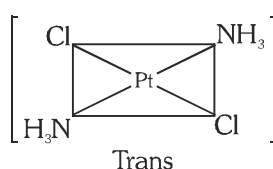
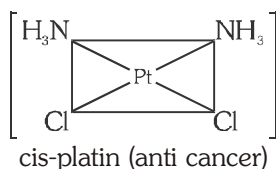
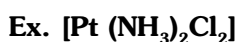
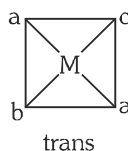
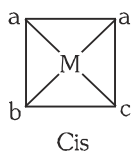
such as Ma_2b_2 , Ma_2bc , Mab cd , $\text{M}(\text{AB})_2$, $\text{M}(\text{AB})\text{cd}$

Geometrical Isomers With Coordination Number = 4 (Square Planar Complexes)

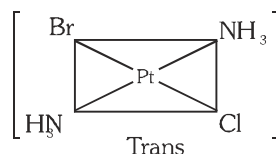
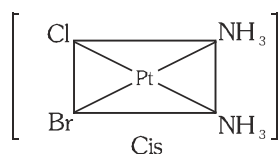
- (i)** Complexes with general formula, Ma_2b_2 (where both a and b are monodentate) can have Cis-and trans isomers.



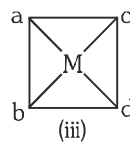
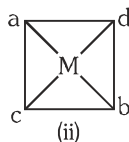
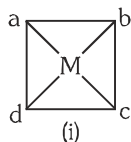
- (ii)** Complexes with general formula Ma_2bc can have Cis - and trans-isomers.



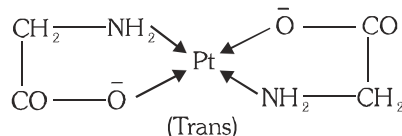
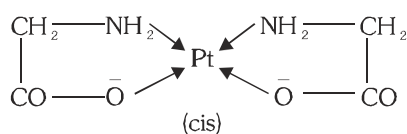
Ex. $[\text{Pt}(\text{NH}_3)_2\text{ClBr}]$



(iii) Complexes with general formula, **Mabcd** can have three isomers.

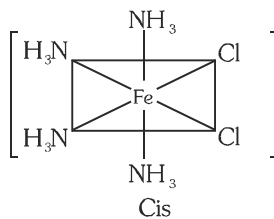
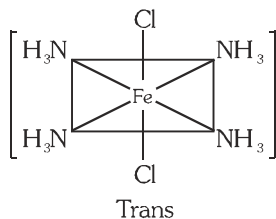


(iv) Diglycinato platinum (II) complexes

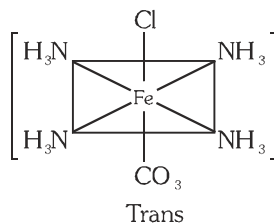
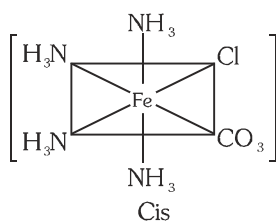


Geometrical isomers with Coordination number = 6

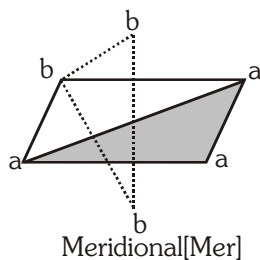
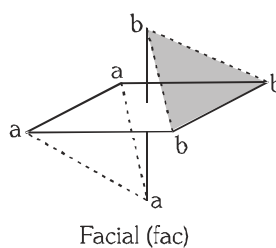
(i) $[\text{Fe}(\text{NH}_3)_4\text{Cl}_2]$



(ii) $[\text{Fe}(\text{NH}_3)_4\text{ClCO}_3]$



(iii) Facial and Meridional isomerism (Ma_3b_3)



Note : Other 6-Coordinated geometrical isomers are –

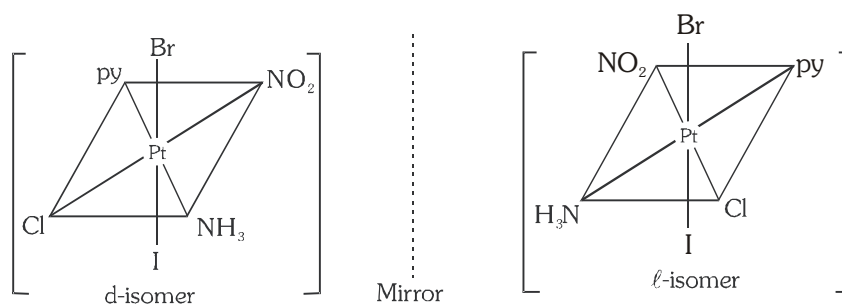
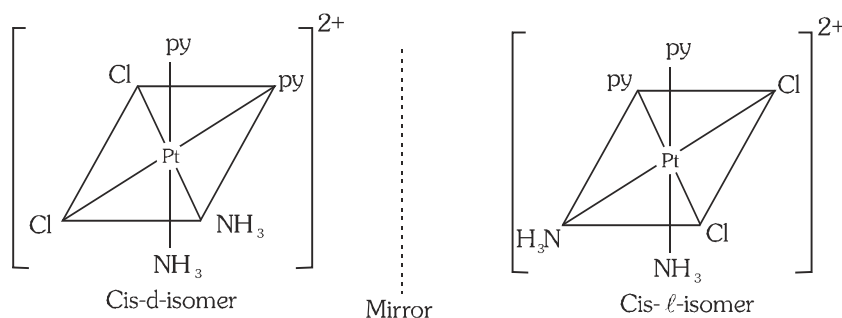
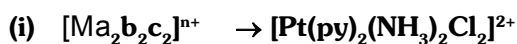
General formula	Total No. of geometrical isomers
Mabcdef	15 (30 optical isomers)
Ma ₂ bcd	9
Ma ₂ b ₂ cd	6
Ma ₂ b ₂ c ₂	5
Ma ₃ bcd	4
Ma ₃ b ₂ c	3
Ma ₃ b ₃	2
Ma ₄ bc	2
Ma ₄ b ₂	2
Ma ₅ b	Nil
Ma ₆	Nil

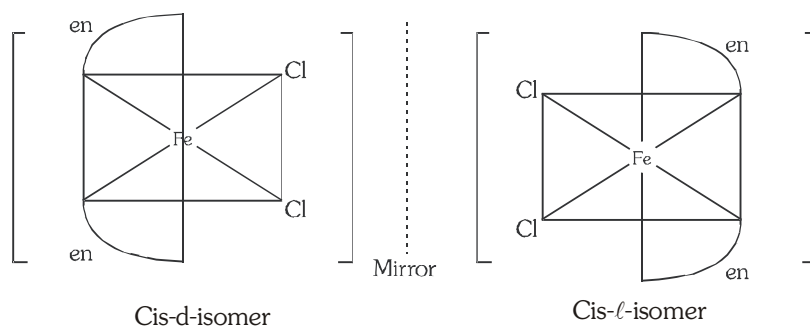
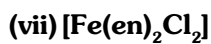
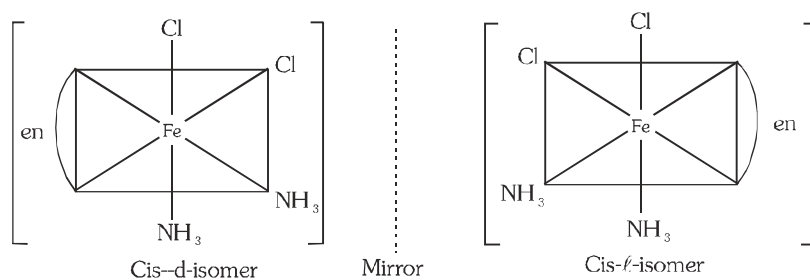
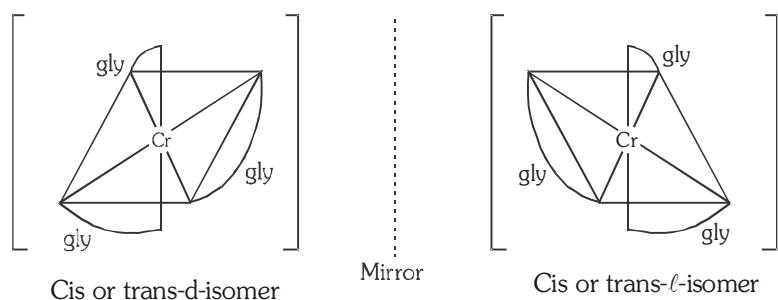
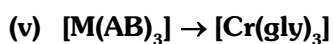
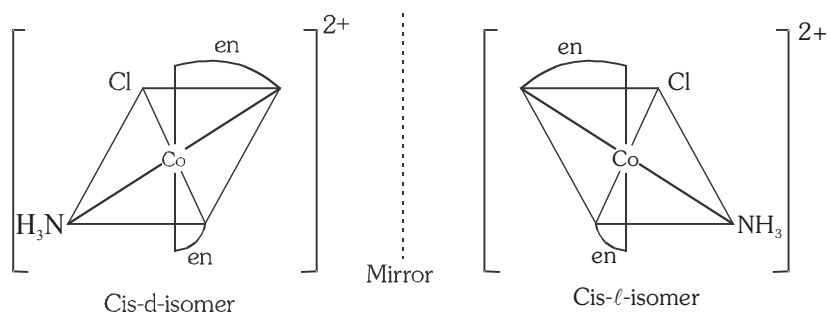
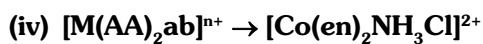
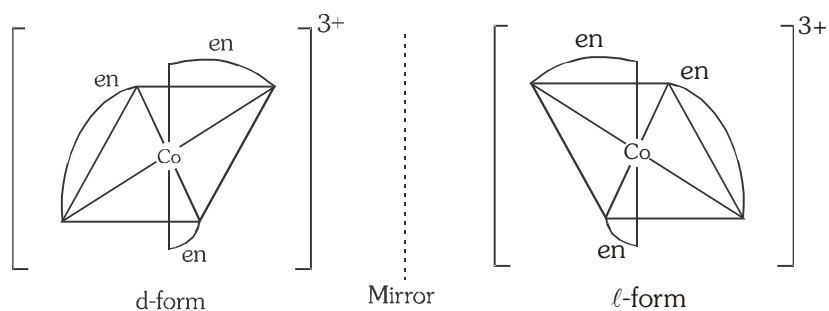
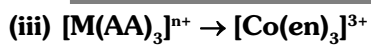
Here M = central atom ; a, b, c, d, e, f = Monodentate ligands

(B) Optical Isomers

- Optically active complexes are those which are non-superimposable over the mirror image structure.
- An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.
- The complex which rotates plane polarised light to left hand side is **laevo rotatory i.e. 'ℓ' or '—'** and if the complex rotates the plane polarised light to right hand side then it is **dextro rotatory 'd' or '+'**.
- Thus complexes which have same physical and chemical properties but differ in their action towards plane polarised light are called as **optical isomers**.
- The 'd' and 'ℓ' isomers of a compound are called as **Enantiomers or Enantiomorphs**.

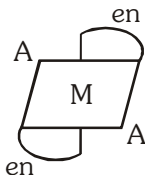
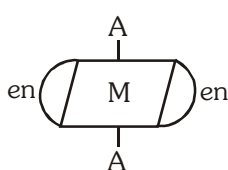
Optical isomers with Coordination number = 6





BEGINNER'S BOX-5

- Which of the following sets is/are example of co-ordination isomerism in complexes ?
 (1) $[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{CN})_6]$ and $[\text{Co}(\text{CN})_6] [\text{Cr}(\text{NH}_3)_6]$
 (2) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$
 (3) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Cr}(\text{NH}_3)_5\text{SO}_4]\text{Br}$
 (4) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and $[\text{Pt}(\text{NH}_3)_4] [\text{PtCl}_4]$
- Which of the following does/do not exhibit optical isomerism
 (1) Tetrahedral complexes (2) Square planar complexes
 (3) Octahedral complexes (4) Polynuclear complexes
- The number of geometrical isomers of $[\text{Co}(\text{NH}_3)_3(\text{NO}_3)_3]$ are :
 (1) 0 (2) 2 (3) 3 (4) 4
- Which of the following coordination entity form racemic mixture when mixed in equimolar concentration
 (1) $[\text{Cr}(\text{OX})_3]^{3-}$ (2) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ (3) $[\text{Co}(\text{en})\text{Cl}_4]^-$ (4) All
- The number of isomeric forms in which $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{1+}$ ion can occur is
 (1) 2 (2) 3 (3) 4 (4) 1
- The total number of possible isomer for the complex comp. :- $[\text{Cu}(\text{NH}_3)_4] [\text{PtCl}_4]$
 (1) 3 (2) 6 (3) 5 (4) 4
- The complexes $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$ and $[\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{Cl}_2$ are the examples of
 (1) Coordination isomerism (2) Ionisation isomerism
 (3) Geometrical isomerism (4) Linkage isomerism
- The type of isomerism exhibited $[\text{Rh}(\text{en})_2\text{Cl}_2][\text{Rh}(\text{en})\text{Cl}_4]$ and $[\text{Rh}(\text{en})_3][\text{RhCl}_6]$ is
 (1) Linkage (2) Coordination
 (3) Ligand (4) Ionisation
- Which of the following will give maximum number of isomers :-
 (1) $[\text{Co}(\text{py})_3(\text{NH}_3)_3]^{3+}$ (2) $[\text{Ni}(\text{en})(\text{NH}_3)_4]^{2+}$
 (3) $[\text{Fe}(\text{C}_2\text{O}_4)(\text{en})_2]^{2-}$ (4) $[\text{Cr}(\text{NO}_2)_2(\text{NH}_3)_4]^+$
- The Complexes given below are :-



- (1) Geometrical isomers (2) Position isomers (3) Optical isomers (4) Identical

3.6 ORGANOMETALLIC COMPOUNDS

Compounds in which C-atom is directly bonded with less electronegative element.

(Ge, Sb, B, Si, P, As) Also form organometallic compounds.

Ex. $\begin{cases} R-Zn-R & \text{dialkyl zinc (Frankland reagent)} \\ R-Mg-X & \text{Alkyl Magnesium halide (Grignards reagent)} \end{cases}$

(b) $\begin{array}{l} \text{Sodium acetate} \quad \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{ONa} \\ \text{Sodium ethoxide} \quad \text{C}_2\text{H}_5-\text{O}-\text{Na} \\ \text{Sodium Mercaptide} \quad \text{H}_3\text{C}-\text{SNa} \end{array} \left. \vphantom{\begin{array}{l} \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{ONa} \\ \text{C}_2\text{H}_5-\text{O}-\text{Na} \\ \text{H}_3\text{C}-\text{SNa} \end{array}} \right\} \text{These are not organometallic compounds because in these compounds metal is not directly attached with carbon atom.}$

(c) $\text{B}(\text{OCH}_3)_3$ is not OMC $\rightarrow \begin{array}{c} \text{H}_3\text{CO} \\ \diagup \\ \text{B}-\text{OCH}_3 \\ \diagdown \\ \text{H}_3\text{CO} \end{array}$ and $\text{CH}_3\text{B}(\text{OCH}_3)_2$ is OMC $\rightarrow \begin{array}{c} \text{OCH}_3 \\ \diagup \\ \text{CH}_3-\text{B} \\ \diagdown \\ \text{OCH}_3 \end{array}$

(d) Carbides and carbonates are not considered OMC because in these compounds metal carbon bond has ionic nature.

Classification of Organometallic Compounds

OMC can be classified into three main categories –

σ - bonded OMC : These compounds are formed mostly by non transition and metalloid elements.

Ex. $R-Mg-X$ (Grignard's reagent)

$(\text{CH}_3)_2\text{Zn}$ (Dimethyl zinc or Frankland's reagent)

R_2Cd (dialkyl cadmium)

$(\text{C}_2\text{H}_5)_4\text{Pb}$ (Tetra ethyl lead) – used as antiknocking agent in petrol.

$(\text{C}_2\text{H}_5)_3\text{Al} + \text{TiCl}_4$ (Ziegler natta catalyst) – Heterogeneous catalyst, used in polymerisation of alkene.

π - bonded OMC : These are usually formed by transition metals.

Ex. Ferrocene $[\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2]$ where η = No. of carbon atoms combined with metal atom.

Zeise's salt $[\text{PtCl}_3(\eta^2-\text{C}_2\text{H}_4)]$

Dibenzene chromium $[\text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2]$

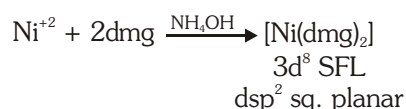
σ and π - bonded OMC : Transition metals of gp. 6, 7, 8, 9 and 10 in their zero oxidation state form such type of OMC. The carbonyl compounds of these metals have both σ and π bonds.

Ex. $[\text{Ni}(\text{CO})_4], [\text{Fe}(\text{CO})_5], [\text{Mn}_2(\text{CO})_{10}]$

$[\text{M}(\text{CO})_6]$ $[\text{M} = \text{Cr}, \text{Mo}, \text{W}]$

3.7 APPLICATION OF COORDINATION CHEMISTRY

(a) Test of Ni^{+2} : Ni^{+2} ion give rosy red ppt when react with dmg in weak alkaline medium.



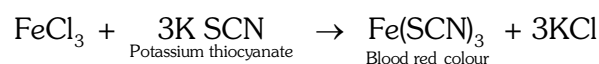
(b) Test of S^{2-} : $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})] \rightarrow \text{Na}_4[\text{Fe}(\text{CN})_5(\text{NOS})]$

sodium nitro prousside violet colour

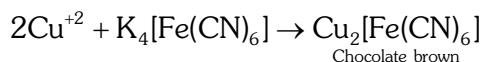
(c) Test of Fe^{+2} & Fe^{+3} :



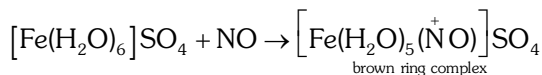
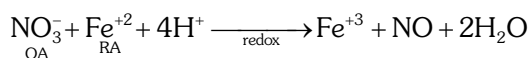
(d) Test of Fe^{+3}



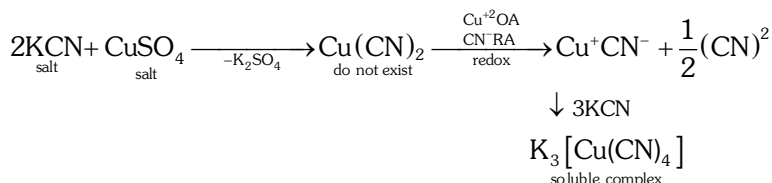
(e) Test of Cu⁺²



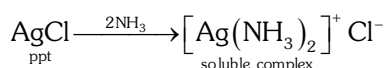
(f) Brown ring test : Test for Nitrate ion



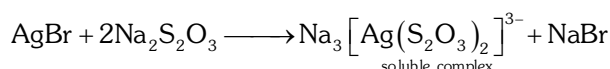
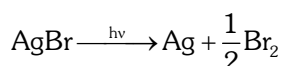
(g) If excess of KCN & KI is added in CuSO₄ insoluble CuCN & CuI is formed which later turn into soluble complex.



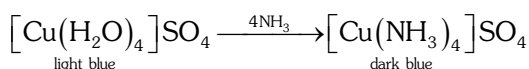
(h) AgCl or AgBr ppt (Not AgI) are soluble in ammonia & NH₄OH



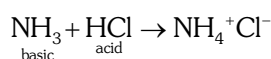
(i) In photography : undecomposed AgBr is removed from photography film by using hyposolution [Na₂S₂O₃·5H₂O]



(j) Light blue colour of aqueous solution of CuSO₄ turn into dark blue in presence of ammonia



But in the presence of acid in above there is no colour change



(k) Rusting spots of iron [Fe₂O₃·xH₂O] can be removed by using oxalic acid.

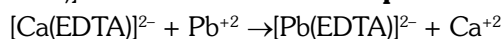
(l) cyano complex are used for electroplating of Ag or Au due to high stability.

e.g. [Ag(CN)₂]⁻

(m) **Wilkinson catalyst** [RhCl(PPh₃)₃] is used for hydrogenation of alkene. (Homogeneous catalysis)

(n) [EDTA]⁴⁻ is used for **estimation of hardness of water**.

(o) [Ca(EDTA)]²⁻ is **used to remove Pb poison**.



(p) **Biological importance**

Chlorophyll (Mg)

haemoglobin (Fe⁺²)

Myoglobin (Fe⁺²)

Vit B₁₂ (Co)

Corboxypeptide (Zn)

Insulin (Zn)

JAHN TELLER EFFECT

In octahedral field if the d electrons are symmetrically arranged, they will repel all six ligands equally. Thus the structure will be a completely regular octahedron.

If the d electrons are unsymmetrically arranged, they will repel some ligands in the complex more than others. Thus the structure is distorted. The e_g orbitals point directly at the ligands. Thus unsymmetric filling of the e_g orbitals results in some ligands being repelled more than others. This causes a significant distortion of the octahedral shape. In contrast the t_{2g} orbitals do not point directly at the ligands, but point in between the ligand directions. Thus unsymmetric filling of the t_{2g} orbitals has only a very small effect on the stereochemistry. Distortion caused by unsymmetric filling of the t_{2g} orbitals is usually too small to measure.

If the d_{z^2} orbital contains one more electron than the $d_{x^2-y^2}$ orbital then the ligands approaching along +z and -z will face greater repulsion than the other four ligands. The repulsion and distortion result in elongation of the octahedron along the z-axis. This is called tetragonal distortion or tetragonal elongation.

If the $d_{x^2-y^2}$ orbital contains the extra electron, then elongation will occur along the x and y axes. This means that the ligands approach more closely along the z axis. Thus there will be four long bonds and two short bonds. This is equivalent to compressing the octahedron along the z axis, and is called tetragonal compression.

Example-I

Many Cu(+II) salts and complexes also show tetragonally distorted octahedral structures. Cu^{2+} has a d^9 configuration:



To minimize repulsion with the ligands, two electrons occupy the d_{z^2} orbital and one electron occupies the $d_{x^2-y^2}$ orbital. Thus the two ligands along +z and -z are repelled more strongly than the other four ligands.

Therefore according to Jahn Teller effect distortion in regular octahedral geometry occurs when unsymmetrical configuration is present in e_g orbitals of central metal ion/atom.

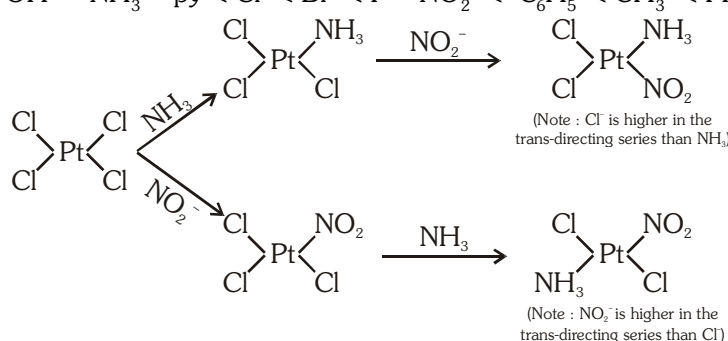
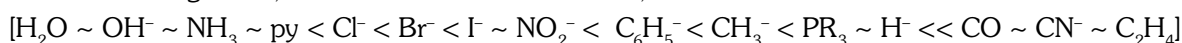
Example-II

High spin complexes in which J.T. effect is i.e. d^1 , d^2 , d^3 (negligible), d^4 , d^6 , d^7 , d^9 observed.

TRANS EFFECT (The kinetic trans effect)

The kinetic trans effect, defined as the relationship between the rate of substitution of square planar complexes and the nature of the species trans to the ligands being displaced.

A trans-directing series, such as the one shown below, can be constructed :



In a substitution reaction in which there is more than one possibility as to which chloride will be replaced, the trans directing series is used to predict which structure will be possible.

BEGINNER'S BOX-6

- $\text{K}_4[\text{Fe}(\text{CN})_6]$ reacts with FeCl_3 to form :-
 (1) $\text{K}_3[\text{Fe}(\text{CN})_6]$ (2) $\text{K}_4[\text{Fe}(\text{CN})_3\text{Cl}_3]$ (3) $\text{K}_3[\text{Fe}(\text{CN})_5\text{Cl}]$ (4) $\text{KFe}[\text{Fe}(\text{CN})_6]$
- A blue colouration is not obtained when :-
 (1) NH_4OH is added to CuSO_4 (2) CuSO_4 solution reacts with $\text{K}_4[\text{Fe}(\text{CN})_6]$
 (3) FeCl_3 reacts with $\text{K}_4[\text{Fe}(\text{CN})_6]$ (4) Anhydrous white CuSO_4 is dissolved in water
- A reagent used for identifying nickel ion is :-
 (1) Potassium ferrocyanide (2) Phenolphthalin
 (3) Dimethyl glyoxime (4) EDTA
- Match the following
Complex
 (A) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
 (B) $\text{K}_3[\text{Cu}(\text{CN})_4]$
 (C) $[\text{Ca}(\text{EDTA})]^{2-}$
 (D) $\text{K}_2[\text{Cd}(\text{CN})_4]$
Property
 (P) reacts with H_2S gas
 (Q) estimation of hardness
 (R) removal of lead poisoning
 (S) anti cancer drug
 (T) coordination number of metal is = 4
 (1) (A)-S, T, (B) T, (C) Q, R (D) P, T
 (2) (A)-S (B) T, (C) Q, R (D) P, T
 (3) (A)-P, (B) T, (C) Q, R (D) P, T
 (4) (A)-R (B) T, (C) Q, R (D) P, T

5. A person suffering from lead poisoning should be fed with :-
 (1) Hypo (2) Cis-platin (3) $[\text{Ca}(\text{EDTA})]^{2-}$ (4) DMG
6. Zeigler natta catalyst is :
 (1) $[\text{RhCl}(\text{PPh}_3)_3]$ (2) $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{TiCl}_4$ (3) $\text{K}(\text{PtCl}_3(\eta^2 - \text{C}_2\text{H}_4))$ (4) Pt/Rh
7. In which of the following process OMC is formed with the help of other OMC :
 (1) $\text{SnCl}_4 + \text{Butyl lithium} \longrightarrow \text{Bu}_4\text{Sn} + 4\text{LiCl}$
 (2) $\text{C}_2\text{H}_5\text{I} + 4\text{Pb}/\text{Na (alloy)} \longrightarrow (\text{C}_2\text{H}_5)_4\text{Pb} + 4\text{NaI} + 3\text{Pb}$
 (3) $\text{Ni} + 4\text{CO} \longrightarrow [\text{Ni}(\text{CO})_4]$
 (4) $\text{K}_2[\text{PtCl}_4] + \text{CH}_2 = \text{CH}_2 \longrightarrow \text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] + \text{KCl}$
8. Which is/are organometallic compound :-
 (I) Grignard reagent (II) Sodium methoxide (III) trimethyl boron (IV) TEL
 (1) Only I (2) I & II (3) I, II, IV (4) I, III, IV
9. Which of the following is an organometallic compound :
 (1) $\text{Ti}(\text{OCOCH}_3)_4$ (2) $\text{Ti}(\text{OC}_6\text{H}_5)_4$ (3) $\text{Ti}(\text{OC}_2\text{H}_5)_3\text{C}_2\text{H}_5$ (4) $\text{Ti}(\text{OC}_2\text{H}_5)_4$

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	4	3	1			2	3	3	2
BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	4	3	3	1	4	1	1	3	4
BEGINNER'S BOX-3	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	4	4	2	2	3	1	3	3	3	1
BEGINNER'S BOX-4	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	1	3	2	3		4	4	3	1
BEGINNER'S BOX-5	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	1	2	2	1,2	1	4	4	2	4	4
BEGINNER'S BOX-6	Que.	1	2	3	4	5	6	7	8	9	
	Ans.	4	2	3	1	3	2	1	4	3	

NCERT QUESTIONS (REASONING)

Q.1 Explain the term Degenerate orbitals :

Ans. Orbitals which have same energy in a subshell are known as degenerate orbitals.

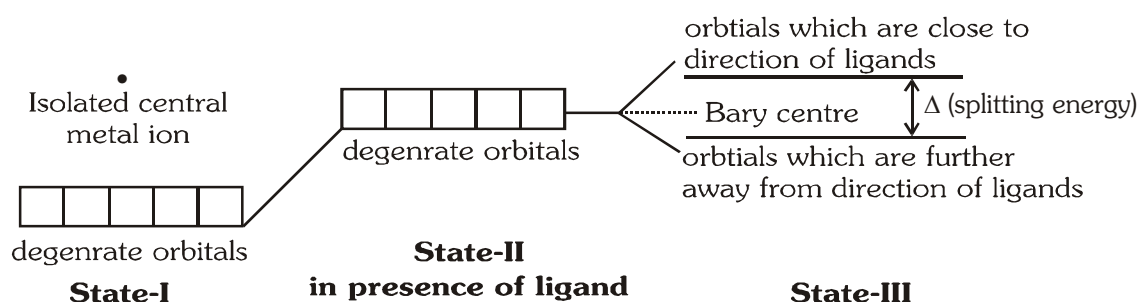
Q.2 What is crystal field splitting ?

Ans. According to CFT the interaction between a transition metal and ligands arises from the attraction between the positively charged metal cation and negative charge of ligand.

As a ligand approaches the metal ion, the electrons of ligand will be closer to some of the d-orbitals and farther away from other causing a loss of degeneracy.

The electrons in the d-orbitals and those in the ligand repel each other due to repulsion between like charges. Thus the d-electrons closer to the ligands will have a higher energy than those further away as a results in the d-orbitals splitting in energy.

This loss of degeneracy of d-orbital is known as crystal field splitting.



The state I represents degeneracy of all the five d-orbitals in the isolated central ion. The state II represents hypothetical degeneracy of all the orbitals at a higher energy level if the negative charge of all the ligands is assumed to be uniformly affecting the electrons in the d-orbitals of the metal ion. The state III represents crystal field splitting.

Q.3 Define (a) crystal field stabilisation energy (b) Pairing energy ?

Ans. (a) Crystal field stabilisation energy : The lowering in the energy of a transition metal ion in a given ligand environment due to crystal field effects.

(b) Pairing energy : The energy required to pair the electrons.

Q.4 Explain the term

(a) Inner orbital complex and outer orbital complexes ?

(b) Low spin and high spin complexes ?

Ans. (a) The empty 'd' orbitals involved in hybridisation may be inner (n-1)d or outer "nd" orbitals and these complexes are called as **Inner orbital complexes** and **outer orbital complexes** respectively.

For example in d^2sp^3 hybridisation (n-1)d, ns and np orbitals are mixed it forms inner orbital complex and in sp^3d^2 ns, np and nd orbitals are mixed so it forms outer orbitals complex.

(b) When the strong field ligand approaches to metal ion value to splitting energy (Δ) is greater than, pairing energy, so it is unfavourable to put electron into high energy orbitals. Therefore, the lower energy orbitals are completely filled before population of the upper sets starts according to the Aufbau principle. Such type of complexes are called low spin complex.

For low spin complexes

splitting energy (Δ) > pairing energy (P)

Weak field ligand causes a small splitting of the d-orbitals where splitting energy is less than pairing energy. It is easier to put electrons into the higher energy set of orbitals than to pair up in the same low energy orbitals because two electrons in the same orbitals repel each other. So one electron is put into each of the five d-orbitals before any pairing occur in accordance with hund rule.

Such complexes are known as high spin complex.

For high spin complexes splitting energy (Δ) < pairing energy (P)

Q.5 In octahedral complex if central metal have configuration d^1, d^2, d^3 always make inner orbital complex, Why ?

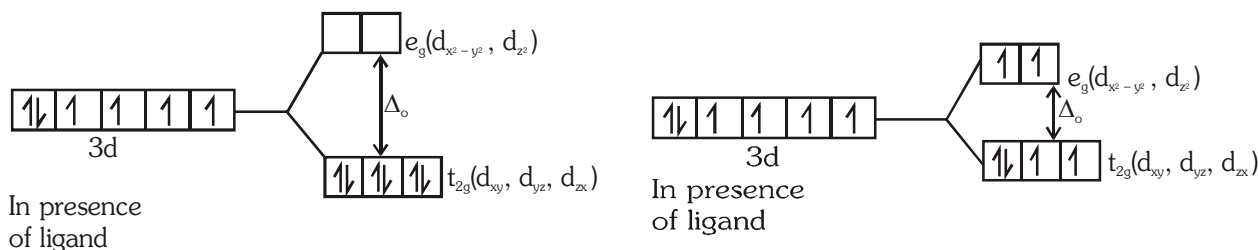
Ans. Central metal ion which have d^1, d^2, d^3 configuration have at least two vacant orbitals in any ligand environment or with any central metal ion with any oxidation state. So always make inner orbital complex.

Q.6 Explain the formation of $\text{Na}_4[\text{Fe}(\text{CN})_6]$ and $\text{Na}_4[\text{FeF}_6]$? Show which is low spin and which is high spin complex and also calculate the Crystal field stabilisation energy (CFSE) ?

Ans. In given compounds CN^- is strong field ligands and F^- is weak field ligand and in both compounds ions is in +2 oxidation state d^6 configuration.

So in $\text{Na}_4[\text{Fe}(\text{CN})_6]$

$\text{Na}_4[\text{FeF}_6]$



$$\text{For octahedral CFSE} = \left[-0.4(n_{t_{2g}}) + 0.6(n_{e_g}) \right] \Delta_0 + nP$$

where $n_{t_{2g}}$ = number of electron in t_{2g} orbitals

n_{e_g} = number of electron in e_g orbitals

$$\text{Na}_4[\text{Fe}(\text{CN})_6] \text{ CFSE} = -2.4 \Delta_0 + 3P. \quad [n_{t_{2g}} = 6, n_{e_g} = 0]$$

$$\text{Na}_4[\text{Fe}(\text{F})_6] \text{ CFSE} = -0.4 \Delta_0 + P [n_{t_{2g}} = 4, n_{e_g} = 2]$$

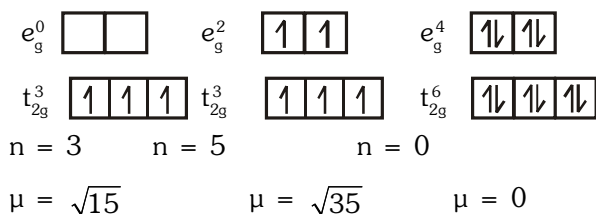
where P = pairing energy to pair up electron.

Q.7 Calculate the paramagnetism into following compound ?



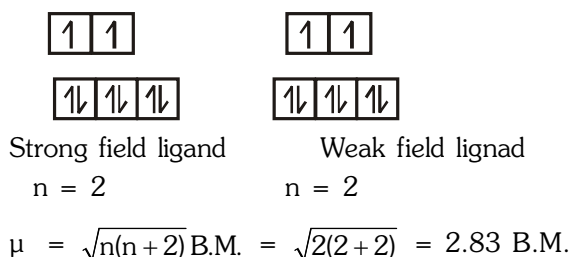
Ans. In all compound H_2O is a weak field ligand so pairing of electron will not occur in

(I) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (II) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (III) $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$



Q.8 Why the d^8 configuration always shows paramagnetism 2.83 B.M in octahedral complex?

Ans. In given d^8 configuration for octahedral complex for both strong field ligand and weak field ligand is always have two unpaired electron.



EXERCISE-I (Conceptual Questions)**TERMINOLOGY OF COORDINATION COMPOUND**

- In the complex ion $[\text{Fe}(\text{EDTA})]^-$ the coordination number and oxidation state of central metal ion is :-
 (1) C. N. = 6 O. N. = +3
 (2) C. N. = 1 O. N. = -1
 (3) C. N. = 4 O. N. = +2
 (4) C. N. = 3 O. N. = +3
- The coordination number and oxidation number of the central metal ion in the complex $[\text{Pt}(\text{en})_2]^{+2}$ is :-
 (1) C. N. = 2, O. N. = +2
 (2) C. N. = 6, O. N. = +4
 (3) C. N. = 4, O. N. = +4
 (4) C. N. = 4, O. N. = +2
- Select bidentate or didentate ligand from the following .
 (1) CO (2) SCN^-
 (3) CH_3COO^- (4) $\text{C}_2\text{O}_4^{2-}$
- The oxidation and coordination number of Pt in $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ is respectively :-
 (1) + 1, 3 (2) + 2, 4
 (3) + 3, 6 (4) + 2, 5
- The CN and ON of X in the compound $[\text{X}(\text{SO}_4)(\text{NH}_3)_5]$ will be :-
 (1) 10 and 3 (2) 1 and 6
 (3) 6 and 4 (4) 6 and 2
- What is the oxidation number of Fe in $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$ ion?
 (1) +2 (2) +3 (3) +1 (4) 0
- The oxidation state of iron in $\text{Na}_4[\text{Fe}(\text{CN})_5(\text{NOS})]$ is
 (1) +1 (2) +2 (3) +3 (4) zero
- Incorrect statement about DMG:-
 (1) It is tetradentate ligand
 (2) Chelating ligand
 (3) dioxime of diacetyl
 (4) in gravimetric determination of Ni is used

IUPAC - NOMENCLATURE

- $\text{K}_3[\text{Fe}(\text{CN})_6]$ is :-
 (a) Potassium hexacyano ferrate (II)
 (b) Potassium hexacyano ferrate (III)
 (c) Potassium ferri-cyanide
 (d) Hexacyano ferrate (III) potassium
 Correct answer is :-
 (1) Only (a) and (b) (2) Only (b) and (c)
 (3) Only (a) and (c) (4) Only (b) and (d)

Build Up Your Understanding

- Give the IUPAC name of the complex compound $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}](\text{NO}_3)_2$.
 (1) Bromoaquatetraamine Cobalt (III) nitrate
 (2) Bromoaquatetraaminocobalt (III) nitrate
 (3) Bromoaquatetraammine cobalt (III) nitrate
 (4) Tetraammineaquabromido cobalt (III) nitrate
- Which of the following complex is anion :-
 (1) Fluoro pentaammine cobalt (III)
 (2) Trioxalato ferrate (III)
 (3) Penta Carbonyl iron (0)
 (4) Dichloro diammine platinum
- The chloro-bis (ethylenediamine) nitro cobalt (III) ion is :-
 (1) $[\text{Co}(\text{NO}_2)_2(\text{en})_2\text{Cl}_2]^+$ (2) $[\text{CoCl}(\text{NO}_2)_2(\text{en})_2]^+$
 (3) $[\text{Co}(\text{NO}_2)\text{Cl}(\text{en})_2]^+$ (4) $[\text{Co}(\text{en})\text{Cl}_2(\text{NO}_2)_2]^+$
- Which of the following complexes is not a chelate
 (1) bis (dimethylglyoximate) nickel(II)
 (2) Potassium ethylenediaminetetrathiocyanato chromate(III)
 (3) Tetrammine dichlorocobalt(III) nitrate
 (4) Trans-diglycinatoplatinum(II)
- The correct IUPAC name of the complex $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ is
 (1) Cyclopentadienyl iron (II)
 (2) Bis (cyclopentadienyl) iron (II)
 (3) Dicyclopentadienyl ferrate (II)
 (4) Ferrocene
- The correct name of $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{PtCl}_4]$ is :-
 (1) Tetraammine dichloro platinum (IV) tetrachloro platinate (II)
 (2) Dichloro tetra ammine platinum (IV) tetrachloro platinate (II)
 (3) Tetrachloro platinum (II) tetraammine platinate(IV)
 (4) Tetrachloro platinum (II) dichloro tetraamine platinate (IV)
- The IUPAC name of $\text{K}_2[\text{Cr}(\text{CN})_2\text{O}_2(\text{O})_2(\text{NH}_3)]$ is:-
 (1) Potassiumamminedicyano dioxoperoxochromate(VI)
 (2) Potassiumamminecyanoperoxodioxo chromium (VI)
 (3) Potassiumamminecyanoperoxodioxo chromium (VI)
 (4) Potassiumamminecyanoperoxodioxo chromate (IV)
- The IUPAC name for $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ is :-
 (1) Hexaammine cobalt (III) hexacyanochromate (III)
 (2) Hexacyanochromium cobalt hexaammine (VI)
 (3) Hexaammine cobalt (III) hexacyanochromium (VI)
 (4) Hexacyanochromium (III) hexaammine cobalt (III)

18. The IUPAC name for $[\text{Co}(\text{NCS})(\text{NH}_3)_5]\text{Cl}_2$ is :-
 (1) Pentaammine (thiocyanato-N) cobalt (III) chloride
 (2) Pentaammine (thiocyanato-S) cobalt (III) chloride
 (3) Pentaammine (isothiocyanato-N,S)cobalt (III) chloride
 (4) Pentaammine (mercapto-N) cobalt (III) chloride
19. IUPAC name of $\text{K}_2[\text{OsCl}_5\text{N}]$ will be
 (1) Potassium pentachloroazido osmate (VIII)
 (2) Potassium pentachloroazido osmate (VI)
 (3) Potassium pentachloro nitrido osmate (VI)
 (4) Potassium nitro osmate (III)

WERNER'S THEORY & EAN

20. Which of the following has least conductivity in aqueous solution.
 (1) $\text{Co}(\text{NH}_3)_4\text{Cl}_3$ (2) $\text{Co}(\text{NH}_3)_3\text{Cl}_3$
 (3) $\text{Co}(\text{NH}_3)_5\text{Cl}_2$ (4) $\text{Co}(\text{NH}_3)_6\text{Cl}_3$
21. If EAN of a central metal ion X^{+2} in a complex is 34, and atomic number of X is 28. The number of monodentate ligands present in complex are:-
 (1) 3 (2) 4 (3) 6 (4) 2
22. The EAN of cobalt in the complex ion $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ is :-
 (1) 27 (2) 36 (3) 33 (4) 35
23. The effective atomic number of Cr (atomic no. 24) in $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ is
 (1) 35 (2) 27 (3) 33 (4) 36
24. Which gives only 25% mole of AgCl , when reacts with AgNO_3 :-
 (1) $\text{PtCl}_2 \cdot 4\text{NH}_3$ (2) $\text{PtCl}_4 \cdot 5\text{NH}_3$
 (3) $\text{PtCl}_4 \cdot 4\text{NH}_3$ (4) $\text{PtCl}_4 \cdot 3\text{NH}_3$
25. In the metal carbonyls of general formula $\text{M}(\text{CO})_x$ (Which follows EAN rule) if M is Ni, Fe and Cr the value of x will be respectively:-
 (1) 6, 5, 6 (2) 4, 5, 6
 (3) 4, 4, 5 (4) 4, 6, 6
26. A compound has the empirical formula $\text{CoCl}_3 \cdot 5\text{NH}_3$. When an aqueous solution of this compound is mixed with excess silver nitrate, 2 mol of AgCl precipitate per mol of compound. On reaction with excess HCl , no NH_4^+ is detected. Hence it is
 (1) $[\text{Co}(\text{NH}_3)_5\text{Cl}_2]\text{Cl}$
 (2) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
 (3) $[\text{Co}(\text{NH}_3)_5\text{Cl}_3]$
 (4) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{NH}_3$
27. Which of the following pair the EAN of central metal atom is not same?
 (1) $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{NH}_3)_6]^{3+}$
 (2) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ and $[\text{Cr}(\text{CN})_6]^{3-}$
 (3) $[\text{FeF}_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$
 (4) $[\text{Ni}(\text{CO})_4]$ and $[\text{Ni}(\text{CN})_4]^{2-}$

VALENCE BOND THEORY

28. Which of the following compound is paramagnetic
 (1) Tetracyanonickelate (II) ion
 (2) Tetraamminezinc (II) ion
 (3) Hexamine chromium (III) ion
 (4) Diammine silver (I) ion
29. The shape of the complex $[\text{Ag}(\text{NH}_3)_2]^+$ is :
 (1) Octahedral (2) Square planar
 (3) Tetrahedral (4) Linear
30. Hexafluoroferrate (III) ion is an outer orbital complex. The number of unpaired electrons are
 (1) 1 (2) 5
 (3) 4 (4) Unpredictable
31. The shape of $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ is :
 (1) Square planar (2) Pyramidal
 (3) Octahedral (4) Tetrahedral
32. Among the following ions, which one has the highest paramagnetism ?
 (1) $[\text{FeF}_6]^{3-}$ (2) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 (3) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ (4) $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$
33. In the complex ion ML_6^{n+} , M^{n+} has five d-electrons and L is weak field ligand. According to crystal field theory, the magnetic properties of the complex ion correspond to how many unpaired electrons
 (1) 0 (2) 5 (3) 2 (4) 3
34. A magnetic moment of 1.73 BM will be shown by one among of the following compounds .
 (1) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ (2) $[\text{Ni}(\text{CN})_4]^{2-}$
 (3) TiCl_4 (4) $[\text{CoCl}_6]^{3-}$
35. The magnetic property and the shape of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ complex ions are :
 (1) Paramagnetic, Octahedral
 (2) Diamagnetic, square planar
 (3) Paramagnetic, tetrahedral
 (4) None of the above
36. Amongst the following ions which one has the highest paramagnetism
 (1) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ (2) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
 (3) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ (4) $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$
37. Which of the following complexes is an inner orbital complex ?
 (1) $[\text{CoF}_6]^{3-}$ (2) $[\text{FeF}_6]^{3-}$
 (3) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ (4) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
38. The wrong statement is :-
 (1) Halide ligands forms high spin complex
 (2) Strong ligands form low spin complex
 (3) $[\text{FeF}_6]^{3-}$ is inner orbital complex
 (4) $[\text{NiCl}_4]^{2-}$ is outer orbital complex

- 39.** What is Incorrect for $K_4[Fe(CN)_6]$
 (1) O.N of Iron is +2
 (2) It exhibit diamagnetic character
 (3) It exhibit paramagnetic character
 (4) It involved d^2sp^3 hybridisation
- 40.** In which of the following molecules, central atom used orbitals of different principle quantum number in the hybridisation :-
 (1) $[Fe(CO)_5]$ (2) IF_7
 (3) $Ni(CO)_4$ (4) XeO_4
- 41.** What are the geometric shape and the oxidation number of the copper atom, respectively, for the complex ion, $[Cu(NH_3)_4(OH_2)_2]^{2+}$?
 (1) Tetrahedral; + 2
 (2) Square planar; - 2
 (3) Linear; + 3
 (4) Octahedral; + 2
- 42.** For FeF_6^{3-} and $Fe(CN)_6^{3-}$ magnetic moment of the fluoride complex is expected to be:-
 (1) The same as the magnetic moment of the cyanide complex
 (2) Larger than the magnetic moment of the cyanide complex because there are more unpaired electrons in the fluoride complex
 (3) Smaller than the magnetic moment of the cyanide complex because there are more unpaired electrons in the fluoride complex
 (4) Larger than the magnetic moment of the cyanide complex because there are fewer unpaired electrons in the fluoride complex
- 43.** Which of the following contains one unpaired electron in the 4p orbitals :-
 (1) $[Cu(NH_3)_2]^+$ (2) $[Cu(NH_3)_4]^{2+}$
 (3) $[Cu(CN)_4]^{3-}$ (4) $[Ni(CN)_4]^{2-}$
- 44.** Which of the following complexes are low spin and diamagnetic ?
 (a) $K_4[Os(CN)_6]$
 (b) $[Mo(CO)_6]$
 (c) $[Mn(CN)_6]^{4-}$
 Select the correct answer using the codes given below:
 (1) a, b and c (2) a and b only
 (3) a and c only (4) b and c only
- 45.** How many unpaired electrons are present in the Brown Ring complex $[Fe(H_2O)_5(NO)]SO_4$
 (1) 4 (2) 3
 (3) 0 (4) 5
- 46.** Which of the following statements about $Fe(CO)_5$ is correct?
 (1) It is paramagnetic and high spin complex
 (2) It is diamagnetic and high spin complex
 (3) It is diamagnetic and low spin complex
 (4) It is paramagnetic and low spin complex
- 47.** Which is true for $[Ni(en)_2]^{2+}$, $Z(Ni) = 28$?
 (1) paramagnetism, dsp^2 , square planar, C.N. of Ni = 2
 (2) diamagnetism, dsp^2 , square planar, C.N. of Ni = 4
 (3) diamagnetism, sp^3 , tetrahedral, C.N. of Ni = 4
 (4) paramagnetism, sp^3 , tetrahedral, C.N. of Ni = 4
- 48.** Arrange the following in order of decreasing number of unpaired electrons :
 I : $[Fe(H_2O)_6]^{2+}$ II : $[Fe(CN)_6]^{3-}$
 III : $[Fe(CN)_6]^{4-}$ IV : $[Fe(H_2O)_6]^{3+}$
 (1) IV, I, II, III (2) I, II, III, IV
 (3) III, II, I, IV (4) II, III, I, IV

CFT, COLOUR OF THE COMPLEX AND STABILITY

- 49.** Which one of these ions absorbs energy from visible spectrum :-
 (1) $[Cu(NH_3)_4]^+$ (2) $[Cu(NH_3)_4]^{+2}$
 (3) $[Zn(H_2O)_6]^{+2}$ (4) $[Co(H_2O)_6]^{+3}$
- 50.** In the complex $[Ni(H_2O)_2(NH_3)_4]^{+2}$ the magnetic moment (μ) of Ni is :-
 (1) Zero (2) 2.83 BM
 (3) 1.73 BM (4) 3.87 BM
- 51.** Which of the following system has maximum number of unpaired electrons :-
 (1) d^5 (Octahedral, low spin)
 (2) d^8 (Tetrahedral)
 (3) d^6 (Octahedral, low spin)
 (4) d^3 (Octahedral)
- 52.** In an octahedral crystal field, the t_{2g} orbitals are
 (1) Raised in energy by $0.4 \Delta_0$
 (2) Lowered in energy by $0.4 \Delta_0$
 (3) Raised in energy by $0.6 \Delta_0$
 (4) Lowered in energy by $0.6 \Delta_0$
- 53.** If $\Delta_0 < P$, the correct electronic configuration for d^4 system will be :-
 (1) $t_{2g}^4 e_g^0$ (2) $t_{2g}^3 e_g^1$
 (3) $t_{2g}^0 e_g^4$ (4) $t_{2g}^2 e_g^2$

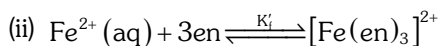
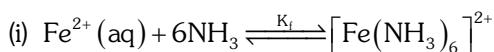
54. Match List-I (Complex ions) with List-II (Number of Unpaired Electrons) and select the correct answer using the codes given below the lists :-

List-I (Complex ions)	List-II (Number of Unpaired Electrons)
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A. $[\text{CrF}_6]^{4-}$	i. One
B. $[\text{MnF}_6]^{4-}$	ii. Two
C. $[\text{Cr}(\text{CN})_6]^{4-}$	iii. Three
D. $[\text{Mn}(\text{CN})_6]^{4-}$	iv. Four
	v. Five

Code :	A	B	C	D
(1)	iv	i	ii	v
(2)	ii	v	iii	i
(3)	iv	v	ii	i
(4)	ii	i	iii	v

55. Consider the following complex formation reactions and comment on their formation constant value



- (1) $K_f > K'_f$ (2) $K_f < K'_f$
 (3) $K_f = K'_f$ (4) can not be compared

56. Select most stable complex :-

- (1) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ (2) $[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{+3}$
 (3) $[\text{Co}(\text{en})_3]^{+3}$ (4) $[\text{Co}(\text{NH}_3)_4(\text{en})]^{+3}$

57. What will be the theoretical value of 'spin only' magnetic moment when $\text{Fe}(\text{SCN})_3$ reacts with a solution containing F^- ions to yield a complex ?

- (1) 2.83 B.M. (2) 3.87 B.M.
 (3) 5.92 B.M. (4) 1.73 B.M.

58. Which one of the following high-spin complexes has the largest CFSE (Crystal field stabilization energy)?

- (1) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (2) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
 (3) $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ (4) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

59. Match List-I (Complex ions) with List-II (CFSE) and select the correct answer using the codes given below the lists :

Column-I	Column-II			
(P) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	1. $0.6 \Delta_0$			
(Q) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	2. $0.4 \Delta_0$			
(R) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	3. 0			
(S) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	4. $1.2 \Delta_0$			
P	Q	R	S	
(1)	3	1	2	4
(2)	1	2	3	4
(3)	4	3	2	1
(4)	None of these			

ISOMERISM

60. A square planar complex is cis platin $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, shows :

- (1) Geometrical isomerism (2) Optical isomerism
 (3) Linkage isomerism (4) None

61. The two compounds sulphato penta-ammine cobalt (III) bromide and sulphato penta-ammine cobalt (III) chloride represent :

- (1) Linkage isomerism
 (2) Ionisation isomerism
 (3) Co-ordination isomerism
 (4) No isomerism

62. Which of the following complex can not exhibit geometrical isomerism :-

- (1) $[\text{Pt}(\text{NH}_3)_2\text{ClNO}_2]$ (2) $[\text{Pt}(\text{gly})_2]$
 (3) $[\text{Cu}(\text{en})_2]^{+2}$ (4) $[\text{Pt}(\text{H}_2\text{O})(\text{NH}_3)\text{BrCl}]$

63. Which one of the following compounds will exhibit linkage isomerism :-

- (1) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ (2) $[\text{Co}(\text{NH}_3)_3\text{NO}_2]\text{Cl}_2$
 (3) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ (4) $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$

64. Out of the following which complex will show geometrical isomerism ?

- (1) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ (2) $\text{Ni}(\text{CO})_4$
 (3) $\text{Na}_3[\text{Ni}(\text{CN})_4]$ (4) $\text{K}[\text{Ag}(\text{CN})_2]$

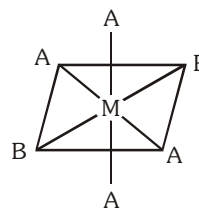
65. Which of the following complexes will show optical isomerism ?

- (1) $[\text{Cr}(\text{NH}_3)_6]^{2+}$ (2) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
 (3) $[\text{Pt}(\text{NH}_3)_3\text{Br}]\text{NO}_3$ (4) $[\text{Cr}(\text{en})_3]\text{Cl}_3$

66. The compound $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ represent

- (1) Linkage isomerism
 (2) Hydration isomerism
 (3) Ligand isomerism
 (4) None of these

67. The isomer -



can be marked as -

- (1) Cis isomer (2) Leavo isomer
 (3) Dextro isomer (4) Trans isomer

- 68.** A Planar Complex (Mabcd) gives :-
 (1) Two Optical isomer
 (2) Two geometrical isomer
 (3) Three optical isomer
 (4) Three geometrical isomers
- 69.** Theoretically the No. of geometrical isomers expected for octahedral complex [Mabcdef] is:-
 (1) Zero (2) 30 (3) 15 (4) 9
- 70.** Which of the following complex produce ppt with AgNO_3 and exist in two geometrical isomeric form
 (1) $\text{PtCl}_2 \cdot 4\text{NH}_3$ (2) $\text{PtCl}_2 \cdot 3\text{NH}_3$
 (3) $\text{PtCl}_4 \cdot 4\text{NH}_3$ (4) $\text{PtCl}_4 \cdot 2\text{NH}_3$
- 71.** $\text{Cis}[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ and $\text{trans}[\text{Pd}(\text{en})_2\text{Br}_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ are :-
 (1) Ionisation isomer
 (2) Geometrical isomer
 (3) Hydrate isomer
 (4) None of these
- 72.** Which of the following octahedral complex have maximum stereoisomers :-
 (1) $[\text{M}(\text{CN})_6]^\pm$ (2) $[\text{M}(\text{en})(\text{CN})_4]^\pm$
 (3) $[\text{M}(\text{en})_2(\text{CN})_2]^\pm$ (4) $[\text{M}(\text{en})_3]^\pm$
- 73.** Which of the following complex does not show geometrical isomerism ?
 (1) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ (2) $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$
 (3) $[\text{Cr}(\text{en})_3]^{3+}$ (4) $[\text{Pt}(\text{gly})_2]$
- 74.** Select the correct statement :
 (1) Potassium ferrocyanide and potassium ferricyanide can be differentiated by measuring the solid state magnetic moment.
 (2) The complex $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ can be differentiated by adding aqueous solution of barium chloride
 (3) The complex $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}$ can be differentiated by adding aqueous solution of silver nitrate.
 (4) All of these
- 75.** Which of the following complex compounds does not exhibit geometrical isomerism ?
 (1) $[\text{PtCl}_2(\text{NH}_3)_2]$ (2) $[\text{PdCl}_2\text{BrI}]$
 (3) $[\text{Pt}(\text{NH}_3)(\text{py})(\text{Cl})(\text{Br})]$ (4) $[\text{Pt}(\text{NH}_3)_3(\text{Br})]$
- 76.** The pair of molecules that exhibit geometrical isomerism are
 (1) $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
 (2) $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$
 (3) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$
 (4) All of the above show geometric isomerism

ORGANOMETALLIC COMPOUNDS

- 77.** Which of the following is π -acid ligand
 (1) NH_3 (2) CO
 (3) gly. (4) ethylene diamine
- 78.** Which of the following statement is/are wrong:-
 (a) Al_4C_3 is an organometallic compound
 (b) Metal carbonyls are organometallic compounds
 (c) TEL is π bonded organometallic compound
 (d) Frankland reagent is σ -bonded organometallic compound
 The answer is:-
 (1) c and d (2) a and c
 (3) a and b (4) All are correct
- 79.** Compounds which contain one or more metal carbon bonds are called :
 (1) Organic compound (2) Complex compound
 (3) Metal carbides (4) OMC compounds.
- 80.** Which one of the following is used as a heterogeneous catalyst ?
 (1) Wilkinson's catalyst (2) Tetraethyl lead
 (3) Zeigler Natta catalyst (4) Grignard's reagent
- 81.** Which of the following statement is true
 (1) FeCO_3 and Fe_3C are organometallic compounds.
 (2) In ferrocene ligand is cyclopentadienyl.
 (3) $\text{Pb}(\text{C}_2\text{H}_5)_4$ is π -bonded OMC
 (4) In zeise salt central metal is Sp^3 hybridised.
- 82.** Synergic bonding involves :-
 (1) The transference of electrons from ligands to metal
 (2) The transference of electrons from filled metal orbitals to anti-bonding orbitals of ligands
 (3) Both the above
 (4) None of these
- 83.** OMC form during purification of a metal is :-
 (1) $\text{Ni}(\text{CO})_4$ (2) $\text{Pb}(\text{C}_2\text{H}_5)_4$
 (3) $\text{Li}-\text{C}_4\text{H}_9$ (4) $\text{Na}_2[\text{Ni}(\text{CN})_4]$
- 84.** Which of the following is not an organometallic compound :-
 (1) $(\text{C}_2\text{H}_5)_2\text{Zn}$ (2) $\text{CH}_3\text{B}(\text{OCH}_3)_2$
 (3) $\text{B}(\text{OCH}_3)_3$ (4) $\text{Ni}(\text{CO})_4$

APPLICATION OF COORDINATION CHEMISTRY

- 85.** The brown ring test for nitrites and nitrates is due to the formation of a complex ion with formula :-
 (1) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ (2) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 (3) $[\text{Fe}(\text{H}_2\text{O})(\text{NO})_5]^{2-}$ (4) $[\text{Fe}(\text{NO})(\text{CN})_5]^{2+}$
- 86.** In a ferric salt on adding KCN a prussian blue is obtained which is :-
 (1) $\text{K}_3[\text{Fe}(\text{CN})_6]$ (2) $\text{Fe}_3[\text{Fe}(\text{CN})_6]_4$
 (3) $\text{FeSO}_4[\text{Fe}(\text{CN})_6]$ (4) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$

- 87.** Hypo is used in photography because it is :-
 (1) A strong reducing agent
 (2) A strong oxidising agent
 (3) A strong Complexing agent
 (4) Photo sensitive Compound
- 88.** The solubility of AgBr in hypo solution is due to the formation of :-
 (1) Ag_2SO_3 (2) $\text{Ag}_2\text{S}_2\text{O}_3$
 (3) $[\text{Ag}(\text{S}_2\text{O}_3)]^-$ (4) $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$
- 89.** Which of the following is related to Nessler's reagent?
 (1) $\text{PtCl}_4 + \text{KCl} \rightarrow$ (2) $\text{AgCl} + \text{NH}_3 \rightarrow$
 (3) $\text{AgBr} + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow$ (4) $\text{HgI}_2 + \text{KI} \rightarrow$
- 90.** $\text{K}_4[\text{Fe}(\text{CN})_6]$ reacts with FeCl_3 to form :-
 (1) $\text{K}_3\text{Fe}(\text{CN})_6$ (2) $\text{K}_4[\text{Fe}(\text{CN})_3\text{Cl}_3]$
 (3) $\text{K}_3[\text{Fe}(\text{CN})_5\text{Cl}]$ (4) $\text{KFe}[\text{Fe}(\text{CN})_6]$
- 91.** A reagent used for identifying nickel ion is :-
 (1) Potassium ferrocyanid (2) Phenolphthalein
 (3) Dimethyl glyoxime (4) EDTA
- 92.** Which one of the following statement is false for nickel-dimethylglyoximate complex ?
 (1) The stability of complex is only due to the presence of intra-molecular hydrogen bonding
 (2) The complex is stable, only because dimethyl glyoxime ligand is a stronger ligand
 (3) The complex is stable as it has five membered chelate rings as well as intra molecular hydrogen bonding
 (4) (1) and (2) both

- 93.** $\text{CuCl}_2 + \text{K}_4[\text{Fe}(\text{CN})_6] \rightarrow$ Chocolate brown ppt(X)
 Select the correct statement for (X) :
 (1) Its IUPAC name is copper (I) hexacyanoferrate (II)
 (2) It reacts with excess potassium cyanide forming an another soluble complex which has tetrahedral geometry.
 (3) It has 'spin only' magnetic moment equal to $\sqrt{36}$ B.M.
 (4) 2 and 3 both
- 94.** It is an experiment fact that :
 $\text{DMG} + \text{Ni(II)salt} + \text{NH}_4\text{OH} \longrightarrow$ Red ppt.
 Which of the following is wrong about this red ppt:
 (1) It is a non-ionic complex
 (2) It involves intra molecular H-bonding
 (3) Ni(II) is sp^3 hybridised
 (4) It is a diamagnetic complex
- 95.** Wilkinson's catalyst react with H_2 to form an octahedral complex in which Rh(Z = 45) has the following electronic configuration in the ligand field $t_{2g}^{2,2,2}, e_g^{0,0}$. Then which of the following is correct about this new complex
 (1) It is paramagnetic
 (2) Its IUPAC name is chlorodihydriodotris (triphenylphosphine) rhodium (III)
 (3) Hybridisation of Rh(I) is d^2sp^3
 (4) None of these

EXERCISE-I (Conceptual Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	4	4	2	4	3	2	1	2	4	2	3	3	2	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	1	1	1	3	2	2	2	3	4	2	2	4	3	4	2
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	1	1	2	1	1	2	3	3	3	1	4	2	2	2	2
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	3	2	1	2	2	4	2	2	3	2	3	3	4	1	1
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	4	3	2	1	4	2	4	4	3	3	4	3	3	4	4
Que.	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
Ans.	1	2	2	4	3	2	3	1	3	1	4	3	4	4	4
Que.	91	92	93	94	95										
Ans.	3	4	2	3	2										

EXERCISE-II (Previous Year Questions)**AIPMT/NEET & AIIMS (2006-2018)****AIPMT 2006**

- Copper sulphate dissolves in excess of KCN to give
 (1) $\text{Cu}(\text{CN})_2$ (2) CuCN
 (3) $[\text{Cu}(\text{CN})_4]^{3-}$ (4) $[\text{Cu}(\text{CN})_4]^{2-}$
- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$ exhibits
 (1) linkage isomerism, geometrical isomerism and optical isomerism
 (2) linkage isomerism, ionization isomerism and optical isomerism
 (3) linkage isomerism, ionization isomerism and geometrical isomerism
 (4) ionization isomerism, geometrical isomerism and optical isomerism

AIIMS 2006

- The pair in which both species have same magnetic moment (spin only value) is –
 (1) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, $[\text{CoCl}_4]^{2-}$
 (2) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 (3) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
 (4) $[\text{CoCl}_4]^{2-}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
- The number of possible isomers of an octahedral complex $[\text{Co}(\text{C}_2\text{O}_4)_2(\text{NH}_3)_2]^-$ is –
 (1) 1 (2) 2 (3) 3 (4) 4
- The ligands in anti cancer drug cisplatin are
 (1) NH_3 , Cl (2) NH_3 , H_2O
 (3) Cl , H_2O (4) NO , Cl
- Given below, catalyst and corresponding process/reaction are matched. The mismatch is –
 (1) $[\text{RhCl}(\text{PPh}_3)_2]$: Hydrogenation
 (2) $\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$: Polymerization
 (3) V_2O_5 : Haber–Bosch process
 (4) Nickel: Hydrogentaion
- Among the following the species having square planar geometry for central atom are
 (i) XeF_4 (ii) SF_4
 (iii) $[\text{NiCl}_4]^{2-}$ (iv) $[\text{PdCl}_4]^{2-}$
 (1) (i) and (iv) (2) (i) and (ii)
 (3) (ii) and (iii) (4) (iii) and (iv)

AIPMT 2007

- Which of the following will give a pair of enantiomorphs
 (1) $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ (2) $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$
 (3) $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_6]$ (4) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_2$

- The d electron configurations of Cr^{2+} , Mn^{2+} , Fe^{2+} and Ni^{2+} are $3d^4$, $3d^5$, $3d^6$ and $3d^8$ respectively which one of the following aqua complexes will exhibit the minimum paramagnetic behaviour
 (1) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (2) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
 (3) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ (4) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

AIPMT 2008

- Which of the following complexes exhibits the highest paramagnetic behaviour? Where gly = glycine, en = ethylenediamine and bpy = bipyridyl moities
 (1) $[\text{Co}(\text{OX})_2(\text{H}_2\text{O})_2]^-$ (2) $[\text{Ti}(\text{NH}_3)_6]^{3+}$
 (3) $[\text{V}(\text{gly})_2(\text{OH})_2(\text{NH}_3)_2]^+$ (4) $[\text{Fe}(\text{en})(\text{bpy})(\text{NH}_3)_2]^{2+}$
- In which of the following coordination entities the magnitude of Δ_o (CFSE in octahedral field) will be maximum?
 (1) $[\text{Co}(\text{CN})_6]^{3-}$ (2) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$
 (3) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ (4) $[\text{Co}(\text{NH}_3)_6]^{3+}$

AIPMT 2009

- Which of the following complex ions is expected to absorb visible light?
 (1) $[\text{Zn}(\text{NH}_3)_6]^{2+}$ (2) $[\text{Sc}(\text{H}_2\text{O})_3(\text{NH}_3)_3]^{3+}$
 (3) $[\text{Ti}(\text{en})_2(\text{NH}_3)_2]^{4+}$ (4) $[\text{Cr}(\text{NH}_3)_6]^{3+}$
- Out of TiF_6^{2-} , CoF_6^{3-} , Cu_2Cl_2 and NiCl_4^{2-} colourless species are:
 (1) CoF_6^{3-} and NiCl_4^{2-}
 (2) TiF_6^{2-} and CoF_6^{3-}
 (3) Cu_2Cl_2 and NiCl_4^{2-}
 (4) TiF_6^{2-} and Cu_2Cl_2
- Which of the following does not show optical isomerism?
 (1) $[\text{Co}(\text{en})_3]^{3+}$ (2) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$
 (3) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]^0$ (4) $[\text{Co}(\text{en})\text{Cl}_2(\text{NH}_3)_2]^+$
- Which one of the following complexes is **not** expected to exhibit isomerism :-
 (1) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ (2) $[\text{NiCl}_4]^{2-}$
 (3) $[\text{Ni}(\text{en})_3]^{2+}$ (4) $[\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$

AIPMT 2010

- Which of the following complex ion is not expected to absorb visible light?
 (1) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ (2) $[\text{Ni}(\text{CN})_4]^{2-}$
 (3) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ (4) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

17. The existence of two different coloured complexes with the composition of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ is due to:-
 (1) Ionization isomerism
 (2) Linkage isomerism
 (3) Geometrical isomerism
 (4) Coordination isomerism

18. Crystal field stabilization energy for high spin d^4 octahedral complex is :-
 (1) $-0.6 \Delta_0$ (2) $-1.8 \Delta_0$
 (3) $-1.6 \Delta_0 + P$ (4) $-1.2 \Delta_0$

AIIMS 2010

19. In which of the following compound C–O bond length is maximum :-
 (1) $[\text{Fe}(\text{CO})_5]^-$ (2) $[\text{Ni}(\text{CO})_4]$
 (3) $[\text{Cr}(\text{CO})_6]$ (4) $[\text{Mn}(\text{CO})_5]^+$
20. The CFSE for octahedral $[\text{CoCl}_6]^{4-}$ is 18000 cm^{-1} . The CFSE for tetrahedral $[\text{CoCl}_4]^{2-}$ will be
 (1) $18,000 \text{ cm}^{-1}$ (2) $16,000 \text{ cm}^{-1}$
 (3) $8,000 \text{ cm}^{-1}$ (4) $20,000 \text{ cm}^{-1}$

AIPMT Pre. 2011

21. Of the following complex ions, which is diamagnetic in nature ?
 (1) $[\text{NiCl}_4]^{2-}$
 (2) $[\text{Ni}(\text{CN})_4]^{2-}$
 (3) $[\text{CuCl}_4]^{2-}$
 (4) $[\text{CoF}_6]^{3-}$
22. The complex $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ are the examples of which type of isomerism ?
 (1) Linkage isomerism
 (2) Ionization isomerism
 (3) Coordination isomersim
 (4) Geometrical isomerism
23. The complex $[\text{Pt}(\text{Py})(\text{NH}_3)\text{BrCl}]$ will have how many geometrical isomers ?
 (1) 3 (2) 4
 (3) 0 (4) 2

AIPMT Mains 2011

24. Which of the following carbonyls will have the strongest C–O bond ?
 (1) $\text{Fe}(\text{CO})_5$ (2) $\text{Mn}(\text{CO})_6^+$
 (3) $\text{Cr}(\text{CO})_6$ (4) $\text{V}(\text{CO})_6^-$

25. Which of the following complex compounds will exhibit highest paramagnetic behaviour :-
 (At. No. Ti = 22, Cr = 24, Co = 27, Zn = 30)
 (1) $[\text{Zn}(\text{NH}_3)_6]^{2+}$ (2) $[\text{Ti}(\text{NH}_3)_6]^{3+}$
 (3) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ (4) $[\text{Co}(\text{NH}_3)_6]^{3+}$

AIIMS 2011

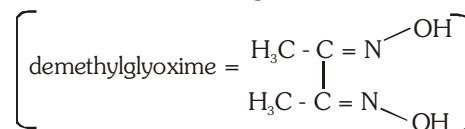
26. The wave length of light absorbed is highest in:
 (1) $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ (2) $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$
 (3) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (4) $[\text{Co}(\text{en})_3]^{3+}$
27. Which of the following is diamagnetic:
 (1) $[\text{Cu}(\text{NH}_3)_4]^{+2}$ (2) $[\text{NiCl}_4]^{2-}$
 (3) $[\text{PtCl}_4]^{2-}$ (4) $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$

AIPMT Pre. 2012

28. Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour?
 (1) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ (2) $[\text{Co}(\text{NH}_3)_6]^{3+}$
 (3) $[\text{Ni}(\text{NH}_3)_6]^{2+}$ (4) $[\text{Zn}(\text{NH}_3)_6]^{2+}$

AIPMT Mains 2012

29. Red precipitate is obtained when ethanol solution of dimethylglyoxime is added to ammoniacal Ni(II). Which of the following statements is not true ?



- (1) Red complex has a tetrahedral geometry.
 (2) Dimethylglyoxime functions as bidentate ligand.
 (3) Red complex has a square planar geometry.
 (4) Complex has symmetrical H-bonding.
30. Low spin complex of d^6 -cation in an octahedral field will have the following energy :-
 (Δ_0 = Crystal field splitting energy in an octahedral field, P = Electron pairing energy)

- (1) $-\frac{2}{5} \Delta_0 + 2P$ (2) $-\frac{2}{5} \Delta_0 + P$
 (3) $-\frac{12}{5} \Delta_0 + P$ (4) $-\frac{12}{5} \Delta_0 + 3P$

NEET-UG 2013

31. A magnetic moment of 1.73 BM will be shown by one among the following :-
 (1) $[\text{CoCl}_6]^{4-}$ (2) $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 (3) $[\text{Ni}(\text{CN})_4]^{2-}$ (4) TiCl_4

AIPMT 2014

32. Which of the following complexes is used to be as an anticancer agent?
- (1) $\text{mer}[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
 - (2) $\text{cis}[\text{PtCl}_2(\text{NH}_3)_2]$
 - (3) $\text{cis-K}_2[\text{PtCl}_2\text{Br}_2]$
 - (4) Na_2CoCl_4

AIIMS 2014

33. Which of the following compound has minimum coordination number :-
- (1) $\text{Co}_2(\text{CO})_8$
 - (2) $\text{Mn}_2(\text{CO})_{10}$
 - (3) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
 - (4) $[\text{Co}(\text{NH}_3)_4\text{Cl}]$
34. Which of the following compound show both linkage & ionisation isomerism :-
- (1) $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{NO}_2)$
 - (2) $[\text{Co}(\text{NO}_2)(\text{Py})_2(\text{NH}_3)_2]\text{NO}_2$
 - (3) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$
 - (4) $[\text{Co}(\text{NO}_2)\text{Br}(\text{NH}_3)_4]\text{Cl}$

AIPMT 2015

35. Cobalt (III) chloride forms several octahedral complexes with ammonia. Which of the following will not give test of chloride ions with silver nitrate at 25°C ?
- (1) $\text{CoCl}_3 \cdot 4\text{NH}_3$
 - (2) $\text{CoCl}_3 \cdot 5\text{NH}_3$
 - (3) $\text{CoCl}_3 \cdot 6\text{NH}_3$
 - (4) $\text{CoCl}_3 \cdot 3\text{NH}_3$
36. Which of these statements about $[\text{Co}(\text{CN})_6]^{3-}$ is true:-
- (1) $[\text{Co}(\text{CN})_6]^{3-}$ has four unpaired electrons and will be in a low-spin configuration.
 - (2) $[\text{Co}(\text{CN})_6]^{3-}$ has four unpaired electrons and will be in a high spin configuration.
 - (3) $[\text{Co}(\text{CN})_6]^{3-}$ has no unpaired electrons and will be in a high-spin configuration.
 - (4) $[\text{Co}(\text{CN})_6]^{3-}$ has no unpaired electrons and will be in a low-spin configuration.

Re-AIPMT 2015

37. The name of complex ion, $[\text{Fe}(\text{CN})_6]^{3-}$ is :-
- (1) Tricyanoferrate (III) ion
 - (2) Hexacyanidoferrate (III) ion
 - (3) Hexacyanoiron (III) ion
 - (4) Hexacyanitoferrate (III) ion
38. The hybridization involved in complex $[\text{Ni}(\text{CN})_4]^{2-}$ is (At.No. Ni = 28)
- (1) d^2sp^2
 - (2) d^2sp^3
 - (3) dsp^2
 - (4) sp^3

39. The sum of coordination number and oxidation number of the metal M in the complex $[\text{M}(\text{en})_2(\text{C}_2\text{O}_4)]\text{Cl}$ (where en is ethylenediamine) is:-
- (1) 7
 - (2) 8
 - (3) 9
 - (4) 6
40. Number of possible isomers for the complex $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ will be : (en = ethylenediamine)
- (1) 3
 - (2) 4
 - (3) 2
 - (4) 1

AIIMS 2015

41. Colour of ruby is due to presence of Cr_2O_3 in Al_2O_3 the reason of colour property
- (1) charge transfer of O^{2-} to Al^{+3}
 - (2) charge transfer of O_2^- to Cr^{3+}
 - (3) charge transfer of O^- to Cr^{3+}
 - (4) d-d transition in Cr^{3+}
42. Electronic configuration of Co in a octahedral complex is $t_{2g}^6 e_g^0$ with a ligand L, than L is
- (1) SCN^-
 - (2) oxalate
 - (3) F^-
 - (4) Cl^-

NEET-I 2016

43. Which of the following has longest C-O bond length? (Free C-O bond length in CO is $1.128\text{\AA}$).
- (1) $\text{Ni}(\text{CO})_4$
 - (2) $[\text{Co}(\text{CO})_4]^0$
 - (3) $[\text{Fe}(\text{CO})_4]^{2-}$
 - (4) $[\text{Mn}(\text{CO})_6]^+$

NEET-II 2016

44. The correct increasing order of trans-effect of the following species is :
- (1) $\text{Br}^- > \text{CN}^- > \text{NH}_3 > \text{C}_6\text{H}_5^-$
 - (2) $\text{CN}^- > \text{Br}^- > \text{C}_6\text{H}_5^- > \text{NH}_3$
 - (3) $\text{NH}_3 > \text{CN}^- > \text{Br}^- > \text{C}_6\text{H}_5^-$
 - (4) $\text{CN}^- > \text{C}_6\text{H}_5^- > \text{Br}^- > \text{NH}_3$
45. Jahn-Teller effect **not** observed in high spin complexes of :-
- (1) d^4
 - (2) d^9
 - (3) d^7
 - (4) d^8

AIIMS 2016

46. Which of the following complex is most stable among the following :-
- (1) $\text{Na}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$
 - (2) $[\text{Cu}(\text{NH}_3)_4]^{+2}$
 - (3) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$
 - (4) $\text{Na}_3[\text{CoF}_6]$

47. Select the incorrect statement for same type of ligands :-
 (1) Neutral ligands can be strong than anionic ligands
 (2) Chelating ligands are stronger than non chelating
 (3) π -bond containing ligands are classical
 (4) electron pair donating ability depends on electronegativity of donor atom
48. Which of the following ion will form complex with EDTA most rapidly :-
 (1) Bi^{+3} (2) Zn^{+2}
 (3) Cd^{+2} (4) Ag^{+}
49. Regarding brown ring complex formation, which of the following statement is wrong :-
 (1) NO formation takes place
 (2) $\text{Fe}_2(\text{SO}_4)_3$ is used in this process
 (3) Fe^{+2} and NO_3^- both are reduced
 (4) Formula of brown ring complex is $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{+2}$
50. Which of the following homoleptic complex has square planar geometry :-
 (1) $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{-3}$ (2) $[\text{Co}(\text{EDTA})]^{-2}$
 (3) $[\text{Pt}(\text{trien})]^{+2}$ (4) $[\text{Ni}(\text{H}_2\text{O})_4]^{+2}$
51. An octahedral complex having formula $\text{Ma}_2\text{b}_2\text{c}_2$, which of the following combination is possible to exhibit optical isomerism.
 (1) $a = \text{Cl}^-$, b & $c = (\text{en})$
 (2) a & b & $c = \text{EDTA}$
 (3) a & $b = \text{C}_2\text{O}_4^{2-}$, $c = \text{en}$
 (4) $a = \text{H}_2\text{O}$, $b = \text{NH}_3$, $c = \text{Cl}^-$

NEET(UG) 2017

52. An example of a sigma bonded organometallic compound is :
 (1) Grignard's reagent
 (2) Ferrocene
 (3) Cobaltocene
 (4) Ruthenocene
53. Pick out the correct statement with respect to $[\text{Mn}(\text{CN})_6]^{3-}$:-
 (1) It is sp^3d^2 hybridised and tetrahedral
 (2) It is d^2sp^3 hybridised and octahedral
 (3) It is dsp^2 hybridised and square planar
 (4) It is sp^3d^2 hybridised and octahedral

54. Correct increasing order for the wavelengths of absorption in the visible region the complexes of Co^{3+} is :-

- (1) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Co}(\text{en})_3]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$
 (2) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{en})_3]^{3+}$
 (3) $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{en})_3]^{3+}$, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
 (4) $[\text{Co}(\text{en})_3]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$

AIIMS 2017

55. If $[\text{CoCl}(\text{NH}_3)_5]^{+2}$ absorb yellow light then what is the colour of the compound.
 (1) Violet (2) Red
 (3) Pale yellow (4) Yellow orange

NEET(UG) 2018

56. The type of isomerism shown by the complex $[\text{CoCl}_2(\text{en})_2]$ is
 (1) Geometrical isomerism
 (2) Coordination isomerism
 (3) Ionization isomerism
 (4) Linkage isomerism
57. The geometry and magnetic behaviour of the complex $[\text{Ni}(\text{CO})_4]$ are
 (1) square planar geometry and diamagnetic
 (2) tetrahedral geometry and diamagnetic
 (3) square planar geometry and paramagnetic
 (4) tetrahedral geometry and paramagnetic
58. Iron carbonyl, $\text{Fe}(\text{CO})_5$ is
 (1) tetranuclear (2) mononuclear
 (3) trinuclear (4) dinuclear

AIIMS 2018

59. Which of the following forms most stable aqua octahedral complex ion :-
 (1) Mn^{+2} (2) Fe^{+2}
 (3) Co^{+2} (4) Ni^{+2}
60. Which of the following pair are diamagnetic :-
 (1) $[\text{Co}(\text{ox})_3]^{-3}$ & $[\text{Fe}(\text{CN})_6]^{-4}$
 (2) $[\text{Fe}(\text{CN})_6]^{-3}$ & $[\text{Co}(\text{ox})_3]^{-3}$
 (3) $[\text{CoF}_6]^{-3}$ & $[\text{Co}(\text{CN})_6]^{-3}$
 (4) $[\text{CoF}_6]^{-3}$ & $[\text{Fe}(\text{CN})_6]^{-3}$
61. Which of the following species is more reducible :-
 (1) $[\text{V}(\text{CO})_5]$ (2) $[\text{Co}(\text{CO})_6]^{-1}$
 (3) $[\text{Fe}(\text{CO})_5]$ (4) $[\text{Mo}(\text{CO})_6]$
62. Which ligand shows least back bonding :-
 (1) CO (2) C_2H_4
 (3) PPh_3 (4) CN^-

63. $[\text{Cr}(\text{CO})_6]$ react with excess of NO, formed compound will be :-

- (1) $[\text{Cr}(\text{CO})_5(\text{NO})]$
 (2) $[\text{Cr}(\text{CO})_4(\text{NO})]$
 (3) $[\text{Cr}(\text{CO})_4(\text{NO})_2]$
 (4) $[\text{Cr}(\text{NO})_4]$

64. How many of the following behaves as a 1 : 1 type electrolyte ratio in solution - (1) a salt formed by Zeise (2) Wilkinson catalyst (3) Cis-platine (4) Ferrocene (5) Grignard reagent

- (1) 0 (2) 2 (3) 3 (4) 5

65. Which of the following has best π accepting tendency to form synergic bond :-

- (1) CO (2) PPh_3
 (3) NO_2 (4) en

EXERCISE-II (Previous Year Questions)

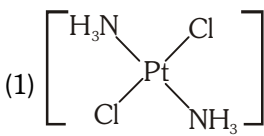
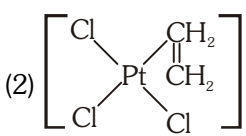
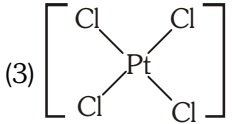
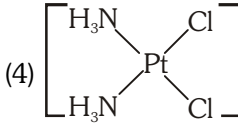
ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	3	2	3	1	3	1	2	2	2	1	4	4	3	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	2	3	1	1	3	2	3	1	2	3	1	3	3	1	4
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	2	2	4	4	4	4	2	3	3	1	4	2	3	4	4
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	1	3	1	2	3	4	1	2	4	1	1	2	2	4	1
Que.	61	62	63	64	65										
Ans.	1	3	4	2	1										

EXERCISE-III (Analytical Questions)

- A complex compound of cobalt has molecular formula containing five NH_3 molecules, one nitro group and two chlorine atom for one cobalt atom. One mole of this compound produces three moles of ion in aqueous solution. On reaction with excess of AgNO_3 solution two moles of AgCl get precipitated. The ionic formula of the compound.
 (1) $[\text{Co}(\text{NH}_3)_4 \text{NO}_2 \text{Cl}] \text{NH}_3\text{Cl}$
 (2) $[\text{Co}(\text{NH}_3)_5 \text{Cl}] \text{ClNO}_2$
 (3) $[\text{Co}(\text{NH}_3)_5 \text{NO}_2] \text{Cl}_2$
 (4) $[\text{Co}(\text{NH}_3)_5 (\text{NO}_2) \text{Cl}] \text{Cl}$
- Which of the following is react with AgCl ?
 (1) KCN (2) NH_4OH
 (3) $\text{Na}_2\text{S}_2\text{O}_3$ (4) All
- Which one of the following shows maximum paramagnetic character ?
 (1) $[\text{Fe}(\text{CN})_6]^{3-}$ (2) $[\text{Fe}(\text{CN})_6]^{4-}$
 (3) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (4) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
- Which statement is incorrect :-
 (1) $\text{Ni}(\text{CO})_4$ - Tetrahedral, paramagnetic
 (2) $[\text{Ni}(\text{CN})_4]^{2-}$ - Square planar, diamagnetic
 (3) $\text{Ni}(\text{CO})_4$ - Tetrahedral, diamagnetic
 (4) $[\text{NiCl}_4]^{2-}$ - Tetrahedral, paramagnetic
- CuSO_4 when reacts with KCN forms CuCN , which is insoluble in water. It is soluble in excess of KCN , due to formation of the following complex :-
 (1) $\text{K}_2[\text{Cu}(\text{CN})_4]$ (2) $\text{K}_3[\text{Cu}(\text{CN})_4]$
 (3) CuCN_2 (4) $\text{Cu}[\text{KC}(\text{CN})_4]$
- Considering H_2O as a weak field ligand, the number of unpaired electrons in $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ will be (At. no. of $\text{Mn} = 25$) :-
 (1) Four (2) Three
 (3) Five (4) Two
- Which of the following coordination compounds would exhibit optical isomerism ?
 (1) tris-(ethylenediamine) cobalt (III) bromide
 (2) pentaamminenitrocobalt (III) iodide
 (3) diamminedichloroplatinum (II)
 (4) trans-dicyanobis (ethylenediamine) chromium (III) chloride
- Among $[\text{Ni}(\text{CO})_4]$, $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{NiCl}_4]^{2-}$ species, the hybridization states at the Ni atom are, respectively (At. no. of $\text{Ni} = 28$):-
 (1) dsp^2 , sp^3 , sp^3 (2) sp^3 , dsp^2 , dsp^2
 (3) sp^3 , dsp^2 , sp^3 (4) sp^3 , sp^3 , dsp^2

Check Your Understanding

- Which of the following is considered to be an anti-cancer species ?
 (1)  (2) 
 (3)  (4) 
- Which of the following does not have a metal-carbon bond ?
 (1) $\text{Ni}(\text{CO})_4$ (2) $\text{Al}(\text{OC}_2\text{H}_5)_3$
 (3) $\text{C}_2\text{H}_5\text{MgBr}$ (4) $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$
- An aqueous solution of CoCl_2 on addition of excess of concentrated HCl turns blue due to formations of :
 (1) $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]$ (2) $[\text{Co}(\text{H}_2\text{O})_2\text{Cl}_4]^{2-}$
 (3) $[\text{CoCl}_4]^{2-}$ (4) $[\text{Co}(\text{H}_2\text{O})_2\text{Cl}_2]$
- The correct order for the wavelength of absorption in the visible region is :
 (1) $[\text{Ni}(\text{NO}_2)_6]^{4-} < [\text{Ni}(\text{NH}_3)_6]^{2+} < [\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
 (2) $[\text{Ni}(\text{NO}_2)_6]^{4-} < [\text{Ni}(\text{H}_2\text{O})_6]^{2+} < [\text{Ni}(\text{NH}_3)_6]^{2+}$
 (3) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} < [\text{Ni}(\text{NH}_3)_6]^{2+} < [\text{Ni}(\text{NO}_2)_6]^{4-}$
 (4) $[\text{Ni}(\text{NH}_3)_6]^{2+} < [\text{Ni}(\text{H}_2\text{O})_6]^{2+} < [\text{Ni}(\text{NO}_2)_6]^{4-}$
- The IUPAC name of the coordination compound $\text{K}_3[\text{Fe}(\text{CN})_6]$ is
 (1) potassium hexacyanoferrate (II)
 (2) potassium hexacyanoferrate (III)
 (3) potassium hexacyanoiron (II)
 (4) tripotassium hexacyanoiron (III)
- Which one of the following cyano complexes would exhibit the lowest value of paramagnetic behaviour ?
 (1) $[\text{Cr}(\text{CN})_6]^{3-}$ (2) $[\text{Mn}(\text{CN})_6]^{3-}$
 (3) $[\text{Fe}(\text{CN})_6]^{3-}$ (4) $[\text{Co}(\text{CN})_6]^{3-}$
- The value of the 'spin only' magnetic moment for one of the following configurations is 2.84 BM. The correct one is
 (1) d^4 (in strong ligand filed)
 (2) d^4 (in weak ligand filed)
 (3) d^3 (in weak as well as in strong fields)
 (4) d^5 (in strong ligand filed)

- 16.** A square planar complex is formed by hybridization of which atomic orbitals
 (1) s, p_x, p_y, d_{yz} (2) $s, p_x, p_y, d_{x^2-y^2}$
 (3) s, p_x, p_y, d_{z^2} (4) s, p_x, p_y, d_{xy}
- 17.** The most stable complex among the following is
 (1) $K_3[Al(C_2O_4)_3]$ (2) $[Pt(en)_2]Cl_2$
 (3) $[Ag(NH_3)_2]Cl$ (4) $K_2[Ni(EDTA)]$
- 18.** Coordination compounds have great importance in biological systems. In this context which of the following statements is incorrect?
 (1) Cyanocobalamin is vitamin B_{12} and contains cobalt
 (2) Haemoglobin is the red pigment of blood and contains iron
 (3) Chlorophylls are green pigments in plants and contain calcium
 (4) Carboxypeptidase - A is an enzyme and contains zinc
- 19.** Nickel ($Z=28$) combines with a uninegative monodentate ligand X^- to form a paramagnetic complex $[NiX_4]^{2-}$. The number of unpaired electron (s) in the nickel and geometry of this complex ion are, respectively.
 (1) one, square planar (2) two, square planar
 (3) one, tetrahedral (4) two, tetrahedral
- 20.** In $Fe(CO)_5$, the $Fe-C$ bond possesses
 (1) ionic character (2) σ -character only
 (3) π -character only (4) both σ & π character
- 21.** How many EDTA (ethylenediaminetetraacetic acid) molecules are required to make an octahedral complex with a Ca^{2+} ion?
 (1) One (2) Two (3) Six (4) Three
- 22.** The "spin-only" magnetic moment [in units of Bohr magneton, (μ_B)] of Ni^{2+} in aqueous solution would be (At. No. $Ni=28$)
 (1) 0 (2) 1.73 (3) 2.84 (4) 4.90
- 23.** The coordination number of Ni^{+2} is 4
 $NiCl_2 + KCN$ (Complex) $\rightarrow$ A (Complex)
 $A + Conc.HCl$ (Maximun) $\rightarrow$ B (Chloro complex)
 The IUPAC name of A and B are
 (1) potassium tetracyanonickelate(II), potassium tetrachloronickelate(II),
 (2) tetracyanopotassiumnickelate(II), tetrachloropotassiumnickelate (II),
 (3) tetracyanonickel (II), tetrachloronickel (II)
 (4) potassiumtetracyanonickel (II), potassiumtetrachloronickel (II).
- 24.** Which one of the following is tridentate ligand
 (1) NO_2^- (2) oxalate ion
 (3) glycinate ion (4) dien
- 25.** Both Co^{3+} and Pt^{4+} have a coordination number of six. Which of the following pairs of complexes will show approximately the same electrical conductance for their 0.001 M aqueous solutions
 (1) $CoCl_3 \cdot 4NH_3$ and $PtCl_4 \cdot 4NH_3$
 (2) $CoCl_3 \cdot 3NH_3$ and $PtCl_4 \cdot 5NH_3$
 (3) $CoCl_3 \cdot 6NH_3$ and $PtCl_4 \cdot 5NH_3$
 (4) $CoCl_3 \cdot 6NH_3$ and $PtCl_4 \cdot 3NH_3$
- 26.** Which of the following has a square planar geometry
 (1) $[PtCl_4]^{2-}$ (2) $[CoCl_4]^{2-}$ (3) $[FeCl_4]^{2-}$ (4) $[NiCl_4]^{2-}$
- 27.** Hybridisation of Ni in $Ni(CO)_4$ is
 (1) dsp^2 (2) dsp^3 (3) d^2sp^3 (4) sp^3
- 28.** Hybridisation and shape of central metal atom of Wilkinson's catalyst is :-
 (1) dsp^2 , Square planer
 (2) sp^3 , Tetrahedral
 (3) sp^3d , Trigonal bipyramidal
 (4) sp^3d^2 , Octahedral
- 29.** Which of the following is not an organo metallic compound :-
 (1) $(C_2H_5)_2Zn$ (2) $CH_3B(OCH_3)_2$
 (3) $B(OCH_3)_3$ (4) $Ni(CO)_4$
- 30.** Which of the following facts about the complex $[Cr(NH_3)_6]Cl_3$ is wrong?
 (1) The complex is an outer orbital complex
 (2) The complex gives white precipitate with silver nitrate solution
 (3) The complex involves d^2sp^3 hybridisation and is octahedral in shape
 (4) The complex is paramagnetic
- 31.** Among the ligands NH_3 , en , CN^- and CO the correct order of their increasing field strength, is:-
 (1) $CO < NH_3 < en < CN^-$
 (2) $NH_3 < en < CN^- < CO$
 (3) $CN^- < NH_3 < CO < en$
 (4) $en < CN^- < NH_3 < CO$
- 32.** Which one of the following complex ions has geometrical isomers?
 (1) $[Co(en)_3]^{3+}$ (2) $[Ni(NH_3)_5Br]^+$
 (3) $[Co(NH_3)_2(en)_2]^{3+}$ (4) $[Cr(NH_3)_4(en)]^{3+}$
 [en = ethylenediamine]

33. Which among the following will be named as dibromidobis (ethylene diamine) chromium (III) bromide ?

- (1) $[\text{Cr}(\text{en})\text{Br}_2]\text{Br}$ (2) $[\text{Cr}(\text{en})_3]\text{Br}_3$
(3) $[\text{Cr}(\text{en})_2\text{Br}_2]\text{Br}$ (4) $[\text{Cr}(\text{en})\text{Br}_4]^-$

34. The octahedral complex of a metal ion M^{3+} with four monodentate ligands L_1 , L_2 , L_3 and L_4 absorb wavelength in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is:

- (1) $\text{L}_3 < \text{L}_2 < \text{L}_4 < \text{L}_1$
(2) $\text{L}_1 < \text{L}_2 < \text{L}_4 < \text{L}_3$
(3) $\text{L}_4 < \text{L}_3 < \text{L}_2 < \text{L}_1$
(4) $\text{L}_1 < \text{L}_3 < \text{L}_2 < \text{L}_4$

35. Which of the following statements is/are correct ?

- (1) $[\text{Ag}(\text{NH}_3)_2]^+$ is linear with sp hybridised Ag^+ ion.
(2) NiCl_4^{2-} , VO_4^{3-} and MnO_4^- have tetrahedral geometry.
(3) $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Pt}(\text{NH}_3)_4]^{2+}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ have dsp^2 hybridisation of the metal ions.
(4) All the above

36. Which of the following statements is not true about the complex ion $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$?

- (1) It has two geometrical isomers – cis and trans
(2) Both the cis and trans isomers display optical activity.
(3) Only the cis isomer displays optical activity.
(4) Only the cis isomer has non-superimposable mirror image.

37. In Ziegler's salt $\text{C}=\text{C}$ bond length is :-

Note : $\left\{ \begin{array}{l} \text{C}-\text{C} \text{ bond length in ethane is } 1.54 \text{ \AA} \\ \text{C}=\text{C} \text{ bond length in ethene is } 1.34 \text{ \AA} \\ \text{C}\equiv\text{C} \text{ bond length in ethyne is } 1.20 \text{ \AA} \end{array} \right\}$

- (1) 1.37 Å (2) 1.19 Å (3) 1.87 Å (4) 1.34 Å

38. $[\text{Pt}(\text{NH}_3)(\text{NH}_2\text{OH})(\text{NO}_2)(\text{py})]^+$ will form how many geometrical isomers ?

- (1) 2 (2) 3 (3) 4 (4) 5

39. Which of the following statements is/are correct ?

- (1) The stability constant of $[\text{Co}(\text{NH}_3)_6]^{3+}$ is greater than that of $[\text{Co}(\text{NH}_3)_6]^{2+}$
(2) Among F^- , Cl^- , Br^- and I^- , F^- forms strongest complexes due to small size.
(3) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is thermodynamically more stable than $[\text{Zn}(\text{NH}_3)_4]^{2+}$
(4) All the above

40. All the metal ions contains $t_{2g}^6 e_g^0$ configurations. Which of the following complex will be paramagnetic ?

- (1) $[\text{FeCl}(\text{CN})_4(\text{O}_2)]^{4-}$ (2) $\text{K}_4[\text{Fe}(\text{CN})_6]$
(3) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (4) $[\text{Fe}(\text{CN})_5(\text{O}_2)]^{-5}$

41. $\text{FeCl}_3 + \text{K}_3[\text{Fe}(\text{CN})_6] + \text{H}_2\text{O}_2 \rightarrow \text{Precipitate}$. The colour of the precipitate is :-

- (1) Sky blue (2) Brown
(3) Prussian blue (4) White

EXERCISE-III (Analytical Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	4	3	1	2	3	1	3	4	2	3	1	2	4	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	2	4	3	4	4	1	3	1	4	3	1	4	1	3	1
Que.	31	32	33	34	35	36	37	38	39	40	41				
Ans.	2	3	3	4	4	2	1	2	4	1	3				

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

- Assertion:** The aqueous solution of $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ is acidic in nature
Reason : It ionises to give a complex ion.
 (1) A (2) B (3) C (4) D
- Assertion :** In the complex $K_2[PtCl_6]$, coordination number of Pt is 6.
Reason : In the complex six coordinate bonds are formed between Pt and chloro ligands.
 (1) A (2) B (3) C (4) D
- Assertion :** Tetrahedral complex do not exhibit geometrical isomerism.
Reason : In tetrahedral complex all the four positions are identical.
 (1) A (2) B (3) C (4) D
- Assertion :** $[Fe(CO)_5]$ is inner orbital complex.
Reason : In the given complex oxidation state of Iron is zero.
 (1) A (2) B (3) C (4) D
- Assertion :** $[Fe(CN)_6]^{3-}$ is paramagnetic in nature.
Reason : $[Fe(CN)_6]^{3-}$ is low spin complex.
 (1) A (2) B (3) C (4) D
- Assertion :** Hexachloroplatinate is a complex anion
Reason: Complex has negatively charged ligands
 (1) A (2) B (3) C (4) D
- Assertion :** $[Ni(CN)_4]^{2-}$ has zero unpaired electron while that of $[NiCl_4]^{2-}$ has two unpaired e^-
Reason: $[Ni(CN)_4]^{2-}$ has strong crystal field while $[NiCl_4]^{2-}$ has weak crystal field
 (1) A (2) B (3) C (4) D
- Assertion :** Cis - $[Fe(en)_2 Cl_2]^+$ can form racemic mixture.
Reason : Cis - $[Fe(en)_2 Cl_2]^+$ is square planar complex .
 (1) A (2) B (3) C (4) D
- Assertion:** Square planar complex Ma_2b_2 has two optical isomers
Reason : Mirror image of Ma_2b_2 is non-super imposable.
 (1) A (2) B (3) C (4) D
- Assertion :** AgI is coloured while AgF is colourless.
Reason : Unpaired e^- is present in AgI
 (1) A (2) B (3) C (4) D
- Assertion :** $[CoF_6]^{3-}$ is high spin complex.
Reason : F^- is strong field ligand.
 (1) A (2) B (3) C (4) D
- Assertion :** Ferrocene is π -bonded organometallic compound.
Reason : Ferrocene is a sandwich compound.
 (1) A (2) B (3) C (4) D
- Assertion :** Solution of Na_2CrO_4 in water is intensely coloured.
Reason: Ox. state of Cr in Na_2CrO_4 is +6.
 (1) A (2) B (3) C (4) D
- Assertion :** Potassium ferrocyanide is diamagnetic whereas potassium ferricyanide is paramagnetic.
Reason : Crystal field splitting in ferrocyanide ion is greater than that of ferricyanide ion.
 (1) A (2) B (3) C (4) D
- Assertion :-** In a mixture of Cd (II) and Cu(II), (Cd^{+2}) gets precipitated in presence of KCN by H_2S .
Reason :- The stability constant of $[Cu(CN)_4]^{3-}$ is greater than $[Cd(CN)_4]^{2-}$
 (1) A (2) B (3) C (4) D
- Assertion :-** aq. solution of $CoCl_2$ is pink in colour. It turns blue in presence of conc. HCl.
Reason :- It is due to formation of $(CoCl_4)^{2-}$.
 (1) A (2) B (3) C (4) D

17. Assertion : Triethylenediamine is a bidentate monoanion.

Reason : Complex containing propylenediamine ligand shows ligand isomerism.

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

18. Assertion : $[\text{Co}^{\text{III}}(\text{gly})_3]$ is called inner-metallic complex because,

Reason : Both the coordination number and charge of the cation are satisfied simultaneously by ligands.

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

19. Assertion : All tetrahedral complexes are mainly high spin and the low spin configurations are rarely observed.

Reason: Δ_t is always much smaller even with stronger field ligands and it is never energetically favourable to pair up the electrons.

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

20. Assertion : NH_2NH_2 although possesses two electron pairs for donation but not acts as a chelating agent.

Reason: The coordination by NH_2NH_2 leads to a three member highly unstable strained ring

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

21. Assertion : The correct order for the wave length of absorption in the visible region is ; $[\text{Ni}(\text{NO}_2)_6]^{4-} < [\text{Ni}(\text{NH}_3)_6]^{2+} < [\text{Ni}(\text{H}_2\text{O})_6]^{2+}$

Reason: The stability of different complexes depends on the strength of the ligand field of the various ligands.

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

22. Assertion : The 'spin only' magnetic moment of a green complex, potassium amminetetraacyanidonitrosonium chromate(I) is 1.73 BM.

Reason : To have two d-orbitals empty for d^2sp^3 hybridisation, the pairing of electrons take place leaving behind one unpaired electron as CN^- is a stronger ligand.

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

23. Assertion : Pentaamminethiocyanato-N-chromium(III) tetrachloridozincate(II) is a coloured compound and is an example of ionisation isomerism.

Reason : The compound is paramagnetic and therefore, d-d transition is possible

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

24. Assertion :- $\text{Cu}[\text{Hg}(\text{SCN})_4]$ and $\text{Hg}[\text{Co}(\text{NCS})_4]$ are isomers.

Reason :- SCN^- is an ambidentate ligand.

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

25. Assertion :- Coordination number of Pt in Zeise's salt is 5.

Reason :- C_2H_4 act as bidentate ligand

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

26. Assertion :- Fe^{+3} not used in brown ring test of NO_3^- .

Reason :- NO_3^- is first converted into NO_2 .

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

27. Assertion : $[\text{Co}(\text{H}_2\text{O})_6]^{+3} \rightarrow [\text{Co}(\text{H}_2\text{O})_6]^{+2}$ changes its colour on reduction.

Reason : Crystal field stabilisation energy increases on reduction

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

28. Assertion :- Zone refining is based on the fact that impurities are more soluble in molten state than in solid in the presence of oxygen.

Reason :- This method is used to prepare pure metal oxides.

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

29. Assertion :- If in $[\text{Co}(\text{NH}_3)_6]^{+3}$, NH_3 is replaced by H_2O , same wavelength will be absorbed by the complex :

Reason :- It is a high spin species.

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

EXERCISE-IV (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	1	1	2	2	2	1	3	4	3	3	2	2	3	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	
Ans.	1	4	2	1	1	2	1	4	4	4	3	3	4	4	

S. No.	CONTENTS	Page
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3.	Ether	41
4.	Carbonyl compounds	44
5.	Carboxylic acid	57
6.	Acid derivatives	63
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8.	Exercise-II (Previous Years Questions)	77
9.	Exercise-III (Analytical Questions)	87
10.	Exercise-IV (Assertion & Reason)	91

NEET SYLLABUS

Alcohols : Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only); identification of primary, secondary and tertiary alcohols, mechanism of dehydration, uses with special reference to methanol and ethanol. **Phenols** : Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophilic substitution reactions, uses of phenols. **Ethers** : Nomenclature, methods of preparation, physical and chemical properties uses. Aldehydes and Ketones : Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties and reactivity of alpha hydrogen in aldehydes, Carboxylic acid : Nomenclature, acidic nature, methods of preparation, physical and chemical properties;

OBJECTIVES

After studying this unit, we will be able to :

- Name alcohols, phenols and ethers according to the IUPAC system of nomenclature;
- Discuss the reactions involved in the preparation of alcohols from
(i) alkenes (ii) aldehydes, ketones and carboxylic acids;
- Discuss the reactions involved in the preparation of phenols from
(i) haloarenes (ii) benzene sulphonic acids
(iii) diazonium salts and (iv) cumene;
- Discuss the reactions for preparation of ethers from
(i) alcohols and
(ii) alkyl halides and sodium alkoxides/aryloxides;
- Correlate physical properties of alcohols, phenols and ethers with their structures;
- Discuss chemical reactions of the three classes of compounds on the basis of their functional groups.
- Write the common and IUPAC names of aldehydes, ketones and carboxylic acids;
- Write the structures of the compounds containing functional groups namely carbonyl and carboxyl groups;
- Describe the important methods of preparation and reactions of these classes of compounds;
- Correlate physical properties and chemical reactions of aldehydes, ketones and carboxylic acids, with their structures;
- Explain the mechanism of a few selected reactions of aldehydes and ketones;
- Understand various factors affecting the acidity of carboxylic acids and their reactions;
- Describe the uses of aldehydes, ketones and carboxylic acids.

"If you fail, never give up because FAIL means "first attempt in Learning"

– End is not the end, in fact END means "Efforts never dies"

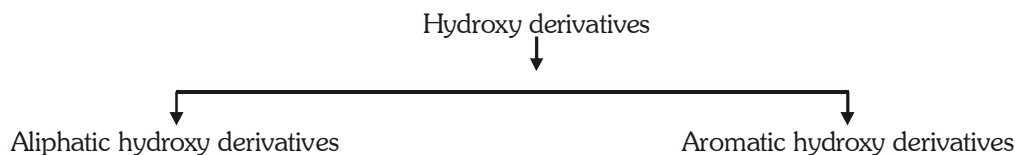
– If you get No as an answer, remember NO means "Next Opportunity"

So Let's be positive. "Dr. A.P.J. Abdul Kalam of feel LIFE"

A.P.J. Abdul Kalam

OXYGEN CONTAINING COMPOUND

1.0 HYDROXY DERIVATIVES



1.1 Aliphatic Hydroxy Derivatives

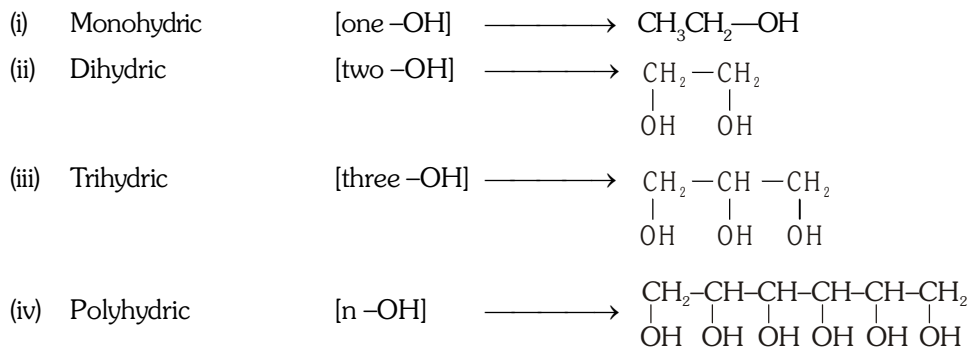
Hydroxy derivatives in which —OH is directly attached to sp^3 'C' (Alcoholic compounds).

1.2 Aromatic Hydroxy Derivatives

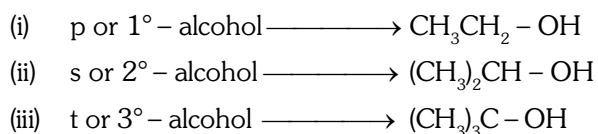
Hydroxy derivatives in which —OH is directly attached to sp^2 'C' or benzene ring (Phenolic compounds).

Aliphatic hydroxy derivatives :

(a) Classification according to number of —OH groups :



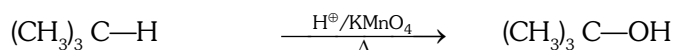
(b) Classification according to nature of carbon :



2.0 MONOHYDRIC ALCOHOL

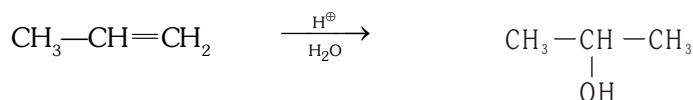
2.1 General Methods of Preparation

(i) From alkanes (By oxidation):

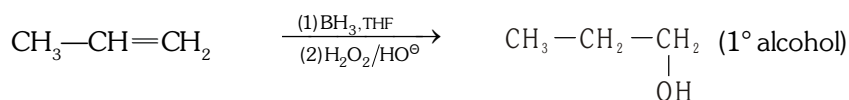


(ii) From alkenes :

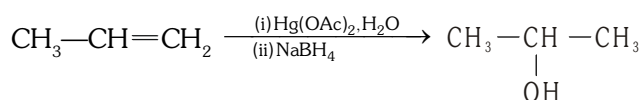
(a) By hydration :



(b) By hydroboration oxidation :



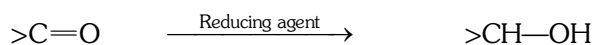
(c) By oxymercuration demercuration :



(iii) From alkyl halides (By hydrolysis) :

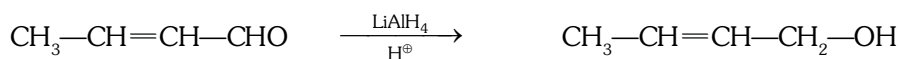
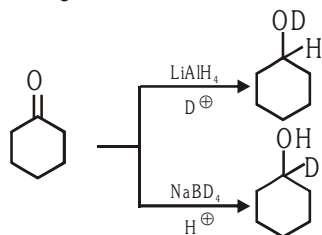
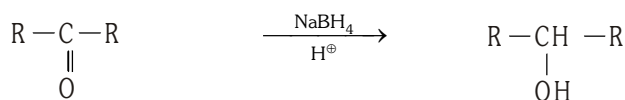
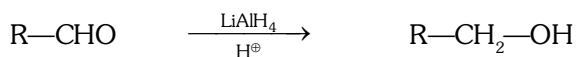
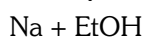
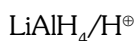


(iv) From carbonyl compounds (By reduction) :



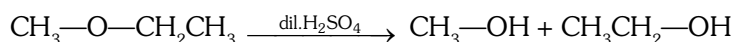
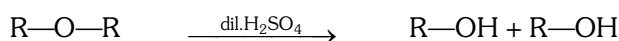
GOLDEN KEY POINTS

Reducing agents may be,

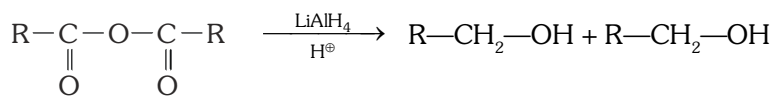
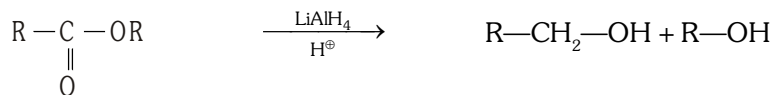
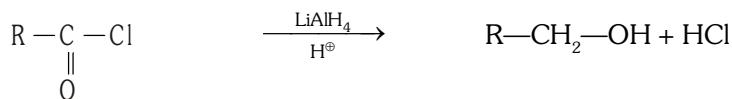
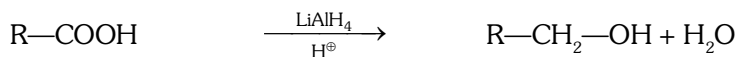


Crotonaldehyde

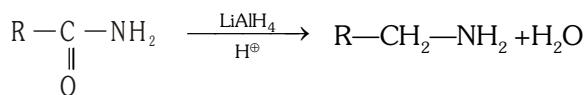
(v) From ethers :



(vi) From acid and derivatives (By reduction) :

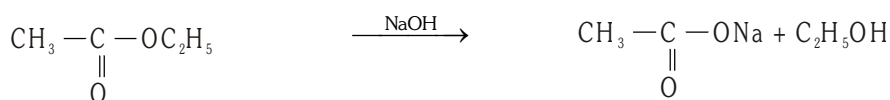
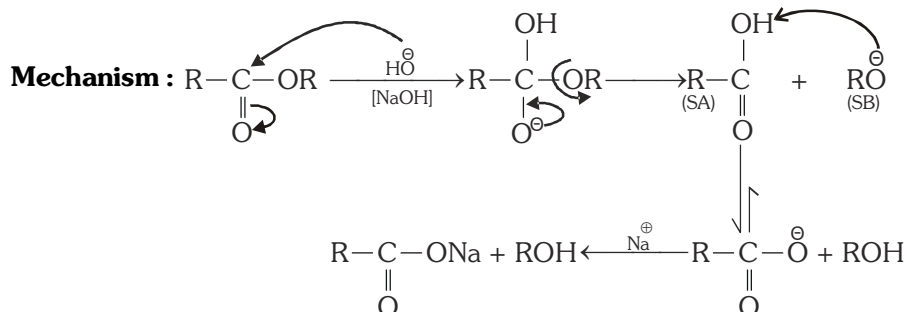
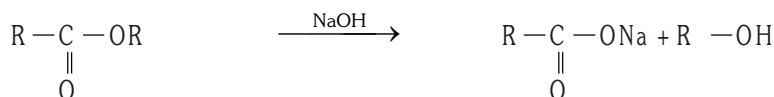


Note : Amide on reduction gives amine not alcohol.

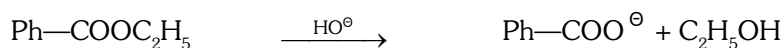


(vii) From esters (By hydrolysis) :

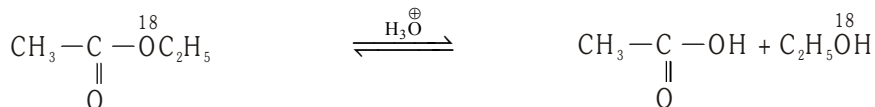
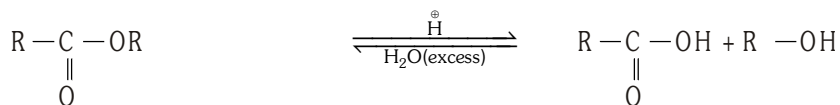
(a) By alkaline hydrolysis :



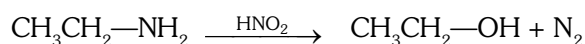
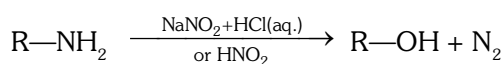
Hydrolysis is Nucleophilic substitution reaction (NSR) and Order of reaction is 2. Alkaline hydrolysis is also called as saponification



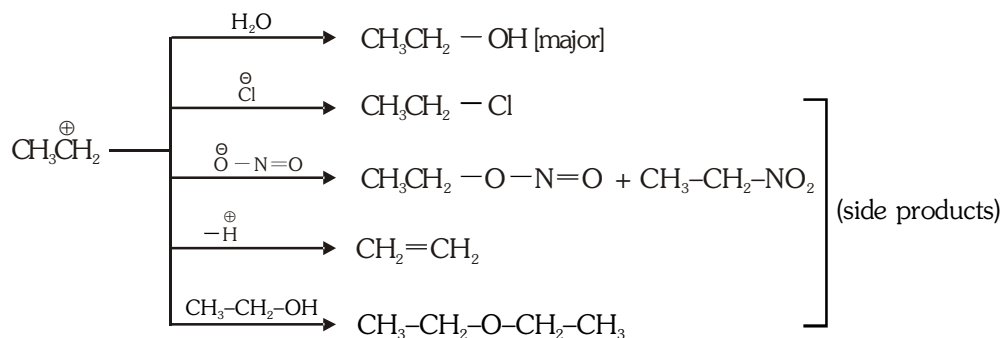
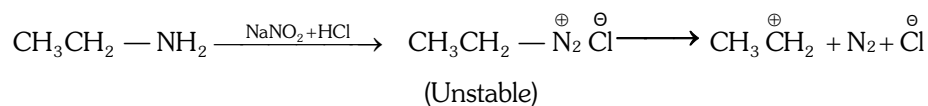
(b) By acidic hydrolysis :



(viii) From p-amines :



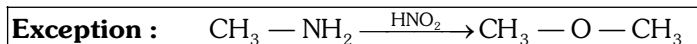
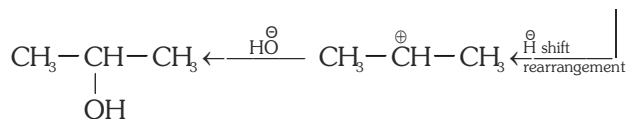
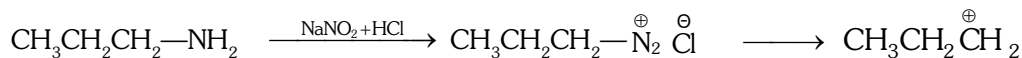
Mechanism :



Intermediate is carbocation so rearrangement may be possible.

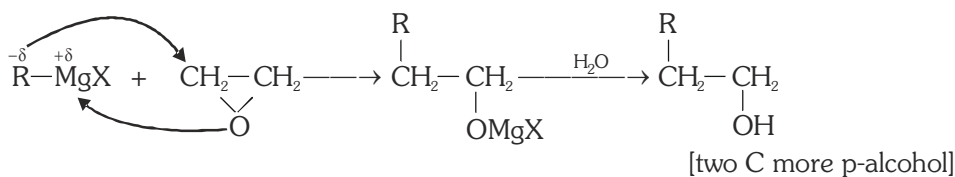
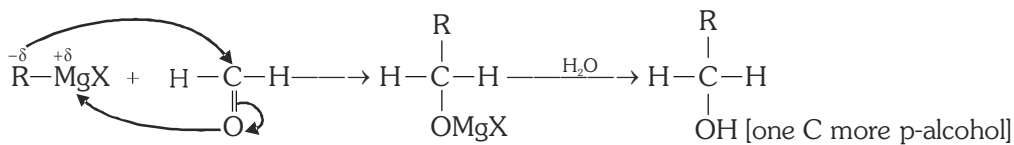
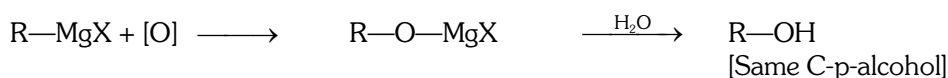
Illustrations

Illustration 1. $\text{CH}_3\text{CH}_2\text{CH}_2\text{—NH}_2 \xrightarrow{\text{NaNO}_2+\text{HCl}} ?$
Solution. **Mechanism :**

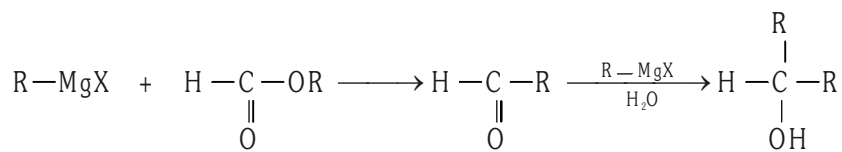
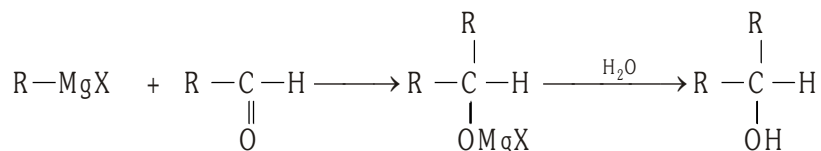


(ix) From Grignard reagent :

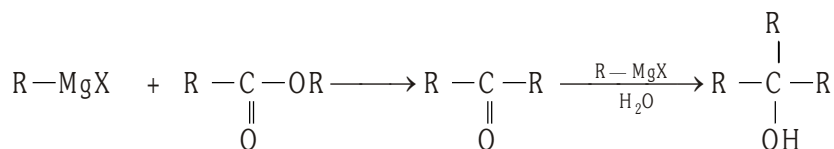
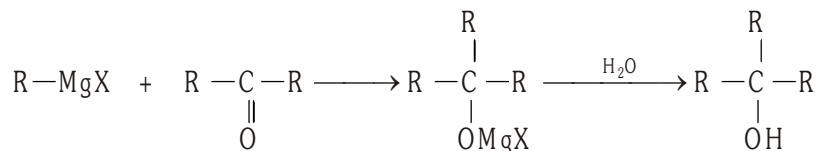
(a) p-alcohol :



(b) s-alcohol :



(c) t-alcohol :

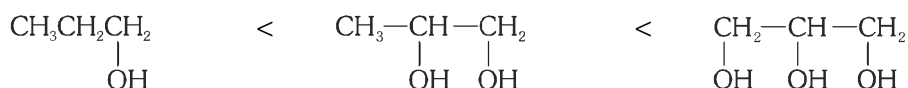
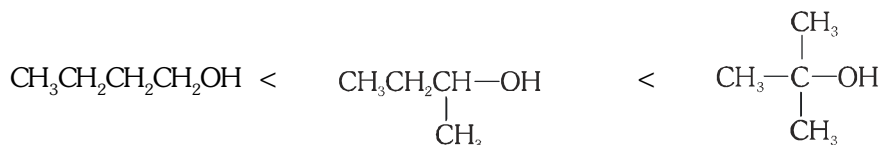


Physical properties :

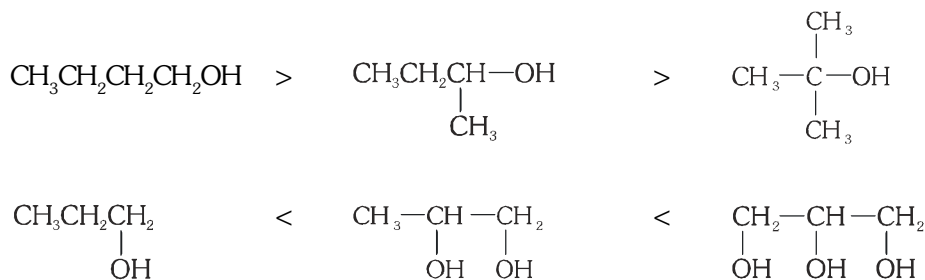
- (i) C_1 to C_{11} are colourless liquids and higher alcohols are solids.
- (ii) Density of monohydric alcohol is less than H_2O .
- (iii) Density $\propto$ mol. wt. (for monohydric alcohol).

Z:\NODE02\B0A1-B0\TARGET\CHEM\ENG\MODULE-6\02 OXYGEN CONTAINING COMPOUND\01-THEORY.P65

Order of solubility :



(v) **Boiling points :** $BP \propto \frac{\text{molecular weight}}{\text{No. of side chains}}$



Illustrations

Solution. H-bonding in alcohol.

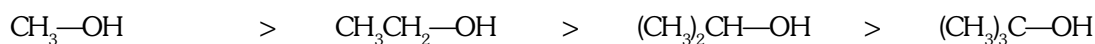
Solution. Dimer formation in carboxylic acid.



Monohydric alcohol shows following reactions

- (A) Reaction involving cleavage of $\text{O} \vdash \text{H}$
 (B) Reaction involving cleavage of $\text{C} \vdash \text{OH}$
 (C) Reaction involving complete molecule of alcohol

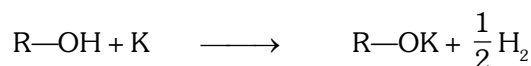
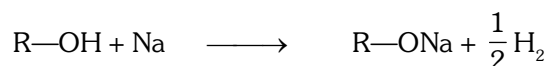
(A) Reaction involving cleavage of $\text{O}-\text{H}$: Reactivity order (Acidic nature) is



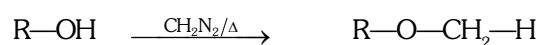
(i) Acidic nature :



Alcohols are less acidic than H_2O and neutral for litmus paper and give H_2 with active metals (Na, K)

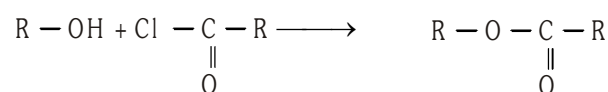


(ii) Alkylation:

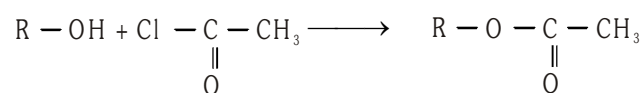


(Williamson synthesis)

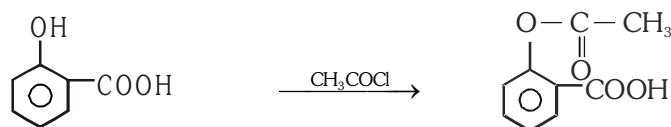
(iii) Acylation :



(Acylation)



(Acetylation)



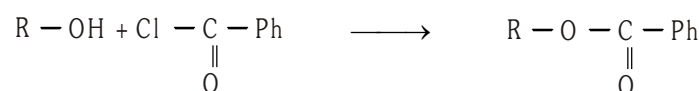
Salicylic acid

Acetoxy benzoic acid

Acetyl salicylic acid

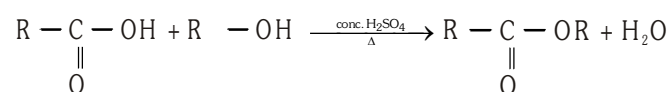
Aspirin [Used as analgesic and antipyretic]

(iv) Benzoylation : (Schotten Baumann's Reaction) :



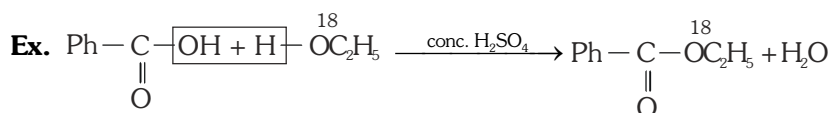
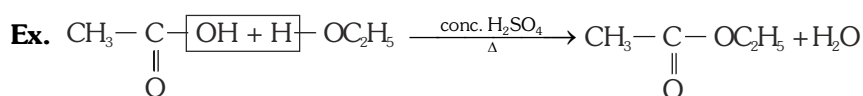
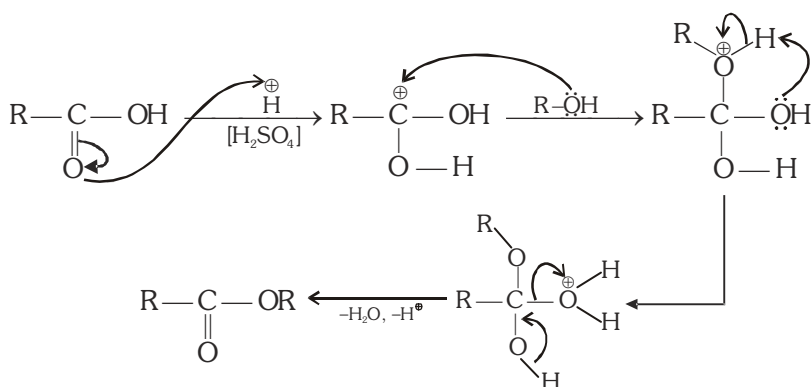
(Benzoylation)

(v) Esterification :

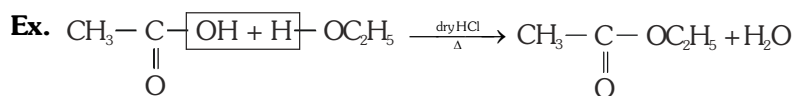


Conc. H_2SO_4 is used as catalyst and dehydrating agent.

Mechanism :

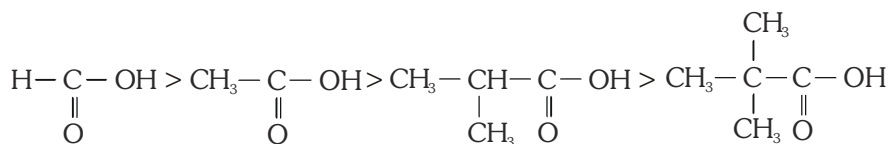


Dry HCl can also be used as dehydrating agent.

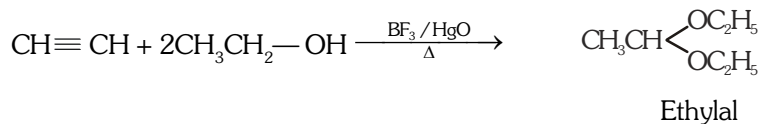
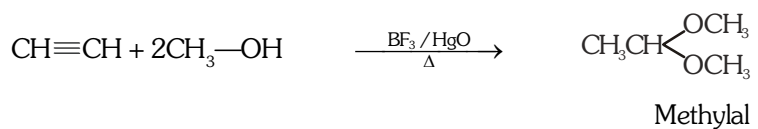


GOLDEN KEY POINTS

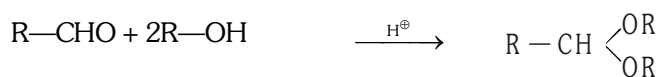
- Reactivity for esterification $\propto \frac{1}{\text{Steric hindrance}}$.
- Reactivity of $\text{R}-\text{OH}$ [If acid is same] : $\text{CH}_3-\text{OH} > 1^\circ > 2^\circ > 3^\circ$ alcohol
- Reactivity of RCOOH [If alcohol is same] :



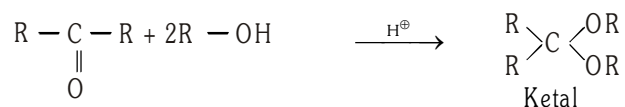
(vi) Reaction with $\text{CH}\equiv\text{CH}$:



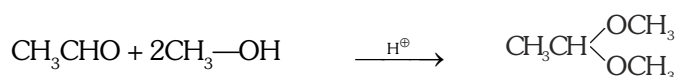
(vii) Reaction with carbonyl compounds :



Acetal

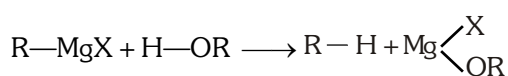


Ketal

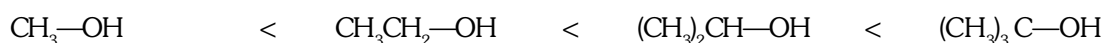


Methylal

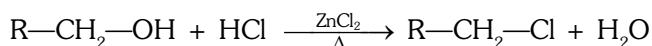
(viii) Reaction with Grignard reagent :



(B) Reaction involving cleavage of $C-\dot{O}H$: Reactivity order or basic nature is

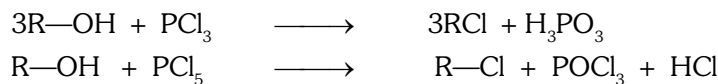


(i) Reaction with halogen acid :

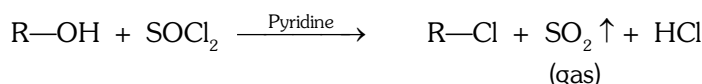


Reactivity order of the acids is $HI > HBr > HCl$

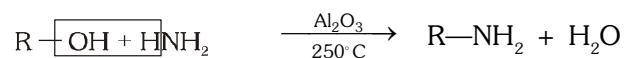
(ii) Reaction with phosphorous halides :



(iii) Reaction with thionyl chloride ($SOCl_2$) :



(iv) Reaction with NH_3 : Alumina (Al_2O_3) is used as dehydrating agent.

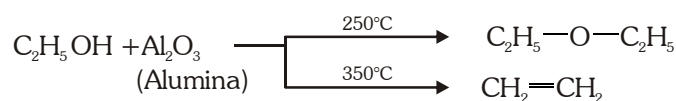
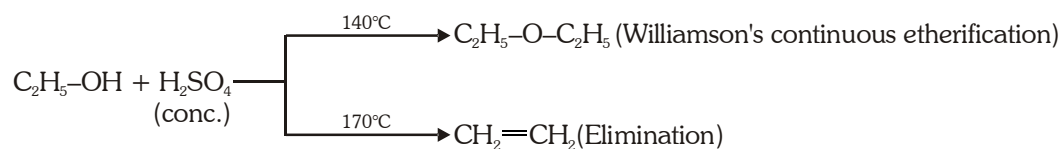


(C) Reaction involving complete molecule of alcohol :

(i) Dehydration : Removal of H_2O

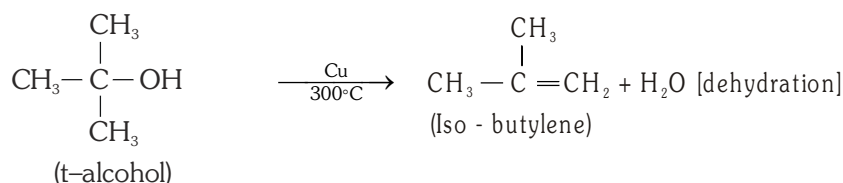
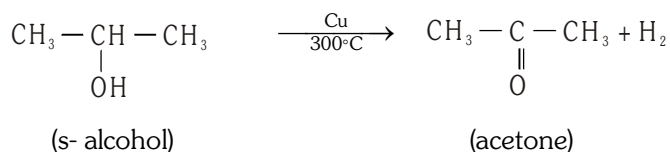
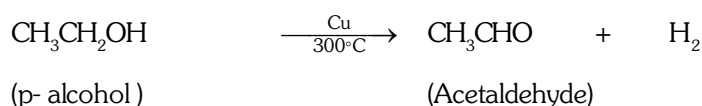
(a) Intermolecularly removal of H_2O [formation of ether]

(b) Intramolecularly removal of H_2O [formation of alkene]

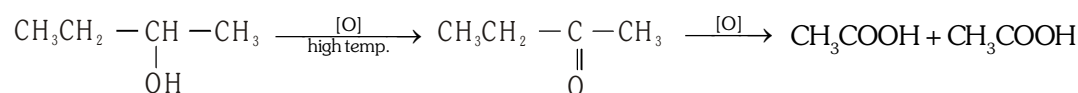
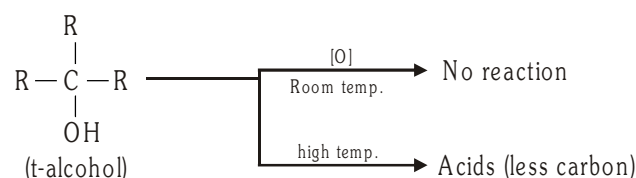
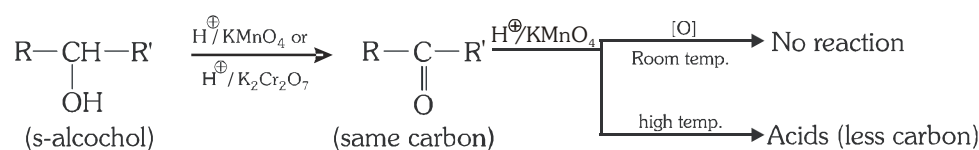
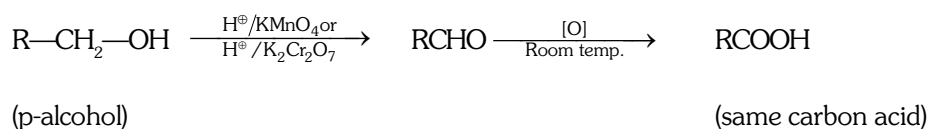


Ease of dehydration follows the order : **$3^\circ ROH > 2^\circ ROH > 1^\circ ROH$**

(ii) Catalytic Dehydrogenation :



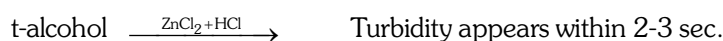
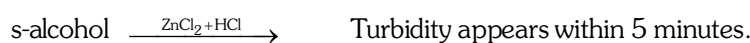
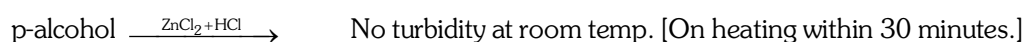
(iii) Oxidation :

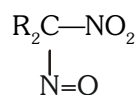
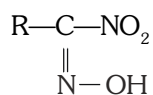
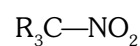
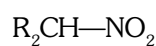
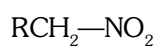
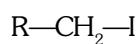
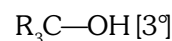
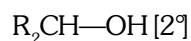
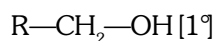


Carbonyl group goes with smaller alkyl group [Popoff's rule suggested for oxidation of unsymmetrical ketones]

(iv) Distinction between 1°, 2° and 3° alcohols :

(a) **Lucas test :** A mixture of HCl(conc.) and anhydrous ZnCl₂ is called Lucas reagent.



(b) Victor - Meyer test :p-alcohol $\longrightarrow$ Red colours-alcohol $\longrightarrow$ Blue colourt-alcohol $\longrightarrow$ No colour

No reaction

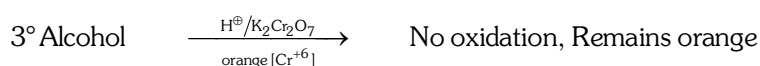
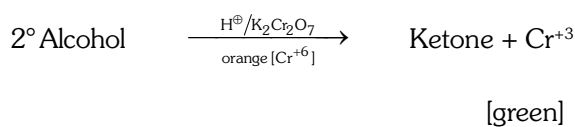
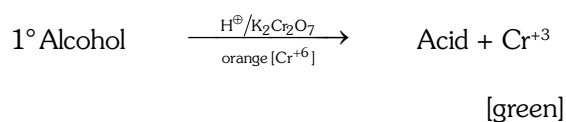
Nitrolic acid (blue)

Pseudonitrol (blue)

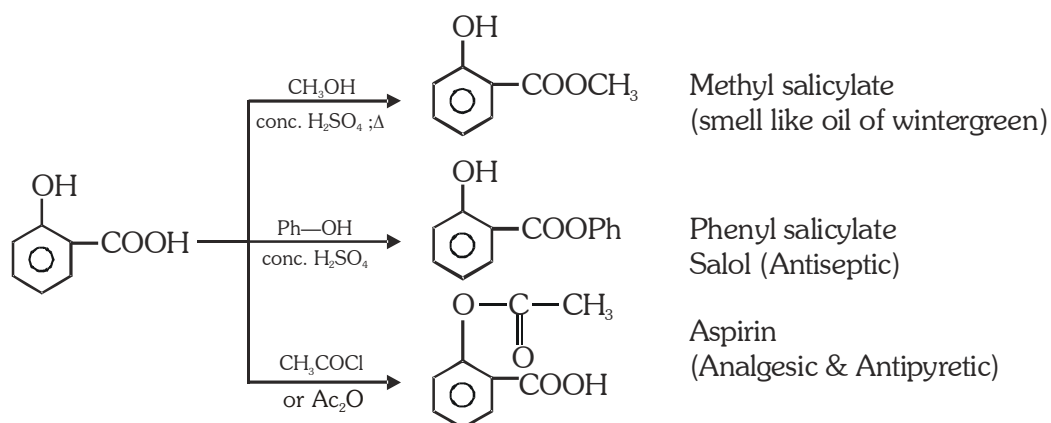
Colourless



Sodium nitrolate (Red) No reaction (Remains blue)

(C) Dichromate test :**(v) Distinction between CH_3-OH and C_2H_5OH**

	CH_3OH	CH_3CH_2OH
B.P.	65°C	78°C
$I_2 + NaOH$	No ppt	Yellow ppt of CHI_3
$Cu/300^\circ C$	Smell of formalin [$HCHO$]	No smell
Salicylic acid	Smell like oil of wintergreen	No smell



BEGINNER'S BOX-1

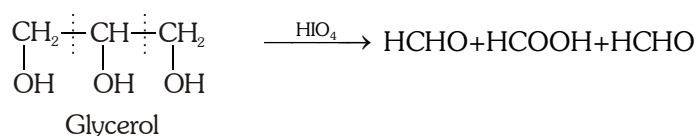
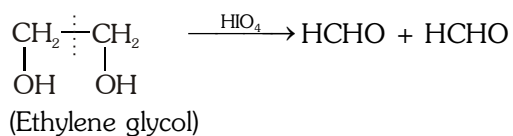
- Which of the following reactions of alkanols does not involve C-O bond breaking
 - $\text{CH}_3\text{CH}_2\text{OH} + \text{SOCl}_2$
 - $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + \text{PBr}_3$
 - $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{COOH}$
 - $\text{ROH} + \text{HX}$
- Which of the following alkanols is most soluble in water
 - 1-Butanol
 - 2-Butanol
 - Isobutyl alcohol
 - t-Butyl alcohol
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{PCl}_3} \text{A} \xrightarrow{\text{Alc. KOH}} \text{B} \xrightarrow{\text{H}_3\text{O}^+} \text{C}$
Find product 'C' is
 - $\text{CH}_3\text{CH}=\text{CH}_2$
 - $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$
 - $\text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\text{CH}_3$
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$

Important facts about alcohols

- Toxicity [ethyl alcohol < Iso propyl alcohol < methyl alcohol]
- Absolute alcohol : Ethyl alcohol - 99.5%-100%
- Power alcohol : Rectified spirit + C_6H_6 + Petrol for generation of power
- Methylated spirit : Methanol + Pyridine + mineral naptha + rectified spirit.
- 70% CH_3OH is known as wood spirit.
- 90% $\text{C}_2\text{H}_5\text{OH}$ is known as Raw spirit.
- $\text{C}_2\text{H}_5\text{OH}$ is technically called WASH.
- Rectified spirit contains 95.5% alcohol and 4.5% H_2O .

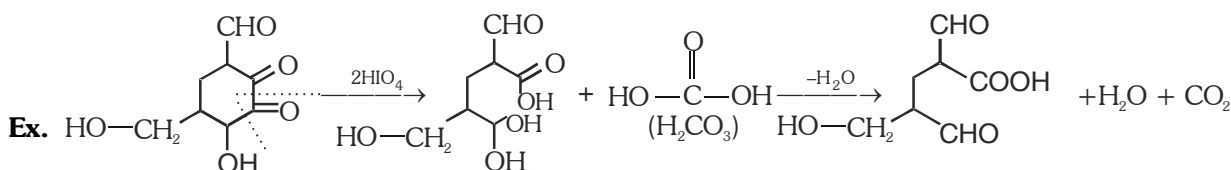
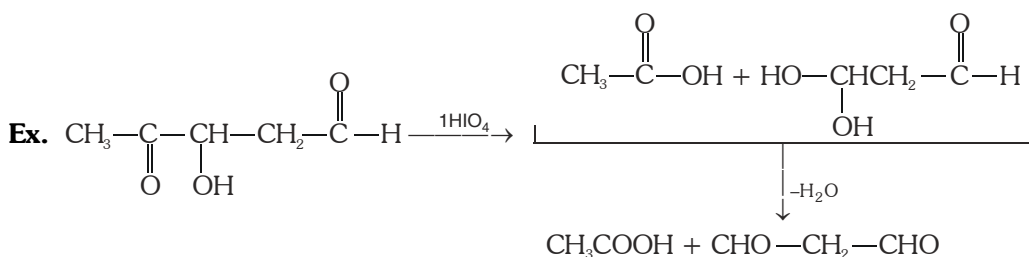
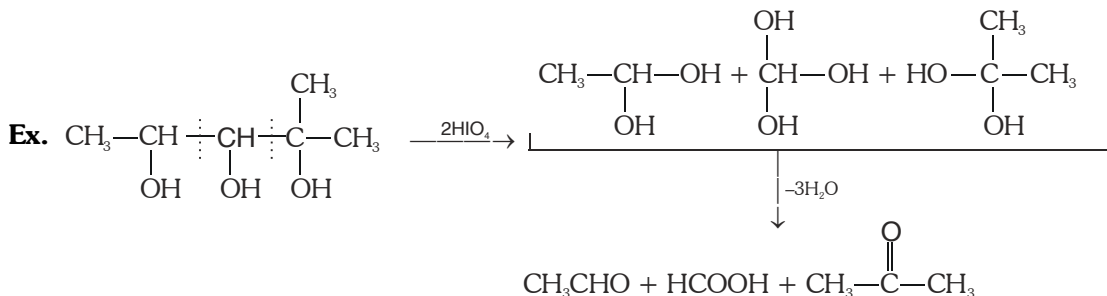
GOLDEN KEY POINTS

Oxidation by HIO_4 [per iodic acid] or $(\text{CH}_3\text{COO})_4\text{Pb}$ [lead tetraacetate] :



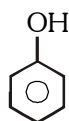
Condition for oxidation by HIO_4 or $(\text{CH}_3\text{COO})_4\text{Pb}$

- (i) At least 2 $-\text{OH}$ or 2 $>\text{C}=\text{O}$ or 1 $-\text{OH}$ and 1 $>\text{C}=\text{O}$ should be at vicinal carbons.
- (ii) One HIO_4 breaks one $\text{C}-\text{C}$ bond and adds one $-\text{OH}$ to each carbon.

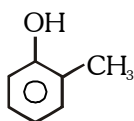


4.0 AROMATIC HYDROXY DERIVATIVES

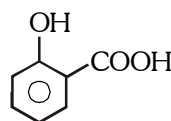
Phenolic compounds : Compounds in which $-\text{OH}$ group is directly attached to sp^2c [Benzene ring]



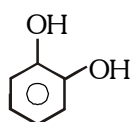
Phenol



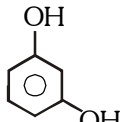
o-Cresol



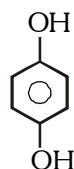
Salicylic acid



Catechol



Resorcinol



Quinol

All phenolic compounds give colour with neutral FeCl_3 .

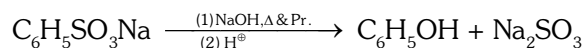


PHENOL (C₆H₅OH)

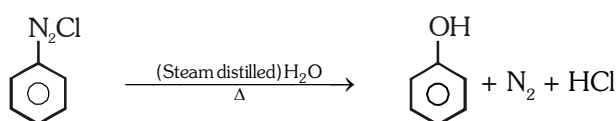
Phenol is also known as carboic acid. In phenol —OH group is attached with sp² hybridised carbon.

4.1 General Methods of Preparation

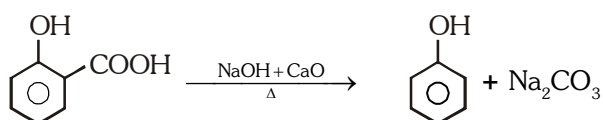
(1) From benzene sulphonic acid : When sodium salt of benzene sulphonic acid is fused with NaOH phenol is obtained.



(2) From benzene diazonium chloride : When benzene diazonium chloride solution is warmed with water, phenol is obtained with evolution of nitrogen.

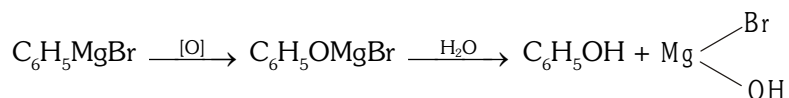


(3) By distilling a phenolic acid with sodalime (decarboxylation):

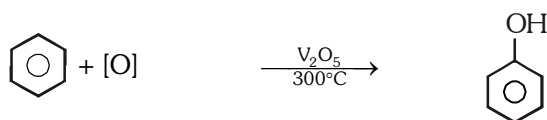


Salicylic acid

(4) From Grignard reagent : The Grignard reagent on reaction with oxygen and subsequent hydrolysis yields phenol.



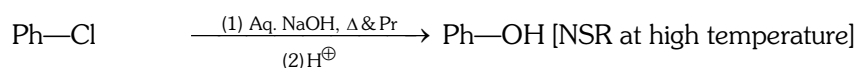
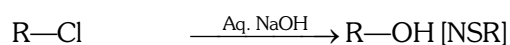
(5) From benzene :



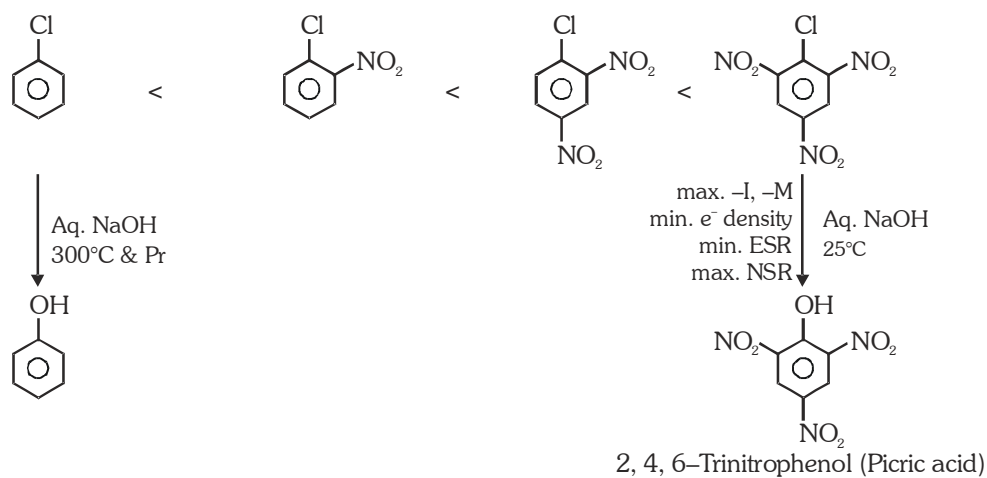
(6) From chloro benzene :



Stable by resonance



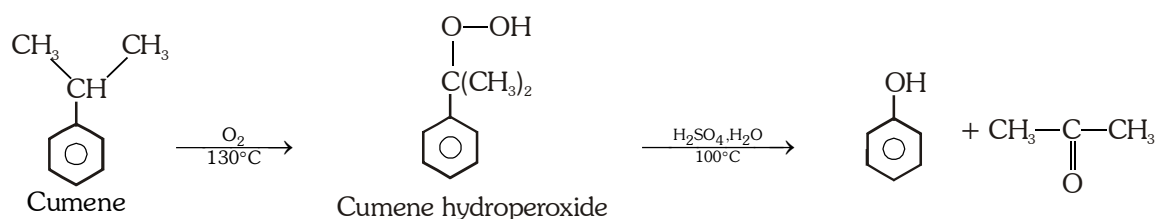
Order for NSR :



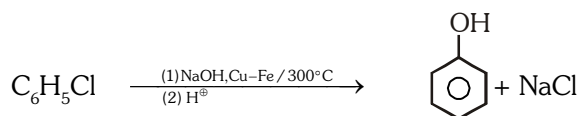
(7) Industrial preparation of phenol: Phenol can be prepared commercially by :

- (a) Cumene
- (b) Dow's process

(a) From cumene (Isopropyl benzene) : Cumene is oxidised with oxygen into cumene hydroperoxide in presence of a catalyst. This is decomposed by dil. H_2SO_4 into phenol and acetone.

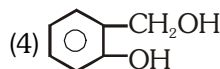
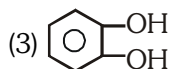
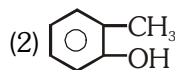
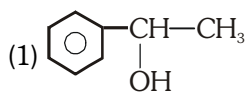


(b) Dow process : This process involves alkaline hydrolysis of chloro benzene-(obtained by above process) followed by acidification.



BEGINNER'S BOX-2

1. Which of the following compounds does not show phenolic properties :-



2. The number of dihydric phenols possible with the molecular formula $C_6H_6O_2$ is :-

(1) 2

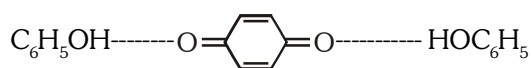
(2) 3

(3) 4

(4) 5

4.2 Physical Properties

- (i) Phenol is a colourless, crystalline solid.
- (ii) It attains pink colour on exposure to air and light. (slow oxidation)



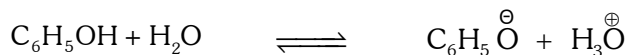
Phenoquinone (pink colour)

- (iii) It is poisonous in nature but acts as antiseptic and disinfectant.
- (iv) Phenol is slightly soluble in water, readily soluble in organic solvents.
- (v) Solubility of phenol in water is much lower than alcohols because of larger hydrocarbon part in the molecule.
- (vi) Due to intermolecular H-Bonding, phenol has relatively high boiling point than the corresponding hydrocarbons, aryl halides.

4.3 Chemical Properties

(A) Reactions due to -OH group :

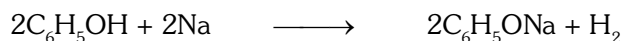
- (i) **Acidic Nature** : Phenol is a weak acid. The acidic nature of phenol is due to the formation of stable phenoxide ion in solution. The phenoxide ion is stable due to resonance. The negative charge is spread through out the benzene ring which is stabilising factor in the phenoxide ion. Electron withdrawing groups ($-\text{NO}_2$, $-\text{Cl}$) increase the acidity of phenol while electron releasing groups ($-\text{CH}_3$ etc.) decrease the acidity of phenol.



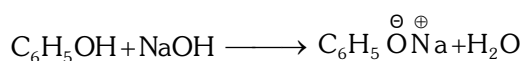
Phenol is stronger acid than alcohols but weaker than the carboxylic acids and even carbonic acid.

GOLDEN KEY POINTS

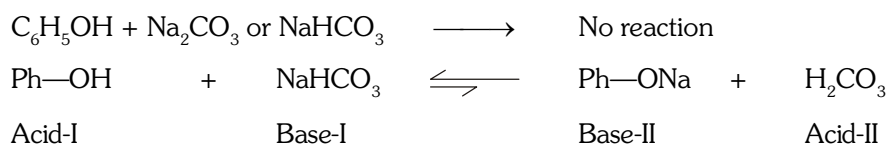
- The acidic nature of phenol is observed as the following:
 - (i) Phenol changes blue litmus to red.
 - (ii) Highly electro positive metals react with phenol.



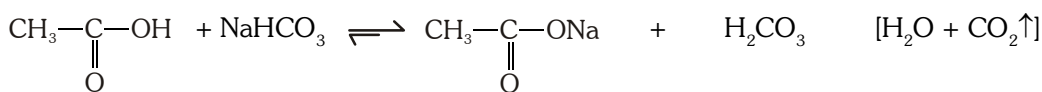
(iii) Phenol reacts with strong alkalies to form phenoxides.



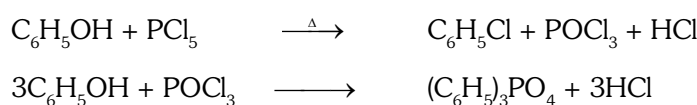
(iv) However phenol does not decompose Na_2CO_3 or NaHCO_3 because phenol is weaker acid than carbonic acid.



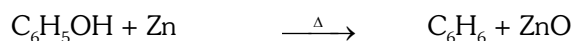
Note : Acetic acid reacts with NaHCO_3 and gives effervescence of CO_2 .



(ii) Reaction with PCl_5 : Phenol reacts with PCl_5 to form chloro benzene. POCl_3 formed as biproduct reacts with phenol to form triphenyl phosphate.

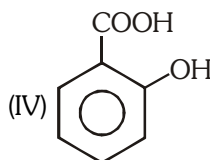
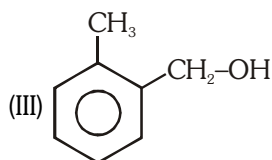
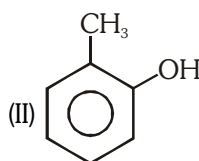
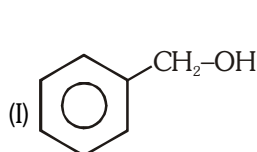


(iii) Reaction with Zn dust: When phenol is distilled with zinc dust benzene is obtained.



Illustrations

Illustration 4. In which of the following compound deoxygenation is possible when heated with Zn



(1) I, II, III

(2) I, III, IV

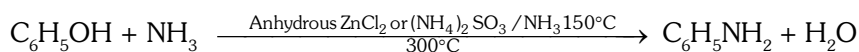
(3) II, IV

(4) II, III

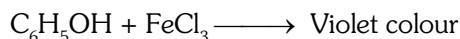
Solution

Ans.(3) Observed in phenolic compound.

(iv) Reaction with NH_3 (Bucherer reaction): Phenol reacts with NH_3 in presence of anhydrous ZnCl_2 to form aniline.

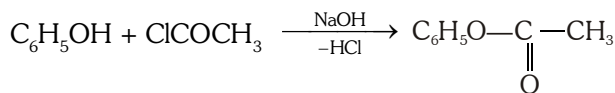


- (v) **Reaction with FeCl_3 :** Phenol gives violet colouration with FeCl_3 solution (neutral) due to formation of a complex.

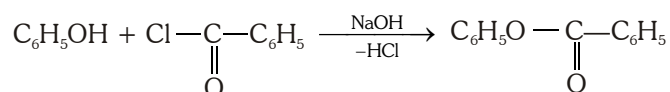


This reaction is used to differentiate phenol from alcohols.

- (vi) **Acetylation :** Phenol reacts with acid chlorides or acid anhydrides in alkali solution to form phenyl esters.

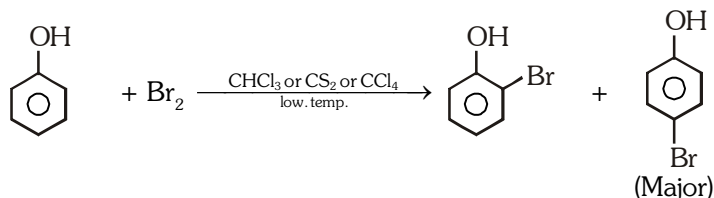


- (vii) **Benzoylation (Schotten-Baumann reaction)**

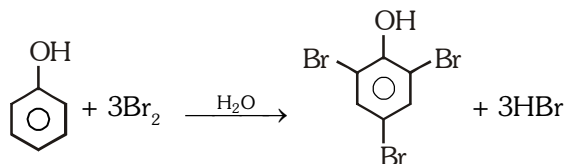


- (B) **Reaction of Benzene Ring :** The $-\text{OH}$ group is ortho and para directing. It activates the benzene nucleus.

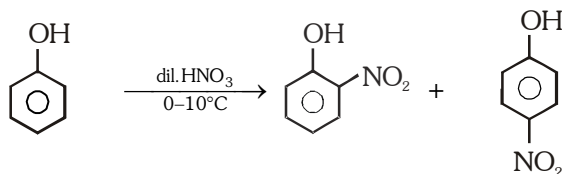
- (i) **Halogenation :** Phenol reacts with bromine in CCl_4 to form mixture of o- and p-bromo phenol.



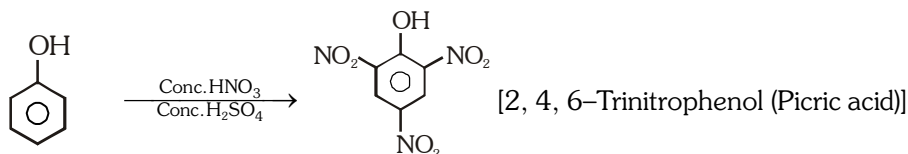
Phenol reacts with bromine water to form a white ppt. of 2,4,6-tribromo phenol. (Test for phenol)



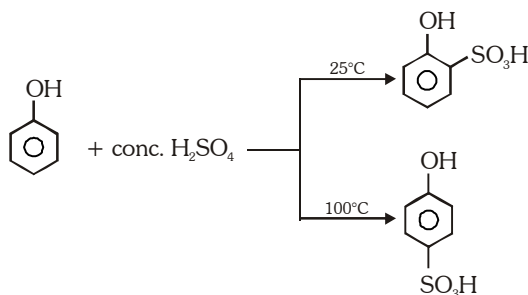
- (ii) **Nitration :** Phenol reacts with dil. HNO_3 at $0^\circ\text{--}10^\circ\text{C}$ to form o- and p- nitro phenols.



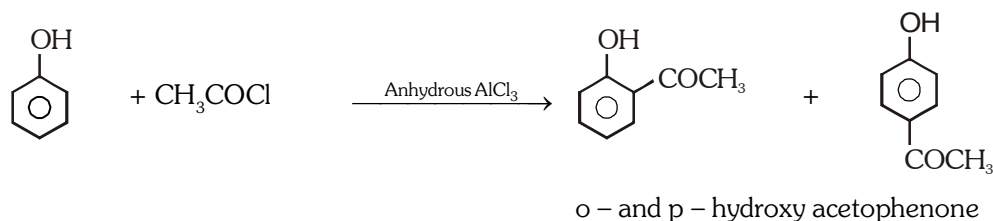
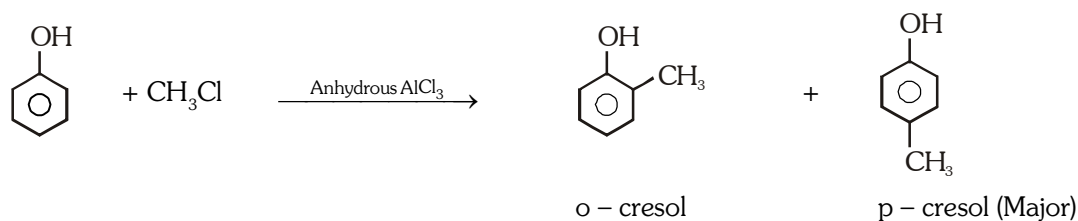
When phenol is treated with nitrating mixture it forms 2,4,6- trinitro phenol (picric acid) but it is not good method to form picric acid because nitric acid oxidise phenol into p-Bezoquinone



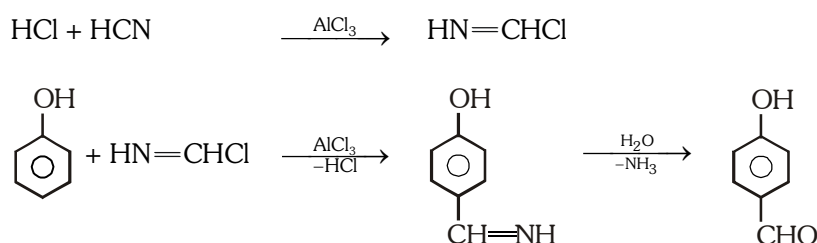
- (iii) **Sulphonation:** Phenol reacts with fuming H_2SO_4 to form o- and p-hydroxy benzene sulphonic acid at different temperatures.



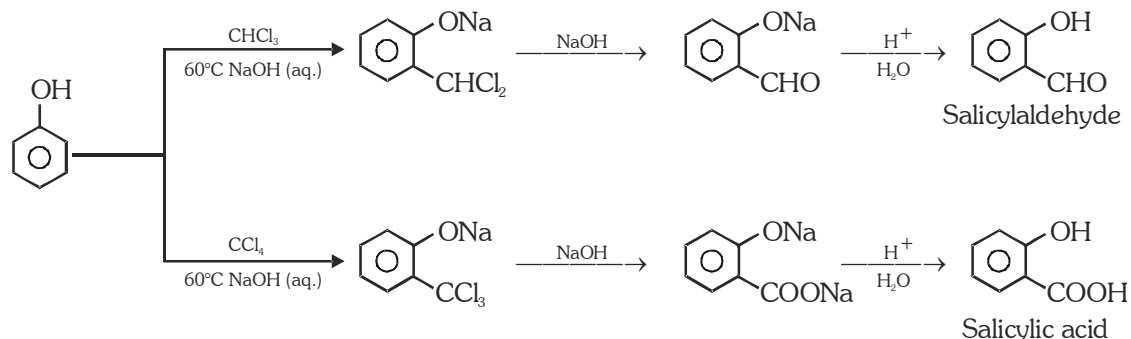
(iv) Friedel - Craft 's reaction:



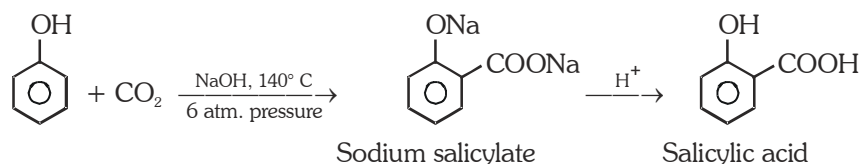
(v) Gattermann aldehyde synthesis : When phenol is treated with liquid HCN and HCl gas in presence of anhydrous AlCl_3 it yields mainly p- hydroxy benzaldehyde (formylation)



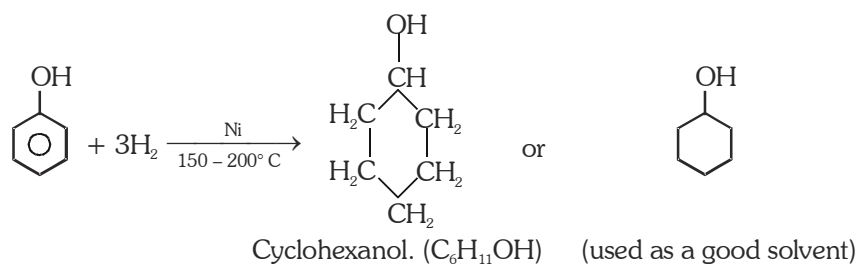
(vi) Reimer-Tiemann reaction : Phenol on refluxing with chloroform and NaOH (aqueous) followed by acid hydrolysis yields o-hydroxy benzaldehyde. When CCl_4 is used salicylic acid is formed.



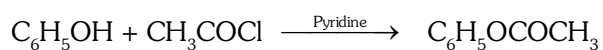
(vii) Kolbe's Schmidt reaction : It involves the reaction of $\text{C}_6\text{H}_5\text{OH}$ with CO_2 and NaOH at 140°C followed by acidification to form salicylic acid.



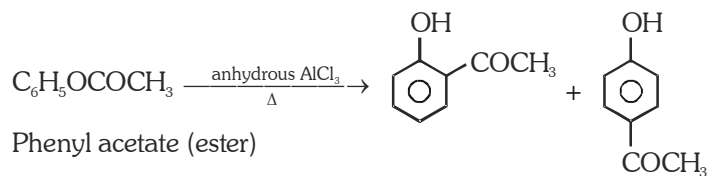
(viii) Hydrogenation: Phenol when hydrogenated in presence of Ni at $150\text{-}200^\circ\text{C}$ forms cyclohexanol.



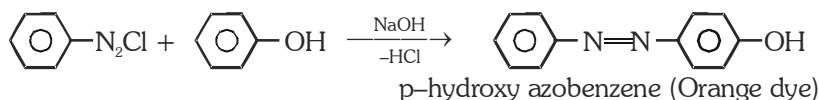
(ix) Fries rearrangement reaction:



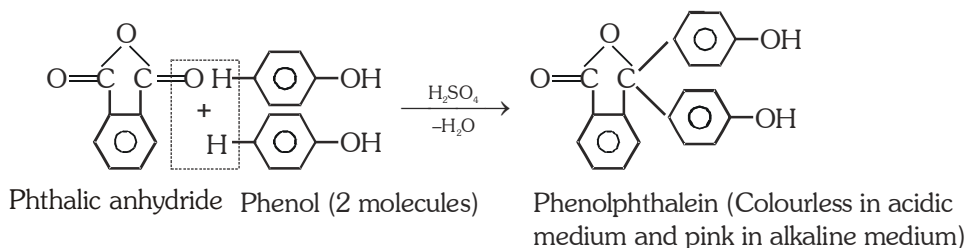
Phenyl Acetate



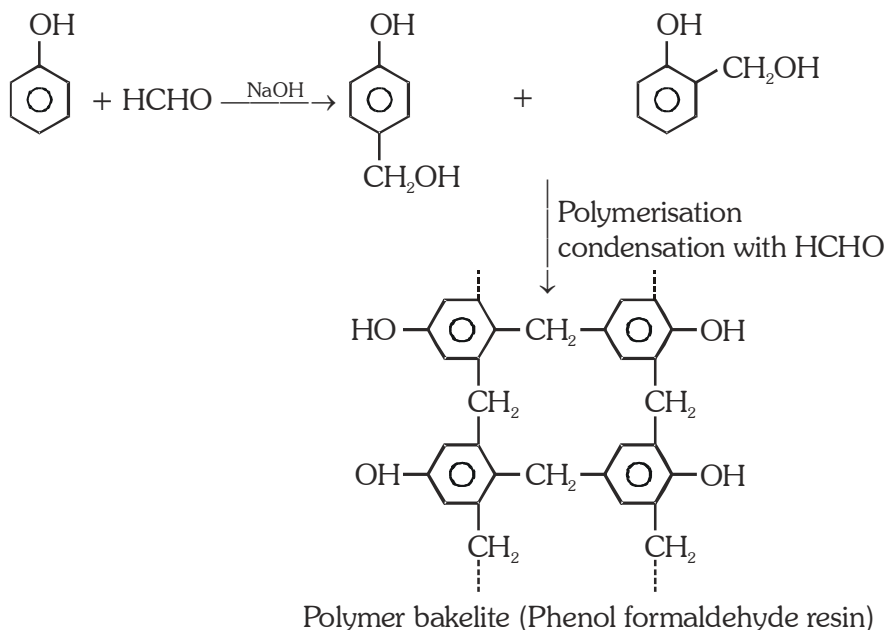
(x) Coupling reactions: Phenol couples with benzene diazonium chloride in presence of an alkaline solution to form a dye (p- hydroxy azobenzene) orange dye.



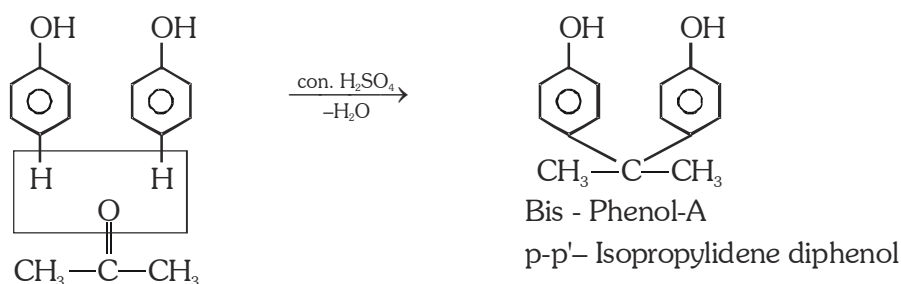
Phenol couples with phthalic anhydride in presence of conc. H_2SO_4 to form a dye (phenolphthalein) used as an indicator.



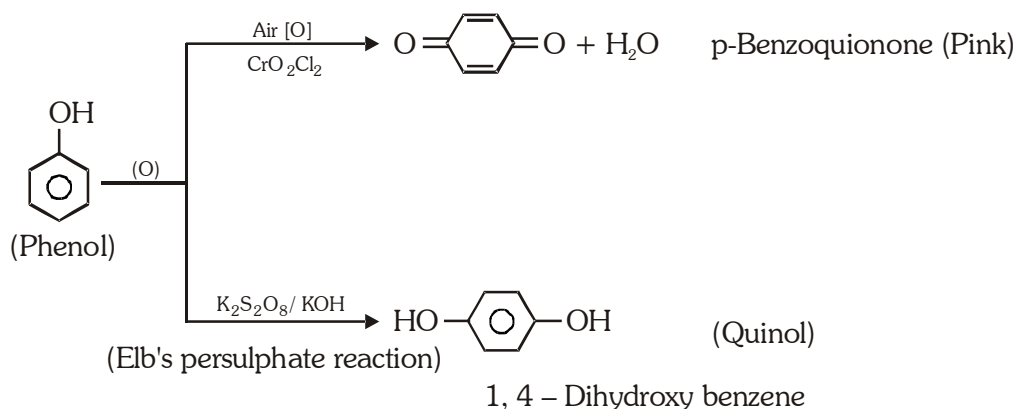
(xi) Lederer Manasse (Condensation with formaldehyde) : Phenol condenses with HCHO (excess) in presence of NaOH or weak acid (H^+) to form a polymer known as bakelite (resin).



(xii) Reaction with acetone: (Condensation with acetone)



(xiii) Oxidation:



BEGINNER'S BOX-3

- Reimer-Tiemann formylation reaction involves addition of :-
 - Chloroform on phenoxide ion
 - Trichloromethyl carbanion on phenoxide ion
 - Dichlorocarbene on phenoxide ion
 - Hydroxide ion on phenol
- Phenol reacts with benzenediazonium chloride solution to form a compound of the structure :-
 -
 -
 -
 -
- Phenol $\xrightarrow[\text{conc. H}_2\text{SO}_4]{\text{NaNO}_2}$ Green colour $\xrightarrow{\text{H}_2\text{O}}$ red colour $\xrightarrow{\text{NaOH}}$ Blue colour

This reaction is associated with the name of :-

- Gattermann
- Hofmann
- Liebermann
- Reimer-Tiemann

Test of Phenol :

- Phenol turns blue litmus to red.
- Aqueous solution of phenol gives a violet colour with a drop of ferric chloride.
- Phenol gives Liebermann's nitroso test.
- Aqueous solution of phenol gives a white ppt. of 2,4,6-tribromophenol with bromine water.
- Phenol combines with phthalic anhydride in presence of conc. H_2SO_4 to form phenolphthalein which gives pink colour with alkali.

Differences between phenol and alcohol (C₂H₅OH) :

- (1) Phenol is more acidic than aliphatic alcohol due to resonance in phenoxide ion.
- (2) Phenol gives violet colour with FeCl₃ while aliphatic alcohol does not give.
- (3) Phenol gives triphenyl phosphate with PCl₅ while aliphatic alcohol does not.
- (4) Phenol on oxidation gives quinone while alcohol gives aldehyde or ketone and acids.

Uses of Phenol :

Phenol is used :

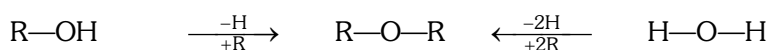
- (1) As an antiseptic in soaps and lotions. "Dettol" (mixture of chloroxylenol and terpineol)
- (2) In manufacture of azodyes, phenolphthalein, picric acid (explosive), cyclohexanol (Solvent for rubber), plastics (bakelite) etc.
- (3) In manufacture of drugs like aspirin, salol, phenacetin etc.
- (4) As preservative for ink.

5.0 ETHER

R—O—R (Dialkyl ether), alkoxy alkane. It's General formula is C_nH_{2n+2}O.

CH₃—O—CH₂CH₃ (Methoxy ethane) or Ethyl methyl ether

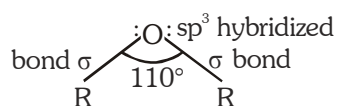
Ether is monoalkyl derivative of R—OH and dialkyl derivative of H₂O



Classification : They may be classified as :

- (a) Simple or symmetrical ether. e.g. R—O—R
- (b) Mixed or unsymmetrical ether e.g. R—O—R'

Structure :

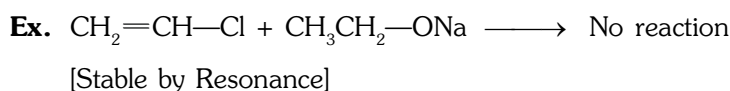
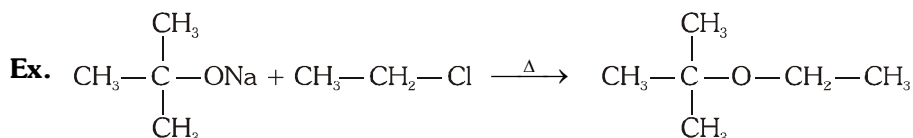
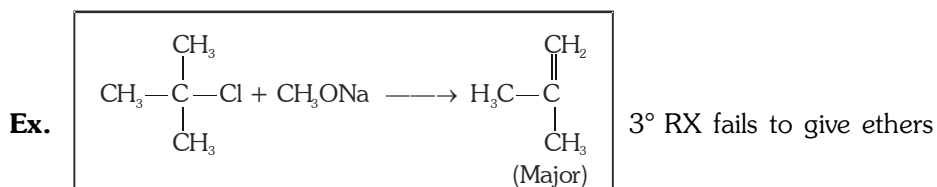
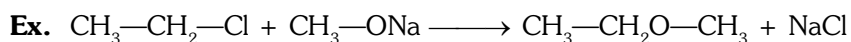
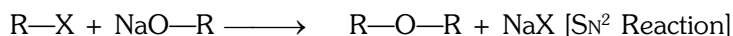


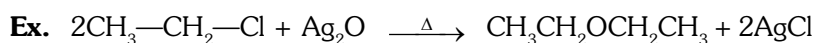
The molecule of ether is bent due to presence of lone pair. The bond angle is 110°. It is greater than that of water (105°) due to the repulsion between bulkier alkyl groups. Due to bent structure, it possesses dipole moment and hence are polar molecules.

5.1 General Methods of Preparation

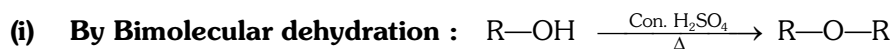
(a) From alkyl halides :

(i) By Williamson's synthesis :

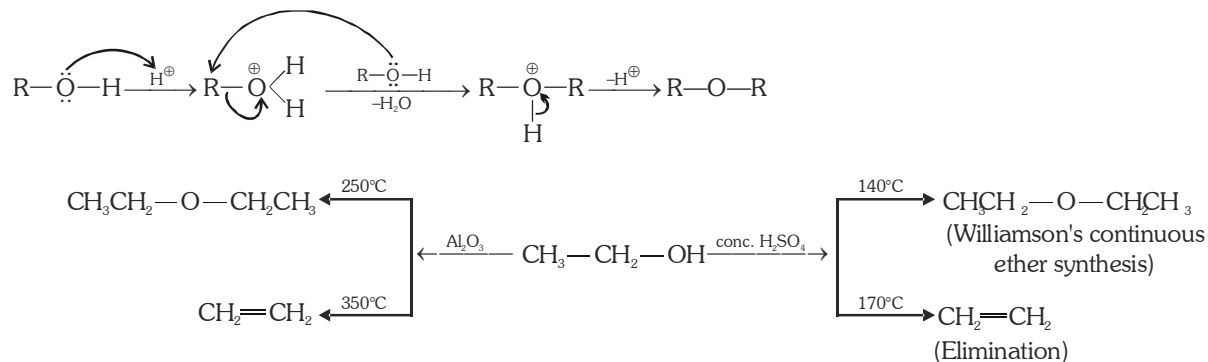




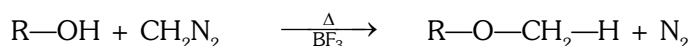
(b) From R-OH:



Mechanism :



(ii) **Reaction with CH₂N₂** (diazomethane) :



5.2 Physical Properties

- (i) CH_3OCH_3 , $CH_3OCH_2CH_3$ are gases and higher ethers are volatile liquids.
- (ii) Ether are less polar.
- (iii) Ethers are less soluble in H_2O .
- (iv) Ethers have less BP than corresponding alcohol.

Illustrations

Illustration 5. Ethers are less soluble in H_2O . Why ?

Solution. Due to less polarity, it forms weaker H-Bonding with H_2O .

Illustration 6. Ethers have less BP than corresponding alcohol. Why ?

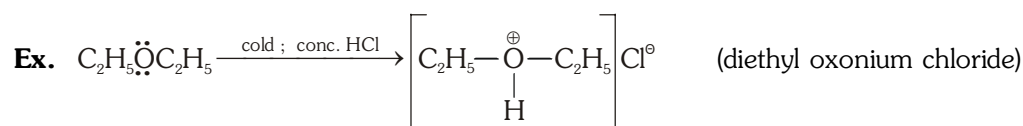
Solution. No H-Bonding in ether molecules.

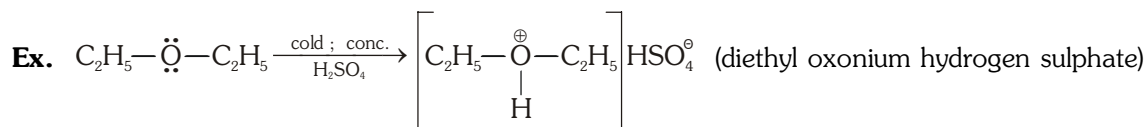
5.3 Chemical properties

Ethers are less polar so less reactive and do not react with active metals [Na,K], cold dil. acid, oxidising and reducing agent. They do not have any active functional group.

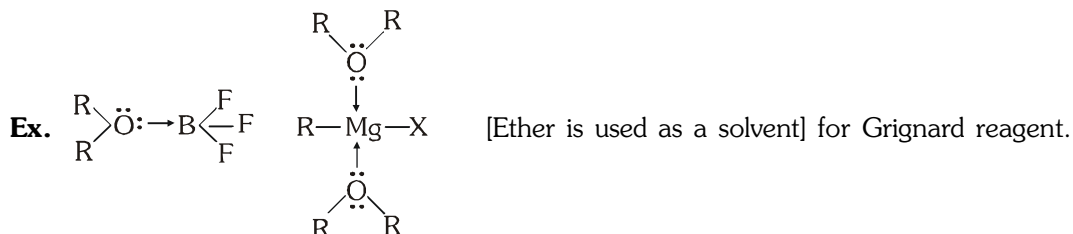
(1) Basic nature : Due to presence of $\ell.p$ on oxygen atom ether behave as lewis base

Ethers react with cold conc. acid and form oxonium salts.

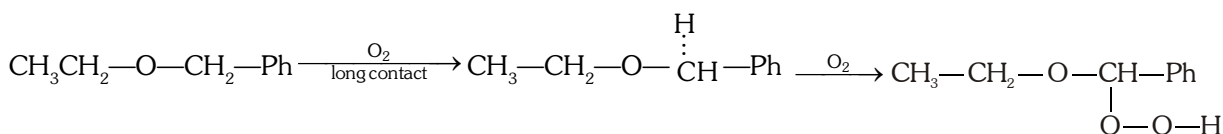
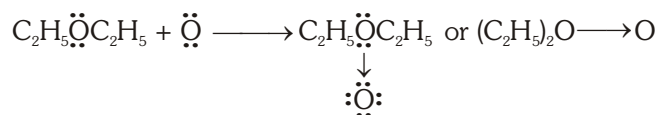
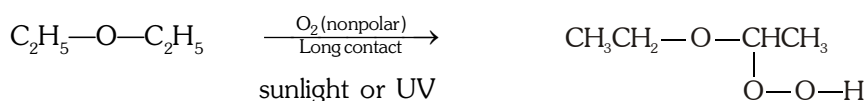




Ethers form dative bond with Lewis acids like BF_3 , AlCl_3 , RMgX etc.



(2) Formation of peroxides : Ether add up atmospheric oxygen or ozonised oxygen. It is explained by Free radical mechanism as intermediate is free radical.



Peroxides are unstable and explosives.

GOLDEN KEY POINTS

Test for peroxides

Ether (peroxide) $\xrightarrow{\text{FeSO}_4/\text{KCNs}}$ Red colour

Ether (Peroxides) + $\text{Fe}^{+2} \longrightarrow \text{Fe}^{+3} \xrightarrow{\text{CNS}^-} \text{Fe}(\text{CNS})_3$
(Red)

(3) Reaction with PCl_5 : $\text{ROR} + \text{PCl}_5 \xrightarrow{\text{heat}} 2\text{RCl} + \text{POCl}_3$

(4) Reduction : $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 \xrightarrow[\text{heat}]{\text{Red P} + \text{HI}} 2\text{CH}_3\text{CH}_3$

(5) Reaction with HX : $\text{R}-\text{O}-\text{R}' + \text{HI} \longrightarrow \text{R}-\text{OH} + \text{R}'-\text{I}$

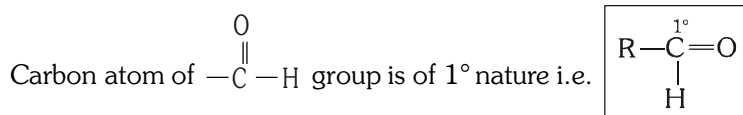
Uses of ether :

- General anaesthetic agent.
- Solvent for oil, fats, resins, Grignard reagent.
- For providing inert & moist free medium to organic reaction e.g. Wurtz reactions.
- In perfumery.
- Di-isopropyl ether $\longrightarrow$ In petrol as an antiknock comp.
- Mixture of alcohol and ether is used as a substitute of petrol. Trade name "**Natalite**"

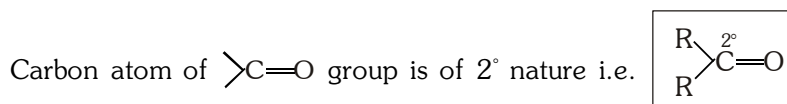
6.0 CARBONYL COMPOUNDS

Organic Compounds having $>\text{C}=\text{O}$ group are called carbonyl compounds and $>\text{C}=\text{O}$ group is known as carbonyl group. Its general formula is $\text{C}_n\text{H}_{2n}\text{O}$ ($n = 1, 2, 3, \dots$). Carbonyl compounds are grouped into two categories.

(a) Aldehydes : Aldehyde group is $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—H}$ (also known as formyl group). It is a monovalent group



(b) Ketones : The carbonyl group ($>\text{C}=\text{O}$) is a Ketonic group when its both the valencies are satisfied by alkyl group. It is a bivalent group.

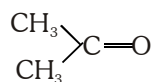


Ketones are further classified as :

(i) **Simple or Symmetrical ketones :** Having two similar alkyl groups. $\begin{array}{c} \text{R} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R} \end{array} \text{=O}$

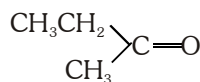
(ii) **Mixed or unsymmetrical ketones :** Having two different alkyl groups. $\begin{array}{c} \text{R} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R}' \end{array} \text{=O}$

Ex. (Ketones) : Symmetrical

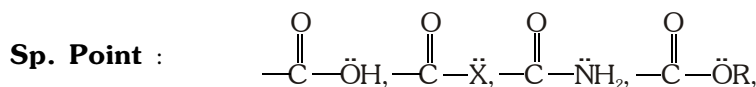


(Acetone or Dimethyl ketone)
Propanone

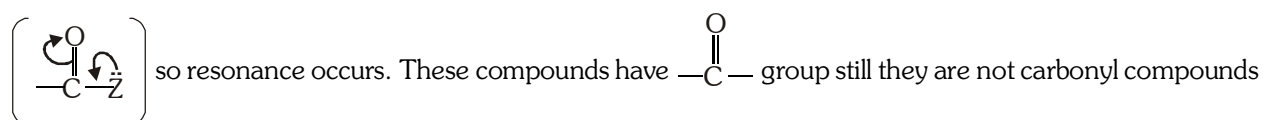
Unsymmetrical



(Ethyl methyl ketone)
Butanone

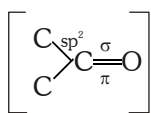


In all the compounds given above, lone pair of electrons and double bond are in conjugate system.



because these compounds have characteristic reactions different from carbonyl compounds.

Structure : In $>\text{C}=\text{O}$ compounds C-atom is sp^2 hybridised which forms two σ bonds and one π bond. The unhybridised atomic orbital of C-atom and the parallel 2p orbital of oxygen forms the π bond in $>\text{C}=\text{O}$ group



The C—C—O / H—C—O bond angle is of 120°

Due to electro-negativity difference in C & O atoms, the $>\text{C}=\text{O}$ group is polar.

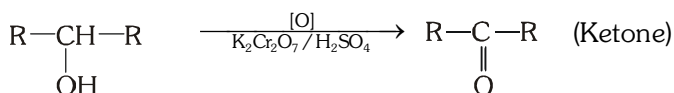
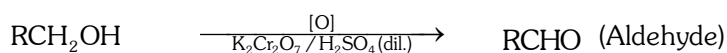
$\text{>C}^{\delta+}=\text{O}^{\delta-}$ Hence aldehydes and Ketones possess considerable dipole moment.

6.1 General Methods of Preparation

(A) For both Aldehydes and Ketones

(1) By Oxidation of Alcohols :

(a) **By $\text{K}_2\text{Cr}_2\text{O}_7$ / H_2SO_4** : Oxidation of primary alcohols gives aldehyde and oxidation of secondary alcohols gives Ketones.

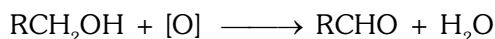


Aldehydes are quite susceptible to further oxidation to acids -



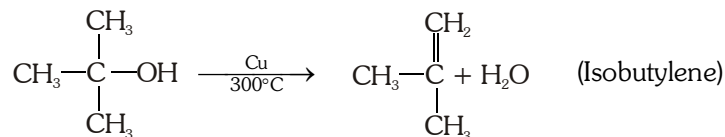
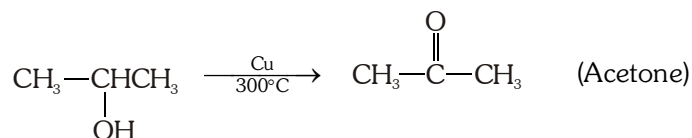
Thus oxidation of primary alcohols is made at the temperature much above the boiling point of aldehyde and thus aldehydes are vapourised out and prevented from being oxidised.

(b) **Mild Oxidising Agent** : 1° alcohols will get oxidised with CrO_3 / Pyridine, (**collin's reagent**) or P.C.C (Pyridinium chloro chromate $\text{CrO}_3 + \text{C}_5\text{H}_5\text{N} + \text{HCl}$) to aldehyde and 2° alcohols to ketone.

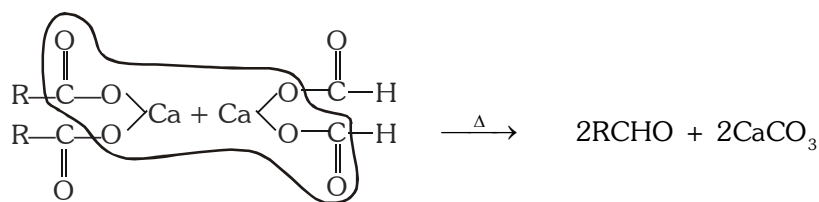


By this reaction, **good yield of aldehyde** is possible.

(2) Dehydrogenation of alcohols :



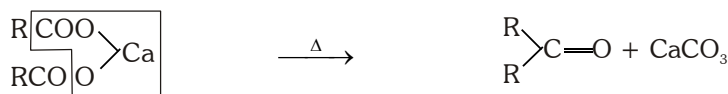
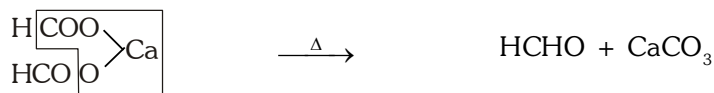
(3) By dry distillation of Ca-salts of carboxylic acid :



Calcium alkanoate

Calcium formate

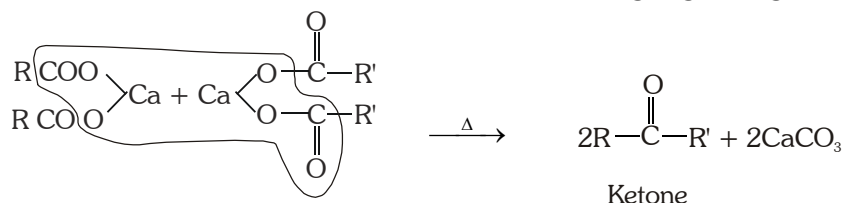
($\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{R}$ and HCHO are also formed)



Calcium-alkanoate

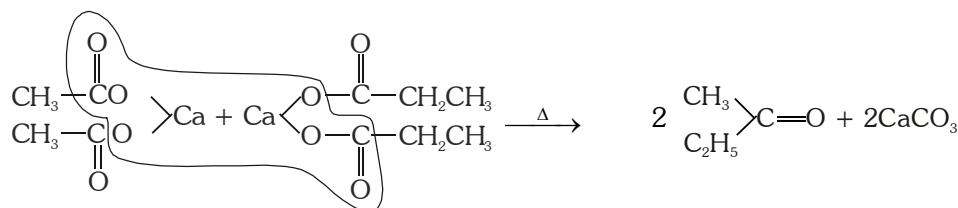
Ketone

Calcium salts of acids other than formic acid on heating together give unsymmetrical ketone



Ketone

To prepare ethyl methyl ketone Calcium acetate and Calcium propionate are used :

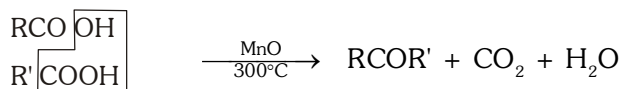
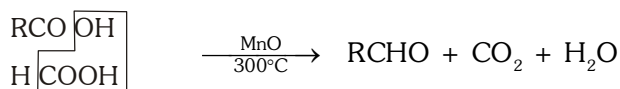
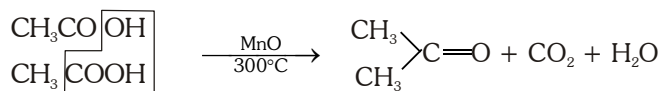
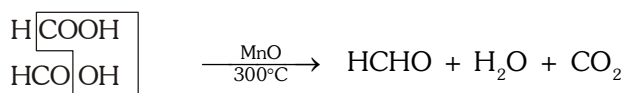


Calcium Acetate

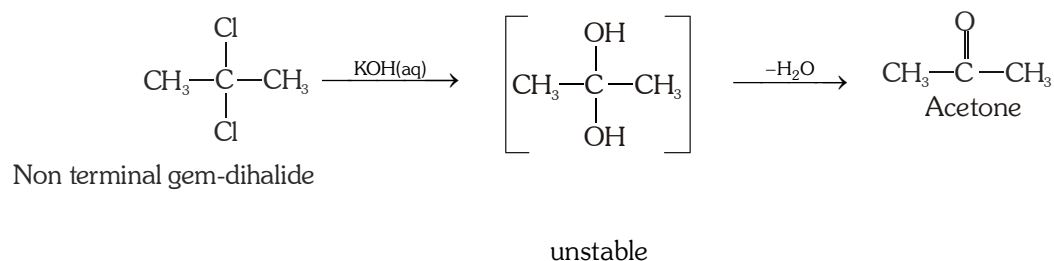
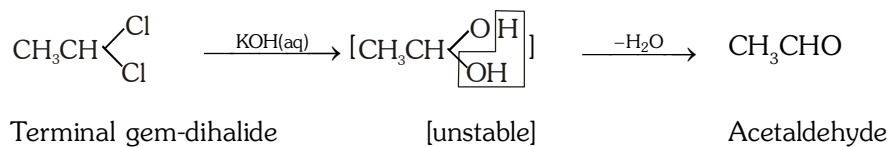
Calcium propionate

Ethyl methyl ketone

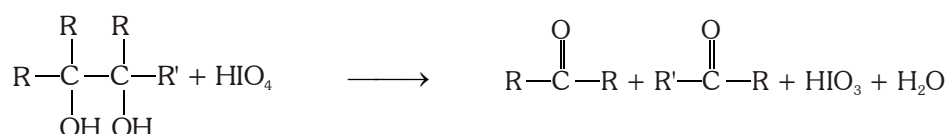
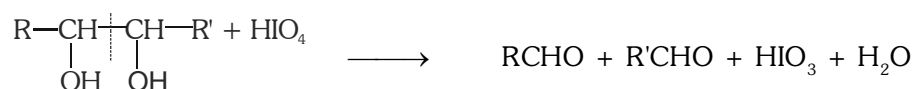
(4) By Thermal decomposition of carboxylic acids : Vapour of carboxylic acids when passed over $\text{MnO}/300^\circ\text{C}$ give carbonyl compounds



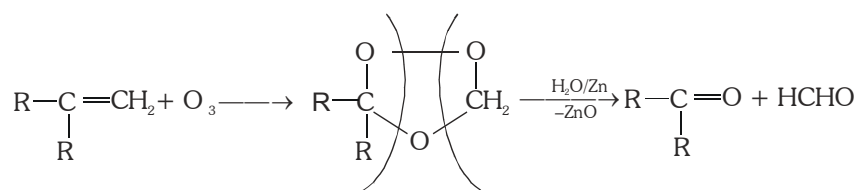
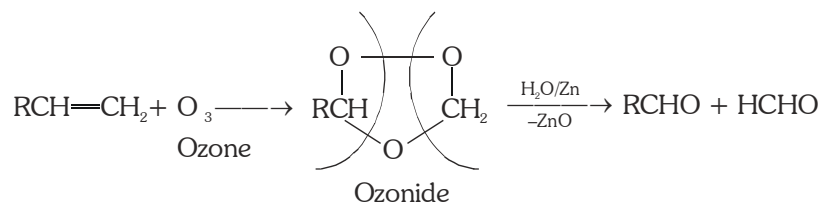
- (5) By Hydrolysis of gem dihalides :** Terminal gem-dihalides on hydrolysis give aldehydes while the non-terminal gem-dihalides give ketones.



- (6) By Oxidation of diols :** With periodic acid (HIO_4) or lead tetra acetate $(\text{CH}_3\text{COO})_4\text{Pb}$ vicinal diols get oxidised to form carbonyl compounds

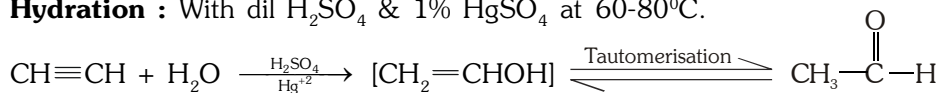


- (7) By Ozonolysis of alkenes :** This reaction is used to determine the position of double bond in alkene. Zn is used to decompose H_2O_2 formed during hydrolysis.

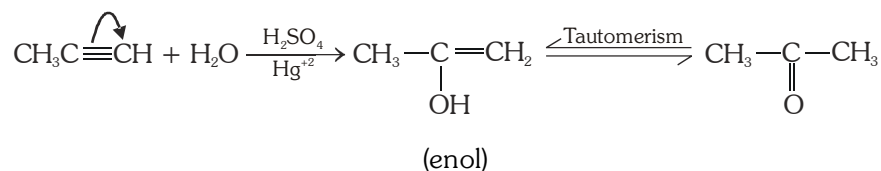


- (8) From Alkyne :**

(a) Hydration : With dil H_2SO_4 & 1% HgSO_4 at $60-80^\circ\text{C}$.

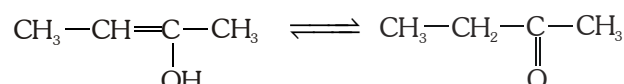
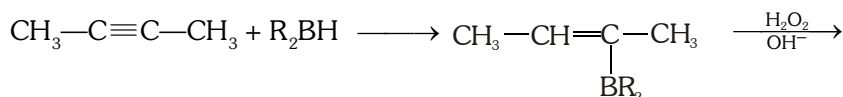
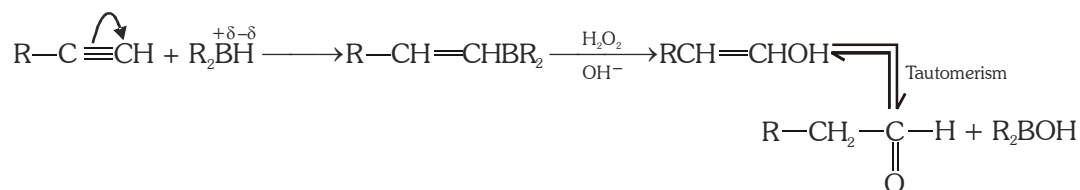


Other alkynes mainly give ketone :



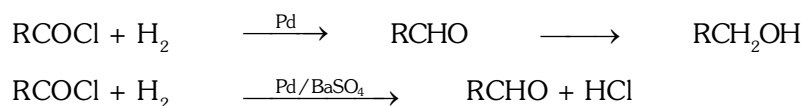
(b) Hydroboration : Reaction with B_2H_6 or R_2BH give alkenyl dialkyl borane.

1-alkyne gives $\longrightarrow$ aldehyde
other alkynes $\longrightarrow$ ketone

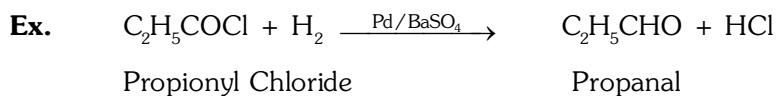


(B) For Aldehydes only

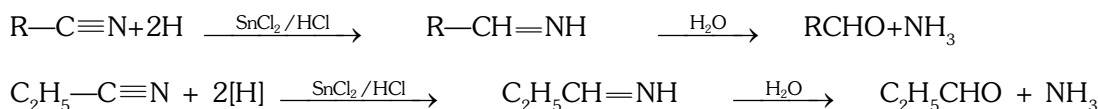
(1) Rosenmund's reduction :



$BaSO_4$ controls the further reduction of aldehyde to alcohols. Formaldehyde can not be prepared by this method.

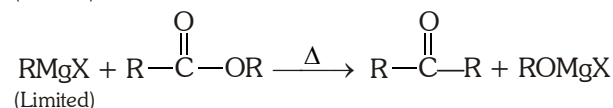
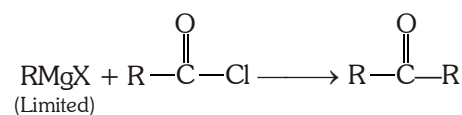
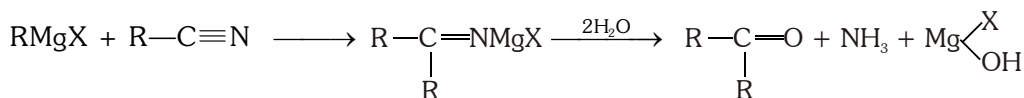


(2) Stephen's reduction :



(C) For Ketones only

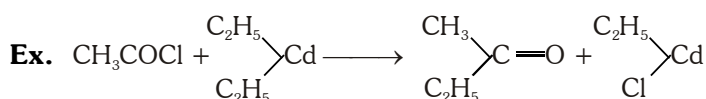
(1) From Grignard's reagent :



(2) From dialkyl Cadmium : $R'CdR'$ (dialkyl Cadmium) is an organometallic compound.



This reaction is superior than Grignard Reaction because the ketones formed, further reacts with Grignard reagent to form 3° alcohols.



6.2 Physical Properties

State : Only formaldehyde is gas, all other carbonyl compounds upto C_{11} are liquids and C_{12} & onwards solid.

Solubility : C_1 to C_3 (formaldehyde, acetaldehyde and propionaldehyde) and acetone are freely soluble in water due to polarity of $\overset{\delta+}{>C}=\overset{\delta-}{O}$ bond and can form H—bond with water molecule. C_5 onwards are insoluble in water.



H-bonding

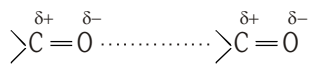
$$\text{Solubility} \propto \frac{1}{\text{Molecular weight}}$$

Boiling point :

$$\text{Boiling point} \propto \text{Molecular weight}$$

Boiling point order is - **Alcohol > Ketone > Aldehydes > Alkane** (of comparable molecular mass)

This is because in alcohols intermolecular H-bonding is present but in carbonyl compounds H-bonding doesn't exist, instead dipole-dipole & vander waal force of attraction is present. Alkanes are non polar.



Density : Density of carbonyl compounds is lower than water.

BEGINNER'S BOX-4

- Acids do not give the characteristic reactions of $C=O$ group because of :-
(1) Dimerisation (2) Resonance (3) Cyclic structures (4) Attached alkyl radical
- The vapour density of a compound is 45. Its molecular formula will be -
(1) C_2H_5O (2) $C_3H_6O_2$ (3) $C_4H_{10}O$ (4) $C_5H_{14}O$
- 23 gm of sodium of reaction with methyl alcohol gives :
(1) Half mole of H_2 (2) One mole of H_2 (3) One mole of O_2 (4) none

6.3 Chemical Properties

Carbonyl compounds undergo following reactions :

6.3.1 Nucleophilic addition reactions (Already discussed in Reaction Mechanism Part-2)

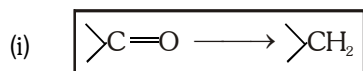
6.3.2 Other reactions

6.3.3 Reactions of only aldehyde

6.3.4 Reactions of only ketones

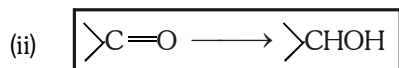
6.3.2 Other reactions

(a) **Reduction** : The nature of product depends upon the reducing agent used.



Reducing agents are

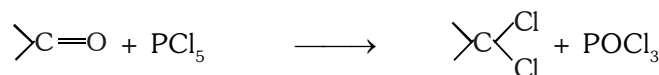
- Red P/HI at 150°C
- Zn-Hg/HCl [Clemensen's reduction]
- (i) N_2H_4 (ii) $\ominus OH/\Delta$ [Wolf Kishner reduction]



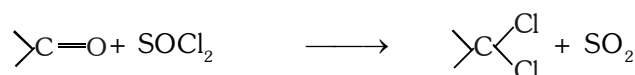
Reducing agents are

- Metal + H_2
- $LiAlH_4$
- $NaBH_4$
- $Na + C_2H_5OH$

(b) **Reaction with PCl_5 & $SOCl_2$** :

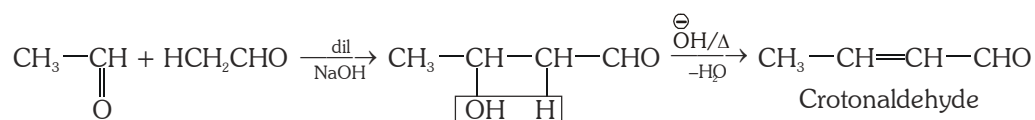


Phosphorus penta chloride



Thionyl chloride

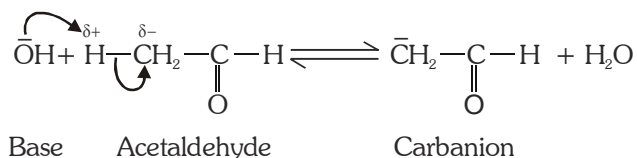
(c) **Aldol Condensation** : Carbonyl compounds which contain α -H atoms undergo condensation with dil. NaOH to give aldol. Aldol contains both alcoholic and carbonyl group, which on heating in alkaline medium gets converted into α, β -unsaturated carbonyl compound.



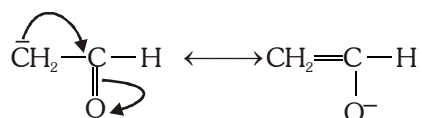
Mechanism of aldol condensation : It takes place in the following two stages :

- Formation of Carbanion
- Combination of carbanion with other carbonyl molecule.

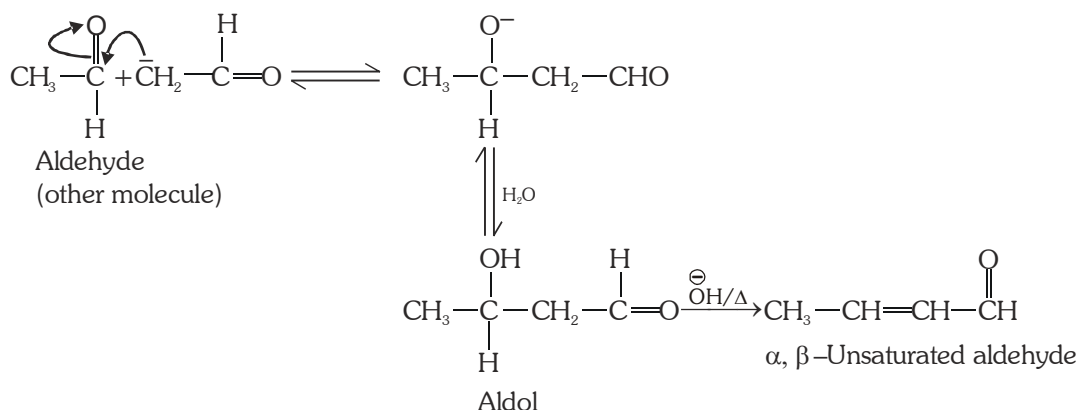
(i) **Formation of Carbanion** : α -H atom of $>C=O$ group are quite acidic which can be removed easily as proton, by a base



Carbanion thus formed is stable because of resonance -

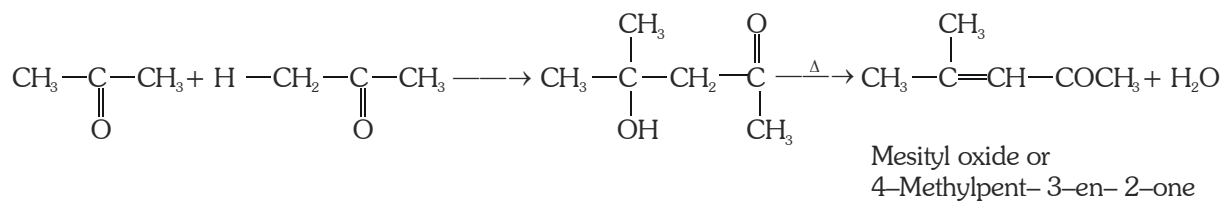


(ii) Combination of carbanion with other carbonyl molecule :

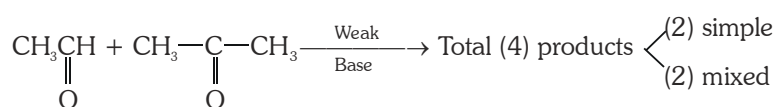


Identical carbonyl compounds $\longrightarrow$ Simple or self aldol condensation.
Different carbonyl compounds $\longrightarrow$ Mixed or crossed aldol condensation.

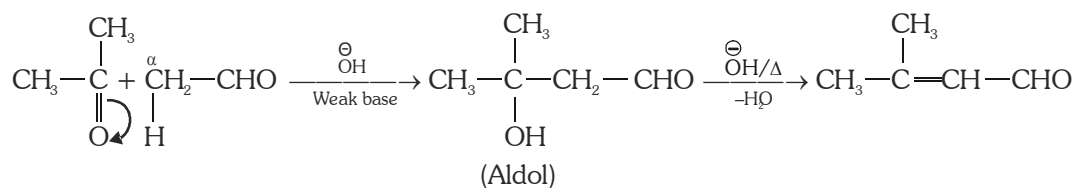
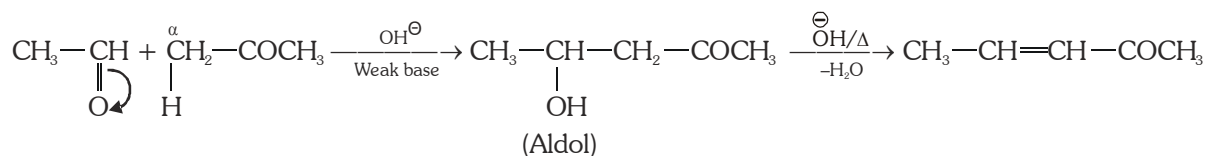
Simple or Self condensation :



Mixed or Crossed aldol Condensation :



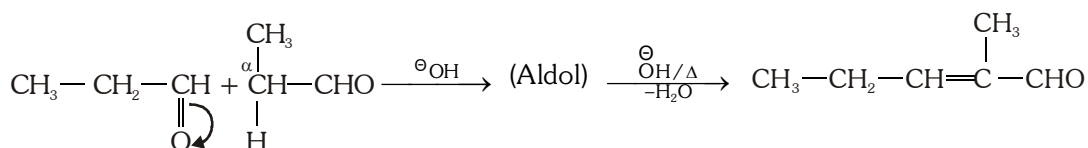
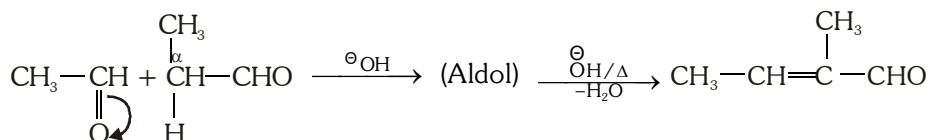
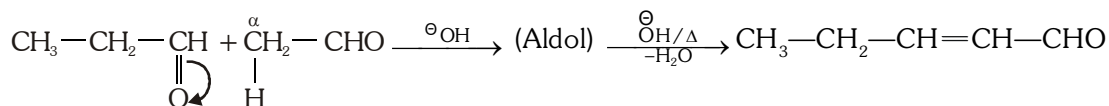
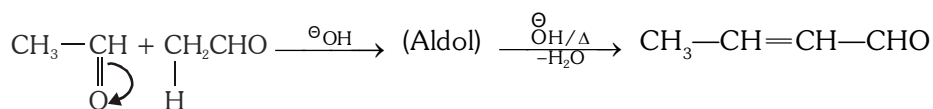
Mixed aldol condensation products of the above reaction are :



Illustrations

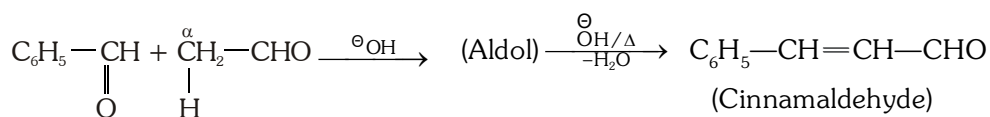
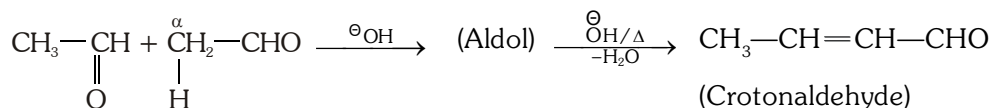
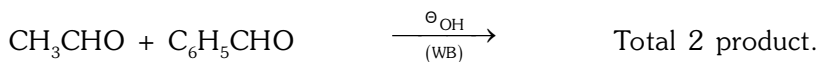
Illustration 7. $\text{CH}_3\text{CHO} + \text{CH}_3\text{CH}_2\text{CHO} \xrightarrow[\text{(WB)}]{^\ominus\text{OH}}$ Total 4 products. Write structure of products ?

Solution.

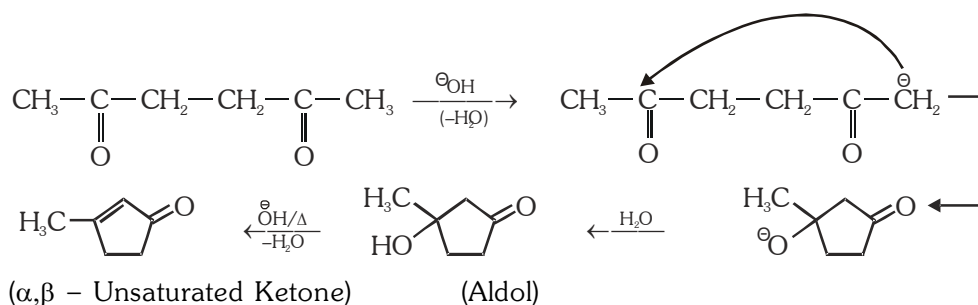


GOLDEN KEY POINTS

- If in crossed aldol condensation reaction, only one carbonyl compound have α -H then total two products are formed.



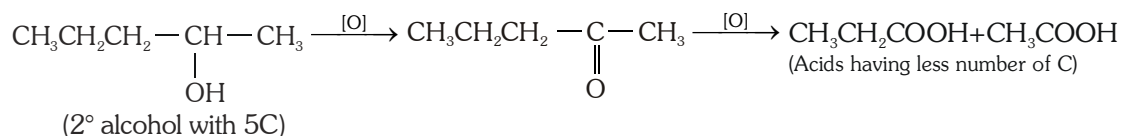
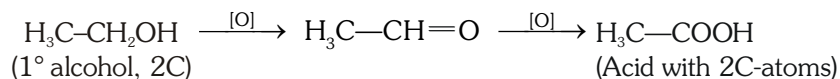
- Intramolecular** aldol condensation :



Here one more product having 3 membered ring is also possible, but 5 membered ring is more stable than 3 membered ring so above product is formed as a major product.

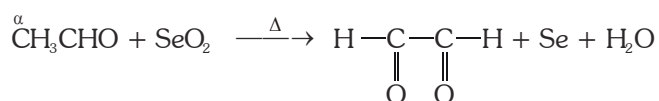
(d) Oxidation reactions :

- (i) By $K_2Cr_2O_7/H_2SO_4$:** On oxidation with $K_2Cr_2O_7/H_2SO_4$ 1° alc. gives aldehyde, which on further oxidation gives acid with same number of carbons. If 2° alcohol is oxidised at elevated temperature using $KMnO_4/H^+$, it gets oxidised to give acids with less number of C-atom.

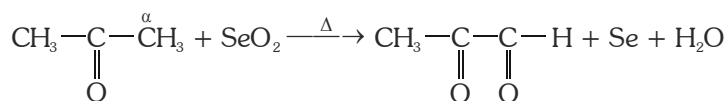


- (ii) SeO_2 (Selenium dioxide) :** Ketones or aldehydes on oxidation with SeO_2 give dicarbonyl compounds. This reaction is possible only in compounds containing $\alpha-CH_2-$ unit.

HCHO doesn't show this reaction.



Glyoxal

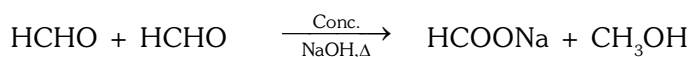


Methyl glyoxal (Pyruvaldehyde)

6.3.3 Reactions of only aldehydes :

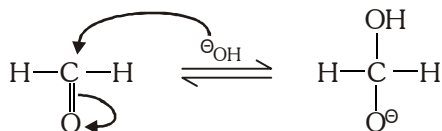
- (a) Cannizzaro's reaction :** Those aldehydes which do not contain α - H atom give this reaction, with conc. NaOH or KOH; Products are Salt of carboxylic acid + alcohol

In this reaction one molecule of carbonyl compounds is oxidised to acid, while other is reduced to alcohol, such type of reactions are called redox reaction.

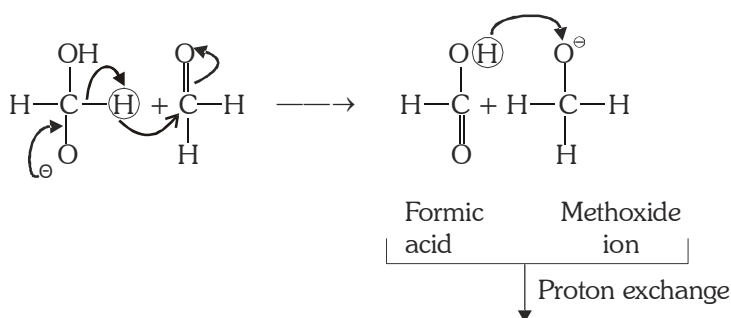


Mechanism involved in cannizzaro's reaction :

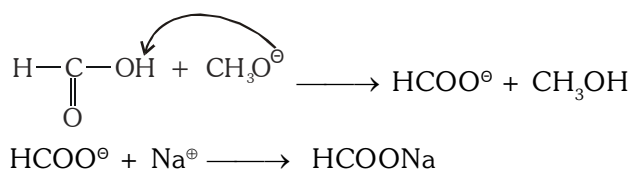
- (a) Rapid reversible addition of $\bar{O}H$ to one molecule of HCHO.



(b) Transfer of hydride ion $\text{H}^\ominus$ to second molecule of HCHO

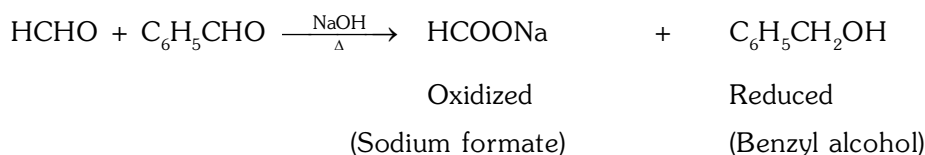


(c) Proton exchange

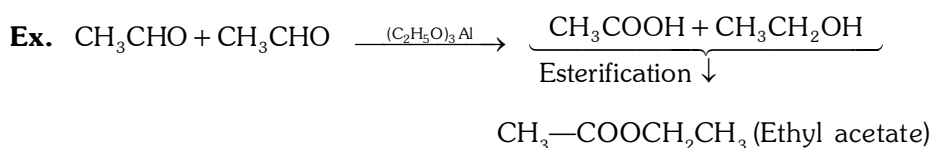
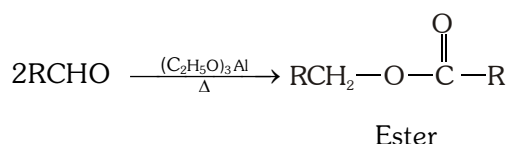


When molecules are same	→ Simple cannizaro reaction (disproportionation reaction)
Two different molecules	→ Mixed cannizaro reaction (Redox reaction)

In mixed or crossed cannizaro reaction more reactive aldehyde is oxidised and less reactive aldehyde is reduced.

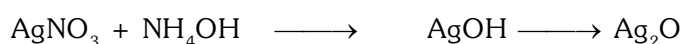
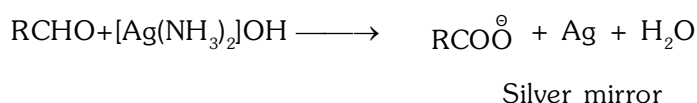
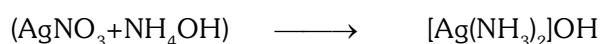


(b) Tischenko reaction : It is a modified cannizaro reaction. All aldehydes undergo this reaction in presence of $(\text{C}_2\text{H}_5\text{O})_3\text{Al}$, to form ester.



(c) Reducing character : Aldehydes are easily oxidised so they are strong reducing agents.

(i) Tollen's reagent : It oxidises aldehydes. Tollen's reagent is ammoniacal silver nitrate solution

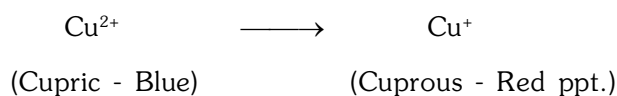
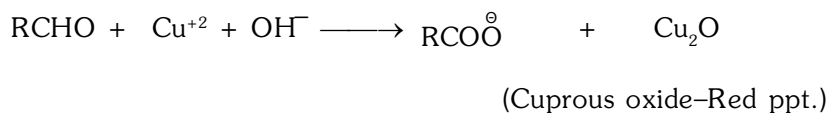


(ii) Fehling's solution : It is a mixture of aqueous CuSO_4 , NaOH and sodium potassium tartarate.

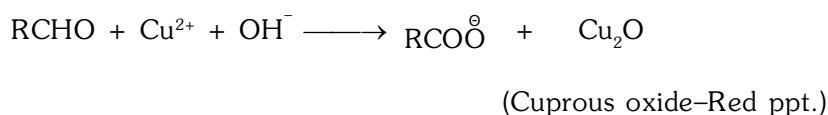
Fehling solution A– (aq.) solution of CuSO_4

Fehling solution B– Roschelle salt (Sodium potassium tartarate + NaOH)

Fehling solution A + Fehlings solution B(Dark blue colour of cupric tartarate)



(iii) Benedict's solution : It is a mixture of CuSO_4 + sodium citrate + NaOH . It provides Cu^{+2} . It is reduced by aldehyde to give red ppt of cuprous oxide.

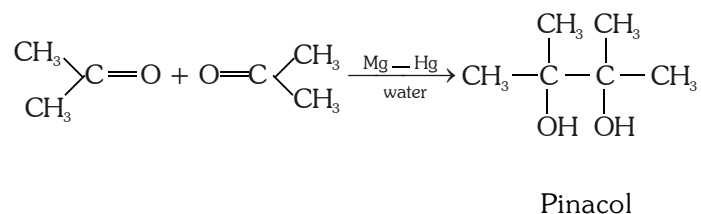


(iv) Schiff's reagent : Dilute solution of p-rosaniline hydrochloride or magenta dye, is a pink coloured dye and is known as schiff' dye.

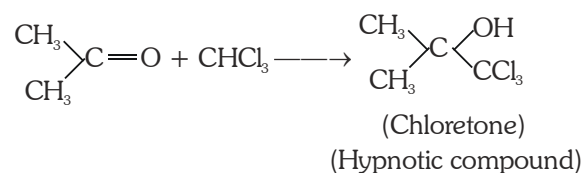
Its pink colour is discharged by passing SO_2 gas and the colourless solution obtained is called schiff's reagent, Aldehyde reacts with this reagent to restore the pink colour.

6.3.4 Reaction of Only Ketones

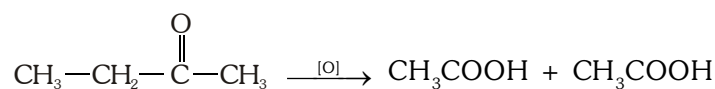
(1) Reduction : Acetone is reduced by magnesium amalgam and water to give pinacol.



(2) Reaction with chloroform :

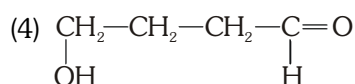
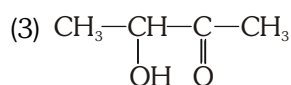
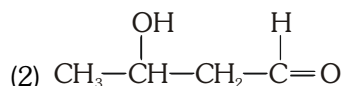
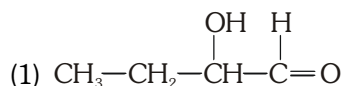


(3) Oxidation reaction : According to popoff's rule $>\text{C}=\text{O}$ group stays with smaller alkyl group.



BEGINNER'S BOX-5

1. The compounds capable in reaction with Tollen's reagent is (are):
 (1) Formaldehyde (2) Formic acid (3) Acetaldehyde (4) All the above
2. Acetaldehyde reacts with NaOH to form :-



3. Fehling's solution is a :-
 (1) Solution of magenta dye bleached by SO_2
 (2) Ammonical solution of AgNO_3
 (3) Mixture of a solution of CuSO_4 and a solution of caustic soda and sodium potassium tartarate
 (4) Alcoholic solution of 2,4-dinitrophenylhydrazine

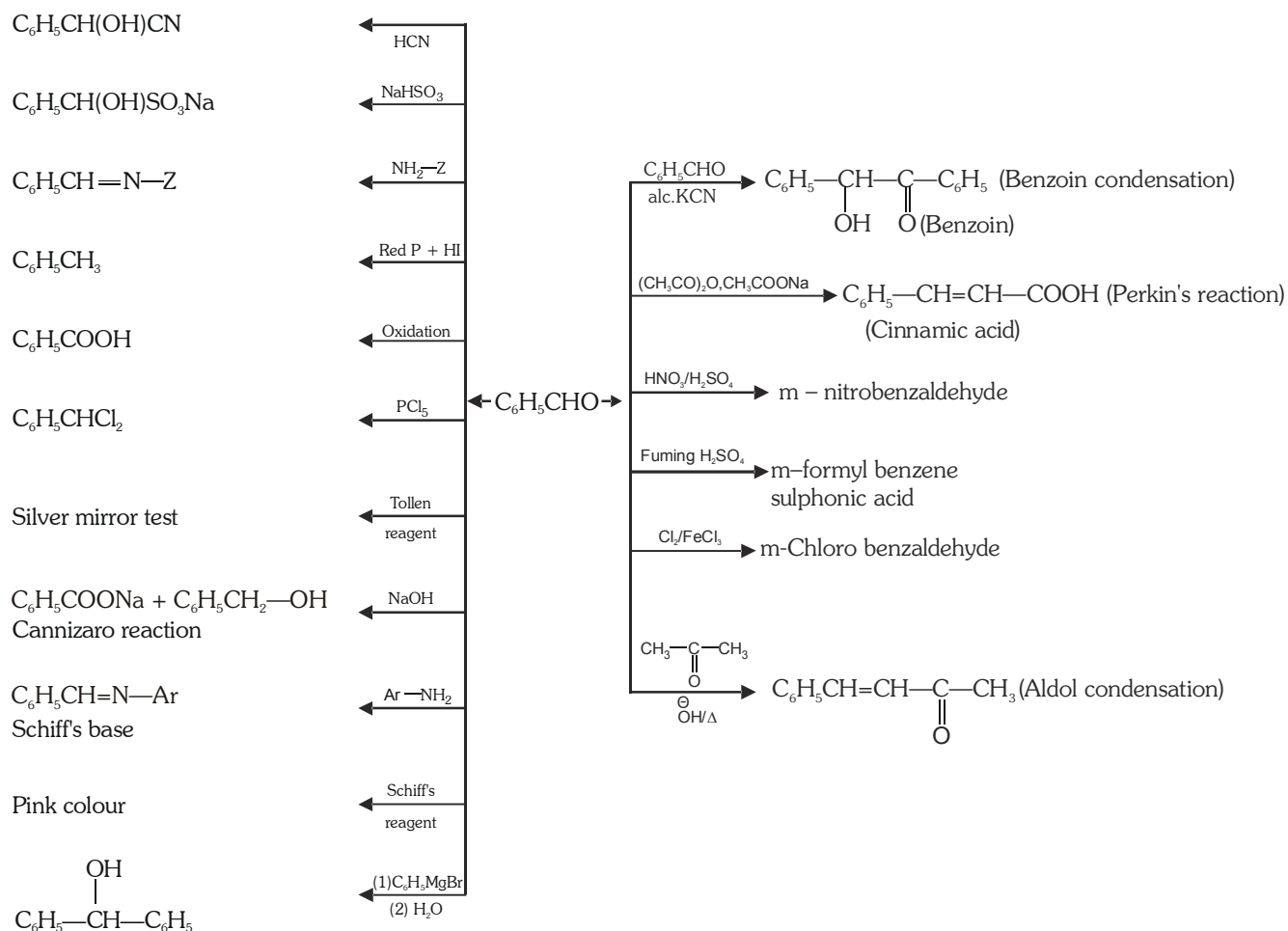
7.0 BENZALDEHYDE ($\text{C}_6\text{H}_5\text{CHO}$) [OIL OF BITTER ALMONDS (COMPONENT OF BITTER ALMOND)]

7.1 General Methods of Preparation

C_6H_6	$\text{CO/HCl} + \text{ZnCl}_2$	(Gattermann-koch aldehyde synthesis)
$\text{C}_6\text{H}_5\text{CH}_3$	(1) CrO_2Cl_2 (2) H_2O	(Etard reaction)
$\text{C}_6\text{H}_5\text{COCl}$	Pd/BaSO_4	(Rosenmund reaction)
$\text{C}_6\text{H}_5\text{CN}$	(i) SnCl_2/HCl (ii) H_2O	(Stephen's reaction)
$(\text{C}_6\text{H}_5\text{COO})_2\text{Ca}$	$(\text{HCOO})_2\text{Ca}/\Delta$	
$\text{C}_6\text{H}_5\text{CHCl}_2$	aq. KOH	
$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	$[\text{O}]$ (controlled oxidation)	
$\text{C}_6\text{H}_5\text{MgBr}$	HCOOC_2H_5	
C_6H_6	(1) $\text{HCN/HCl} + \text{ZnCl}_2$ (2) H_2O	(Gattermann aldehyde synthesis)

$\rightarrow \text{C}_6\text{H}_5\text{CHO}$

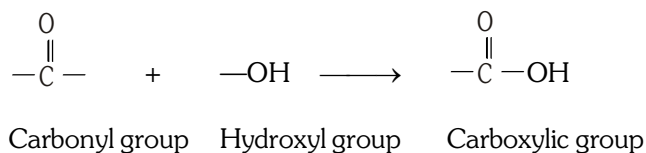
7.2 Chemical Properties



8.0 CARBOXYLIC ACID

Organic compounds having -COOH group are called Carboxylic acids. This functional group is composed of

Carbonyl (>C=O) and hydroxyl (-OH) group.



The properties of the carboxylic group are not simply the combined properties of these two groups, but it has its own distinctive properties. The acidic nature of carboxylic acids is due to the presence of replaceable H-atom in the Carboxylic group. The general formula is $C_nH_{2n}O_2$.

Classification :

Monocarboxylic acid (RCOOH) : Having one carboxylic group, also called monobasic acid.

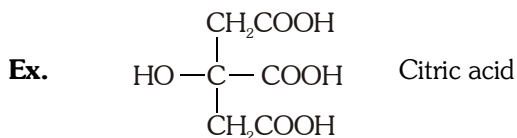
General formula - $C_nH_{2n}O_2$ ($n = 1, 2, 3, \dots$). Higher mono carboxylic acids are called **fatty acids**.

Ex. CH_3COOH acetic acid

Dicarboxylic acid : Having two carboxylic groups, also called dibasic acid.



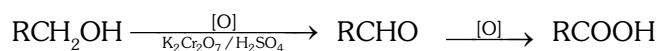
Tricarboxylic acid : Having three carboxylic groups also called tribasic acid.



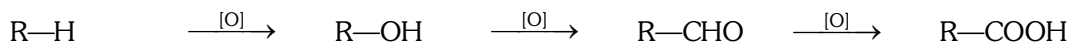
Structure : The carbon atom of $-\text{COOH}$ group is sp^2 hybridised, this C-atom is in centre and thus bond angle around C-atom is 120° .

8.1 General Methods of Preparation

8.1.1 By Oxidation of alcohols & carbonyl compounds : Oxidation is carried out by acidified $\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4 .



Acids are third oxidation products of alkane.



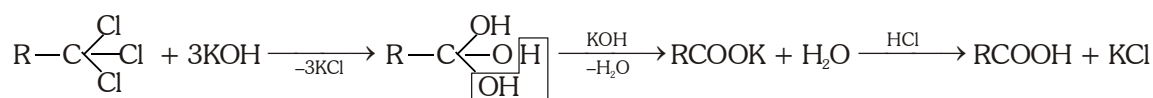
GOLDEN KEY POINTS

- Aldehyde on oxidation give acids having same no. of C-atoms.
- Ketones on oxidation give acids having less no. of C-atoms.
- Oxidation of Ketones occurs on prolonged treatment with strong oxidising agent.

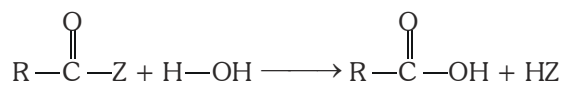
8.1.2 By hydrolysis of alkane nitriles or cyanides : Complete hydrolysis takes place in acidic medium (dil. HCl). In alkaline medium there is partial hydrolysis.



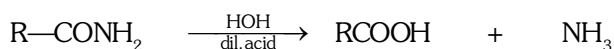
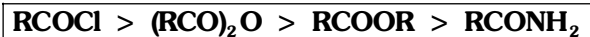
8.1.3 By alkaline hydrolysis of 1, 1, 1-trihaloalkane :



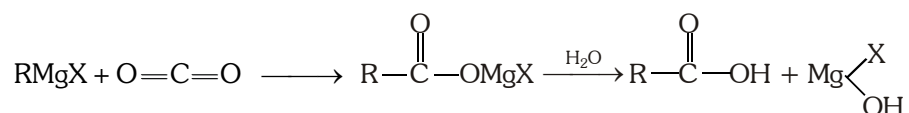
8.1.4 By hydrolysis of acid derivatives :



Reactivity order of acid derivatives :



8.1.5 From Grignard's reagent :



Carbon dioxide

Solid CO_2 (dry ice) is used

8.2 Physical Properties

Carboxylic acids from C_1-C_4 are completely soluble in water.

$$\text{Solubility} \propto \frac{1}{\text{molecular weight}}$$

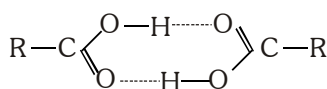
Solubility is due to intermolecular H - bonding with water molecules.

Boiling point : $B. P. \& M. P. \propto \text{Molecular weight,}$

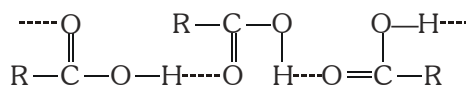
Acids > alcohol

This is because in acids two oxygen atoms take part in H - bonding (while in alcohol only one O - atom takes part).

In vapour or soluble state lower acids occur in the form of dimers.



But in liquid state it exists in polymer form.

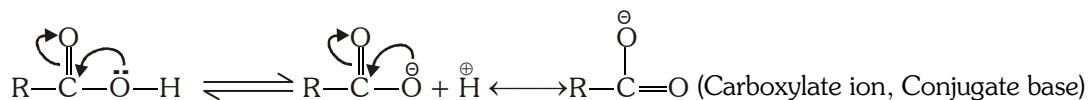


Melting point : Acids having even number of C-atoms have higher melting point as compared to having odd number of C - atoms. The carboxyl group and terminal methyl group in even member acids lie on opposite side to provide more close packing in crystal lattice which results in high melting point.

8.3 Chemical Properties

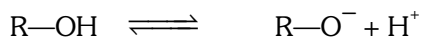
8.3.1 Reaction due to - H atom of - COOH group

(a) Acidic character :



Carboxylate ion is stabilised by resonance so carboxylic acids show considerable acidic character.

In case of alcohol alkoxide ion is not stabilised so they are neutral.



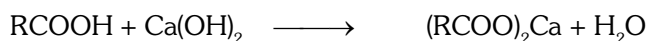
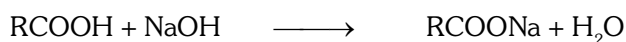
alkoxide ion

(a) Carboxylic acids turn blue litmus to red.

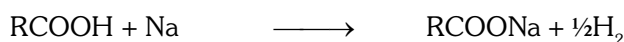
(b) Addition of carboxylic acid to NaHCO_3 in water gives out effervescence of CO_2 .



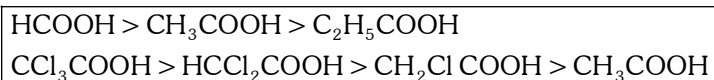
(c) Form salts with alkalis.



(d) Action of metals.

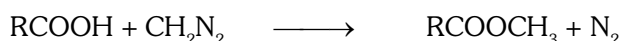


The acidic character order is :



Acidic character may be explained on the basis of I effect and resonance.

(b) Reaction with CH_2N_2 : Methyl ester can be prepared by this method.



Methyl ester

8.3.2 Reaction due to - OH group

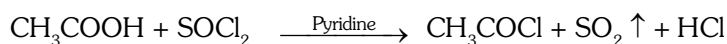
(a) Esterification :



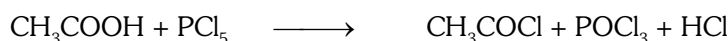
(b) Reaction with NH_3 :



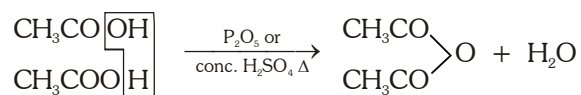
(c) Reaction with thionyl chloride :



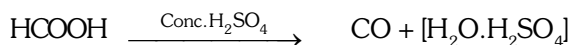
(d) Reaction with PCl_5 :



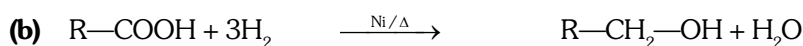
(e) Reaction with P₂O₅ (dehydrating agent) :



HCOOH is dehydrated by Conc. H₂SO₄

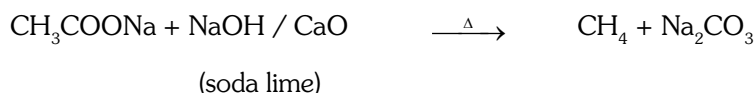


8.3.3 Reaction due to $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$ group of COOH :

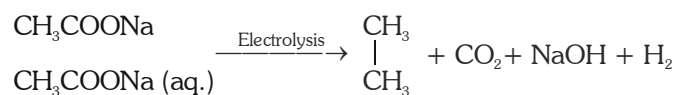


8.3.4 Reaction due to —COOH group :

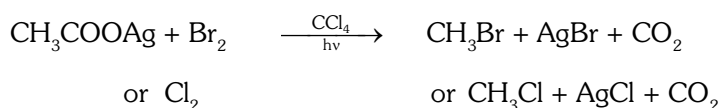
(a) Decarboxylation :



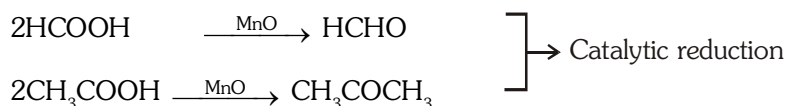
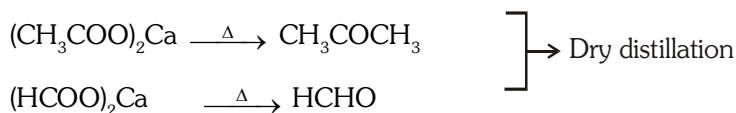
(b) Kolbe's electrolysis :



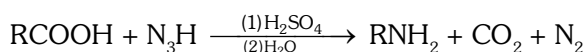
(c) Hunsdiecker reaction :



(d) Formation of carbonyl compounds :



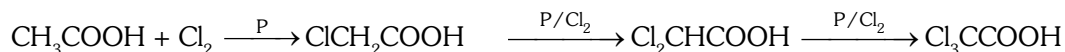
(e) Schmidt reaction : The amine formed has one C - atom less than the reactant acid.



Hydrazoic acid

8.3.5 Reaction due to alkyl (R) group :

(a) **Halogenation [HVZ reaction] : Hell volhard Zelinsky reaction]** : In this reaction α - H atoms are replaced by halogen atoms.



GOLDEN KEY POINTS

Test for HCOOH and CH₃COOH

Test	HCOOH	CH ₃ COOH
1. Reducing character		
Reducing agents -		
Tollen reagent	Silver mirror	×
Fehling solution	Cu ₂ O red ppt.	×
K ₂ Cr ₂ O ₇	Cr ⁺³ (green)	×
2. Decarboxylation.	Na ₂ CO ₃ + H ₂	CH ₄

Uses of Formic Acid :

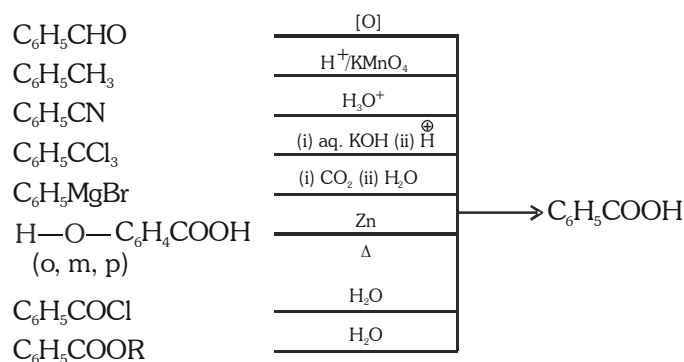
- (i) As an antiseptic
- (ii) For preservation of fruits.
- (iii) For leather tanning.
- (iv) In dying wool and cotton fabrics.

Uses of Acetic Acid :

- (i) Vinegar (6 - 10% solution) used as **table acid** and manufacture of pickles.
- (ii) For manufacture of rubber from latex and casein from milk CH₃COOH is used as coagulant.
- (iii) As a solvent and laboratory reagent.

9.0 BENZOIC ACID (C₆H₅COOH)

9.1 General Method of Preparation :

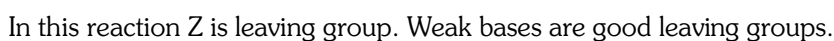


Z:\NODE02\B0A1-B0\TARGET\CHEM\ENG\MODULE-6\02 OXYGEN CONTAINING COMPOUND\01-THEORY.P65


$$\begin{array}{ccc} \text{O} & & \text{O} \\ \parallel & & \parallel \\ \text{R}-\text{C}-\text{OH} & \xrightarrow[\text{+ Z}]{-\text{OH}} & \text{R}-\text{C}-\text{Z} \\ \text{Acid} & & \text{Acid derivative} \end{array}$$

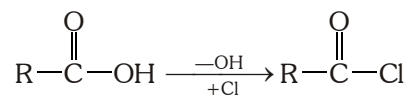
Ex. $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{Acetyl group}$

Mechanism :


$$\overline{\text{CH}_3\text{COCl} > \text{CH}_3\text{COOCOCH}_3 > \text{CH}_3\text{COOC}_2\text{H}_5 > \text{CH}_3\text{CONH}_2}$$

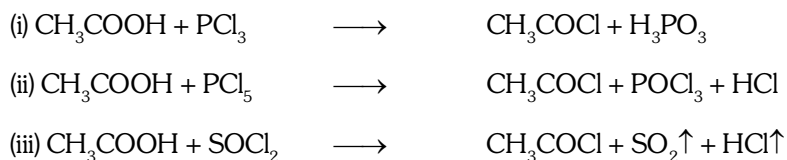
10.1 Acetyl Chloride

Replacement of —OH group from a —COOH group by Cl— atom gives acid chloride.

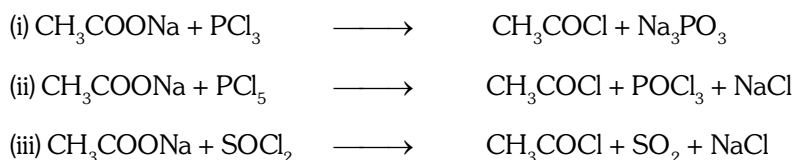


10.1.1 General Method of Preparation :

(a) By heating CH_3COOH with PCl_3 , PCl_5 & SOCl_2 :



(b) By heating the salt of acids with PCl_3 , PCl_5 or SOCl_2 :



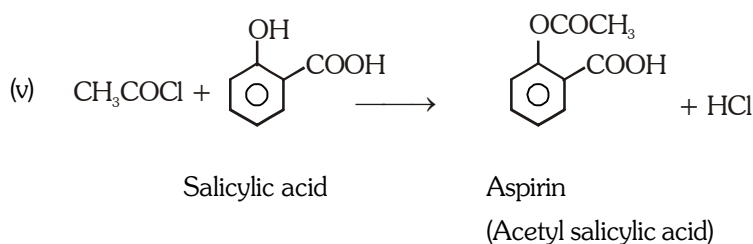
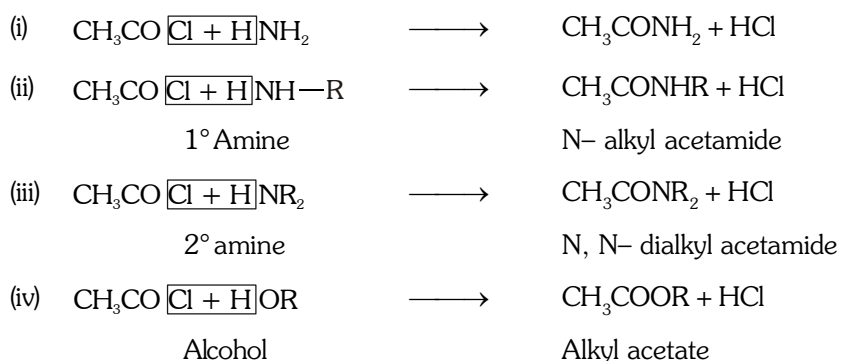
10.1.2 Physical properties :

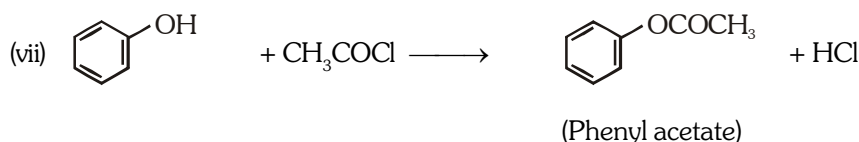
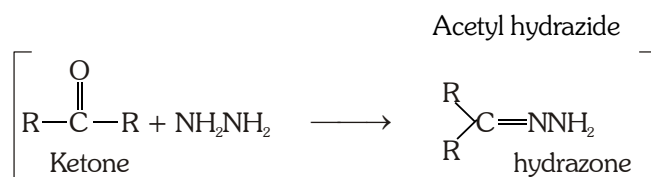
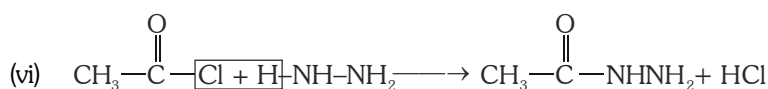
- (i) Pungent smelling liquid.
- (ii) Boiling point 52°C .
- (iii) Soluble in organic solvent, slowly soluble in water.
- (iv) It produces fumes in moist air due to the formation of HCl.

10.1.3 Chemical properties :

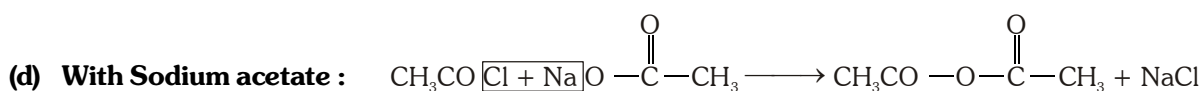
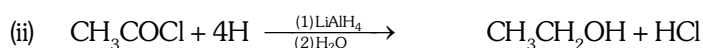
(a) Hydrolysis : $\text{CH}_3\text{CO}[\text{Cl} + \text{H}]\text{OH} \longrightarrow \text{CH}_3\text{COOH} + \text{HCl}$

(b) Reaction with active H - containing compounds (Acetylation) :

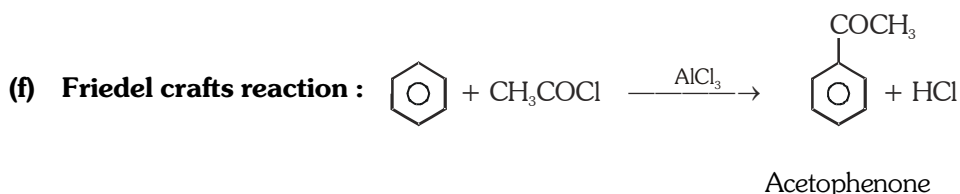
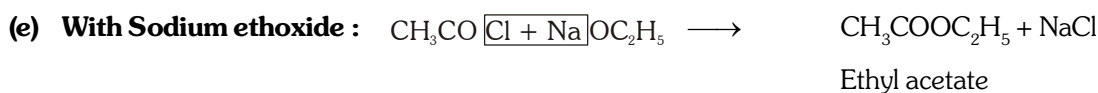




(c) Reduction :



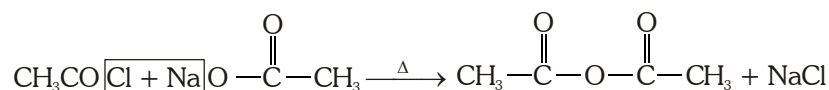
Acetic anhydride



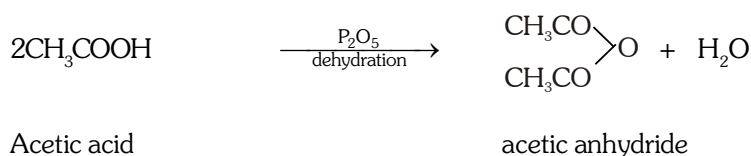
10.2 Acetic Anhydride (Ethanoic Anhydride)

10.2.1 General Method of Preparation :

(a) By heating acetyl Chloride with anhydrous sodium acetate [Lab. Method] :



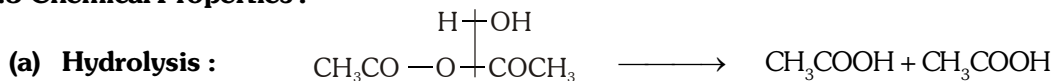
(b) By Dehydration of acetic acid :



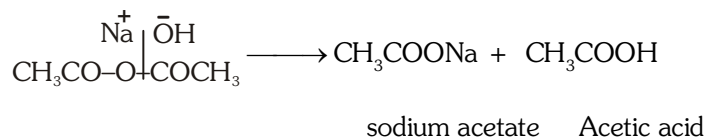
10.2.2 Physical Properties :

- (i) It is pungent smelling liquid.
- (ii) Sparingly soluble in water, soluble in ether & alcohol.
- (iii) Boiling point 139°C.

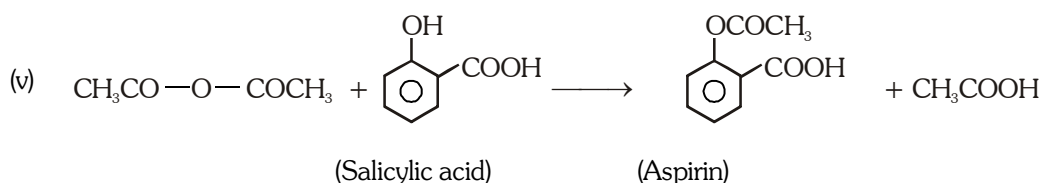
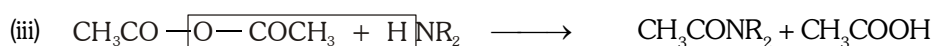
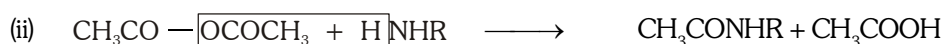
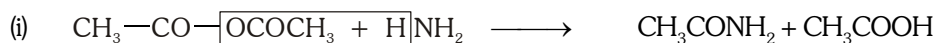
10.2.3 Chemical Properties :



Hydrolysis order : **Alkaline > Acidic > neutral**



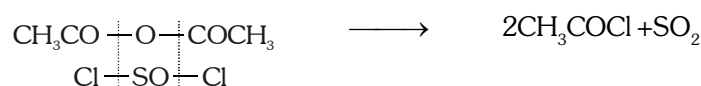
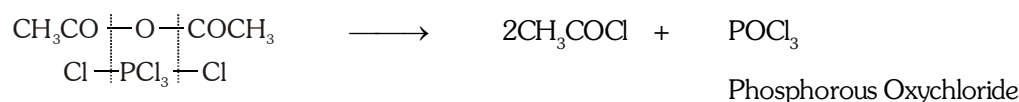
(b) **Reaction with active H - containing compounds (Acetylation) :**



(c) **Reduction :** With LiAlH_4 in ether gives ethyl alcohol



(d) **Reaction with PCl_5 & SOCl_2 :**



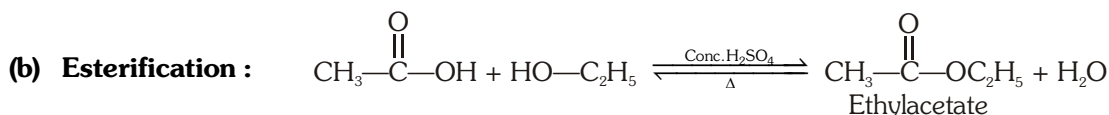
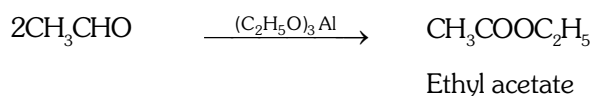
10.2.4 Uses

- (i) As an acetylating agent
- (ii) In the manufacture of cellulose acetate, aspirin, phenacetin, acetamide, & acetophenone etc.
- (iii) For detection and estimation of hydroxyl and amino group.

10.3 Ethyl acetate

10.3.1 General Method of Preparation :

(a) **Tischenko reaction :** By treating acetaldehyde with aluminium ethoxide. (Modified cannizaro reaction)



BEGINNER'S BOX-6

1. Alkanoic acids can be prepared by hydrolysis of:-

(1) Trihaloalkanes	(2) 1,1,1-trihaloalkanes
(3) Grignard reagents	(4) Ketones
2. Acids have much higher boiling points than isomeric esters because :-
 - (1) Acids form dimers by H-Bonding
 - (2) Acids are volatile in steam
 - (3) Esters are non-volatile
 - (4) Acids can ionise to give protons in aqueous solution
3. Which of the following compounds can form intermolecular H-bonds :-

(1) Ethyl acetate	(2) Methyl formate
(3) Acetamide	(4) Acetic anhydride
4. Reaction of ethyl acetate with sodium ethoxide gives acetoacetic ester. This reaction is known with the name of :-

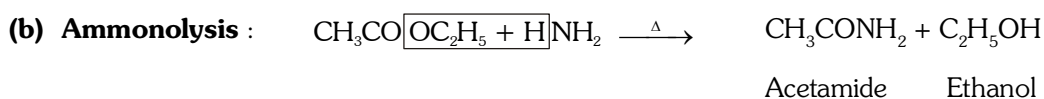
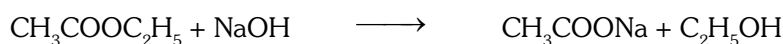
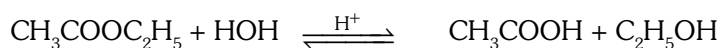
(1) Claisen	(2) Clemmensen
(3) Cannizaro	(4) Etard

10.3.2 Physical Properties

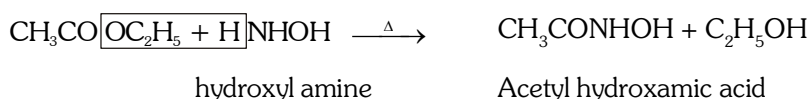
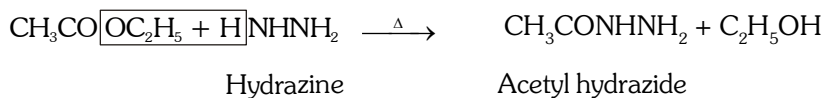
- (i) Fruity smell liquid.
- (ii) Boiling point 77° C.
- (iii) Slightly soluble in water, soluble in organic solvent.

10.3.3 Chemical Properties :

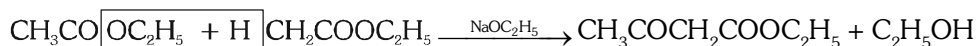
(a) Hydrolysis : In acidic medium reaction is reversible and in alkaline medium reaction is irreversible.



(c) Reaction with NH_2NH_2 & NH_2OH :



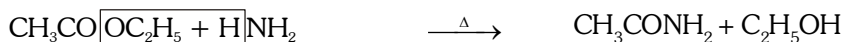
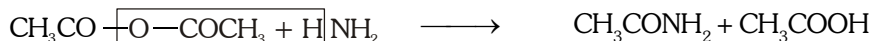
(e) Claisen condensation :



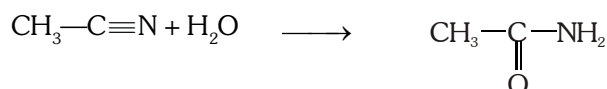
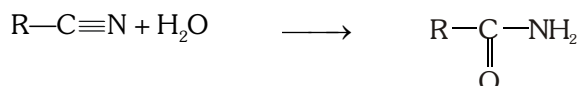
10.4 Acetamide

10.4.1 General Method of Preparation :

(a) Ammonolysis of acid derivatives :

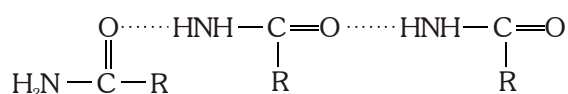


(b) Hydrolysis of alkyl cyanides : By the partial hydrolysis of alkyl cyanides.



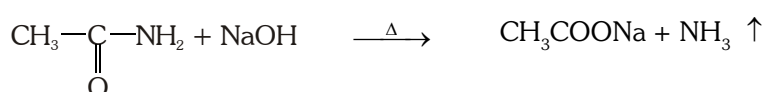
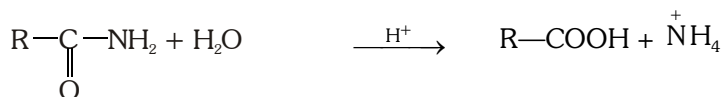
10.4.2 Physical Properties :

- (i) Acetamide is white crystalline solid.
- (ii) Pure acetamide is odourless.
- (iii) Impure acetamide - Smell like mouse.
- (iv) Lower amides are soluble in water, due to H-bonding.
- (v) Their higher M. P. and B. P. are due to intermolecular H-bonding.

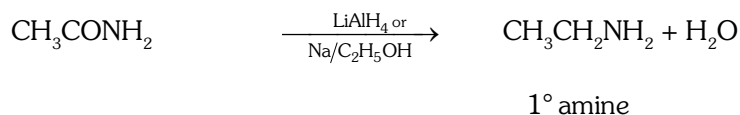


10.4.3 Chemical Properties :

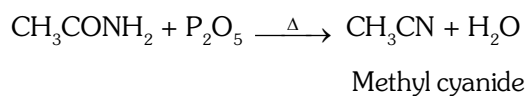
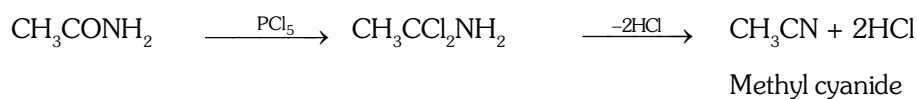
(a) Hydrolysis : Amides are hydrolysed rapidly in acidic medium. In alkaline medium hydrolysis is carried out in temperature condition.



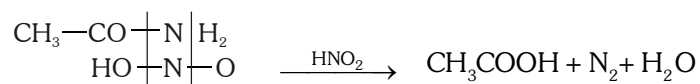
(b) Reduction to primary amines : Amine contains same number of carbon atoms.



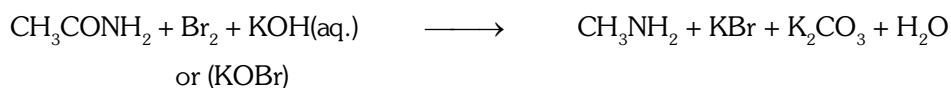
(c) Dehydration with PCl_5 , SOCl_2 or P_2O_5 :



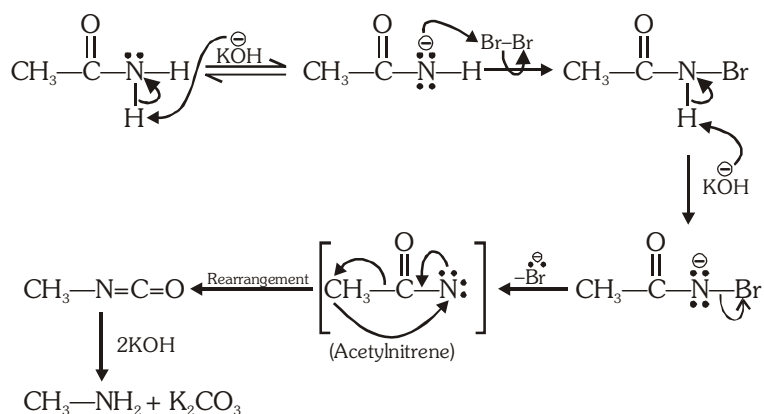
(d) Reaction with nitrous acid :



(e) Hoffmann's bromamide degradation reaction : Amides on reaction with bromine, and NaOH or KOH yield primary amines, having one C-atom less than the amides.



Mechanism :



ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3							
	Ans.	3	4	2							

BEGINNER'S BOX-2	Que.	1	2								
	Ans.	1	2								

BEGINNER'S BOX-3	Que.	1	2	3							
	Ans.	3	2	3							

BEGINNER'S BOX-4	Que.	1	2	3							
	Ans.	2	4	1							

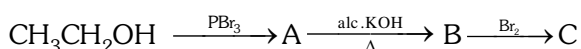
BEGINNER'S BOX-5	Que.	1	2	3							
	Ans.	4	2	3							

BEGINNER'S BOX-6	Que.	1	2	3	4						
	Ans.	2	1	3	1						

Build Up Your Understanding

ALCOHOL

- 1.** The compound A, B and C in the reaction sequence



are given by the set

- (1) $\text{C}_2\text{H}_5\text{Br}$, $\text{CH}_3\text{CH}_2\text{OH}$, CH_3CHBr_2 .
- (2) $\text{C}_2\text{H}_5\text{Br}$, $\text{CH}\equiv\text{CH}$, $\text{CH}_2=\text{CHBr}$
- (3) $\text{C}_2\text{H}_5\text{Br}$, $\text{CH}_2=\text{CH}_2$, $\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$
- (4) $\text{C}_2\text{H}_5\text{Br}$, $\text{CH}_3\text{CH}_2\text{OH}$, $\text{BrCH}_2-\text{CH}_2\text{Br}$

- 2.** Primary amines can be converted into alkanols by reaction with

- (1) Aqueous HCl (2) Tilden's reagent
(3) NaNO_2 and dil. HCl (4) Hypochlorous acid

- 3.** Which of the following alcohols gives a red colour in Victor Meyer test

- (1) $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--OH}$ (2) $\begin{array}{c} \text{CH}_3\text{--CH--OH} \\ | \\ \text{CH}_3 \end{array}$
- (3) $(\text{CH}_3)_3\text{C--OH}$ (4) $\begin{array}{c} \text{CH}_3\text{--CH--CH}_2\text{--CH}_3 \\ | \\ \text{OH} \end{array}$

4. Methanol on heating with salicylic acid and a few drops of conc. H_2SO_4 gives the smell of

- (1) Bitter almonds (2) Oil of wintergreen
(3) Rotten eggs (4) Mustard oil

5. Which of the following does not turn orange colour of chromic acid to green

- (1) 1° alcohol (2) 2° alcohol
(3) 3° alcohol (4) Allyl alcohol

- 6.** p, s and t-alcohols can be distinguished by :-

- (1) Reimer-Tiemann reaction
- (2) Tollen's reagent
- (3) Lucas test
- (4) Lassaigne's test

- 7.** Consider the following reaction :

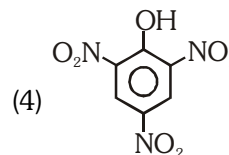
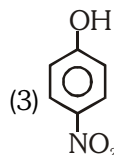
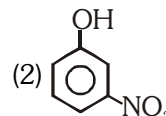
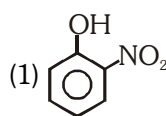


Among the following, which one cannot be formed as a product under any conditions ?

- (1) $\text{C}_2\text{H}_5\text{OSO}_3\text{H}$
- (2) $\text{H}_2\text{C}=\text{CH}_2$
- (3) $\text{HC}\equiv\text{CH}$
- (4) $\text{CH}_3\text{--CH}_2\text{--O--CH}_2\text{--CH}_3$

PHENOL

- 8.** Nitration of phenol with conc. nitric acid gives :-

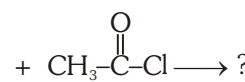
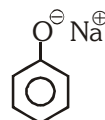


- 9.** Deoxygenation of phenol can be achieved by distillation with :-

- (1) Raney nickel
- (2) Lithium aluminium hydride
- (3) Sodium borohydride
- (4) Zinc dust

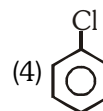
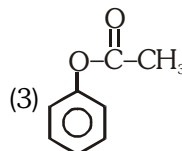
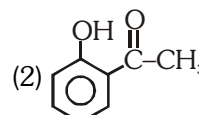
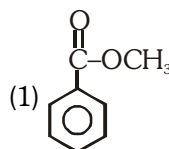
- 10.** Which of the following compounds shows intramolecular hydrogen bonding :-

- (1) p-Nitrophenol (2) Ethanol
(3) o-Nitrophenol (4) Methanamine

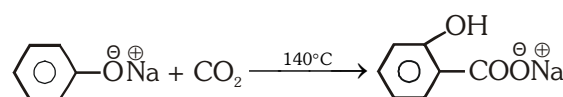


- 11.**

Sodium phenate



- 12.** The reaction



is called :-

- (1) Schotten Bauman reaction
- (2) Kolbe Schmidt reaction
- (3) Reimer–Tiemann reaction
- (4) Lederer–Manasse reaction

13. Phenol can be distinguished from ethanol by reactions with the following except :-

- (1) Iodine and alkali (2) Ferric chloride
(3) Acetyl chloride (4) Bromine water

14. Phenol on treatment with methyl chloride in the presence of anhydrous AlCl_3 gives chiefly :-

- (1) o-cresol (2) m-cresol
(3) anisole (4) p-cresol

15. Phenol on heating with NaNO_2 and a few drops of conc. H_2SO_4 mainly gives :-

- (1) p-nitrophenol (2) p-nitrosophenol
(3) o-nitrophenol (4) m-nitrosophenol

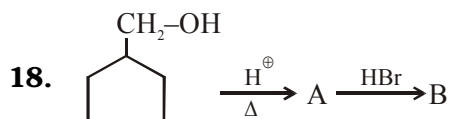
16. Phenol and benzoic acid are distinguished by :-

- (1) Lucas reagent (2) Victor Meyer test
(3) Caustic soda (4) Sodium bicarbonate

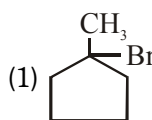
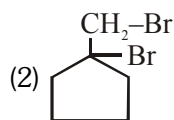
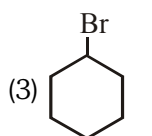
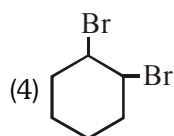
17. Phenol can be distinguished from ethanol by the reaction with

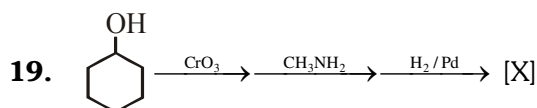
- (1) Na (2) Br_2/Water
(3) Neutral AlCl_3 (4) 1 and 2 Both

ETHER

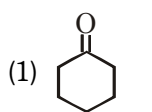
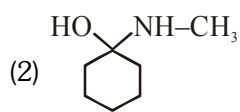
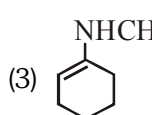
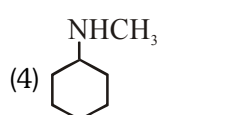


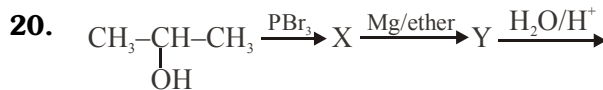
What is the structure of B :-

- (1)  (2) 
(3)  (4) 

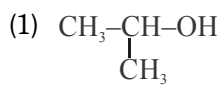
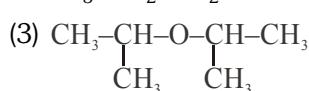


Product [X] of given reaction is :-

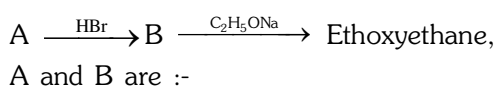
- (1)  (2) 
(3)  (4) 



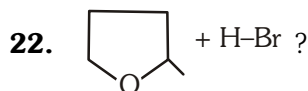
The final product is :-

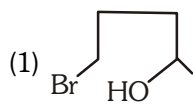
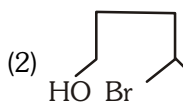
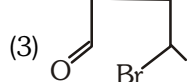
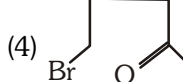
- (1) 
(2) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH}$
(3) 
(4) $\text{CH}_3-\text{CH}_2-\text{CH}_3$

21. In the reaction sequence



- (1) C_2H_6 , $\text{C}_2\text{H}_5\text{Br}$
(2) CH_4 , CH_3Br
(3) $\text{CH}_2=\text{CH}_2$, $\text{C}_2\text{H}_5\text{Br}$
(4) $\text{CH}\equiv\text{CH}$, $\text{CH}_2=\text{CHBr}$



- (1)  (2) 
(3)  (4) 

23. $\text{CH}_3-\text{CH}_2-\text{OH} + \text{Ph}-\text{CH}_2-\text{OH} \xrightarrow[140^\circ\text{C}]{\text{H}^+}$ of which is not obtained?

- (1) $\text{CH}_3-\text{CH}_2-\text{OCH}_2-\text{CH}_3$
(2) $\text{Ph}-\text{CH}_2-\text{OCH}_2-\text{Ph}$
(3) $\text{Ph}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$
(4) $\text{Ph}-\text{CH}_2-\text{O}-\text{CH}_2-\text{O}-\text{CH}_3$

24. Oxonium ion of ether has the structure :-

- (1) $\text{C}_2\text{H}_5-\text{O}-\underset{\text{CH}_3}{\text{CH}}-\overset{\oplus}{\text{O}}-\text{H}$
(2) $\text{CH}_3-\text{CH}_2-\overset{\oplus}{\text{O}}-\text{CH}_2-\text{CH}_3$
(3) $(\text{C}_2\text{H}_5)_2\text{O} \rightarrow \text{O}$
(4) $\text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\overset{\oplus}{\text{O}}-\text{H}$

- 26.** Which of the following does not react with aq. NaOH :-
- (1) Phenol (2) Benzoic acid
(3) CH_3COOH (4) $\text{CH}_3\text{-O-C}_6\text{H}_5$

27. Acetaldehyde on warming with Fehling's solution gives a red precipitate of :-

- (1) Elemental copper
- (2) Cuprous oxide
- (3) Cupric oxide
- (4) Mixture of all of the above

- 28.** Acetone does not form :-
- (1) A phenylhydrazone with phenylhydrazine
 - (2) A sodium bisulphite adduct with sodium bisulphite
 - (3) A silver mirror with Tollen's reagent
 - (4) An oxime with hydroxylamine

- 29.** CH_3CHO and CH_3COCH_3 can not be distinguished by :-
- (1) Fehling solution (2) Grignard reagent
(3) Schiff's reagent (4) Tollen's reagent

- $$\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow[\text{(2) Br}_2/\text{CCl}_4]{\text{(1) moist Ag}_2\text{O, } \Delta} \text{A} \xrightarrow[\text{Ether}]{\text{Mg}} \text{B} \xrightarrow{\text{CH}_3\text{CN/H}_3\text{O}^+} \text{C}$$

(1) $\text{CH}_3\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$

- (2) $\text{CH}_3\text{CH}_2\text{-CN}$
 (3) $\text{CH}_3\text{CH}_2\text{-}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{-CH}_3$
 (4) $\text{CH}_3\text{-CH}_2\text{-}\underset{\text{COOH}}{\underset{|}{\text{CH}}}\text{-CH}_3$

32. $\text{Ph}-\overset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}}-\text{CH}_3 + \text{aq. KOH} \rightarrow \text{A} \xrightarrow[\text{H}^+]{\text{KCN}} \text{B} ?$

- (1) 50% d + 50% *l* (2) 80% d + 20% *l*
(3) Meso compound (4) optically active

33.  can be obtained by :-

- $$(1) \text{C}_6\text{H}_5\text{COCl} + (\text{Ph})_2\text{Cd}$$

- $$(2) \quad \text{C}_6\text{H}_5\text{COCl} + \text{C}_6\text{H}_5\text{OH} \rightarrow \text{C}_6\text{H}_5\text{COOC}_6\text{H}_5 + \text{HCl}$$

- $$(3) \text{C}_6\text{H}_6 + \text{CO} + \text{ZnCl}_2 + \text{HCN}$$

- (4) None of the above

- $$(1) \text{ Ph}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H}$$

- (2) $\text{CH}_3\text{-O-C}_6\text{H}_4\text{-C(=O)-H}$

- (3) $\text{CH}_3\text{---}\text{C}_6\text{H}_4\text{---CH}_2\text{---C(=O)---Ph}$

- (4) 

- (1) Rosenmund reduction
- (2) Etard reaction
- (3) Cannizzaro reaction
- (4) Friedel-Craft reaction

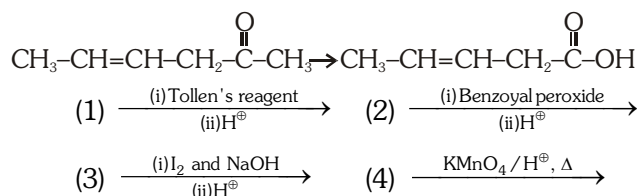
- (1) Steam distillation
- (2) Hydrolysis of sodium bisulphite adducts
- (3) Fractional crystallisation
- (4) Sublimation

- (1) Nucleophilic substitutions
- (2) Electrophilic addition reactions
- (3) Nucleophilic addition reactions
- (4) Free radical substitution reactions

38. $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ and $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ are readily distinguished by their reaction with :-
 (1) Iodine and alkali
 (2) 2,4-dinitrophenylhydrazine
 (3) Tollen's reagent
 (4) All the above

39. Formaldehyde and acetaldehyde are readily distinguished by reaction with :-
 (1) A solution of 2,4-dinitrophenylhydrazine
 (2) Fehling's solution
 (3) Tollen's reagent
 (4) Iodine and alkali

40. Which is the most suitable reagent for the following conversion



41. Formaldehyde reacts with conc. alkali to form :-
 (1) A resinous mass
 (2) Formic acid
 (3) A mixture of methanol and sodium formate
 (4) Methanol

42. Which of the following compounds does not give aldol condensation :-
 (1) CH_3CHO (2) $\text{CH}_3\text{CH}_2\text{CHO}$
 (3) HCHO (4) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$

43. Cannizzaro reaction is given by :-
 (1) Aldehydes containing α -hydrogen atoms
 (2) Aldehydes as well as ketones containing α -hydrogen atoms
 (3) Aldehydes not containing α -hydrogen atoms
 (4) Aldehydes containing β -hydrogen atoms

44. Benzaldehyde reacts with formaldehyde in the presence of alkali to form :-

- (1) CH_3-OH and $\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^- \text{Na}^+$
 (2) $\text{C}_6\text{H}_5-\text{CH}_2-\text{OH}$ and $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^- \text{Na}^+$
 (3) $\text{C}_6\text{H}_5-\text{COOH}$ and $\text{CH}_3\text{CH}_2-\text{OH}$
 (4) $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ and $\text{C}_6\text{H}_5-\text{CH}_2-\text{OH}$

45. Which of the following can be converted to $\text{CH}_3-\text{CH}=\text{CH}-\text{CHO}$:-

- (1) Acetone (2) Acetaldehyde
 (3) Propanaldehyde (4) Formaldehyde

46. The product of reaction with primary amine and aldehyde is -

- (1) $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ (2) $\text{R}-\text{ONO}$
 (3) $\text{R}'-\text{CH}=\text{N}-\text{R}$ (4) $\text{R}-\text{NO}_2$

47. Brady's reagent is

- (1) $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
 (2) $\text{KMnO}_4/\text{NaIO}_4$
 (3) $\text{O}_2\text{N}-\text{C}_6\text{H}_3(\text{NO}_2)-\text{NH.NH}_2$
 (4) $\text{O}_2\text{N}-\text{C}_6\text{H}_3(\text{NO}_2)-\text{F}$

48. A compound with molecular formula $\text{C}_3\text{H}_6\text{O}$, not gives silver mirror with Tollen's reagent but forms oxime with hydroxyl amine. Compound will be -

- (1) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OH}$
 (2) $\text{CH}_3\text{CH}_2\text{CHO}$
 (3) $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_3$
 (4) CH_3COCH_3

49. Aldehyde and ketone are distinguished by reagent

- (1) Fehling solution (2) H_2SO_4
 (3) NaHSO_3 (4) NH_3

50. Carbonyl group is converted into methylene group by -

- (1) Acidic reduction
 (2) Raney Ni
 (3) Basic hydrolysis
 (4) Normal Hydrogenation

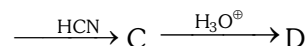
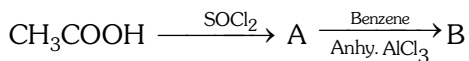
51. When acetaldol is treated with excess of acid then unsaturated product will be :-

- (1) Alcohol (2) Aldehyde
 (3) Acid (4) Alkyl halide

52. The reagent used for the separation of acetaldehyde from acetophenone is -

- (1) NaHSO_3 (2) $\text{C}_6\text{H}_5\text{NHNH}_2$
 (3) NH_2OH (4) $\text{NaOH} + \text{I}_2$

61. In a set of reactions acetic acid yielded a product D



The structure of D would be –

- (1)
- (2)
- (3)
- (4)

ACID DERIVATIVE

62. The compounds A and B in the reaction sequence



are given by the set :-

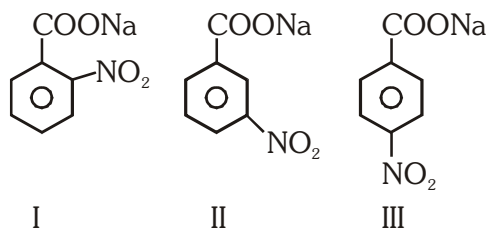
- (1) $\text{CH}_3\text{CO}-\text{O}-\text{COCH}_3$, $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
 (2) $\text{CH}_3\text{CO}-\text{O}-\text{COCH}_3$, $\text{C}_6\text{H}_5\text{OCOCH}_3$
 (3) CH_3COCH_3 , $\text{C}_6\text{H}_5\text{OCOCH}_3$
 (4) $\text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{O}-\text{C}(=\text{O})-\text{CH}_3$,
 $\text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_5$

63. $\text{CH}_3-\text{CH}_2-\text{COOH} \xrightarrow{\text{P}/\text{Cl}_2} \text{A} \xrightarrow[\text{KOH}]{\text{Alc.}} \text{B}$

structure of B is :-

- (1) $\text{CH}_2=\text{CH}-\text{COOH}$
 (2) $\text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\text{COOH}$
 (3) $\text{CH}_2-\underset{\text{Cl}}{\text{CH}}-\text{COOH}$
 (4) $\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$

64. Correct reactivity order of decarboxylation is



- (1) I > II > III
 (2) I > III > II
 (3) III > II > I
 (4) III > I > II

65. Which is most reactive towards hydrolysis.

- (1)
- (2)
- (3)
- (4)

66. Which of the following reagents may be used to distinguish between phenol and benzoic acid ?

- (1) Victor-Mayer test
 (2) Neutral FeCl_3
 (3) Aqueous NaOH
 (4) Tollen's reagent

67. Acyl chlorides undergo :-

- (1) Nucleophilic addition reactions
 (2) Nucleophilic substitution reactions
 (3) Electrophilic substitution reactions
 (4) Electrophilic addition reactions

68. The reaction of ethanol on acetic anhydride is an example of :-

- (1) Nucleophilic addition
 (2) Nucleophilic substitution
 (3) Electrophilic addition
 (4) Free radical substitution

69. The reduction of acetamide gives :-

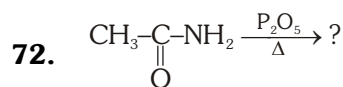
- (1) $\text{CH}_3\text{CH}_2\text{NH}_2$
- (2) $(\text{CH}_3)_2\text{CHNH}_2$
- (3) $(\text{CH}_3)_3\text{CNH}_2$
- (4) $(\text{CH}_3\text{CH}_2)_2\text{NH}$

70. Which is used in preparation of aldehyde by rosenmund reduction

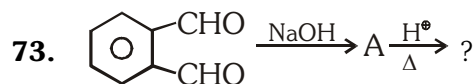
- (1) Ester
- (2) Acid
- (3) Acid halide
- (4) Alcohol

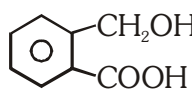
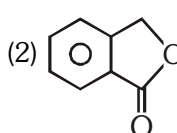
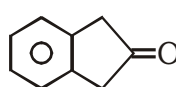
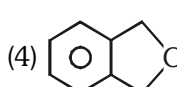
71. Which is maximum reactive :-

- (1) CH_3CONH_2
- (2) $\text{CH}_3\text{COOCH}_3$
- (3) CH_3COCl
- (4) $\text{CH}_3\text{COOC}_2\text{H}_5$



- (1) CH_3COOH
- (2) CH_3-CN
- (3) CH_3-CH_3
- (4) CH_3-CHO



- (1) 
- (2) 
- (3) 
- (4) 

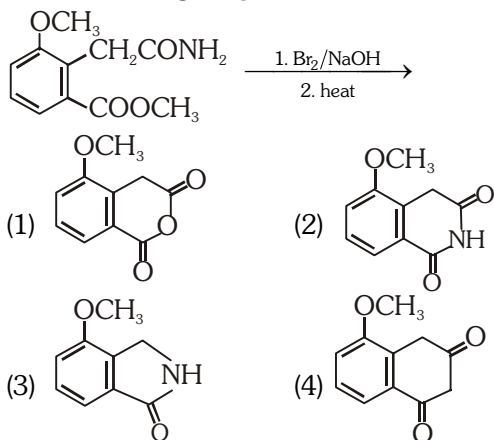
EXERCISE-I (Conceptual Questions)

ANSWER KEY

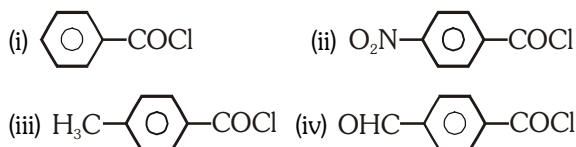
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Ans.	3	3	1	2	3	3	3	4	4	3	3	2	3	4	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	4	2	3	4	4	3	1	4	2	2	4	2	3	2	3
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	4	1	1	3	4	2	3	3	4	3	3	3	3	2	2
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	3	3	4	1	1	2	1	4	2	2	2	2	1	2	4
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73		
Ans.	1	2	1	1	2	2	2	2	1	3	3	2	2		

EXERCISE-II (Previous Year Questions)**AIPMT/NEET & AIIMS (2006-2018)****AIIMS 2006**

1. The following sequence of reactions gives

**AIPMT 2007**

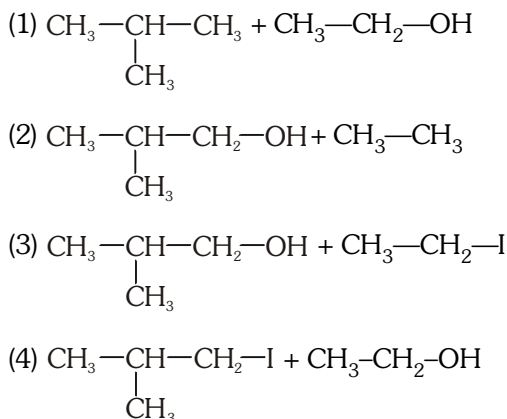
2. Consider the following compounds:



The correct order of reactivity towards hydrolysis is:-

- (1) (i) > (ii) > (iii) > (iv) (2) (iv) > (ii) > (i) > (iii)
 (3) (ii) > (iv) > (i) > (iii) (4) (ii) > (iv) > (iii) > (i)
3. Which one of the following on treatment with 50% aq. NaOH yields the corresponding alcohol and acid
- (1) C_6H_5CHO (2) $CH_3CH_2CH_2CHO$
 (3) CH_3COCH_3 (4) CH_3CHO

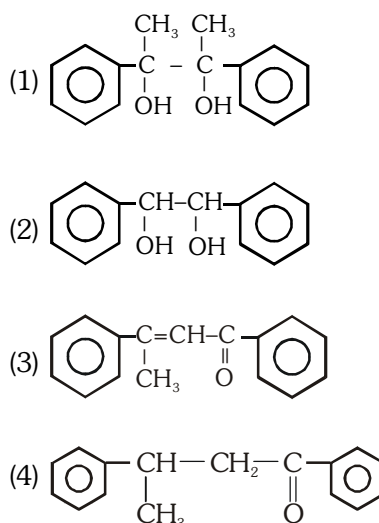
4. In the reaction : $CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-O-CH_2-CH_3 + HI \longrightarrow \dots\dots\dots$
 which of following compounds will be formed :



5. The product formed in aldol reaction is :-
 (1) a β -hydroxy aldehyde or ketone
 (2) an α -hydroxy aldehyde or ketone
 (3) an α, β -unsaturated ester
 (4) a β -hydroxy acid

AIPMT 2008

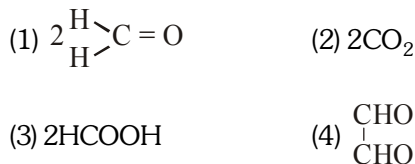
6. Acetophenone when reacted with a base, C_2H_5ONa , yields a stable compound which has the structure :-



7. A strong base can abstract an α -hydrogen from
 (1) Ketone (2) Alkane
 (3) Alkene (4) Amine

AIPMT 2009

8. $H_2COH.CH_2OH$ on heating with periodic acid gives :-

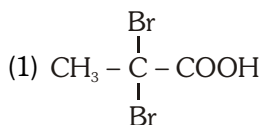


9. Consider the following reaction,
 ethanol $\xrightarrow{PBr_3}$ X $\xrightarrow{alc. KOH}$ Y
 $\xrightarrow[(ii) H_2O]{(i) H_2SO_4 \text{ room temperature}}$ Z ;

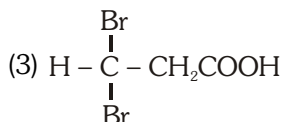
the product Z is :-

- (1) CH_3CH_2OH
 (2) $CH_2=CH_2$
 (3) $CH_3CH_2-O-CH_2-CH_3$
 (4) $CH_3-CH_2-O-SO_3H$

- 10.** Propionic acid with Br_2/P yields a dibromo product. Its structure would be :-

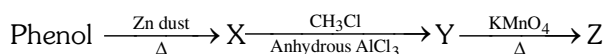


- (2) $\text{CH}_2\text{Br} - \text{CHBr} - \text{COOH}$



- (4) $\text{CH}_2\text{Br} - \text{CH}_2 - \text{COBr}$

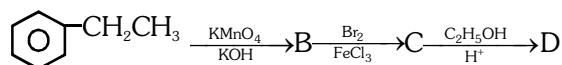
- 11.** Consider the following reaction :



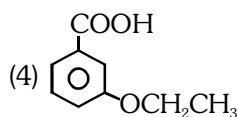
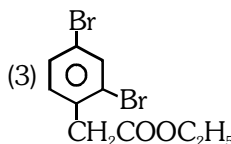
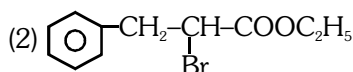
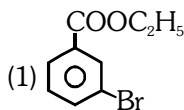
the product Z is :-

- (1) Benzene (2) Toluene
(3) Benzaldehyde (4) Benzoic acid

- 12.** In a set of reactions, ethyl benzene yielded a product D



'D' would be :-



AIPMT 2010

- 13.** Which of the following reactions will not result in the formation of carbon-carbon bonds?

- (1) Friedel-Crafts acylation
- (2) Reimer-Tieman reaction
- (3) Cannizzaro reaction
- (4) Wurtz reaction

- 14.** When glycerol is treated with excess of HI, it produces :-

- (1) allyl iodide
- (2) propene
- (3) glyceryl triiodide
- (4) 2-iodopropane

- 15.** Match the compounds given in List-I with their characteristic reactions given in List-II. Select the correct option.

List-I

Compounds

- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
 (b) $\text{CH}_3\text{C}\equiv\text{CH}$
 (c) $\text{CH}_3\text{CH}_2\text{COOCH}_3$
 (d) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$

List-II

Reactions

- (i) Alkaline hydrolysis
- (ii) With KOH (alcohol) and CHCl_3 produces bad smell
- (iii) Gives white ppt. with ammonical AgNO_3
- (iv) With Lucas reagent cloudiness appears after 5 minutes

Options :

- | | (a) | (b) | (c) | (d) |
|-----|-------|-------|-------|-------|
| (1) | (iii) | (ii) | (i) | (iv) |
| (2) | (ii) | (iii) | (i) | (iv) |
| (3) | (iv) | (ii) | (iii) | (i) |
| (4) | (ii) | (i) | (iv) | (iii) |

AIIMS 2010

- 16.** The suitable reagent to convert $\text{CH}_3\text{-CH=CH-CHO}$ into $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$ is :-

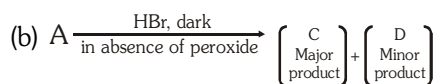
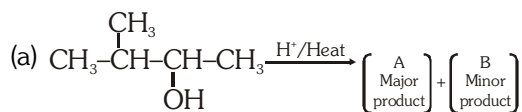
- (1) NaBH_4
- (2) LiAlH_4
- (3) Zn-Hg/HCl
- (4) H_2/Pd

17. $\text{CH}_3-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{COOCH}_3 \xrightarrow{\text{NaBH}_4} :-$

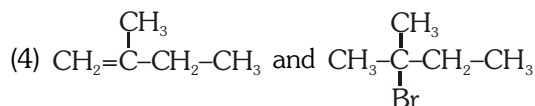
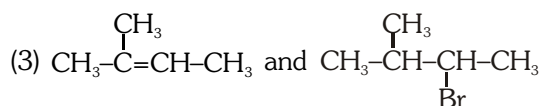
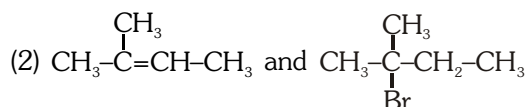
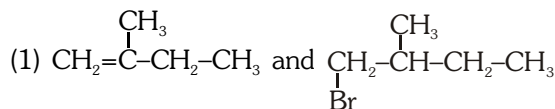
- (1) $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_2\text{COOCH}_3$
- (2) $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{CH}_2-\text{OH}$
- (3) $\text{CH}_3-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2\text{CH}_2-\text{OH}$
- (4) $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_2\text{COOH}$

AIPMT Pre. 2011

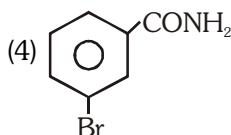
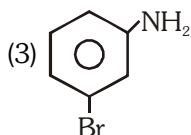
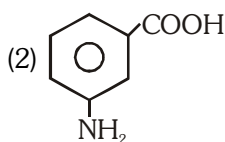
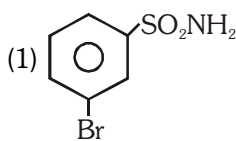
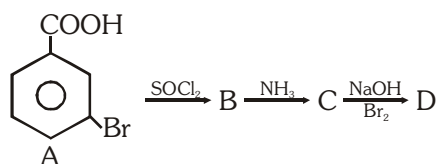
18. In the following reactions,



the major products (A) and (C) are respectively :-



19. In a set of reactions m-bromobenzoic acid gave a product D. Identify the product D



20. Clemmensen reduction of a ketone is carried out in the presence of which of the following ?

- (1) Glycol with KOH
- (2) Zn-Hg with HCl
- (3) LiAlH_4
- (4) H_2 and Pt as catalyst

AIPMT Mains 2011

21. An organic compound 'A' on treatment with NH_3 gives 'B' which on heating gives 'C'. 'C' when treated with Br_2 in the presence of KOH produces ethylamine. Compound 'A' is :-

- (1) $\text{CH}_3\text{CH}_2\text{COOH}$
- (2) CH_3COOH
- (3) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
- (4) $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}\text{COOH}$

22. Match the compounds given in List-I with List-II and select the suitable option using the code given below.

List-I	List-II
(a) Benzaldehyde	(i) Phenolphthalein
(b) Phthalic anhydride	(ii) Benzoin condensation
(c) Phenyl benzoate	(iii) Oil of wintergreen
(d) Methyl salicylate	(iv) Fries rearrangement

Code :

(a)	(b)	(c)	(d)
(1) (ii)	(i)	(iv)	(iii)
(2) (iv)	(i)	(iii)	(ii)
(3) (iv)	(ii)	(iii)	(i)
(4) (ii)	(iii)	(iv)	(i)

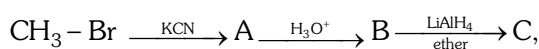
AIIMS 2011

23. Decarboxylation occurs with maximum rate in:

- (1) CH_3COOH
- (2) $\text{C}_6\text{H}_5-\text{COOH}$
- (3) $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$
- (4) $\text{CH}_3\text{COCH}_2\text{COOH}$

AIPMT Pre. 2012

24. In the following sequence of reactions



the end product (C) is:

- (1) Acetaldehyde
- (2) Ethyl alcohol
- (3) Acetone
- (4) Methane

O=Cc1ccccc1Cl $\xrightarrow{50\% \text{ KOH}}$

- $$\text{C}_6\text{H}_5\text{COCl} \xrightarrow[\text{Pd}-\text{BaSO}_4]{\text{H}_2} \text{'A'}$$

$$(1) \quad \text{CH}_2 - \text{CH}_2 \xrightarrow[\text{Heat}]{\text{H}_3\text{O}^+} \text{O}$$

- E

33. Which of the following will not be soluble in sodium hydrogen carbonate?

- (1) 2, 4, 6-trinitrophenol
- (2) Benzoic acid
- (3) o-Nitrophenol
- (4) Benzenesulphonic acid

AIIMS 2014

34. Which of the following reagents cannot be used to prepare acetophenone :-

- (1) $C_6H_5COCl + (CH_3)_2Cd$
- (2) $C_6H_5COCl + CH_3MgBr$
- (3) $C_6H_5CN + C_2H_5MgBr$
- (4) $C_6H_6 + (CH_3CO)_2O/AlCl_3$

AIPMT 2015

35. An organic compound 'X' having molecular formula $C_5H_{10}O$ yields phenyl hydrazone and gives negative response to the Iodoform test and Tollen's test. It produces n-pentane on reduction. 'X' could be :-

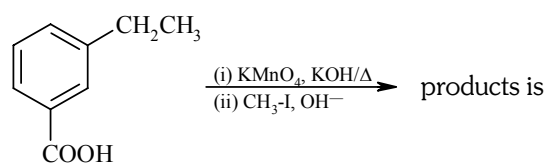
- (1) 2-pentanone
- (2) 3-pentanone
- (3) n-amyl alcohol
- (4) pentanal

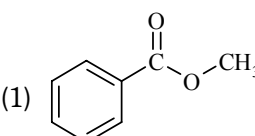
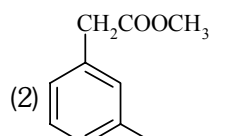
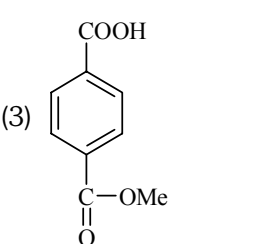
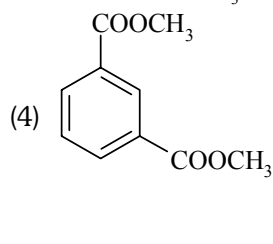
RE-AIPMT 2015

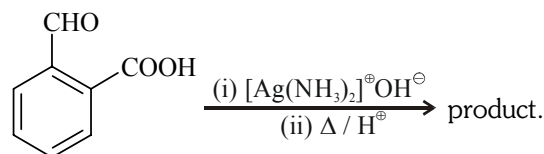
36. Reaction of phenol with chloroform in presence of dilute sodium hydroxide finally introduces which one of the following functional group ?

- (1) $-CHCl_2$
- (2) $-CHO$
- (3) $-CH_2Cl$
- (4) $-COOH$

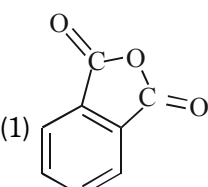
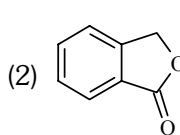
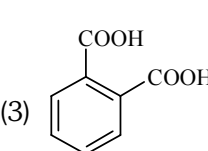
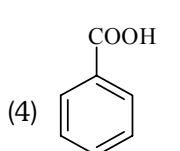
AIIMS 2015

37.  products is

- (1) 
- (2) 
- (3) 
- (4) 

38.  product.

Product of above reaction is

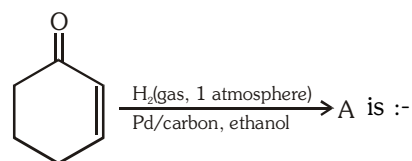
- (1) 
- (2) 
- (3) 
- (4) 

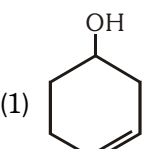
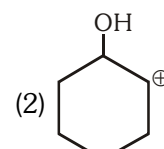
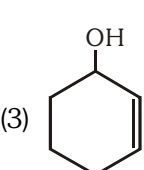
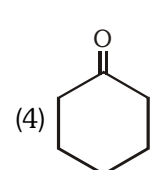
39. Correct order of boiling point is

- (i) $CH_3(CH_2)_3OH$
- (ii) $C_2H_5-O-C_2H_5$
- (iii) $CH_3-(CH_2)_3CH_3$
- (iv) $CH_3-(CH_2)_3-Cl$
- (1) $i > iv > ii > iii$
- (2) $iii > ii > iv > i$
- (3) $i > ii > iii > iv$
- (4) $iv > iii > ii > i$

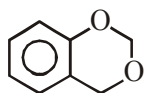
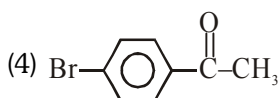
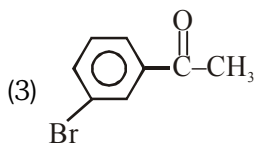
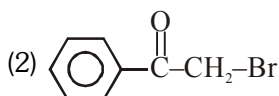
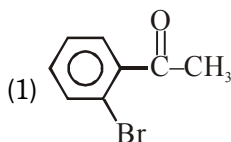
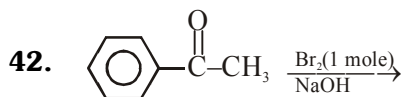
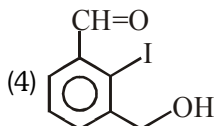
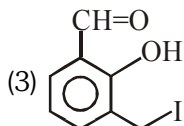
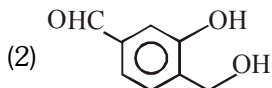
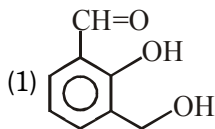
NEET-II 2016

40. The **correct** structure of the product A formed in the reaction

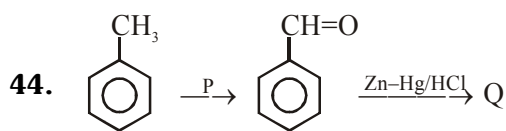
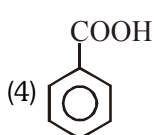
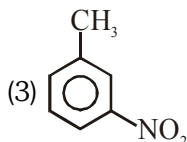
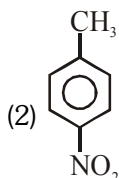
 A is :-

- (1) 
- (2) 
- (3) 
- (4) 

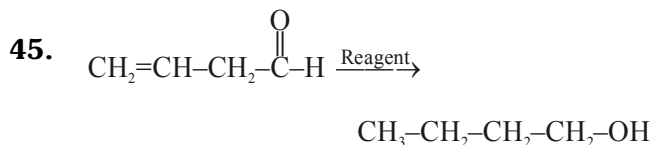
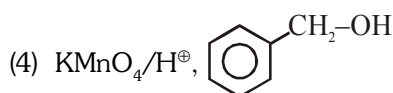
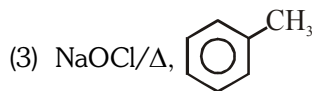
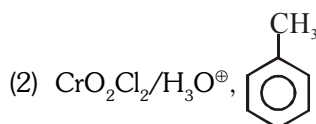
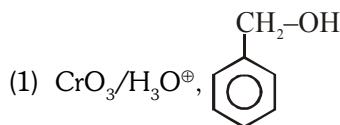
41. $\xrightarrow[\text{(ii) CHCl}_3, \text{NaOH}]{\text{(i) HI}}$ product (major) :-


$$\frac{\text{(i) HI}}{\text{(ii) CHCl}_3, \text{NaOH}} \rightarrow \text{product (major)} :-$$


(1) 

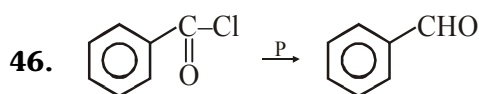


P & Q respectively are :-



Appropriate reagent for above conversion will be:-

- (1) Metal + H₂ (2) LiAlH₄
(3) NaBH₄ (4) All



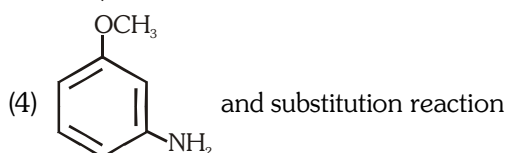
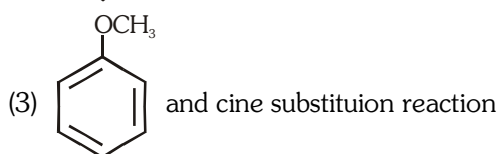
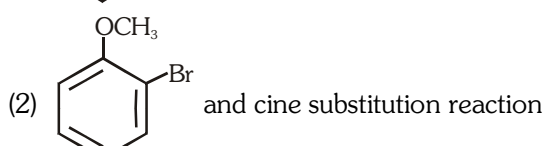
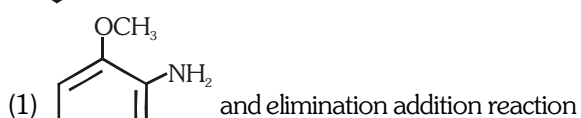
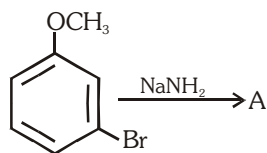
P will be :-

- (1) Pd/BaSO₄ + H₂ (2) LiAlH₄
(3) NaBH₄ (4) Pd + H₂

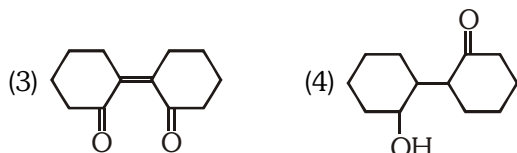
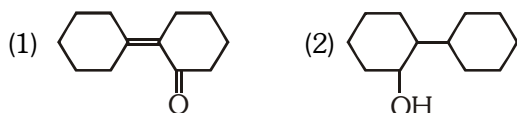
47. The heating of phenyl-methyl ethers with HI produces

- (1) iodobenzene
- (2) phenol
- (3) benzene
- (4) ethyl chlorides

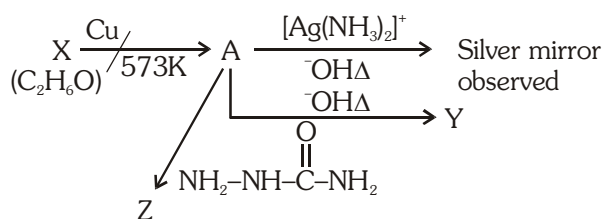
48. Identify A and predict the type of reaction



49. Of the following, which is the product formed when cyclohexanone undergoes aldol condensation followed by heating ?



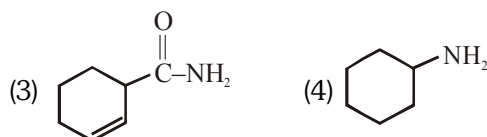
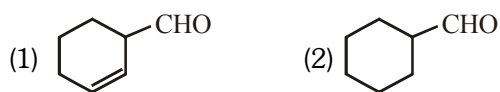
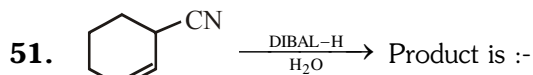
50. Consider the reactions :-



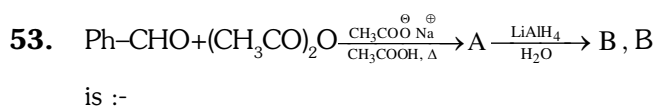
Identify A, X, Y and Z

- (1) A-Methoxymethane, X-Ethanol, Y-Ethanoic acid, Z-Semicarbazide.
- (2) A-Ethanal, X-Ethanol, Y-But-2-enal, Z-Semicarbazone
- (3) A-Ethanol, X-Acetaldehyde, Y-Butanone, Z-Hydrazone
- (4) A-Methoxymethane, X-Ethanoic acid, Y-Acetate ion, Z-hydrazine

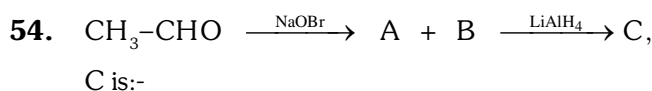
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52. Which of the following is the better reactant for the production of m-cresol.



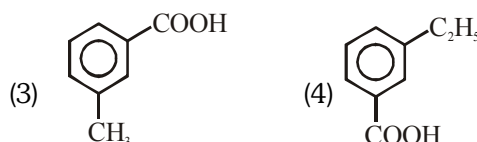
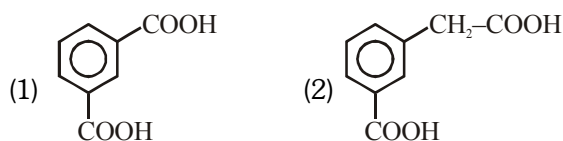
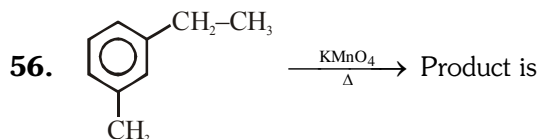
- (1) $\text{Ph-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$
- (2) $\text{Ph-CH=CH-CH}_2\text{-OH}$
- (3) $\text{Ph-CH}_2\text{-CH}_2\text{-COOH}$
- (4) Ph-CH=CH-CHO



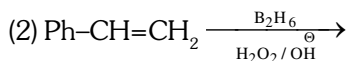
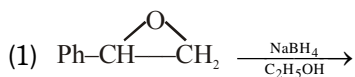
- (1) $\text{CH}_3\text{-OH}$ (2) CH_3CHO
- (3) HCHO (4) HCOOH

55. Reagent can not be used to convert alcohol into alkyl halide

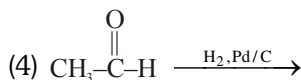
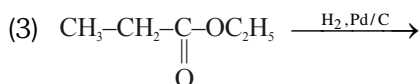
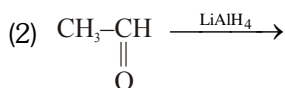
- (1) Red P/ Br_2 (2) KI / acetone
- (3) SOCl_2 (4) HCl/ZnCl_2



57. $\text{Ph-CH=CH}_2 \xrightarrow{\text{Reagent}} \text{Ph-CH}_2\text{-CH}_2\text{-OH}$
Which reagent is suitable for given conversion.



58. Which of the following cannot form ethanol ?



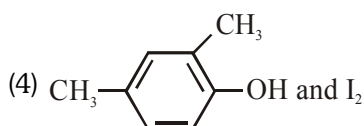
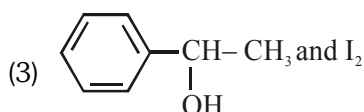
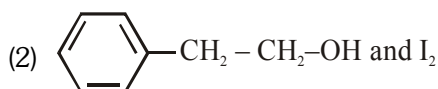
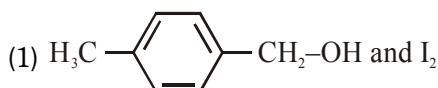
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59. Carboxylic acid have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their

- (1) formation of intramolecular H-bonding
- (2) formation of carboxylate ion
- (3) more extensive association of carboxylic acid via van der Waals force of attraction
- (4) formation of intermolecular H-bonding.

60. Compound A, $\text{C}_8\text{H}_{10}\text{O}$, is found to react with NaOI (produced by reacting Y with NaOH) and yields a yellow precipitate with characteristic smell.

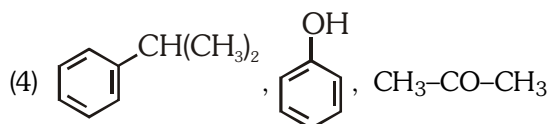
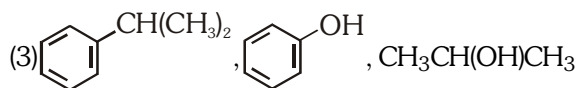
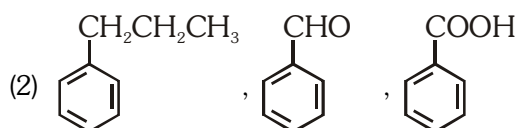
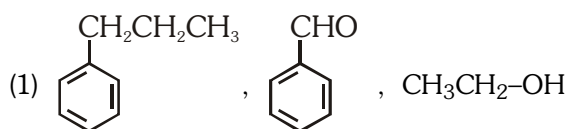
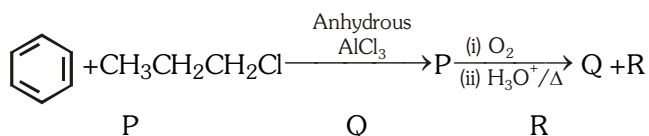
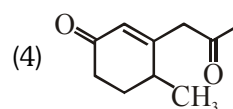
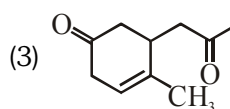
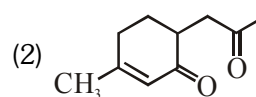
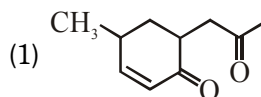
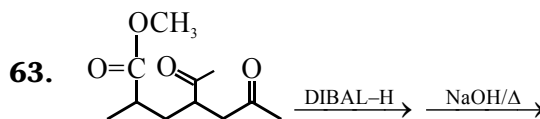
A and Y are respectively

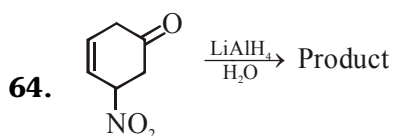


61. The compound A on treatment with Na gives B, and with PCl_5 gives C. B and C react together to give diethyl ether. A, B and C are in the order

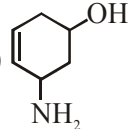
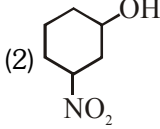
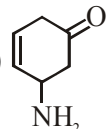
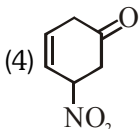
- (1) $\text{C}_2\text{H}_5\text{OH}$, C_2H_6 , $\text{C}_2\text{H}_5\text{Cl}$
- (2) $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_2\text{H}_5\text{Cl}$, $\text{C}_2\text{H}_5\text{ONa}$
- (3) $\text{C}_2\text{H}_5\text{Cl}$, C_2H_6 , $\text{C}_2\text{H}_5\text{OH}$
- (4) $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_2\text{H}_5\text{ONa}$, $\text{C}_2\text{H}_5\text{Cl}$

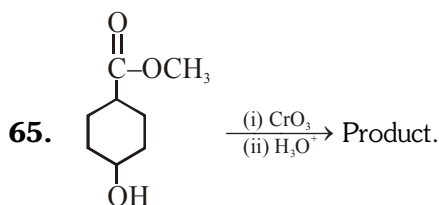
62. Identify the major products P, Q and R in the following sequence of reaction :

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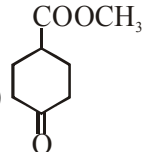
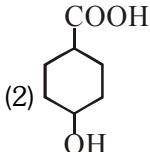
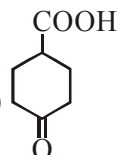
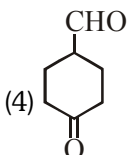


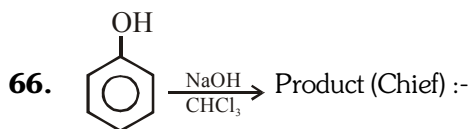
Product of the above reaction is

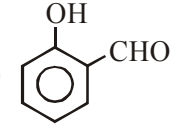
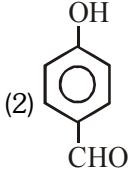
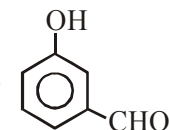
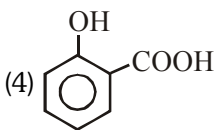
- (1)  (2) 
 (3)  (4) 

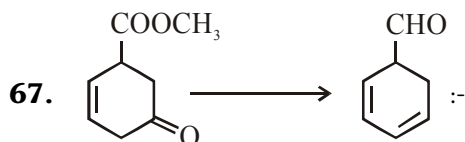


Product of reaction is :-

- (1)  (2) 
 (3)  (4) 

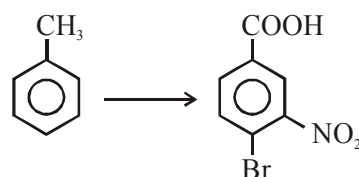


- (1)  (2) 
 (3)  (4) 

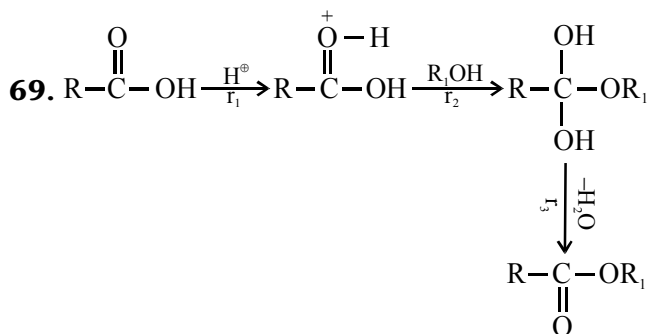


- (1) NaBH_4 , DIBAL-H, $\text{H}_3\text{O}^+/\Delta$
 (2) DIBAL-H, $\text{H}_3\text{O}^+/\Delta$, NaBH_4
 (3) B_2H_6 , NaBH_4 , $\text{H}_3\text{O}^+/\Delta$
 (4) $\text{H}_3\text{O}^+/\Delta$, DIBAL-H, NaBH_4

68. Correct sequence of reagents to get the given product-

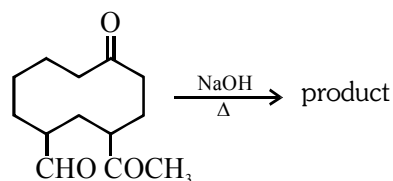


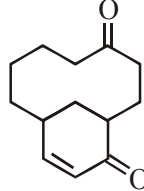
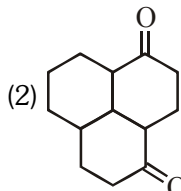
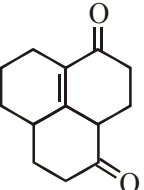
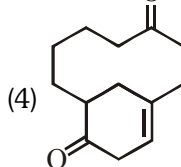
- (1) Br_2/Fe , $\text{HNO}_3/\text{H}_2\text{SO}_4$, KMnO_4/H^+
 (2) KMnO_4/H^+ , $\text{Br}_2/\text{FeBr}_3$, $\text{HNO}_3/\text{H}_2\text{SO}_4$
 (3) KMnO_4/H^+ , $\text{HNO}_3/\text{H}_2\text{SO}_4$, $\text{Br}_2/\text{FeBr}_3$
 (4) $\text{Br}_2/\text{FeBr}_3$, KMnO_4/H^+ , $\text{HNO}_3/\text{H}_2\text{SO}_4$

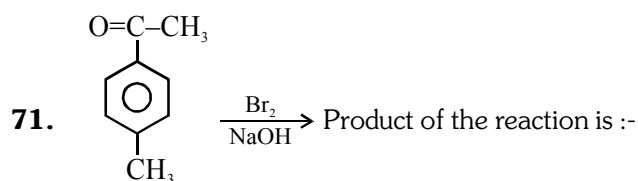


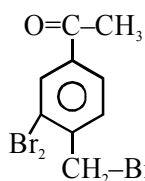
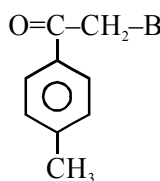
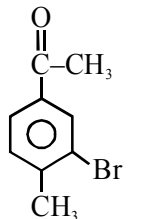
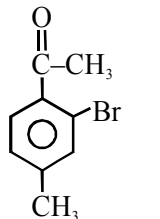
- (1) Fast, Slow, Fast (2) Slow, Fast, Fast
 (3) Fast, Fast, Slow (4) Slow, Fast, Slow

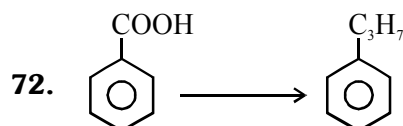
70. For the reaction :-



- (1)  (2) 
 (3)  (4) 

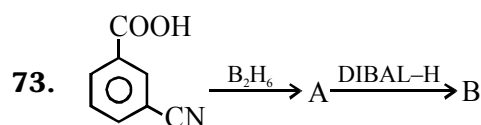


- (1)  (2) 
- (3)  (4) 

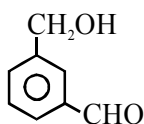
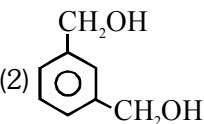
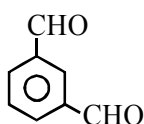
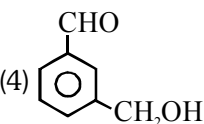


Select the correct sequence of reagents to carry out the above conversion :-

- (1) SOCl_2 , $\text{Cd}(\text{C}_2\text{H}_5)_2$, $\text{NH}_2\text{-NH}_2/\text{OH}^\ominus$
 (2) SOCl_2 , $\text{C}_2\text{H}_5\text{MgBr}$, Zn-Hg/HCl
 (3) SOCl_2 , $\text{CH}_3\text{-Li}$, $\text{NH}_2\text{-NH}_2/\text{OH}^\ominus$
 (4) $\text{Cd}(\text{CH}_3)_2$, SOCl_2 , $\text{NH}_2\text{-NH}_2/\text{OH}^\ominus$



The product 'B' is :-

- (1)  (2) 
- (3)  (4) 

EXERCISE-II (Previous Year Questions)

ANSWER KEY

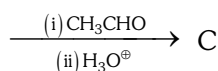
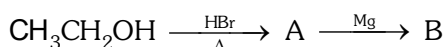
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	3	1	3	1	3	1	1	1	1	4	1	3	4	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	4	1	2	3	2	1	1	4	2	1	4	3	1	3	2
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	1	2	3	3	2	2	4	1	1	4	1	2	2	2	1
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	1	2	4	1	2	1	1	1	1	2	1	2	1	4	3
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73		
Ans.	4	4	1	1	3	1	1	1	1	1	2	1	1		

EXERCISE-III (Analytical Questions)

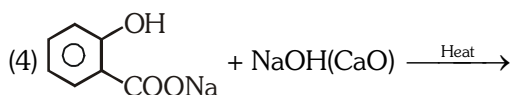
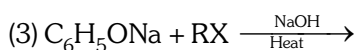
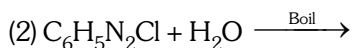
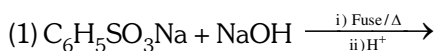
- Methanol can be distinguished from ethanol by the following except
 (1) Reaction with iodine and alkali
 (2) Reaction with salicylic acid and H_2SO_4
 (3) Reaction with Lucas reagent
 (4) Boiling point

- Ethanol on heating with acetic acid in the presence of a few drops of sulphuric acid gives the smell of
 (1) Oil of wintergreen (2) Oil of mustard
 (3) An ester (4) Oil of bitter almonds

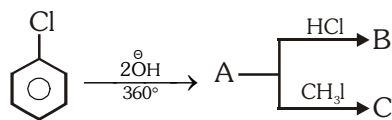
- The compounds A, B and C in the reaction sequence are given by the set :-



- (1) $\text{CH}_3\text{CH}_2\text{Br}$, $\text{CH}_3\text{CH}_2\text{MgBr}$, $(\text{CH}_3)_3\text{C}-\text{OH}$
 (2) $\text{CH}_3\text{CH}_2\text{Br}$, $(\text{CH}_3\text{CH}_2)_2\text{Mg}$, $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$
 (3) $\text{CH}_3\text{CH}_2\text{Br}$, $\text{CH}_3\text{CH}_2\text{MgBr}$, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$
 (4) CH_3CHBr_2 , $\text{CH}_3\text{CH}(\text{MgBr})_2$, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$
- Which of the following reactions will not lead to a phenol :-

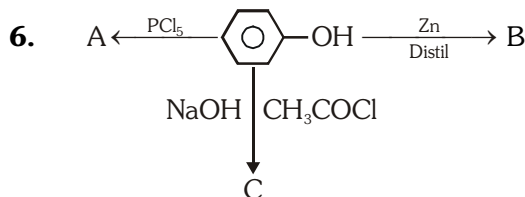


- The structures of the compounds / ions A, B and C in the reaction sequence are given by the set :-



- (1) $\text{C}_6\text{H}_5\text{OH}$, $\text{C}_6\text{H}_5\text{Cl}$, $\text{C}_6\text{H}_5\text{CH}_3$
 (2) $\text{C}_6\text{H}_5\text{O}^-$, $\text{C}_6\text{H}_5\text{OH}$, $\text{C}_6\text{H}_5\text{OCH}_3$
 (3) $\text{C}_6\text{H}_5\text{O}^-$, $\text{C}_6\text{H}_5\text{Cl}$, $\text{C}_6\text{H}_5\text{I}$
 (4) $\text{C}_6\text{H}_5\text{O}^-$, $\text{C}_6\text{H}_5\text{OH}$, $\text{C}_6\text{H}_5\text{I}$

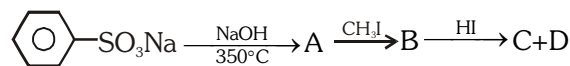
Check Your Understanding



The compounds A, B and C in the above reaction sequence are :-

- (1) Chlorobenzene, benzene, methyl benzoate
 (2) Triphenyl phosphate, benzene, phenyl acetate
 (3) Benzyl chloride, benzene, phenyl acetate
 (4) Benzyl chloride, benzene, phenylacetyl chloride

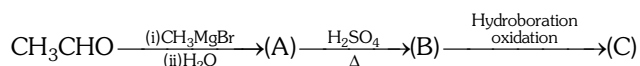
- In the reaction sequence —



A, B, C and D are given by the set :-

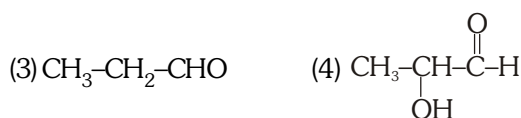
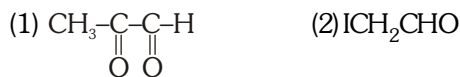
- (1) Sodium phenate, anisole, $\text{C}_6\text{H}_5\text{I}$, CH_3OH
 (2) Sodium phenate, phenetole, $\text{C}_2\text{H}_5\text{I}$, $\text{C}_6\text{H}_5\text{OH}$
 (3) Sodium phenate, anisole, $\text{C}_6\text{H}_5\text{OH}$, CH_3I
 (4) Sodium phenate, phenetole, $\text{C}_6\text{H}_5\text{I}$, $\text{C}_2\text{H}_5\text{OH}$

- Compound A and C in the following reaction are



- (1) Identical (2) Functional isomer
 (3) Positional isomer (4) Optical isomer

- Which of the following aldehydes does not form iodoform on heating with iodine and alkali :-



- A carbonyl compound gives pink colour with Schiff's reagent and a yellow precipitate when boiled with iodine and caustic alkali. It also gives a red precipitate with Fehling's solution. It is likely to be:-
 (1) Formaldehyde (2) Propionaldehyde
 (3) Acetaldehyde (4) Crotonaldehyde

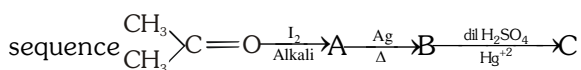
11. A carbonyl compound gives a positive iodoform test but does not reduce Tollen's reagent or Fehling's solution. It forms a cyanohydrin with HCN, which on hydrolysis gives a hydroxy acid with a methyl side chain. The compound is :-

- (1) Acetaldehyde
- (2) Propionaldehyde
- (3) Acetone
- (4) Crotonaldehyde

12. Which of the following statement is wrong :-

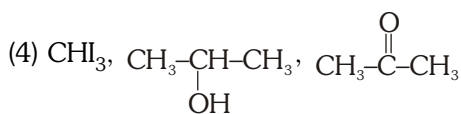
- (1) All methyl ketones give a positive iodoform test
- (2) Acetaldehyde is the only aldehyde that gives iodoform test
- (3) All secondary alcohols give positive iodoform test
- (4) Any alcohol that can be oxidised to an acetyl group gives a positive iodoform test

13. The compounds A, B and C in the reaction

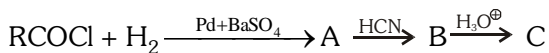


are given by the set :-

- (1) CHI_3 , $\text{H}_2\text{C}=\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{-OH}$
- (2) CHI_3 , $\text{HC}\equiv\text{CH}$, CH_3CHO
- (3) CHI_3 , $\text{CH}_3\text{-C}\equiv\text{CH}$, CH_3COCH_3



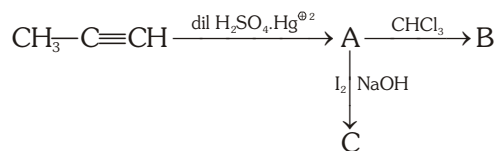
14. In the reaction sequence



A, B and C are given by the set :-

- (1) RCHO , $\text{RCH}(\text{OH})\text{CN}$, $\text{RCH}(\text{OH})\text{CH}_2\text{NH}_2$
- (2) RCHO , $\text{RCH}(\text{OH})\text{CN}$, $\text{RCH}(\text{OH})\text{COOH}$
- (3) RCHO , $\text{R}-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})-\text{OH}$
- (4) RCHO , $\text{R-CH}_2\text{-CN}$, $\text{R-CH}_2\text{-COOH}$

15. In the reaction sequence



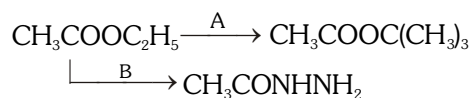
A, B and C are given by the set :-

- (1) $\text{CH}_3\text{CH}_2\text{CHO}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$, CHI_3
- (2) CH_3COCH_3 , $\text{CCl}_3\text{-C}(=\text{O})\text{-CH}_3$, CHI_3
- (3) CH_3COCH_3 , $\text{CCl}_3\text{-C}(\text{OH})(\text{CH}_3)_2$, CHI_3
- (4) $\text{CH}_3\text{CH}_2\text{CHO}$, $\text{CCl}_3\text{-CH}(\text{OH})\text{-CH}_2\text{-CH}_3$, CHI_3

16. Match the reactions given in column-I with the suitable reagent given in column-II

Column-I	Column-II
(i) Benzophenone → Diphenylmethane	(a) LiAlH_4
(ii) Benzaldehyde → 1-Phenyl ethanol	(b) Dibal-H
(iii) Cyclohexanone → Cyclohexanol	(c) Zn(Hg)/conc. HCl
(iv) Phenylbenzoate → Benzaldehyde	(d) CH_3MgBr
(1) (i)-(c), (ii)-(d), (iii)-(a), (iv)-(b)	
(2) (i)-(c), (ii)-(d), (iii)-(b), (iv)-(a)	
(3) (i)-(d), (ii)-(c), (iii)-(a), (iv)-(b)	
(4) (i)-(d), (ii)-(a), (iii)-(c), (iv)-(b)	

17. The reagents A and B in the reaction sequence



are given by the set :-

- (1) $\text{CH}_3\text{-CH}(\text{OH})\text{-CH}_3$, $\text{H}_2\text{N-NH}_2$
- (2) $\text{CH}_3\text{-CH}(\text{OH})\text{-CH}_3$, $\text{H}_2\text{N-OH}$
- (3) $\text{CH}_3\text{-C}(\text{OH})(\text{CH}_3)_2$, $\text{H}_2\text{N-NH}_2$
- (4) $\text{CH}_3\text{-C}(\text{OH})(\text{CH}_3)_2$, $\text{H}_2\text{N-OH}$

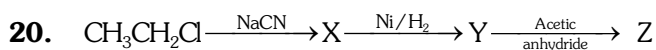
18. Methyl amine reacts with acetyl chloride and forms :-

- (1) CH_3NH_2
- (2) CH_3NHNa
- (3) $\text{CH}_3\text{NHCOCH}_3$
- (4) $(\text{CH}_3)_2\text{NCOCH}_3$

19. Intermediates formed during reaction of



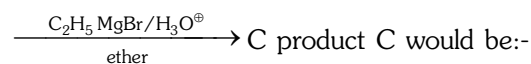
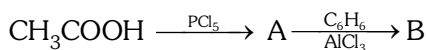
- (1) RCONHBr and RNCO
- (2) RNHCOBr and RNCO
- (3) $\text{RNH}-\text{Br}$ and RCONHBr
- (4) RCONBr_2



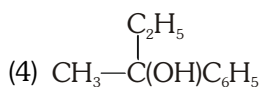
Z in the above reaction sequence is :-

- (1) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCOCH}_3$
- (2) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$
- (3) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONHCH}_3$
- (4) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONHCOCH}_3$

21. In a set of the given reactions, acetic acid yielded a product C.



- (1) $\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_5$
- (2) $\text{CH}_3\text{COC}_6\text{H}_5$
- (3) $\text{CH}_3\text{CH}(\text{OH})\text{C}_6\text{H}_5$

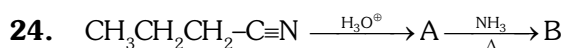


22. CH_3CHO and CH_3COCH_3 can not be distinguished by :-

- (1) Fehling solution
- (2) Grignard reagent
- (3) Schiff's reagent
- (4) Tollen's reagent

23. When propan-1-ol is dehydrated, the product obtained is again hydrated and further oxidised to form a compound. The compound is -

- (1) $\text{HC}\equiv\text{C}-\text{CH}_2-\text{OH}$
- (2) $\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$
- (3) $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ | \quad | \\ \text{OH} \quad \text{OH} \end{array}$
- (4) $\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_3 \\ | \quad | \\ \text{OH} \quad \text{OH} \end{array}$



Product 'B' is :-

- (1) $\text{CH}_3-\text{CH}_2\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$
- (2) $\text{CH}_3\text{CH}_2\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H}$
- (3) $\text{CH}_3\text{CH}_2\text{CH}_2-\text{NC}$
- (4) $\text{CH}_3\text{CH}_2\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{NH}_2$

25. Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in the above reaction is :-

- (1) Ethyl chloride
- (2) Ethyl ethanoate
- (3) Diethyl ether
- (4) 2-Butanone

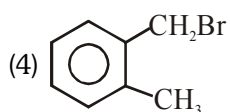
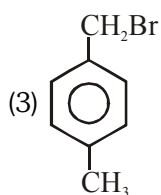
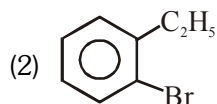
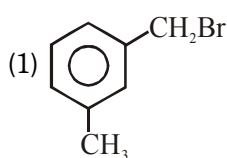
26. Phenol is heated with a solution of mixture of KBr and KBrO_3 . The major product obtained in the above reaction is :-

- (1) 4-Bromophenol
- (2) 2,4,6-Tribromophenol
- (3) 2-Bromophenol
- (4) 3-Bromophenol

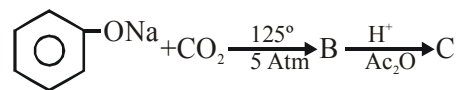
27. Trichloroacetaldehyde was subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate and another compound. The other compound is:-

- (1) 2,2,2-Trichloropropanol
- (2) Chloroform
- (3) 2,2,2-Trichloroethanol
- (4) Trichloromethanol

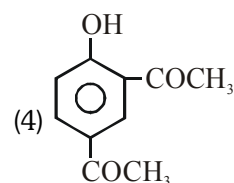
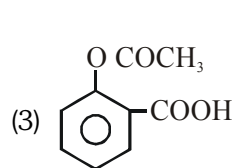
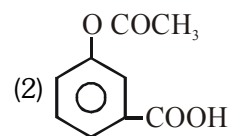
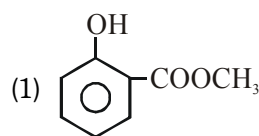
28. Compound (A), C_8H_9Br , gives a yellow precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A):



29. Sodium phenoxide when heated with CO_2 under pressure at $125^\circ C$ yields a product which on acetylation produces C



The major product C would be :



EXERCISE-III (Analytical Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	3	3	3	2	2	3	3	3	3	3	3	2	2	3
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	
Ans.	1	3	3	1	1	4	2	2	4	2	2	3	4	3	

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

- Assertion :-** Chlorobenzene and benzyl chloride can be distinguished by treatment with AgNO_3 .
Reason :- Chlorobenzene does not give white ppt with AgNO_3 due to resonance.
 (1) A (2) B (3) C (4) D
- Assertion :-** Benzyl alcohol turns blue litmus red.
Reason :- Benzyl alcohol is not an isomer of p-cresol.
 (1) A (2) B (3) C (4) D
- Assertion :-** Phenol is stronger acid than alcohols.
Reason :- Phenol is stabilized by resonance whereas alcohols are not.
 (1) A (2) B (3) C (4) D
- Assertion :-** Addition of CH_3OH to phenyl magnesium bromide gives benzene.
Reason :- CH_3OH is a stronger acid than benzene.
 (1) A (2) B (3) C (4) D
- Assertion :-** Ethers behave as bases in the presence of mineral acids.
Reason :- Ethers have lone pairs of electrons on oxygen.
 (1) A (2) B (3) C (4) D
- Assertion :-** Phenols give o- and p-Nitrophenol on nitration with conc. HNO_3 and H_2SO_4 mixture.
Reason :- -OH group in phenol shows -M effect.
 (1) A (2) B (3) C (4) D
- Assertion :-** Formic acid is a stronger acid than benzoic acid.
Reason :- pK_a of formic acid is higher than that of benzoic acid.
 (1) A (2) B (3) C (4) D
- Assertion :-** Ketones on reaction with Grignard reagents, followed by hydrolysis yield tertiary alcohols.
Reason :- All ketones show haloform reaction.
 (1) A (2) B (3) C (4) D
- Assertion :-** $>\text{C}=\text{O}$ group is present both in aldehydes and acid derivatives.
Reason :- Aldehydes give nucleophilic addition across $>\text{C}=\text{O}$ bond but acid derivatives do not exhibit such reactions.
 (1) A (2) B (3) C (4) D
- Assertion :-** Benzamide and methyl benzoate are derivatives of benzoic acid.
Reason :- Benzamide is less easily hydrolysed as compared to methyl benzoate.
 (1) A (2) B (3) C (4) D
- Assertion :-** Dehydration of alcohols always takes place in basic medium.
Reason :- OH^- is a good leaving group
 (1) A (2) B (3) C (4) D
- Assertion :-** Acetamide on reaction with KOH and bromine gives acetic acid.
Reason :- Bromine catalyses hydrolysis of acetamide.
 (1) A (2) B (3) C (4) D
- Assertion :-** Mixture of benzaldehyde and acetaldehyde in hot alkaline medium gives cinnamaldehyde.
Reason :- Benzaldehyde is a stronger electrophile than acetaldehyde.
 (1) A (2) B (3) C (4) D

14. Assertion :- Acetophenone shows aldol condensation.

Reason :- Acetophenone contains carbonyl group.

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

15. Assertion :- Benzyl phenyl ether forms phenol and benzyl iodide with HI

Reason :- Because benzyl carbocations is more stable than phenyl carbocation.

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

16. Assertion :- m-Nitrophenol is less acidic than p-nitrophenol.

Reason :- p-Nitrophenol has intermolecular-H-bonding.

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

17. Assertion :- Benzene sulphonic acid on heating with NaOH gives phenoxide.

Reason :- Sulphonic group is a poor leaving group.

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

18. Assertion :- Acetamide on reaction with Br_2/NaOH give $\text{CH}_3\text{-NH}_2$.

Reason :- Carbon of amide functional group becomes part of Na_2CO_3 .

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

19. Assertion :- $\text{Ph-O-C}_2\text{H}_5$ can be prepared from PhONa and ethyl iodide.

Reason :- Aryl halides are less reactive substrates for nucleophilic substitution reaction.

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

20. Assertion :- $\text{C}_6\text{H}_5\text{CH(OH)CH}_3$ gives benzoic acid with NaOBr followed by hydrolysis.

Reason :- First dehydration occur then oxidation

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

21. Assertion :- Ethyl acetoacetate forms butane-1,4-diol with NaBH_4 .

Reason :- NaBH_4 can reduces ketone and esters group.

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

22. Assertion :- Methoxy ethane has less boiling point than propanol.

Reason :- Methoxy ethane is more polar than propanol.

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

23. Assertion :- Isopropyl benzene reacts with O_2 and acid gives phenol.

Reason :- Initially isopropyl benzene converts into 2-phenyl propan-2-ol.

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

24. Assertion :- Benzaldehyde with alkaline CuSO_4 gives red-brown precipitate.

Reason :- Red precipitate is due to Cu_2O .

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

25. Assertion :- Methoxy ethane has more boiling point than propanol.

Reason :- Attraction is more in methoxy ethane than propanol.

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

EXERCISE-IV (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	4	2	1	1	4	3	3	2	2	4	4	3	2	1
Que.	16	17	18	19	20	21	22	23	24	25					
Ans.	2	3	1	1	3	4	3	3	4	4					

S. No.	CONTENTS	Page
1.	Amines	93
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3.	Nitro-benzene	102
4.	Exercise-I (Conceptual Questions)	105
5.	Exercise-II (Previous Years Questions)	110
6.	Exercise-III (Analytical Questions)	114
7.	Exercise-IV (Assertion & Reason)	116

NEET SYLLABUS

Amines : Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary secondary and tertiary amines. **Cyanides and Isocyanides** (will be mentioned at relevant places) **Diazonium salt** : preparation, chemical reactions and importance in synthetic organic chemistry.

OBJECTIVES

After studying this unit, we will be able to :

- *Describe amines as derivatives of ammonia having a pyramidal structure;*
- *Classify amines as primary, secondary and tertiary;*
- *Name amines by common names and IUPAC system;*
- *Describe some of the important methods of preparation of amines;*
- *Explain the properties of amines;*
- *Distinguish between primary, secondary and tertiary amines;*
- *Describe the method of preparation of diazonium salts and their importance in the synthesis of a series of aromatic compounds including azo dyes.*

*"Learning gives creativity
Creativity leads to thinking
Thinking provides knowledge
Knowledge makes you great."*

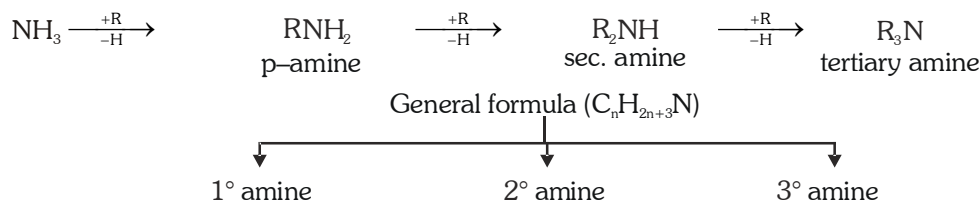
A.P.J. Abdul Kalam

NITROGEN CONTAINING COMPOUND

1.0 Amines

Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by alkyl group(s).

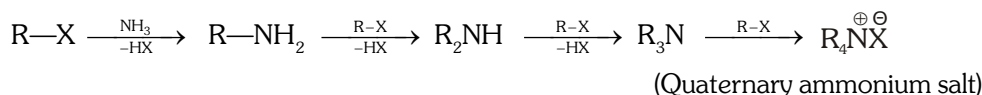
Amines are classified as primary, secondary and tertiary depending on the number of alkyl groups attached to nitrogen atom.



2.0 General methods of preparation

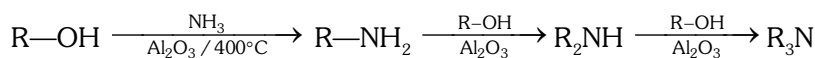
(1) Ammonolysis of alkyl halides and alcohols :

- (a) **From Ammonolysis of alkyl halides [Hofmann's ammonolysis]** : When an aqueous solution of ammonia is heated with alkyl halide all the three types of amines and quaternary ammonium salt are formed.



If ammonia is taken in excess, 1° amine is the main product.

- (b) **Ammonolysis of alcohols** : When ROH and NH₃ are passed over Al₂O₃ or ThO₂ at 350° C all the three types of amines are formed.



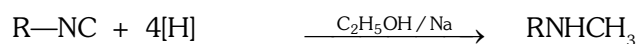
- Quaternary ammonium hydroxide is not formed.
- If excess of ammonia is used, then main product will be primary amine.

(2) By reduction :

- (a) **With RCONH₂** : $\text{RCONH}_2 \xrightarrow[\text{or Na/C}_2\text{H}_5\text{OH}]{\text{LiAlH}_4} \text{RCH}_2\text{NH}_2$
- (b) **With RCN** : $\text{RCN} + 4[\text{H}] \xrightarrow{\text{Na/C}_2\text{H}_5\text{OH}} \text{RCH}_2\text{NH}_2$

This reaction (b) is called mendius reaction.

The reduction of alkyl isocyanides gives secondary amines.



- (c) **With Oximes** : $\text{R-CH=N-OH} + 4[\text{H}] \xrightarrow[\text{Na/C}_2\text{H}_5\text{OH}]{\text{LiAlH}_4 \text{ or}} \text{RCH}_2\text{-NH}_2 + \text{H}_2\text{O}$

- (d) **With RNO₂** : $\text{RNO}_2 + 6[\text{H}] \xrightarrow[\text{or Fe+HCl}]{\text{Sn/HCl}} \text{RNH}_2 + 2\text{H}_2\text{O}$

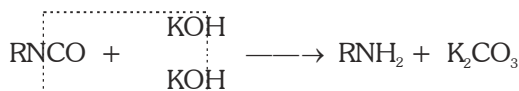
Sn/HCl is used in laboratory preparation

(3) By hydrolysis of :

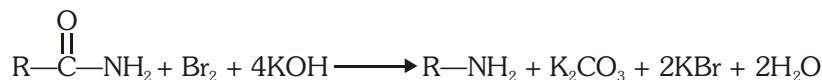
- (a) **R-NC** : Alkyl isocyanide undergoes hydrolysis with mineral acid and forms alkyl amine.



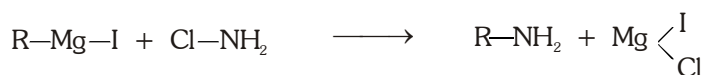
(b) **RNCO** : Alkyl isocyanate undergoes hydrolysis on heating with KOH and forms alkyl amine.



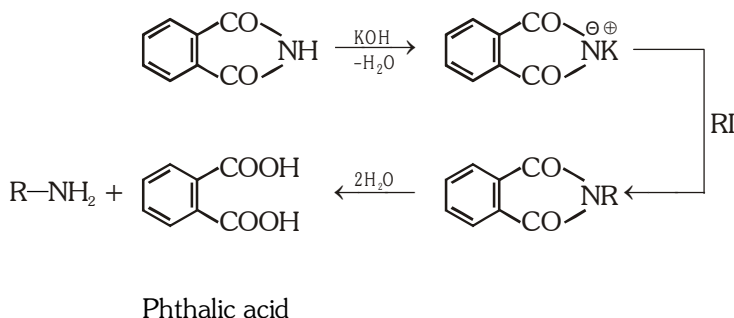
(4) **By Hofmann's bromamide reaction (Hofmann's Hypobromite reaction)** : This is a general method for the conversion of alkanamides into primary amines having one less carbon.



(5) **From Grignard reagent** : Alkyl magnesium iodide reacts with chloramine to yield alkyl amine.

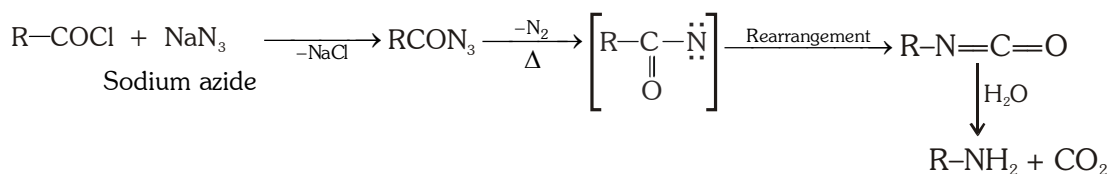


(6) **Gabriel phthalimide synthesis** : Phthalimide is first treated with KOH to obtain potassium phthalimide which is then treated with alkyl iodide. Then alkyl phthalimide on hydrolysis yields alkylamine. This method is used in the formation of pure aliphatic primary amines.

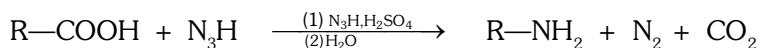


* Aniline is not formed by this reaction.

(7) **Curtius reaction** :

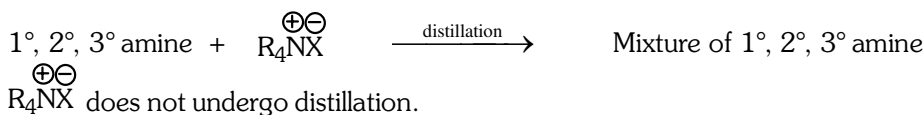


(8) **Schmidt reaction** : In presence of conc. H₂SO₄ alkanic acid reacts with hydrazoic acid (N₃H) followed by hydrolysis to yield alkylamine.



GOLDEN KEY POINTS

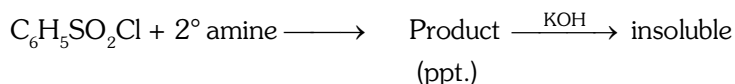
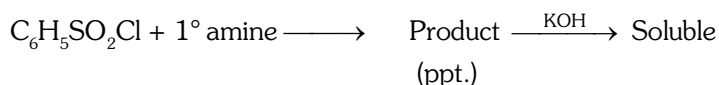
• Separation of 1°, 2° and 3° amines



Mixture of 1°, 2°, 3° amine can be separated by following methods.

(i) **Fractional distillation** : The mixture of amines may be separated by fractional distillation because their boiling points are quite different. It is used in industry.

(ii) **Hinsberg method** : In this method mixture of amines is separated by using benzene sulphonyl chloride (Hinsberg's reagent).



3° amine does not react with benzene sulphonyl chloride. (No ppt. formed)

(iii) **Hofmann method** : In this method mixture of amines is separated by using ethyl oxalate.

1° amine + ethyl oxalate $\longrightarrow$ solid product

2° amine + ethyl oxalate $\longrightarrow$ liquid product

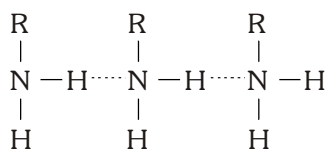
3° amine + ethyl oxalate $\longrightarrow$ No reaction

3.0 PHYSICAL PROPERTIES

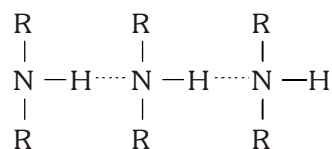
(i) CH_3NH_2 is gas and $\text{C}_2\text{H}_5\text{NH}_2$ is a volatile liquid.

(ii) Higher amines have fishy smell.

(iii) H-Bonding (weaker as compared to $\text{H}-\text{O}-\text{H}$).



(1° amine)



(2° amine)

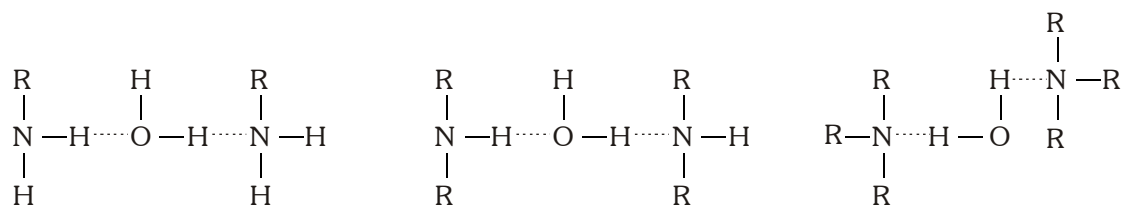
In 3° amine (due to absence of H-atom) H-bonding is not possible.

(iv) **Boiling point** : Due to weak intermolecular H-bonding the B.P. of 1° and 2° amines are lower than those of alcohols of comparable molecular weight. The boiling point of 3° amines which form no H-bonds are near to those of alkanes of comparable molecular weight.

Boiling point $\propto$ molecular weight

Order of B.P. :	1° amine	>	2° amine	>	3° amine
so order of volatility :	3° amine	>	2° amine	>	1° amine

(v) **Solubility** : Low molecular weight amines are soluble in water. The water solubility of amines decreases with increasing size of alkyl group.



(1° amine)

(2° amine)

(3° amine)

Order of solubility $\longrightarrow$ p- amine > s- amine > t- amine

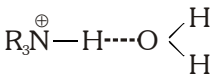
4.0 Chemical properties

- (i) Basic character of amines is due to the presence of lone pair of electrons on the N - atom.
- (ii) Basic strength depends on electron donating tendency.
- (iii) Order of basic character in aqueous solution : $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$
 $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$

GOLDEN KEY POINTS

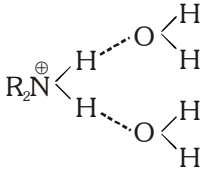
- Tertiary amine is less basic than secondary due to following reasons :
 - (i) **Steric hindrance** : In tertiary amines (R_3N), three alkyl groups attached to N are bulkier and as such exert steric hindrance.
 - (ii) **Decrease in hydration** :

In tertiary amine



Protonated t-amine can form H-bonding with water molecule only at one point
[less stable]

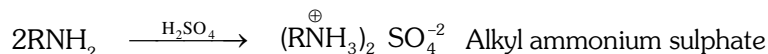
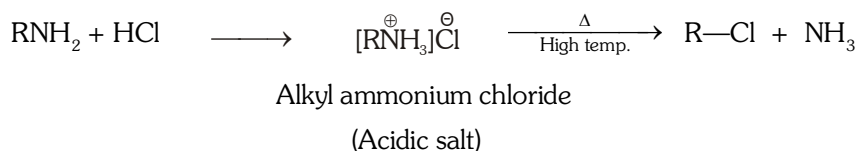
In secondary amine



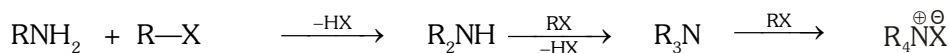
Protonated s-amine can form H-bonding with water molecules at two points
(more stable)
- Conjugate acid of 3° amine are less stable as compared to 2° amine due to low hydration so less basic.
- The basic strength of aniline is less than aliphatic amines as the lone pair of electron present on N-atom interacts with the delocalized π -orbital of benzene ring. Hence it is less available for protonation on N-atom.

(1) Reactions showing basic nature :

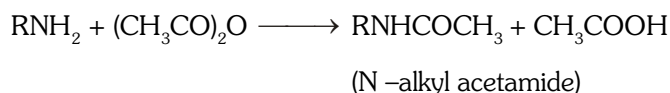
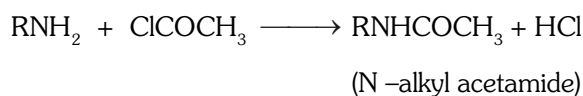
It reacts with acids to form salts.



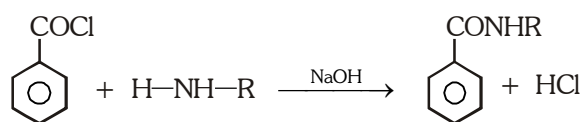
- (2) **Reaction with alkyl halides** : Alkyl amine reacts with alkyl halides and forms sec., ter. amines and quaternary ammonium salt.



- (3) **Acetylation** : Acetylation takes place when alkyl amine combines with acetyl chloride or acetic anhydride.



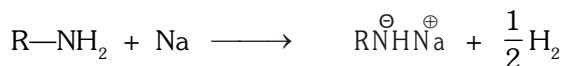
(4) Benzoylation (Schotten Baumann reaction) :



Benzoylchloride

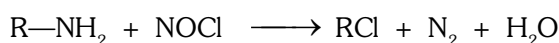
N-alkyl benzamide

(5) Acidic nature : Amines are very weak acids only 1° and 2° amines show acidic nature with active metals.

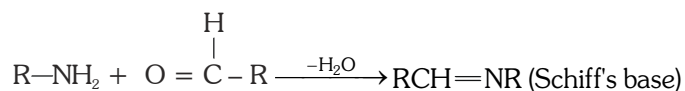


N- alkyl sodamide

(6) Reaction with Tilden reagent :

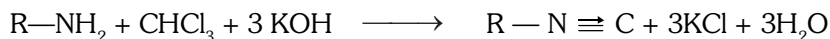


(7) Reaction with aldehydes :

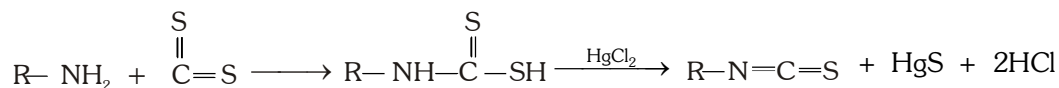


(8) Carbylamine Reaction (Isocyanide test) : When alkyl amine heated with chloroform and alc. KOH alkyl isocyanide is formed which has very bad smell.

This test is also given by aniline . This is a test for p- amines.



(9) Hofmann's mustard oil test : When alkyl amine is heated with carbon disulphide and mercuric chloride alkyl isothiocyanate is formed which has smell like mustard oil.



Alkyl isothiocyanate

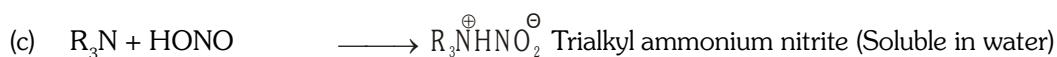


(10) Reaction with HNO₂ :

(a) Primary amines react with nitrous acid to produce nitrogen gas [seen as bubbles]



Dialkylnitroso amine (Yellow oily layer)



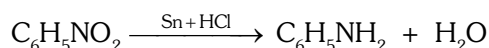
Points to Remember :

- (i) Nitrosoamines are carcinogens (Cancer causing agents)
- (ii) Amines can have chiral N-atom but cannot be resolved into enantiomeric forms because of rapid inversion of one enantiomeric form into the other.
- (iii) The Schiff's bases formed by reaction of 1° amines and aldehyde/ketones are also called anils.
- (iv) The mixture of 1°, 2°, 3° amines can be distinguished by Hofmann's test or Hinsberg's reagent or nitrous acid test.

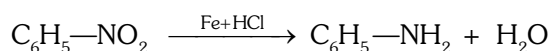
5.0 ANILINE (C₆H₅NH₂)

5.1 General Methods of Preparation

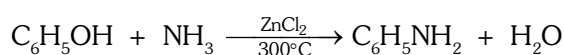
(1) Lab method:



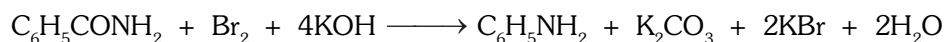
(2) Industrial method :



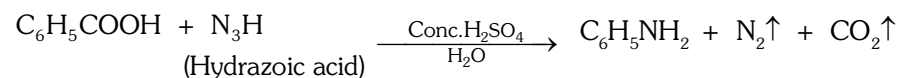
(3) From Phenol :



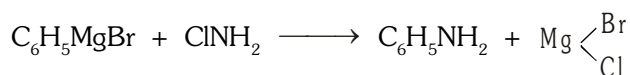
(4) From benzamide (Hofmann's bromamide reaction):



(5) From benzoic acid (Schmidt reaction) :



(6) From Grignard reagent :



(7) From phenyl isocyanide :

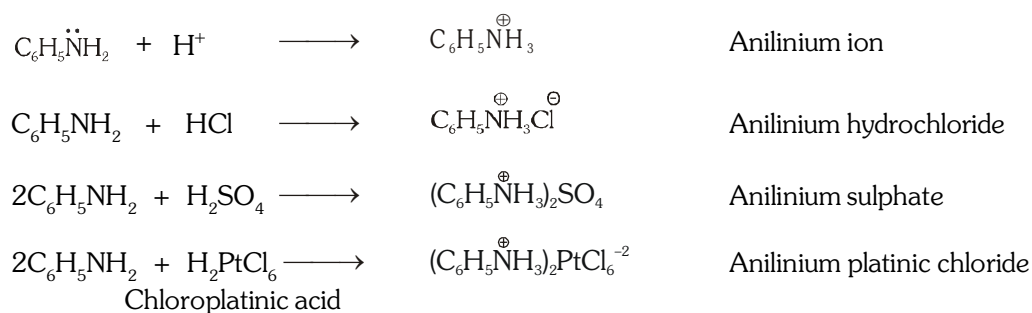


5.2 Physical Properties

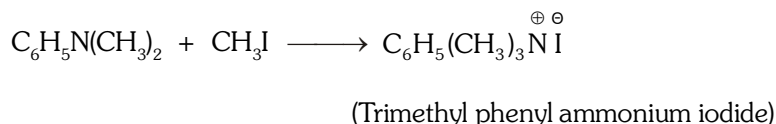
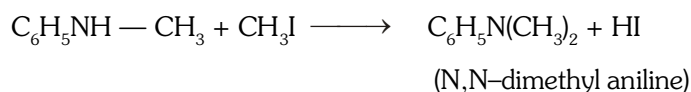
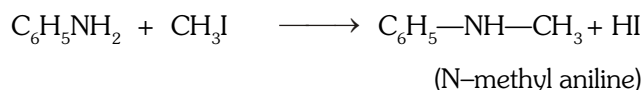
- (i) Fresh, aniline is a colourless oily liquid. On standing the colour becomes dark brown due to action of air and light.
- (ii) It's B.P. is 183°C.
- (iii) It is heavier than water.
- (iv) It has characteristic unpleasant odour. It is toxic in nature.

Reactions due to —NH₂ group

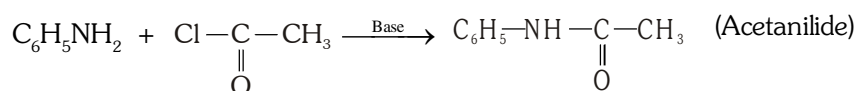
(1) **Basic nature :** Aniline is weak base but it forms salt with strong acids. It accepts a proton.



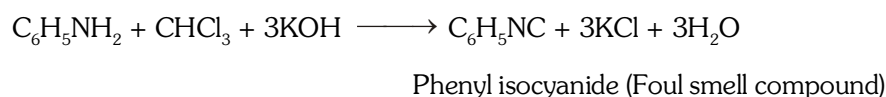
- (2) **Alkylation** : Aniline reacts with alkyl halides forming secondary, tertiary and quaternary ammonium salts depending on the concentration of alkyl halides.



- (3) **Acylation** : Aniline reacts with acid chlorides or anhydrides to form corresponding amides called anilides. [The reaction of $\text{C}_6\text{H}_5\text{NH}_2$ with benzoyl chloride is example of "**Schotten Baumann reaction**"]



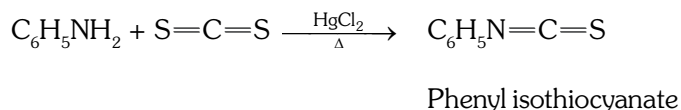
- (4) **Carbylamine reaction** :



Note : (1) Intermediate species is dichloro carbene [$:\text{CCl}_2$].

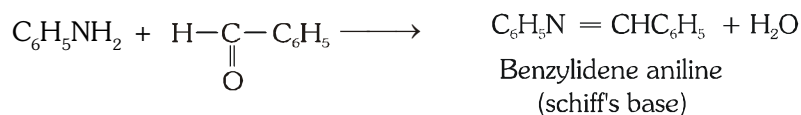
(2) This is test of aniline and other primary amine, known as **Isocyanide test**.

- (5) **Hoffmann's mustard oil reaction** : When aniline is heated with alc. CS_2 and excess of HgCl_2 phenyl isothiocyanate having a characteristic smell of mustard oil is formed.

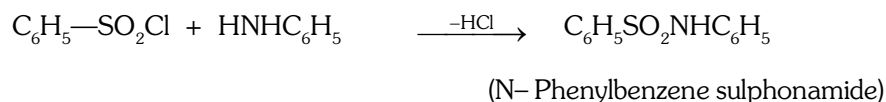


This is a test of aniline and other primary amines.

- (6) **Reaction with aldehydes** : Aniline condenses with aldehydes to form schiff's base.



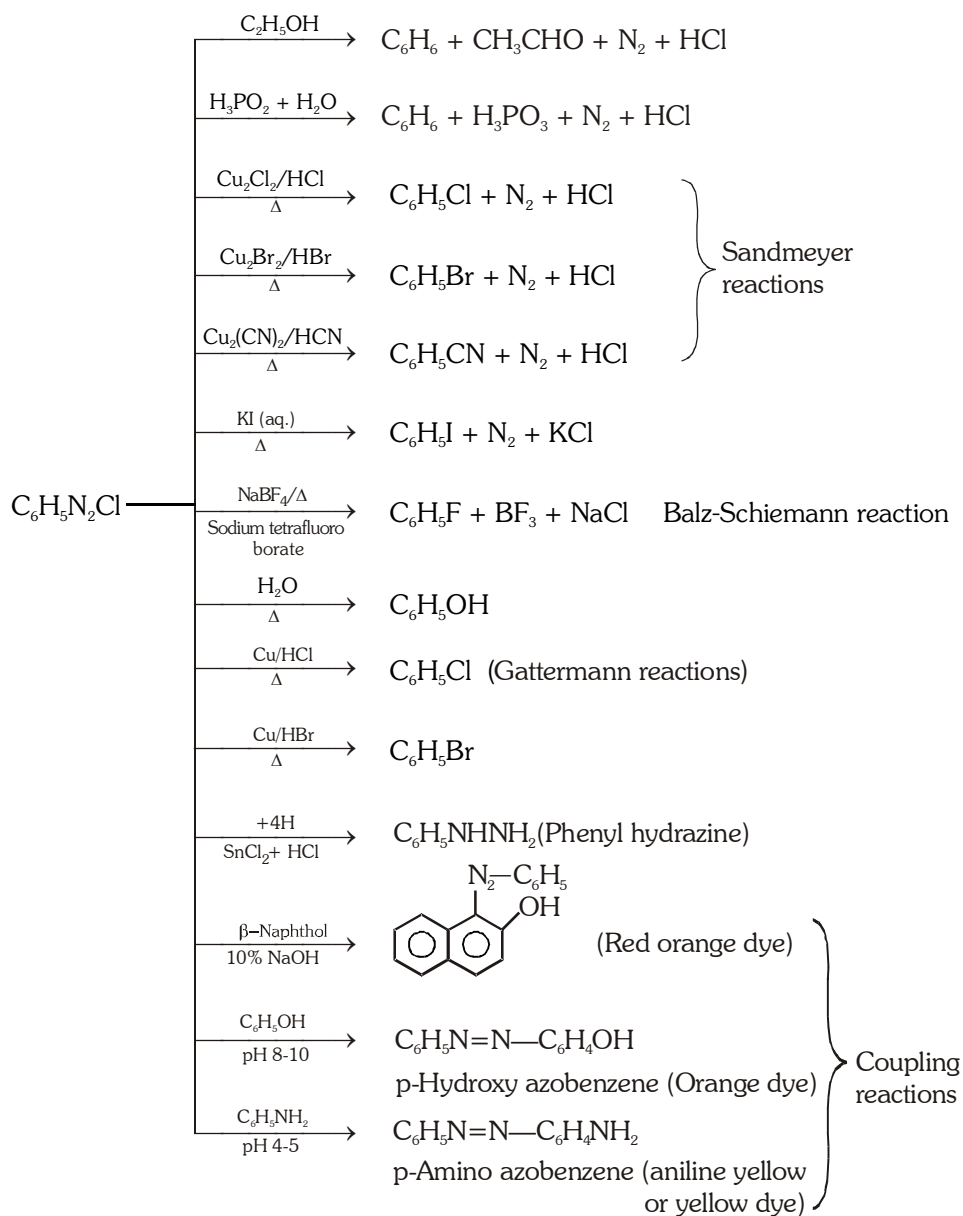
- (7) **Reaction with Hinsberg's reagent** :



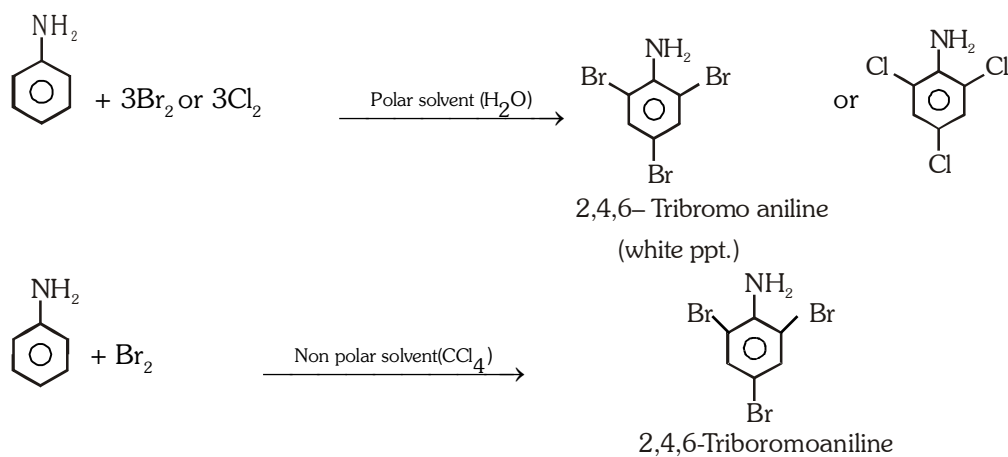
- (8) **Diazotisation** : Diazotisation is a reaction in which ice cooled solution of aniline in an inorganic acid reacts with sodium nitrite solution leading to the formation of diazonium salt.



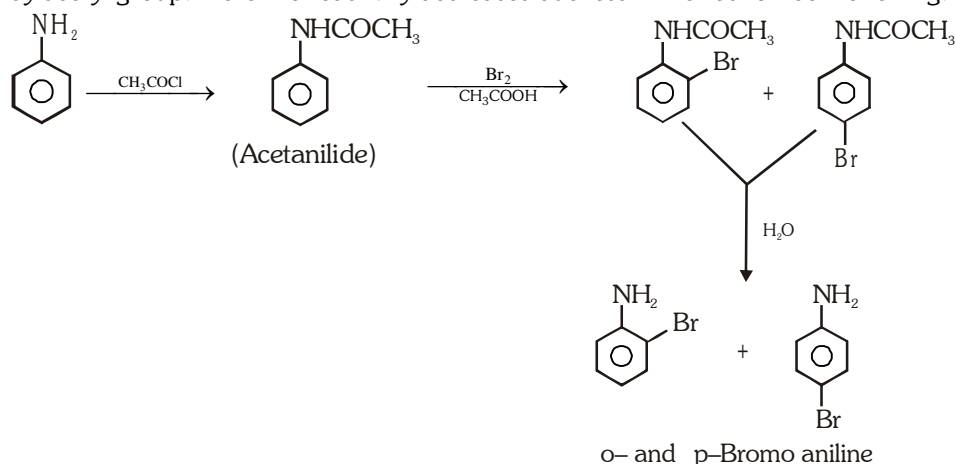
Benzene diazonium chloride is a useful synthetic reagent. It is used in the preparation of many organic compounds



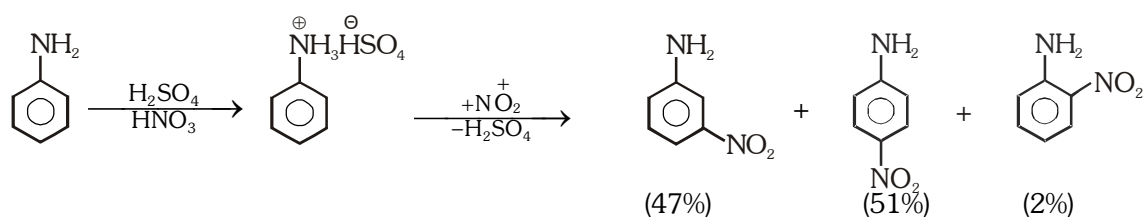
(1) Halogenation : In polar and nonpolar medium Chlorine and bromine react with aniline and form trichloro and tribromo aniline respectively.



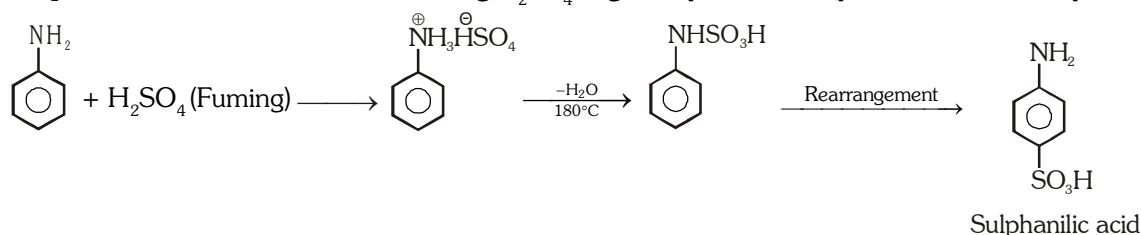
Note : However, monobromo or chloro derivative of aniline can be prepared if $-NH_2$ group is first protected by acetyl group. Here the reactivity decreases due less +M effect on benzene ring.



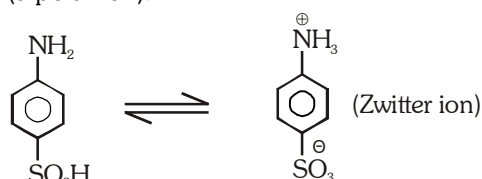
(2) Nitration :



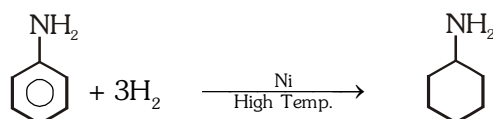
(3) Sulphonation : Aniline reacts with fuming H_2SO_4 to give sulphanilic acid. (p-Amino-benzene sulphonic acid)



- This process is called baking.
- Sulphanilic acid is an important intermediate in the manufacturing of dyes and drugs.
- The compounds in which both proton donating & proton accepting groups present are called amphotile (dipolar ion).

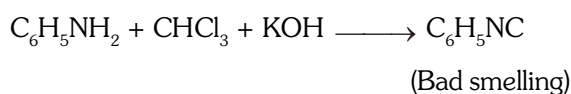


(4) Catalytic hydrogenation : Aniline undergoes hydrogenation in presence of Ni at high temp. to form cyclohexanamine.



5.3 Tests of Aniline

(i) Carbylamine test : Aniline gives carbylamine test or Isocyanide test.



(ii) Dye test : Aniline is first diazotised. On adding alkaline solution. of β -naphthol to the diazotised product a red-orange dye is formed.

(iii) On heating with bromine water, a white ppt. is formed.

BEGINNER'S BOX-1

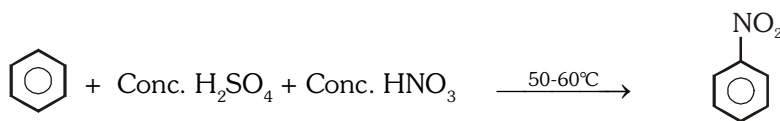
- Which one of following reaction is Schotten–Baumann reaction
(1) Acetylation of RNH_2 (2) Acylation of RNH_2
(3) Benzoylation of RNH_2 (4) All of them
- Which of the following pair will yield primary amine on hydrolysis
(1) CH_3NCO , CH_3NC (2) CH_3CN , CH_3NC
(3) $(\text{CH}_3)_2\text{NH}$, $\text{CH}_3\text{—CH=NOH}$ (4) None of the above
- Methylamine on treatment with chloroform and ethanolic caustic alkali gives foul smelling compound, the compound is
(1) CH_3NCO (2) CH_3CNO (3) CH_3CN (4) CH_3NC

6.0 NITRO BENZENE [$\text{C}_6\text{H}_5\text{NO}_2$]

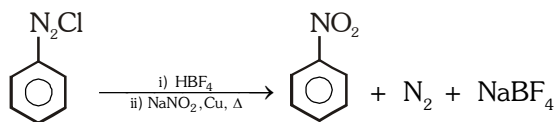
It is also called as artificial oil of bitter almonds or oil of mirbane as its odour is like that of bitter almonds.

6.1 General Methods of Preparation

(1) Lab method :



(2) From diazonium salt :



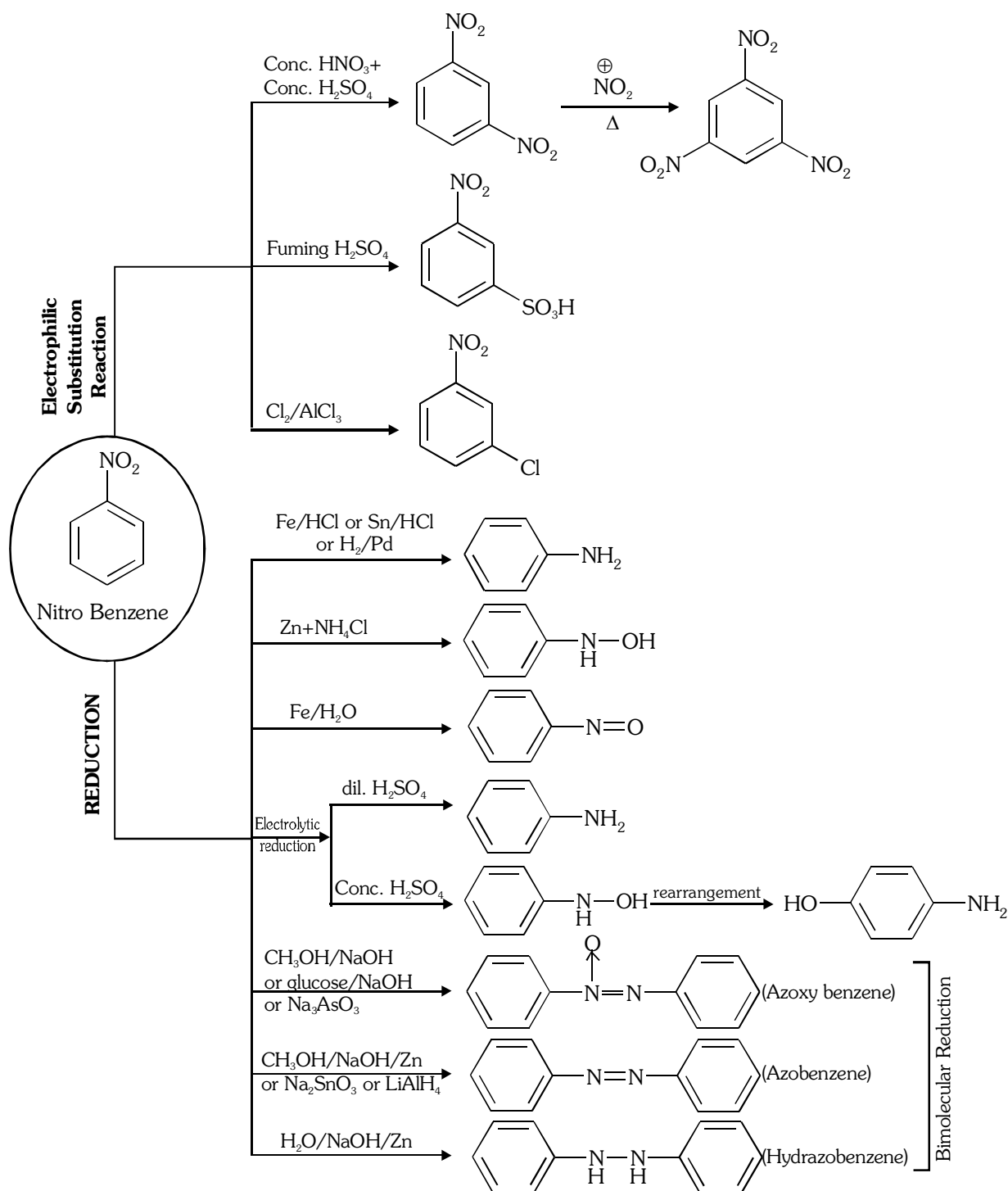
6.2 Physical Properties

- Nitro benzene is light yellow oily liquid
- It has smell of bitter almonds
- It is steam volatile. Its vapours are poisonous in nature.
- It is heavier than water
- Its B. P. is 211°C
- Smell of nitro benzene and benzaldehyde is same

6.3 Chemical Properties

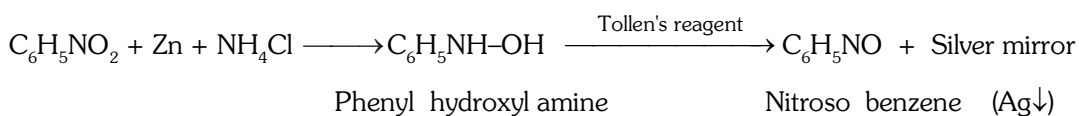
Nitrobenzene shows following chemical reactions –

- Reactions due to NO_2 group.
- Reactions due to benzene ring : (A) Electrophilic substitution (B) Nucleophilic substitution



6.4 Test of Nitrobenzene

Mullikan Barker Test : Ethanolic solution of nitrobenzene is treated with zinc dust and NH_4Cl solution. The mixture is heated and filter in a test tube containing Tollen's reagent a grey or black precipitate (Ag mirror) is formed.

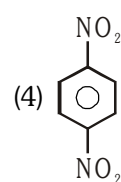
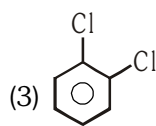
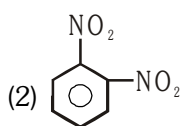
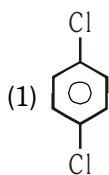


6.5 Uses

- (i) As a solvent
- (ii) In manufacture of aniline and azo dye

BEGINNER'S BOX-2

- Nitration of which of the following compound is difficult :-
 (1) Benzene (2) Nitrobenzene (3) Toluene (4) Phenol
- Nitration of nitrobenzene in presence of fuming nitric acid will generate a :-
 (1) Solid product (2) Gaseous product (3) Semi-solid product (4) Liquid product
- $C_6H_5NO_2 \xrightarrow{Sn/HCl} A \xrightarrow{NaNO_2/HCl} B$; To obtain benzene from B, the suitable reagent is :
 (1) $SnCl_2 + HCl$ (2) H_3PO_2 (3) $C_2H_5N_2Cl$ (4) Methanol
- When nitrobenzene is heated with conc. HNO_3 and conc. H_2SO_4 the product would be obtained :-
 (1) T.N.T. (2) D.N.B. (3) D.D.T. (4) T.E.L.
- Which of the following has the maximum value of dipole moment ?



ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3							
	Ans.	4	1	4							

BEGINNER'S BOX-2	Que.	1	2	3	4	5					
	Ans.	2	1	2	2	2					

EXERCISE-I (Conceptual Questions)**AMINE**

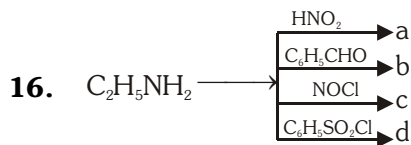
- Among the following which one is not formed in Hoffmann degradation
 (1) RNCO (2) $\text{R}-\ddot{\text{N}}\text{H}_2$
 (3) RCONHBr (4) RNC
- $\text{CH}_3\text{CH}_2\text{CONH}_2 \xrightarrow[\text{Br}_2]{\text{NaOH}} \text{A}$,
 Aqueous solution of A
 (1) Turns blue litmus to red
 (2) Turns red litmus to blue
 (3) Does not affect the litmus
 (4) Decolourise the litmus
- Ethanamine can be obtained if the following compound is heated with $[\text{KOH} + \text{Br}_2]$
 (1) Ethanamide (2) Methanamide
 (3) Propionamide (4) All the above
- $\text{CH}_3\text{CONH}_2 \xrightarrow[\text{I}]{\text{P}_2\text{O}_5} \text{A} \xrightarrow[\text{II}]{\text{Na/EtOH}} \text{B}$
 Reaction II is called
 (1) Clemensen
 (2) Stephen
 (3) Mendius
 (4) Bauveault-blank reduction
- CH_3CONH_2 , Br_2 & KOH give CH_3NH_2 as the product. The intermediates of the reaction are :-
 (a) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHBr}$ (b) $\text{CH}_3-\text{N}=\text{C}=\text{O}$
 (c) CH_3NHBBr (d) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{N} \begin{matrix} \text{Br} \\ \text{Br} \end{matrix}$
 The correct answer is :-
 (1) a, b (2) a, c (3) b, d (4) c, d
- In which case alkylamine is not formed :-
 (1) $\text{R}-\text{X} + \text{NH}_3 \longrightarrow$
 (2) $\text{R}-\text{CH}=\text{NOH} + [\text{H}] \xrightarrow[\text{alc.}]{\text{Na}}$
 (3) $\text{R}-\text{CN} + \text{H}_2\text{O} \xrightarrow{\text{H}^+}$
 (4) $\text{RCONH}_2 + 4[\text{H}] \xrightarrow{\text{LiAlH}_4}$

Build Up Your Understanding

- Tertiary amine is obtained in the reaction :-
 (1) Aniline $\xrightarrow{\text{CH}_3\text{I}} \xrightarrow{\text{CH}_3\text{I}}$
 (2) Aniline $\xrightarrow{\text{CH}_3\text{I}}$
 (3) Nitrobenzene $\xrightarrow{\text{Sn/HCl}}$
 (4) None of the above
- $\text{C}_2\text{H}_5\text{NH}_2$ cannot be prepared by the reduction of
 (1) $\text{C}_2\text{H}_5\text{NO}_2$ (2) $\text{CH}_3\text{CH}=\text{NOH}$
 (3) $\text{C}_2\text{H}_5\text{NC}$ (4) CH_3CN
- Gabriel reaction for the synthesis of amines, involves the use of
 (1) 1° amide (2) 2° amide
 (3) Imides (4) Aliphatic amide
- Gabriel phthalimide reaction is used in the synthesis of
 (1) Primary aromatic amines
 (2) Secondary amines
 (3) Primary aliphatic amines
 (4) Tertiary amines
- The reaction : $[\text{C}_2\text{H}_5\text{Br} + \text{NH}_3]$ is in fact an example of
 (1) Ammonolysis only
 (2) Nucleophilic substitution only
 (3) Ammonolysis as well as nucleophilic substitution
 (4) None
- Melting points are normally the highest for
 (1) Tertiary amides (2) Secondary amides
 (3) Primary amides (4) Amines
- Solubility of ethylamine in water is due to
 (1) Low molecular weight
 (2) Ethyl group is present in ethyl alcohol
 (3) Formation of H-bonding with water
 (4) Being a derivative of ammonia
- Which of the following compound liberates CO_2 when treated with NaHCO_3
 (1) $\text{CH}_3\text{COCH}_2\text{NH}_2$ (2) CH_3NH_2
 (3) $(\text{CH}_3)_4\text{N}^+\text{OH}^-$ (4) $\text{CH}_3\text{NH}_3^+\text{Cl}^-$

15. The product obtained by the alkaline hydrolysis of $C_2H_5-N=C=O$ when treated with t-butyl magnesiumbromide, the compound obtained will be

- (1) t-butylamine (2) n-butylamine
(3) Isobutane (4) n-butane



Which product is a Schiff's base :-

- (1) a (2) b (3) c (4) d

17. Acidic nature of amino group is shown by the reaction :-

- (1) $R-NH_2 + NOCl \rightarrow RCl + N_2 + H_2O$
(2) $2RNH_2 + 2Na \rightarrow 2RNH.Na + H_2$
(3) $R.CH_2NH_2 + HNO_2 \rightarrow R.CH_2OH + N_2 + H_2O$
(4) $R.NH_2 + HCl \rightarrow R\overset{\oplus}{N}H_3 \overset{\ominus}{Cl}$

18. The reagent used in the conversion of $C_2H_5NH_2$ to C_2H_5Cl would be

- (1) SO_2Cl_2 (2) $SOCl_2$
(3) $NOCl$ (4) All

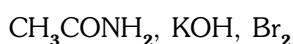
19. Hydrogen attached to nitrogen is released in the reaction

- (1) $RCONH_2 + NaNH_2$
(2) $RNH_2 + Na$
(3) Both the above
(4) None of the above

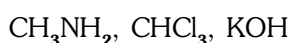
20. If primary amines are treated with ketones the product is

- (1) Urea (2) Guanidine
(3) Amide (4) Schiff's base

21. Reactants of reaction – I are



Reactants of reaction-II are



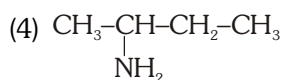
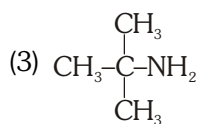
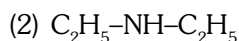
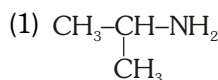
The intermediate species of reaction-I and reaction-II are respectively

- (1) Carbonium ion, carbene
(2) Nitrene, carbene
(3) Carbene, nitrene
(4) Carbocation, carbanion

22. N, N-dimethyl acetamide is obtained in the reaction

- (1) Acetyl chloride and methanamine
(2) Acetyl chloride and ethanamine
(3) Acetyl chloride and dimethylamine
(4) Acetyl chloride and diethylamine

23. This compound does not respond to carbylamine reaction :-



24. Blue litmus can be turned to red by the compound



25. Match List I with List II and select the correct answer using the codes given below :-

List I

[Reagent]

List II

[Used as test reagent for]

A. Ammonical $AgNO_3$

a. Primary amine

B. HIO_4

b. Aldehyde

C. Cold dil. Alkaline $KMnO_4$

c. Vicinal-OH groups

D. Chloroform + $NaOH$

d. Double bond

Codes :

	A	B	C	D
(1)	b	c	a	d
(2)	d	b	a	c
(3)	b	c	d	a
(4)	d	c	b	a

26. Which one of the following aromatic amino compound gives alcohol with HNO_2 :-

- (1) N,N-Dimethylaniline (2) Benzylamine
(3) N-methylaniline (4) Aniline

ANILINE

27. Electrolytic reduction of nitrobenzene in weakly acidic medium gives

- (1) Aniline
(2) p-Hydroxyaniline
(3) N-Phenylhydroxylamine
(4) Nitrosobenzene

28. $\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{\text{Br}_2/\text{CCl}_4} ?$ The product is :-

- (1) Only o-bromoaniline
(2) 2, 4, 6-tribromoaniline
(3) o-and p-bromoaniline

(4) Only p-bromoaniline

29. Before proceeding for the nitration of aminobenzene, the NH_2 group is first protected by:-

- (1) Alkylation
(2) Acetylation
(3) Formylation
(4) Chloromethylation

30. Aniline is purified by :-

- (1) Azeotropic distillation
(2) Steam distillation
(3) distillation in presence of magnesium
(4) Fractional distillation

31. Reaction $\text{C}_6\text{H}_5\text{NH}_2 + \text{HAuCl}_4 \longrightarrow$

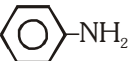
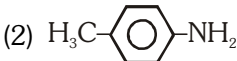
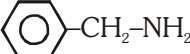
$[\text{C}_6\text{H}_5\text{NH}_3]^+[\text{AuCl}_4]^-$ shows ... behaviour of aniline :-

- (1) Acidic (2) Neutral
(3) Basic (4) Amphoteric

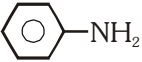
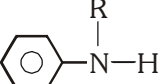
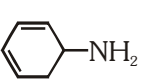
32. Aniline on treatment with bromine water yields white precipitate of :-

- (1) o-Bromoaniline
(2) p-Bromoniline
(3) 2, 4, 6-Tribromoaniline
(4) m-Bromoaniline

33. Which compound does not show diazo reaction:-

- (1)  (2) 
(3)  (4) 

34. Which of the following amines give N-nitroso derivative with NaNO_2 and HCl :-

- (1) $\text{C}_2\text{H}_5\text{NH}_2$ (2) 
(3)  (4) 

35. Which of the following involves nitrene as an intermediate ?

- (1) Carbylamine reaction
(2) Hofmann bromamide reaction
(3) Reimer Tiemann reaction
(4) Friedal crafts reaction

36. Which of the following does not reduce Tollen's reagent :-

- (1) CH_3CHO (2) HCOOH
(3) $\text{C}_6\text{H}_5\text{NHOH}$ (4) $\text{C}_6\text{H}_5\text{NH}_2$

37. Aniline can be obtained by :-

- (1) Benzoyl chloride and ammonia
(2) Reduction of benzamide
(3) Phenol and ammonia in presence of ZnCl_2
(4) Benzoic anhydride and ammonia

38. Aniline on direct nitration produces :-

- (1) o-Nitroaniline (2) m-Nitroaniline
(3) p-Nitroaniline (4) All

39. Nitration of acetanilide followed by hydrolysis gives

- (1) o-Nitroaniline (2) p-Nitroaniline
(3) o- & p-Nitroaniline (4) o-Nitroanilinium ion

40. $\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow[0-5^\circ\text{C}]{\text{NaNO}_2/\text{HCl}} \text{A}$, Which is the incorrect structure of the product 'A' :-

- (1) $\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{Cl}$ (2) $[\text{C}_6\text{H}_5\text{N}_2]^+\text{Cl}^-$
(3) $[\text{C}_6\text{H}_5-\text{N}\equiv\text{N}]^+\text{Cl}^-$ (4) $[\text{C}_6\text{H}_5-\text{N}\equiv\text{N}]^+\text{Cl}^-$

41. Chloroform and ethanolic KOH is used as a reagent in the following reaction :-

- Hoffmann carbylamine reaction
- Hoffmann degradation reaction
- Reimer-Tiemann reaction
- Hoffmann mustard oil reaction

Code is :-

- Only for a
- Only for a and b
- Only for b and d
- Only for a and c

42. Acetanilide when treated with bromine in acetic acid mainly gives :-

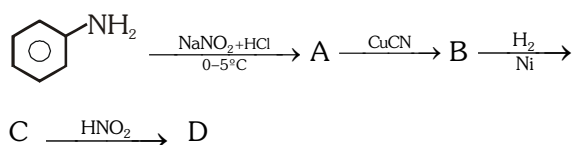
- o-Bromoacetanilide
- N-Bromoacetanilide
- p-Bromoacetanilide
- m-Bromoacetanilide

43. Aromatic nitriles (ArCN) are not prepared by reaction

- $\text{ArX} + \text{KCN}$
- $\text{ArN}_2^+ + \text{CuCN}$
- $\text{ArCONH}_2 + \text{P}_2\text{O}_5$
- $\text{ArCONH}_2 + \text{SOCl}_2$

NITRO GROUP, CYANIDE & ISOCYANIDE

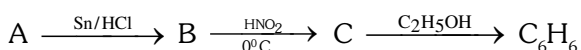
44. Aniline in a set of reactions yielded end product D



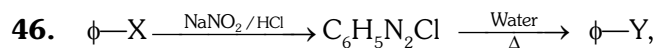
The structure of the product D would be

- $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
- $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$
- $\text{C}_6\text{H}_5\text{NHOH}$
- $\text{C}_6\text{H}_5\text{NHCH}_2\text{CH}_3$

45. In the reaction sequence identify the functional group present in A, B, C :-



- NO_2 , NH_2 , $\text{N}=\text{N}$
- NO_2 , NH_2 , OH
- $-\text{OH}$, $-\text{NH}_2$, $-\text{NO}$
- $-\text{NH}_2$, $-\text{NO}_2$, $-\text{N}=\text{N}-$



In the above sequence X and Y are :-

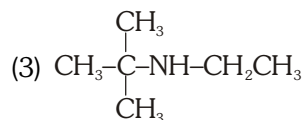
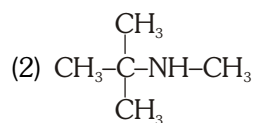
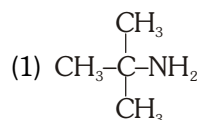
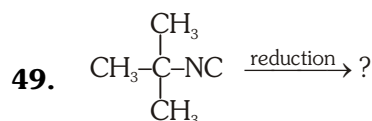
- o-, p- and m-directing
- o-, p- and o-, p-directing
- m and m directing
- m and o, p directing

47. Which of the following compound gives an explosive on decarboxylation :-

- 2,4,6-Trinitrobenzoic acid
- 2,4-Dinitrobenzoic acid
- o-Aminobenzoic acid
- o-Hydroxybenzoic acid

48. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was:-

- Methylisocyanate
- Methylamine
- Ammonia
- Phosgene



(4) None

50. Reaction of RCN with sodium and alcohol leads to the formation of :-

- RCONH_2
- $\text{RCOO}^-\text{NH}_4^+$
- RCH_2NH_2
- $\text{R}(\text{CH}_2)_3\text{NH}_2$

51. $C_6H_5NO_2 \xrightarrow{SnCl_2/HCl} A \xrightarrow[0^\circ C]{NaNO_2/HCl} B$; In the above sequence Benzene from B, is suitably obtained by using :-

- (1) Ethanol
- (2) H_3PO_2
- (3) Both the above
- (4) Methanol

52. Which reagent is used to get iodo benzene from benzene diazonium acid sulphate $[C_6H_5N_2HSO_4]$:

- (1) $CuBr, \Delta$
- (2) Cu powder + HI
- (3) KI, Δ
- (4) None

53. Which of the following is used as a solvent in the Friedel-Crafts reaction :-

- (1) Toluene
- (2) Nitrobenzene
- (3) Benzene
- (4) Aniline

54. Match list I with II and choose the correct answer from the codes given below :-

List I

(A) Aniline

(B) Nitrobenzene

(C) Sulphanilamide

(D) Trinitrotoluene

List II

a. Used in making azo dyes

b. Sulpha drug

c. Solvent in the Friedel Crafts reaction

d. Used as explosive

Code is :-

	A	B	C	D
(1)	a	c	b	d
(2)	a	b	c	d
(3)	c	d	a	b
(4)	d	c	b	a

55. In the Sandmeyer's reaction, $-N=N-X$ group of diazonium salt is replaced by :-

- (1) Halide group
- (2) Nitro group
- (3) $-OH$ group
- (4) $-NHNH_2$ group

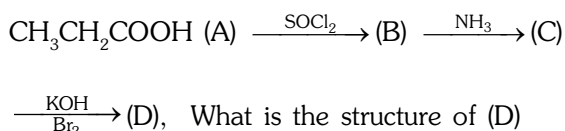
EXERCISE-I (Conceptual Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	2	3	3	1	3	1	3	3	3	3	3	3	4	3
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	2	2	3	3	4	2	3	2	4	3	2	1	2	2	2
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	3	3	4	3	2	4	3	4	3	1	4	3	1	1	1
Que.	46	47	48	49	50	51	52	53	54	55					
Ans.	2	1	1	2	3	3	3	2	1	1					

EXERCISE-II (Previous Year Questions)**AIPMT/NEET & AIIMS (2006-2018)****AIPMT 2006**

1. In a set of reactions propionic acid yielded a compound (D) ;



- (1) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ (2) $\text{CH}_3\text{CH}_2\text{CONH}_2$
 (3) $\text{CH}_3\text{CH}_2\text{NHCH}_3$ (4) $\text{CH}_3\text{CH}_2\text{NH}_2$

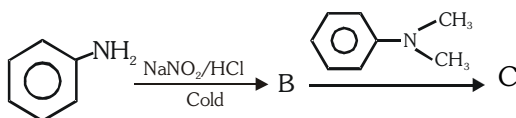
AIPMT 2007

2. Which one of the following on reduction with LiAlH_4 yields a secondary amine

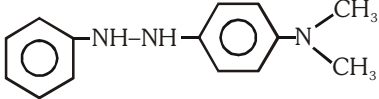
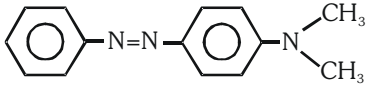
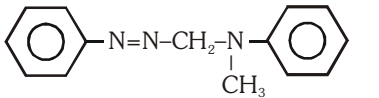
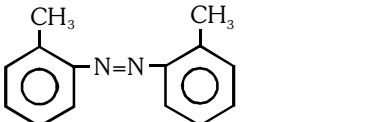
- (1) Methyl isocyanide
 (2) Acetamide
 (3) Methyl cyanide
 (4) Nitro ethane

AIPMT 2008

3. In a reaction of aniline a coloured product C was obtained.

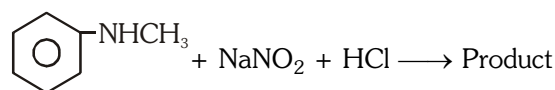


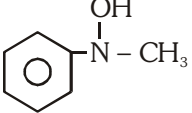
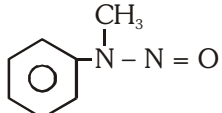
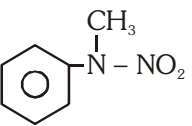
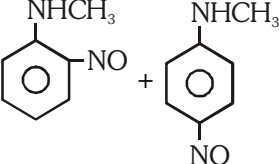
The structure C would be :

- (1) 
 (2) 
 (3) 
 (4) 

AIPMT 2009

4. Predict the product :



- (1)  (2) 
 (3)  (4) 

AIPMT 2010

5. Which of the following statements about primary amines is 'False' ?

- (1) Alkyl amines are stronger bases than ammonia
 (2) Alkyl amines are stronger bases than aryl amines
 (3) Alkyl amines react with nitrous acid to produce alcohols
 (4) Aryl amines react with nitrous acid to produce phenols

6. Acetamide is treated with the following reagents separately. Which one of these would yield methyl amine ?

- (1) PCl_5 (2) NaOH/Br_2
 (3) Sodalime (4) Hot conc. H_2SO_4

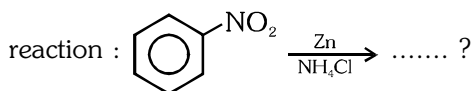
AIIMS 2010

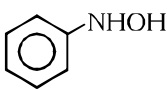
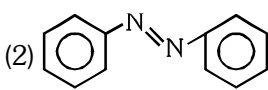
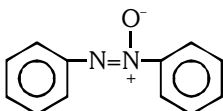
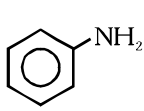
7. Which of the following gives a soluble complex on reaction with benzene sulphonyl chloride (which of the following compounds after reacting with benzene sulphonyl chloride is soluble in alkali solution) :-

- (1) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$
 (2) $\text{CH}_3\text{CH}_2\text{NHCH}_3$
 (3) $\text{CH}_3\text{CH}_2\text{OH}$
 (4) $(\text{CH}_3)_3\text{N}$

AIPMT Pre. 2011

8. What is the product obtained in the following



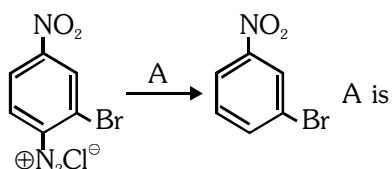
- (1)  (2) 
 (3)  (4) 

AIPMT Mains 2012

9. An organic compound C_3H_9N (A), when treated with nitrous acid, gave an alcohol and N_2 gas was evolved. (A) on warming with $CHCl_3$ and caustic potash gave (C) which on reduction gave isopropylmethylamine. Predict the structure of (A):

- (1) $CH_3 - \underset{\text{CH}_3}{\text{N}} - CH_3$ (2) $CH_3CH_2CH_2-NH_2$
 (3) $\begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} \text{CH} - NH_2$ (4) $CH_3CH_2-NH-CH_3$

NEET UG 2013

10. In the reaction  A is

- (1) H^+/H_2O (2) $HgSO_4/H_2SO_4$
 (3) Cu_2Cl_2 (4) H_3PO_2 and H_2O

11. Nitrobenzene on reaction with conc. HNO_3/H_2SO_4 at $80-100^\circ C$ forms which one of the following products ?

- (1) 1, 2, 4-Trinitrobenzene
 (2) 1, 2-Dinitrobenzene
 (3) 1, 3-Dinitrobenzene
 (4) 1, 4-Dinitrobenzene

AIIMS 2013

12. Reaction of aniline with HNO_2 followed by treatment of dilute acid gives :-

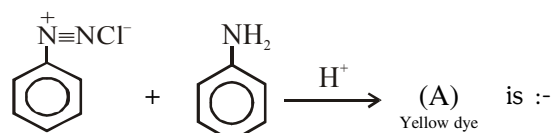
- (1) C_6H_5NHOH (2) C_6H_5OH
 (3) $C_6H_5NHNH_2$ (4) C_6H_6

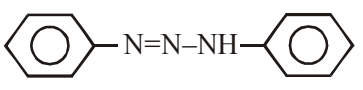
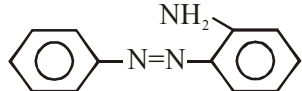
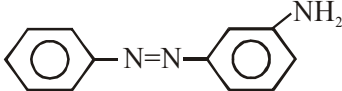
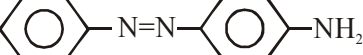
13. Which of the following will give carbylamine test?

- (1) CH_3NH_2 (2) CH_3NHCH_3
 (3) $(CH_3)_3N$ (4) CH_3CONH_2

AIPMT 2014

14. In the following reaction, the product (A)



- (1) 
 (2) 
 (3) 
 (4) 

15. Which of the following will be most stable diazonium salt $RN_2^+X^-$?

- (1) $CH_3N_2^+X^-$ (2) $C_6H_5N_2^+X^-$
 (3) $CH_3CH_2N_2^+X^-$ (4) $C_6H_5CH_2N_2^+X^-$

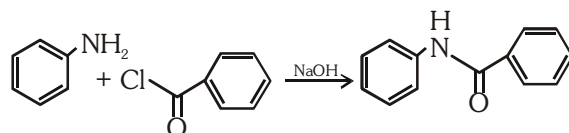
AIPMT 2015

16. The electrolytic reduction of nitrobenzene in strongly acidic medium produces :-

- (1) Azoxybenzene (2) Azobenzene
 (3) Aniline (4) p-Aminophenol

RE-AIPMT 2015

17. The following reaction



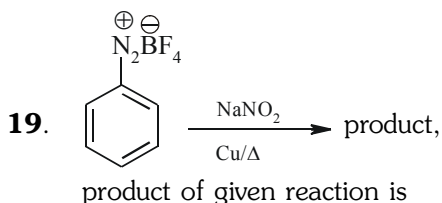
is known by the name :

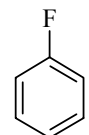
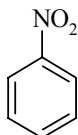
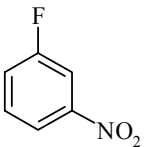
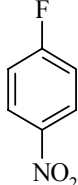
- (1) Acetylation reaction
 (2) Schotten-Baumann reaction
 (3) Friedel-Craft's reaction
 (4) Perkin's reaction

18. Method by which Aniline cannot be prepared is :-

- (1) reduction of nitrobenzene with H_2/Pd in ethanol
- (2) potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution
- (3) hydrolysis of phenylisocyanide with acidic solution
- (4) degradation of benzamide with bromine in alkaline solution

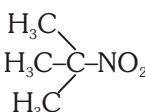
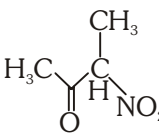
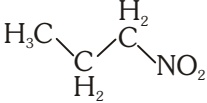
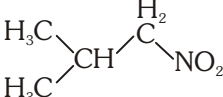
AIIMS 2015



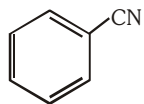
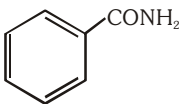
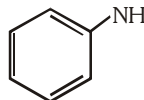
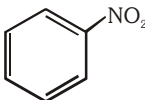
- (1) 
- (2) 
- (3) 
- (4) 

NEET-II 2016

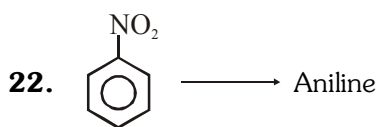
20. Which one of the following nitro-compounds does not react with nitrous acid ?

- (1) 
- (2) 
- (3) 
- (4) 

21. A given nitrogen-containing aromatic compound (A) reacts with Sn/HCl , followed by HNO_2 to give an unstable compound (B). (B), on treatment with phenol, forms a beautiful coloured compound (C) with the molecular formula $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}$. The structure of compound (A) is :-

- (1) 
- (2) 
- (3) 
- (4) 

AIIMS 2016



Aniline will not be prepared in presence of :-

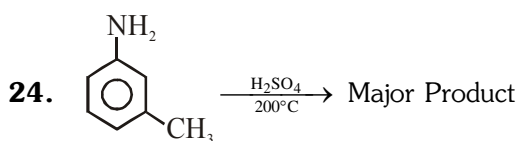
- (1) $\text{Sn} + \text{HCl}$
- (2) $\text{Fe} + \text{HCl}$
- (3) $\text{Zn} + \text{NH}_4\text{Cl}$
- (4) H_2/Pd

NEET(UG) 2017

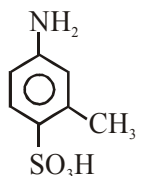
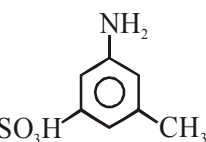
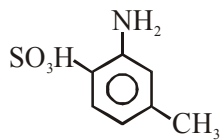
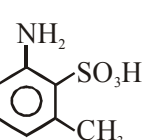
23. Which of the following reactions is appropriate for converting acetamide to methanamine ?

- (1) Hoffmann hypobromamide reaction
- (2) Stephens reaction
- (3) Gabriels phthalimide synthesis
- (4) Carbylamine reaction

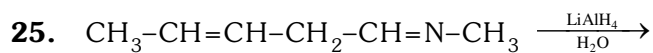
AIIMS 2017



Major product of this reaction is :-

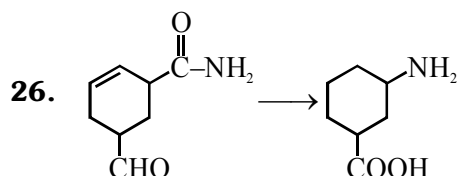
- (1) 
- (2) 
- (3) 
- (4) 

AIIMS 2018



product.

- (1) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_3$
- (2) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_3$
- (3) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}=\text{N}-\text{CH}_3$
- (4) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{N}-\text{CH}_3$



Select the correct sequence of reagents for the above conversion.

- (1) H_2 -Pd/c ; Br_2/KOH , Tollen's Reagent
- (2) Tollen's Reagent, Br_2/KOH , H_2 -Pd-c
- (3) Br_2/KOH , Tollen's Reagent, Br_2/KOH
- (4) H_2 -Pd-c, Tollen's Reagent, Br_2/KOH

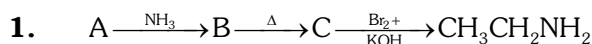
27. Which of the following is incorrect statement regarding diazo salt :-

- (1) On reaction with $\text{C}_2\text{H}_5\text{OH}$, it form benzene
- (2) on reaction with HCN/CuCN it forms 
- (3) It gives nitrobenzene with NaNO_2
- (4) It gives iodobenzene with KI/Δ

EXERCISE-II (Previous Year Questions)

ANSWER KEY

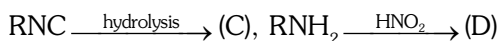
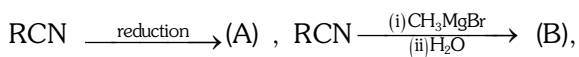
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	1	2	2	4	2	1	1	3	4	3	2	1	4	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27			
Ans.	4	2	2	2	1	4	3	1	1	1	2	3			

EXERCISE-III (Analytical Questions)**Check Your Understanding**

A is :-

- (1) CH_3COOH
- (2) $CH_3CH_2CH_2COOH$
- (3) $CH_3-\underset{\text{CH}_3}{\text{CH}}-COOH$
- (4) CH_3CH_2COOH

2. The correct set of the products obtained in the following reactions

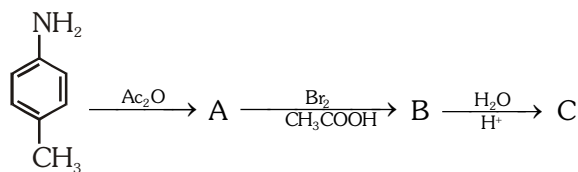


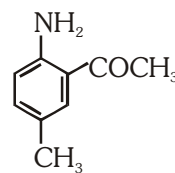
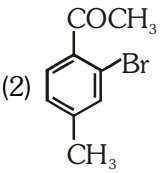
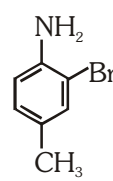
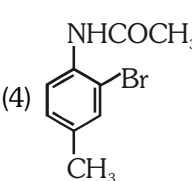
The answer is

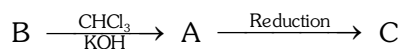
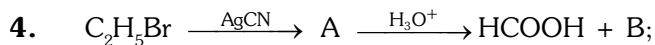
A B C D

- (1) 2°Amine Methyl ketone 1°Amine Alcohol
- (2) 1°Amine Methyl ketone 1°Amine Alcohol
- (3) 2°Amine Methyl ketone 2°Amine Acid
- (4) 1°Amine Methyl ketone 2°Amine Aldehyde

3. The final product C, obtained in this reaction would be

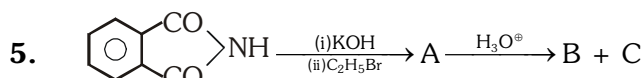


- (1) 
- (2) 
- (3) 
- (4) 



A, B, C respectively in the above sequence are

- (1) Ethane amine, methane nitrile and diethyl amine
- (2) Carbyl amino ethane, ethane amine and primary amine
- (3) Ethyl isocyanide, ethyl amine and methyl isocyanate
- (4) Carbylamino ethane, ethanamine and ethyl methyl amine

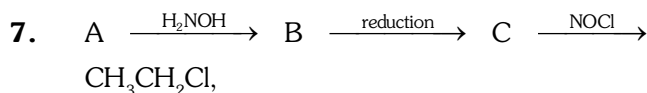


B and C in the above sequence are

- (1) Benzoic acid + aniline
 - (2) Phthalic acid + ethylamine
 - (3) Phthalic acid + aniline
 - (4) Benzoic acid + ethylamine
6. The end-product in the reaction sequence would be :



- (1) Ethyl cyanide
- (2) Ethyl amine
- (3) Methyl amine
- (4) Acetamide

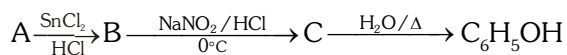


A and C in the above sequence respectively are:-

- (1) Methanal, Methylamine
 - (2) Acetone, ethanamine
 - (3) Ethanal, dimethylamine
 - (4) Acetaldehyde, ethylamine
8. A compound of mol. wt. 180 gm is acetylated to give a compound of mol. wt. 390. The number of amino groups in the compound are :-

- (1) 2
- (2) 4
- (3) 5
- (4) 6

9. In the reaction sequence A, B and C are :-



- (1) Benzene, nitrobenzene, aniline
- (2) Nitrobenzene, aniline and azo-compound
- (3) Nitrobenzene, benzene, aniline
- (4) Benzene, amino compound, aniline

10. Which one of the following tests can be used to identify primary amino group in a given organic compound

- (1) Iodoform test
- (2) Victor Meyer's test
- (3) Carbylamine reaction
- (4) Libermann's reaction

11. At 0°C temperature reaction of aniline with HNO_2 and subsequent treatment with alkaline β -naphthol solution produces a precipitate whose colour would be :-

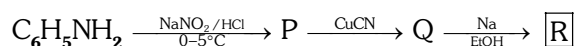
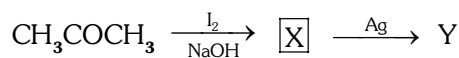
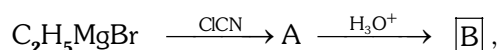
- (1) Black
- (2) Purple
- (3) White
- (4) Orange

12. $\text{CH}_3\text{Cl} \xrightarrow{\text{KCN}} \xrightarrow{+4\text{H}} \text{A} \xrightarrow{\text{NaNO}_2/\text{HCl}} \text{Ethanol} + ?$

Apart from ethanol as the main product, the other products would be

- (1) $\text{H}_2\text{C}=\text{CH}_2$
- (2) $\text{CH}_3\text{CH}_2\text{-ONO}$
- (3) $\text{CH}_3\text{CH}_2\text{-Cl}$
- (4) All the above

13. Identify B, X and R respectively in the following sequence of reactions



- (1) $\text{C}_2\text{H}_5\text{COOH}$, CHI_3 , $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$
- (2) $\text{C}_2\text{H}_5\text{COOH}$, CH_3I , $\text{C}_6\text{H}_5\text{COOH}$
- (3) $\text{C}_2\text{H}_5\text{CH}_2\text{NH}_2$, CH_3I , $\text{C}_6\text{H}_5\text{COOH}$
- (4) $\text{C}_2\text{H}_5\text{COOH}$, $\text{C}_2\text{H}_5\text{I}$, $\text{C}_6\text{H}_5\text{CONH}_2$

14. Using Fe/HCl , which one of the following reaction is possible [Here $\phi = \text{C}_6\text{H}_5$]

- (1) $\phi\text{-NO}_2 \rightarrow \phi\text{-NH-NH-}\phi$
- (2) $\phi\text{-NO}_2 \rightarrow \phi\text{-NH}_2$
- (3) $\phi\text{-NO}_2 \rightarrow \phi\text{-NHOH}$
- (4) $\phi\text{-NO}_2 \rightarrow \phi\text{-N=N-}\phi$

15. An aromatic compound A on treatment with $\text{Zn}/\text{NH}_4\text{Cl}$, and subsequent filtration in ammonical silver nitrate solution gives a black precipitate. Hence compound A bears the group :-

- (1) -COOH
- (2) -NO_2
- (3) -CHO
- (4) -NH_2

EXERCISE-III (Analytical Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	2	3	4	2	2	4	3	2	3	4	4	1	2	2

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

1. **Assertion :-** Boiling point of trimethyl amine is higher than that of n-propyl amine.

Reason :- H-bonding is stronger in tertiary amines.

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

2. **Assertion :-** $\text{H}-\text{C}-\text{N}-\text{CH}_3$ and $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 \end{array}$

$\text{CH}_3-\text{C}-\text{NH}-\text{CH}_3$ are metamers.

Reason :- There is adjustment of $-\text{CH}_2-$ group in the molecule.

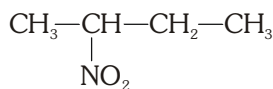
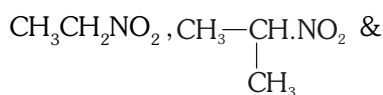
(1) A (2) B (3) C (4) D

3. **Assertion :-** Pyrole is alicyclic compound.

Reason :- It is aliphatic in nature and has cyclic chain.

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

4. **Assertion :-** The following compound are given below –



all three compounds are soluble in NaOH.

Reason :- All above compound have lower boiling than CH_3NO_2 .

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

5. **Assertion :-** Acetonitrile is another name of ethanenitrile.

Reason :- α -H atom of acetonitrile exhibit acidic character.

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

6. **Assertion :-** Benzene diazonium chloride on reaction with ethanol gives benzene.

Reason :- Ethanol is good oxidising agent.

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

7. **Assertion :-** Diazonium salt is prepared at low temperature.

Reason :- Diazonium salt is hydrolysed to give phenol.

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

8. **Assertion :-** Carbylamine reaction involves reaction between 1° amine and chloroform in basic medium to give isocyanide.

Reason :- Methylene ($:\text{CH}_2$) carbene is formed as a reaction intermediate.

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

9. **Assertion :-** Suitable method for preparation of primary amine is when haloalkane is treated with excess of NH_3 .

Reason :- In this reaction primary, secondary, tertiary amines are formed.

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

Que.	1	2	3	4	5	6	7	8	9
Ans.	4	4	4	3	2	3	1	3	3

BIOMOLECULES

4.0 INTRODUCTION :

Complex organic compound which governs the common activities of the living organism are called biomolecules. Living systems are made up of various complex biomolecules like carbohydrates, proteins, nucleic acids, lipids, etc. In addition, some simple molecules like vitamins and mineral salts also play an important role in the functions of organisms.

4.1 CARBOHYDRATES

Carbohydrates are primarily produced by plants and form a very large group of naturally occurring organic compounds. Some common examples are cane sugar, glucose, starch, etc. Most of them have a **general formula, $C_x(H_2O)_y$** , and were considered as hydrates of carbon from where the name carbohydrate was derived. For example, the molecular formula of glucose ($C_6H_{12}O_6$) fits into this general formula, $C_6(H_2O)_6$. **But all the compounds which fit into this formula may not be classified as carbohydrates. Rhamnose, $C_6H_{12}O_5$ is a carbohydrate but does not fit in this definition.** Chemically, *the carbohydrates may be defined as optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis.* Some of the carbohydrates, which are sweet in taste, are also called sugars. **The most common sugar, used in our homes is named as sucrose whereas the sugar present in milk is known as lactose.**

4.1.1 Classification of Carbohydrates :

Carbohydrates are classified on the basis of their behaviour on hydrolysis. They have been broadly divided into following three groups.

(i) Monosaccharides :

A carbohydrate that cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone is called a **monosaccharide**. Some common examples are glucose, fructose, ribose, etc.

Monosaccharides are further classified on the basis of number of carbon atoms and the functional group present in them. If a monosaccharide contains an aldehyde group, it is known as an **aldose** and if it contains a keto group, it is known as a **ketose**. Number of carbon atoms constituting the monosaccharide is also introduced in the name as is evident from the examples given in Table

Different Types of Monosaccharides

Carbon Atom	General term	Aldehyde	Ketone
3	Triose	Aldotriose	Ketotriose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose
7	Heptose	Aldoheptose	Ketoheptose

(ii) Oligosaccharides :

Carbohydrates that yield two to ten monosaccharide units, on hydrolysis, are called oligosaccharides. They are further classified as disaccharides, trisaccharides, tetrasaccharides, etc., depending upon the number of monosaccharides, they provide on hydrolysis. Amongst these the most common are disaccharides. The two monosaccharide units obtained on hydrolysis of a disaccharide may be same or different. For example, sucrose on hydrolysis gives one molecule each of glucose and fructose whereas maltose gives two molecules of glucose only.

(iii) Polysaccharides :

Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called polysaccharides. Some common examples are starch, cellulose, glycogen, etc. Polysaccharides are not sweet in taste, hence they are also called **non-sugars**.

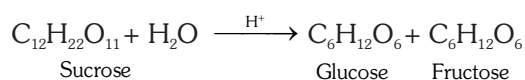
The carbohydrates may also be classified as either reducing or non-reducing sugars. All those carbohydrates which reduce Fehling's solution and Tollens' reagent are referred to as reducing sugars. All monosaccharides whether aldose or **ketose are reducing sugars**.

In disaccharides, if the reducing groups of monosaccharides i.e., aldehydic or ketonic groups are bonded, these are **non-reducing sugars e.g. sucrose**. On the other hand, sugars in which these functional groups are free, are called reducing sugars, for example, maltose and lactose.

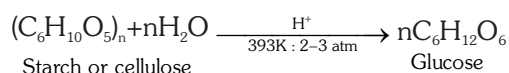
4.1.2 GLUCOSE (ALDOHEXOSE)

Preparation of Glucose

1. **From sucrose (Cane sugar):** If sucrose is boiled with dilute HCl or H₂SO₄ in alcoholic solution, glucose and fructose are obtained in equal amounts.

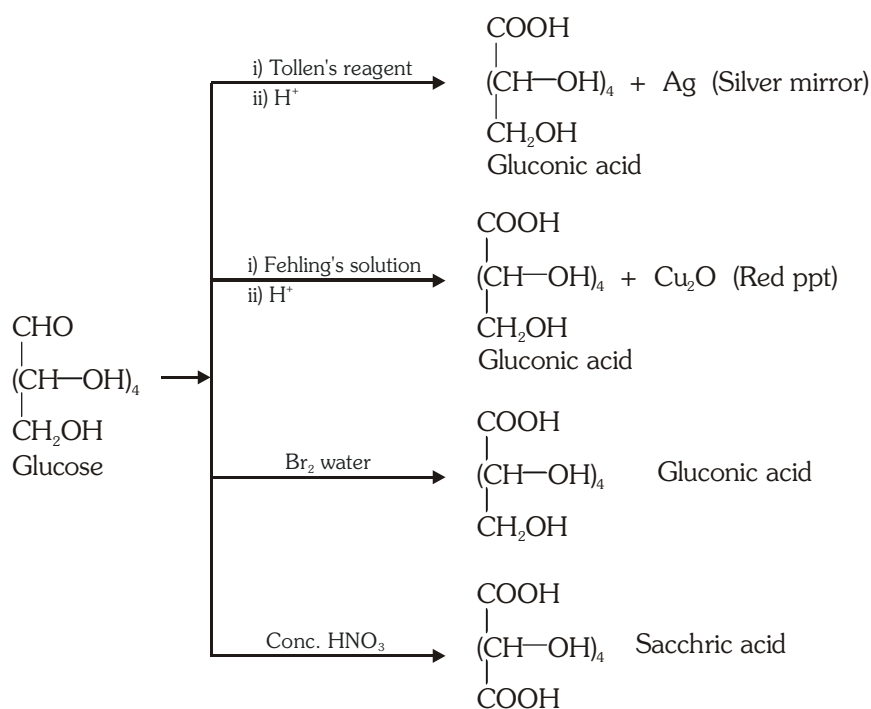


2. **From starch :** Commercially glucose is obtained by hydrolysis of starch by boiling it with dilute H₂SO₄ at 393 K under pressure.

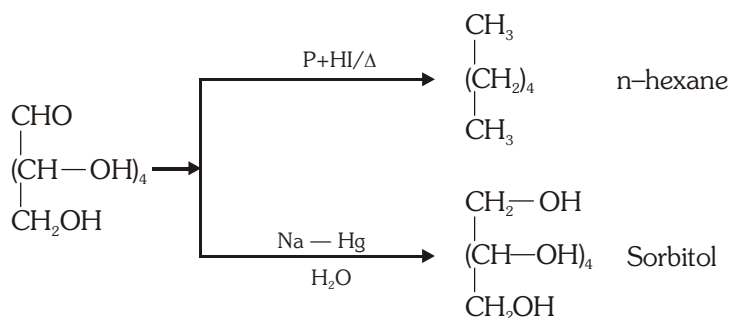


Chemical reactions of Glucose :

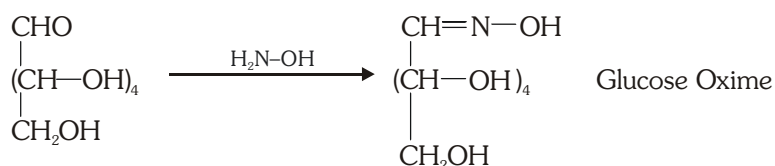
1. **Oxidation :**



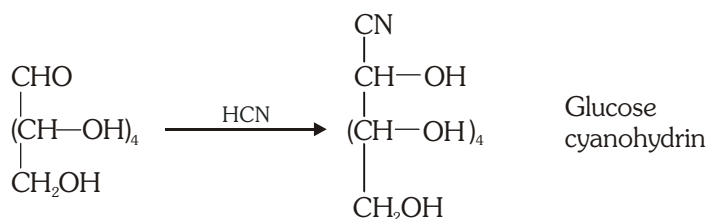
2. Reduction :



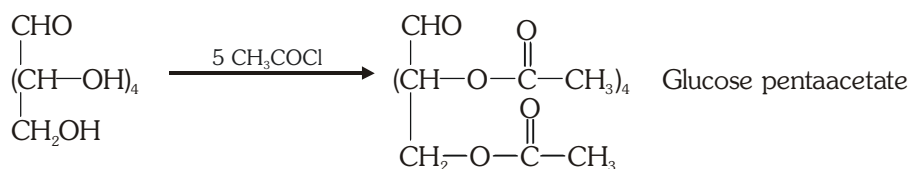
3. Reaction with hydroxyl amine :



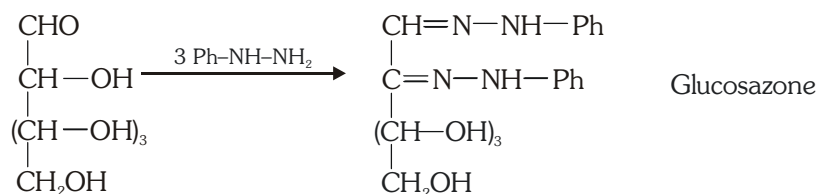
4. Reaction with hydrogen cyanide :



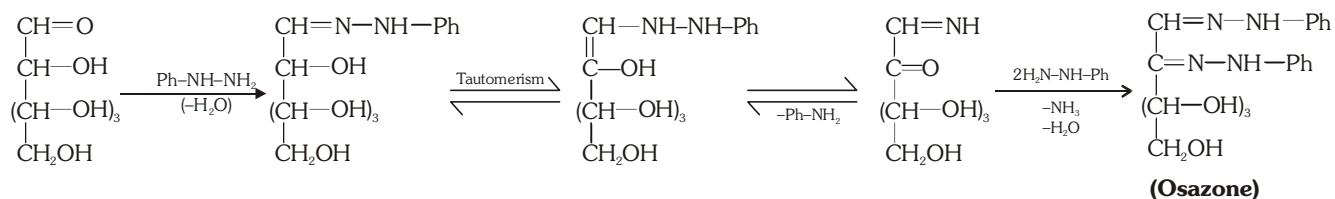
5. Acetylation :



6. Reaction with phenyl hydrazine :

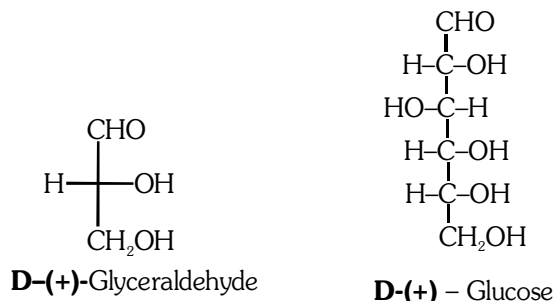


Mechanism :



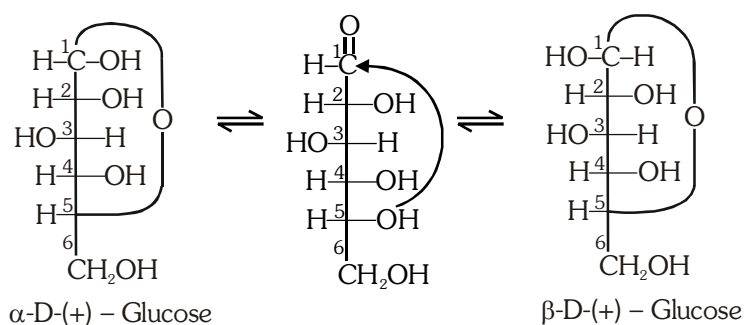
Configuration in monosaccharides :

For assigning the configuration of monosaccharides, it is the lowest asymmetric carbon atom (as shown below) which is compared. As in (+) glucose, —OH on the lowest asymmetric carbon is on the right side which is comparable to (+) glyceraldehyde, so it is assigned D-configuration.

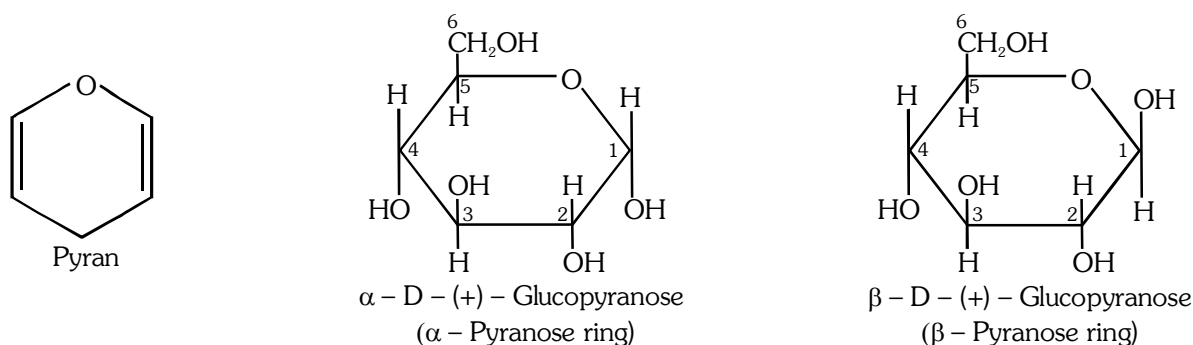


Cyclic structure of Glucose :-

It was found that glucose forms a six-membered ring in which —OH at C-5 is involved in ring formation. This explains the absence of —CHO group and also existence of glucose in two forms as shown below. These two cyclic forms exist in equilibrium with open chain structure.



The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C₁, called anomeric carbon (the aldehyde carbon before cyclisation). Such isomers, i.e., α -form and β -form, are called **anomers**. The six membered cyclic structure of glucose is called **pyranose structure** (α - or β -), in analogy with pyran. Pyran is a cyclic organic compound with one oxygen atom and five carbon atoms in the ring. The cyclic structure of glucose is more correctly represented by **Haworth structure** as given below.

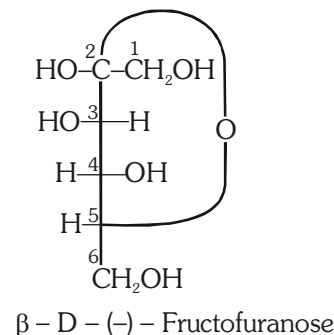
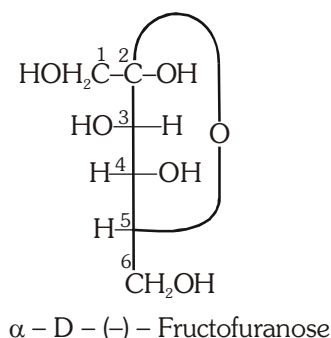
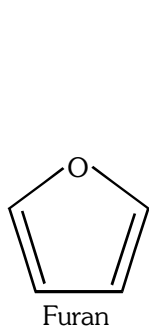
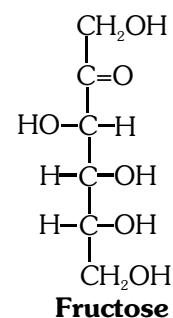


4.1.3 FRUCTOSE (KETOHEXOSE)

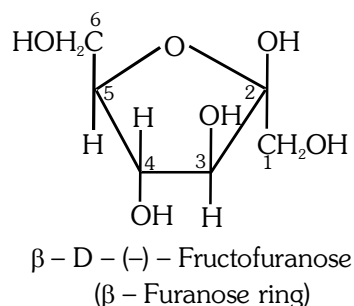
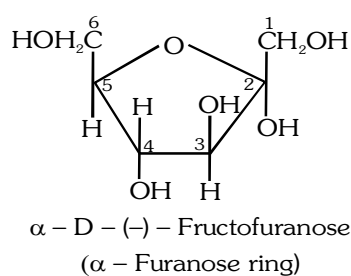
Structure of Fructose :

Fructose also has the **molecular formula $C_6H_{12}O_6$** and on the basis of its reactions it was found to contain **a ketonic functional group at carbon number 2** and six carbons in straight chain as in the case of glucose. It belongs to **D-series and is a laevorotatory compound**. It is appropriately written as **D-(-)-fructose**. Its open chain structure is as shown.

It also exists in two cyclic forms which are obtained by the addition of $-OH$ at C5 to the $(>C=O)$ group. The ring, thus formed is a five membered ring and is named as **furanose** with analogy to the compound furan. Furan is a five membered cyclic compound with one oxygen and four carbon atoms.



The cyclic structures of two anomers of fructose are represented by Haworth structures as given.

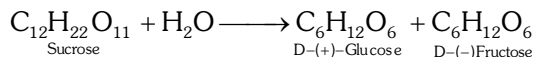


COMPARISON OF GLUCOSE AND FRUCTOSE			
S. No.	Property	Glucose	Fructose
1.	Molecular formula	$C_6H_{12}O_6$	$C_6H_{12}O_6$
2.	Nature	Polyhydroxy aldehyde	Polyhydroxy ketone
3.	Melting point	146°C	102°C
4.	Optical nature	Dextro rotatory	Leavo rotatory
5.	Tollen's reagent	Silver mirror	Silve mirror
6.	Fehling's solution	Red ppt	Red ppt
7.	Molisch test	Violet colour	Violet colour
8.	Phenyl hydrazine	Forms osazone	Forms osazone
9.	Oxidation by conc. HNO_3	Saccharic acid	Mixture of glycollic acid, Tartaric acid and Trihydroxy Gluteric acid

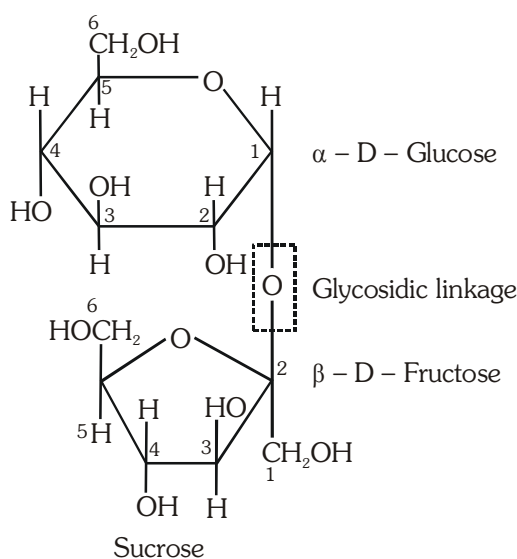
4.1.4 DISACCHARIDES

The two monosaccharides are joined together by an oxide linkage formed by the loss of a water molecule. Such a linkage between two monosaccharide units through oxygen atom is called **glycosidic linkage**.

- (i) **Sucrose** : One of the common disaccharides is **sucrose** which on hydrolysis gives equimolar mixture of D-(+)-glucose and D-(-) fructose.

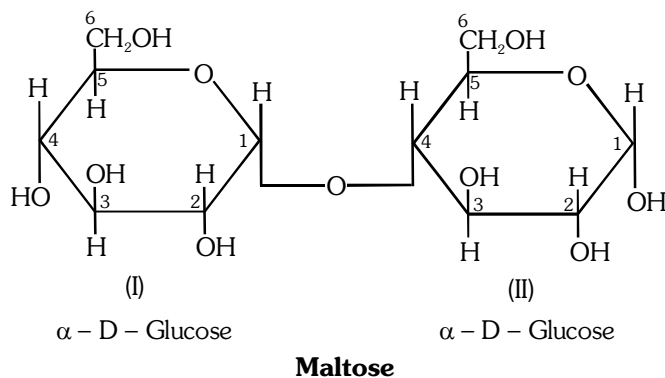


These two monosaccharides are held together by a glycosidic linkage between C₁ of α-glucose and C₂ of β-fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a **non reducing sugar**.

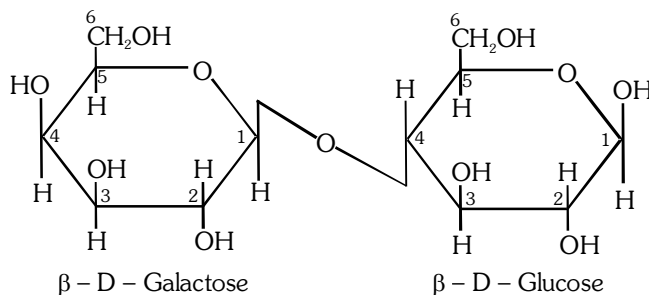


Hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (-) and the product is named as invert sugar.

- (ii) **Maltose**: Another disaccharide, maltose is composed of two α-D-glucose units in which C₁ of one glucose (I) is linked to C₄ of another glucose unit (II). The free aldehyde group can be produced at C₁ of second glucose in solution and it shows reducing properties so it is a **reducing sugar**.



- (iii) **Lactose** : It is more commonly known as milk sugar since this disaccharide is found in milk. It is composed of β -D-galactose and β -D-glucose. The linkage is between C_1 of galactose and C_4 of glucose. Hence it is also a **reducing sugar**.



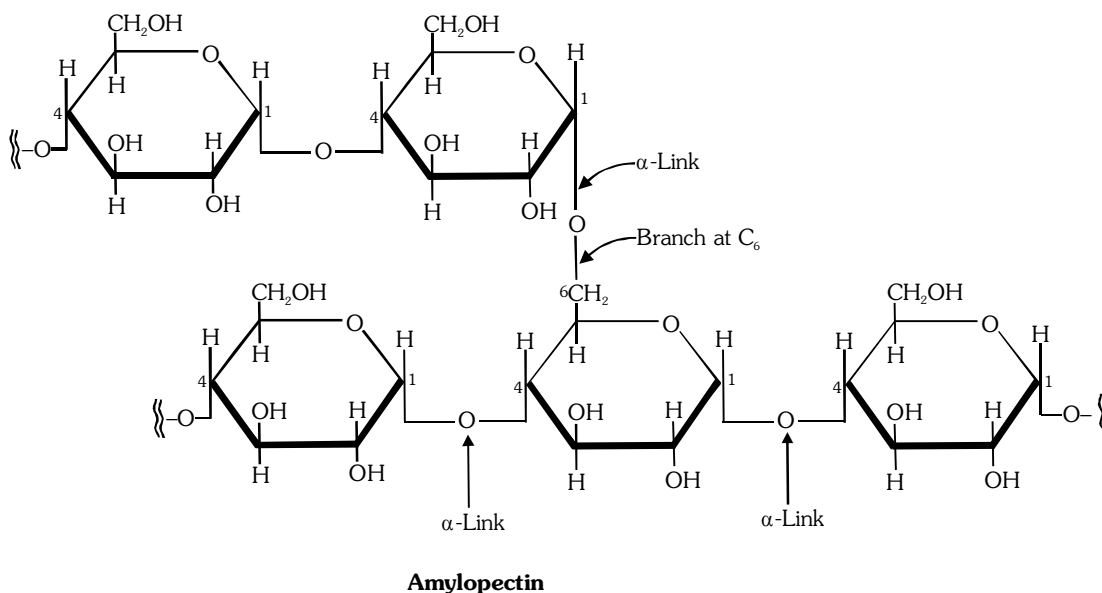
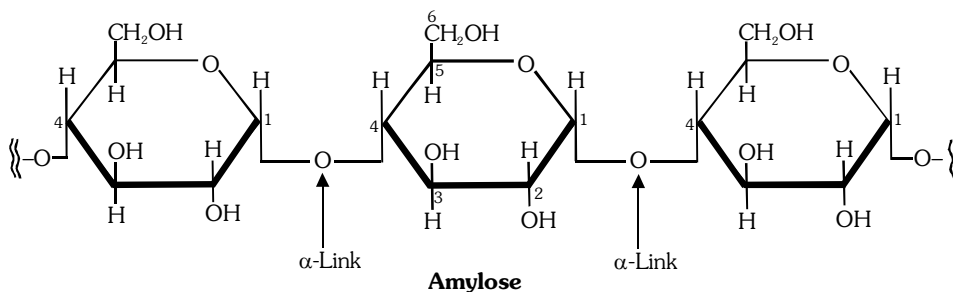
Lactose

4.1.5 POLYSACCHARIDES

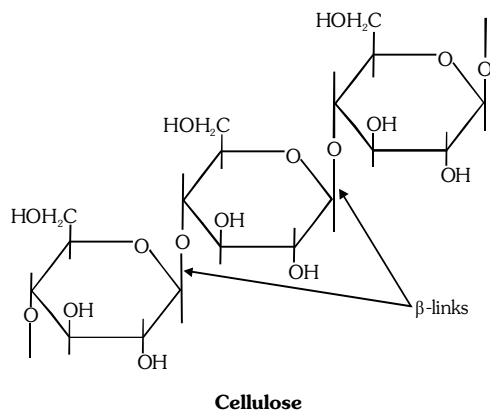
Polysaccharides contain a large number of monosaccharide units joined together by glycosidic linkages. They mainly act as the food storage or structural materials.

- (i) **Starch**: Starch is the main storage polysaccharide of plants. It is the most important dietary source for human beings. High content of starch is found in cereals, roots, tubers and some vegetables. It is a **polymer of α -glucose** and consists of two components—

Amylose and **Amylopectin**. Amylose is hot water soluble component which constitutes about 15-20% of starch. Chemically amylose is a long unbranched chain with 200-1000 α -D-(+)-glucose units held by C_1 - C_4 glycosidic linkage. Amylopectin is insoluble in hot water and constitutes about 80-85% of starch. It is a branched chain polymer of α -D-glucose units in which chain is formed by C_1 - C_4 glycosidic linkage whereas branching occurs by C_1 - C_6 glycosidic linkage.



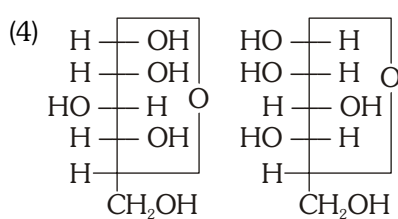
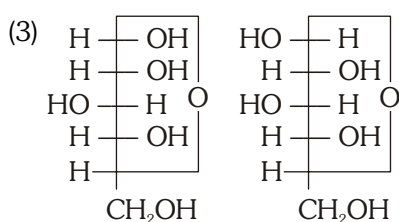
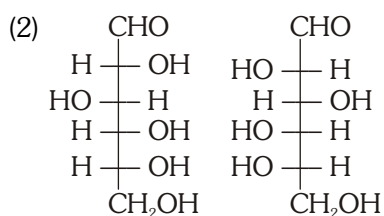
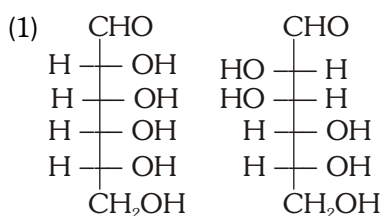
- (ii) **Cellulose** : Cellulose occurs exclusively in plants and it is the most abundant organic substance in plant kingdom. It is a predominant constituent of cell wall of plant cells. Cellulose is a straight chain polysaccharide composed only of **β -D-glucose** units which are joined by glycosidic linkage between C_1 of one glucose unit and C_4 of the next glucose unit.



- (iii) **Glycogen** : The carbohydrates are stored in animal body as glycogen. It is also known as **animal starch** because its structure is similar to amylopectin and is rather more highly branched. It is present in liver, muscles and brain. When the body needs glucose, enzymes break the glycogen down to glucose. Glycogen is also found in yeast and fungi.

BEGINNER'S BOX-1

- Glucose can be tested by following –
 - Tollen's reagent
 - Fehling's solution
 - Both of these
 - None of these
- Glucose on oxidation with nitric acid as well as gluconic acid both gives –
 - Saccharic acid
 - n-Hexane
 - Fructose
 - Glucosazone
- The spontaneous change in specific rotation of an optically active compound is called –
 - Mutarotation
 - Rearrangements
 - Inversion
 - Retention
- Hydrolysis of sucrose brings about a change in sign of rotation from dextro(+) to Laevo(–) and such a sign change is known as –
 - Racemization
 - Inversion
 - Mutarotation
 - None of these
- Which of the following pairs represents anomer:-



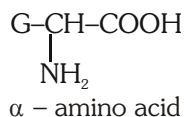
4.2 PROTEINS

The word protein is derived from Greek word, “**proteios**” which means primary or of prime importance.

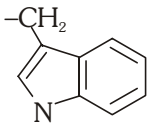
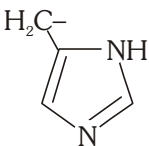
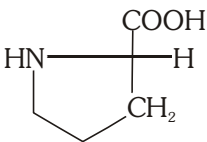
All proteins are polymers of **α -L-amino acids**.

Amino acids : Amino acids contain amino ($-\text{NH}_2$) and carboxyl ($-\text{COOH}$) functional groups.

Depending upon the relative position of amino group with respect to carboxyl group, the amino acids can be classified as α , β , γ , δ and so on. Only α -amino acids are obtained on hydrolysis of proteins. They may contain other functional groups also.



	Name of the amino acids	Characteristic feature of side chain, G	Three letter symbol	One letter code
1.	Glycine	H	Gly	G
2.	Alanine	$-\text{CH}_3$	Ala	A
3.	Valine*	$(\text{H}_3\text{C})_2 \text{CH}-$	Val	V
4.	Leucine*	$(\text{H}_3\text{C})_2 \text{CH}-\text{CH}_2-$	Leu	L
5.	Isoleucine*	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}_2-\text{CH}- \\ \\ \text{CH}_3 \end{array}$	Ile	I
6.	Arginine*	$\begin{array}{c} \text{HN}=\text{C}-\text{NH}-(\text{CH}_2)_3- \\ \\ \text{NH}_2 \end{array}$	Arg	R
7.	Lysine*	$\text{H}_2\text{N}-(\text{CH}_2)_4-$	Lys	K
8.	Glutamic acid	$\text{HOOC}-\text{CH}_2-\text{CH}_2-$	Glu	E
9.	Aspartic acid	$\text{HOOC}-\text{CH}_2-$	Asp	D
10.	Glutamine	$\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CH}_2-\text{CH}_2- \end{array}$	Gln	Q
11.	Asparagine	$\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CH}_2- \end{array}$	Asn	N
12.	Threonine*	$\text{H}_3\text{C}-\text{CHOH}-$	Thr	T
13.	Serine	$\text{HO}-\text{CH}_2-$	Ser	S
14.	Cysteine	$\text{HS}-\text{CH}_2-$	Cys	C

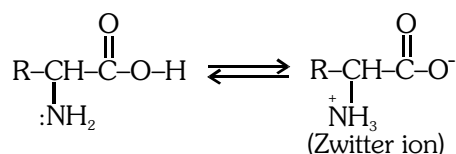
15.	Methionine*	$\text{H}_3\text{C}-\text{S}-\text{CH}_2-\text{CH}_2-$	Met	M
16.	Phenylalanine*	$\text{C}_6\text{H}_5-\text{CH}_2-$	Phe	F
17.	Tyrosine	(p) $\text{HO}-\text{C}_6\text{H}_4-\text{CH}_2-$	Tyr	Y
18.	Tryptophan*		Trp	W
19.	Histidine*		His	H
20.	Proline ^(a)		Pro	P

* essential amino acid, a = entire structure

4.2.1 Classification of Amino Acids : Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule.

- The amino acids, which can be synthesised in the body, are known as **non-essential amino acids**. On the other hand, those which cannot be synthesised in the body and must be obtained through diet, are known as **essential amino acids**.

Amino acids are usually colourless, crystalline solids. These are water-soluble, high melting solids and behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic (carboxyl group) and basic (amino group) groups in the same molecule.



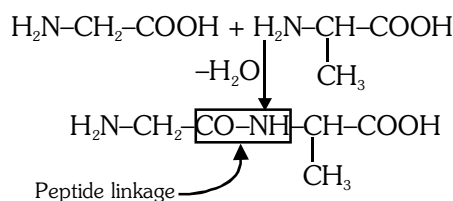
In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as **zwitter ion**. This is neutral but contains both positive and negative charges.

In zwitter ionic form, amino acids show **amphoteric** behaviour as they react both with acids and bases.

Except glycine, all other naturally occurring α-amino acids are optically active, since the α-carbon atom is asymmetric. These exist both in 'D' and 'L' forms. Most naturally occurring amino acids have L-configuration. **L-Aminoacids** are represented by writing the $-\text{NH}_2$ group on left hand side.

4.2.2 Structure of Proteins :

Proteins are the polymers of α-amino acids and they are connected to each other by **peptide bond** or **peptide linkage**. Chemically, peptide linkage is an amide formed between $-\text{COOH}$ group and $-\text{NH}_2$ group.



Glycylalanine [Gly-Ala]

The reaction between two molecules of similar or different amino acids, proceeds through the combination of the amino group of one molecule with the carboxyl group of the other. This results in the elimination of a water molecule and formation of a **peptide bond** $-\text{CO}-\text{NH}-$.

Proteins can be classified into two types on the basis of their molecular shape.

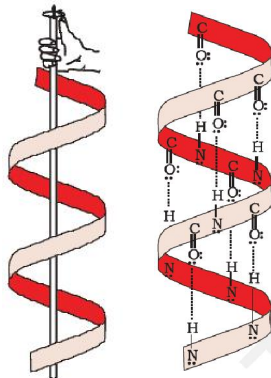
(a) Fibrous proteins

When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre-like structure is formed. Such proteins are generally insoluble in water. Some common examples are keratin (present in hair, wool, silk) and myosin (present in muscles), etc.

(b) Globular proteins

This structure results when the chains of polypeptides coil around to give a spherical shape. These are usually soluble in water. Insulin and albumins are the common examples of globular proteins.

Structure and shape of proteins can be studied at four different levels, i.e., primary, secondary, tertiary and quaternary, each level being more complex than the previous one.



- (i) **Primary structure of proteins:** Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that is said to be the primary structure of that protein. Any change in this primary structure (i.e., the sequence of amino acids) creates a different protein.
- (ii) **Secondary structure of proteins:** The secondary structure of protein refers to the shape in which a long polypeptide chain can exist. They are found to exist in two different types of structures viz. α -helix and β -pleated sheet structure. These structures arise due to the regular folding of the backbone

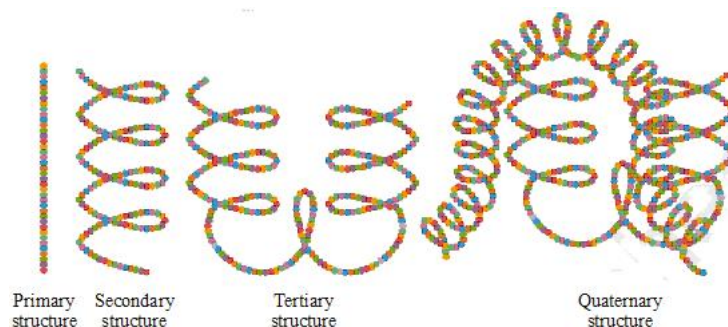
of the polypeptide chain due to hydrogen bonding between $-\text{C}(=\text{O})-$ and $-\text{NH}-$ groups of the peptide bond.

α -Helix is one of the most common ways in which a polypeptide chain forms all possible hydrogen bonds by twisting into a right handed screw (helix) with the $-\text{NH}$ group of each amino acid residue hydrogen bonded to the $>\text{C}=\text{O}$ of an adjacent turn of the helix.

In β -structure all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by intermolecular hydrogen bonds. The structure resembles the pleated folds of drapery and therefore is known as β -pleated sheet.

- (iii) **Tertiary structure of proteins:** The tertiary structure of proteins represents overall folding of the polypeptide chains i.e., further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular. The main forces which stabilise the 2° and 3° structures of proteins are hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction.
- (iv) **Quaternary structure of proteins :** Some of the proteins are composed of two or more polypeptide chains referred to as sub-units. The spatial arrangement of these subunits with respect to each other is known as quaternary structure.

A diagrammatic representation of all these four structures is given in figure.



4.2.3 Denaturation of Proteins :

Physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called **denaturation** of protein. The coagulation of egg white on boiling is a common example of denaturation. Another example is curdling of milk which is caused due to the formation of lactic acid by the bacteria present in milk.

During denaturation secondary and tertiary structures are destroyed but primary structure remains unchanged.

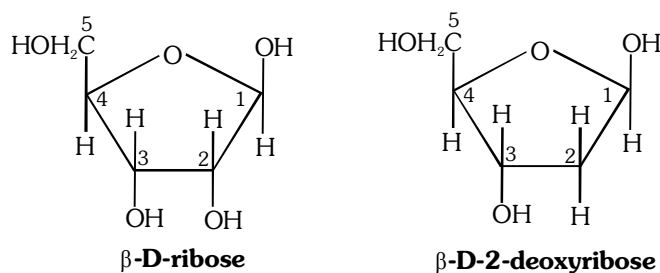
4.3 NUCLEIC ACIDS

Introduction :

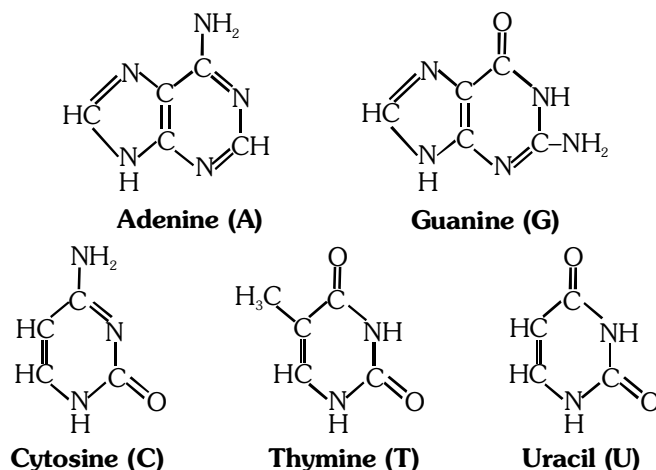
It has been observed that nucleus of a living cell is responsible for the transmission of inherent characters, also called **heredity**. The particles in nucleus of the cell, responsible for heredity, are called chromosomes which are made up of proteins and another type of biomolecules called **nucleic acids**. These are mainly of two types, the **deoxyribonucleic acid (DNA)** and **ribonucleic acid (RNA)**. Since nucleic acids are long chain polymers of **nucleotides**, so they are also called polynucleotides.

4.3.1 Chemical composition of Nucleic Acids :

Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compounds (called bases). In DNA molecules, the sugar moiety is **β -D-2-deoxyribose** whereas in RNA molecule, **it is β -D-ribose**.

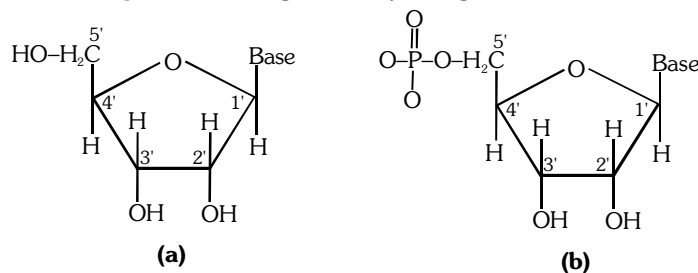


DNA contains four bases viz. **adenine** (A), **guanine** (G), **cytosine** (C) and **thymine** (T). RNA also contains four bases, the first three bases are same as in DNA but the fourth one is uracil (U).



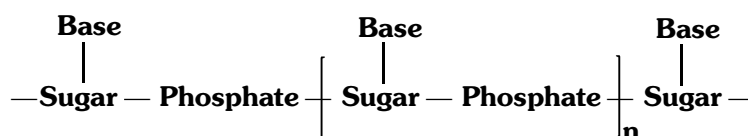
4.3.2 Structure of Nucleic Acids :-

A unit formed by the attachment of a base to 1' position of sugar is known as **nucleoside**. In nucleosides, the sugar carbons are numbered as 1', 2', 3', etc. in order to distinguish these from the bases. When nucleoside is linked to phosphoric acid at 5'-position of sugar moiety, we get a nucleotide.

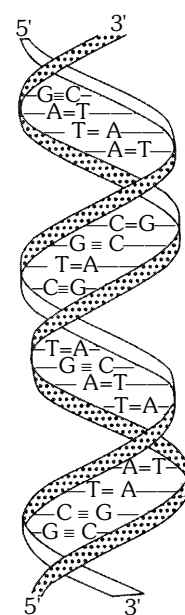


Structure of (a) a nucleoside and (b) a nucleotide

Nucleotides are joined together by **phosphodiester linkage** between 5' and 3' carbon atoms of the pentose sugar. A simplified version of nucleic acid chain is as shown below. Fig.



Information regarding the sequence of nucleotides in the chain of a nucleic acid is called its primary structure. Nucleic acids have a secondary structure also. James Watson and Francis Crick gave a double strand helix structure for DNA (Fig.). Two nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases. The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine. In secondary structure of RNA, helices are present which are only single stranded. Sometimes they fold back on themselves to form a double helix structure. RNA molecules are of three types and they perform different functions. They are named as **messenger RNA (m-RNA)**, **ribosomal RNA (r-RNA)** and **transfer RNA (t-RNA)**.



Double strand helix structure for DNA

BEGINNER'S BOX-2

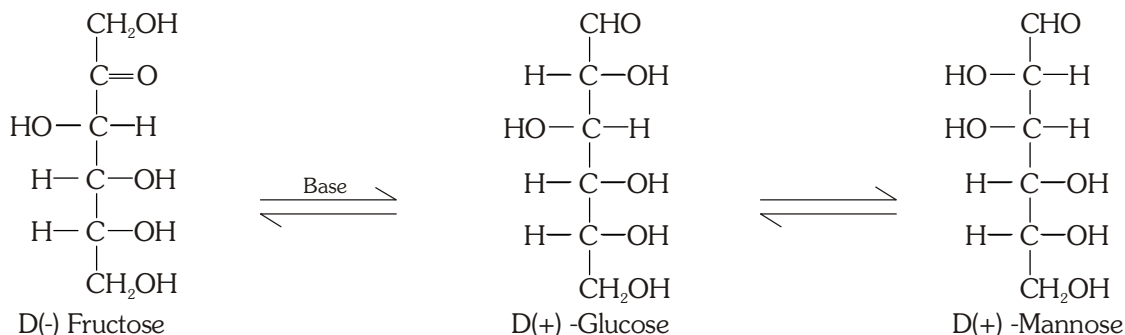
1. Zwitter ion is –
 (1) neutral ion (2) positive charge ion (3) negative ion (4) None of these
2. In β -sheet of proteins, conformers are held together by (Secondary structure of protein) –
 (1) Intermolecular H-bond (2) Intramolecular H-bond
 (3) Conformers not held together (4) None of these
3. DNA contains following purines bases –
 (a) Adenine (b) Guanine (c) Thymine (d) Cytosine
 (1) a, c (2) a, b (3) a, c, d (4) a, b, c, d
4. Which of the following statement is/are true –
 (1) DNA has deoxyribose while RNA has ribose sugar (2) DNA contains thymine while RNA has uracil
 (3) Both of these (4) None of these
5. RNA on translation gives –
 (1) Protein (2) DNA (3) Both (4) None of these

GOLDEN KEY POINTS

TEST FOR BIOMOLECULES

(I) Lobry de Bruyn van Eikenstein rearrangement :

Glucose contains —CHO group and hence reduces fehling's solution. Fructose, on the other hand, contains >C=O group but still reduces Fehling's solution. This is due to the reason that under basic conditions of the reagent, fructose undergoes a reversible isomerization and is converted into a mixture of glucose and mannose - both of which contain —CHO group and hence reduce fehling's solution.



This conversion of fructose into a mixture of glucose and mannose under basic conditions is called Lobry de Bruyn van Eikenstein rearrangement.

(II) Test of carbohydrates : Molish test is used for detection of all types of carbohydrates, i.e., monosaccharides, disaccharides and polysaccharides.

Molisch reagent (1% alcoholic solution of α - naphthol) is added to the aqueous solution of a carbohydrate followed by conc. H_2SO_4 along the sides of the test tube. A violet ring is formed at the junction of the two layers.

(III) Tests of Proteins:

Biuret test: An alkaline solution of a protein when treated with a few drops of 1% CuSO_4 solution, produces a violet colouration. The colour is due to the formation of a coordination complex of Cu^{+2} with >C=O and —NH— groups of the peptide linkages.

4.4 VITAMINS

	Vitamin	Sources	Deficiency diseases
(i)	Vitamin-A (Retinol or eye vitamin)	Milk, cod liver oil, butter, carrots, green leaves, tomatoes, eggs, etc.	Night blindness, xerophthalmia (i.e. hardening of cornea of eye) and xerosis.
(ii)	Vitamin-B ₁ Thiamine or Aneurin	Pulses, nuts, green vegetables, Polished rice. yeast and egg yolk.	Beriberi (a disease of nervous system) and loss appetite.
(iii)	Vitamin - B ₂ or Riboflavin or Lactoflavin	Milk, meat, green vegetables and yeast.	Inflammation of tongue or dark red tongue (glossitis), and cheilosis (cracking or fissuring the lips and corners of the mouth)
(iv)	Vitamin-B ₆ or Pyridoxine or Adermine	Rice, bran, yeast, meat, fish, egg, yolk, maize, spinach and lettuce.	Specific dermatitis called acrodynia, pellagra (shrivelled skin) anaemia and convulsions.
(v)	Vitamin-B ₁₂ or Cyanocobblamin	Milk, liver, kidney and eggs.	Inflammation of tongue, mouth etc. and pernicious anaemia.
(vi)	Vitamin-C or L-Ascorbic acid	Citrous fruits, amla, (oranges, lemons), sprouted pulses, germinated grains and leafy vegetables.	Scurvy and brittleness of bones, swelling and bleeding of gums and loosening of teeth.
(vii)	Vitamin D or Ergocalciferol (or antirachitic Vitamin of sunshine vitamin)	Fish liver oil, cod liver oil, milk and eggs.	Rickets (softening and bending of bones) in children, controls Ca and P metabolism.
(viii)	Vitamin-E or Tocopherols (α , β and γ) or Antisterility factor	Eggs, milk, fish, wheat germ, oil, cotton seed oil etc.	Sterility (loss of sexual power and reproduction)
(ix)	Vitamin-H (Biotin)	Yeast, liver, Kidney and milk.	Dermatitis, loss of hair and paralysis.
(x)	Vitamin-K or Phylloquinones or Antihemorrhagic vitamin	Cabbage, alfalfa, spinach and carrot tops.	Hemorrhage and lengthens time of blood clotting.
(xi)	Coenzyme Q ₁₀	Chloroplasts of green plants and mitochondria of animals	Low order of immunity of body against many diseases

4.5 HORMONES

Hormones are biomolecules which are produced in the ductless (endocrine) glands and are carried to different parts of the body by the blood stream where they control various metabolic processes. These are required in minute quantities and unlike fats and carbohydrates these are not stored in the body but are continuously produced.

Some important hormones along with the sources and functions are summarised below :

NAME	ORGAN OF SECRETION	FUNCTIONS
I. Steroidal hormones		
A. Sex hormones		
(a) Androgens (Testosterone)	Testes	Control the development and normal functioning of Androsterone and male sex organs.
(b) Estrogens (Estrone, Estradiol, Estriol)	Ovary	Control the development and normal functioning of female sex organs.
(c) Gestogens (Progesterone)	Corpus luteum	Control the development and maintenance of pregnancy.
B. Adrenal cortex hormones or corticoids (Cortisone, Corticosterone, Aldosterone etc.)	Adrenal cortex	Regulate the metabolism of fats, proteins and carbohydrates; control the balance of water and minerals in the body.
II. Peptide hormones		
(i) Oxytocin	Posterior pituitary gland	Controls the contraction of the uterus after child birth and releases milk from the mammary glands.
(ii) Vasopressin	Posterior pituitary gland	Controls the reabsorption of water in the kidney.
(iii) Angiotensin II	Blood plasma of persons with high blood pressure.	Potent vasoconstrictor i.e. contracts the blood vessels.
(iv) Insulin	Pancreas	Controls the metabolism of glucose, maintains glucose level in the blood.
III. Amine hormones		
(i) Adrenaline or Epinephrine	Adrenal medulla	It is an amine compound and was the first hormone to be isolated. Prepares animals and humans for emergency in many ways by raising the pulse rate, blood pressure etc. stimulates the breakdown of liver glycogen into blood glucose and fats into fatty acids during emergency. These properties make adrenaline as one of the most valuable drugs used in medicine.
(ii) Thyroxine	Thyroid gland	Controls metabolism of carbohydrates, lipids and proteins.

GOLDEN KEY POINTS

- Monosaccharides which differ in configuration at first chiral carbon are called anomers. thus, α -D-glucose and β -D-glucose are anomers and so are α -D-fructose and β -D-fructose.
- The C_1 carbon atom in aldoses and C_2 carbon atom in ketoses around which the configuration of anomers differs is called anomeric or the glycosidic carbon.
- Monosaccharides which differ in configuration at any one carbon atom are called epimers. Thus, glucose and mannose which differ in Configuration at C_2 are called C_2 -epimers while glucose and galactose which differ in configuration at C_4 are called C_4 epimers.
- All monosaccharides (aldoses and ketoses) and disaccharides except sucrose reduce fehling's solution, Benedict's solution and Tollen's reagent and hence are called reducing sugars. Others (sucrose, starch, cellulose) which do not reduce these reagents are called non-reducing carbohydrates.
- The spontaneous change of specific rotation with time to an equilibrium value is called mutarotation. All reducing carbohydrates i.e. monosaccharides (glucose, fructose, mannose etc.) and disaccharides (maltose, lactose etc.) undergo mutarotation in aqueous solutions.
- Since glucose (grape sugar) is dextrorotatory, it is also called dextrose. Similarly, fructose being laevorotatory is also called laevulose.
- α -Amino acids are the building blocks of proteins or proteins are the condensation polymers of α -amino acids.
- All the α -amino acids forming proteins have L- configuration while all the naturally occurring carbohydrates have D-configuration.
- DNA undergoes replication and controls transmission of hereditary effects from one generation to the other while RNA controls synthesis of proteins.
- Vitamin D_2 is also called sunshine vitamin since it is obtained by sunlight irradiation of ergosterol present in oils and fats.
- The α -helix structure of proteins is also called 3.6_{13} helix since each turn of the helix has approx. 3.6 amino acids and a 13-member ring is formed by H-bonding.
- The deficiency of protein causes the disease called Kwashiorkor.
- Thiamine is vitamin B_1 while thymine is a pyrimidine base which occurs in DNA.

COMPETITION WINDOW

- All monosaccharides and reducing disaccharides (maltose, lactose etc.) react with three molecules of $C_6H_5NHNH_2$ to form crystalline osazones which are used for their identification and characterization. Further all monosaccharides which differ in configuration at C_1 and C_2 give the same osazone, i.e. glucose, fructose and Mannose.
- Both starch and cellulose are condensation polymers of glucose. Starch is a polymer of α -glucose, whereas cellulose is polymer of β -glucose.
- At isoelectric point, the amino acids primarily exist as the neutral dipolar or zwitterion and hence have the minimum solubility. All amino acid have their own isoelectric point.
- In amino acids. $-COO^\ominus$ group acts as the base while $-NH_3^+$ acts as the acid.

- The biological activity of proteins is due to their secondary and tertiary structures.
- Adenosine (ribose + adenine) is a nucleoside while adenosine monophosphate (AMP), adenosine diphosphate and adenosine triphosphate (ATP) are all nucleotides.
- ATP is called energy currency of the cells. It is a nucleotide containing adenine as the purine base, ribose as the sugar and three inter-linked phosphate groups.
- Energy is stored in living cells in form of ATP.
- Haemoglobin is a globular protein and the red colour of haemoglobin is due to the iron-protoporphyrin complex called the heme.
- Water soluble vitamins are B-complex and C.
- Water insoluble vitamins are A,D,E, and K.
- Vitamins which act as antioxidants are C,D and E.
- Calorific value of various food stuffs follows the Sequence : Fats > Carbohydrates > proteins.

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5					
	Ans.	3	1	1	2	3					
BEGINNER'S BOX-2	Que.	1	2	3	4	5					
	Ans.	1	1	2	3	1					

POLYMER

Polymer is defined as a high molecular weight compound formed by the combination of a large number of one or more types of small molecules (Monomers)

CLASSIFICATION OF POLYMERS :

5.1 BASED ON SOURCE

(a) Natural polymers (b) Semi-Synthetic polymers (c) Synthetic polymers

(a) **Natural polymers:** These are of natural origin and these are found in plants and animals.

Natural polymers are also called as biopolymers.

Example Proteins (Polymers of amino acids), Polysaccharides (Polymers of mono saccharides), rubber (Polymers of isoprene) silk, wool, starch, cellulose, enzymes, haemoglobin etc.

(b) **Semi Synthetic polymers :**

Examples Nitro cellulose, cellulose acetate, cellulose xanthate, etc.

(c) **Synthetic Polymers :** These are artificial polymers. For example Polythene, nylon, PVC, bakelite, dacron.

5.2 BASED ON STRUCTURE OF POLYMERS.

(1) **Linear polymers**

→ These polymers consist of long and straight chains.

→ Ex. Polyvinyl chloride, high density polythene.

(2) **Branched chain polymers**

→ These polymers contain linear chain having some branches.

Ex. – Low density polythene.

(3) **Cross linked polymers**

→ Contain strong covalent bond between various linear polymer chains.

Ex. – Bakelite, Melamine

5.3 BASED ON MODE OF POLYMERISATION :

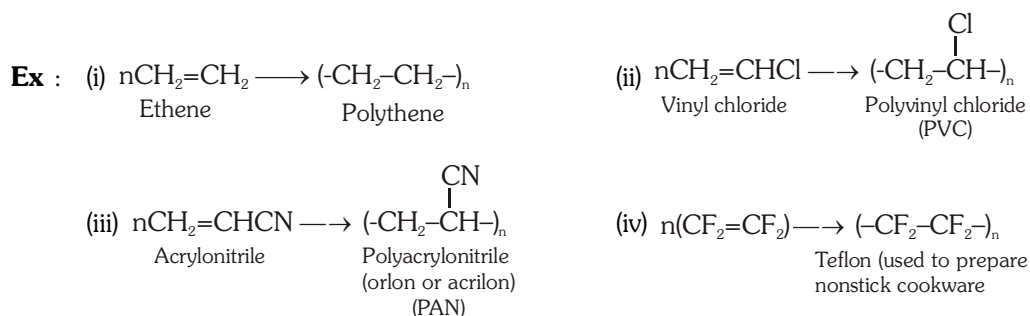
(1) **Addition polymer : (Chain growth polymerisation)**

→ Formed by the repeated addition of monomer molecules

→ Without elimination of any thing.

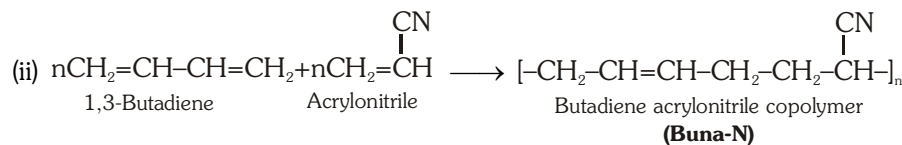
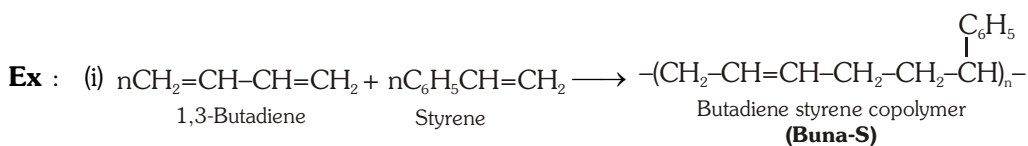
Types :

(a) **Homopolymers :** Addition polymers formed by the polymerisation of a single monomeric species.

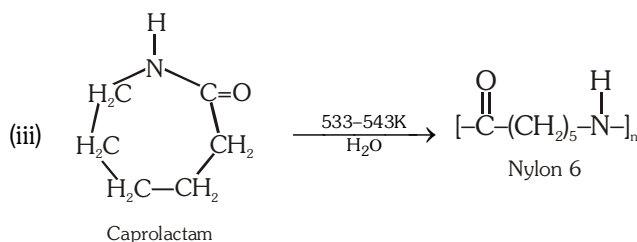
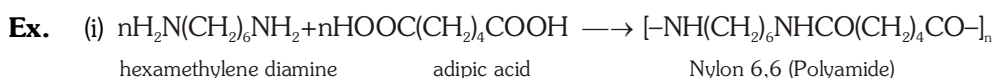
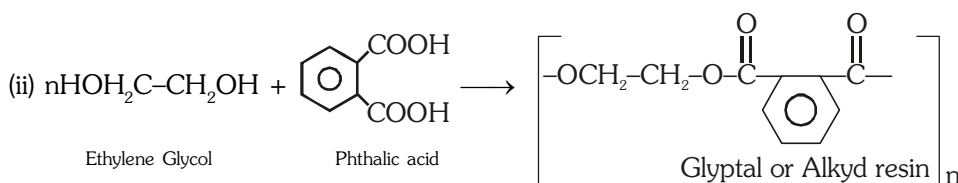
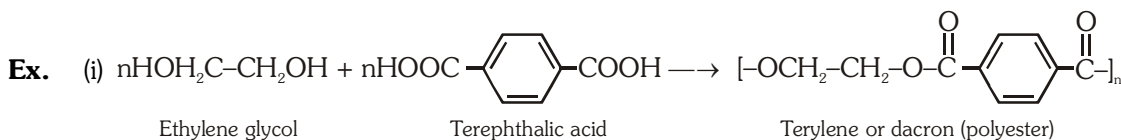
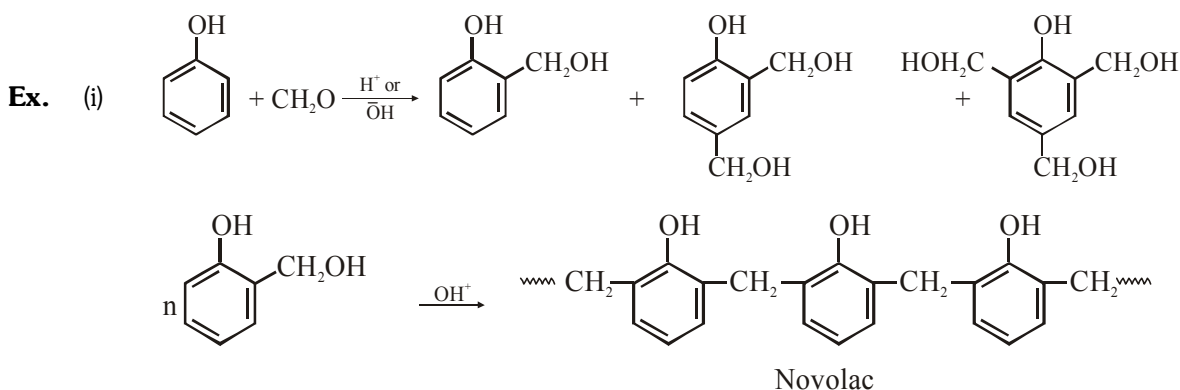


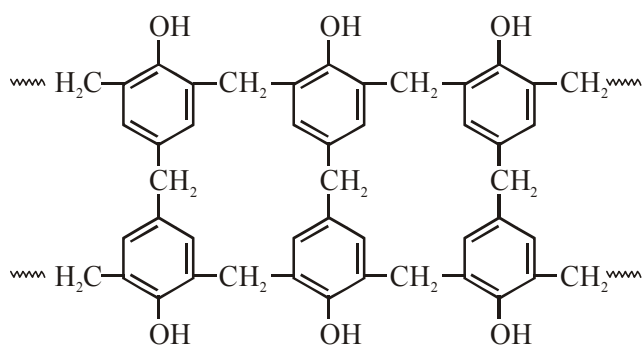
(b) Copolymers :

Addition polymers formed by the polymerisation of two different monomers.

**(2) Condensation polymers : (Step growth polymerisation)**

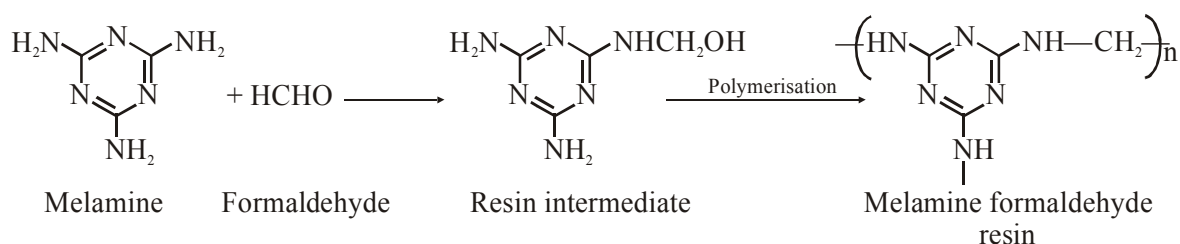
In these polymerisation reaction, the elimination of small molecules such as water, alcohol, hydrogen chloride take place.

(a) Polyamide :**(b) Polyester :****(c) Formaldehyde polymer (Bakelite and related polymers) -****(i) Bakelite :**



Bakelite

(ii) Melamine - formaldehyde polymer -



5.4 BASED ON MOLECULAR FORCES :

(1) Elastomers :

- The polymer chains are held together by the weakest intermolecular forces.
- These weak binding forces permit the polymer to be stretched.

Ex. : Buna-S, Buna-N, neoprene

(2) Fibres :

- Fibres are the thread forming solids which possess high tensile strength and strong intermolecular forces.

Ex. : Nylon 66, polyesters (terylene)

(3) Thermoplastic :

- These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling.

Ex. : Polythene, Polystyrene ; polyvinyls.

(4) Thermosetting plastic :

- These polymers are cross linked or heavily branched molecules.
- These cannot be reused

Ex. : Bakelite, urea - formaldehyde.

Note: Correct order for Intermolecular forces in various classes of polymers.

Thermosetting > Fibres > Thermoplastic > Elastomers.

5.5 PREPARATION OF SOME IMPORTANT POLYMERS.

(1) Low density polythene :

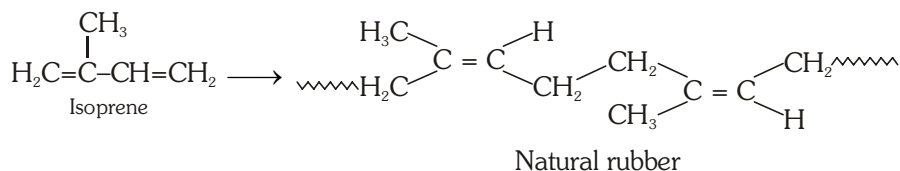
- Formed by free radical addition in presence of peroxide.
- Chemically inert and poor conductor of electricity.
- Used in the insulation of electric wires and squeeze bottles, flexible pipes.

(2) High density polythene :

- Formed in presence of titanium tetrachloride (TiCl_4) + triethyl aluminium ($\text{C}_2\text{H}_5)_3\text{Al}$ [Ziegler – Natta catalyst]
- It is chemically inert and more tougher and harder.
- It is used for manufacturing buckets, bottles.

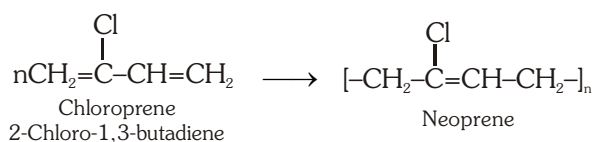
(3) Natural rubber :

- Linear polymer of cis-isoprene (2-methyl-1,3-butadiene) and is also called as **cis-1,4-polyisoprene**



- **Vulcanisation of rubber** : Natural rubber becomes soft at high temperature. To improve upon these physical properties, a process of vulcanisation is carried out. This process consists of heating a mixture of raw rubber with sulphur. On vulcanisation, sulphur forms cross links at the reactive sites of double bond.

(4) Synthetic rubber (Neoprene)



5.6 BIODEGRADABLE POLYMERS

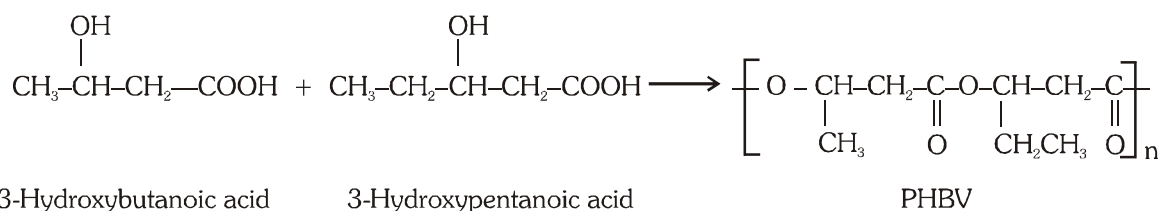
Introduction

A large number of polymers are quite resistant to the environmental degradation processes and are thus responsible for the accumulation of polymeric solid waste materials. These solid wastes cause acute environmental problems and remain undegraded for quite a long time. In view of the general awareness and concern for the problems created by the polymeric solid wastes, certain new biodegradable synthetic polymers have been designed and developed. These polymers contain functional groups similar to the functional groups present in biopolymers.

Examples :

(1) Poly (β -hydroxybutyrate- β -hydroxy valerate) (PHBV)

It is obtained by the copolymerisation of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid. PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment.



(2) Nylon 2-nylon 6

It is an alternating polyamide copolymer of glycine ($\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$) and amino caproic acid [$\text{H}_2\text{N}(\text{CH}_2)_5\text{COOH}$].

BEGINNER'S BOX-1

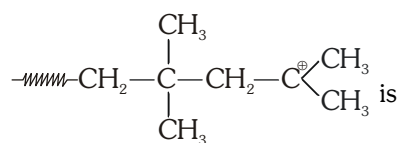
1. Which of the following is a biodegradable polymer

- | | |
|------------------------|---------------|
| (1) Cellulose | (2) Polythene |
| (3) Polyvinyl chloride | (4) Nylon-6 |

2. Which one of the following is a chain growth polymer

- | | |
|------------------|-----------------|
| (1) Nucleic acid | (2) Polystyrene |
| (3) Protein | (4) Starch |

3. The monomer of the polymer –



- | | |
|---|---|
| (1) $\text{CH}_3\text{CH}=\text{CHCH}_3$ | (2) $\text{CH}_3\text{CH}=\text{CH}_2$ |
| (3) $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$ | (4) $\text{H}_2\text{C}=\text{C}\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$ |

4. Which of the following polymer is biodegradable

- | | |
|---|---|
| (1) $(-\text{CH}_2-\underset{\text{Cl}}{\text{C}}=\text{CH}-\text{CH}_2-)_n$ | (2) $(-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-)_n$ |
| (3) $(-\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-\underset{\text{CH}_2-\text{CH}_3}{\text{CH}}-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-)_n$ | (4) $(-\underset{\text{H}}{\text{N}}-(\text{CH}_2)_6-\underset{\text{H}}{\text{N}}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-(\text{CH}_2)_4-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-)_n$ |

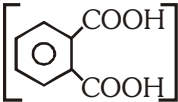
5. Which of the following is not correctly matched –

- | | |
|---|--|
| (1) Neoprene $\left[-\text{CH}_2-\underset{\text{Cl}}{\text{C}}=\text{CH}-\text{CH}_2- \right]_n$ | (2) Nylon-6,6 $\left[-\text{NH}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_4\overset{\text{O}}{\underset{\text{O}}{\text{C}}}- \right]_n$ |
| (3) Terylene $\left[-\text{OCH}_2-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{C}_6\text{H}_4-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}- \right]_n$ | (4) PMMA $\left[-\text{CH}_2-\underset{\text{COOCH}_3}{\overset{\text{CH}_3}{\text{C}}}- \right]_n$ |

6. Monomer of $\left[\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_2- \right]_n$ is –

- | | |
|----------------------|-------------|
| (1) 2-methyl propene | (2) Styrene |
| (3) Propylene | (4) Ethene |

MONOMERS AND POLYMERS

S.N.	Monomer	Polymer	Type of Polymers
1.	$\text{CH}_2=\text{CH}_2$ (Ethylene)	Poly ethene	Addition polymer
2.	$\text{CH}_2=\text{CHCH}_3$ (Propylene)	Poly propylene	Addition homo polymer
3.	$\text{CH}_2=\text{CHCl}$ (Vinyl chloride)	Polyvinyl chloride (PVC)	Homopolymer, chain growth
4.	$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$ (Styrene)	Polystyrene (styron)	Addition homo polymer, linear chain
5.	$\text{CH}_2=\text{CH}-\text{CN}$ (Acrylonitrile)	Ployacrylonitrile (PAN) or Orlon	Addition homopolymer
6.	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ (1,3 Butadiene) + Styrene	BUNA-S rubbers	Addition copolymer
7.	$\text{CH}_2=\text{CHOCOCH}_3$ (Vinyl acetate)	Poly vinyl acetate (PVA)	Addition homopolymer
8.	$\text{CF}_2=\text{CF}_2$ (Tetrafluoro ethylene)	Teflon	Chain growth homopolymer (Nonstick cookwares)
9.	$\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{CH}=\text{CH}_2$ (Isoprene)	Natural Rubber	Additon homopolymer
10.	$\text{CH}_2=\underset{\text{Cl}}{\text{C}}-\text{CH}=\text{CH}_2$ (Chloroprene)	Neoprene (Artificial Rubber)	Addition homopolymer
11.	Ethylene Glycol + terephthalic acid	Terylene or Dacron (Polyester)	Condensation Copolymer, step growth
12.	Hexamethylene diamine + adipic acid	Nylon-6,6 (Polyamide)	Copolymer, step growth linear
13.	Formaldehyde + urea	Urea formaldehyde resin	Copolymer, step growth
14.	Formaldehyde + Phenol	Bakelite	Copolymer, step growth
15.	Methyl methacrylate $\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{COOCH}_3$	Poly methyl meth acrylate (PMMA)	Addition homopolymer
16.	Ethylene Glycol + Phthalic acid 	Glyptal or alkyd resin	Copolymer, linear step growth, thermo plastic
17.	Melamine + formaldehyde	Melamine formaldehyde resin	Copolymer, step growth thermosetting polymer
18.	Hexamethylene diamine + sebacic acid	Nylon - 6,10	Copolymer, step growth linear
19.	Caprolactam	Nylon - 6	Homopolymer, step growth linear

ANSWER KEY

BEGINNER'S BOX-1

Que.	1	2	3	4	5	6				
Ans.	1	2	4	3	3	1				

CHEMISTRY IN EVERY DAY LIFE

6.1 DRUGS

Drugs :

Drugs are the chemicals of low molecular masses which interact with macromolecular target and produce a biological response.

Medicines :

Medicines are the drug which are therapeutic and used for diagnosis, prevention and treatment of diseases.

CLASSES OF DRUGS

(A) Antiseptics :

Which prevent or destroy the growth of the harmful micro organism on living organism externally like wound, cut or skin surface. Common antiseptics are-

Dettol, Savlon, Cetavlon, acriflavin, Iodine, methylene blue, mercurochrome, Furacine, Soframicine

Dettol is a mixture of chloroxylenol and terpineol.

Bithional -It is added to soap to impart antiseptic properties

Iodoform is also used as an antiseptic for wounds. Boric acid in dilute aqueous solution is weak antiseptic for eyes.

(B) Disinfectants :

The chemical compounds capable of completely destroying the micro organism on non-living objects are termed as disinfectants. These are toxic to living tissues.

These are utilized for sterilization of floor, toilets instruments and cloths.

Same substance can act as an antiseptic as well as disinfectant by varying the concentration.

eg. 1% solution of phenol in disinfectant while 0.2% solution of phenol is antiseptic.

(C) Analgesics :

The substance which are used to get relief from pain. These are of two types -

(a) Narcotics or habit forming drugs

(b) Non-narcotics or non-addictive

(a) Narcotics : These are alkaloids and mostly opium products, causes sleep and unconsciousness when taken in higher doses.

e.g. Morphine, codeine, heroin

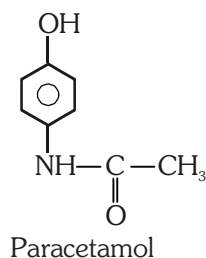
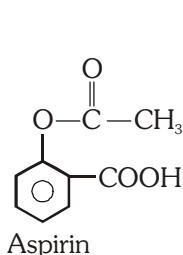
(b) Non-narcotics : Analgesics belonging to this category are effective antipyretics also.

e.g. Aspirin, Novalgin, Ibuprofen and Naproxen

(D) Antipyretics :

To bring down the body temp. in high fever are called antipyretics.

e.g - (a) Aspirin, (b) Analgin (Novalgin), (c) Paracetamol, (d) Phenacetin



(E) Antimalarials :

Drug which is used to prevent or cure malaria.

e.g. Quinine, Chloroquine, Paraquine and Primaquine etc.

(F) Tranquilizers :

The chemical substances which acts on the central nervous system and has a calming effect.

Since these are used for mental diseases so are known as psychotherapeutic drugs.

They are of two types - (a) Sedative or hypnotics (b) Mood elevators

(a) **Sedative** : Reduce nervous tension and promote relaxation. e.g. Reserpine, barbituric acid and its derivatives as luminal, seconal & veronal.

(b) **Mood elevators or Antidepressants** : A drug used for treatment of highly depressed patient, who has lost confidence.

e.g. Benzedrine (amphetamine), Iproniazid and phenelzine

Chlordiazepoxide and meprobamate are relatively mild tranquilizers suitable for relieving tension.

(G) Anesthetics :

These are chemical substances used for producing general or local insensibility to pain and other sensation.

These are of two types (a) General (b) Local

(a) **General** : - Produce unconsciousness and are given at the time of major surgical operations.

e.g. - Gaseous form → Nitrous oxide, ethylene, cyclopropane etc.

Liquid form → Chloroform, divinyl ether and sodium pentothal etc.

(b) **Local anaesthetics**: Produce loss of sensation on a small portion of the body. It is used for minor operations.

e.g. Jelly form → Oxylocain

Spray form → Ethyl chloride

Injection form → Procain

(H) Antibiotics : Initially antibiotic were the chemical substances produced from some micro organism (fungi bacteria or mold) and are used to inhibit the growth or even destroy micro organism.

But now, antibiotics are substances produced wholly or partially by chemical synthesis which in low concentrations inhibits the growth or destroy micro-organism by intervening in their metabolic processes.

These are effective in the treatment of infections diseases.

The range of bacteria or other micro-organisms that are affected by a certain antibiotic is expressed as its spectrum of action.

Three types of spectrum of action :

(i) **Broad spectrum antibiotics** – Antibiotics which kill or inhibit a wide range of gram-positive and gram-negative bacteria. e.g. Ofloxacin, Ampicillin, Amoxycillin, Chlorapheniol

(ii) **Narrow spectrum antibiotics** – Those effective mainly against gram-positive or gram-negative bacteria are narrow spectrum antibiotics. e.g. – penicillin G

(iii) **Limited spectrum antibiotic** – Those effective against a single organism or disease are limited spectrum antibiotics. e.g. – dysidazirine – toxic toward certain strain of cancer cell.

6.2 ARTIFICIAL SWEETENING AGENTS

Natural sweeteners, e.g., sucrose add to calorie intake and therefore many people prefer to use artificial sweeteners. Ortho-sulphobenzimide, also called saccharin, is the first popular artificial sweetening agent. It is about 550 times as sweet as cane sugar. It is excreted from the body in urine unchanged. It appears to be entirely inert and harmless when taken. Some other commonly marketed artificial sweeteners and their relative sweetness value in comparison to canesugar is :-

Artificial Sweetner	Sweetness value in Comparison to cane sugar
Aspartame	100
Saccharin	550
Sucralose	600
Alitame	2000

6.3 FOOD PRESERVATIVES

Food preservatives prevent spoilage of food due to microbial growth. The most commonly used preservatives include table salt, sugar, vegetable oils and sodium benzoate. Sodium benzoate is used in limited quantities and is metabolised in the body. Salts of sorbic acid and propanoic acid are also used as preservatives.

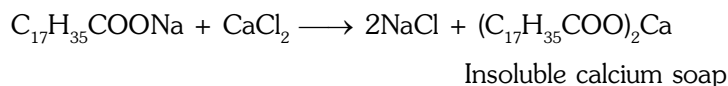
6.4 CLEANSING AGENTS

These are soaps and synthetic detergents. These improve cleansing properties of water. These help in removal of fats which bind other materials to the fabric or skin.

6.4.1 Soaps

Soaps are sodium or potassium salts of long chain fatty acids, e.g., stearic, oleic and palmitic acids. Soaps containing sodium salts are formed by heating fat (i.e., glyceryl ester of fatty acid) with aqueous sodium hydroxide solution. This reaction is known as saponification.

Soap does not work in hard water due to presence of calcium and magnesium ion in hard water. These ions form insoluble calcium & magnesium soap respectively.



These insoluble soap separate as scum in water and are useless as cleansing agent.

Types of soaps

- Toilet soaps • Transparent soaps • Medicated soaps • Shaving soaps • Laundry soaps

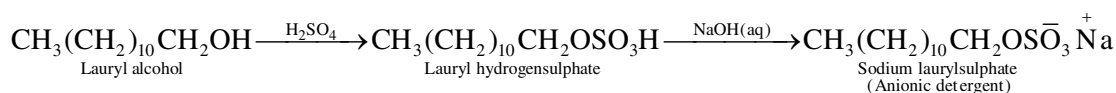
6.4.2 Synthetic Detergents

Synthetic detergents are cleansing agents which have all the properties of soaps, but which actually do not contain any soap. These can be used both in soft and hard water as they give foam even in hard water.

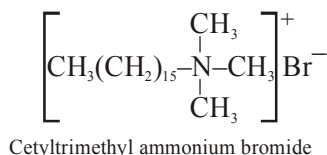
Synthetic detergents are mainly classified into three categories:

- (i) Anionic detergents (ii) Cationic detergents and (iii) Non-ionic detergents

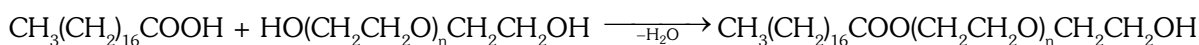
- (i) **Anionic Detergents:** Anionic detergents are sodium salts of sulphonated long chain alcohols or hydrocarbons. Alkyl hydrogensulphates formed by treating long chain alcohols with concentrated sulphuric acid are neutralised with alkali to form anionic detergents. The anionic part of the molecule is involved in the cleansing action. Mostly used for household work and in toothpastes.



- (ii) **Cationic Detergents:** Cationic detergents are quarternary ammonium salts of amines with acetates, chlorides or bromides as anions. Cationic part possess a long hydrocarbon chain and a positive charge on nitrogen atom. Hence, these are called cationic detergents. Cetyltrimethylammonium bromide is a popular cationic detergent and is used in hair conditioners.



- (iii) **Non-ionic Detergents:** Non-ionic detergents do not contain any ion in their constitution. One such detergent is formed when stearic acid reacts with polyethyleneglycol.



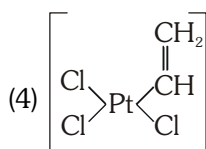
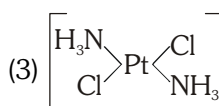
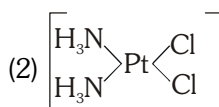
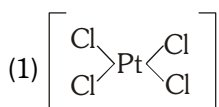
Liquid dish washing detergents are non-ionic type.

GOLDEN KEY POINTS

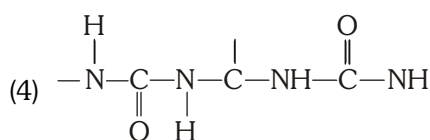
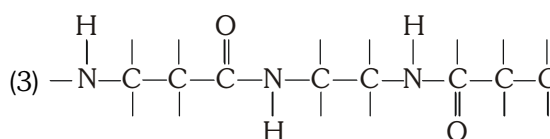
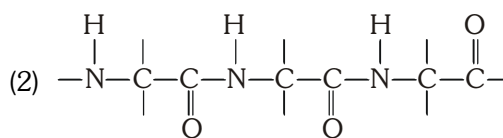
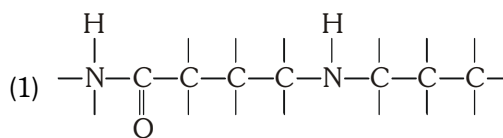
- Aspirin is used to prevent heart attacks besides being antipyretic and analgesic agents.
- Derivatives of barbituric acid, viz. veronal, amytal, nembutal, luminal and seconal are hypnotic tranquillizer while meprobamate equanil, valium and serotonin are non-hypnotic tranquillizers.
- Soaps, detergents and phospholipids are called surfactants since they lower the surface tension of water.
- All surfactants consist of two characteristic groups, i.e., apolar head group which is water-soluble (hydrophilic group) and a non-polar hydrocarbon tail which is oil-soluble (lyophilic or lipophilic group).
- Sodium soaps are hard while potassium soaps are soft. Therefore, washing soaps are mostly sodium soaps while liquid soaps having creams and toilet soaps are potassium salts.
- Unlike soaps, detergents can be used in hard water. The reason being that magnesium and calcium salts of detergents are soluble in water while those of soaps are insoluble in water.
- Aspirin, phenacetin and paracetamol act both as antipyretics and analgesics.
- The alkaloid morphine and its derivatives such as codeine (morphine methyl ether) and heroin (morphine diacetate) are important narcotic analgesic.
- Aspirin is a non-narcotic analgesic but is toxic to liver. It also undergoes hydrolysis in the stomach producing salicylic acid which causes bleeding from the stomach wall. Therefore, other non-narcotic analgesics such as naproxen, ibuprofen and diclofenac sodium or potassium are preferred to aspirin.
- Enovid E which is a mixture of norethindron (a progestogen) and ethynysestradiol (an estrogen) is the most commonly used oral contraceptive.
- AZT (3'-Azido-3-deoxythymidine) is used against AIDS i.e. HIV-infections.
- Sulpha drugs are effective against bacterial infections.
- Ciprofloxacin and norfloxacin are quinolone based antibacterial drugs.
- Artificial sweeteners have no caloric value and hence are useful for diabetic persons.

EXERCISE-I (Conceptual Questions)**BIOMOLECULES**

- The nitrogenous base having two possible hydrogen bonding sites is –
 (1) Thymine (2) Cytosine
 (3) Guanine (4) None
- The correct statement in respect of protein haemoglobin is that it –
 (1) Maintains blood sugar level
 (2) Acts as an oxygen carrier in the blood
 (3) Forms antibodies and offers resistance to diseases
 (4) acts as a catalyst for biological reactions
- A sequence of how many nucleotides in messenger RNA makes a codon for an amino acid ?
 (1) 4 (2) 1
 (3) 2 (4) 3
- The hormone that helps in the conversion of glucose to glycogen is –
 (1) Bile acids (2) Adrenaline
 (3) Insulin (4) Cortisone
- The helical structure of protein is stabilized by –
 (1) Hydrogen bonds (2) ether bonds
 (3) peptide bonds (4) dipeptide bonds
- Which of the following is considered to be an anticancer species

**Build Up Your Understanding**

7. Which of the following structures represents the peptide chain –



8. Which functional group participates in disulphide bond formation in proteins –
 (1) Thioether (2) Thiol
 (3) Thioester (4) Thiolactone
9. The cell membranes are mainly composed of –
 (1) Phospholipids (2) Proteins
 (3) Fats (4) Carbohydrates
10. Which is simplest amino acid –
 (1) Alanine (2) Asparagine
 (3) Glycine (4) Tyrosine
11. Which of the following biomolecules is insoluble in water –
 (1) α -Keratin (2) Haemoglobin
 (3) Ribonuclease (4) Adenine
12. Which one of the following statements is true for protein synthesis (translation) –
 (1) Amino acids are directly recognized by m-RNA
 (2) The third base of the codon is less specific
 (3) Only one codon codes for an amino acid
 (4) Every t-RNA molecule has more than one amino acid attachment site

- 13.** The presence or absence of hydroxy group on which carbon atom of sugar differentiates RNA and DNA ?
 (1) 3rd (2) 4th (3) 1st (4) 2nd
- 14.** The change in the optical rotation of freshly prepared solution of glucose is known as :-
 (1) tautomerism
 (2) racemisation
 (3) specific rotation
 (4) mutarotation
- 15.** Synthesis of each molecule of glucose in photosynthesis involves :-
 (1) 18 molecules of ATP
 (2) 10 molecules of ATP
 (3) 8 molecules of ATP
 (4) 6 molecules of ATP
- 16.** Which one of the following bases is not present in DNA ?
 (1) Cytosine (2) Thymine
 (3) Quinoline (4) Adenine
- 17.** Lysine; $\text{H}_2\text{N}-(\text{CH}_2)_4-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}$ is :-
 (1) α -Amino acid
 (2) γ -amino acid
 (3) Amino acid synthesised
 (4) β -Amino acid
- 18.** In fibrous protein, polypeptide chains are held together by :-
 (1) Vander waals forces
 (2) Disulphide linkage
 (3) Electrostatic forces attraction
 (4) None of these
- 19.** Which is correct in following -
 (1) Monosaccharides also known as sugars
 (2) Polysaccharides are non sugars
 (3) Maltose and Lactose are reducing sugar
 (4) All of these
- 20.** Structure of glycogen is similar to :-
 (1) Alylose (2) Amylopectin
 (3) Cellulose (4) Glucose
- 21.** Which of the following gives osazone different from the other three :-
 (1) Glucose (2) Mannose
 (3) Galactose (4) Fructose
- 22.** Anomers of glucose (α -form & β -form) are differ in the stereochemistry at which carbon -
 (1) C-1 (2) C-2
 (3) C-3 (4) All of these
- 23.** Sucrose in presence of invertase on hydrolysis gave -
 (1) Glucose (2) Fructose
 (3) Ethyl alcohol (4) 1 & 2 both
- 24.** Which of the following B group vitamins can be stored in our body.
 (1) Vitamin B₁ (2) Vitamin B₂
 (3) Vitamin B₆ (4) Vitamin B₁₂
- 25.** Which of the following are polysaccharides -
 (a) Starch (b) cellulose
 (c) dextrans (d) glycogen
 (1) a, b & c (2) a, b, d
 (3) a & c (4) a,b, c, d
- 26.** Cellulose can not be tested by followings -
 (1) Fehling's solution (2) Tollen's reagent
 (3) Both of these (4) None of these
- 27.** On hydrolysis of proteins, the product is/are -
 (1) Amino acids (2) Peptides
 (3) Enzymes (4) 1 & 2 both
- 28.** Which of the following do not have hemiacetal group:-
 (1) Fructose (2) Maltose
 (3) Sucrose (4) Glucose
- 29.** In amino acids, more number of amino than carboxyl groups makes it -
 (1) acidic (2) Basic
 (3) Neutral (4) None of these
- 30.** Which amino acids are called non essential -
 (1) those which can be synthesized in the body.
 (2) those which have more amino groups as compared to carboxyl groups
 (3) those which have equal number of amino acid and carboxyl groups
 (4) None of these

- 31.** Which of the following is not essential amino acid –
 (1) Serine (2) Lysine
 (3) Threonine (4) Tryptophan
- 32.** In acidic & alkaline solution amino acids exists as a –
 (1) Positive ion & negative ion respectively
 (2) Negative ion & positive ions respectively
 (3) Neutral in both medium
 (4) None of these
- 33.** In which of following shapes are found in tertiary structure of proteins –
 (1) Fibrous (2) Globular
 (3) Both of these (4) None of these
- 34.** The example of globular protein is
 (1) Silk (2) Collagen
 (3) Haemoglobin (4) All of these
- 35.** If a native protein is subjected to physical or chemical treatment which may disrupt its various forms without affecting its primary structure, are called –
 (1) Inactive protein
 (2) Denatured protein
 (3) Both of these
 (4) None of these
- 36.** The coagulation of egg protein while boiling of egg is called –
 (1) Reversible protein denaturation
 (2) Irreversible protein denaturation
 (3) Renaturation
 (4) None of these
- 37.** An enzyme molecule may contain protein and non-protein part. Non-protein part is known as:-
 (1) Holoenzyme (2) Cofactor
 (3) Inverted enzyme (4) None of these
- 38.** Cofactor which gets attached to the enzyme at the time of reaction are known as
 (1) Coenzymes (2) Apoenzyme
 (3) Prosthetic group (4) None of these
- 39.** Mainly DNA is localized in –
 (1) Cytoplasm (2) Nucleus
 (3) Mitochondria (4) Chloroplasts
- 40.** RNA contains following pyrimidine bases –
 (a) Thymine (b) Uracil
 (c) Cytosine (d) Adenine
 (1) b & c (2) a, b, c
 (3) a, b, d (4) All of these
- 41.** DNA molecules can duplicate themselves-called –
 (1) Replication
 (2) Translation
 (3) Transcription
 (4) None of these
- 42.** Which of the following carbohydrates are branched polymer of glucose.
 (1) Glycogen (2) Amylopectin
 (3) Cellulose (4) Both (1) & (2)
- 43.** Vitamin K
 (1) Is phyloquinone
 (2) Soluble in oils and fats
 (3) Deficiency lengthens the blood clotting
 (4) All of these
- 44.** Which of the following is not an amino acid
 (1) Histidine (2) Benzidine
 (3) Alanine (4) Proline
- 45.** Vitamin C is called :
 (1) Antisterility (2) Antiscorvy
 (3) both of these (4) None of these
- 46.** Reducing sugars are one which :
 (1) reduce fehling's solutions
 (2) not reduce tollen's reagent
 (3) Have bonded aldehydic or ketonic groups
 (4) All of these
- 47.** Multiple deficiencies caused by lack of more than one vitamin are more common in human beings. This condition of vitamin deficiency is known as
 (1) avitaminosis (2) xerophthalmia
 (3) convulsions (4) None of these

48. Which vitamin is synthesized in human body from carotene

- (1) Vitamin-A (2) Vitamin-C
(3) Vitamin-K (4) All of these

49. Which of the following is correct about H-bonding in nucleotide –

- (1) A-T G-C (2) A-G T-C
(3) G-T A-C (4) A-A T-T

POLYMER

50. Which of the following is monomer unit of polystyrene :-

- (1) $-\text{CH}_2-\underset{\text{CN}}{\text{CH}}-$ (2) $-\text{CF}_2-\text{CF}_2-$
(3) $-\text{CH}_2-\underset{\text{Cl}}{\text{CH}}-$ (4) $-\underset{\text{C}_6\text{H}_5}{\text{CH}}-\text{CH}_2-$

51. Weakest intermolecular forces are present in :-

- (1) Neoprene (2) Terylene
(3) Polystyrene (4) Bakelite

52. Thermosetting polymer, Bakelite is formed by the reaction of phenol with :-

- (1) $\text{CH}_3\text{CH}_2\text{CHO}$ (2) CH_3CHO
(3) HCHO (4) HCOOH

53. Which one is classified as a condensation polymer?

- (1) Teflon (2) Acrylonitrile
(3) Dacron (4) Neoprene

54. Novolac is a :

- (1) linear polymer of urea and formaldehyde
(2) crosslink polymer of urea and formaldehyde
(3) linear polymer of phenol and formaldehyde
(4) crosslink polymer of phenol and formaldehyde

55. Which of the following is not a semisynthetic polymer.

- (1) cis-polyisoprene (2) cellulose nitrate
(3) cellulose acetate (4) vulcanised rubber

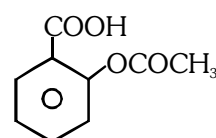
CHEMISTRY IN EVERYDAY LIFE

56. Aspirin is also known as –

- (1) Methyl salicylic acid (2) acetyl salicylate
(3) Methyl salicylate (4) Acetyl salicylic acid

57. Paracetamol is :-

- (1) Analgesic (2) Antipyretic
(3) Both (4) Antiseptic



58. is used as

- (1) Antiseptic (2) Analgesic
(3) Antibiotic (4) Micro organism

59. Which among the following is a tranquilizer ?

- (1) Equanil (2) promethazine
(3) Omeprazole (4) Cimetidine

EXERCISE-I (Conceptual Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	2	4	3	1	2	2	2	1	3	1	2	4	4	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	3	1	2	4	2	3	1	4	4	4	3	4	3	2	1
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	1	1	3	3	2	2	2	1	2	1	1	4	4	2	2
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	
Ans.	1	1	1	1	4	1	3	3	3	1	4	3	2	1	

EXERCISE-II (Previous Year Questions)**AIPMT/NEET & AIIMS (2006-2018)****AIPMT 2006**

- Which one of the following is a peptide hormone –
 (1) Glucagon (2) Testosterone
 (3) Thyroxin (4) Adrenaline
- During the process of digestion, the proteins present in food materials are hydrolysed to amino acids. The two enzymes involved in the process –



are respectively –

- (1) Amylase and Maltase
- (2) Diastase and Lipase
- (3) Pepsin and Trypsin
- (4) Invertase and Zymase

AIIMS 2006

- The pair in which both species have iron is –
 (1) Nitrogenase, cytochromes
 (2) Carboxypeptidase, haemoglobin
 (3) Haemocyanin, nitrogenase
 (4) Haemoglobin, cytochromes
- Thymine is –
 (1) 5-Methyluracil (2) 4-Methyluracil
 (3) 3-Methyluracil (4) 1-Methyluracil
- Lysine is least soluble in water in the pH range
 (1) 3 to 4 (2) 5 to 6
 (3) 6 to 7 (4) 8 to 9
- Methyl- α -D-glucoside and methyl- β -D-glucoside are –
 (1) Epimers
 (2) Anomers
 (3) Enantiomers
 (4) Conformational diastereomers

AIPMT 2007

- Which one of the following vitamins is water-soluble –
 (1) Vitamin A (2) Vitamin B
 (3) Vitamin E (4) Vitamin K
- RNA and DNA are chiral molecules, their chirality is due to –
 (1) D-sugar Component
 (2) L-sugar component
 (3) Chiral bases
 (4) Chiral phosphate ester units

- Which one of the following polymers is prepared by condensation polymerization
 (1) Styrene (2) Nylon-66
 (3) Teflon (4) Rubber

AIPMT 2008

- In DNA, the complimentary bases are :
 (1) Adenine and thymine ; guanine and uracil
 (2) Adenine and guanine ; thymine and cytosine
 (3) Uracil and adenine ; cytosine and guanine
 (4) Adenine and thymine ; guanine and cytosine
- Which one of the following is an amine hormone :
 (1) Oxypurin (2) Insulin
 (3) Progesterone (4) Thyroxine
- Which of the following statement is not true :
 (1) Natural rubber has the trans-configuration at every double bond.
 (2) Buna-S is a copolymer of butadiene and styrene.
 (3) Natural rubber is a 1, 4-polymer of isoprene.
 (4) In vulcanization, the formation of sulphur bridges between different chains make rubber harder and stronger.
- Green chemistry means such reaction which :
 (1) reduce the use and production of hazardous chemicals.
 (2) are related to the depletion of ozone layer
 (3) study the reaction in plants
 (4) produce colour during reactions

AIPMT 2009

- Which one of the following is employed as a tranquilizer ?
 (1) Chlorpheninamine (2) Equanil
 (3) Naproxen (4) Tetracycline
- Structures of some common polymers are given. Which one is not correctly presented ?
 (1) Nylon 66 $\text{[NH(CH}_2)_6\text{NHCO(CH}_2)_4\text{CO]}_n$
 (2) Teflon $\text{-(CF}_2\text{-CF}_2\text{)-}_n$
 (3) Neoprene $\left[\text{CH}_2 - \underset{\text{Cl}}{\text{C}} = \text{CH} - \text{CH}_2 - \text{CH}_2 \right]_n$
 (4) Terylene $\left[\text{OC} - \text{C}_6\text{H}_4 - \text{COOCH}_2\text{-CH}_2\text{-O} \right]_n$
- The segment of DNA which acts as the instrumental manual for the synthesis of the protein is :-
 (1) Nucleoside (2) Nucleotide
 (3) Ribose (4) Gene

17. Which of the following hormones contains iodine ?
 (1) Thyroxine (2) Insulin
 (3) Testosterone (4) Adrenaline

AIPMT 2010

18. Which one of the following is employed as a tranquilizer drug ?
 (1) Mifepristone (2) Promethazine
 (3) Valium (4) Naproxen
19. Which one of the following does not exhibit the phenomenon of mutarotation ?
 (1) (-) Fructose (2) (+) Sucrose
 (3) (+) Lactose (4) (+) Maltose
20. Which of the following structures represents Neoprene polymer ?
 (1) $\left(\text{CH}_2 - \underset{\text{C}_6\text{H}_5}{\text{CH}} \right)_n$ (2) $\left(\text{CH}_2 - \underset{\text{Cl}}{\text{C}} = \text{CH} - \text{CH}_2 \right)_n$
 (3) $\left(\text{CH}_2 - \underset{\text{CN}}{\text{CH}} \right)_n$ (4) $\left(\text{CH}_2 - \underset{\text{Cl}}{\text{CH}} \right)_n$

AIPMT Main 2010

21. Fructose reduces Tollen's reagent due to :-
 (1) primary alcoholic group
 (2) secondary alcoholic group
 (3) enolisation of fructose followed by conversion to aldehyde by base.
 (4) asymmetric carbons

AIIMS 2010

22. The most basic α -amino acid is :-
 (1) Lysine (2) Histidine
 (3) Glutamine (4) Glycine
23. Units of lactose are :-
 (1) α -D Glucose and α -D-Glucose
 (2) α -D Glucose and β -D galactose
 (3) β -D Glucose and α -D galactose
 (4) β -D-Glucose and β -D galactose

AIPMT Pre. 2011

24. Which one of the following statements is not true regarding (+) Lactose ?
 (1) On hydrolysis (+) Lactose gives equal amount of D(+) glucose and D(+) galactose
 (2) (+) Lactose is a β -glycoside formed by the union of a molecule of D(+) glucose and union of a molecule of D(+) glucose and a molecule of D(+) galactose
 (3) (+) Lactose is a reducing sugar and does not exhibit mutarotation
 (4) (+) Lactose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ contains 8-OH groups

25. Which one of the following is employed as Antihistamine ?
 (1) Chloramphenicol (2) Diphenyl hydramine
 (3) Norethindrone (4) Omeprazole

26. Of the following which one is classified as polyester polymer ?
 (1) Terylene (2) Bakelite
 (3) Malamine (4) Nylon-66

AIPMT Mains 2011

27. Which of the following is not a fat soluble vitamin ?
 (1) Vitamin A (2) Vitamin B complex
 (3) Vitamin D (4) Vitamin E
28. Which of the statements about 'Denaturation' given below are correct ?
Statements
 (a) Denaturation of proteins causes loss of secondary and tertiary structures of the protein
 (b) Denaturation leads to the conversion of double strand of DNA into single strand.
 (c) Denaturation affects primary structure which gets distorted
Options :
 (1) (a), (b) and (c) (2) (b) and (c)
 (3) (a) and (c) (4) (a) and (b)

AIIMS 2011

29. Find the hydrolysis product when a phosphodiester bonds of nucleotide breaks:
 (1) 3-OH-deoxyribose-5 PO_4^{3-}
 (2) 5-OH-deoxyribose-3- PO_4^{3-}
 (3) 2-OH-deoxyribose-2- PO_4^{3-}
 (4) 4-OH-deoxyribose-2- PO_4^{3-}
30. Find the hydrolysis product of maltose
 (1) α -D Glucose + α -D-Glucose
 (2) α -D Glucose + α -D-Fructose
 (3) α -D Glucose + α -D-galactose
 (4) α -D Fructose + α -D-Galactose

AIPMT Pre 2012

31. Deficiency of vitamin B_1 causes the disease
 (1) Cheilosis (2) Sterility
 (3) Convulsions (4) Beri-Beri

32. Which one of the following sets of monosaccharides forms sucrose?

- (1) β -D-Glucopyranose and α -D-fructofuranose
- (2) α -D-Glucopyranose and β -D-fructopyranose
- (3) α -D-Galactopyranose and α -D-Glucopyranose
- (4) α -D-Glucopyranose and β -D-fructofuranose

33. Which one of the following is not a condensation polymer?

- (1) Dacron
- (2) Neoprene
- (3) Melamine
- (4) Glyptal

34. Which of the following statements is false?

- (1) The repeat unit in natural rubber is isoprene
- (2) Both starch and cellulose are polymers of glucose
- (3) Artificial silk is derived from cellulose
- (4) Nylon-66 is an example of elastomer

AIPMT Mains 2012

35. Which one of the following sets forms the biodegradable polymer?

- (1) $\text{HO} - \text{CH}_2 - \text{CH}_2 - \text{OH}$ &



- (2) $\text{C}_6\text{H}_5 - \text{CH} = \text{CH}_2$ and $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$

- (3) $\text{CH}_2 = \text{CH} - \text{CN}$ and $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$

- (4) $\text{H}_2\text{N} - \text{CH}_2 - \text{COOH}$ and $\text{H}_2\text{N} - (\text{CH}_2)_5 - \text{COOH}$

36. Chloroamphenicol is an :-

- (1) Antiseptic and disinfectant
- (2) Antibiotic broad spectrum
- (3) Antifertility drug
- (4) Antihistaminic

NEET UG 2013

37. Nylon is an example of :-

- (1) Polythene
- (2) Polyester
- (3) Polysaccharide
- (4) Polyamide

38. Antiseptics and disinfectants either kill or prevent growth of microorganisms. Identify which of the following statements is **not true** :-

- (1) Disinfectants harm the living tissues
- (2) A 0.2% solution of phenol is an antiseptic while 1% solution acts as a disinfectant
- (3) Chlorine and Iodine are used as strong disinfectants
- (4) Dilute solutions of Boric acid and Hydrogen Peroxide are strong antiseptics

39. Which is the monomer of Neoprene in the following?

- (1) $\text{CH}_2 = \text{CH} - \text{C} \equiv \text{CH}$
- (2) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$
- (3) $\text{CH}_2 = \underset{\text{CH}_3}{\text{C}} - \text{CH} = \text{CH}_2$
- (4) $\text{CH}_2 = \underset{\text{Cl}}{\text{C}} - \text{CH} = \text{CH}_2$

AIIMS 2013

40. Which of the following is non reducing sugar:-

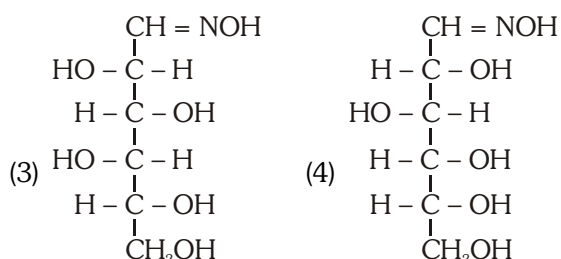
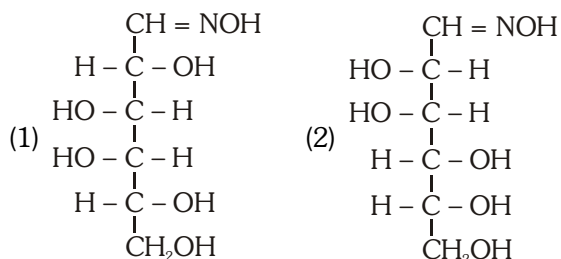
- (1) Sucrose
- (2) Maltose
- (3) Lactose
- (4) Mannose

AIPMT 2014

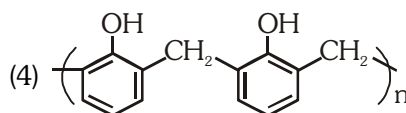
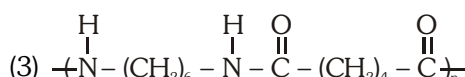
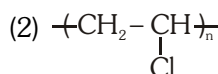
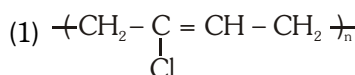
41. Artificial sweetner which is stable under cold conditions only is :-

- (1) Saccharine
- (2) Sucralose
- (3) Aspartame
- (4) Alitame

42. D (+) glucose reacts with hydroxylamine and yields an oxime. The structure of the oxime would be :



43. Which one of the following is an example of a thermosetting polymer?



44. Which of the following organic compounds polymerizes to form the polyester Dacron?
- (1) Propylene and para $\text{HO} - (\text{C}_6\text{H}_4) - \text{OH}$
 - (2) Benzoic acid and ethanol
 - (3) Terephthalic acid and ethylene glycol
 - (4) Benzoic acid and para $\text{HO} - (\text{C}_6\text{H}_4) - \text{OH}$

AIIMS 2014

45. "Maltose" is made up of ?
- (1) α -D-Glucose + α -D-Glucose
 - (2) α -D-Glucose + β -D-Glucose
 - (3) α -D-Glucose + β -D-Fructose
 - (4) α -D-Glucose + α -D-Galactose
46. Nylon 2-Nylon 6 is the copolymer of :-
- (1) Glycine + Adipic acid
 - (2) Glycine + Amino caproic acid
 - (3) Adipic acid + Hexamethylene diamine
 - (4) Amino caproic acid + Alanine
47. RNA and DNA are made up of:-
- (1) Sugar, Phosphate and vitamin A
 - (2) Sugar, Phosphate and bases
 - (3) Nucleic Acid, Vitamins and sugar
 - (4) Sugar, Amino acid and Phosphate

Re-AIPMT 2015

48. Caprolactam is used for the manufacture of :
- (1) Terylene
 - (2) Nylon - 6, 6
 - (3) Nylon - 6
 - (4) Teflon

AIPMT 2015

49. Bithional is generally added to the soaps as an additive to function as a/an :-
- (1) Dryer
 - (2) Buffering agent
 - (3) Antiseptic
 - (4) Softner
50. Biodegradable polymer which can be produced from glycine and aminocaproic acid is :-
- (1) PHBV
 - (2) Buna - N
 - (3) Nylon 6, 6
 - (4) Nylon 2- nylon 6

NEET-I 2016

51. In a protein molecule various amino acids are linked together by :
- (1) α -glycosidic bond
 - (2) β -glycosidic bond
 - (3) peptide bond
 - (4) dative bond

52. The **correct** statement regarding RNA and DNA, respectively is :

- (1) The sugar component in RNA is arabinose and the sugar component in DNA is 2'-deoxyribose.
- (2) The sugar component in RNA is ribose and the sugar component in DNA is 2'-deoxyribose.
- (3) The sugar component in RNA is arabinose
- (4) The sugar component in RNA is 2'-deoxyribose and the sugar component in DNA is arabinose.

53. Which one given below is a non-reducing sugar ?

- (1) Maltose
- (2) Lactose
- (3) Glucose
- (4) Sucrose

54. Natural rubber has

- (1) All cis-configuration
- (2) All trans-configuration
- (3) Alternate cis-and trans-configuration
- (4) Random cis-and trans-configuration

55. Which of the following is an analgesic ?

- (1) Novalgin
- (2) Penicillin
- (3) Streptomycin
- (4) Chloromycetin

NEET-II 2016

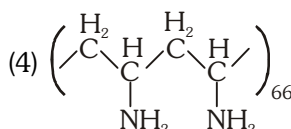
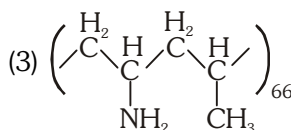
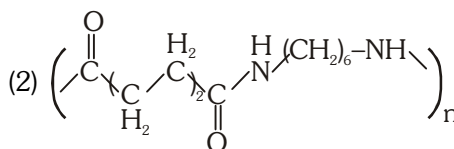
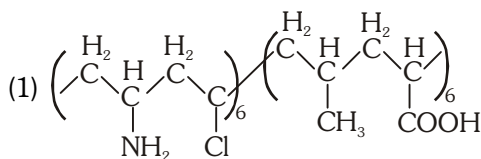
56. The central dogma of molecular genetics states that the genetic information flows from :-

- (1) $\text{DNA} \rightarrow \text{RNA} \rightarrow \text{Proteins}$
- (2) $\text{DNA} \rightarrow \text{RNA} \rightarrow \text{Carbohydrates}$
- (3) $\text{Amino acids} \rightarrow \text{Proteins} \rightarrow \text{DNA}$
- (4) $\text{DNA} \rightarrow \text{Carbohydrates} \rightarrow \text{Proteins}$

57. Which one of the following compounds shows the presence of intramolecular hydrogen bond ?

- (1) Cellulose
- (2) Concentrated acetic acid
- (3) H_2O_2
- (4) HCN

58. Which one of the following structures represents nylon 6,6 polymer ?



AIIMS 2016

- NEET(UG) 2017

- AIIMS 2017

-
- Chemical structures of the four nucleosides are shown:
- (1) Adenine: Nc1ncnc2[nH]cnc12
 - (2) Guanine: O=c1nc2[nH]cnc2c(=O)[nH]1
 - (3) Cytosine: Nc1cc[nH]c(=O)n1
 - (4) Uracil: O=c1cc[nH]c(=O)[nH]1

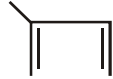
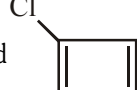
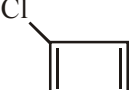
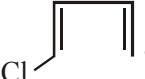
- | | Column-I | | Column-II |
|---|------------------------|---|---------------|
| a | 3-Hydroxybutanoic acid | p | Biodegradable |
| b | Bakellite | q | Chloroprene |
| c | Neoprene | r | Phthalic acid |
| d | Glyptal | s | Phenol |

- E

73. Which of the following are essential amino acids:-

- (1) Tryptophan, Lysine, Histidine
- (2) Serine, Lysine, Tryptophan
- (3) Serine, Histidine, Tryptophan
- (4) Serine, Histidine, Lysine

74. Which of the following are monomers of natural rubber and neoprene respectively:-

- (1)  and 
- (2)  and 
- (3)  and 
- (4)  and 

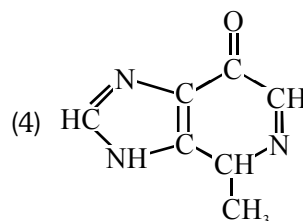
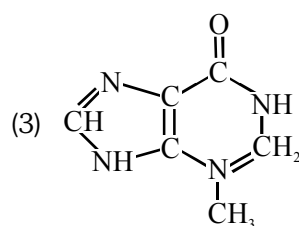
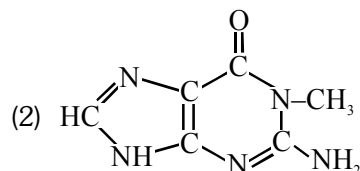
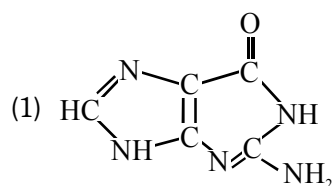
75. Among given polypeptide chain reacts with acetic anhydride and pyridine then which of the following after degradation by enzyme gives N-acetylated :-
Trp – Lys – Gly – Asn – Ala

- (1) Trp + Lys + Asn
- (2) Trp + Lys
- (3) Trp + Ala
- (4) Trp + Lys + Gly

76. Find out the incorrect statement :-

- (1) Iodine is antiseptic
- (2) Chillisalt peter is rich source of iodine
- (3) Histamine is a potent vasodilator
- (4) Chlordiazepoxide is mild tranquilizer suitable for reliving tention

77. Which of the following is the correct structure of Guanine :-



78. Which of the following statement is incorrect ?

- (1) Serotonin is a tranquilizer
- (2) Novestrol is an anti-fertility drug
- (3) Chloramphenicol is narrow spectrum antibiotic drug
- (4) Competitive inhibitor binds with enzyme

EXERCISE-II (Previous Year Questions)

ANSWER KEY

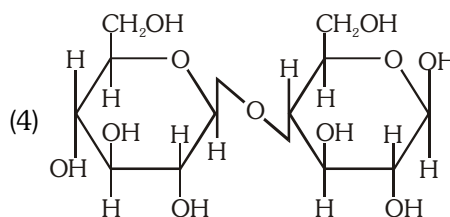
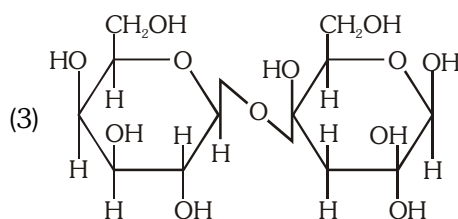
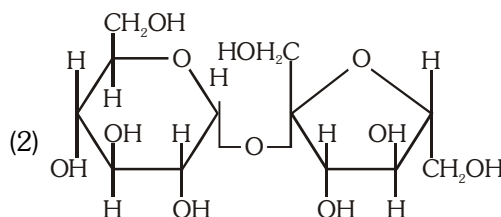
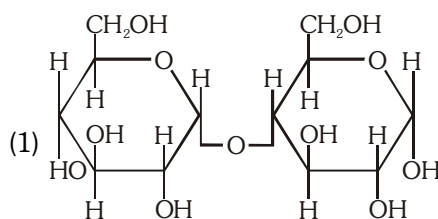
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	3	4	1	4	2	2	1	2	4	4	1	1	2	3
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	4	1	3	2	2	3	1	4	3	2	1	2	4	1	1
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	4	4	2	4	4	2	4	4	4	1	3	4	4	3	1
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	2	2	3	3	4	3	2	4	1	1	1	1	2	3	4
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	4	1	3	1	1	2	1	1	4	4	3	1	1	1	2
Que.	76	77	78												
Ans.	2	1	3												

EXERCISE-III (Analytical Questions)

- Glucose on heating with dilute sodium hydroxide undergoes in a reversible isomerisation (known as Lobry de Bruyn-van Eikenstein rearrangement) and gives –
(1) D-glucose (2) D-mannose
(3) D-fructose (4) All of these
- In which of the following properties of an open chain structure of glucose could not be explained by Baeyer –
(1) Glucose contain aldehyde group, but does not give schiff's test
(2) Glucose does not react with sodium hydrogen sulphite and ammonia
(3) The pentaacetate of glucose does not react with hydroxy amine indicates absence of $-\text{CHO}$ group
(4) All of these
- When glucose was crystallized from a concentrated solution at 30°C & 98°C . It gave α & β form of glucose respectively what are the angle of rotation $[\alpha_D]$ for both forms –
(1) $(+) 111^{\circ}$ & $(+) 19.2^{\circ}$ (2) $(+) 19.2^{\circ}$ & $(-) 111^{\circ}$
(3) $(+) 111^{\circ}$ & $(-) 19.2^{\circ}$ (4) $(-) 111^{\circ}$ & $(-) 19.2^{\circ}$
- Dinucleotide is obtained by joining two nucleotides together by phosphodiester linkage. Between which carbon atoms of pentose sugar of nucleotides are these linkages presents.
(1) $5'$ and $3'$ (2) $1'$ and $5'$
(3) $5'$ and $5'$ (4) $3'$ and $3'$
- Which of the following statements is not true about glucose.
(1) It is an aldohexase
(2) On heating with HI it forms h-hexane
(3) It is present in furanose form
(4) It does not give 2,4-DNP test
- Which statement is incorrect in following –
(1) Sucrose is dextrorotatory
(2) After hydrolysis of sucrose, dextrorotatory glucose and laevorotatory fructose will obtained
(3) Laevorotation of fructose is more than dextrorotation of glucose
(4) Cane sugar gives nonequimolar mixture of D-(+)-glucose and D-(-)-fructose

Check Your Understanding

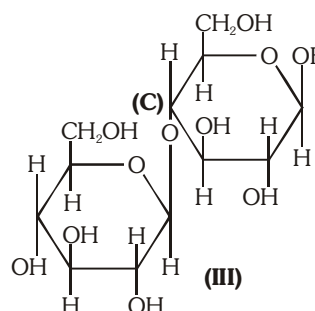
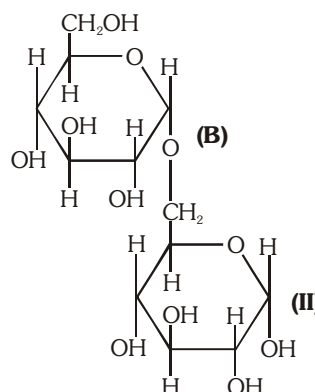
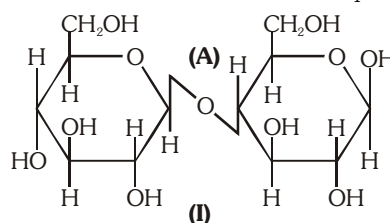
7. Which of the following disaccharide is a non-reducing sugar :-



8. On hydrolysis of one mole of maltose two moles of D-glucose are obtained. These two glucose units are linked together through a α -glycoside linkage between –
(1) C-2 of one unit and C-4 of another unit
(2) C-1 of one unit and C-2 of another unit
(3) C-1 of one unit and C-4 of another unit
(4) C-2 of one unit and C-3 of another unit
9. Which statement is/are incorrect –
(1) Natural starch has approximately 10-20% of amylose and 80-90% of amylopectin.
(2) Amylose is water soluble and gives blue colour with iodine
(3) Amylopectin is a branched chain polysaccharides insoluble in water and does not give blue colour with iodine
(4) Starch is not hydrolysed by enzyme amylase present in saliva

- 10.** Which of the following statement is true for proteins –
 (1) Proteins are high molecular mass complex biopolymers of amino acids present in all living cells
 (2) Protein may contains phosphorous & iodine
 (3) Proteins may contains iron, copper, zinc and manganese
 (4) All of these
- 11.** Which of following are essential amino acids –
 (a) Aspartic acid (b) Leucine
 (c) Valine (d) Glycine
 (e) Alanine
 (1) a, b & c (2) a, b, d & e
 (3) b & c (4) a, c, d & e
- 12.** At a certain hydrogen ion concentration (pH), the dipolar ion exists as a neutral ion and does not migrate to either electrode. What is the name of pH point for amino acids –
 (1) isoelectric point (2) isoprotonic point
 (3) isotonic point (4) None of these
- 13.** Which of the following reactions of glucose can be explained only by its cyclic structure.
 (1) Glucose forms penta acetate
 (2) Glucose reacts with hydroxylamine to form an oxime
 (3) Penta acetate of glucose does not react with hydroxylamine
 (4) Glucose is oxidised by nitric acid to gluconic acid
- 14.** Protein found in biological system with definite configuration and biological activity is called –
 (1) Amino acids (2) Native protein
 (3) Conformer protein (4) Inactive protein
- 15.** If disruptive agent is removed, the proteins recovers its original physical and chemical properties and biological activity, this process is known as –
 (1) Denaturation (2) Renaturation
 (3) Transcription (4) Translation
- 16.** Which of following statement is not true for enzyme –
 (1) Some enzymes can be non proteins also
 (2) Prosthetic groups which get attached to enzyme at the time of reaction are known as cofactor.
 (3) Enzymes provides lower activation pathways there by increasing the rate of reaction
 (4) None of these

- 17.** Which of following statements is incorrect –
 (1) Proteins have a polyamide chain while nucleic acids contains a poly phosphate ester chain
 (2) Nucleic acids are long chain polymers of nucleotides
 (3) RNA is major source of genetic information which is copied into a DNA molecules
 (4) Proteins are synthesized in a process involving translation of RNA.
- 18.** Complete hydrolysis of DNA or RNA yields following –
 (1) Ribose in RNA & deoxyribose in DNA
 (2) Hetrocyclic nitrogenous purines base
 (3) Hetrocyclic nitrogenous pyrimidines
 (4) All of these
- 19.** Three structures are given below in which two glucose units are linked. Which of these linkages between glucose units are between C_1 and C_4 and which linkages are between C_1 and C_6 .



- (1) (A) is between C_1 and C_4 ; (B) and (C) are between C_1 and C_6
 (2) (A) and (B) are between C_1 and C_4 ; (C) is between C_1 and C_6
 (3) (A) and (C) are between C_1 and C_4 ; (B) is between C_1 and C_6
 (4) (A) and (C) are between C_1 and C_6 ; (B) is between C_1 and C_4

- 20.** Nucleosides are –
 (1) Base + sugar = Nucleoside
 (2) N-glycosides of purine or pyrimidine bases with pentose sugar
 (3) Both of these
 (4) None of these
- 21.** RNA molecules in turn directs the synthesis of specific proteins which are characteristic of each kind of organism. This process is known as –
 (1) Translation (2) Transcription
 (3) Replication (4) None of these
- 22.** A single stand of DNA can act as a template on which a molecule of RNA is synthesized in a specific manner. This process is known as –
 (1) Replication (2) Transcription
 (3) Translation (4) None of these
- 23.** Which statements is/are correct –
 (1) Transcription is used as a synonym for RNA synthesis
 (2) Translation is used as a synonym for protein synthesis
 (3) Translation is unidirectional but transcription can sometimes be reversed
 (4) All of these
- 24.** Insulin is known as hypoglycemic factor because
 (1) It inhibits anabolic processes and promotes catabolic processes
 (2) It decreases glucose concentration in blood
 (3) It does not facilitate entry of glucose into the cells
 (4) None of these
- 25.** Which is correct statement –
 (1) Starch is polymer of α -glucose
 (2) Amylose is a component of cellulose
 (3) Proteins are composed of only one type of amino acid
 (4) In cyclic structure of fructose, there are four carbons and one oxygen atom
- 26.** $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\ddot{\text{N}}\text{H}- \end{array}$ (peptide bond) which statement is incorrect about peptide bond –
 (1) C–N bond length in proteins is longer than usual bond length of C–N bond
 (2) Spectroscopic analysis show planar structure of $\begin{array}{c} -\text{C}-\text{NH}- \\ \parallel \\ \text{O} \end{array}$ group
 (3) C–N bond length in proteins is smaller than usual bond length of C–N bond
 (4) None of above

EXERCISE-III (Analytical Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	4	1	1	3	4	2	3	4	4	3	1	3	2	2
Que.	16	17	18	19	20	21	22	23	24	25	26				
Ans.	2	3	4	3	3	1	2	4	2	1	1				

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

- Assertion :-** D-(+) Glucose and L-(-) fructose are enantiomers.
Reason :- Glucose molecule is mirror image of fructose molecule.
 (1) A (2) B (3) C (4) D
- Assertion :-** Teflon has high thermal stability and chemical inertness.
Reason :- Teflon is highly cross-linked polymer.
 (1) A (2) B (3) C (4) D
- Assertion :-** Polypropylene is an addition polymer.
Reason :- The monomer unit of polypropylene is $\text{CH}_3\text{-CH=CH}_2$
 (1) A (2) B (3) C (4) D
- Assertion :-** Carboxypeptidase is an exopeptidase.
Reason :- It cleaves the N-terminal bond.
 (1) A (2) B (3) C (4) D
- Assertion :-** Natural rubber is cis-1,4-polyisoprene.
Reason :- Isoprene is 2-methyl-1,3-butadiene.
 (1) A (2) B (3) C (4) D
- Assertion :-** Maltose is composed of galactose.
Reason :- Glucose and galactose differ from C_3 position.
 (1) A (2) B (3) C (4) D
- Assertion :-** β -pleated sheet structure of protein shows maximum extension.
Reason :- Intermolecular hydrogen bonding is present in them
 (1) A (2) B (3) C (4) D
- Assertion :-** All enzymes are made up of proteins which have three dimensional structure.
Reason :- Secondary structure of protein are sequence of aminoacids.
 (1) A (2) B (3) C (4) D
- Assertion :-** Melamine resin has secondary amine functionality.
Reason :- Melamine resin is condensation polymer of melamine and acetaldehyde.
 (1) A (2) B (3) C (4) D
- Assertion :-** Sucrose and saccharin have nearly same sweetness index.
Reason :- Both compounds are the component of carbohydrate.
 (1) A (2) B (3) C (4) D
- Assertion :-** Glucose does not give 2,4-DNP test.
Reason :- Glucose does not have free carbonyl group.
 (1) A (2) B (3) C (4) D
- Assertion :-** Tryptophan is less basic than Histidine
Reason :- Tryptophan has sp^3 hybridised nitrogen but Histidine has sp^2 hybridisation.
 (1) A (2) B (3) C (4) D
- Assertion :-** Bakelite is a thermosetting polymer.
Reason :- It has highly branched structure.
 (1) A (2) B (3) C (4) D
- Assertion :-** Calcium salt of fatty acid can be used as soap.
Reason :- They are water soluble.
 (1) A (2) B (3) C (4) D

15. Assertion :- Aspirin is used to reduce the chance of heart attack.

Reason :- Aspirin increase the rate of prostaglandin synthesis.

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

16. Assertion :- At neutral pH, Tyrosine act as an acid

Reason :- pK_a of phenol is more than 7.

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

17. Assertion :- Antihistamine does not effect acid secretion of stomach.

Reason :- Antacid and antihistamine acts on different receptors.

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

18. Assertion :- Glucose reacts with Br_2 to form saccharic acid.

Reason :- Acid will be formed by oxidation of alcohol with Br_2 .

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

19. Assertion :- Non competitive inhibitors alters the active site of enzymes.

Reason :- Non competitive inhibitors always bind with active site.

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

20. Assertion :- Generally RNA are single stranded.

Reason :- They interact with amino acids.

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

21. Assertion :- Natural Rubber has elastic property.

Reason :- It has linear structure.

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

22. Assertion :- Cimitidine is an antacid

Reason :- It increases the interaction of histamine with receptors present in stomach wall.

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

23. Assertion :- α – glucose has lesser melting point than β -glucose.

Reason :- β – glucose is more thermodynamic stable.

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

24. Assertion :- Sucrose is dextrorotatory but its aqueous solution is laeverotatory.

Reason :- Dextro rotation of glucose is less than laevo rotation of fructose.

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

25. Assertion :- Novolac on heating with formaldehyde gives bakelite.

Reason :- Bakelite is thermosetting polymer and an infusible solid.

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

EXERCISE-IV (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	3	2	1	2	4	2	3	3	4	1	3	2	4	3
Que.	16	17	18	19	20	21	22	23	24	25					
Ans.	2	4	4	3	2	2	3	2	1	2					