CHAPTER 03

CHEMICAL EQUILIBRIUM

> *The proportion of ingredients is important, but the final result is also a matter of how you put them together. Equilibrium is key.*
>
> **"ALAIN DUCASSE"**

INTRODUCTION

Chemical equilibrium are important in numerous biological and environmental processes. For example, equilibrium involving O_2 molecules and the protein hemoglobin play a crucial role in the transport and delivery of O_2 from our lungs to our muscles. Similar equilibrium involving CO moleucles and hemoglobin account for the toxicity of CO. State of chemical equilibrium, these may be classified in three groups.

(i) The reactions that proceed nearly to completion and only negligible concentrations of the reactants are left. In some cases., it may not be even possible to detect these experimentally.

(ii) The reactions in which only small amounts of products are formed and most of the reactants remain unchanged at equilibrium state

(iii) The reactions in which the concentrations of the reactants and products are comparable. When the system is in equilibrium.

Ex. Chemical equilibrium is a condition :

(A) where all species have same concentration
(B) where all species have constant concentration with respect to time.
(C) where all species have concentration = 1
(D) all of above

Sol. **(B)** Chemical equilibrium defined as when all species have constant concentration with respect to time.

Ex. Example of physical equilibria, is :

(A) $H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$	**(B)** $CaCO_3(s) \rightleftharpoons CaO\,(s) + CO_2(g)$
(C) $H_2O\,(s) \rightleftharpoons H_2O\,(\ell)$	**(D)** $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2(g)$

Sol. **(C)** Physical equilibria does not include any chemical change.

Ex. At equilibrium :

(A) the energy of system is minimum	**(B)** the entropy of system is maximum
(C) the energy of system is maximum	**(D)** the entropy of system is minimum

Sol. **(A,B)** It is the compromising stage of minimum energy and maximum entropy.

ETOOS KEY POINTS

(i) Whenever question doesn't ask about direction, then we take forward direction only.
(ii) In a reversible reaction if forward reaction is exothermic then the backward reaction will be endothermic and vice versa.

Law of Mass action or Law of chemical equilibrium

The law of mass action was given by **Guldberg** and **Waage** (1864). It states that the rate of a chemical reaction is directly proportional to the product of active masses of the reacting substances.

Derivation of equilibrium constant : Consider a reversible homogeneous chemical reaction which has attained equilibrium state at a particular temperature : $A + B \rightleftharpoons C + D$

Let the active masses of A, B, C and D be [A] [B] [C] and [D] respectively at equilibrium.

According to law of mass action :

Rate of forward reaction $(R_f) \propto [A]\,[B]$
Rate of backward reaction $(R_b) \propto [C]\,[D]$

$R_f = k_f\,[A]\,[B]$ and $R_b = k_b[C][D]$

Where k_f and k_b are forward and backward rate or velocity constants respectively.

At equilibrium state :

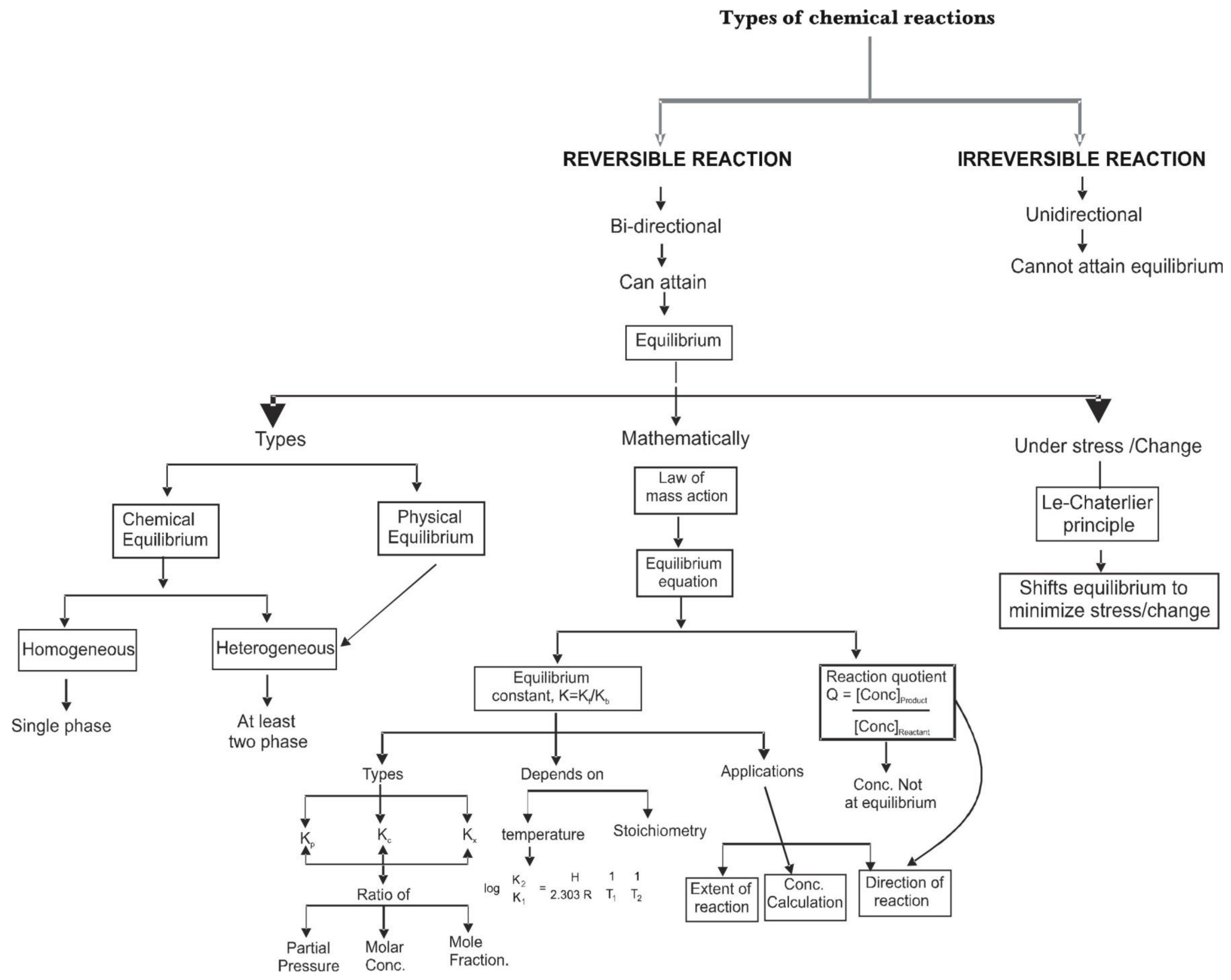
$$R_f = R_b$$

$$k_f[A]\,[B] = k_b\,[C]\,[D]$$

$$\frac{k_f}{k_b} = \frac{[C][D]}{[A][B]}$$

$$K_C = \frac{[C][D]}{[A][B]}; \qquad \because\ K_C = \frac{k_f}{k_b}$$

K_c is known as equilibrium constant. K_c has a definite value for every chemical reaction at particular temperature.


Types of chemical reactions
REVERSIBLE REACTION
Bi-directional
Can attain
Equilibrium
IRREVERSIBLE REACTION
Unidirectional
Cannot attain equilibrium
Types
Chemical Equilibrium
Physical Equilibrium
Homogeneous
Single phase
Heterogeneous
At least two phase
Mathematically
Law of mass action
Equilibrium equation
Equilibrium constant, K=K_f/K_b
Types
K_p
K_c
K_x
Ratio of
Partial Pressure
Molar Conc.
Mole Fraction.
Depends on
temperature
Stoichiometry
log K_2/K_1 = H/2.303 R 1/T_1 1/T_2
Applications
Extent of reaction
Conc. Calculation
Direction of reaction
Reaction quotient Q = [Conc]_Product / [Conc]_Reactant
Conc. Not at equilibrium
Under stress /Change
Le-Chaterlier principle
Shifts equilibrium to minimize stress/change

SOLVED EXAMPLE

Ex. 1 When 1.0 mole of N_2 and 3.0 moles of H_2 was heated in a vessel at 873 K and a pressure of 3.55 atm. 30% of N_2 is converted into NH_3 at equilibrium. Find the value of K_P for the reaction.

(A) $3.1 \times 10^{-2}\,atm^{-2}$ **(B)** $4.1 \times 10^{-2}\,atm^{-2}$ **(C)** $5.1 \times 10^{-2}\,atm^{-2}$ **(D)** $6.1 \times 10^{-2}\,atm^{-2}$

Sol. **(C)**

	$N_2(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$	
	1 mole		3 moles		0	Initial moles
	1–0.3		3.0 – 0.9		0.6 moles	at equilibrium
	= 0.7 moles		=2.1 moles			

Total no. of moles at equilibrium = 3.4

$$K_P = \frac{\left(\frac{0.6}{3.4} \times 3.55\right)^2}{\left(\frac{0.7}{3.4} \times 3.55\right)\left(\frac{2.1}{3.4} \times 3.55\right)^3} = 5.1 \times 10^{-2}\ atm^{-2}$$

Ex. 2 $2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3(g)$

If the partial pressure of SO_2, O_2 and SO_3 are 0.559, 0.101 and 0.331 atm respectively. What would be the partial pressure of O_2 gas, to get equal moles of SO_2 and SO_3.

(A) 0.188 atm **(B)** 0.288 atm **(C)** 0.388 atm **(D)** 0.488atm

Sol. **(B)**

$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3(g)$

$$K_P = \frac{[P_{SO_3}]^2}{[P_{SO_2}]^2[P_{O_2}]} = \frac{(0.331)^2}{(0.559)^2\,(0.101)} = 3.47$$

If SO_2 and SO_3 have same number of moles, their partial pressure will be equal and

$$P_{SO_3} = P_{SO_2} \quad \therefore \quad P_{O_2} = \frac{1}{3.47} = 0.288 atm$$

Ex. 3 K_P for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at 400°C is 3.28×10^{-4}. Calculate K_c.

(A) 0.3 mole^{-2} litre^2 **(B)** 0.4 mole^{-2} litre^2 **(C)** 1.0 mole^{-2} litre^2 **(D)** 0.6 mole^{-2} litre^2

Sol. **(C)** $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$\Delta n = -2$ and $K_P = K_C\,(RT)^{\Delta n}$

$3.28 \times 10^{-4} = K_c\,(0.0821 \times 673)^2$

and $K_c = 1.0$ mole^{-2} litre^2.

Ex. 4 A mixture of H_2 and I_2 in molecular proportion of 2 : 3 was heated at 444°C till the reaction

$H_2 + I_2 \rightleftharpoons 2HI$ reached equilibrium state. Calculate the percentage of iodine converted into HI.

(K_C at 444°C is 0.02)

(A) 3.38 % **(B)** 4.38% **(C)** 5.38% **(D)** 6.38%

Sol. **(C)**

	H_2	+ I_2	$\rightleftharpoons$	$2HI$
Initial moles	2	3		0
Equi.conc.	$\frac{2-x}{v}$	$\frac{3-x}{v}$		$\frac{2x}{v}$

$$K_C = \frac{4x^2}{(2-x)(3-x)} = 0.02$$

$199\,x^2 + 5x - 6 = 0$

$x = 0.1615$

Out of 3 moles, 0.1615 moles I_2 is converted into HI.

$$\therefore \text{ Percentage of } I_2 \text{ converted to HI} = \frac{0.1615 \times 100}{3} = 5.38\%$$

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. According to law of mass action rate of a chemical reaction is proportional to

(A) Concentration of reactants

(B) Molar concentration of reactants

(C) Concentration of products

(D) Molar concentration of products

2. In a reaction the rate of reaction is proportional to its active mass, this statement is known as

(A) Law of mass action

(B) Le-chatelier principle

(C) Faraday law of electrolysis

(D) Law of constant proportion

3. The active mass of 64 gm of HI in a two litre flask would be

(A) 2 **(B)** 1

(C) 5 **(D)** 0.25

4. Under a given set of experimental conditions, with increase in the concentration of the reactants, the rate of a chemical reaction

(A) Decreases

(B) Increases

(C) Remains unaltered

(D) First decreases and then increases

5. The law of mass action was enunciated by

(A) Guldberg and Waage **(B)** Bodenstein

(C) Birthelot **(D)** Graham

6. For the system $3A + 2B \rightleftharpoons C$, the expression for equilibrium constant is

(A) $\dfrac{[3A][2B]}{C}$ **(B)** $\dfrac{[C]}{[3A][2B]}$

(C) $\dfrac{[A]^3[B]^2}{[C]}$ **(D)** $\dfrac{[C]}{[A]^3[B]^2}$

7. In the reversible reaction $A + B \rightleftharpoons C + D$, the concentration of each C and D at equilibrium was 0.8 mole/litre, then the equilibrium constant K_c will be

(A) 6.4 **(B)** 0.64

(C) 1.6 **(D)** 16.0

8. 4 moles of A are mixed with 4 moles of B. At equilibrium for the reaction $A + B \rightleftharpoons C + D$, 2 moles of C and D are formed. The equilibrium constant for the reaction will be

(A) $\dfrac{1}{4}$ **(B)** $\dfrac{1}{2}$

(C) 1 **(D)** 4

9. On a given condition, the equilibrium concentration of HI, H_2 and I_2 are 0.80, 0.10 and 0.10 mole/litre. The equilibrium constant for the reaction $H_2 + I_2 \rightleftharpoons 2HI$ will be

(A) 64 **(B)** 12

(C) 8 **(D)** 0.8

10. In which of the following, the reaction proceeds towards completion

(A) $K = 10^2$ **(B)** $K = 10^{-2}$

(C) $K = 10$ **(D)** $K = 1$

11. A reversible chemical reaction having two reactants in equilibrium. If the concentrations of the reactants are doubled, then the equilibrium constant will

(A) Also be doubled **(B)** Be halved

(C) Become one-fourth **(D)** Remain the same

12. The equilibrium constant in a reversible reaction at a given temperature

(A) Depends on the initial concentration of the reactants

(B) Depends on the concentration of the products at equilibrium

(C) Does not depend on the initial concentrations

(D) It is not characteristic of the reaction

13. Pure ammonia is placed in a vessel at temperature where its dissociation constant (α) is appreciable. At equilibrium

(A) K_p does not change significantly with pressure

(B) α does not change with pressure

(C) Concentration of NH_3 does not change with pressure

(D) Concentration of H_2 is less than that of N_2

14. For the system $A(g) + 2B(g) \rightleftharpoons C(g)$, the equilibrium concentrations are **(A)** 0.06 mole/litre **(B)** 0.12 mole/litre **(C)** 0.216 mole/litre. The K_{ep} for the reaction is

(A) 250 **(B)** 416

(C) $K \times 10^{-3}$ **(D)** 125

Exercise # 2

SINGLE OBJECTIVE | AIIMS LEVEL

1. Equilibrium constant for the reactions,

$2\,NO + O_2 \rightleftharpoons 2\,NO_2$ is K_{C_1};

$NO_2 + SO_2 \rightleftharpoons SO_3 + NO$ is K_{C_2} and

$2\,SO_3 \rightleftharpoons 2\,SO_2 + O_2$ is K_{C_3} then correct reaction is :

(A) $K_{C_3} = K_{C_1} \times K_{C_2}$

(B) $K_{C_3} \times K_{C_1} \times K^2_{C_2} = 1$

(C) $K_{C_3} \times K_{C_1} \times K_{C_2} = 1$

(D) $K_{C_3} \times K^2_{C_1} \times K_{C_2} = 1$

2. At a certain temperature, the following reactions have the equilibrium constant as shown below:

$S(s) + O_2(g) \rightleftharpoons SO_2(g);\ K_c = 5 \times 10^{52}$

$2S(s) + 3O_2(g) \rightleftharpoons 2SO_3(g);\ K_c = 10^{29}$

What is the equilibrium constant K_c for the reaction at the same temperature ?

$2SO_2(s) + O_2(g) \rightleftharpoons 2SO_3(g)$

(A) 2.5×10^{76} **(B)** 4×10^{23}

(C) 4×10^{-77} **(D)** None of these

3. Sulfide ion in alkaline solution reacts with solid sulfur to form polysulfide ions having formulae S_2^{2-}, S_3^{2-}, S_4^{2-} and so on. The equilibrium constant for the formation of S_2^{2-} is $K_1 = 12$ & for the formation of S_3^{2-} is $K_2 = 132$, both from S and S^{2-}. What is the equilibrium constant for the formation of S_3^{2-} from S_2^{2-} and S?

(A) 11 **(B)** 12

(C) 132 **(D)** None of these

4. When alcohol ($C_2H_5OH(\ell)$) and acetic acid ($CH_3COOH(\ell)$) are mixed together in equimolar ratio at 27ºC, 33% of each is converted into ester. Then the K_C for the equilibrium

$C_2H_5OH(\ell) + CH_3COOH(\ell) \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$

is :

(A) 4 **(B)** 1/4

(C) 9 **(D)** 1/9

5. One litre of 2M acetic acid and one litre of 3M ethyl alcohol are mixed to form ester according to the given equation :

$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O.$

If each solution is diluted by adding equal volume (1 litre) of water by how many times the initial forward rate is reduced ?

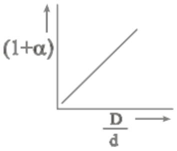
(A) 4 times **(B)** 2 times

(C) 0.5 times **(D)** 0.25 times

6. In the dissociation of N_2O_4 into NO_2, $(1 + \alpha)$ values with the vapour densities ratio $\left(\frac{D}{d}\right)$ is as given by :

[α-degree of dissociation, D-vapour density before dissociation, d-vapour density after dissociation]

(A)



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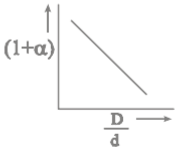
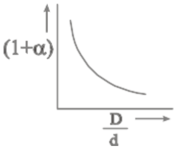
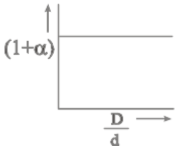


(C)

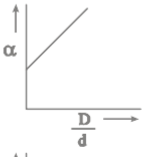


(D)

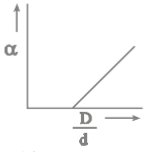


7. In the above question, α varies with $\frac{D}{d}$ according to :

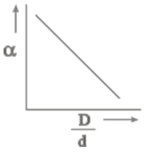
(A)



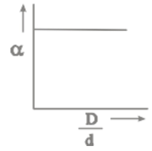
(B)



(C)



(D)



8. For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, if percentage dissociation of N_2O_4 are 20%, 45%, 65% & 80%, then the sequence of observed vapour densities will be :

(A) $d_{20} > d_{45} > d_{65} > d_{80}$

(B) $d_{80} > d_{65} > d_{45} > d_{20}$

(C) $d_{20} = d_{45} = d_{65} = d_{80}$

(D) $(d_{20} = d_{45}) > (d_{65} = d_{80})$

Exercise # 3

PART - 1

MATRIX MATCH COLUMN

1. Match the following :

Column I (Assume only reactant were present initially)	Column II
(A) For the equilibrium $NH_4I(s) \rightleftharpoons NH_3(g) + HI(g)$, if pressure is increased at equilibrium	**(p)** Forward shift
(B) For the equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ volume is increased at equilibrium	**(q)** No shift in equilibrium
(C) For the equilibrium $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$ inert gas is added at constant pressure at equilibrium	**(r)** Backward shift
(D) For the equilibrium $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ Cl_2 is removed at equilibrium.	**(s)** Final pressure is more than initial pressure

2. Match the following : (Assume only reactants were present initially).

Column □	Column □ □
(A) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (t = 300ºC)	**(p)** $\Delta n_g > 0$
(B) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ (t = 50ºC)	**(q)** $K_p < K_c$
(C) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$	**(r)** K_p not defined
(D) $CH_3COOH(\ell) + C_2H_3OH(\ell) \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$	**(s)** $P_{initial} > P_{eq.}$

3.

Column-I (Reactions)	Column-II (Favourable conditions)
(A) Oxidation of nitrogen $N_2(g) + O_2(g) + 180.5\ kJ \rightleftharpoons 2NO(g)$	**(p)** Addition of inert gas at constant pressure
(B) Dissociation of $N_2O_4(g)$ $N_2O_4(g) + 57.2\ kJ \rightleftharpoons 2NO_2(g)$	**(q)** Decrease in pressure
(C) Oxidation of $NH_3(g)$ $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) + 905.6\ kJ$	**(r)** Decrease in temperature
(D) Formation of $NO_2(g)$ $NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g) + 200\ kJ$	**(s)** Increase in temperature

4.

Column-I (Reaction)	Column-II (If □ isnegligiable w.r.t. 1)
(A) $2X(g) \rightleftharpoons Y(g) + Z(g)$	**(p)** $\alpha = 2 \times \sqrt{K_c}$
(B) $X(g) \rightleftharpoons Y(g) + Z(g)$	**(q)** $\alpha = 3 \times \sqrt{K_c}$
(C) $3X(g) \rightleftharpoons Y(g) + Z(g)$	**(r)** $\alpha = (2K_c)^{1/3}$
(D) $2X(g) \rightleftharpoons Y(g) + 2Z(g)$	**(s)** $\alpha = \sqrt{K_c}$

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. For a reversible reaction, if the concentrations of the reactants are doubled, the equilibrium constant will be **[CBSE AIPMT 2000]**

(A) one-fourth **(B)** halved
(C) doubled **(D)** the same

2. For the equilibrium,

$MgCO_3(s) \square\square\overset{\Delta}{\square}\square\, MgO(s) \square\, CO_2(g)$

which of the following expressions is correct?

[CBSE AIPMT 2000]

(A) $K_p \square p_{CO_2}$ **(B)** $K_p \square \frac{[MgO][CO_2]}{[MgCO_3]}$

(C) $K_p \square \frac{p_{MgO} \square p_{CO_2}}{p_{MgCO_3}}$ **(D)** $K_p \square \frac{p_{MgO} \square p_{CO_2}}{p_{MgCO_3}}$

3. Reaction, $BaO_2(s) \square BaO(s) + O_2(g), \Delta H = +ve$

In equilibrium condition, pressure of O_2 depends on **[CBSE AIPMT 2002]**

(A) increased mass of BaO_2
(B) increased mass of BaO
(C) increased temperature of equilibrium
(D) increased mass of BaO_2 and BaO both

4. The reaction quotient (Q) for the reaction, $N_2(g) + 3H_2(g) \square\ 2NH_3(g)$ is given by

$Q \square \frac{[NH_3]^2}{[N_2][H_2]^3}$

The reaction will proceed towards right side, if **[CBSE AIPMT 2003]**

(A) $Q > K_c$ **(B)** $Q = 0$
(C) $Q = K_c$ **(D)** $Q < K_c$

where, K_c is the equilibrium constant.

5. In the two gaseous reaction (i) and (ii) at 250°C

(i) $NO(g) + \frac{1}{2}O_2(g) \square NO_2(g), K_1$

(ii) $2NO_2(g) \square 2NO(g) + O_2(g), K_2$

the equilibrium constants K_1 and K_2 are related as **[CBSE AIPMT 2005, 1994]**

(A) $K_2 \square \frac{1}{K_1}$ **(B)** $K_2 \square K_1^{1/2}$

(C) $K_2 \square \frac{1}{K_1^2}$ **(D)** $K_2 \square K_1^2$

6. For the reaction,
$CH_4(g) + 2O_2(g) \square CO_2(g) + 2H_2O(l)$,
$\Delta rH = -170.8\ kJ\ mol^{-1}$
Which of the following statement is not true ?

[CBSE AIPMT 2006]

(A) At equilibrium, the concentrations of $CO_2(g)$ and $H_2O(l)$ are not equal
(B) The equilibrium constant for the reaction is given by $k_p \square \frac{[CO_2]}{[CH_4][O_2]}$
(C) Addition of CH4(g) or O2(g) at equilibrium will cause a shift to the right
(D) The reaction is exothermic

7. The value of equilibrium constant of the reaction,

$HI(g) \square \frac{1}{2}H_2(g) \square \frac{1}{2}I_2(g)$ is 8.0.

The equilibrium constant of the reaction,

$H_2(g) + I_2(g) \square 2HI(g)$ will be

[CBSE AIPMT 2008]

(A) $\frac{1}{16}$ **(B)** $\frac{1}{64}$

(C) 16 **(D)** $\frac{1}{8}$

8. If the concentration of OH^- ions in the reaction, $Fe(OH)_3(s) \square Fe^{3+}(aq) + 3OH^-(aq)$ is decreased by 1/4 times, then equilibrium concentration of $Fe3^+$ will increase by

[CBSE AIPMT 2008]

(A) 8 times **(B)** 16 times
(C) 64 times **(D)** 4 times

9. 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,
$CN^- + CH_3COOH \square HCN + CH_3COO^-$
would be

[CBSE AIPMT 2009]

(A) 3.0×10^5 **(B)** 3.0×10^{-5}
(C) 3.0×10^{-4} **(D)** 3.0×10^4

10. In which of the following equilibrium K_c and K_p are not equal ? **[CBSE AIPMT 2010]**

(A) $2NO(g) \square N_2(g) + O_2(g)$
(B) $SO_2(g) + NO_2(g) \square SO_3(g) + NO(g)$
(C) $H_2(g) + I_2(g) \square 2HI(g)$
(D) $2C(s) + O_2(g) \square 2CO_2(g)$

MOCK TEST

STRAIGHT OBJECTIVE TYPE

1. Solid ammonium carbamate dissociates to give ammonia and carbon dioxide as follows.

$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

At equilibrium, ammonia is added such that partial pressures of NH_3 now equals the original totoal pressure. Calculate the ratio of the total pressure now to the original total pressure.

(A) $\frac{31}{27}$ **(B)** $\frac{60}{40}$ **(C)** $\frac{31}{9}$ **(D)** $\frac{62}{27}$

2. In the Haber process for the industrial manufacture of ammonia involving the reaction,

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ at 200 atm pressure in the presence of a catalyst, a temperature of about 500°C is used. This is considered as optimum temperature for the process because

(A) yield is maximum at this temperature

(B) catalyst is active only at this temperature

(C) energy needed for the reaction is easily obtained at this temperature

(D) rate of the catalytic reaction is fast enough while the yield is also appreciable for this exothermic reaction at this temperature.

3. For the equilibrium of the reaction, $HgO(s) \rightleftharpoons Hg(g) + \frac{1}{2}O_2(g)$, k_p for the reaction at total pressure of P is :

(A) $K_p = \frac{2}{3^{3/2}}P^{3/2}$ **(B)** $K_p = \frac{2}{3^{1/2}}P^{1/2}$ **(C)** $K_p = \frac{1}{3^{2/3}}P^{3/2}$ **(D)** $K_p = \frac{1}{3^{2/3}}P$

4. The average person can see the red colour imparted by the complex $[Fe(SCN)]^{2+}$ to an aqueous solution if the concentration of the complex is 6×10^{-6} M or greater. What minimum concentration of KSCN would be required to make it possible to detect 1 ppm (part per million) of Fe(III) in a natural water sample? The instability constant for

$Fe(SCN)^{2+} \rightleftharpoons Fe^{3+} + SCN^-$ is 7.142×10^{-3}.

(A) 0.0036 M **(B)** 0.0037 M **(C)** 0.0035 M **(D)** None of these

5. $\frac{1}{2}N_2(g) + O_2(g) \rightleftharpoons NO_2(g)$ ...K_1

$2NO_2(g) \rightleftharpoons N_2O_4(g)$ ...K_2

Given that above reactions have equilibrium constants K_1 and K_2 respectively. What would be the expression for the equilibrium constant K for the following reaction in terms of K_1 and K_2?

(A) $K_1 K_2$ **(B)** $\frac{1}{K_1(K_2)^2}$ **(C)** $\frac{1}{K_2(K_1)^2}$ **(D)** $\frac{1}{K_1K_2}$

6. The value of K_p for the reaction at 27°C

$Br_2(\ell) + Cl_2(g) \rightleftharpoons 2BrCl(g)$

is '1 atm'. At equilibrium in a closed container partial pressure of BrCl gas ia 0.1 atm and at this temperature the vapour pressure of $Br_2(\ell)$ is also 0.1 atm. Then what will be minimum moles of $Br_2(\ell)$ to be added to 1 mole of Cl_2, to get above equilibrium situation :

(A) $\frac{10}{6}$ moles **(B)** $\frac{5}{6}$ moles **(C)** $\frac{15}{6}$ moles **(D)** 2 moles

7. The two equilibria, $AB(aq) \rightleftharpoons A^+(aq) + B^-(aq)$ and $AB(aq) + B^-(aq) \rightleftharpoons AB_2^-(aq)$ are simultaneously maintained in a solution with equilibrium constants, K_1 and K_2 respectively. If $[A^+]$ and $[AB_2^-]$ are y and x respectively, under equilibrium produced by adding the substance AB to the solvents, then K_1 / K_2 is equal to

(A) $\frac{y}{x}(y - x)^2$ **(B)** $\frac{y^2(x + y)}{x}$ **(C)** $\frac{y^2(x + y)}{x}$ **(D)** $\frac{y}{x}(x - y)$

[**Note** : Use the information of the preceding problem]

CHAPTER 05

SURFACE CHEMISTRY

The nature of the chemical bond is the problem at the heart of all chemistry.

''BRYCE CRAWFORD''

INTRODUCTION

The properties of substances are different at the surfaces and in the bulk, because the molecules present in the bulk are equally attracted in all direction having net force zero but the molecules present at surface experience attraction unequally. Due to unbalanced forces these molecules present at surface tends to take up molecules of a gas or any other substance in order to release the surface tension which they are experiencing. This tendency is more prominent in transition metals. The surface is more activated in case of finely divided state or rough surface. In this unit we will study phenomenon related to surface.

Surface chemistry is the branch of chemistry which deals with the study of nature of surface and the species present on it. This phenomenon is studied with the help of adsorption and colloidal state which are quite useful to understant the physical and chemical characteristics of the substance.

EDOS KEY POINTS

Actually every substance irrespective of its nature can be crystalloid or colloid under suitable conditions. For example:

(I) NaCl though a crystalloid in water behaves like a colloid in benzene.

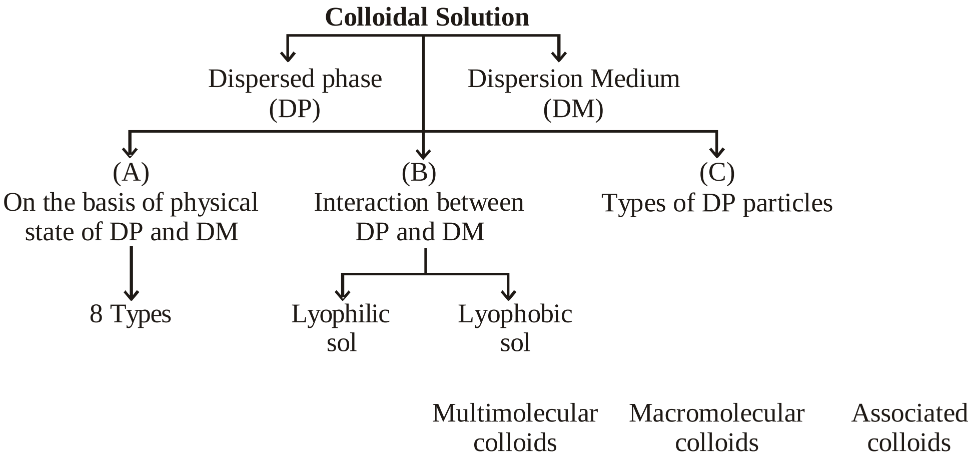
(II) Soap is a colloid in water, while it behaves like a crystalloid in benzene.

Therefore colloidal state now a days may be defined as following "A substance is said to be in the colloidal state, when it is dispersed in another medium in the form of very small particles having diameter between 10^{-4} to 10^{-7} cm (100 mμ to 1 mμ).

Molecular size in true solution	**Colloidal particle size**	**Coarse suspension particle size**
10^{-7} to 10^{-8} cm	10^{-5} to 10^{-7} cm	10^{-3} to 10^{-5} cm

TYPESOF COLLOIDAL SOLUTIONS

They considered as a heterogeneous system consisting of the following three essential components:



(i) **A dispersed phase:** It is also known as discontinuous or inner phase. It consists of discrete particles significantly larger than ordinary molecules and in this small particles of solute is diffused in solvent.

(ii) **A dispersion medium or continuous phase or the outer phase :** It is the medium in which dispersed phase is present. This consists of continuously interlinked molecules.

(iii) **A stabilising agent:** This is a substance which tends to keep the colloidal particles apart. Some colloids are self stabilizers.

Dispersed phase + Dispersion medium = Dispersion system (Colloidal solution)

Each of the two phases constituting a colloidal system may be a gas, a liquid or a solid. For example, in milk, the fat globules are dispersed in water. Hence fat globules form a dispersed phase and water is the dispersion medium.

(iv) **Sol :** If dispersion of a solid in a liquid, solid or gaseous medium, the resulting solution is called sol.

(COLLOIDAL SOLUTION)

Classification based on interaction of phases :-

(1) LYOPHILIC AND LYOPHOBIC SOLS

Colloidal solution in which the dispersed phase has considerable affinity for the dispersion phase, are called Lyophilic sols (solvent - liking)

For example - dispersion of gelatin, starch, gum and proteins in water.

Colloidal solutions in which the dispersed phase has no affinity or attaraction for the medium or for the solvent are called Lyophobic colloidal (Solvent hating) solutions.

COMPARISION OFLYOPHOBIC AND LYOPHILIC SOLS

General Characteristics of Catalysts :-

(i) A catalyst remains unchanged in mass and chemical composition but can change their physical state.

(ii) Onlya very small amount of catalyst is sufficient to catalyse a reaction.

(iii) A catalyst does not initiate a reaction.

(iv) Solid catalyst is more efficient when used in finely divided form.

(v) Generally catalyst does not change the nature of products.

(vi) A catalyst does not change the equilibrium state of a reversible reaction but helps to achieve the equilibrium state or position of equilibrium in lesser time.

(vii) The catalyst is generally specific in nature.

(viii) Change rate constant of reaction.

(ix) Does not change free energy of reaction.

(x) Participate in mechanism of reaction.

SOLVED EXAMPLE

Ex. 1 Which of the following process does not occur at the interface of phases

(A) Crystallisation

(B) Heterogeneous catalysis

(C) Homogeneous catalysis

(D) Corrosion

Sol. **(C)** Homogeneous catalysis does not at the interface of phases as in case of homogenous catalysis reactant and catalyst have same phase and their distribution is uniform throughout.

Ex. 2 At the equilibrium position in the process of adsorption ...

(A) $\Delta H > 0$ **(B)** $\Delta H = T\Delta S$

(C) $\Delta H > T\Delta S$ **(D)** $\Delta H < T\Delta S$

Sol. **(B)** As we know that, at equilibrium $\Delta G = 0$

$$\Delta H - T\Delta S = 0$$

$$\Delta H = T\Delta S$$

Hence, at equilibrium enthalpy change is equal to product of temperature and entropy change.

Ex. 3 Which of the following interface cannot be obtained

(A) Liquid-liquid **(B)** Solid-liquid

(C) Liquid-gas **(D)** Gas-gas

Sol. **(A)** Gas-gas interface can not be obtained as they are completely miscible in nature. e.g., air is a mixture of various gases such as. O_2, N_2, CO_2 etc.

Ex. 4 The term 'sorption' stands for.....

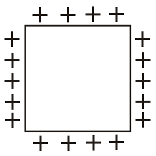
(A) Absorption

(B) Adsorption

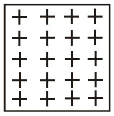
(C) Both absorption and adsorption

(D) Desorption

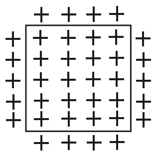
Sol. **(C)** Sorption stands for both absorption and adsorption. We can understand this by using following figures.



adsoption



abroption



sorption

Ex. 5 Extent of physisorption of a gas increases with......

(A) Increase intemperature

(B) Decrease in temperature

(C) Decrease in surface area of adsorbent

(D) Decrease in strength of van der Waal's forces

Sol. **(B)** Extent of physisorption of a gas increases with decreases in temperature. Beacause in physisorption particles are held to the surface by weak van der Waal's force of attrection hence on increasing temperature they get desorbed easily.

Ex. 6 Extent of adsorption of adsorbate from solution phase increases with.....

(A) Increase in amount of adsorbate in solution

(B) Decrease in surface area of adsorbent

(C) Increase in temperature of solution

(D) Decrease in amount of adsorbate in solution

Sol. **(A)** Extent of adsorption of adsorbate from solution phase increase with increase in amount of adsorbate in solution. As amount of adsorption in the solution increase interaction of adsorption with adsorbent increase which lead to increase in extent of adsorption.

Ex. 7 Which one of the follwing is not applicable to the phenomenon of adsorption

(A) $\Delta H > 0$ **(B)** $\Delta G < 0$

(C) $\Delta S < 0$ **(D)** $\Delta H < 0$

Sol. **(A)** For phenomenon of adsorption $\Delta H < 0$. i.e., enthalpy change during phenomenon of adsorption is negative beacause during adsorption, there is always a decrease in residual forces of the surface which lead to decrease in surface energy which appears as heat.

So, adsorption is an exothermic process and $\Delta H < 0$

Ex. 8 Which of the follwing is not a favourable condition for physical adsorption

(A) High pressure

(B) Negative ΔH

(C) Higher critical temperature of adsorbate

(D) High temperaure

Sol. **(D)** Physisorption is a process in which adsorbate get adsorbed on the adsorbent surface by weak van der Waal's force of attraction. On increasing temperaure the interaction between adsorbate and adsorbent becomes weak and adsorbate particles get desorbed.

Ex. 9 Physical adsobtion of a gaseous spesies may change to chemical adsorption with....

(A) Decrease in temperature

(B) Increase in temperature

(C) Increase in surface area of adsorbent

(D) Decrease in surface area of adsorbent

Sol. **(B)** On increasing temperature physisorption changes to chemisorption. As temperature increases. energy of activatin of adsorbate particles increaese which lead to formation of chemical bond between adsorbate and adsorbent.

Hence, physisorption transform into chemisorption.

Exercise # 1 SINGLE OBJECTIVE NEET LEVEL

1. Chemisorption
(A) Involves the weak attractive interactions between adsorbent and adsorbate
(B) Is irreversible in nature
(C) Decreases with increase of temperature
(D) Involves multilayer formation of adsorbent on adsorbate

2. Chemisorption
(A) Increases with temperature
(B) Decreases with temperature
(C) Remains unaffected by change of temperature
(D) Either increases or decreases with temperature

3. Which among the following statement is false
(A) The adsorption may be monolayered or multilayered
(B) Particle size of adsorbent will not affect the amount of adsorption
(C) Increase of pressure increases amount of adsorption
(D) Increase of temperature may decrease the amount of adsorption

4. Wood charcoal is used to decolourise sugar because it
(A) Adsorbs coloured material
(B) Absorbs decolorised material
(C) Reduces coloured material
(D) None of these

5. If the absorbate is held on a surface by weak Vander Waal's forces, the absorption process is called
(A) Physical adsorption
(B) Chemical adsorption
(C) Heat of adsorption
(D) Enthalpy of adsorption

6. When the temperature is raised, the viscosity of liquid decreases, this is because
(A) Decreased volume of the solution
(B) Increase in temperature increases the average kinetic energy of molecules, which overcome the attractive force between them
(C) Decreased covalent and hydrogen bond forces
(D) Increased attraction between molecules

7. A solid acts as an adsorbent because it has
(A) A definite shape **(B)** Small pores in it
(C) Unsaturated valencies **(D)** A high lattice energy

8. Point out the wrong statement :
Physical adsorption is characterised by
(A) Attraction due to weak Vander Waal's forces
(B) Irreversible nature of adsorption
(C) Multimolecular adsorption layers
(D) Decrease in adsorption with increase in temperature

9. When the temperature is lowered and pressure is raised, the adsorption of a gas on a solid
(A) Decreases
(B) Increases
(C) Remains unaffected
(D) Decreases first then increases

10. In physical adsorption, the gas molecules are held on solid surface by
(A) Chemical forces
(B) Electrostatic forces
(C) Gravitational forces
(D) Vander Waal's forces

11. Adsorption is multilayer in the case of
(A) Physical adsorption **(B)** Chemisorption
(C) Both **(D)** None of both

12. Physical adsorption
(A) Involves the weak attractive interaction between the adsorbent and adsorbate
(B) Involves the chemical interactions between the adsorbent and adsorbate
(C) Is irreversible in nature
(D) Increases with increase of temperature

13. The charge on sol is due to the adsorbed
(A) H^+ **(B)** OH^-
(C) O^{2-} **(D)** S^{2-}

14. In the adsorption of acetic acid on activated charcoal, the acetic acid is an
(A) Adsorber **(B)** Absorber
(C) Adsorbent **(D)** Adsorbate

15. Sticking of one substance at the surface of another is called
(A) Absorption **(B)** Chemisorption
(C) Adsorption **(D)** Desorption

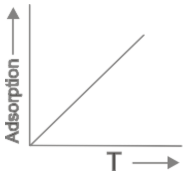
16. The charge on colloidal particles is due to
(A) Presence of electrolyte
(B) Very small size of particles
(C) Adsorption of ions from the solution
(D) None of these

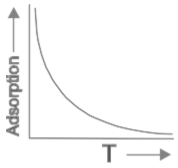
Exercise # 2

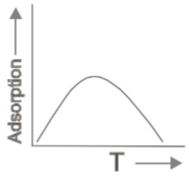
SINGLE OBJECTIVE

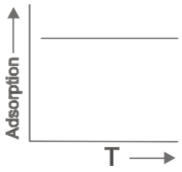
AIIMS LEVEL

1. Following is the variation of physical adsorption with temperature:

(A)


(B)


(C)


(D)


2. Adsorption is the phenomenon in which a substance:
   - (A) accumulates on the surface of the other substance
   - (B) goes into the body of the other substances
   - (C) remains close to the other substance
   - (D) none of these

3. Finely divided catalyst has greater surface area and has greater catalytic activity than the compact solid. If a total surface area of 6291456 cm^2 is required for adsorption in a catalysed gaseous reaction, then how many splits should be made to a cube of exactly 1 cm in length to achieve required surface area. (Given : One split of a cube gives eight cubes of same size)
   - (A) 60
   - (B) 80
   - (C) 20
   - (D) 22

4. Which of the following statements about chemisorption is not applicable?
   - (A) It involves chemical forces between adsorbent and absorbate
   - (B) It is irreversible in nature
   - (C) It involves high heat of adsorption
   - (D) It does not require activation energy

5. Volume of N_2 at NTP required to form a mono layer on the surface of iron catalyst is 8.15 ml/gram of the adsorbent. What will be the surface area of the adsorbent per gm if each nitrogen molecule occupies $16 \times 10^{-22} m^2$.
   - (A) $16 \times 10^{-16} cm^2$
   - (B) $0.35 m^2/g$
   - (C) $39 m^2/g$
   - (D) $22400 cm^2$

6. There is desorption of physical adsorption when:
   - (A) temperature is increased
   - (B) temperature is decreased
   - (C) pressure is increased
   - (D) concentration is increased

7. Softening of hard water is done using sodium aluminium silicate (zeolite). The causes :
   - (A) adsorption of Ca^{2+} and Mg^{2+} ions of hard water replacing Na^+ ions.
   - (B) adsorption of Ca^{2+} and Mg^{2+} ions of hard water replacing Al^{3+} ions
   - (C) both **(A)** and **(B)**
   - (D) none of these

8. The rate of chemisorption :
   - (A) decreases with increase of pressure
   - (B) increases with increase of pressure
   - (C) is independent of pressure
   - (D) is independent of temperature

9. Which one is false in the following statement ?
   - (A) A catalyst is specific in its action
   - (B) A very small amount of the catalyst alters the rate of a reaction
   - (C) The number of free vacancies on the surface of the catalyst increases on sub-division
   - (D) Ni is used as a catalyst in the manufacture of ammonia

10. A catalyst increases rate of reaction by:
    - (A) Decreasing enthalpy
    - (B) Decreasing internal energy
    - (C) Decreasing activation energy
    - (D) Increasing activation energy

11. Colloidal solution of gold prepared by different methods of different colours because of :
    - (A) different diameters of colloidal gold particles
    - (B) variable valency of gold
    - (C) different concentration of gold particles
    - (D) impurities produced by different methods

12. Peptisation is :
    - (A) conversion of a colloidal into precipitate form
    - (B) conversion of precipitate into colloidal sol
    - (C) conversion of metal into colloidal sol by passage of electric current
    - (D) conversion of colloidal sol into macromolecules

Exercise # 3 PART - 1 MATRIX MATCHCOLUMN

1. Match list I with list II and select the correct answer :

List I	**List II**
(A) Coagulation	**(p)** Scattering of light
(B) Dialysis	**(q)** Formation of colloidal solution from precipitates.
(C) Peptization	**(r)** Purification of colloids
(D) Tyndall effect	**(s)** Accumulation of colloidal sols

2. Match list I with list II and select the correct answer :

List I	**List II**
(A) Mechanical property of colloid	**(p)** Dialysis
(B) Purification	**(q)** Peptization
(C) Gold number	**(r)** Brownian movement
(D) Formation of a sol	**(s)** Protection

3.

Column (I)	**Column (II)**
(A) Gold sol	**(p)** Bredig's Arc method
(B) Purification of colloidal solution	**(q)** Negatively charged
(C) As_2S_3 sol	**(r)** Ultra centrifugation
(D) Zeta potential	**(s)** Electro kinetic potential
(E) Casein	**(t)** Double decomposition reaction
	(u) Protective colloid

4.

Column (I)	**Column (II)**
(A) Tyndall effect	**(p)** Zig-zag motion
(B) Brownian movement	**(q)** Sky is blue
(C) Electrophoresis	**(r)** Coagulation of colloids
(D) Hardy schulze rule	**(s)** Charge on colloidal solution
(E) Froth floatation	**(t)** Emulsion of pine oil
	(u) Gold number

5. Match the entries Listed in Column I with appropriate entries listed in Column II.

Column (I)	**Column (II)**
(A) Silicic acid	**(p)** Forms negatively charged sol
(B) Arsenic sulphide	**(q)** Forms macromolecular colloid
(C) Gum arabic	**(r)** Forms lyophobic sol
(D) Gold	**(s)** Forms a non-elastic gel

6. Match the entries Listed in Column I with appropriate entries Listed in Column II.

Column (I)	**Column (II)**
(A) Lyophilic colloids	**(p)** Scatter light
(B) Lyophobic colloids	**(q)** Irreversible in nature
(C) Macromolecular colloids	**(r)** Can act as protective colloids
(D) Associated colloids	**(s)** Can act as emulsifiers

Exercise # 4

PART - 1

PREVIOUS YEAR (NEET/AIPMT)

1. The method usually employed for the precipitation of a colloidal solution is **[CBSE ALPMT 2000]**

(A) Dialysis
(B) Addition of electrolytes
(C) Adsorption is more for some specific substance
(D) Condensation

2. Which is not correct regarding the adsorption of a gas on surgace of solid? **[CBSE ALPMT 2001]**

(A) On increasing temperature adsorption increases continuously
(B) Enthalpy and entropy change is negative
(C) Adsorption is more for some specific substance
(D) Reversible

3. Position of non-polar and polar parts in micelle is **[CBSE ALPMT 2002]**

(A) Polar at outter surface but non-polar at inner surface
(B) Polar at inner surface but non-polar at outer surface
(C) Distributed all over the surface
(D) Present in the surface only

4. According to the adsorption theory of catalysis, the speed of the reaction increases because **[CBSE ALPMT 2003]**

(A) Adsorption produces heat which increases the speed of the reaction
(B) Adsorption lowers the activation energy of the reaction
(C) The concentration of reactant moleculer at the active centres of the catalyst becomes high due to adsorption
(D) In the process of adsorption, the activation energy of the molecules becomes large

5. Which of the following forms cationic micelles above certain concentration? **[CBSE ALPMT 2004]**

(A) Sodium ethyl sulphate
(B) Sodium acetate
(C) Urea
(D) Cetyl trimethyl ammounium bromide

6. Which one of the following forms micelles in aqueous solution above certain concentration? **[CBSE ALPMT 2005]**

(A) Urea
(B) Dodecyl trimethyl ammounium chloride
(C) Pyridinium chloride
(D) Glucose

7. For adsorption of a gas on a solid, the plot of lox $\frac{x}{m}$ vs log p is linear with slope equal to (n being a whole number) **[CBSE ALPMT 2006]**

(A) k **(B)** log k

(C) n **(D)** $\frac{1}{n}$

8. The Langmuir adsorption isotherm is deduced by using the assumption that **[CBSE ALPMT 2007]**

(A) the adsorption takes place in multilayers
(B) the adsorption sites are equivalent in their ability to adsorb the particles
(C) the heat of adsorption varies with coverage
(D) the adsorbed molecules interact with each other

9. If x is amount of adsorbate and m is amount of adsorbent, which of the following relations is not related to adsorption process? **[CBSE ALPMT 2011]**

(A) $\frac{x}{m} = f\,(T)$ at cons tan t P

(B) $p = f(T)$ at cons tan t $\left(\frac{x}{m}\right)$

(C) $\frac{x}{m} = p \times T$

(D) $\frac{x}{m} = f\,(p)$ at cons tan t T

10. The protecting power of lyophilic colloidal sol is expressed in terms of **[CBSE ALPMT 2012]**

(A) Coagulation value
(B) Gold number
(C) Critical micelle concentration
(D) Oxidation number

MOCK TEST

STRAIGHT OBJECTIVE TYPE

1. According to the adsorption theory of catalysis, the speed of the reaction increases because
(A) Adsorption lowers the activation energy of the reaction
(B) The concentration of reactant molecules at the active centres of the catalyst becomes high due to adsorption
(C) In the process of adsorption, the activation energy of the molecules becomes large
(D) Adsorption produces heat which increases the speed of the reaction

2. In Freundlich adsorption, isotherm adsorption is proportional to pressure P as
(A) P^0 **(B)** P **(C)** P^n **(D)** $P^{1/n}$

3. Which one of the following characteristics is not correct for physical adsorption
(A) Adsorption on solids is reversible **(B)** Adsorption increases with increase in temperature
(C) Adsorption is spontaneous **(D)** Both enthalpy and entropy of adsorption are negative

4. Which of the following is not a characteristic of chemisorption
(A) ΔH is of the order of 400 kJ **(B)** Adsorption is irreversible
(C) Adsorption may be multimolecular layer **(D)** Adsorption is specific

5. The viscosity of the solvent depends on
(A) Isothermic nature **(B)** Solute - solute interaction
(C) Solute -solvent interaction **(D)** Density of the liquid

6. The transition metal used as a catalyst is
(A) Nickel **(B)** Platinum **(C)** Cobalt **(D)** All of these

7. Which of the following is true about catalyst
(A) It initiates reaction **(B)** It changes equilibrium point
(C) It increase average kinetic energy **(D)** It accelerates the rate of reaction

8. Which of the following types of metals form the most efficient catalysts
(A) Alkali metals **(B)** Alkaline earth metals **(C)** Transition metals **(D)** All of these

9. Formation of ammonia from H_2 and N_2 by Haber's process using Fe is an example of
(A) Heterogeneous catalysis **(B)** Homogeneous catalysis
(C) Enzyme catalysis **(D)** Non-catalytic process

10. Paste is
(A) Suspension of solid in a liquid **(B)** Mechanical dispersion of a solid in liquid
(C) Colloidal solution of a solid in solid **(D)** None of these

11. A precipitate is changed to colloidal solution by the following process
(A) Dialysis **(B)** Ultrafiltration **(C)** Peptization **(D)** Electrophoresis

12. An aerosol is a
(A) Dispersion of a solid or liquid in a gas **(B)** Dispersion of a solid in a liquid
(C) Dispersion of a liquid in a liquid **(D)** Solid solution

13. Lyophilic sols are
(A) Irreversible sols **(B)** They are prepared from inorganic compound
(C) Coagulated by adding electrolytes **(D)** Selfstabilizing

14. The volume of a colloidal particle, V_C as compared to the volume of a solute particle in a true solution V_S could be
(A) $\frac{V_C}{V_S} \simeq 1$ **(B)** $\frac{V_C}{V_S} \simeq 10^{23}$ **(C)** $\frac{V_C}{V_S} \simeq 10^{-3}$ **(D)** $\frac{V_C}{V_S} \simeq 10^{3}$

15. The disperse phase in colloidal iron (III) hydroxide and colloidal gold is positively and negatively charged, respectivley. Which of the following statements is NOT correct
(A) Magnesium chloride solution coagulates, the gold sol more readily than the iron (III) hydroxide sol
(B) Sodium sulphate solution causes coagulation in both sols
(C) Mixing the sols has no effect
(D) Coagulation in both sols can be brought about by electrophoresis

CHAPTER 15

REACTION MECHANISM

You mix a bunch of ingredients and once in a great while Chemistry happens.

''Bill Watterson''

INTRODUCTION

Reaction mechanism is the step by step sequence of elimentry reaction by which overall chemical change occurs. A chemical mechanism is the theoritical conjecture that tries to describe in detail what takes place at each stage of an overall chemical reaction. The detailed steps of a reaction are not observable in most cases. The conjectured mechanism is choosen because it is thermodynamically feasible and has experimental support in isolated intermediates or other quantitative and qualitative characteristics of the reaction. A complete mechanism must also explain the reason for the reactants and catalyst used, the stereochemistry observed in reactants and products, all products formed and the amount of each.

Types of Reactions

In organic chemistry the following types of reaction are more important,

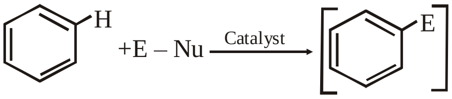
(I) Substitution reaction
(II) Elimination reaction
(III) Addition reaction
(IV) Rearrangement reaction
(V) Isomerisation reactions

(I) Substitution Reaction:

Reactions in which one atom or a group of substrate is replaced by other atom or group are called as substitution reactions.

(A) Electrophilic substitution reactions
(B) Nucleophilic substitution reactions
(C) Free radical substitution reactions

(A) Electrophilic substitution reactions[ESR] : Characteristic reaction of arenes is ESR

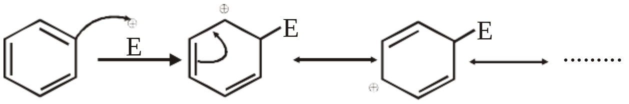


Mechanism :

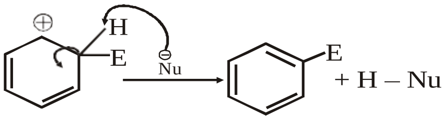
Formation of $\overset{\oplus}{E}$

$$E - Nu \xrightarrow{\text{Catalyst}} \overset{\oplus}{E} + \overset{\ominus}{Nu}$$

Attack of $\overset{\oplus}{E}$

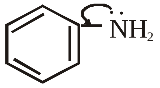


Abstraction of $\overset{\oplus}{H}$



Ex. Give reactivity order for electrophilic substitution reaction.

(i)



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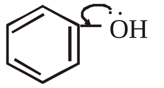
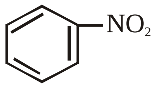


Less EN of nitrogen so more + M so more e^- density So more reactive	Less + M of – OH due to more EN

(ii)



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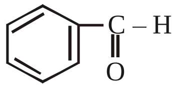
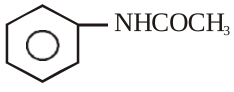
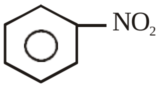


More – M of – NO_2 & more –1 so e^- density decrease (more) so less reactive	less – M of – CHO & less–1 so e^- density decreases (less) so more reactive.

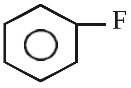
(iii)



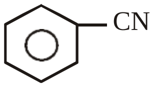
+M



–M (more)



–I



–M (less)

ESR order I > III > IV > II

1. Rate determining step

The slowest step of the mechanism known as rate determining step of the reaction.Order of reaction or rate law of reaction is calculated with the help of mechanism of the reaction and generally using rate determine step (R.D.S). An organic reaction can be represented as

$$\textbf{Reactant (substrate) + Reagent} \xrightarrow{\text{Solvent}} \textbf{Product}$$

Homolytic bond dissociation

Ex. $A–B \longrightarrow A^{o} + B^{o}$

Hetrolytic bond dissociation

Ex. $A–B \longrightarrow A^{\oplus} + B^{\ominus}$

2. Types of Reagents

A reagent generates three type of attacking species. Which are nucleophile, electrophile and radical.

(a) Electrophiles (b) Nucleophiles (c) Radicals

(a) Electrophiles : Electrophiles are electron deficient species.

Ex. $\overset{\oplus}{H}$ $\overset{\oplus}{Cl}$, $\overset{\oplus}{Br}$, $\overset{\oplus}{NO_2}$, $\overset{\oplus}{CH_3}$ (positively charged species), PCl_5, SO_2, SO_3 BH_3 (species with vacant orbital at central atom, carbenes) etc.

(b) Nucleophiles : It is the electron rich species having atleast one unshared pair of electron. It can be neutral or negativetely charged it is always a lewis base.

Ex. CN^-, OH^-, Br^-, I^-, NH_3, H_2O etc.

(c) Radicals : It is electron deficient species with seven electrons around an atom.

Ex. $\dot{C}H_3$ $C_2H_5^{\bullet}$, $C_2H_5O^{\bullet}$, $CH_3COO^{\bullet}$, $X^{\bullet}$ etc.

3. Nucleophilicity

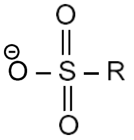
The tendency to give e^- pair to an electron deficient carbon atom is defined as nucleophilicity.

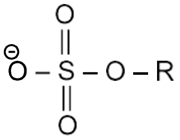
Leaving group Ability/Nucleofugality

(a) Order of leaving ability of halide ion

$$\overset{\ominus}{I} > \overset{\ominus}{Br} > \overset{\ominus}{Cl} > \overset{\ominus}{F}$$

(b) Other good leaving groups are





Alkyl sulphate ion

SOLVED EXAMPLE

Ex.1 In the case homologous series of alkanes, which one of the following statements is incorrect

(A) The members of the series are isomers of each other

(B) The members of the series have similar chemical properties

(C) The members of the series have the general formula C_nH_{2n+2} ,where n is an integer

(D) The difference between any two successive members of the series corresponds to 14 unit of relative atomic mass

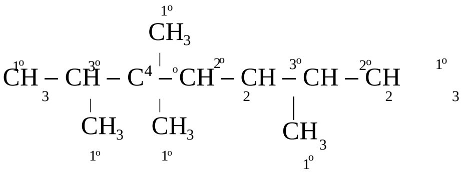
Sol. **(A)** The difference between any two successive members of the homologous series – CH_2– i.e., the molecular weight of every two adjacent members differ by 14. ($CH_2 = 12 + 2 = 14$)

Ex.2 How many primary, secondary, tertiary and quaternary carbons are present in the following hydrocarbon

$CH_3 - CH(CH_3) - C(CH_3)_2 - CH_2 - CH(CH_3) - CH_2 - CH_3$

	Primary	Secondary	Tertiary	Quaternary
(A)	6	2	2	1
(B)	2	6	3	0
(C)	2	4	3	2
(D)	2	2	4	3

Sol. **(A)**



$$\overset{1^o}{C}H_3 - \underset{\underset{1^o}{CH_3}}{\overset{3^o}{C}H} - \underset{\underset{1^o}{CH_3}}{\overset{\overset{1^o}{CH_3}}{C^4}} -{}^o\overset{2^o}{C}H_2 - \underset{\underset{1^o}{CH_3}}{\overset{3^o}{C}H} - \overset{2^o}{C}H_2 - \overset{1^o}{C}H_3$$

$1^o \Rightarrow$ Primary 6, $2^o \Rightarrow$ Secondary 2

$3^o \Rightarrow$ Tertiary 2, $4^o \Rightarrow$ Quanternary1

Ex.3 The octane number of a sample of petrol is 40. It means that its knocking property is equal to the mixture of

(A) 40% n-heptane + 60% iso-octane **(B)** 40% petrol + 60% iso-octane

(C) 60% n-heptane + 40% iso-octane **(D)** 60% petrol + 40% iso-octane

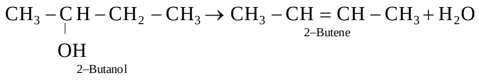
Sol. **(C)** Octane number of fuel is the percentage of iso- octane in mixture.

Ex.4 Formation of 2-butene as major product by dehydration of 2-butanol is according to

(A) Markownikoff rule **(B)** Saytzeff rule

(C) Peroxide effect **(D)** Anti-Markownikoff rule

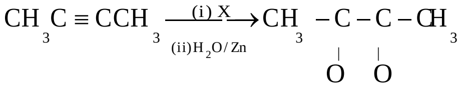
Sol. **(B)**



$$\underset{\text{2–Butanol}}{CH_3 - \underset{OH}{C}H - CH_2 - CH_3} \rightarrow \underset{\text{2–Butene}}{CH_3 - CH = CH - CH_3} + H_2O$$

According to this rule H atom goes from that β- carbon which is less hydrogenated.

Ex.5

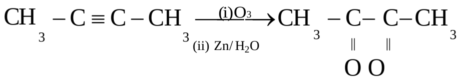


$$CH_3C \equiv CCH_3 \xrightarrow[(ii)H_2O/Zn]{(i)\ X} CH_3 - \underset{O}{C} - \underset{O}{C} - CH_3$$

X in the above reaction is

(A) HNO_3 **(B)** O_2 **(C)** O_3 **(D)** $KMnO_4$

Sol. **(C)**



$$CH_3 - C \equiv C - CH_3 \xrightarrow[(ii)\ Zn/H_2O]{(i)O_3} CH_3 - \underset{\overset{\|}{O}}{C} - \underset{\overset{\|}{O}}{C} - CH_3$$

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

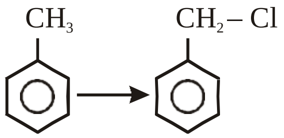
1. To which of the following four types does this reaction belong $B^- + R - A \rightarrow B - R + A^-$

(A) Unimolecular electrophilic substitution
(B) Bimolecular electrophilic substitution
(C) Unimolecular nucleophilic substitution
(D) Bimolecular nucleophilic substitution

2. An alkyl halide may be converted into an alcohol by

(A) Elimination
(B) Addition
(C) Substitution
(D) Dehydrohalogenation

3.



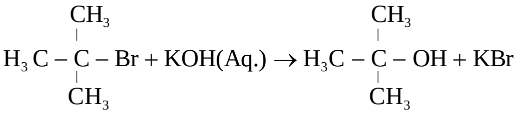
The above reaction proceeds through

(A) Nucleophilic substitution
(B) Electrophilic substitution
(C) Free radical substitution
(D) More than one of the above processes

4. Geometry of reaction intermediate in SN^1 reaction is

(A) Tetrahedral
(B) Planar
(C) Triangular bipyramidal
(D) None of these

5.



$$H_3C - \underset{CH_3}{\overset{CH_3}{C}} - Br + KOH(Aq.) \rightarrow H_3C - \underset{CH_3}{\overset{CH_3}{C}} - OH + KBr$$

above reaction is

(A) SN^1 **(B)** SN^2
(C) E_1 **(D)** Both **(A)** and **(B)**

6. In electrophilic substitution reaction nitrobenzene is

(A) Meta-directing
(B) Ortho-directing
(C) Para-directing
(D) Not reactive and does not undergo any substitution
(E) Non-selective

7. The most common type of reaction in aromatic compounds is

(A) Elimination reaction
(B) Addition reaction
(C) Electrophilic substitution reaction
(D) Rearrangement reaction

8. The function of $AlCl_3$ in Friedel-Craft's reaction is

(A) To absorb HCl
(B) To absorb water
(C) To produce nucleophile
(D) To produce electrophile

9. Which of the following can't be used in Friedal Craft's reactions

(A) $FeCl_3$ **(B)** $FeBr_2$
(C) $AlCl_3$ **(D)** NaCl

10. The nitration of a compound is due to the

(A) NO_2 **(B)** NO_3
(C) NO **(D)** NO_2^+

11. Dehydrohalogenation of an alkyl halide is a/an

(A) Nucleophilic substitution reaction
(B) Elimination reaction
(C) Both nucleophilic substitution and elimination reaction
(D) Rearrangement

12. Addition of HCl to vinyl chloride gives 1, 1-dichloroethane because of

(A) Mesomeric effect of Cl
(B) Inductive effect of Cl
(C) Restricted rotation around double bond
(D) None of these

13. Formation of ethylene from acetylene is an example of

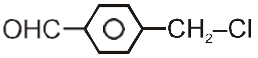
(A) Elimination reaction
(B) Substitution reaction
(C) Addition reaction
(D) Condensation reaction

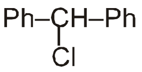
14. Conversion of CH_4 to CH_3Cl is an example of which of the following reaction

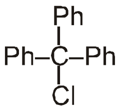
(A) Electrophilic substitution
(B) Free radical addition
(C) Nucleophilic substitution
(D) Free radical substituion

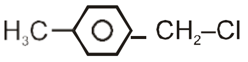
Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

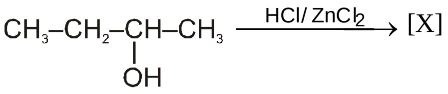
1. Which of the following alkyl halide is most reactive towards H_2O ?

(A) 

(B) 
$Ph-\underset{Cl}{CH}-Ph$

(C) 
$Ph-\underset{Cl}{\overset{Ph}{C}}-Ph$

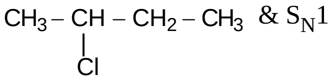
(D) 

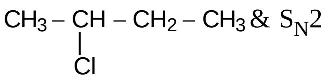
2. 
$CH_3-CH_2-\underset{OH}{CH}-CH_3 \xrightarrow{HCl/\,ZnCl_2} [X]$

Identify X and the mechanism of the reaction.

(A) $CH_3-CH_2-CH_2-CH_2-Cl$ & S_N1

(B) $CH_3-CH_2-CH_2-CH_2-Cl$ & S_N2

(C) 
$CH_3-\underset{Cl}{CH}-CH_2-CH_3$ & S_N1

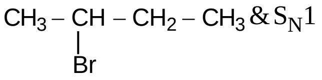
(D) 
$CH_3-\underset{Cl}{CH}-CH_2-CH_3$ & S_N2

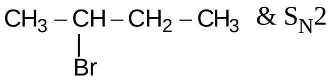
3. $\underset{\text{1-butanol}}{CH_3(CH_2)_2CH_2OH} \xrightarrow{HBr} X,$

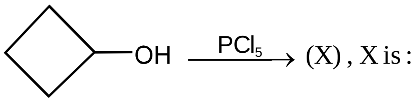
Identify X and the mechanism of the reaction

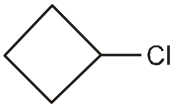
(A) $CH_3-CH_2-CH_2-CH_2-Br$ & S_N1

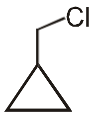
(B) $CH_3-CH_2-CH_2-CH_2-Br$ & S_N2

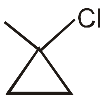
(C) 
$CH_3-\underset{Br}{CH}-CH_2-CH_3$ & S_N1

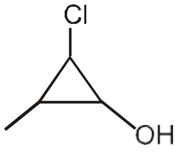
(D) 
$CH_3-\underset{Br}{CH}-CH_2-CH_3$ & S_N2

4. 

(A) 

(B) 

(C) 

(D) 

5. What is the final product of reaction.

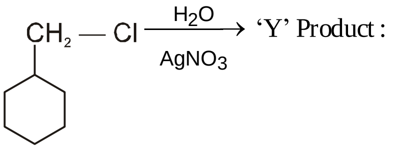
$CH_3-C\equiv CH \xrightarrow{Na} \xrightarrow{CH_3-CH_2-I}$ Product

(A) $CH_2=CH-CH_2-CH_3$

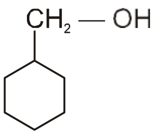
(B) $CH_3-CH_2-C\equiv C-CH_2-CH_3$

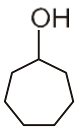
(C) $CH\equiv C-CH_2-CH_2-CH_3$

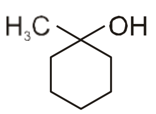
(D) $CH_3-C\equiv C-CH_2-CH_3$

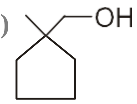
6. 

'Y' Product :

(A) 

(B) 

(C) 

(D) 

7. S_N2 mechanism proceeds through intervention of :

(A) Carbonium ion

(B) Transition state

(C) Free radical

(D) Carbanion

8. When the concentration of alkyl halide is tripled and the concentration of $\overset{\ominus}{OH}$ ion is reduced to half, the rate of S_N2 reaction increases by:

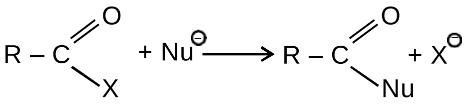
(A) 3 times

(B) 2 times

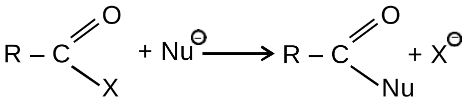
(C) 1.5 times

(D) 6 times

9. The reaction



is slowest when X is :



(A) Cl

(B) NH_2

(C) OC_2H_5

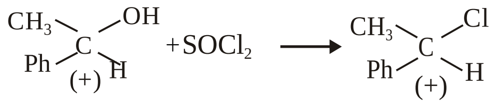
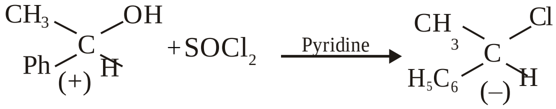
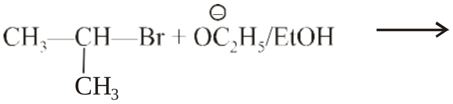
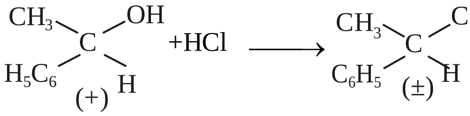
(D) $OCOCH_3$

Exercise # 3

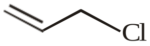
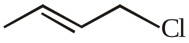
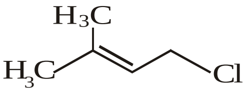
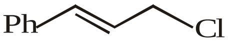
PART - 1

MATRIX MATCHCOLUMN

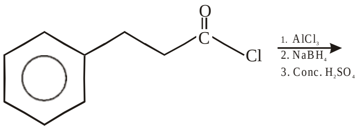
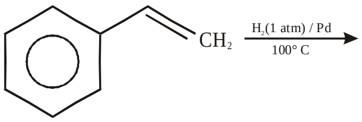
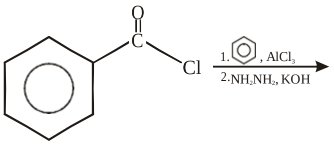
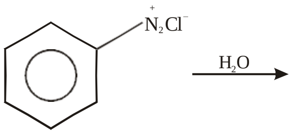
1. Match the column I with column II.

Column-I (reaction)		**Column-II (Mechanism)**
(A)		**(p)** S_N1
(B)		**(q)** S_N2
(C)	 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-Br + \overset{\ominus}{O}C_2H_5/EtOH \longrightarrow$	**(r)** S_Ni
(D)		**(s)** E_2

2. Match the column I with column II.

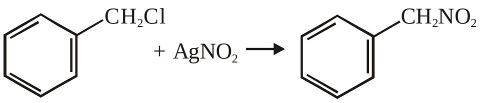
Column-I **(Substrate)**		**Column-II** **(Relative rate of solvolysis in 50%** aqueousethanol at 45°C)
(A)		**(p)** 7700
(B)		**(q)** 1
(C)		**(r)** 91
(D)		**(s)** 1,30,000

3. Match the entries listed in Column I with appropriate entries listed in Column II.

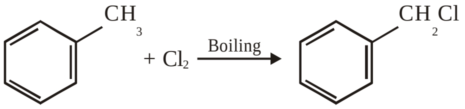
Column-I		**Column-II**
(A)		**(p)** Electrophilic sustitution
(B)		**(q)** A hydrocarbon is the final product
(C)		**(r)** Aromaticity is destroyed
(D)		**(s)** Nucleophilic substitution

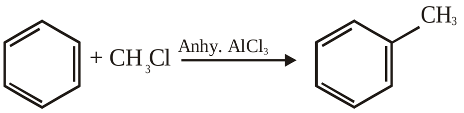
Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. Which one of the following is a free radical substitution reaction? **[CBSE AIPMT 2003]**

(A) 

(B) $CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$

(C) 

(D) 

2. Which of the following reactions is an example of nucleophilic substitution reaction? **[CBSE AIPMT 2009]**

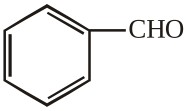
(A) $RX + KOH \rightarrow ROH + KX$

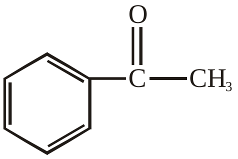
(B) $2\,RX + 2NA \rightarrow R - R + 2NaX$

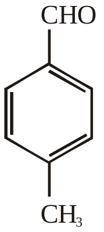
(C) $RX + H_2 \rightarrow RH + HX$

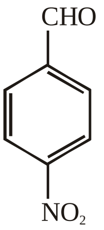
(D) $RX + Mg \rightarrow RMgX$

3. Which one is most reactive towards nucleophilic addition reaction? **[CBSE AIPMT 2014]**

(A) 

(B) 

(C) 

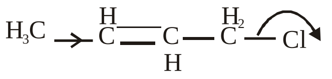
(D) 

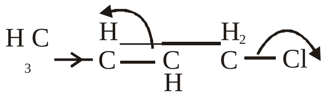
4. Which of the following organic compounds has same hybridisation as its combustion (CO_2) product? **[CBSE AIPMT 2014]**

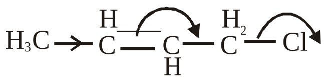
(A) Ethane **(B)** Ethyne

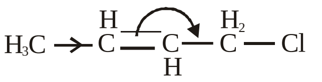
(C) Ethene **(D)** Ethanol

5. Which of the following is the most correct electron displacement for a nucleophilic reaction to take place? **[CBSE AIPMT 2015]**

(A) 

(B) 

(C) 

(D) 

6. In an S_N1 reaction on chiral centres there is **[CBSE AIPMT 2015]**

(A) 100 % racemisation

(B) inversion more than retention leading to partial racemisation

(C) 100% retention

(D) 100% inversion

7. The correct statement regarding a carbonyl compound with a hydrogen atom on its alpha-carbon, is **[NEET 2016, Phase I]**

(A) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration

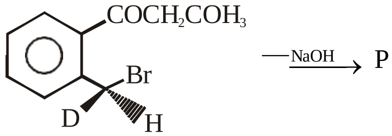
(B) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation

(C) a carbonyl compound with a hydrogen atom on its alphs-carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism

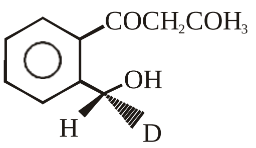
(D) a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol

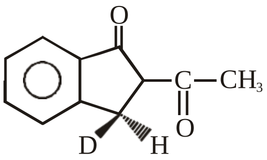
MOCK TEST

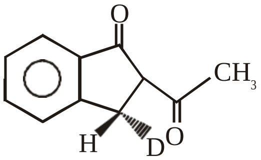
STRAIGTH OBJECTIVE TYPE

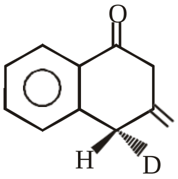
1. 

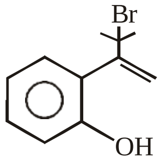
Which of the following statement is correct

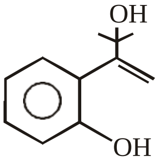
(A) P = 

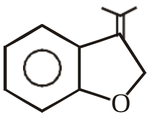
(B) P = 

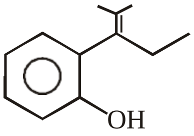
(C) P = 

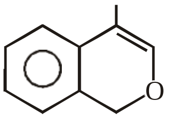
(D) P = 

2.  $\xrightarrow{NaOH}$ Product, Product is

(A) 

(B) 

(C) 

(D) 

3. $CH_3 - CH_2SH \xrightarrow[\text{(ii) ethylene oxide}]{\text{(i) } CH_3O^{\ominus}}$ Product, Product is :

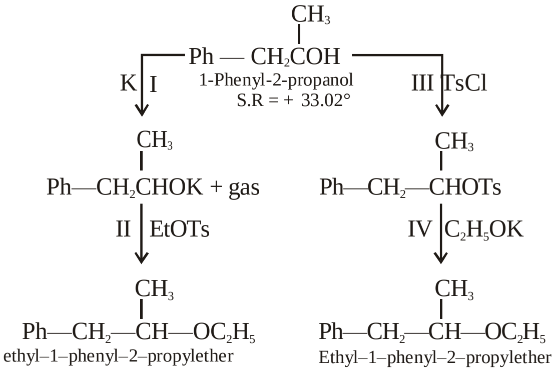
(A) $CH_3 - CH_2 - S - CH_2 - CH_2 - OH$

(B) $CH_3 - CH_2O^{\ominus}$

(C) $CH_3 - CH_2 - O - CH_2 - CH_2 - OH$

(D) 

4. Read the following road map carefully



(A) Both the ethers obtained by the two routes have opposite but equal optical rotation.
(B) One of the either is obtained as a recemic mixture.
(C) Step II & III both are S_N2 reaction and both have inversion
(D) Step II has inversion but step III has retention.

CHAPTER 10

HYDROGEN AND ITS COMPOUNDS

Hydrogen is a light, odorless gas, which, given enough time, turns into people.

"EDWARD ROBERT HARRISON"

INTRODUCTION

Hydrogen, the most abundant element in the universe and the third most abundant on the surface of the globe, is being visualised as the major future source of energy.

Hydrogen has the simplest atomic structure among all the elements around us in Nature. In atomic form it consists of only one proton and one electron. However, in elemental form it exists as a diatomic (H_2) molecule and is called dihydrogen. It forms more compounds than any other element. Do you know that the global concern related to energy can be overcome to a great extent by the use of hydrogen as a source of energy? In fact, hydrogen is of great industrial importance as we will learn in this unit.

Hydrogen is the lightest element and also the lightest gas in the periodic table.

It is the lightest non-metal. It is the simplest element in periodic table having only 1e⁻, 1p & no neutron.

Electronic configuration of H is $1s^1$

Number of e^- = 1	Number of orbital = 1
Number of shells = 1	Number of subshell = 1

It is discovered by Henry Cavendish & it was called inflammable element.

The name hydrogen was given by **Lavoisier**

HYDROGEN

Hydro (Water) Gene (Producer) or generator

means according to Lavoisier the gas which produce water on burning with oxygen.

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

POSITION OF H_2 IN PERIODIC TABLE

Hydrogen is the first element of Periodic table but still it could not be assigned a proper position either in Mendeleef periodic table or in Modern periodic table because of following reasons.

It may kept in 1st/IA or 17th/VIIA group due to following reason.

RESEMBLES WITH 1ST/ IA ALKALI METALS

(i) Electronic configuration : Like alkali metals hydrogen also has only one electron in outer most shell.

- $H = 1s^1$ $K = 4s^1$
- $Li = 2s^1$ $Rb = 5s^1$ — ns^1
- $Na = 3s^1$

(ii) Electropositive characters : Like alkali metals hydrogen also have the tendency to loose one electron to form cation.

Ex. $Na \rightarrow Na^+ + e^-$

$H \rightarrow H^+ + e^-$

(Proton)

(iii) Oxidation numbers : Like alkali metals hydrogen can also exhibit the oxidation number of +1 in most of its compound.

Ex. Na^+Cl^- K^+Cl

H^+Cl^- = +1

(iv) Reaction with electronegative elements (non-metals) : Like alkali metals H also reacts with Oxygen, Sulphur, Halogens to form oxides, sulphides and halides respectively.

$O \xrightarrow{\text{gives}}$ H_2O, like Na_2O, K_2O

$S \xrightarrow{\text{gives}}$ H_2S, like Na_2S, K_2S

with halogen $\xrightarrow{\text{gives}}$ HX, like NaX, KX

(v) Liberation at Cathode :

$2Na^+Cl \xrightarrow{\text{electrolysis}} 2Na + Cl_2$

(liberated at cathode) (liberated at anode)

$2H^+Cl^- \xrightarrow{\text{electrolysis}} (H_2 + Cl_2)$

like alkali metals H also get liberated at cathode on electrolysis.

Preparationof hydrogen

(I) Passing steam over hot iron (Lane process)

$3Fe + 4\,H_2O \rightarrow Fe_3P_4 + H_2\uparrow$

(II) By the action of water on hydrolith

$CaH_2 + H_2O \longrightarrow Ca(OH)_2 + 3H_2$

(III) By the electrolysis of water

(IV) Bosch process

$C(s) + H_2O\,(g) \longrightarrow CO + H_2$

$+$

$H_2O(g) \xrightarrow{FeCrO_4} CO_2 + H_2$

$\downarrow$

25 atm

$\boxed{H_2O}$

CO_2 absorbed

Properties of molecular hydrogen

Metals like Pd, Pt, Ni, Co etc. adsorb large quantities of the gas due to vacancies between these atoms. This is known as **"occlusion"**.

Reaction with vegetable oils

Vegetable oil $+ H_2 \xrightarrow[Ni]{473\ K}$ Vegetable gheef (Slid fat)

This process is known as "hydrogenation" or "hardening of oils"

Isotopes of hydrogen

(a) Hydrogen (Protium)	(b) Deuterium	(c) Tritium
${}_1H^1$ or H	${}_1H^2$ or D	${}_1H^3$ or T
(P = 1, e = 1, n = 0)	(P = 1, e = 1, n = 1	(P = 1, e = 1, n = 2)

Different forms ofhydrogen

Atomic hydrogen

$H_2 \xrightarrow{\text{electric arc}} 2H$

(Molecular hydrogen) (Atomic hydrogen)

Nascent hydrogen

$Zn + dil.H_2SO_4 \longrightarrow ZnSO_4 + 2H$

Ortho and Para hydrogen

If two nuclei have same spin then it is called "Ortho H_2".

If two nuclei have different spin then it is called "Para H_2".

HYDRIDES

Ionic or salt like hydrides : s block

Li H, NaH, KH, RbH, SrH_2, BaH_2 etc.

Be & Mg hydrides are covalent in nature

Molecular or covalent hydrides : p block

NH_3, PH_3, H_2O, CH_4 etc.

Metallic or Interstitial hydrides : trasition elements

SOLVED EXAMPLE

Ex. 1 How does the atomic hydrogen or oxy-hydrogen torch function for cutting and welding purposes ? Explain.

Sol. Atomic hydrogen is produced when molecular hydrogen is passed through an electric arc struck between tungsten electrodes (3773–4273 K).

$H_2(g) \xrightarrow{\text{electric arc}} H(g) + H(g)$: $\Delta H = 436.0$ kJ mol^{-1}

The life span of atomic hydrogen is about 0.3 sec and therefore, it immediately gets converted into the molecular hydrogen (H_2) liberating a large amount of energy which is used for cutting and welding purposes in the form of atomic hydrogen torch.

Ex. 2 What do you understand by the term " non-stoichiometric hydrides" ? Do you expect this type of hydrides to be formed by alkali metals ? Justify your answer.

Sol. These are hydrides which have low hydrogen content. In these hydrides the ratio of the metal to hydrogen atoms is fractional and they are called non-stoichiometric hydrides. Furthermore, even this fractional ratio of atoms is not fixed but varies with the temperature and the pressure conditions. This type of hydrides are formed by d-and f-block elements. In these hydrides, the hydrogen atoms occupy holes in the metal lattice. Usually some holes always remain unoccupied and hence these metals form non-stoichiometric hydrides.

Alkali metals are highly reducing as they transfer their lone electron to the H atom, thereby, forming H^- ions. In other words, alkali metals hydrides are ionic in nature. SInce such hydrides are formed by complete transfer of an electron, therefore, the ratio of metal to hydrogen is always fixed. Therefore, alkali metals form only stoichiometric hydrides. They do not form non-stoichiometric hydrides at all.

Ex. 3 What do you understand by **(i)** electron-deficient, **(ii)** electron-precise, and **(iii)** electron rich compounds of hydrogen ? Provide justification with suitable examples.

Sol. **(i)** Hydrides of elements of group–13 such as BH_3, AIH_3, etc., do not have sufficient number of electrons to form normal covalent bond and hence are called electron-deficient hydrides. To make up this deficiency, they generally exist in polymeric forms such as B_2H_6, B_4H_{10}, $(AIH_3)_n$, etc.

(ii) Hydrides of elements of group-14 like CH_4, SiH_4, GeH_4, etc. have exact number of electrons to form covalent bonds and hence are called electron-precise hydrides. All these hydrides have tetrahedral shapes.

(iii) Hydrides of elements of group 15, 16 and 17, like NH_3, PH_3, H_2O, H_2S, HF, HCl, etc. have more electrons than required to form normal covalent bonds and hence are called electron-rich hydrides. The excess electron in these hydrides are present as lone pairs of electrons.

Ex. 4 Which of the following is correct for hydrogen ?

(A) It is always collected at cathode.

(B) Its ionization energy is very low incomparision with alkalimetals.

(C) It can form bonds in +1 as well as in –1 oxidation states.

(D) Its oxide is not stable.

Sol. **(C)** $2Na + H_2 \longrightarrow 2\overset{+1}{Na}\overset{-1}{H}$;

$N_2 + 3H_2 \longrightarrow 2\overset{-3}{N}\overset{+1}{H_3}$

Ex. 5 Metal which does not react with cold water but evolves H_2 with steam is :

(A) Na **(B)** K

(C) Pt **(D)** Fe

Sol. **(D)**

$4H_2O(g) + 3Fe(s) \xrightarrow{1000\text{ K}} Fe_3O_4 + 4H_2\uparrow$

Ex. 6 Saline hydride are known to react with water violently producing fire, Can, CO_2, a well known fire extinguisher, be used in this case ? Explain.

Sol. Saline hydride (Such as NaH, CaH_2, etc), react with water violently to form the corresponding metal hydroxides with the evolution of dihydrogen. The dihydrogen gas so liberated undergoes spontaneous combustion causing fire. This is because of exothermic nature of combustion reactions.

$NaH(s) + H_2O(\ell) \longrightarrow NaOH\,(aq) + H_2(g)$

$CaH_2(s) + 2H_2O\,(\ell) \longrightarrow Ca(OH)_2\,(aq) + 2H_2\,(g)$

The fire so produced cannot be extinguished by CO_2 because it reacts with the hot metal hydride and forms formate ions

$NaH + CO_2 \longrightarrow HCOONa$

However, send (because of its stable nature) is more effective fire extinguisher in such a case.

Exercise # 1 SINGLE OBJECTIVE NEET LEVEL

1. Which is used hydrogen generators

(A) NaH **(B)** HI

(C) S_6H_3 **(D)** None of these

2. Metal hydride on treatment with water gives

(A) H_2O_2 **(B)** H_2O

(C) Acid **(D)** Hydrogen

3. Hydrogen burns in air with a

(A) Light bluish flame **(B)** Yellow flame

(C) Green flame **(D)** None of these

4. Which pair does not show hydrogen isotopes

(A) Ortho hydrogen and para hydrogen

(B) Protium and deuterium

(C) Deuterium and tritium

(D) Tritium and protium

5. Which is distilled first

(A) Liquid CO_2 **(B)** Liquid N_2

(C) Liquid O_2 **(D)** Liquid H_2

6. On reaction with Mg, very dilute nitric acid produces

(A) NH_3 **(B)** Nitrous oxide

(C) Nitric oxide **(D)** Hydrogen

7. Among the following, identify the compound which cannot act as both oxidising and reducing agents

(A) H_2O_2 **(B)** H_2

(C) SO_2 **(D)** Cl_2

8. Which of the following reaction produces hydrogen

(A) $Mg + H_2O$ **(B)** $BaO_2 + HCl$

(C) $H_2S_4O_8 + H_2O$ **(D)** $Na_2O_2 + 2HCl$

9. Hydrogen resembles in many of its properties

(A) Halogen **(B)** Alkali metals

(C) Both **(A)** and **(B)** **(D)** None of these

10. Ortho and para hydrogen differ in

(A) Proton spin **(B)** Electron spin

(C) Nuclear charge **(D)** Nuclear reaction

11. Action of water or dilute mineral acids on metals can give

(A) Monohydrogen **(B)** Tritium

(C) Dihydrogen **(D)** Trihydrogen

12. Hydrogen from HCl can be prepared by

(A) Mg **(B)** Cu

(C) P **(D)** Pt.

13. Which of the following can adsorb largest volume of hydrogen gas

(A) Finely divided platinum

(B) Finely divided nickel

(C) Colloidal palladium

(D) Colloidal platinum

14. The nuclei of tritium (H^3) atom would contain neutrons

(A) 1 **(B)** 2

(C) 3 **(D)** 4

15. The colour of hydrogen is

(A) Black **(B)** Yellow

(C) Orange **(D)** Colourless

16. Ordinary hydrogen at room temperature is a mixture of

(A) 75% of o-Hydrogen + 25% of p-Hydrogen

(B) 25% of o-Hydrogen + 75% of p-Hydrogen

(C) 50% of o-Hydrogen + 50% of p-Hydrogen

(D) 1% of o-Hydrogen + 99% of p-Hydrogen

17. Hydrogen cannot reduce

(A) Hot CuO **(B)** Fe_2O_3

(C) Hot SnO_2 **(D)** Hot Al_2O_3

18. Hydrogen does not combine with

(A) Antimony **(B)** Sodium

(C) Bismuth **(D)** Helium

19. The adsorption of hydrogen by metals is called

(A) Dehydrogenation **(B)** Hydrogenation

(C) Occlusion **(D)** Adsorption

20. Which of the following produces hydrolith with dihydrogen

(A) Mg **(B)** Al

(C) Cu **(D)** Ca

21. The metal which displaces hydrogen from a boiling caustic soda solution is

(A) As **(B)** Zn

(C) Mg **(D)** Fe

22. Metals like platinum and palladium can absorb large volumes of hydrogen under special conditions. Such adsorbed hydrogen by the metal is known as

(A) Adsorbed hydrogen **(B)** Occluded hydrogen

(C) Reactive hydrogen **(D)** Atomic hydrogen

23. Which is poorest reducing agent

(A) Nascent hydrogen

(B) Atomic hydrogen

(C) Dihydrogen

(D) All have same reducing strength

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. Hydrogen will not reduce

(A) Heated cupric oxide

(B) Heated ferric oxide

(C) Heated stannic oxide

(D) Heated aluminium oxide

2. HCl is added to following oxides. Which one would give H_2O_2

(A) MnO_2 **(B)** PbO_2

(C) BaO **(D)** None of these

3. Which of the following pair will not produce dihydrogen gas

(A) Cu + HCl(dil.) **(B)** Fe + H_2SO_4

(C) Mg + steam **(D)** Na + alcohol

4. The amount of H_2O_2 present in 1 L of 1.5 N H_2O_2 solution is

(A) 2.5 g **(B)** 25.5g

(C) 3.0 g **(D)** 8.0 g

5. Hydrogen is evolved by the action of cold dil.HNO_3 on

(A) Fe **(B)** Mn

(C) Cu **(D)** Al

6. Hydrogen can behave as a metal

(A) At very high temperature

(B) At very low temperature

(C) At very high pressure

(D) At very low pressure

7. D_2O is preferred to H_2O, as a moderator, in nuclear reactors because

(A) D_2O slows down fast neutrons better

(B) D_2O has high specific heat

(C) D_2O is cheaper

(D) None of these

8. Out of the two allotropic forms of dihydrogen, the form with lesser molecular energy is

(A) Ortho **(B)** Meta

(C) Para

(D) All have same energy

9. Saline hydrides react explosively with water, such fires can be extinguished by

(A) Water **(B)** Carbon dioxide

(C) Sand **(D)** None of these

10. Nascent hydrogen consists of :

(A) Hydrogen atoms with excess of energy

(B) Hydrogen molecules with excess energy

(C) Hydrogen ions in excited state

(D) solvated protons

11. Hydrogen molecule differs from chlorine molecule in the following respect :

(A) hydrogen molecule is non-polar but chlorine molecule is polar.

(B) hydrogen molecule is polar while chlorine molecule is non-polar.

(C) hydrogen molecule can form intermolecular hydrogen bonds but chlorine molecule does not.

(D) hydrogen molecule cannot participate in co-ordinate bond formation but chlorine molecule can.

12. Which one of the following properties shows that hydrogen resembles alkali metals?

(A) It shows metallic character like alkali metals.

(B) It is diatomic like alkali metals.

(C) Its ionization energy is of the same order as that of alkali metals.

(D) When hydrogen halides and alkali metal halides are electrolysed, hydrogen and alkali metals are liberated at the cathode.

13. Hydrogen has three isotopes, the number of possible diatomic molecules will be :

(A) 3 **(B)** 6

(C) 9 **(D)** 12

14. The first ionization energy for in KJ mol^{-1} H, Li, F, Na has one of the following values 1681, 520, 1312, 495. Which of these values corresponds to that of hydrogen ?

(A) 1681 **(B)** 1312

(C) 520 **(D)** 495

15. Reaction between following pairs will produce hydrogen except :

(A) Cu + HCl **(B)** Fe + H_2O (g)

(C) Mg + H_2O (hot) **(D)** Na + Alcohol

Exercise # 3 PART - 1 MATRIX MATCHCOLUMN

1. Match the compounds given in coloumn–I with their characteristics/uses given in coloumn – II

Column – I	**Column – II**
(A) Heavy water	**(p)** Causes sequestration of C^{2+} and Mg^{2+} ions.
(B) Hydrolith	**(q)** Hydrated sodium aluminium silicate
(C) Calgon	**(r)** In molten state on electrolysis produces H_2 gas at anode
(D) Zeolites	**(s)** Used as tracer compound for studying reaction mechanism
	(t) Used as moderator in nuclear reactors

2. Match the processes/reactions listed in coloumn–I with the resultant product(s) listed in coloumn – II

Column – I	**Column – II**
(A) Prolonged electrolysis of water (H_2O)	**(p)** H_2O_2
(B) Electrolysis of 50% H_2SO_4	**(q)** H_2
(C) Water gas shift reaction	**(r)** CO_2
(D) Auto-oxidation of 2–Ethylnthrquinol	**(s)** D_2O
	(t) CO

3. Match the entries listed in Column I with appropriate entries listed in Column II.

Column – I **(Hydride)**	**Column – II** **(Types of Hydride)**
(A) BeH_2	**(p)** Complex
(B) AsH_3	**(q)** Lewis acid
(C) B_2H_6	**(r)** Interstitial
(D) LaH_3	**(s)** Covalent
(E) $LiAlH_4$	**(t)** Intermediate

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. The structure of H_2O_2 is **[CBSE AIPMT 2006]**

(A) planar **(B)** non-planar

(C) spherical **(D)** linear

2. The correct order of the mobility of the alkali metal ions in aqueous solution is **[CBSE AIPMT 2006]**

(A) $Li^+ > Na^+ > K^+ > Rb^+$

(B) $Na^+ > K^+ > Rb^+ > Li^+$

(C) $K^+ > Rb^+ > Na^+ > Li^+$

(C) $Rb^+ > K^+ > Na^+ > Li^+$

3. The correct order of increasing thermal stability of K_2CO_3, $MgCO_3$, $CaCO_3$ and $BeCO_3$ is **[CBSE AIPMT 2007]**

(A) $BeCO_3 < MgCO_3 < K_2CO_3 < CaCO_3$

(B) $BeCO_3 < MgCO_3 < CaCO_3 < K_2CO_3$

(C) $MgCO_3 < BeCO_3 < CaCO_3 < K_2CO_3$

(D) $K_2CO_3 < MgCO_3 < CaCO_3 < BeCO_3$

4. In which of the following the hydration energy is higher than the lattice energy? **[CBSE AIPMT 2007]**

(A) $BaSO_4$ **(B)** $MgSO_4$

(C) $RaSO_4$ **(D)** $SrSO_4$

5. The sequence of ionic mobility in aqueous solution is **[CBSE AIPMT 2008]**

(A) $K^+ > Na^+ > Rb^+ > Cs^+$ **(B)** $Cs^+ > RB^+ > K^+ > Na^+$

(C) $Rb^+ > K^+ > Cs^+ > Na^+$ **(D)** $Na^+ > K^+ > Rb^+ > Cs^+$

6. The alkali metals form salt like hydrides by the direct synthesis at elevated temperature. The thermal stability of these hydrides decreases in which of the following orders ? **[CBSE AIPMT 2008]**

(A) CsH > RbH > KH > NaH > LiH

(B) KH > NaH > LiH > CsH > RbH

(C) NaH > LiH > KH > RbH > CsH

(D) LiH > NaH > KH > RbH > CsH

7. Equimolar solutions of the following were prepared in water separately. Which one of the solutions will record the highest pH ? **[CBSE AIPMT 2008]**

(A) $SrCl_2$ **(B)** $BaCl_2$

(C) $MgCl_2$ **(D)** $CaCl_2$

8. Which one of the following is present as an active ingredient in bleaching powder for bleaching action ? **[CBSE AIPMT 2011]**

(A) $Ca(OCl)_2$ **(B)** CaO_2Cl_2

(C) $CaCl_2$ **(D)** $CaOCl_2$

9. On heating which of the following releases CO_2 most easily ? **[CBSE AIPMT 2015]**

(A) K_2CO_3 **(B)** Na_2CO_3

(C) $MgCO_3$ **(D)** $CaCO_3$

10. Solubility of the alkaline earth's metal sulphates in water decreases in the sequence **[CBSE AIPMT 2015]**

(A) Mg > Ca > Sr > Ba **(B)** Ca > Sr > Ba > Mg

(C) Sr > Ca > Mg > Ba **(D)** Ba > Mg > Sr > Ca

11. "Metals are usually not found as nitrates in their ores". **[CBSE AIPMT 2015]**

Out of the following two (I and II) reasons which is/are true for the above observation?

I. Metal nitrates are highly unstable

II. Metal nitrates are highly soluble in water.

(A) I and II are ture **(B)** I and II are false

(C) I is false but if is true **(D)** I is true but II is false

12. In context with beryllium, which one of the following statements is incorrect ? **[NEET 2016, Phase II]**

(A) It is rendered passive by nitric acid

(B) It forms Be_2C

(C) Its salts rarely hydrolyse

(D) Its hydride is electron-deficient and polymeric

13. Which of the following statements about hydrogen is incorrect ? **[NEET 2016, Phase I]**

(A) Hydrogen never acts as cation in ionic salts

(B) Hydronium ion, H_3O^+ exists freely in solution

(C) Dihydrogen does not act as a reducing agent

(D) Hydrogen has three isotopes of which tritium is the most common

14. Which of the following statements is false? **[NEET 2016, Phase I]**

(A) Ca^{2+} ions are important in blood clotting

(B) Ca^{2+} ions are not important in maintaining the regular beating of the heart

(C) Mg^{2+} ions are important in the green parts of plants

(D) Mg^{2+} ions form a complex with ATP

15. The product obtained as a result of a reaction of nitrogen with CaC_2 is **[NEET 2016, Phase I]**

(A) CaCN **(B)** $CaCN_3$

(C) Ca_2CN **(D)** $Ca(CN)_2$

16. Ionic mobillity of which of the following alkali metal ions is lowest when aqueous solution of their salts are put under an electric field ? **[NEET 2017]**

(A) Na **(B)** K

(C) Rb **(D)** Li

MOCK TEST

1. Hydrogen is :

(A) electropositive. **(B)** electronegative.

(C) both electropositive as well as electronegative. **(D)** neither electropositive nor electronegative.

2. Reaction between following pairs will produce hydrogen except :

(A) Cu + HCl **(B)** Fe + H_2O (g) **(C)** Mg + H_2O (hot) **(D)** Na + Alcohol

3. The colour of hydrogen is :

(A) black **(B)** yellow **(C)** orange **(D)** colourless

4. Which of the following explanations justifies for not placing hydrogen in either the group of alkali metals or halogens ?

(A) The ionization energy of hydrogen is too high for group of alkali metals and too low for halogen group.

(B) Hydrogen atom does not contain any neutron.

(C) Hydrogen is much lighter than alkali metals or halogens.

(D) Hydrogen can form compounds with almost all other elements.

5. Hydrogen accepts an electron to form inert gas configuration. In this it resembles :

(A) halogen **(B)** alkali metals **(C)** chalcogens **(D)** alkaline earth metals

6. Which of the following is a interstitial hydride ?

(A) $TiH_{1.5-1.8}$ **(B)** B_2H_6 **(C)** LiH **(D)** H_2S

7. Hydrogen does not combine with :

(A) Sb **(B)** Na **(C)** He **(D)** Bi

8. The hydride ion H^- is a stronger base than its hydroxide ion OH^-. Which of the following reactions will occur if sodium hydride (NaH) is dissolved in water?

(A) $H^-(aq) + H_2O \longrightarrow H_3O^-(aq)$ **(B)** $H^-(aq) + H_2O(l) \longrightarrow OH^-(aq) + H_2(g)$

(C) $H^-(aq) + H_2O(l) \longrightarrow$ No reaction **(D)** None of these.

9. Which of the following will cause softening of hard water ?

(A) Passing it through anion exchange resin. **(B)** Passing it through sand.

(C) Passing it through cation exchange resin. **(D)** Passing it through alumina.

10. Permutit is a technical name given to :

(A) aluminates of Ca and Na. **(B)** hydrated silicates of Al and Na.

(C) silicates of Ca and Na. **(D)** silicates of Ca and Mg.

11. When H_2O_2 is oxidised by a suitable oxidant, one of the products is :

(A) O^{2-} **(B)** HO^{2-} **(C)** OH^- **(D)** O_2

12. The dihedral angle in gaseous H_2O_2 is :

(A) 180° **(B)** 90° **(C)** 111.5° **(D)** 109°–28′

13. What would happen when a small quantity of H_2O_2 is added to a solution of $FeSO_4$?

(A) Colour of $FeSO_4$ disappears. **(B)** H_2 is evolved.

(C) An electron is added to Fe^{2+}. **(D)** An electron is lost by Fe^{2+}.

CHAPTER 02

ATOMIC STRUCTURE

Nothing exists excpet atoms and empty space: everything else is opinion

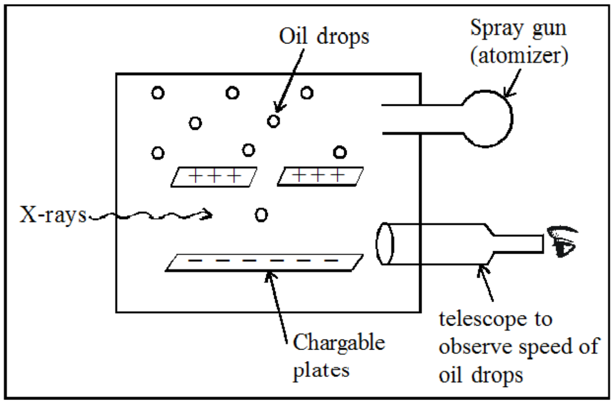
"DEMOCRITUS"

INTRODUCTION

The continued subdivisions of matter would ultimately yield atoms which would not be further divisible. The word atom has been derived from the Greek word 'a-tomio' which means uncutable or non divisible. These earlier ideas were mere speculations and there was no way to test them experimentally. These ideas remained dorment for a very long time and were revived again be scientists in thenineteenth century.

The atomic theory of matter was first proposed on a firm scientific basis by John Dalton, a British school teacher in 1808. His theory, called Dalton's atomic theory, regarded the atom as the ultimate particle of matter.

In this unit we start with the experimental observations made by scientists towards the end of nineteenth and beginning of twentieth century. These established that atoms can be further divided into sub atomic particles, i.e., electrons, protons and neutrons a concept very different from that of Dalton.



measured by R.A. Milikan in 1909 by the Milikan's oil drop experiment.

- The apparatus used by him is shown in fig.
- An oil droplet falls through a hole in the upper plate. The air between the plates is then exposed to X-rays which eject electrons from air molecules. Some of these e⁻ are captured by the oil droplet and it acquires a negative charge.

The metal plates were given an electric charge, and as the electric field between the plates was increased, it was possible to make some of the drops travel upwards at the same speed as they were previously falling.

By measuring the speed, and knowing things like the strength of the field and the density of the oil, radius of oil drops, Milikan was able to calculate the magnitude of the charge on the oil drops. He found that the smallest charge to be found on them was approximately **1.59×10^{-19} C**. This was recognised as the charge on an e^-. The modern value is **1.602×10^{-19} C**.

Mass of the electron :

Mass of the e^- can be calculate from the value of e/m and the value of e

$$m = \frac{e}{e/m} = \frac{-1.602\times10^{-19}}{-17588\times10^{8}} = 9.1096\times10^{-28}\,\text{g} \quad \text{or} \quad = 9.1096\times10^{-31}\,\text{kg}$$

This is termed as the rest mass of the electron i.e. mass of the electron when moving with low speed. The mass of a moving e^- may be calculate by applying the following formula.

$$\text{Mass of moving } e^- = \frac{\text{rest mass of } e^-}{\sqrt{1-(v/c)^2}}$$

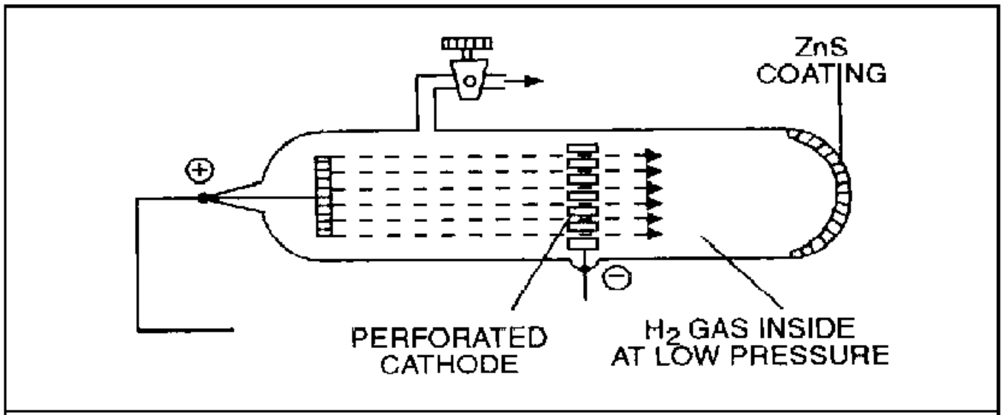
Where v is the velocity of the e^- and c is the velocity of light.

When $v = c \Rightarrow$ mass of $e^- = \infty$

$v > c \Rightarrow$ mass of e^- = imaginary

(ii) Anode rays or Positive rays (Discovery of Proton)

- The first experiment that lead to the discovery of the +ve particle was conducted by 'Goldstein'.
- He used a perforated cathode in the modified cathode ray tube.



Production of Anode rays or Positive rays

1. Frequency, $\nu = \frac{c}{\lambda}$

2. Energy/photon, $E = h\nu = \frac{hc}{\lambda}$

   Also, $E = \frac{12375}{\lambda} eV$, if λ is in Å

3. Electronic energy change during transition, $\Delta E = E_{n_2} - E_{n_1}$

   $n_2 > n_1$, emission spectra if electron jumps from n_2 to n_1 shell and absorption spectra if electron excites from n_1 to n_2 shell.

4. Radius of nth Bohr orbit of H atom, $r_n = \frac{n^2h^2}{4\pi^2 me^2 K}$ (where $K = 9 \times 10^9$)

   r_1 for H = 0.529 Å ; r_n for H like atom $r_n = 0.529 \times \frac{n^2}{Z}$ Å

5. Velocity of electron in nth Bohr orbit of H atom, $v = \frac{2\pi KZe^2}{nh}$

   $v = 2.18 \times 10^8 \frac{Z}{n} cm / sec$.

6. Energy of electron in nth Bohr orbit of H atom, $E = \frac{2\pi^2 mZ^2e^4K^2}{n^2h^2}$

   where n = 1, 2, 3..........

   [$E = -13.6 \times \frac{Z^2}{n^2}$ kcal/mole (1 cal = 4.18 J)]

   E_1 for H = -21.72×10^{-12} erg = – 13.6 eV, E_1 for H like atom = E_1 for H $\times Z^2$

7. Wavelength emitted during transition in H atom,

   $$\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = \frac{2\pi^2 me^4}{ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{(in C.G.S.)}$$

8. Photoelectric effect $h\nu = w + \frac{1}{2}mu^2$ or $h\nu$ = I.E. + K.E.

9. Possible transitions for a jump from n_2 to n_1 = $\sum(n_2 - n_1)$

10. Angular momentum of electron in an orbit = n. (h/2π)

11. Angular momentum of electron in an orbital = (nh/2π) $\sqrt{\left[\ell(\ell+1)\right]}$

12. Total spin = $\pm\left(\frac{1}{2} \times n\right)$; where n is no. of unpaired electrons.

SOLVED EXAMPLE

Ex. 1 If an electron in H atom has an energy of –78.4 kcal/mol. The orbit in which the electron is present is :-

(A) 1st **(B)** 2nd
(C) 3rd **(D)** 4th

Sol. $E^n = \frac{-313.6}{n^2}$ kcal / mol ∴ $-78.4 = \frac{-313.6}{n^2}$

∴ n = 2

Ex. 2 What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition, n = 4 to n = 2 in the He^+ spectrum ?

(A) n = 4 to n = 2 **(B)** n = 3 to n = 2
(C) n = 3 to n = 1 **(D)** n = 2 to n = 1

Sol. $\bar{\nu} = \frac{1}{\lambda} = \left(\frac{1}{2^2} - \frac{1}{4^2}\right) RZ^2 = \frac{3}{4} R$

In H–spectrum for the same $\bar{\nu}$ or λ as Z = 1, n = 1, $n_2 = 2$

So, **(D)** is the correct answer.

Ex. 3 Difference between nth and (n + 1)th Bohr's radius of H–atom is equal to its (n – 1)th Bohr's radius. The value of n is :-

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

Sol. $r_n \propto n^2$

But $r_n + 1 - r_n = r_n - 1$

$(n + 1)^2 - n^2 = (n - 1)^2$

n = 4

So **(D)** is the correct answer

Ex. 4 The dissociation energy of H_2 is 430.53 kJ mol^{-1}. If H_2 is dissociated by illumination with radiation of wavelength 253.7 nm. The fraction of the radiant energy which will be converted into kinetic energy is given by :-

(A) 8.86% **(B)** 2.33%
(C) 1.3% **(D)** 90%

Sol. $\frac{hc}{\lambda} = \frac{430.53 \times 10^3}{6.023 \times 10^{23}} + \text{K.E.}$

$$\text{K.E.} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{253.7 \times 10^{-9}} - \frac{430.53 \times 10^3}{6.023 \times 10^{23}}$$

$= 6.9 \times 10^{-20}$

∴ Fraction = $\frac{6.9 \times 10^{-20}}{7.83 \times 10^{-19}} = 0.088 = 8.86\%$

Ex. 5 Principal, azimuthal and magnetic quantum numbers are respectively related to :-

(A) size, orientation and shape
(B) size, shape and orientation
(C) shape, size and orientation
(D) none of these

Sol. Principal gives size, i.e. azimuthal gives shape and magnetic quantum number gives the orientation.

So, **(B)** is the correct answer.

Ex. 6 If the radius of 2nd Bohr orbit of hydrogen atom is r_2. The radius of third Bohr orbit will be :-

(A) $\frac{4}{9} r_2$ **(B)** $4r_2$
(C) $\frac{9}{4} r_2$ **(D)** $9r_2$

Sol. $r = \frac{n^2 h^2}{4\pi^2 mZe^2}$

∴ $\frac{r_2}{r_3} = \frac{2^2}{3^2}$ ∴ $r_3 = \frac{9}{4} r_2$

So, **(C)** is the correct answer.

Ex. 7 Light of wavelength λ shines on a metal surface with intensity x and the metal emits Y electrons per second of average energy, Z. What will happen to Y and Z if x is doubled ?

(A) Y will be double and Z will become half
(B) Y will remain same and Z will be doubled
(C) Both Y and Z will be doubled
(D) Y will be doubled but Z will remain same

Sol. When intensity is doubled, number of electrons emitted per second is also doubled but average energy of photoelectrons emitted remains the same. So, **(D)** is the correct answer.

Ex. 8 Which of the following is the ground state electronic configuration of nitrogen :-

(A)


(B)


(C)


(D)


Sol. In **(A)** and **(D)**, the unpaired electrons have spin in the same direction.

So, **(A)** and **(D)** are the correct answer.

Exercise # 1 SINGLE OBJECTIVE NEET LEVEL

1. A neutral atom (Atomic no. > 1) consists of
(A) Only protons
(B) Neutrons + protons
(C) Neutrons + electrons
(D) Neutron + proton + electron

2. The nucleus of the atom consists of
(A) Proton and neutron
(B) Proton and electron
(C) Neutron and electron
(D) Proton, neutron and electron

3. The size of nucleus is of the order of
(A) 10^{-12} m **(B)** 10^{-8} m
(C) 10^{-15} m **(D)** 10^{-10} m

4. Positive ions are formed from the neutral atom by the
(A) Increase of nuclear charge
(B) Gain of protons
(C) Loss of electrons
(D) Loss of protons

5. The electron is
(A) α-ray particle **(B)** β-ray particle
(C) Hydrogen ion **(D)** Positron

6. The number of electrons in an atom of an element is equal to its
(A) Atomic weight **(B)** Atomic number
(C) Equivalent weight **(D)** Electron affinity

7. The nucleus of the element having atomic number 25 and atomic weight 55 will contain
(A) 25 protons and 30 neutrons
(B) 25 neutrons and 30 protons
(C) 55 protons
(D) 55 neutrons

8. If W is atomic weight and N is the atomic number of an element, then
(A) Number of $e^{-1} = W - N$
(B) Number of ${}_0n^1 = W - N$
(C) Number of ${}_1H^1 = W - N$
(D) Number of ${}_0n^1 = N$

9. The total number of neutrons in dipositive zinc ions with mass number 70 is
(A) 34 **(B)** 40
(C) 36 **(D)** 38

10. Which of the following are isoelectronic with one another
(A) Na^+ and Ne **(B)** K^+ and O
(C) Ne and O **(D)** Na^+ and K^+

11. The number of electrons in one molecule of CO_2 are
(A) 22 **(B)** 44
(C) 66 **(D)** 88

12. Chlorine atom differs from chloride ion in the number of
(A) Proton
(B) Neutron
(C) Electrons
(D) Protons and electrons

13. CO has same electrons as or the ion that is isoelectronic with CO is
(A) N_2^+ **(B)** CN^-
(C) O_2^+ **(D)** O_2^-

14. The mass of an atom is constituted mainly by
(A) Neutron and neutrino
(B) Neutron and electron
(C) Neutron and proton
(D) Proton and electron

15. The atomic number of an element represents
(A) Number of neutrons in the nucleus
(B) Number of protons in the nucleus
(C) Atomic weight of element
(D) Valency of element

16. An atom has 26 electrons and its atomic weight is 56. The number of neutrons in the nucleus of the atom will be
(A) 26 **(B)** 30
(C) 36 **(D)** 56

17. The most probable radius (in pm) for finding the electron in He^+ is
(A) 0.0 **(B)** 52.9
(C) 26.5 **(D)** 105.8

18. The number of unpaired electrons in the Fe^{2+} ion is
(A) 0 **(B)** 4
(C) 6 **(D)** 3

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. A photon of energy hν is absorbed by a free electron of a metal having work function w < hν. Then :

(A) The electron is sure to come out
(B) The electron is sure to come out with a kinetic energy (hν – w)
(C) Either the electron does not come out or it comes with a kinetic energy (hν – w)
(D) It may come out with a kinetic energy less than (hν – w)

2. Light of wavelength λ falls on metal having work function hc/λ_0. Photoelectric effect will take place only if :

(A) $\lambda \geq \lambda_0$ **(B)** $\lambda \geq 2\lambda_0$□1
(C) $\lambda \leq \lambda_0$ **(D)** $\lambda \leq \lambda_0/2$

3. A bulb of 40 W is producing a light of wavelength 620 nm with 80% of efficiency then the number of photons emitted by the bulb in 20 seconds are (1eV = 1.6×10^{-19} J, hc = 12400 eV Å)

(A) 2×10^{18} **(B)** 10^{18}
(C) 10^{21} **(D)** 2×10^{21}

4. If the value of E_n = – 78.4 kcal/mole, the order of the orbit in hydrogen atom is :

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

5. Correct order of radius of the Ist orbit of H, He^+, Li^{2+}, Be^{3+} is :

(A) H > He^+ > Li^{2+} > Be^{3+}
(B) Be^{3+} > Li^{2+} > He^+ > H
(C) He^+ > Be^{3+} > Li^{2+} > H
(D) He^+ > H > Li^{2+} > Be^{3+}

6. What is likely to be orbit number for a circular orbit of diameter 20 nm of the hydrogen atom :

(A) 10 **(B)** 14
(C) 12 **(D)** 16

7. Which is the correct relationship :

(A) E_1 of H = 1/2 E_2 of He^+ = 1/3 E_3 of Li^{2+} = 1/4 E_4 of Be^{3+}
(B) $E_1(H) = E_2(He^+) = E_3(Li^{2+}) = E_4(Be^{3+})$
(C) $E_1(H) = 2E_2(He^+) = 3E_3(Li^{2+}) = 4E_4(Be^{3+})$
(D) No relation

8. If velocity of an electron in I orbit of H atom is V, what will be the velocity of electron in 3rd orbit of Li^{+2}

(A) V **(B)** V/3
(C) 3 V **(D)** 9 V

9. In a certain electronic transition in the hydrogen atoms from an initial state (1) to a final state (2), the difference in the orbital radius $(r_1 - r_2)$ is 24 times the first Bohr radius. Identify the transition.

(A) 5 → 1 **(B)** 25 → 1
(C) 8 → 3 **(D)** 6 → 5

10. The species which has its fifth ionisation potential equal to 340 V is

(A) B^+ **(B)** C^+
(C) B **(D)** C

11. Choose the correct relations on the basis of Bohr's theory.

(A) Velocity of electron ∝ n
(B) Frequency of revolution $\propto \frac{}{n^2}$
(C) Radius of orbit $\propto n^2 Z$
(D) Electrostatic force on electron $\propto \frac{1}{n^4}$

12. **S1 :** Potential energy of the two opposite charge system increases with the decrease in distance.
S2 : When an electron make transition from higher orbit to lower orbit it's kinetic energy increases.
S3 : When an electron make transtition from lower energy to higher energy state its potential energy increases.
S4 : 11eV photon can free an electron from the 1st excited state of He^+ -ion.

(A) T T T T **(B)** F T T F
(C) T F F T **(D)** F F F F

13. **S1 :** Bohr model is applicable for Be^{2+} ion.
S2 : Total energy coming out of any light source is integral multiple of energy of one photon.
S3 : Number of waves present in unit length is wave number.
S4 : e/m ratio in cathode ray experiment is independent of the nature of the gas.

(A) F F T T **(B)** T T F F
(C) F T T T **(D)** T F F F

14. Match the following
(A) Energy of ground state of He^+
(i) + 6.04 eV
(B) Potential energy of I orbit of H-atom
(ii) –27.2 eV
(C) Kinetic energy of II excited state of He^+
(iii) 54.4 V
(D) Ionisation potential of He^+
(iv) – 54.4eV

(A) A – (i), B – (ii), C – (iii), D – (iv)
(B) A – (iv), B – (iii), C – (ii), D – (i)
(C) A – (iv), B – (ii), C – (i), D – (iii)
(D) A – (ii), B – (iii), C – (i), D – (iv)

Exercise # 3

PART - 1

MATRIX MATCHCOLUMN

1.

Column I	Column II
(A) Cathode rays	**(p)** Helium nuclei
(B) Dumb-bell	**(q)** Uncertainty principle
(C) Alpha particles	**(r)** Electromagnetic radiation
(D) Moseley	**(s)** p-orbital
(E) Heisenberg	**(t)** Atomic number
(F) X-rays	**(u)** Electrons

2. Frequency = f, Time period = T, Energy of n^{th} orbit = E_n, radius of n^{th} orbit = r_n, Atomic number = Z, Orbit number = n

Column I	Column II
(A) f	**(p)** n^3
(B) T	**(q)** Z^2
(C) E_n	**(r)** $\frac{1}{n^2}$
(D) $\frac{1}{r_n}$	**(s)** Z

3.

Column I	Column II
(A) Lyman series	**(p)** maximum number of spectral line observed = 6
(B) Balmer series	**(q)** maximum number of spectral line observed = 2
(C) In a sample of H-atom for 5 upto 2 transition	**(r)** 2^{nd} line has wave number $\frac{8R}{9}$
(D) In a single isolated H-atom for 3 upto 1 transition	**(s)** 2^{nd} line has wave number $\frac{3R}{16}$
	(t) Total number of spectral line is 10.

4.

Column I	Column II
(A) Aufbau principle	**(p)** Line spectrum in visible region
(B) de broglie	**(q)** Maximum multiplicity of electron
(C) Angular momentum	**(r)** Photon
(D) Hund's rule	**(s)** $\lambda = h/(mv)$
(E) Balmer series	**(t)** Electronic configuration
(F) Planck's law	**(u)** mvr

Exercise # 4

PART - 1

PREVIOUS YEAR (NEET/AIPMT)

1. The energy of photon is given as : Δe/atom = 3.03×10^{-19} J atom^{-1}, then the wavelength (λ) of the photon is **[CBSE AIPMT 2000]**
(Given, h(Planck's constant) = 6.63×10^{-34} Js, c (velocity of light) = 3.00×10^{8} ms^{-1})

(A) 6.56 nm **(B)** 65.6 nm
(C) 656 nm **(D)** 0.656 nm

2. The following quantum number are possible for how many orbital(s) n = 3, l = 2 and m = + 2? **[CBSE AIPMT 2001]**

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

3. The hydrogen atom, energy of first excited state is – 3.4 eV. Then, KE of same orbit of hydrogen atom is **[CBSE AIPMT 2002]**

(A) + 3.4 eV **(B)** + 6.8 eV
(C) – 13.6eV **(D)** + 13.6 eV

4. The value of Planck's constant is 6.63×10^{-34} Js. The velocity of light is 3.0 × 108 ms–1. Which value is closest to the wavelength in nanometers of a quantum of light with frequencey of 8×10^{15} s^{-1} ? **[CBSE AIPMT 2002]**

(A) 4×10^{1} **(B)** 3×10^{7}
(C) 2×10^{-25} **(D)** 5×10^{-18}

5. The frequency of radiation emitted when the electron falls from n = 4 to n = 1 in a hydrogen atom will be)Given ionisation energy of H = 2.18×10^{-18} J and h = 6.625×10^{-34} Js) **[CBSE AIPMT 2004]**

(A) 1.54×10^{15} s^{-1} **(B)** 1.03×10^{15} s^{-1}
(C) 3.08×10^{15} s^{-1} **(D)** 2.00×10^{15} s^{-1}

6. The energy of second Bohr orbit of the hydrogen atom is –328 kJ mol^{-1}, hence the energy of fourth Bohr orbit would be **[CBSE AIPMT 2005]**

(A) –41 kJ mol^{-1} **(B)** –1312 kJ mol^{-1}
(C) –164 kJ mol^{-1} **(D)** –82 kJ mol^{-1}

7. Given, the mass of electron is 9.11×10^{-31} kg, Planck's constatn is 6.626×10^{-34} Js, the uncertainty involved in the measurement of velocity within a distance of 0.1 Å is **[CBSE AIPMT 2006]**

(A) 5.79×10^{6} ms^{-1} **(B)** 5.79×10^{7} ms^{-1}
(C) 5.79×10^{8} ms^{-1} **(D)** 5.79×10^{5} ms^{-1}

8. The orientation of an atomic orbital is governed by **[CBSE AIPMT 2007]**

(A) azimuthal quantum number
(B) spin quantum number
(C) magnetic quantum number
(D) principal quantum number

9. Consider the following sets of quantum number.

	n	l	m	s
(i)	3	0	0	+1/2
(ii)	2	2	1	+1/2
(iii)	4	3	–2	–1/2
(iv)	1	0	–1	–1/2
(v)	3	2	3	+1/2

Which of the following sets of quantum number is not possible ? **[CBSE AIPMT 2007]**

(A) (ii), (iii) and (iv) **(B)** (i), (ii), (iii) and (iv)
(C) (ii), (iv) and (v) **(D)** (i) and (iii)

10. If uncertainty in position and momentum are equal, then uncertainty in velocity is **[CBSE AIPMT 2008]**

(A) $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$ **(B)** $\sqrt{\frac{h}{2\pi}}$
(C) $\frac{1}{m}\sqrt{\frac{h}{\pi}}$ **(D)** $\sqrt{\frac{h}{\pi}}$

11. The measurement of the electrons position is associated with an uncertainty in momentum, which is equal to 1×10^{-18} gcm s^{-1}, The uncertainty in electron velocity is (mass of an electron is 9×10^{-28} g) **[CBSE AIPMT 2008]**

(A) 1×10^{9} cm s^{-1} **(B)** 1×10^{6} cm s^{-1}
(C) 1×10^{5} cm s^{-1} **(D)** 1×10^{11} cm s^{-1}

12. Maximum number of electrons in a subshell of an atom is determined by the following **[CBSE AIPMT 2009]**

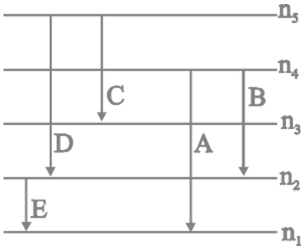
(A) 4/ +2 **(B)** 2 / + 1
(C) 4 /– 2 **(D)** $2n^{2}$

13. The energy absorbed by each molecule (A_2) of a substance is 4.4×10^{-19} J and bond energy per molecule is 4.0×10^{-19} J. The kinetic energy of the molecule per atom will be **[CBSE AIPMT 2009]**

(A) 2.0×10^{-20} J **(B)** 2.2×10^{-19} J
(C) 2.0×10^{-19} J **(D)** 4.0×10^{-20} J

MOCK TEST

1. For a hypothetical H like atom which follows Bohr's model, some spectral lines were observed as shown. If it is known that line 'E' belongs to the visible region, then the lies possibly belonging to ultra violet region will be (n_1 is not necessarily ground state)
[Assume for this atom, no spectral series shows overlaps with other series in the emmission spectrum]



(A) B and D **(B)** D only **(C)** C only **(D)** A only

2. The number of photons emitted in 10 hours by a 60 W sodium lamp (λ of photon = 6000 Å)

(A) 6.50×10^{24} **(B)** 6.40×10^{23} **(C)** 8.40×10^{23} **(D)** 3.40×10^{23}

3. Ratio of frequency of revolution of electron in the 2nd excited state of He^+ and 2nd state of hydrogen is.

(A) $\frac{32}{27}$ **(B)** $\frac{27}{32}$ **(C)** 1/54 **(D)** 27/2

4. A proton accelerated from rest through a potential difference of 'V' volts has a wavelength λ associated with it. An alpha particle in order to have the same wavelength must be accelerated from rest through a potential difference of

(A) V volt **(B)** 4V volt **(C)** 2V volt **(D)** $\frac{V}{8}$ volt

5. If the wave number of 1st line of Balmer series of H-atom is 'x' then the wave number of 1st line of lyman series of the He^+ ion will be

(A) $\frac{36\,x}{5}$ **(B)** $\frac{12\,x}{5}$ **(C)** $\frac{108\,x}{5}$ **(D)** x

6. Consider the ground state of Cr atom (Z = 24). The number of electrons with the azimuthal quantum numbers, λ = 1 and 2 are, respectively :

(A) 16 and 5 **(B)** 12 and 5 **(C)** 16 and 4 **(D)** 12 and 4

7. 4000 Å photon is used to break the iodine molecule, then the % of energy converted to the K.E. of iodine atoms if bond dissociation energy of I_2 molecule is 246.5 kJ/mol

(A) 8% **(B)** 12% **(C)** 17% **(D)** 25%

8. Radius of 3rd orbnit of Li^{2+} ion is 'x' cm then de-broglie wavelength of electrons in the 1st orbit is

(A) $\frac{2\pi x}{3}$ cm **(B)** $6\pi x$ cm **(C)** $3\pi x$ cm **(D)** $\frac{2\pi x}{6}$ cm

9. When an electron makes a transition from (n + 1) state to n state, the frequency of emitted radiation is related to n according to (n > > 1)

(A) $\nu \propto n^{-3}$ **(B)** $\nu \propto \nu\, n^2$ **(C)** $\nu \propto n^3$ **(D)** $\nu \propto n^{2/3}$

CHAPTER 14

GENERAL ORGANIC CHEMISTRY

We define chemistry as the chemistry of carbon compounds.

"AUGUSTKEKULE"

INTRODUCTION

General organic chemistry is the base of organic chemistry If we want to under stand GOC well, then definitely we are going to be a pro in organic chemistry overall.

Topics which mention in GOC

1. Inductive effect
2. Mesomeric effect
3. Resonance effect
4. Hyperconjugation.

We have to remember the condition for every effect and when they are applicable for e.g. If resonance and inductive effect both are operating, then resonance is dominating effect there.

In GOC we also know about the reaction intermediate which is a molecular entity that is promed from the reactants and reacts further to give the directly observed products of a chemcial reaction most chemical reaction are stepwise, that is take more than one chemistry step to complete.

Reaction : Breaking of old bond and formation of new bond is known as chemical reaction

A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism.

Species on which reagent is attacking is known as substrate or reactant.

Species which attack on substrate, is known as reagent.

Type of cleavage of bond

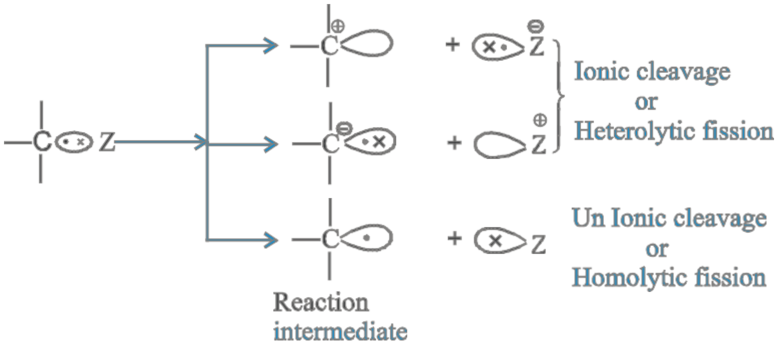
(I) Heterolytical cleavage/fission :

Cleavage in which unequal distribution of electrons takes place during the bond cleavage is known as heterolytical cleavage. Due to unequal distribution of electrons, ions are formed. That's why it is also known as ionic cleavage or heterolytical cleavage.

(II) Homolytical cleavage/fission :

Cleavage in which equal distribution of e^-s takes place during the chemical reaction is known as homolytical cleavage.

- Due to equally distribution of electrons, without charge unpaired electrons species is formed, which is known as free radical and cleavage is known as unionic cleavage/homolytical fission.
- By both cleavage [ionic/non ionic] three type of species are formed [One carrying positive charge, other carrying negative charge and third one is neutral with unpaired electrons] is known as reaction intermidiate.



Attacking reagents

The species which attack on a substrate molecule or intermediate and form a product is called as attacking reagent. These are of two types :

(I) Electrophilic reagent or electrophiles

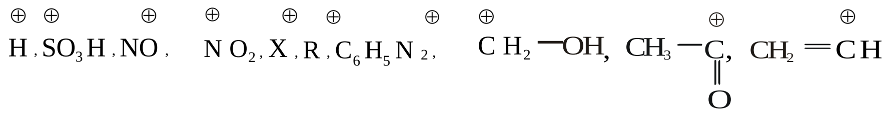
Electrophilic (electro + philic)

(electron + loving)

The reagent which attacks on the **negative of the molecule** or loves electrons are called electrophiles.

Electrophiles may be positively charged or electron deficient molecule (molecule with sextet or septet).

(i) Positively charged electrophiles



$$\overset{\oplus}{H},\ \overset{\oplus}{S}O_3H,\ \overset{\oplus}{N}O,\ \overset{\oplus}{N}O_2,\ \overset{\oplus}{X},\ \overset{\oplus}{R},\ C_6H_5\overset{\oplus}{N}_2,\ \overset{\oplus}{C}H_2—OH,\ CH_3—\underset{\underset{O}{\|}}{\overset{\oplus}{C}},\ CH_2=\overset{\oplus}{C}H$$

(ii) Neutral electrophiles :- Which possess a electron dificiency.

(a) All Lewis acids as :

BF_3, $AlCl_3$, SO_3, $ZnCl_2$, $BeCl_2$, $FeCl_3$, $SnCl_2$, CO_2, $SnCl_4$.

Ex. Which of the following has minimum heat of hydrogenation.

(i) ethene (ii) Propene (iii) cis-2-butene (iv) trans-2-butene

Sol. (iv) maximum stable alkene means minimum reactive.

Ex. If Heat of hydrogenation of 1-butene is 30 Kcal then heat of hydrogenation of 1,3-butadiene is ?

(i) 30 (ii) 60 (iii) 57 (iv) 25

Sol. (iii) 1,3-butadiene requires two moles of hydrogen so heat of hydrogenation should be 60 Kcal but 1,3-butadiene is stabilized by resonance than propane so heat of hydrogenation of 1,3-butadiene will not be twice of 30.

Actual ΔH - $60 > \Delta H > 30$ Kcal.

Ex. Which of the following is maximum stable.

(i) Conjugated alkadiene ($CH_2{=}CH{-}CH{=}CH_2$)

(ii) Isolated alkadiene ($CH_2{=}CH{-}CH_2{-}CH{=}CH_2$)

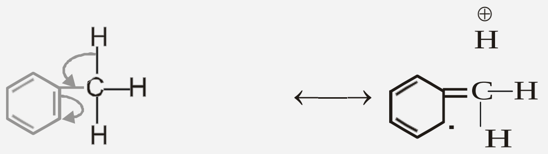
(iii) Cumulated alkadiene ($CH_2{=}C{=}CH_2$)

(iv) All are equal.

Sol. (i) Due to resonance conjugated alkadiene is maximum stable. Isolated is more stable than cumulated alkadiene due to H-effect.

ED OS KEY POINTS

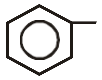
Reactivity of Benzene : H-effect of R groups increases electron density in benzene ring.

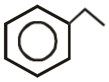


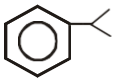
due to CH_3 group there is more e^- density at ortho and para position so CH_3 is ortho/para directing and activating group.

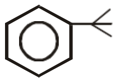
If H-effect is more than e^- density will be more.

Ex. Give electrophilic sustitution reaction order :









Maximum α-H.

So maximum H-effect

So maximum e^- density

So maximum reactive

ESR order I > II > III > IV

1. All the +ve charge species are electrophile except H_3O^+ and NH_4^+.

2. Relative electron withdrawing order (–1 order)

$-NO_2 > -CN > -COOH > -F > -OR > -OH > -C_6H_5 > -CH = CH_2$

3. + I order

$-NO^- > -O > -COO^- > 3°$ alkyl $> 2°$ alkyl $< 1°$ alkyl

4. Greater the number of α-Hydrogen, more stable is carbocation and free radical due to hyperconjugation.

(A) **Carbocation**

$> (Ph)_3\overset{+}{C} > (Ph)_2\overset{+}{C}H > Ph - \overset{+}{C}H_2 > CH_2 = CH - \overset{+}{C}H_2$

$(CH)_3\overset{+}{C} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3 > CH_2 = \overset{+}{C}H > CH \equiv C^{+}$

(B) **Free radical**

$(Ph)_3\overset{\bullet}{C} > (Ph)_2\overset{\bullet}{C}H > Ph\,\overset{\bullet}{C}H_2 > CH_2 = CH - \overset{\bullet}{C}H_2 >$

$(CH_3)_3\overset{\bullet}{C} > (CH_3)_2\overset{\bullet}{C}H > CH_3\overset{\bullet}{C}H_2$

(C) **Carbanion**

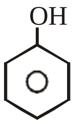
$(Ph)_3\overset{\ominus}{C} > (Ph)_2\overset{\ominus}{C}H > Ph - \overset{\ominus}{C}H_2 > CH_2 = CH - \overset{\ominus}{C}H_2 > \overset{\ominus}{C}H_3 >$

$CH_3\overset{\ominus}{C}H_2 > (CH_3)_2\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$

Acidic Strength

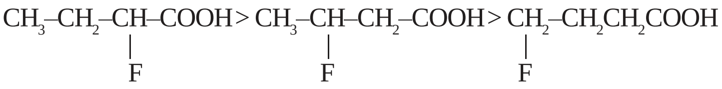
(i) $H_2O > CH \equiv CH > NH_3$

(ii) $CH \equiv CH > CH_2 = CH_2 > CH_3 - CH_3$

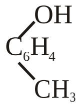
(iii) $R-SO_3H > R-COOH >$  $> R-OH$

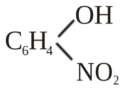
(iv) $HCOOH > CH_3COOH > CH_3CH_2COOH$

(v) $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH$

(vi) 

$CH_3-CH_2-\underset{|\atop F}{CH}-COOH > CH_3-\underset{|\atop F}{CH}-CH_2-COOH > \underset{|\atop F}{CH_2}-CH_2CH_2COOH$

(vii)  Phenol > m > p > 0

(viii)  p > o > m > Phenol

SOLVED EXAMPLE

Ex.1 Which one of the following species is most stable

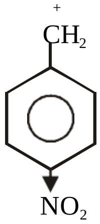
(A) $p-O_2N-C_6H_4-\overset{+}{C}H_2$

(B) $p-CH_3O-C_6H_4-\overset{+}{C}H_2$

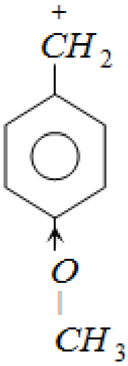
(C) $p-Cl-C_6H_4-\overset{+}{C}H_2$

(D) $C_6H_5-\overset{+}{C}H_2$

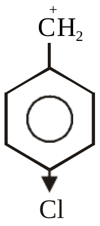
Sol. **(B)**



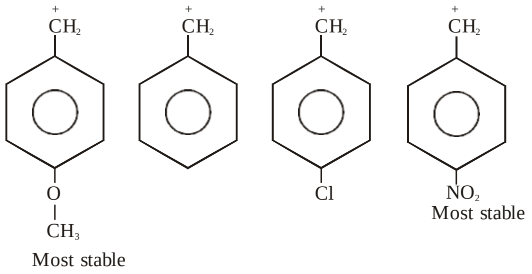
Nitro-group is electron withdrawing therefore decreases stability.



Methoxy group is electron releasing.
Therefore increases stability by donating electron.



Chlorine is also electron withdrawing but its effect is less than $-NO_2$ group.
Hence, correct order of stability.



Ex.2 Which of the following gives most stable carbocation by dehydration

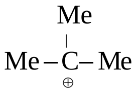
(A) $(CH_3)_2CH-OH$

(B) $(CH_3)_3C-OH$

(C) CH_3-CH_2-OH

(D) $CH_3-CH_2-O-CH_2-CH_3$

Sol. **(B)** 3° alcohols



$Me-\underset{\oplus}{\overset{Me}{C}}-Me$ is most stable carbocation

Ex.3 Which of the following orders regarding relative stability of free radicals is correct

(A) $3° < 2° < 1°$ **(B)** $3° > 2° > 1°$

(C) $1° < 2° > 3°$ **(D)** $3° > 2° < 1°$

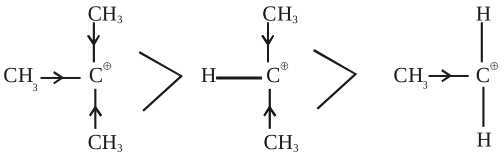
Sol. **(B)** Due to the increasing no. of hyperconjugative structures free radical stabilise following as $3° > 2° > 1°$.

Ex.4 The +I effect of alkyl groups is in the order

(A) $2° > 3° > 1°$ **(B)** $1° > 2° > 3°$

(C) $3° > 2° > 1°$ **(D)** None of these

Sol. **(C)** $3° > 2° > 1°$



Ex.5 Which of the following compounds will show metamerism

(A) $CH_3COOC_2H_5$ **(B)** $C_2H_5-S-C_2H_5$

(C) CH_3-O-CH_3 **(D)** $CH_3-O-C_2H_5$

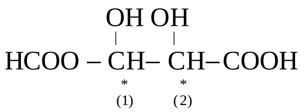
Sol. **(B)** $\underset{\text{Diethyl thioether}}{C_2H_5-S-C_2H_5}$ and $\underset{\text{Methyl propyl thioether}}{CH_3-S-C_3H_7}$ are metamers.

Ex.6 How many carbon atoms in the molecule $HCOO-(CHOH)_2-COOH$ are asymmetric

(A) 1 **(B)** 2

(C) 3 **(D)** None of these

Sol. **(B)**



$HCOO-\underset{(1)}{\overset{OH}{\overset{|}{C^*}}}H-\underset{(2)}{\overset{OH}{\overset{|}{C^*}}}H-COOH$

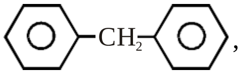
Two carbon atoms in the molecule are asymmetric.

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. The molecular formula of diphenyl methane,



, is $C_{13}H_{12}$

How many structural isomers are possible when one of the hydrogens is replaced by a chlorine atom

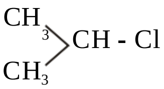
(A) 8 **(B)** 7

(C) 6 **(D)** 4

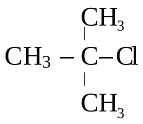
2. SN^1 reaction is faster in

(A) CH_3CH_2Cl

(B)

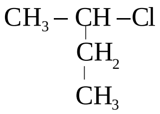


(C)



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl$

(D)



$CH_3-\underset{\underset{CH_3}{CH_2}}{CH}-Cl$

3. How many enantiomer pairs are obtained by monochlorination of 2, 3-dimethylbutane

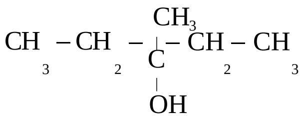
(A) Nil **(B)** Four

(C) Two **(D)** Three

(E) One

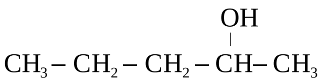
4. Among the following compounds which can be dehydrated very easily is

(A)



$CH_3-CH_2-\overset{CH_3}{\underset{OH}{C}}-CH_2-CH_3$

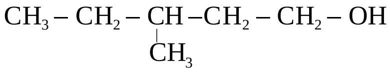
(B)



$CH_3-CH_2-CH_2-\overset{OH}{CH}-CH_3$

(C) $CH_3-CH_2-CH_2-CH_2-CH_2-OH$

(D)



$CH_3-CH_2-\underset{CH_3}{CH}-CH_2-CH_2-OH$

5. Which of the following statements is not characteristic of free radical chain reaction

(A) It gives major product derived from most stable free radical

(B) It is usually sensitive to change in solvent polarity

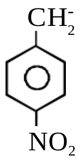
(C) It proceeds in three main steps like initiation, propagation and termination

(D) It may be initiated by U.V. light

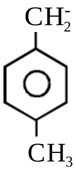
6. Most stable carbanion is

(A) CH_3^- **(B)** $CH_3CH_2^-$

(C)



(D)



7. Which one is electrophilic addition

(A) $CH_3-CH_3+Cl_2 \rightarrow C_2H_5Cl + HCl$

(B) $CH_3CH=O+HCN \rightarrow (CH_3)_2C(OH)CN$

(C) $(CH_3)_2C=O+HCN \rightarrow CH_3CH(OH)CN$

(D) $CH_2=CH_2+Br_2 \rightarrow CH_2BrCH_2Br$

8. A compound has 3 chiral carbon atoms. The number of possible optical isomers it can have

(A) 3 **(B)** 2

(C) 8 **(D)** 4

9. How many chiral isomers can be drawn from 2-bromo, 3-chloro butane

(A) 2 **(B)** 3

(C) 4 **(D)** 5

10. Number of isomers of C_4H_{10} is

(A) 2 **(B)** 3

(C) 4 **(D)** Isomerism not exist

11. The number of possible isomers for compound $C_2H_3Cl_2Br$ is

(A) 2 **(B)** 3

(C) 4 **(D)** 5

12. The optically active tartaric acid is named as D-(+)-tartaric acid because it has a positive

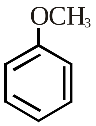
(A) Optical rotation and is derived from D-glucose

(B) pH in organic solvent

(C) Optical rotation and is derived from D(+) glyceraldehyde

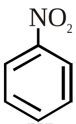
(D) Optical rotation only when substituted by deuterium

13. Among the following compounds (I-III) the correct order of reaction with electrophilic reagent is



I

II



III

(A) II > III > I **(B)** III < I < II

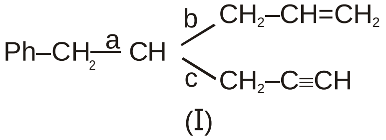
(C) I > II > III **(D)** I = II > III

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. Observe the following statements and choose the correct option.

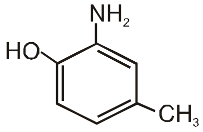
S1 : Inductive effect is more powerful than mesomeric effect.

S2 : The bond polarity order of bonds a, b, and c in the given molecule (I) is c > a > b



(I)

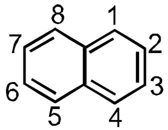
S3 : The hybrid structure has always have equal contribution from all the resonating structures.

S4 : 

shows inductive effect, resonance, hyperconjugation & intramolecular hydrogen bonding.

(A) TFTF **(B)** FTFTC **(C)** FTTF **(D)** TTFF

2. Which of the following is correct about the following compound



(Naphthalene)

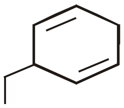
(A) All the C-C bond length are same

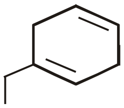
(B) C_1–C_2 bond length is shorter than C_2–C_3 bond length

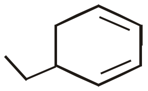
(C) C_1–C_2 bond length is greater than C_2–C_3 bond length

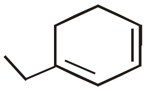
(D) All the C-C bond length are equal to C-C bond length of benzene

3. The stability order of alkene in following compounds is :


(I)

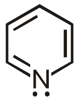

(II)

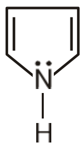

(III)

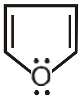

(IV)

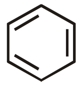
(A) I < II < III < IV **(B)** II < I < III < IV **(C)** II < III < I < IV **(D)** II < IV < I < III

4. Number of π electrons in conjugation for these compounds


Pyridine ,

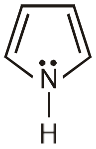

Pyrrole ,


Furan &


Benzene

will be respectively:

(A) 8, 6, 6, 6 **(B)** 6, 4, 6, 6 **(C)** 6, 6, 6, 6 **(D)** 6, 6, 8, 6

5. The hybridisation of nitrogen in  (pyrrole) is :

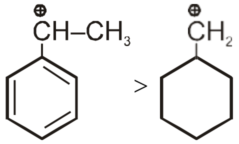
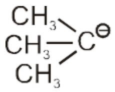
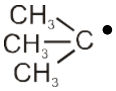
(A) sp^3 **(B)** sp^2 **(C)** sp **(D)** Cann't bepredicted

Exercise # 3

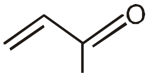
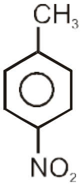
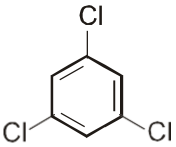
PART - 1

MATRIX MATCHCOLUMN

1.

Column-I **(Stability order)**	**Column-II** **(Responsible effect)**
(A) $\overset{\oplus}{C}H_2–OH > CH_3–\overset{\oplus}{C}H–CH_3$	**(p)** Inductive effect
(B) 	**(q)** Resonance
(C) $CH_3–CH_2^-$ > 	**(r)** Hyperconjugation
(D)  > $CH_3–CH_2^{\bullet}$	**(s)** Mesomeric effect

2. Match the following

Coulmn - I **(Compounds)**	**Coulmn - II** **(Characteristics)**
(A) 	**(p)** Mesomeric effect / resonance
(B) $Ph–CH=CH–CH_3$	**(q)** Inductive effect.
(C) 	**(r)** Hyperconjugative effect
(D) 	**(s)** Nonpolar
	(t) Polar

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. Among the following compounds the decreasing order of reactivity towards electrophilic substitution is **[CBSE AIPMT2000]**

I

II

III

IV

(A) II > I > III > IV **(B)** III > I > II > IV

(C) IV > I > II > IV **(D)** I > II > III > IV

2. In HS^-, I^-, RNH_2, NH_3 order of proton accepting tendency will be **[CBSE AIPMT2001]**

(A) $I^- > NH_3 > RNH_2 > HS^-$

(B) $NH_3 > RNH_2 > HS^- > I^-$

(C) $RNH_2 > NH_3 > HS^- > I^-$

(D) $HS^- > RNH_2 > NH_3 > I^-$

3. The correct order of reactivity towards the electrophilic substitution of the compounds aniline (I). benzene (II) and nitrobenzene (III) is **[CBSE AIPMT 2002]**

(A) II <III > I **(B)** I > II > III

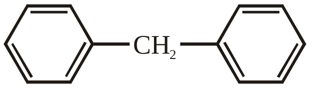
(C) III > II > I **(D)** II > III > I

4. Which of the following is least reactive in a nucleophilic substitution reaction ? **[CBSE AIPMT 2004]**

(A) $(CH_3)_3C-Cl$ **(B)** $CH_2=CHCl$

(C) CH_3CH_2Cl **(D)** $CH_2=CHCH_2Cl$

5. The molecular formula of diphenyl methane



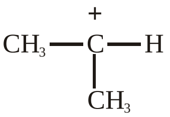
is $C_{13}H_{12}$

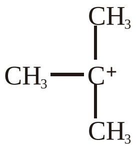
How many structural isomers are possible when one of the hydrogen is replaced by a chlorine atom? **[CBSE AIPMT 2004]**

(A) 6 **(B)** 4

(C) 8 **(D)** 7

6. Which amongst the following is the most stable carbocation? **[CBSE AIPMT2005]**

(A) 
$CH_3-\overset{+}{\underset{CH_3}{C}}-H$

(B) 
$CH_3-\overset{CH_3}{\underset{CH_3}{C^+}}$

(C) $\overset{+}{C}H_3$ **(D)** $CH_3\overset{+}{C}H_2$

7. The correct order regarding the electronegativity of hybrid orbitals of carbon is **[CBSE AIPMT 2005]**

(A) $sp > sp^2 < sp^3$ **(B)** $sp > sp^2 > sp^3$

(C) $sp < sp^2 > sp^3$ **(D)** $sp < sp^2 < sp^3$

8. The order of decreasing reactivity towards an electrophilic reagent, for the following

(i) Benzene (ii) Toluene

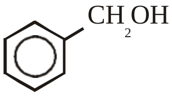
(iii) Chlorobenzene (iv) Phenol

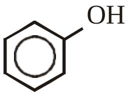
would be **[CBSE AIPMT 2007]**

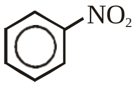
(A) (i) > (ii) > (iii) > (iv) **(B)** (ii) > (iv) > (i) > (iii)

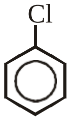
(C) (iv) > (iii) > (ii) > (i) **(D)** (iv) > (ii) > (i) > (iii)

9. Which one of the following is most reactive towards electrophilic attack? **[CBSE AIPMT 2008]**

(A) 

(B) 

(C) 

(D) 

10. Base strength of

(i) $H_3C\overset{\ominus}{C}H_2$ (ii) $H_2C \square \overset{\ominus}{C}H$

(iii) $H \square C \square C^{\ominus}$

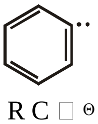
is in the order of **[CBSE AIPMT 2008]**

(A) (ii) > (i) (iii) **(B)** (iii) > (ii) > (i)

(C) (i) > (iii) > (ii) **(D)** (i) > (ii) > (iii)

11. The stability of carbanions in the following

(i) $RC \square \overset{\ominus}{C}$

(B) 

(ii) $R_2C \square \overset{\ominus}{C}H$

(D) $R_3C \square \overset{\ominus}{C}H_2$

is in the order of **[CBSE AIPMT 2008]**

(A) (i) > (ii) > (iii) > (iv) **(B)** (ii) > (iii) > (iv) > (i)

(C) (iv) > (ii) > (iii) > (i) **(D)** (i) > (iii) > (ii) > (iv)

12. In the hydrocarbon

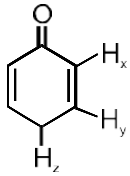
$$\underset{6}{CH_3}-\underset{5}{CH}=\underset{4}{CH}-\underset{3}{CH_2}-\underset{2}{C}\equiv\underset{1}{CH}$$

the state of hybridisation of carbons 1,3 and 5 are in the following sequence **[CBSE AIPMT 2008]**

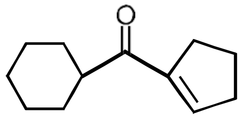
(A) sp^2, sp, sp^3 **(B)** sp, sp^3, sp^2

(C) sp, sp^2, sp^3 **(D)** sp^3, sp^2, sp

MOCK TEST

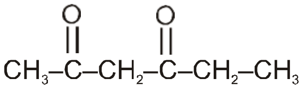
1. Molecule  can be enolised by which hydrogen.

(A) x–H **(B)** y–H **(C)** z–H **(D)** None of these

2. 

How many enolisable –H are present in the above compound ?

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

3. How many total enolic forms (including stereoisomers) are possible for  $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3$.

(A) 3 **(B)** 7 **(C)** 4 **(D)** 5

4. Which statement about tautomerism is incorrect ?

(A) Tautomers always exist in equilibrium.

(B) Tautomers can be separated by physical / chemical process.

(C) Tautomerism is a chemical phenomenon which takes place in liquid and gaseous state and catalysed by acid as well as base.

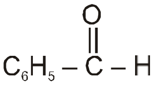
(D) All tautomers are always functional group isomers.

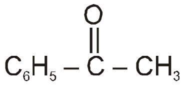
5. The enolic form of acetone contains :

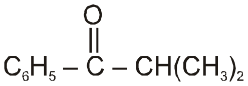
(A) 9 σ bonds, 1 π bond and 2 lone pairs **(B)** 8 σ bond, 2 π bond and 2 lone pairs

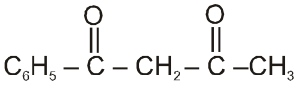
(C) 10 σ bond, 1 π bond and 1 lone pair **(D)** 9 σ bond, 2 π bond and 1 lone pair

6. Keto-enol tautomerism does not observe in :

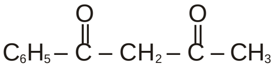
(A)  $C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-H$

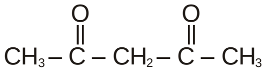
(B)  $C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

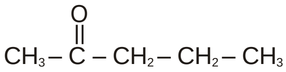
(C)  $C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-CH(CH_3)_2$

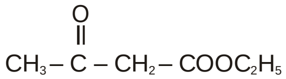
(D)  $C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

7. Which among the following compound will give maximum enol content in solution :

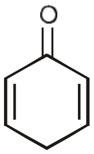
(A)  $C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

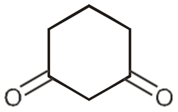
(B)  $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

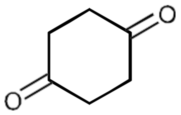
(C)  $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-CH_3$

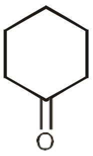
(D)  $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-COOC_2H_5$

8. Arrange the followings in decreasing order of percentage enol content.

(i) 

(ii) 

(iii) 

(iv) 

(A) I > II > III > IV **(B)** II > I > III > IV **(C)** II > III > I > IV **(D)** III > II > IV > I

CHAPTER 13

ISOMERISM

The same number of atoms combined in the same way produces the same crystalline form, and the same crystalline form is independent of the chemical nature of the atoms, and is determined only by their number and relative position.

"EILHARDMITSCHERLICH"

INTRODUCTION

An isomer (isos = "equal", méros = "part") is a molecule with the same molecular formula as another molecule, but with a different chemical structure. That is, isomers contain the same number of atoms of each element, but have different arrangements of their atoms. Isomers do not necessarily share similar properties, unless they also have the same functional groups. There are two main forms of isomerism : ***structural isomerism*** (or constitutional isomerism) and ***stereoisomerism*** (or spatial isomerism).

The name was given by ***Berzilius***.

Isomerism is actually permutation and combination of arrangement of atoms in different style either structurally or 3 –dimensionally to form molecules by the nature.

ETOOS KEY POINTS

(i) Number of electron and lone pairs in both tautomers always remain the same.

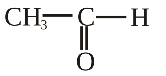
(ii) It is a chemical phenomenon which takes place only in liquids and gaseous phase only. It never takes place in solid state.

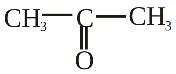
(iii) The process can be catalyzed by the acid as well a bases.

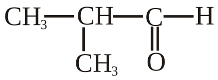
(iv) Tautomers are also F.I. and existin dynamic equilibrium $\rightleftharpoons$ is used to show tautomerism.

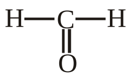
Condition for Tautomerism

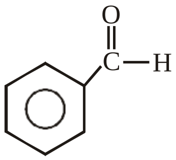
(a) For carbonyl compounds : Carbonyl compounds having **atleast one α-H** show tautomerism

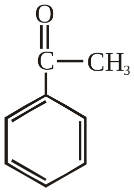
(i) 
$CH_3-\underset{\underset{O}{\|}}{C}-H$ 3 α H, show tautomerism.

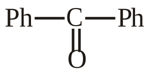
(ii) 
$CH_3-\underset{\underset{O}{\|}}{C}-CH_3$ 6 α H, show tautomerism.

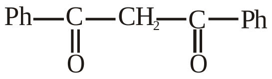
(iii) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-H$ 1 α H, show tautomerism.

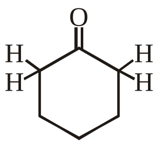
(iv) 
$H-\underset{\underset{O}{\|}}{C}-H$ No α H, No tautomerism.

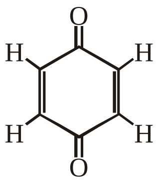
(v) 
No α H, No tautomerism.

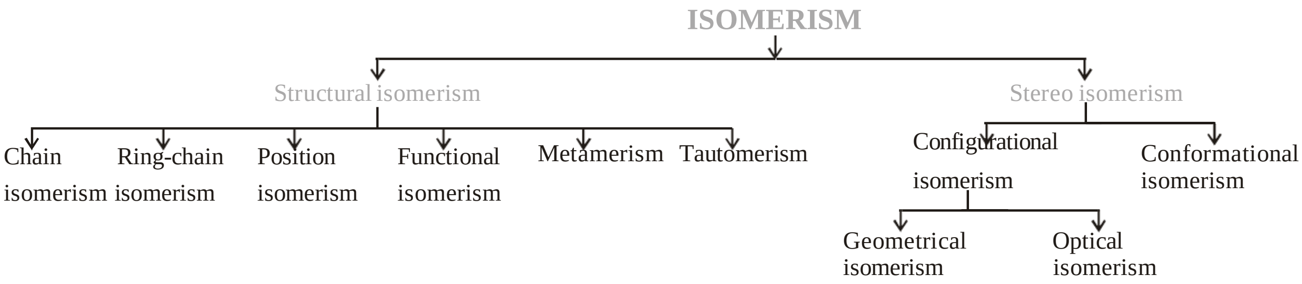
(vi) 
3 α H, show tautomerism (Aceto phenone)

(vii) 
$Ph-\underset{\underset{O}{\|}}{C}-Ph$ No α H, No tautomerism (Benzophenone)

(viii) 
$Ph-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-Ph$ 2 α H, show tautomerism

(ix) 
4 α H, show tautomerism

(x) 
α H, attached sp^2 carbon does not take part in tautomerism



STRUCTURAL ISOMERISM

1	**Chain Isomers**	They have different size of main chain or side chain	They have same nature of locant
2	**Positional Isomers**	They have different position of locant	They should have same size of main chain and side chain and same nature of locant
3	**Functional Isomers**	Different nature of locant	Chain and positional isomerism is not considered
4	**Metamerism**	Different nature of alkyl group along a polyvalent functional group	They should have same nature of functional group chain & positional isomer is ignored
5	**Tautomerism**	Different position of hydrogen atoms	The two functional isomers remains in dynamics equilibrium with each other

Meso compounds are those compounds whose molecules are superimposable on their images in spite of the presence of asymmetric carbon atom.

An equimolar mixture of the enantiomers (d & ℓ) is called **racemic mixture**. The process of converting of d-and ℓ- form of an optically active compound into racemic form is called **racemisation**.

The process by which dℓ mixture is separated into d and ℓ form with the help of chiral reagent or chiral catalyst is known as **resolution**.

Compound containing chiral carbon my or may not be optically active but show optical isomerism.

For optical isomer chiral carbon is not the necessary condition.

Case - 1 When the molecule is unsymmetrical. (It cannot be divided into two halves)

Number of d and ℓ isomers = 2^n
Number of meso form = 0
Total number of optical isomers = 2^n

Where n is the number of chiral carbon atoms

Case - 2 When the molecule is unsymmetrical and number of chiral carbon = even number

Number of d and ℓ isomers = $2^{(n-1)}$
Number of meso isomers = $2^{(n/2-1)}$
Total number of optical isomers = $2^{(n-1)} + 2^{\left(\frac{n}{2}-1\right)}$

Case -3 When the molecule is sysmmetrical number of chiral carbon = odd number

Number of d and ℓ isomers = $2^{(n-1)} - 2^{\frac{(n-1)}{2}}$

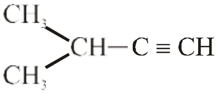
SOLVED EXAMPLE

Ex.1 The possible number of alkynes with the formula C_5H_8 is -

(A) 2 **(B)** 3

(C) 4 **(D)** 5

Sol. **(B)** $CH_3CH_2CH_2C\equiv CH$



$CH_3CH_2C\equiv CCH_3$

Ex.2 How many chain isomers can be obtained form the alkane C_6H_{14} is-

(A) 4 **(B)** 5

(C) 6 **(D)** 7

Sol. **(B)** $CH_3CH_2CH_2CH_2CH_2CH_3$

$CH_3\underset{\substack{|\\CH_3}}{C}HCH_2CH_2CH_3$

(i) **(ii)**

$CH_3\underset{\substack{|\\CH_3}}{C}H-\underset{\substack{|\\CH_3}}{C}HCH_3$

(iii)

Ex.3 An alkane can show structural isomerism if it has .... number of minimum carbon atoms –

(A) 1 **(B)** 2

(C) 3 **(D)** 4

Sol. **(D)** CH_4, $CH_3 – CH_3$, $CH_3 – CH_2 – CH_3$ exist only in one structural form, while $CH_3CH_2CH_2CH_3$ can exist in more than one structure form.

Ex. 4 The molecular formula of a saturated compound is $C_2H_4Cl_2$. The formula permits the existence of two

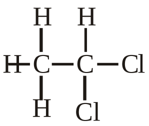
(A) functional isomers

(B) Position isomers

(C) Optical isomers

(D) cis-trans isomers

Sol. **(B)** **(i)**

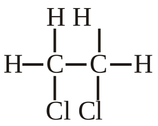


$H-\overset{\substack{H\\|}}{\underset{\substack{|\\H}}{C}}-\overset{\substack{H\\|}}{\underset{\substack{|\\Cl}}{C}}-Cl$

Both are position isomers

1,1-dichloro ethane

(ii)



$H-\overset{\substack{H\\|}}{\underset{\substack{|\\Cl}}{C}}-\overset{\substack{H\\|}}{\underset{\substack{|\\Cl}}{C}}-H$

1,2-dichloro ethane

Ex. 5 Evaporation of an aqueous solution of ammonium cyanate gives urea. This reaction follows the class of -

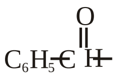
(A) Polymerization **(B)** Isomerization

(C) Association **(D)** Dissociation

Sol. **(B)** $NH_4CNO \xrightarrow{heat} H_2N–CO–NH_2$

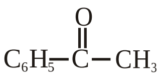
Ex.6 Keto-enol tautomerism is observed in -

(A)



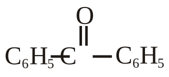
$C_6H_5-\overset{\substack{O\\||}}{C}-H$

(B)



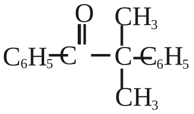
$C_6H_5-\overset{\substack{O\\||}}{C}-CH_3$

(C)



$C_6H_5-\overset{\substack{O\\||}}{C}-C_6H_5$

(D)



$C_6H_5-\overset{\substack{O\\||}}{C}-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-C_6H_5$

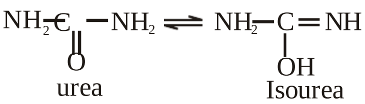
Sol. **(B)** Only compound **(B)** contains α hydrogen atom for showing keto enol tautomerism.

Ex.7 The type of isomerism found in urea molecule is -

(A) Chain **(B)** Position

(C) Tautomerism **(D)** None of these

Sol. **(C)**



$NH_2-\underset{\substack{||\\O}}{C}-NH_2 \rightleftharpoons NH_2-\underset{\substack{|\\OH}}{C}=NH$

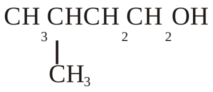
urea Isourea

Ex.8 How many isomers of $C_5H_{11}OH$ will be primary alcohols -

(A) 2 **(B)** 3

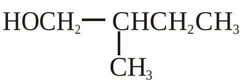
(C) 4 **(D)** 5

Sol. **(C)** $CH_3CH_2CH_2CH_2CH_2OH$

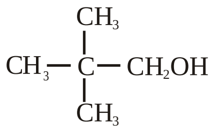


$CH_3\underset{\substack{|\\CH_3}}{C}HCH_2CH_2OH$

(i) **(ii)**



$HOCH_2-\underset{\substack{|\\CH_3}}{C}HCH_2CH_3$



$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_2OH$

(iii) **(iv)**

Ex.9 Which of the following is an isomer of diethyl ether

(A) $(CH_3)_3COH$ **(B)** CH_3CHO

(C) C_3H_7OH **(D)** $(C_2H_5)_2CHOH$

Sol. **(A)** Diethyl ether has 4 carbon atoms, among different alternative alcohols only $(CH_3)_3COH$ has 4 carbon atoms.

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. In ethane and cyclohexane which one of the following pairs of conformations are more stable

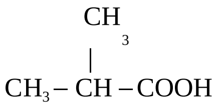
(A) Eclipsed and chair conformations

(B) Staggered and chair conformations

(C) Staggered and boat conformations

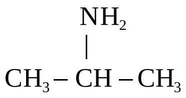
(D) Eclipsed and boat conformations

2. Which of the following may exist in enantiomorphs

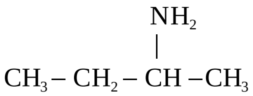
(A) 

$CH_3-\underset{|}{\overset{CH_3}{CH}}-COOH$

(B) $CH_2=CHCH_2CH_2CH_3$

(C) 

$CH_3-\overset{NH_2}{\overset{|}{CH}}-CH_3$

(D) 

$CH_3-CH_2-\overset{NH_2}{\overset{|}{CH}}-CH_3$

3. Which of the following compounds may not exist as enantiomers

(A) $CH_3CH(OH)CO_2H$

(B) $CH_3CH_2CH(CH_3)CH_2OH$

(C) $C_6H_5CH_2CH_3$

(D) $C_6H_5CHClCH_3$

4. Number of isomers of molecular formula $C_2H_2Br_2$ are

(A) 1 **(B)** 2

(C) 3 **(D)** 0

5. Lactic acid shows which type of isomerism

(A) Geometrical isomerism **(B)** Tautomerism

(C) Optical isomerism **(D)** Metamerism

6. Which one of the following is an optically active compound

(A) n-propanol **(B)** 2-chlorobutane

(C) n-butanol **(D)** 4-hydroxyheptane

7. Compounds with same molecular formula but different structural formulae are called

(A) Isomers **(B)** Isotopes

(C) Isobars **(D)** Isoelectronic

(C)

8. Which one of the following compounds shows optical isomerism

(A) $CH_3CHCl-CH_2-CH_3$

(B) $CH_3-CH_2-CHCl-CH_2-CH_3$

(C) $ClCH_2-CH_2-CH_2-CH_3$

(D) $ClCH_2-CH_2-CH_3$

9. Which one of the following objects is 'achiral'

(A) Letter P **(B)** Letter F

(C) Ball **(D)** A pair of hand

10. Total number of isomers of a disubstituted benzene compound is

(A) 1 **(B)** 2

(C) 3 **(D)** 4

11. Separating of d and l enantiomorphs from a racemic mixture is called

(A) Resolution

(B) Dehydration

(C) Rotation

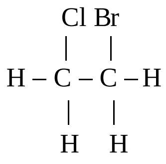
(D) Dehydrohalogenation

12. Number of optical isomers of lactic acid are

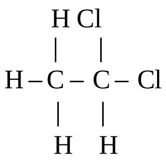
(A) 1 **(B)** 2

(C) 3 **(D)** 4

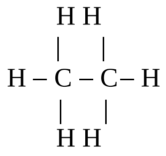
13. Which one of the following contains asymmetric carbon atom

(A) 

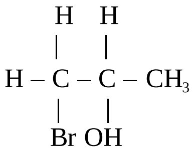
$H-\underset{H}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-H$

(B) 

$H-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-Cl$

(C) 

$H-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H$

(D) 

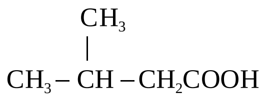
$H-\underset{Br}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{OH}{\underset{|}{\overset{H}{\overset{|}{C}}}}-CH_3$

14. n-butane and isobutane are examples of

(A) Chain isomers **(B)** Geometrical isomers

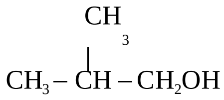
(C) Position isomers **(D)** Tautomers

15. Which of the following has chiral structure

(A) 

$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2COOH$

(B) $CH_3-CH=CH-CH_3$



$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2OH$

(D) $CH_3-CHOH-CH_2CH_3$

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. The number of enantiomers of the compound $CH_3CHBrCHBrCOOH$ is
(A) 0 (B) 1
(C) 3 (D) 4

2. $C_6H_5C \equiv N$ and $C_6H_5N \equiv C$ exhibit which type of isomerism
(A) Position (B) Functional
(C) Dextro isomerism (D) Metamerism

3. Which of the following compounds is not chiral
(A) $DCH_2CH_2CH_2Cl$ (B) CH_3CH_2CHDCl
(C) $CH_3CHDCH_2CH_2Cl$ (D) $CH_2CHClCH_2D$

4. cis and trans 2-butene are
(A) Conformational isomers
(B) Optical isomers
(C) Position isomers
(D) Geometrical isomers

5. Which one of the following is the chiral molecule
(A) CH_3Cl (B) CH_2Cl_2
(C) $CHBr_3$ (D) $CHClBrI$

6. Cyanide and isocyanide are isomers of type
(A) Positional (B) Functional
(C) Tautomer (D) Structural

7. Glucose and fructose are
(A) Optical isomers (B) Functional isomers
(C) Position isomers (D) Chain isomers

8. Which of the following compounds which is an optically active compound
(A) 1-butanol (B) 2-butanol
(C) 3-butanol (D) 4-heptanol

9. d-tartaric acid and l-tartaric acid are
(A) Enantiomers (B) Tautomers
(C) Diastereoisomers (D) Structural isomers

10. Which of the following statements is not true about enantiomers
(A) They have same physical properties
(B) They have different biological properties
(C) They have same chemical properties towards chiral compounds
(D) None of these

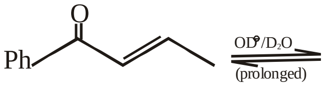
11. Meso-tartaric acid is
(A) Optically inactive
(B) Optically active because of molecular symmetry
(C) Optically inactive due to external compensation
(D) Optically active because of asymmetric carbon atom

12. The number of possible isomers of the compound with molecular formula C_7H_8O is
(A) 3 (B) 5
(C) 7 (D) 9

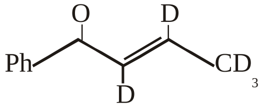
13. The number of isomers for the compound with molecular formula $C_2BrClFI$ is
(A) 3 (B) 4
(C) 5 (D) 6

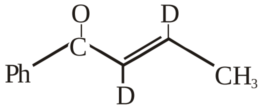
14. Hydrogenation of the adjoining compound in the presence of poisoned palladium catalyst gives
(A) An optically active compound
(B) An optically inactive compound
(C) A racemic mixture
(D) A diastereomeric mixture

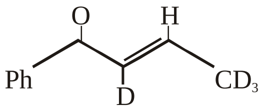
15. How many structural isomer are possible when one of the hydrogen is replaced by a chlorine atom in anthracene?
(A) 3 (B) 7
(C) 4 (D) 6

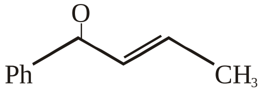
16. 

(P) final product is ?

(A) 

(B) 

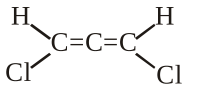
(C) 

(D) 

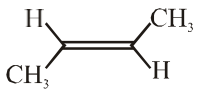
Exercise # 3 PART - 1 MATRIX MATCHCOLUMN

1. Match the following compounds of column I with column II.

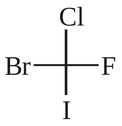
Column - I (Molecule) **Column -I I (Property)**

(A) 

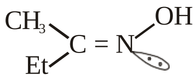
(p) Chiral compound

(B) 

(q) Presence of stereocenter

(C) 

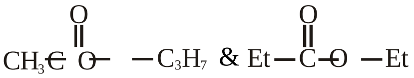
(r) Optically active compound

(D) 

(s) Compound containing plane of symmetry

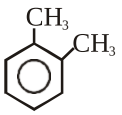
2. Match Column I with Column II :

Column - I **Column-II**

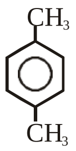
(A) 

$CH_3\overset{O}{\overset{\|}{C}}-O-\ -C_3H_7$ & $Et-\overset{O}{\overset{\|}{C}}-O\ -Et$

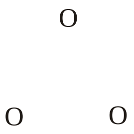
(p) Enantiomer

(B) 

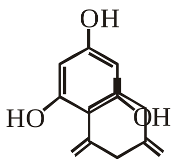
&



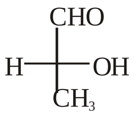
(q) Positional isomers

(C) 

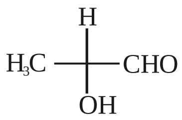
&



(r) Metamers

(D) 

&



(s) Tautomers

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. But-2-ene exhibits cis-trans-isomerism due to **[CBSE AIPMT 2000]**

(A) rotation around $C_2 - C_3$ double bond
(B) rotation around $C_3 - C_4$ sigma bond
(C) rotation around $C_1 - C_2$ bond
(D) restricted rotation around C = C bond

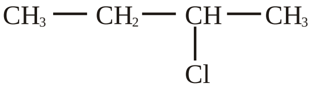
2. The (R) - and (S) - enantiomers of an optically avitve compound differ in **[CBSE AIPMT 2000]**

(A) their solubility in a chiral solvent
(B) their reactivity with a chiral reagent
(C) their optical rotation of plane polarised light
(D) their melting points

3. A compound of molecular formula C_7H_{16} show optical isomerism, compound will be **[CBSE AIPMT 2001]**

(A) 2, 3-dimethyl pentane
(B) 2, 2-dimethyl butane
(C) 2-methyl hexane
(D) None of the above

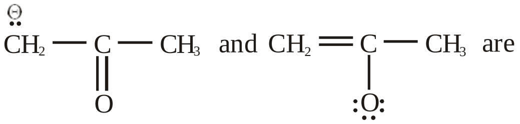
4.



$CH_3-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_3$ obtained by chlorination of n-butane, will be **[CBSE AIPMT 2001]**

(A) meso from **(B)** racemic mixture
(C) d-form **(D)** l-form

5.



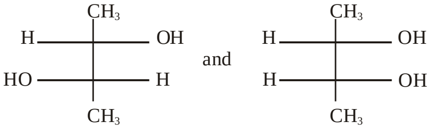
$\overset{\ominus}{\ddot{C}}H_2-\underset{\underset{O}{\|}}{C}-CH_3$ and $CH_2=\underset{\underset{:\ddot{O}:}{|}}{C}-CH_3$ are

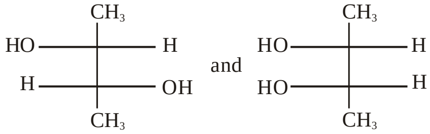
(A) resonating structures
(B) tautomers
(C) geometrical is isomers
(D) optical isomers

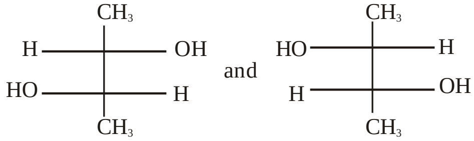
6. Geometrical isomers differ in **[CBSE AIPMT 2002]**

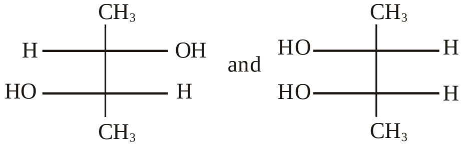
(A) position of functional group
(B) position of atoms
(C) spatial arrangement of atoms
(D) length of carbon chain

7. Which of the following pair of compounds are enantiomers? **[CBSE AIPMT 2003]**

(A)


(B)


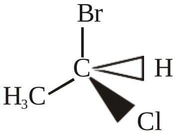
(C)


(D)


8. Which one of the following pairs represents stereoisomerism? **[CBSE AIPMT 2005]**

(A) Chain isomerism and rotational isomerism
(B) Structural isomerism and geometrical isomerism
(C) Linkage isomerism and geometrical isomerism
(D) Optical isomerism and geometrical isomerism

9. The chirality of the compound **[CBSE AIPMT 2005]**



is

(A) R **(B)** S
(C) Z **(D)** E

10. Which of the following is not chiral? **[CBSE AIPMT 2006]**

(A) 2-butanol
(B) 2, 3-dibromo pentane
(C) 3-bromo pentane
(D) 2-hydroxy propanioc acid

11. If there is no rotation of plane polarised light by a compound in a specific solvent, though to be chiral, it may mean that **[CBSE AIPMT 2007]**

(A) the compound is certainly a chiral
(B) the compound is certainly meso
(C) there is no compound in the solvent
(D) the compound may be a racemic mixture

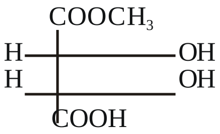
MOCK TEST

1. Dimethyl ether and ethyl alcohol are

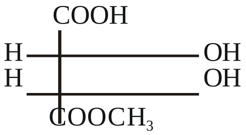
(A) Metamers **(B)** Homologues **(C)** Functional isomers **(D)** Position isomers

2. The correct statement about the compounds A and B is

(A)



(B)



(A) A and B are identical **(B)** A and B are diastereomers

(C) A and B are enantiomers **(D)** None of these

3. Ethyl acetoacetate shows, which type of isomerism

(A) Chain **(B)** Optical **(C)** Metamerism **(D)** Tautomerism

4. Which of the following will have a mesoisomer also

(A) 2, 3-Dichloropentane **(B)** 2, 3-Dichlorobutane **(C)** 2-Chlorobutane **(D)** 2-Hydroxypropanoic acid

5. For which of the following parameters the structural isomers C_2H_5OH and CH_3OCH_3 would be expected to have the same values ? (Assume ideal behaviour)

(A) Boiling points

(B) Vapour pressure at the same temperature

(C) Heat of vaporization

(D) Gaseous densities at the same temperature and pressure

6. Which of the following compounds will exhibit cis-trans isomerism

(A) 2-butene **(B)** 2-butyne **(C)** 2-butanol **(D)** Butanone

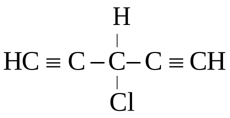
(E) Butanol

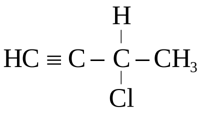
7. Which of the following compounds exhibit stereoisomerism

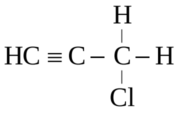
(A) 2-methyl-butane I **(B)** 3-methyl-butanoic acid

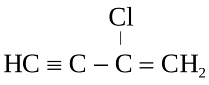
(C) 3-methyl-butyne I **(D)** 2-methyl butanoic acid

8. Which of the following is most likely to show optical isomerism

(A) 
$HC \equiv C-\overset{H}{\underset{Cl}{C}}-C \equiv CH$

(B) 
$HC \equiv C-\overset{H}{\underset{Cl}{C}}-CH_3$

(C) 
$HC \equiv C-\overset{H}{\underset{Cl}{C}}-H$

(D) 
$HC \equiv C-\overset{Cl}{C}=CH_2$

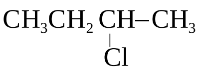
9. Nitroethane can exhibit one of the following kind of isomerism

(A) Metamerism **(B)** Optical activity **(C)** Tautomerism **(D)** Position isomerism

10. $CH_3CH(OH).COOH$ shows

(A) Geometrical isomerism **(B)** Optical isomerism **(C)** Both **(D)** None

11. Which will have enantiomer

(A) 
$CH_3CH_2\underset{Cl}{CH}-CH_3$

$CH_2CH_2CH_2CH_2Cl$ **(C)** $CH_3CH_2CH_2CHCl_2$ **(D)** None

(B)

CHAPTER 20

NEURAL CONTROL AND COORDINATION

"Appetite, craving for food, is a constant and powerful stimulator of the gastric glands."

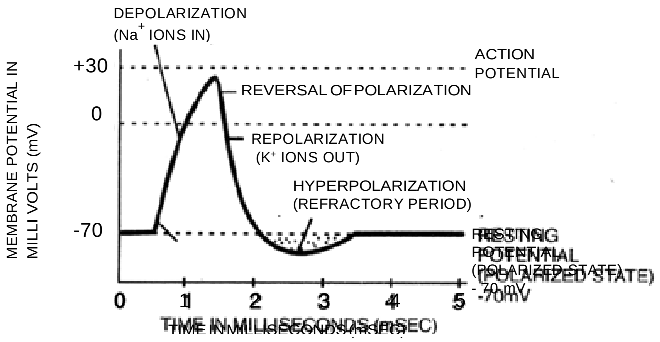
"IVAN PAVLOV (1849-1936)"

INTRODUCTION

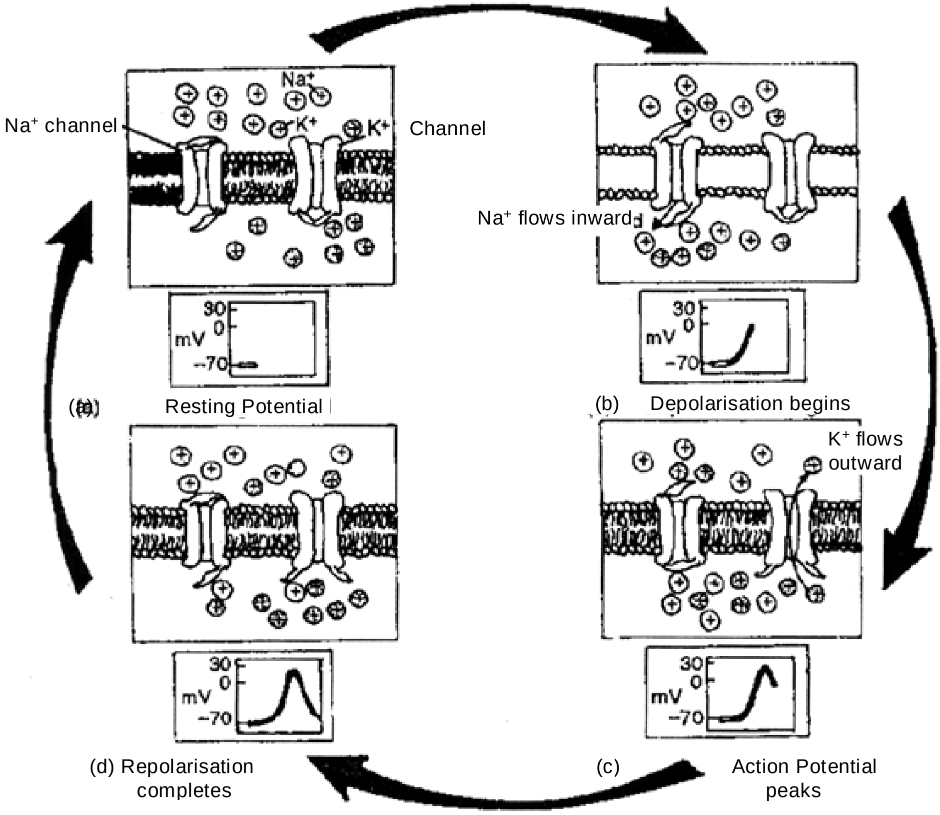
There are various physiological processes takes place in the body of animals. Therefore the body needs to be controlled and regulated to maintain homeostasis. Coordination is the process through which two or more organs interact and complement the functions of one another. So regulation is the means by which adjustement of all variables that determines the nature of physiological function are done. The variables can be an amount, a concerntration a rate or so on. Thus, in our body the neural system and the endocrine system jointly coordinate and integrate all the activities of the organs so that they function in a synchronised fashion.

The neural system provides an organised network of point to point connections for a quick coordination. The endocrine system provides chemical integration through hormones. In this topic, you will learn about the neural system in humans like transmission of nerve impulse, impulse conduction across a synapse, physiology of relex action, sensory reception and sense organs.

NERVEIMPULSE INDUCTION:



Record of potential changes of a nerve impulse



Stages in axon membrane potential during resting, depolarisation, action potential and repolarisation

THE RESTING MEMBRANE POTENTIALINRESTING PHASE:

- The potential difference (a charge) which exists across the cell surface membrane of nerve cells is always, negative inside the cell with respect to the outside. The membrane is said to be **polarised**.
- The potential difference across the membrane at rest is called the **Resting membrane potential** and this is about –70mV (the negative sign indicates that inside the cell is negative with respect to the outside). (Range → – 60 to – 85mV)

ED OS KEY POINTS

1. In the brain of **frog** only 2 skull meninges are presnt. The middle meninge that is the Arachnoid is absent.
2. In rabbit, man and mammals-**3** skull meninges are present.
3. Increase in the amount of cerebro-spinal fluid is diseased condition termed as the **Hydrocephalus**.
4. "**Meningitis**". It arises due to infection or inflamation on injury in the meninges. Infection may be due to virus or bacteria or both.
5. Piamater is the most vascular and conducting and provides nutrition.
6. The power of regeneration is very less in a neuron.
7. The optic lobes of frog are hollow and in them **optocoel** cavity is found.
8. In frog, 2 optic-lobes are present. These are hollow and termed as **Corpora-bigemina**. In mammals, 4 solid optic-lobes are present.
9. Around the brain of fishes, only one menix is found called : **Menix-primitiva**".
10. The **valve of vieussens** joins the optic-lobes with the cerebellum.
11. Cerebral-cortex is made up of gray – matter and is divided into 3 area -

    (i) Sensory area (ii) Motor area (iii) Associated area
12. The sensory and associated areas determine the **shape, colour, sound, taste** and **smell of any object**.
13. Motor area regulates **muscular-contraction**.
14. **Broca's area :** It is known as motor speech area.
15. Broca's area is present in the lateral part of the **frontal-lobe** of the cerebrum. This area makes aware of language; and **translates the written words into speed**.
16. If Broca's area are gets destroyed the animal beecomes unable to speak.
17. The temporal-lobes of cerebrum regulates the mechanism of hearing.
18. Cerebrum is the centre of following :

    (1) Intelligence (2) Emotion (3) Will-power (4) Memory

    (5) Consciousness (6) Experience (7) Knowledge

    (8) Voluntary control (9) Laughing and weeping (10) Defaecation and micturition.
19.. Diencephalon is the centre of carbohydrate – metabolism and fat-metabolism.
20. In rabbit, "**Swammerdam's gland**" are absent. These glands are present at the origin place of spinal nerves in vertebrates & present in frog. It provide extra supply of Ca^{++} for synaptic transmission.
21. Cerebellum made up of three layers and in the middle of cerebellum of brain lobes of flask-shaped cells are found called the "**Purkinje-cells**".
22. In the nerve-cells, "centrosome" are absent so once formed in developement, the nerve-cells do not divide and **remain in Inter-phase stage** throughout their life : and grow in size with the growth of the body.
23. The velocity of nerve-impulse is 5 to 50 times more faster in Myelinated nerve-fibres than in Non-myelinated nerve-fibres.
24. In mammals the speed of nerve impuse is **100-130** m/sec (maximum). In frog, the speed of nerve impulse is 30 m/sec. In reptiles the speed is **15** to **35** m/sec.
25. Acetylcholinesterase enzyme helps in the dissociation of Acetylcholine.
26. In the form of inhibitory neuro-hormons, - GABA are present.

    GABA – gamma amino butyric – acid.

→ Co-ordination : It's the process through which two or more organs interact and complement the functions of one another.

→ Integrated system : In Human's body the neural system and the endocrine system jointly coordinate and integrate all the activities of the organs so that they function in a synchronised fashion and interdependent to each other combinely called integrated system.

→ Distinction in neural system and endocrine systems.

→ The neural system provides an organised network of point to point connections for a quick response (Fast speed) and short span of coordination where as the endocrine system provides chemical integration, slow speed and long lasting effect.

→ Neural system :

→ Neurons : The neural system of all animals is composed of highly specialised cells called neurons also known as structural and functional unit of nervous system.

→ Three major parts of neuron, are dendron, cyton and axon.

→ Nissl's granules : The cell body contains cytoplasm with typical cell organelles and certain granular bodies called Nissl's granules which is also present in dendrites.

→ Limbic system

→ It is a complex structure which includes inner parts of cerebral hemisphere and associated deep structures like amygdala, hippocampus. Along with hypothalamus, it is involved in olfaction autonomous response, regulation of sexual behaviour, expression of emotional reaction (Excitement, pleasure, rage and fear) and motivation.

→ Cranial meninges : Inside skull the brain is covered by cranial meninges, consisting of outer duramater, middle arachnoid, and inner piamater.

→ Cerebral hemispheres : A deep cleft divides the cerebrum longitudinally into two halves, termed as the left and right cerebral hemisphere.

→ Corpus callosum : The cerebral hemispheres are connected by a tract of nerve fibres called corpus callosum.

→ Cerebral cortex : The layer of cells which covers the cerebral hemisphere is called cerebral cortex, thrown in to prominent folds.

→ Gray matter : The cerebral cortex is referred as the gray matter due to grayish appearance and it is due to highly concentrated neuron cell bodies.

→ White matter : Fibres of the tract are covered with myelin sheath which constitute the inner part of cerebral hemispheres and gives the opaque white appearance to the layer hence called the white matter.

→ Association area : The cerebral cortex contains motor area, sensory area and large regions called association areas responsible for complex functions like intersensory association, memory and communication.

→ The neural system coordinate and integrates function as well as metabolic and homeostatic activities of all the organs.

→ Generation and conduction of nerve impulse

→ Excitable cells : Neurons are excitable cells because their membranes are in a polarized state due to differential concentration gradient of ions across the membrane. Different types of ion channels are present on neuronal membrane for which this membrane is selectively permeable.

SOLVED EXAMPLE

Ex.1 Mammalian brain differs from an amphibian brain in possessing

(A) Olfactory lobe (B) Hypothalamus

(C) Corpus callosum (D) Cerebellum

Sol. (C) : Corpus callosum is a thick whitish band of semicircular nerve fibres interconnecting two cerebral hemispheres (found only in mammals).

Ex.2 Brain is

(A) Ectodermal (B) Mesodermal

(C) Endodermal (D) Mesendodermal

Sol. (A)

Ex.3 The autonomic nervous system has control over

(A) Reflex action (B) Skeletal muscles

(C) Sense organs (D) Internal organs

Sol. (D) : Autonomic nervous system regulates and coordinates involuntary activites like heart beating, homeostasis, body temperature, breathing gut peristalsis and secretion of glands.

Ex.4 The hind brain consists of

(A) Pons + cerebellum

(B) Hypothalamus+ cerebellum

(C) Medulla oblongata + cerebellum

(D) Medulla oblongata +cerebellum+ pons

Sol. (D) : Hind brain has two distinct part (i) metencephalon (medulla oblongata) (ii) myelencephalon (cerebellum), transverse band of white matter called pons varoli.

Ex.5 In a myelinated neuron, two adjacent myelin sheaths are separated by gaps called

(A) Nodes of Ranvier (B) Synaptic cleft

(C) Schwann cells (D) Synaptic knob

(E) Neural plate

Sol. (A)

Ex.6 Pituicytes are under the control of

(A) Adenohypophysis (B) Hypothalamus

(C) Neurohypophysis (D) Both (A) and (C)

Sol. (B)

Ex.7 Parasympathetic ganglia are present in

(A) Head and neck

(B) Chains of lateral ganglia

(C) Grey matter of thoracic and lumbar region of spinal cord

(D) All of these

Sol. (A)

Ex.8 Which of the following cranial nerves innervates heart, stomach and lungs

Or

Which of the cranial nerve is mixed

(A) Vagus (B) Accessory

(C) Trigeminal (D) Trochlear

Sol. (A)

Ex.9 Integration of the visual, tactile and auditory inputs occurs in the

Or

Crura cerebrae is found in

(A) Peripheral nervous s.ystem

(B) Corpus callosum

(C) Limbic system

(D) Medulla oblongata

(E) Midbrain

Sol. (E) : Crura cerebrae are thicked ventral portions of the mid-brain of a vertebrate consisting of nervous tracts linking the thalamencephalon with the hind brain.

Ex.10 Which foramen is paired in mammalian brain

(A) Foramen of Luschka

(B) Foramen of Magendie

(C) Foramen of Monro

(D) Inter-ventricular foramen

Sol. (A)

Ex.11 Among the following characteristics, indicate the correct combinations applicable to conditional reflex

P. Acquired by practice or learning

Q. Not acquired by birth

R. Does not abolish by lack of practice

S. Participation of cerebral cortex

T. Originates spontaneously

(A) P, Q, R (B) P, Q, R

(C) P, R, T (D) Q, R, T

Sol. (B)

Ex.12 Which is thickened to form organ of Corti

(A) Reissner's membrane

(B) Basilar membrane

(C) Tectorial membrane

(D) All of the aoove

Sol. (B)

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. Posterior choroids plexus in brain is found in the -
(A) Diencephalon
(B) Cerebrum
(C) Cerebellum
(D) Space b/w pons & medulla (anteriorly) & cerebellum (Posteriorly)

2. Menings surrounding the brain of Human from outside to inside are -
(A) Duramater, arachnoid, piamater
(B) Piamater, arachnoid, duramater
(C) Duramater, piamater, arachnoid
(D) Piamater, duramater, arachnoid

3. Corpus callosum connects -
(A) Two cerebral hemisphere
(B) Two optic lobes
(C) Two olfactory lobes
(D) Optic chiasma

4. Cerebellum is concerned with -
(A) Co-ordination of muscular movement
(B) Memory
(C) Vision
(D) Reflex action

5. Crura cerebri is located in -
(A) Fore brain (B) Hind brain
(C) Mid brain (D) None

6. How many lobes are present in cerebellum-
(A) 1 (B) 3
(C) 5 (D) 7

7. Piamater is -
(A) Inner most meninge (B) Middle meninge
(C) Outer meninge (D) None

8. Leptomenix of brain is formed by the joining of -
(A) Piamater and arachnoid layer
(B) Piamater and duramater
(C) Duramatter and arachnoid layer
(D) Grey matter and white matter

9. Which one of the following menix is present only in mammalian brain -
(A) Duramater (B) Arachnoid
(C) Piamater (D) None of them

10. The function of cerebrospinal fluid surrounding CNS is to -
(A) Protect the brain from external jerks
(B) Provide nourishment and O_2 to the brain
(C) Take away unwanted substance from the brain
(D) All of the above

11. Septum lucidum is part of the -
(A) Pseudocoel (B) Metacoel
(C) Diocoel (D) Rhinocoel

12. Hypothalamus is situated on the -
(A) Upper lateral surface of diencephalon
(B) Lower lateral surface of diencephalon
(C) Ventral side of optic lobes
(D) Dorsal side of optic lobes

13. Epithalamus is situated on the -
(A) Roof of diencephalon
(B) Lateral wall of diencephalon
(C) Dorsal side of optic lobes
(D) Floor of diencephalon

14. Which of the following is not an organ of the central nervous system -
(A) Brain (B) Spinal cord
(C) Medulla oblongata (D) Vagus

15. Intelligency quotient value of Normal person is -
(A) 60 – 70% (B) 90 – 100%
(C) 80 – 90% (D) >100%

16. Which is correct about pons varolii -
(A) Situated between midbrain & M.O.
(B) Pons regulated pneumotaxic centre
(C) Inner gry, outer white matter
(D) All of the above

17. Parkinson's disease is present due to lesion in -
(A) Corpus striatum
(B) RAS
(C) Limbic system
(D) Analysis centre of cerebrum

18. The cavity of brain is lined by -
(A) Neural epithelium
(B) Ependymal epithelium
(C) Cerebrospinal fluid
(D) Glandular epithelium

19. Third ventricle is found in -
(A) Heart of rabbit (B) Brain of rabbit
(C) Heart of frog (D) Kidney of frog

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. GABA (gama amino butyric acid) is a -
(A) Inhibitory neurohormone
(B) Transmittery neuro hormone
(C) Anti coagulant
(D) None

2. Nissl's bodies found in neurons are -
(A) Made of DNA
(B) Masses of ribosome and RER
(C) Help in formation of neurofibrils
(D) Masses of mitochondria

3. ''Nodes of Ranviers'' are found in -
(A) Brain (B) Heart
(C) Axon (D) Eye

4. Afferent nerve fibre conducts impulse from-
(A) C.N.S. to effector (B) Receptor to C.N.S.
(C) Receptor to effector (D) Effector to receptor

5. Chemical substance which take part in synaptic transmission is -
(A) Adrenaline (B) Epinephrine
(C) Colchicine (D) Acetylcholine

6. When a nerve fibers is stimulated the inside of the membrane becomes-
(A) Filled with acetylcholine
(B) Negatively charged
(C) Positively charged
(D) Neutral

7. The parts of the neurons that perform basic cellular functions such as protein synthesis etc. -
(A) Axons (B) Dendrites
(C) Synaptic knobs (D) Soma

8. The nerves leading to the central nervous system are called
(A) Afferent (B) Efferent
(C) Motor (D) None

9. Nerve impulses are initiated by nerve fibers only when the membrane shall become more permeable to -
(A) Adrenaline (B) Phosphorus
(C) Sodium ions (D) Potassium ions

10. Power of regeneration is lowest in -
(A) Brain cell (B) Liver cell
(C) Bone cell (D) Muscle cell

11. Speed of impulse on nerves in mammals is-
(A) 1 meter/sec. (B) 100 meter/sec.
(C) 1000 meter/sec. (D) None of these

12. The functional connection between two neurons is called -
(A) Synapse (B) Synapsis
(C) Chiasma (D) Chiasmata

13. Conduction of nerve impulse is -
(A) Faster in none-myelinated fibres
(B) Faster in myelinated fibres
(C) No difference in the rate of conduction in myelinated & non myelinated fibres
(D) None of the above

14. Enzyme acetyl cholinesterase is concerned with -
(A) Digestion of protein
(B) Synthesis of protein
(C) Digestion of polypeptide
(D) Conduction of nerve impulse

15. During refractory period -
(A) Nerve transmits impulse very slowly
(B) Nerve can not transmit impulse
(C) Nerve transmits impulses very rapidly
(D) None of the above

16. The schwann sheath is -
(A) A non myelinated nerve fibres
(B) Associated with myelin sheath
(C) A connective tissue cell
(D) Associated with myelinated & non myelinated nerve fibre

17. A short period during which a nerve is unable to conduct nerve impulse is called
(A) Synaptic delay (B) Refractory period
(C) Resting potential (D) Critical period

18. Which cell-organelle synthesises acetyl choline -
(A) Golgi complex (B) Ribosome
(C) Mitochondria (D) Lysosome

Exercise # 3

PART - 1

MATRIX MATCHCOLUMN

1. Match Column - I with Column II and select the correct option from the codes given below.

Column I	Column - II
A. Cerebrum	**i.** Controls the pituitary
B. Cerebellum	**ii.** Controls vision and hearing
C. Hypothalamus	**iii.** Controls the rate of heart beat
D. Midbrain	**iv.** Seat of intelligence
	v. Maintains body posture

(A) A-v, B-iv, C-ii, D-i
(B) A-iv, B-v, C-ii, D-i
(C) A-v, B-iv, C-i, D-ii
(D) A-iv, B-v, C-i, D-ii

2. Match Column - I with Column - II and select the correct option from the codes given below.

Column I	Column - II
A. Medulla oblongata	**i.** Involuntary breathing movements
B. Floor of mid brain	**ii.** Accurate voluntary movements
C. Thalamus	**iii.** Seat of memory
D. Cerebral hemispheres	
E. Cerebellum	

(A) A-i, C-ii, D-iii
(B) A-i, E-ii, B-iii
(C) A-i, E-ii, D-iii
(D) E-i, C-ii, B-iii

3. Match Column - I with Column -II and select the correct option from the codes given below.

Column I	Column - II
A. Cornea	**i.** Provides opening for light to enter
B. Iris	**ii.** Transduces blue, green and red light
C. Lens	**iii.** Controls the amount of light that enters
D. Optic nerves	**iv.** Alters the shape of lens
E. Pupil	**v.** Transmit information to the CNS
F. Ciliary muscles	**vi.** Focus light directly on retina
G. Fovea	**vii.** Bends light and protects inner eye

(A) A-vii, B-iii, C-vi, D-v, E-i, F-iv, G-ii
(B) A-i, B-ii, C-iii, D-iv, E-v, F-vi, G-vii
(C) A-vii, B-vi, C-v, D-iv, E-iii, F-ii, G-i
(D) A-vii, B-iv, C-vi, D-v, E-i, F-iii, G-ii

4. Match Column - I with Column - II and select the correct option from the codes given below.

Column - I	Column - II
A. Pinna	**i.** Collects vibrations in the air which produces sound
B. Ear canal	**ii.** Passage for sound wave from pinna to ear drum
C. Tympanic	**iii.** Transfers sound wave to ear membrane ossicles
D. Ear ossicles	**iv.** Increases the efficiency of transmission of sound waves to the inner ear
E. Cochlea	**v.** Has hearing receptors
F. Eustachian	**vi.** Equalizes the pressure on tube both sides of ear drum
G. Auditory nerves	**vii.** Impulse transfer from organ of Corti to auditory cortex in temporal lobe of cerebrum

(A) A-i, B-ii, C-iii, D-iv, E-v, F-vi, G-vii
(B) A-vii, B-vi, C-v, D-iv, E-iii, F-ii, G-i
(C) A-i, B-ii, C-iv, D-iii, E-v, F-vi, G-vii
(D) A-i, B-ii, C-iii, D-iv, E-v, F-vii, G-vi

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. A person suffering from the deficiency of the visual pigment rhodopsin is advised to take more **[CBSEAIPMT-2000]**

(A) radish and potato

(B) apple and grapes

(C) carrot and ripe papaya

(D) guava and ripe banana

2. An action potential in the nerve fibre is produced when positive and negative charges on the outside and the inside of the axon membrane are reversed, because **[CBSEAIPMT-2000]**

(A) more potassium ions enter the axon as compared to sodium ions leaving it.

(B) more sodium ions enter the axon as compared to potassium ions leaving it

(C) all potassium ions leave the axon

(D) All sodium ions enter the axon

3. When we migrate from dark to light, we fail to see for some time but after a time visibility becomes normal. It is an example of **[CBSEAIPMT-2001]**

(A) accommodation **(B)** adaptation

(C) mutation **(D)** photoperiodism

4. Characteristic feature of human cornea is that **[CBSEAIPMT-2001]**

(A) it is secreted by conjunctive and glandular tissue

(B) it is lacrimal gland which secretes tears

(C) blood circulation is absent in cornea

(D) in old age it become hard and white layer deposits on it which causes the cataract

5. What is the intensity of sound in normal conversation ? **[CBSEAIPMT-2001]**

(A) 10-20dB **(B)** 35-60 dB

(C) 70-90 dB **(D)** 120-150dB

6. In which animal nerve cell is present but brain is absent ? **[CBSEAIPMT-2002]**

(A) Sponge **(B)** Earthworm

(C) Cockroach **(D)** *Hydra*

7. Which of the following statements is correct about node of Ranvier ? **[CBSEAIPMT-2002]**

(A) Axolemma is discontinuous

(B) Myelin sheath is discontinuous

(C) Both neurilemma and myelin sheath are discontinuous

(D) Covered by myelin sheath

8. What used to be described as Nissl's granules in a nerve cell are now identified as **[CBSE AIPMT-2003]**

(A) ribosomes **(B)** mitochondria

(C) cell metabolites **(D)** fat granules

9. In the resting state of the neural membrane, diffusion due to concentration gradients, if allowed, would drive **[CBSEAIPMT-2004]**

(A) K^+ into the cell

(B) K^+ and Na^+ out of the cell

(C) Na^+ into the cell

(D) Na^+ out of the cell

10. Injury to vagus nerve in human is not likely to affect **[CBSEAIPMT-2004]**

(A) tongue movements

(B) gastrointestinal movements

(C) pancreatic secretion

(D) cardiac movements

11. Four healthy people in their twenties got involved in injuries resulting in damage and death of a few cells of the following. Which of the cells are least likely to be replaced by new cells? **[CBSEAIPMT-2005]**

(A) Osteocytes

(B) Malpighian layer of the skin

(C) Liver cells

(D) neurons

12. Parkinson's disease (characterised by tremors and progressive rigidity of limbs) is caused by degeneration of brain neurons that are involved in movement control and make use of neurotransmitter **[CBSEAIPMT-2005]**

(A) acetylcholine **(B)** norepinephrine

(C) dopamine **(D)** GABA

13. One of the examples of the action of the autonomous nervous system is **[CBSEAIPMT-2005]**

(A) knee-jerk respone

(B) pupillary reflex

(C) swallowing of food

(D) peristalsis of the intestine

MOCK TEST

1. Read the statements about human neural system and find the wrong one.

(A) The CNS includes the brain and the spinal cord.
(B) The PNS is divided into somatic and autonomic neural system.
(C) The somatic neural system is classified into sympathetic and parasympathetic neural system.
(D) The autonomic neural system transmits impulses from the CNS to the involuntary organs and smooth muscles.
(E) The somatic neural system relays impulses from the CNS to the skeletal muscles.

2. The pneumotaxic centre and respiratory rhythm centres are respectively present in

(A) pons and medulla oblongata
(B) corpus callosum and pons
(C) medulla oblongata and hypothalamus
(D) diencephalona and pons

3. Which area of cerebral cortex is responsible for the interpretation of speech?

(A) Broca's area
(B) Wernicke's area
(C) Premotor area
(D) Association area of sensory cortex

4. Which of the following statements are true for "Motor cortex"?

(i) It is located in the frontal lobe of cerebral cortex.
(ii) It contains pyramidal cells.
(iii) It is responsible for all visual functions.
(iv) It is essential for our thought processes.
(v) It stimulates wakefulness.
(vi) It regulates voluntary muscular movements.

(A) (i), (ii), (iii) and (iv)
(B) (ii), (iii), (iv) and (v)
(C) (ii), (iv), (v) and (vi)
(D) (i), (ii), (iv) and (vi)

5. Parasympathetic ganglia are present in

(A) head and neck
(B) chains of lateral ganglia
(C) grey matter of thoracic and lumbar region of spinal cord
(D) all of these

6. Select the answer with correct matching of the structure, its location and function.

	Structure	Location	Function
(A)	Eustachian tube	Anterior part of internal ear	Equalises air pressure on either sides of tympanic membrane
(B)	Cerebellum	Midbrain	Controls respiration and gastric secretions
(C)	Hypothalamus	Forebrain	Controls body temperature, urge for eating and drinking
(D)	Blind spot	Near the place where optic nerve leaves the eye	Rods and cones are present but inactive here

7. The myelin sheath around the axon is produced by which type of neuroglial cells?

(A) Satellite glial cells
(B) Radial glial cells
(C) Dendrocytes
(D) Schwann cells

8. Which of the following statements are correct and incorrect?

1. Synaptic cleft of neurons secrete adrenaline.
2. Myelinated nerve fibres are enveloped with Schwann cells, which form a myelin sheath around the axon.
3. Non-myelinated nerve fibre is enclosed by a Schwann cell that does not form a myelin sheath.
4. Spinal cord and cranial nerves are made of non-myelinated nerve fibres. Of the four statements.

(A) 1, 2 are correct but 3 and 4 are incorrect
(B) 1, 2 are 3 are correct but 4 is incorrect
(C) 3 and 4 are correct but 1 and 2 are incorrect
(D) 1 and 4 are correct while 2 and 3 are incorrect
(E) 2 and 3 are correct while 1 and 4 are incorrect.

CHAPTER 04

IONIC EQUILIBRIUM

The point of life is to find equillibrium in what is inherently unstable

“PIERREREVERDY”

INTRODUCTION

Ionic equilibrium is the equilibrium established between the unionized molecules and the ions in a solution of weak electrolytes. In this lesson we learn about the equilibrium involving ionic species. The equilibrium involving acids and bases are critically important for a wide variety of reactions.

After reading this lesson, we will be able to discuss

Define and explain various concepts of acids and bases

Define conjugate acid base pairs and identify them in an acid-base equilibrium;

Define pH and correlate it with the nature of queous solutions-neutral, acidic or basic:

Define and explain common ion effect in ionisation of weak acids and bases:

Identify the relationship between solubility and solubility product for salts of AB, AB_2, A_2B_2 and A_2B_3 types

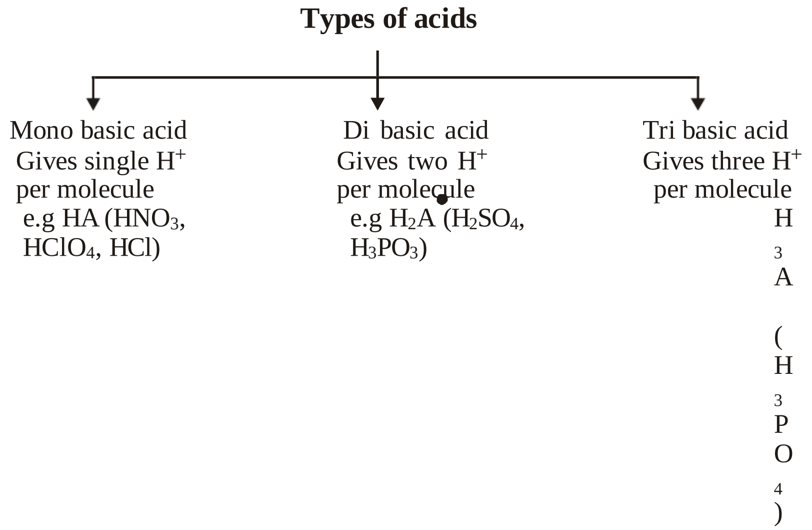
It is number of H^+ ions furnished by a molecule of an acid. An acid may be classified according to its basicity. Thus we may have,

(i) Mono basic or Mono protic acids like HCl, HNO_3, CH_3COOH, HCN etc.

(ii) Dibasic or Diprotic acids like, H_2SO_4, H_2CO_3, H_2SO_3, H_2S etc.

(iii) Tribasic or Triprotic acids like H_3PO_4, H_3AsO_4 etc.

Basicity or Protocity of an Acid



It may be defined as the number of OH^- ions furnished by a molecule of a base. A base can be,

(i) Mono acidic or Monohydroxic like NaOH, NH_4OH, AgOH etc.

(ii) Diacidic or dihydroxic like $Ba(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$ etc.

(iii) Triacidic or trihydroxic like $Fe(OH)_3$, $Al(OH)_3$ etc.

Strength of Acid or Base :

(i) Strength of Acid or Base depends on the extent of its ionisation. Hence equilibrium constant K_a or K_b respectively of the following equilibria give a quantitative measurement of the strength of the acid or base.

(ii) $HA + H_2O \rightleftharpoons H_3O^+ + A^-$;

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

(iii) Similarly

$B + H_2O \rightleftharpoons BH^+ + OH^-$;

$K_b = \frac{[BH^+][OH^-]}{[B]}$ here H_2O isszolvent.

ETD TS

(i) The other ways to represent above equilibrium is :

(a) $HA \overset{H_2O}{\rightleftharpoons} H^+ + A^-$; $K_a = \dfrac{[H^+][A^-]}{[HA]}$

(b) $BOH \overset{H_2O}{\rightleftharpoons} B^+ + OH^-$; $K_b = \dfrac{[B^+][OH^-]}{[BOH]}$

(ii) The larger the value of K_a or K_b, the more complete the ionisation, the higher the concentration of H_3O^+ or OH^- and stronger is the acid or base.

1. A strong electrolyte is defined as a substance which dissociates almost completely into ions in aqueous solution and hence is a very good conductor of electricity **Ex.**, NaOH, KOH, HCl, H_2SO_4, NaCl, KNO_3 etc.

2. A weak electrolyte is defined as a substance which dissociates to a small extent in aqueous solution and hence conducts electricity also to a small extent e.g. NH_4OH, CH_3COOH etc.

3. Degree of dissociation :- The fraction of the total amount of an electrolyte which dissociates into ions is called the degree of dissociation (α),

   i.e. $$\alpha = \frac{\text{Number of moles dissociated}}{\text{Number of moles taken}}$$

4. According to Arrhenius concept of acids and bases, an acid is a substance which gives H^+ ions in the aqueous solution whereas a base is a substance which gives OH^- ions in the aqueous solution.

5. According to Bronsted-Lowry concept of acids and bases, an acid is a substance which can give a proton and a base is a substance which accepts a proton.

6. According to Lewis concept of acids and bases, an acid is a substance which can accept a lone pair of electrons whereas a base is a substance which can donate a lone pair of electrons.

Types of Lewis Bases

(i) Neutral molecules containing a lone pair of electrons on the central atom like : NH_3, $R\ddot{\underset{\cdot\cdot}{O}}H$, $H_2\ddot{O}:$ etc. (ii) All negative ions like F^-, Cl^-, Br^-, I^-, OH^- etc.

Types of Lewis Acids

(i) Molecules having central atom with incomplete octet e.g. BF_3, $AlCl_3$ etc.

(ii) Simple cations e.g. Ag^+, Cu^{2+}, Fe^{3+} etc.

(iii) Molecules having central atom with empty d-orbitals e.g. $SnCl_4$, SiF_4, PF_5 etc.

(iv) Molecules containing multiple bonds between different atoms e.g. O = C = O.

SOLVED EXAMPLE

Ex. 1 Stomach acid is a solution of HCl with concentration of 2.2×10^{-3} M. what is the pH of stomach acid :

(A) 3.92 **(B)** 2.65

(C) 4.92 **(D)** 1.92

Sol. **(B)** HCl is 100 % ionised so

$[H_3O^+] = 2.2 \times 10^{-3}$ M

$pH = -\log(2.2 \times 10^{-3}\ M)$ or $pH = 2.65$

Ex. 2 Calculate the $[H_3O^+]$ of blood, the pH of which is 7.2 (slightly basic).

(A) 5×10^{-8} M **(B)** 6.3×10^{-8} M

(C) 5×10^{-9} M **(D)** 4×10^{-7} M

Sol. **(B)** As pH = 7.2 so $[H_3O^+] = \text{antilog}(-7.2) = 6.3 \times 10^{-8}$ M

Ex. 3 The pH of an aqueous solution at 25°C made up to 0.3 M, with respect to NaOH and 0.5 M, with respect to acetic acid ($pK_a = 4.76$) would be nearly :

(A) 4.25 **(B)** 4.93

(C) 4.75 **(D)** 5.05

Sol. **(B)** $pH = pK_a - \log\dfrac{[\text{acid}]}{[\text{salt}]}$

0.3 M NaOH will react with acid to form 0.3 M CH_3COONa and therefore CH_3COOH concentration will be reduced to 0.2 M.

$$pH = 4.76 - \log\frac{0.2}{0.3} = 4.93$$

Ex. 4 Calculate the pOH and pH of a 0.1 M CH_3COO^- solution ($K_a = 1.8 \times 10^{-5}$).

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

(A) 6.12, 7.88 **(B)** 4.12, 9.88

(C) 5.13, 8.87 **(D)** none of the above

Sol. **(C)** $pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$

$$= 7 + \frac{1}{2} \times 4.74 + \frac{1}{2}\log(0.1)$$

pH = 8.87

pOH = 14 – 8.87 = 5.13

Ex. 5 The pH of a solution of NH_3 is 5.806. If its concentration is 0.95 M then what is the value of its dissociation constant ?

(A) anti log [28 + log (0.95) – 23.242]

(B) anti log [11.612 – log (0.95) – 28]

(C) anti log [11.612 – log (0.95) – 14]

(D) anti log [14 + log (0.95) – 11.612]

Sol. **(B)** Since pH = 14 – pOH and $pOH = \frac{1}{2}pK_b - \frac{1}{2}\log C$

or $pH = 14 - \frac{1}{2}pK_b + \frac{1}{2}\log C$

or $pK_b = 2\left(14 + \frac{1}{2}\log C - pH\right)$

or $K_b = \text{antilog}[11.612 - \log(0.95) - 28]$

Ex. 6 The solubility product of $BaSO_4$ is 1.5×10^{-9}. The precipitation in a 0.01 M Ba^{2+} ions solution will start on adding H_2SO_4 of concentration :

(A) 10^{-9} M **(B)** 10^{-8} M

(C) 10^{-7} M **(D)** 10^{-6} M

Sol. **(D)** $[Ba^{2+}][SO_4^{2-}] = 1.5 \times 10^{-9}$ (K_{sp}) and $[Ba^{2+}] = 0.01$ M

so Required $[SO_4^{2-}] = \dfrac{1.5 \times 10^{-9}}{0.01} = 1.5 \times 10^{-7}$

so $[H_2SO_4] > 1.5 \times 10^{-7}$ for precipitation of $BaSO_4$.

Ex. 7 pH of a saturated solution of $Ca(OH)_2$ is 12. Its solubility product is :

(A) 10^{-6} **(B)** 4×10^{-6}

(C) 5×10^{-7} **(D)** None of these

Sol. **(C)** pH = 12 so $[OH^-] = 10^{-2}$ M

Now $Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+} + 2OH^-$

5×10^{-3}M 10^{-2} M

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

$= (5 \times 10^{-3})(10^{-2})^2 = 5 \times 10^{-7}$

Ex. 8 A sample of 100 ml of 0.10 M acid HA ($K_a = 1 \times 10^{-7}$) is titrated with standard 0.10 M KOH. How many mL of KOH will have to be added when the pH in the titration flask will be 7.00 ?

(A) 0 **(B)** 10

(C) 100 **(D)** 50

Sol. **(D)** $pH = pK_a + \log\dfrac{[\text{Salt}]}{[\text{Acid}]}$

$$7 = 7 + \log\frac{[N_2V_2]}{[N_1V_1 - N_2V_2]}$$

$$1 = \frac{0.1 \times V_2}{0.1 \times 100 - 0.1 \times V_2}$$

or $10 - 0.1V_2 = 0.1V_2$

or $V_2 = 50$ mL

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. Which of the following is non-electrolyte

(A) NaCl **(B)** $CaCl_2$

(C) $C_{12}H_{22}O_{11}$ **(D)** CH_3COOH

2. Ammonium hydroxide is a

(A) Strong electrolyte

(B) Weak electrolyte

(C) Both under different conditions

(D) Non-electrolyte

3. Ammonium hydroxide is a weak base because

(A) It has low vapour pressure

(B) It is only slightly ionized

(C) It is not a hydroxide of any metal

(D) It has low density

4. Electrolytes when dissolved in water dissociate into their constituent ions. The degree of dissociation of an electrolyte increases with

(A) Increasing concentration of the electrolyte

(B) Decreasing concentration of the electrolyte

(C) Decreasing temperature

(D) Presence of a substance yielding a common ion

5. An electrolyte

(A) Gives complex ions in solution

(B) Dissolves in water to give ions

(C) Is ionized in the solid state

(D) Generates ions on passing electric current

6. A monoprotic acid in 1.00 M solution is 0.01% ionised. The dissociation constant of this acid is

(A) 1×10^{-8} **(B)** 1×10^{-4}

(C) 1×10^{-6} **(D)** 10^{-5}

7. Molten sodium chloride conducts electricity due to the presence of

(A) Free electrons

(B) Free ions

(C) Free molecules

(D) Atoms of sodium and chlorine

8. An example for a strong electrolyte is

(A) Urea

(B) Ammonium hydroxide

(C) Sugar

(D) Sodium acetate

9. Which one is strongest electrolyte in the following

(A) NaCl **(B)** CH_3COOH

(C) NH_4OH **(D)** $C_6H_{12}O_6$

10. The equivalent conductance at infinite dilution of a weak acid such as HF

(A) Can be determined by measurement of very dilute HF solution

(B) Can be determined by extrapolation of measurements on dilute solutions of HCl, HBr and HI

(C) Can best be determined from measurements on dilute solutions of NaF, NaCl and HCl

(D) Is an undefined quantity

11. Which of the following is not a Lewis acid

(A) CO **(B)** $SiCl_4$

(C) SO_3 **(D)** Zn^{2+}

12. Review the equilibrium and choose the correct statement $HClO_4 + H_2O \rightleftharpoons H_3O^+ + ClO_4^-$

(A) $HClO_4$ is the conjugate acid of H_2O

(B) H_3O^+ is the conjugate base of H_2O

(C) H_2O is the conjugate acid of H_3O^+

(D) ClO_4^- is the conjugate base of $HClO_4$

13. A solution of $FeCl_3$ in water acts as acidic due to

(A) Hydrolysis of Fe^{3+} **(B)** Acidic impurities

(C) Dissociation **(D)** Ionisation

14. A white substance having alkaline nature in solution is

(A) $NaNO_3$ **(B)** NH_4Cl

(C) Na_2CO_3 **(D)** Fe_2O_3

15. Which of the following can act both as Bronsted acid and Bronsted base

(A) Cl^- **(B)** HCO_3^-

(C) H_3O^+ **(D)** OH^-

16. Lewis acid

(A) Presence of H atom is necessary

(B) Is a electron pair donor

(C) Always a proton donor

(D) Is a electron pair acceptor

17. For two acids A and B, $pK_a = 1.2$, $pK_b = 2.8$ respectively in value, then which is true

(A) A and B both are equally acidic

(B) A is stronger than B

(C) B is stronger than A

(D) Neither A nor B is strong

(E) None of these

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. Which of the following is not correct :

(A) $[H^+] = [OH^-] = \sqrt{K_w}$ for a neutral solution at all temperatures

(B) $[H^+] = [OH^-] = 10^{-7}$ for a neutral solution at all temperatures

(C) $[H^+] > \sqrt{K_w}$ and $[OH^-] < \sqrt{K_w}$ for an acidic solution

(D) $[H^+] < \sqrt{K_w}$ and $[OH^-] > \sqrt{K_w}$ for an alkaline solution

2. Which of the following correctly explains the nature of boric acid in aqueous medium:

(A) $H_3BO_3 \xrightarrow{H_2O} H_3^+O + H_2BO_3^-$

(B) $H_3BO_3 \xrightarrow{2H_2O} 2H_3^+O + HBO_3^{2-}$

(C) $H_3BO_3 \xrightarrow{3H_2O} 3H_3^+O + BO_3^{3-}$

(D) $H_3BO_3 \xrightarrow{H_2O} B(OH)_4^- + H^+$

3. pH for the solution of salt undergoing anionic hydrolysis (say CH_3COONa) is given by:

(A) $pH = 1/2\ [pK_w + pK_a + \log C]$

(B) $pH = 1/2\ [pK_w + pKa - \log C]$

(C) $pH = 1/2\ [pK_w + pK_b - \log C]$

(D) None of these

4. The pH of 0.1 M solution of the following salts increases in the order:

(A) $NaCI < NH_4CI < NaCN < HCI$

(B) $HCI < NH_4CI < NaCI < NaCN$

(C) $NaCN < NH_4CI < NaCI < HCI$

(D) $HCI < NaCI < NaCN < NH_4CI$

5. The pH of the solution obtanied by mixing 10 mL of 10^{-1} N HCI and 10 mL of 10^{-1} N NaOH is:

(A) 8 **(B)** 2

(C) 7 **(D)** None of these

6. pH of water is 7.0 at 25°C. If water is heated to 70°C, the:

(A) pH will decrease and solution becomes acidic

(B) pH will increase

(C) pH will remain constant as 7

(D) pH will decrease but solution will be neutral

7. The ratio of dissociation constant of two weak acids HA and HB is 4. At what moar concentration ratio, the two acids will have same pH in separate solutions:

(A) 2 **(B)** 0.5

(C) 4 **(D)** 0.25

8. The reverse process of neutralisation is:

(A) Hydrolysis **(B)** Decomposition

(C) Dehydration **(D)** Synthesis

9. 10^{-6} M HCI is diluted to 100 times. Its pH is:

(A) 6.0 **(B)** 8.0

(C) 6.95 **(D)** 9.5

10. Which solution will have pH closer to 1.0:

(A) 100 mL of (M/10) HCI + 100 mL of (M/10) NaOH

(B) 55 mL of (M/10) HCI + 45 mL of (M/10) NaOH

(C) 10 mL of (M/10) HCI + 90 mL of (M/10) NaOH

(D) 75 mL of (M/5) HCI + 25 mL of (M/5) NaOH

11. $Ca_3(PO_4)_2$ is insoluble in water. On adding a few drops of HCI to solid $Ca_3(PO_4)_2$ in contact with water, the solid dissolves. The reason is:

(A) The solvent becomes more polar on adding HCI

(B) $Ca_3(PO_4)_2$ combines with HCI to form soluble $CaCI_2$ and H_3PO_4

(C) $Ca(H_2PO_4)_2$ is formed, which dissolves

(D) H_3PO_4, a weak acid is formed and the solubility product of $Ca_3(PO_4)_2$ decrease

12. A certain weak acid has a dissociation contant 1.0×10^{-4} . The equilibrium constant for its reaction with a strong base is:

(A) 1.0×10^{-4} **(B)** 1.0×10^{-10}

(C) 1×10^{-10} **(D)** 1.0×10^{-14}

13. K_a for the acid HA is 1×10^{-6}. The value of K for the reaction $A^- + H_3O^+ \rightleftharpoons HA + H_2O$ is

(A) 1×10^{-6} **(B)** 1×10^{12}

(C) 1×10^{-12} **(D)** 1×10^{6}

14. The degree of hydrolysis of a salt of weak acid and weak base in its 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2M, the percentage hydrolysis of the salt should be:

(A) 100 % **(B)** 50%

(C) 25 % **(D)** None of these

Exercise # 3

PART - 1

MATRIX MATCH COLUMN

1. (Use log 1.8 = 0.26, Ka of formic acid = 1.8×10^{-4}, Ka of acetic acid = 1.8×10^{-5}, K_b of ammonia=1.8×10^{-5}, Ka_1 of $H_2S = 10^{-7}$ and Ka_2 of $H_2S = 10^{-14}$, for the following matchings)

Match the entries of column II for which the equality or inequality given in the column I are satisfied.

Column I	Column II
(A) 10^{-5} M HCl solution > 0.1 M H_2S solution	**(p)** α_{water} (degree of dissociation of water)
(B) CH_3COOH solution at pH equal to 4.74 = NH_4OH solution at pH equal to 9.26	**(q)** $[OH^-]$
(C) 0.1 M CH_3COOH solution = 1.0 M HCOOH solution	**(r)** α (degree of dissociation)
(D) 0.1 M of a weak acid HA_1(Ka = 10^{-5}) solution < 0.01 M of a weak acid HA_2(Ka = 10^{-6}) solution	**(s)** pH

2. Match the effect of addition of 1 M NaOH to 50 ml of 1 M $H_2C_2O_4$ (diprotic acid) in column I with column II (Given: $Ka_1 = 10^{-4}$, $Ka_2 = 10^{-9}$)

Column I	Column II
(A) 25 mL of NaOH	**(p)** Buffer solution
(B) 50 mL of NaOH	**(q)** pH is independent of concentration of species present in the solution.
(C) 75 mL of NaOH	**(r)** anionic hydrolyisis
(D) 100 mL of NaOH	**(s)** pH> 7

3. Match the correct value of Ksp expression in term of solubility (s)

Column-I	Column-II
(A) Al_2O_3	**(p)** $4s^3$
(B) CaO	**(q)** $27s^4$
(C) $Al(OH)_3$	**(r)** $108s^5$
(D) CaF_2	**(s)** s^2

4. Match the effect of addition of 1 M NaOH to 100 mL 1 M CH_3COOH (in Column I) with pH (in Column II) :

Column-I	Column-II
(A) 25 mL of NaOH	**(p)** pK_a
(B) 50 mL of NaOH	**(q)** $pK_a + \log 3$
(C) 75 mL of NaOH	**(r)** $pK_a - \log 3$
(D) 100 mL of NaOH	**(s)** $\frac{1}{2}[pK_w + pK_a - \log 2]$

5. When we titrate sodium carbonate solution (in beaker) with hydrochloric acid.

Column-I	Column-II
(A) At the start of titration	**(p)** Buffer solution of HCO_3^- and CO_3^{2-}
(B) Before the first equivalent point	**(q)** Buffer solution of H_2CO_3 and HCO_3^-
(C) At the first equivalent point	**(r)** Amphiprotic anion, pH = $1/2(pK_{a_1} + pK_{a_2})$
(D) Between the first and second equivalent points	**(s)** Hydrolysis of CO_3^{2-}

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. The conjugate acid of $NH^{\square}_2$ is **[CBSE AIPMT 2000]**

(A) N_2H_4 **(B)** NH_4^+
(C) NH_2OH **(D)** NH_3

2. Which of the following statements about pH and H^+ ion concentration is incorrect ? **[CBSE AIPMT 2000]**

(A) Addition of one drop of concentrated HCl in NH_4OH solution decreases pH of the solution
(B) A solution of the mixture of one equivalent of each of CH_3COOH and NaOH has a pH of 7
(C) pH of pure neutral water is not zero
(D) A cold and concentrated H2SO4 has lower H^+ ions concentration than a dilute solution of H_2SO_4

3. Which one of the following is true for any diprotic acid, H_2X ? **[CBSE AIPMT 2000]**

(A) $K_{a_2} \square K_{a_1}$ **(B)** $K_{a_2} \square K_{a_1}$
(C) $K_{a_2} \square K_{a_1}$ **(D)** $K_{a_2} \square \frac{1}{K_{a_1}}$

4. Ionisation constant of CH_3COOH is 1.7×10^{-5} and concentration of H^+ ions is 3.4×10^{-4}. Then, find out initial concentration of CH_3COOH molecules. **[CBSE AIPMT 2001]**

(A) 3.4×10^{-4} **(B)** 3.4×10^{-3}
(C) 6.8×10^{-4} **(D)** 6.8×10^{-3}

5. Solubility of a M_2S type salt is 3.5×10^{-6}, then find out its solubility product. **[CBSE AIPMT 2007]**

(A) 1.7×10^{-6} **(B)** $17. \times 10^{-16}$
(C) 1.7×10^{-18} **(D)** 1.7×10^{-12}

6. Solubility of MX_2 type electrolytes is 0.5×10^{-4} mol/L, then find out K_{sp} of electrolytes. **[CBSE AIPMT 2002]**

(A) 5×10^{-12} **(B)** 25×10^{-10}
(C) 1×10^{-13} **(D)** 5×10^{-13}

7. Which has highest pH ? **[CBSE AIPMT 2002]**

(A) $CH_3CO^-OK^+$ **(B)** Na_2CO_3
(C) NH_4Cl **(D)** $NaNO_3$

8. Solution of 0.1 N NH_4OH and 0.1 N NH_4Cl has pH 9.25, then find out pK_b of NH_4OH. **[CBSE AIPMT 2002]**

(A) 9.25 **(B)** 4.75
(C) 3.75 **(D)** 8.25

9. The solubility product of AgI at 25ºC is 1.0×10^{-16} $mol^2\ L^{-2}$. The solubility of AgI in 10^{-4} N solution of KI at 25°C is approximately (in mol L^{-1}) **[CBSE AIPMT 2002]**

(A) 1.0×10^{-10} **(B)** 1.0×10^{-8}
(C) 1.0×10^{-16} **(D)** 1.0×10^{-12}

10. The solubility product of a sparingle soluble salt AX_2 is 3.2×10^{-11}. Its solubility (in mol/L) is **[CBSE AIPMT 2004]**

(A) 5.6×10^{-6} **(B)** 3.1×10^{-4}
(C) 2×10^{-4} **(D)** 4×10^{-4}

11. 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 bas (In^-) forms of the indicator given by the expression **[CBSE AIPMT 2004]**

(A) $\log \square\frac{\square In^{\square}\square}{\square HIn\square}\square \square pK_{In} \square pH$

(B) $\log \square\frac{\square HIn\square}{\square In^{\square}\square}\square \square pK_{In} \square pH$

(C) $\log \square\frac{\square HIn\square}{\square In^{\square}\square}\square \square pH \square pK_{In}$

(D) $\log \square\frac{\square In^{\square}\square}{\square HIn\square}\square \square pH \square pK_{In}$

12. At 25°C, the dissociation constant of a base, BOH is 1.0 × 10–12. The concentration of hydroxyl ions in 0.01 M aqueous solution of the base would be **[CBSE AIPMT 2005]**

(A) 2.0×10^{-6} mol L^{-1} **(B)** 1.0×10^{-5} mol L^{-1}
(C) 1.0×10^{-6} mol L^{-1} **(D)** 1.0×10^{-7} mol L^{-1}

13. What if the correct relationship between the pH of isomolar solutions of sodium oxide (pH_1), sodium sulphide (pH_2), sodium selenide (pH_3) and sodium telluride (pH_4) ? **[CBSE AIPMT 2005]**

(A) $pH_1 > pH_2 \approx pH_3 > pH_4$
(B) $pH_1 < pH_2 < pH_3 < pH_4$
(C) $pH_1 < pH_2 < pH_3 \approx pH_4$
(D) $pH_1 > pH_2 > pH_3 > pH_4$

MOCK TEST

1. The following equilibrium is established when hydrogen chloride is dissolved in acetic acid

$$HCl\,(aq) + CH_3COOH\,(aq) \rightleftharpoons Cl^-\,(aq) + CH_3COOH_2^+(aq).$$

The set that characterises the conjugate acid-base pairs is

(A) (HCl, CH_3COOH) and $(CH_3COOH_2^+, Cl^-)$ **(B)** $(HCl, CH_3COOH_2^+)$ and (CH_3COOH, Cl^-)

(C) $(CH_2COOH_2^+, HCl)$ and (Cl^-, CH_3COOH) **(D)** (HCl, Cl^-) and $(CH_3COOH_2^+, CH_3COOH)$.

2. The following equilibrium is established when $HClO_4$ is dissolved in weak acid HF.

$$HF + HClO_4 \rightleftharpoons ClO_4^- + H_2F^+$$

Which of the following is correct set of conjugate acid base pair ?

(A) HF and $HClO_4$ **(B)** HF and ClO_4^- **(C)** HF and H_2F^+ **(D)** $HClO_4$ & H_2F^+

3. Identify the amphoteric species from the following :

(I) H_2O (II) NH_3 (III) $H_2PO_4^-$ (IV) HCO_3^-

(A) I, II **(B)** III, IV **(C)** I, II, III **(D)** I, II, III, I

4. Which of the following relations is correct ?

(A) $\Delta G^o = RT \ln K_{eq}$ **(B)** $[H_3O^+] = 10^{pH}$

(C) $\log \frac{Kw_2}{Kw_1} = \frac{\Delta H^o}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ **(D)** $[OH^-] = 10^{-7}$, for pure water at all temperatures.

5. Which of the following is incorrect ?

(A) K_a (weak acid). K_b (conjugate weak base) = K_w

(B) K_a (strong acid). K_b (conjugate weak base) = K_w

(C) K_a (weak acid). K_b (weak base) = K_w

(D) K_a (weak acid). K_b (conjugate strong base) = K_w

6. K_a for the acid HA is 1×10^{-6}. The value of K for the reaction $A^- + H_3O^+ \rightleftharpoons HA + H_2O$ is

(A) 1×10^{-6} **(B)** 1×10^{12} **(C)** 1×10^{-12} **(D)** 1×10^{6}

7. The pK_a value of NH_4^+ is 9. The pK_b value of NH_4OH would be :

(A) 9 **(B)** 5 **(C)** 7 **(D)** 8

8. Which of the following solution will have a pH exactly equal to 8 ?

(A) 10^{-8} M HCl solution at 25ºC **(B)** 10^{-8} M H^+ solution at 25ºC

(C) 2×10^{-6} M $Ba(OH)_2$ solution at 25ºC **(D)** 10^{-5} M NaOH solution at 25ºC

9. Which of the following solution will have pH close to 1.0 ?

(A) 100 ml of M/10 HCl + 100 ml of M/10 NaOH **(B)** 55 ml of M/10 HCl + 45 ml of M/10 NaOH

(C) 10 ml of M/10 HCl + 90 ml of M/10 NaOH **(D)** 75 ml of M/5 HCl + 25 ml of M/5 NaOH.

10. 0.1mol HCl is dissolved in distilled water of volume V then at $\lim_{V\to\infty}$ $(pH)_{solution}$ is equal to

(A) zero **(B)** 1 **(C)** 7 **(D)** 14

11. Dissociation constant of mono basic acids A, B, C and D are 6×10^{-4}, 5×10^{-5}, 3.6×10^{-6} and 7×10^{-10} respectively. The pH values of their 0.1M aqueous solution are in the order.

(A) D > C > B > A **(B)** A > B > C > D **(C)** D > C > A > B **(D)** None

CHAPTER 05

THERMODYNAMICS AND THERMICHEMISTRY

The production of motion in the steam engine always occurs in circumstances in which it is necessary to recognize, namely when the equilibrium of caloric is restored or when caloric passes from the body at one temperature to another body at a lower temperature.

"SADI CARNOT"

INTRODUCTION

Thermodynamics is the branch of chemistry that deals with energy changes occuring during various physical & chemical processes. It also deals with the transformation between different forms of energy.Chemical energy stored by molecules can be released as heat during chemical reaction when a fuel like methane, cooking gas or coal burns in air . The chemical energy may also be used to mechanical work when a fuel burns in an engine or to provide electrical energy through a galvenic cell like dry cell. Thus, various forms of energy are interrelated and under certain conditions,thease may be transformed from one form into another.The study of thease energy transformation forms the subject matter of thermodynamics. The laws of thermodynamic deals with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules.

In thermochemistry, chemical processes are associated with energy changes in chemical reactions.

Also $P = \frac{F}{A}$

$F = PA$

$dW = PA.dx$

⇒ $\because\ dV = -A\,.\,dx$ (-ive sign indicates work is done by the system i.e. gas is expanding against P_{ext})

⇒ $dW = -P_{ext.}\,dV$

⇒ $$w = -\int P_{external} dV$$

Sign Convention

Work done by the system is –ive.

Work done on the system is +ive

ED OS KEY POINTS

(1) During expansion dV is +ive and hence sign of w is -ive i.e. work is done by the system and hence Expansion Work is always negative.

(2) During compression, dV is -ive which gives +ive value of w i.e. work is done on the system and hence Compression work is always positive.

(II) Non-PV Work - Following are some examples of Non-PV work.

Stretching	Tension (γ), length (l)	$w = -\int \gamma dl$	N m = J
Surface expansion	Surface tension (γ mm), area (σ)	$w = -\iint \gamma d\sigma$	$(N\ m^{-1})\ (m^2) = J$
Electrical	Electrical potential (ϕ),	$w = q \times V$	V × C = J

Units of heat & work :

Calorie : It is defined as the quantity of heat required to raise the temperature of 1g of water by 1°C (14.5 to 15.5°C)

1 cal = 4.184 J = 4.2 J

1 L-atm = 101.3 J = 24.206 cal = 101.3×10^7 erg

1 L-atm > 1 cal. > 1 J. > 1 erg

Ex. Find the work done,when one mole of ideal gas in 10 litre container at 1 atm. is allowed to enter a vaccuated bulb of capacity 100 litre.

Sol. (a) $W = -P\Delta V$

But since gas enters the vaccum bulb and pressure in vaccum is zero.

$W = 0$

Ex. If 1 mole of gas expands from 1 litre to 5 litre against constant atmospheric pressure than calculate thw work done.

Sol. (b) $W = -P\Delta V = -1(5-1) = -4$ litre-atm.

Ex. Calculate the work done when 1 mol of zinc dissolves in hydrochloric acid at 273 K in :

(a) an open beaker

(b) a closed beaker at 300 K.

Sol. (a) From one mole of zinc, the no. of moles of H_2 gas evolved = 1

Hence volume of hydrogen gas evolved = 22.4 litre (when P = 1 atm and T = 273 K)

$\therefore\ w = -P\Delta V = -1 \times 22.4$ litre atm

$$= -22.4 \times \frac{8.314}{0.082}\ J = -2271.14\ J$$

(b) For a closed system $P_{ext} = 0$., therefore, w = 0.

THERMODYNAMICS

1. First law of Thermodynamics

For a finite change : $q = \Delta E - w = \Delta E - P\Delta V$

where q is heat given to system, ΔE is change in internal energy and –w is work done by the system.

$dq = dE - dw = dE - PdV$

2. Work Done in an Irreversible Process

$$w = -P_{ext} \times \Delta V = -P_{ext} \times (V_2 - V_1) = -P_{ext} \times R\left[\frac{P_1T_2 - P_2T_1}{P_1P_2}\right]$$

P_{ext} is the pressure against which volume changes from V_1 to V_2

3. Work Done in Reversible Process, i.e., Maximum Work

Isothermal Conditions

$w_{rev} = -2.303\ nRT \log_{10}(V_2/V_1)$

$w_{rev} = -2.303\ nRT \log_{10}(P_1/P_2)$

w_{rev} is maximum work done.

Adiabatic Conditions

$w_{rev} = [nR/(\gamma - 1)]\ [T_2 - T_1]$

γ is poisson's ratio.

Also for adiabatic process, following conditions hold good :

$PV^{\gamma} = \text{constant}$

$T^{\gamma} P^{1-\gamma} = \text{constant}$

$V^{\gamma - 1} = \text{constant}$

4. Heat Capacities

At constant pressure $C_p = (\delta H/\delta H)_p$

C_p is molar heat capacity at constant pressure.

At constant volume $C_v = (\delta E/\delta T)_v$

C_v is molar heat capacity at constant volume.

$C_p \times c_p \times M$ and $C_v = c_v \times M$

and $C_p - C_v = R/M$

$C_p/C_v = c_p/c_v = \gamma$ (The poisson's ratio)

c_p and c_v are specific heats at constant pressure and volume respectively.

SOLVED EXAMPLE

Ex.1 During 200J work done on the system, 140 J of heat is given out. Calculate the change in internal energy.

Sol. w = 200 J; q = –140 J;

∵ q = ΔE + (–w); where –w is work done by the system

ΔE = q + w

ΔE = –140 + 200 = +60J

Ex. 2 A gas absorbs 200 J of heat and expands against the external pressure of 1.5 atm from a volume of 0.5 litre. Calculate the change in internal energy.

Sol. w = –PΔV = –1.5 × (1.0 – 0.5) = –0.75 litre atm

= –0.75 × 101.3 J = –75.975 J

∵ 1 litre atm = 101.3 J

Now, ΔE = 200 – 75.975 = +124.025 J

Ex. 3 Two litre of N_2 at 0ºC and 5 atm pressure are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm. Assuming gas to be ideal, calculate work of expansion.

Sol. Since the external pressure is greatly different from the pressure of N_2 and thus, process is irreversible.

$w = -P_{ext}(V_2 - V_1)$

$w = -1 \times (V_2 - V_1)$

Given $V_1 = 2$ litre $V_2 = ?$ T = 273 K

$P_1 = 5$ atm $P_2 = 1$ atm

∴ $P_1V_1 = P_2V_2$

∴ $V_2 = \frac{2 \times 5}{1} = 10$ litre

∴ w = –1 × (10 – 2) = –8 litre atm

∴ $= -\frac{8 \times 1.987}{0.0821}$ calorie

$= -\frac{8 \times 1.987 \times 4.184}{0.0821}$ J = –810.10 joule

Ex.4 The enthalpy of vaporisation of liquid diethyl ether –$(C_2H_5)_2O$, is 26.0 kJ mol^{-1} at its boiling point (35.0ºC). Calculate ΔS for conversion of : **(A)** liquid to vapour, and **(B)** vapour to liquid at 35ºC.

Sol. **(A)** $\Delta S_{vap.}$ =

$\frac{\Delta H_{vap.}}{T} = \frac{26 \times 10^3}{308} = +$ JK^{-1} mol^{-1}

(B) $\Delta S_{cond.} = \frac{\Delta H_{cond.}}{T} = -\frac{26 \times 10^3}{308}$ (∵ $H_{cond} = -26$ kJ)

= –84.41 JK^{-1} mol^{-1}

Ex. 5 Calculate the free energy change when 1 mole of NaCl is dissolved in water at 25ºC. Lattice energy of NaCl = 777.8 kJ mol^{-1} ; ΔS for dissolution = 0.043 kJ mol^{-1} and hydration energy of NaCl = –774.1 kJ mol^{-1}.

Sol. $\Delta H_{dissolution}$ = Lattice energy + Hydration energy

= 777.8 – 774.1 = 3.7 kJ mol^{-1}

Now ΔG = ΔH – TΔS

= 3.7 – 298 × 0.043 = 3.7 – 12.814

ΔG = –9.114 kJ mol^{-1}

Ex. 6 The equilibrium constant for the reaction given below is 2.0 × 10^{-7} at 300 K. Calculate the standard free energy change for the reaction;

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Also, calculate the standard entropy change if ΔHº = 28.40 kJ mol^{-1}.

Sol. $\Delta G^o = -2.303 \times 8.314 \times 300 \log [2.0 \times 10^{-7}]$

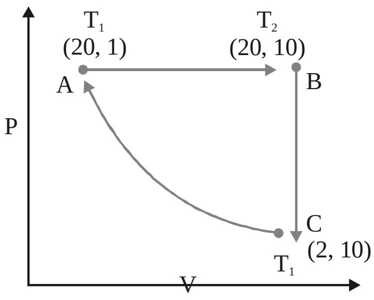
= +38479.8 J mol^{-1} = +38.48 kJ mol^{-1}

Also, ΔGº = ΔHº – TΔSº

∴ $\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} = \frac{28.40 - 38.48}{300}$

= –0.0336 kJ = –33.6 JK^{-1}

Ex. 7 One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps :



(CA) Isothermal compression from 2 atm and 10 litres to 20 atm and 1 litre.

(AB) Isobaric expansion to return the gas to the original volume of 10 litres with T going from T_1 to T_2.

(BC) Cooling at constant volume to bring the gas to the original pressure and temperature.

The steps are shown schematically in the figure shown.

(A) Calculate T_1 and T_2.

(B) Calculate ΔE, q and w in calories, for each step and for the cycle.

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. Internal energy of an ideal gas depends on

(A) Volume **(B)** Temperature

(C) Pressure **(D)** None of these

2. Any series of operations so carried out that at the end, the system is back to its initial state is called

(A) Boyle's cycle **(B)** Reversible process

(C) Adiabatic process **(D)** Cyclic process

3. One calorie is equal to

(A) 0.4184 Joule **(B)** 4.184 Joule

(C) 41.84 Joule **(D)** 418.4 Joule

4. The total internal energy change for a reversible isothermal cycles is

(A) Always 100 calories per degree

(B) Always negative

(C) 0

(D) Always positive

5. The first law of thermodynamics is only

(A) The law of conservation of energy

(B) The law of conservation of mass

(C) The law of conservation of momentum

(D) Both **(A)** and **(B)**

6. A mixture of two moles of carbon monoxide and one mole of oxygen, in a closed vessel is ignited to convert the carbon monoxide to carbon dioxide. If ΔH is the enthalpy change and ΔE is the change in internal energy, then

(A) $\Delta H > \Delta E$

(B) $\Delta H < \Delta E$

(C) $\Delta H = \Delta E$

(D) The relationship depends on the capacity of the vessel

7. Which of the following is always negative for exothermic reaction?

(A) ΔH **(B)** ΔS

(C) ΔG **(D)** None of these

8. The relation between ΔE and ΔH is

(A) $\Delta H = \Delta E - P\Delta V$ **(B)** $\Delta H = \Delta E + P\Delta V$

(C) $\Delta E = \Delta V + \Delta H$ **(D)** $\Delta E = \Delta H + P\Delta V$

9. At constant T and P, which one of the following statements is correct for the reaction,

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$$

(A) ΔH is independent of the physical state of the reactants of that compound

(B) $\Delta H > \Delta E$

(C) $\Delta H < \Delta E$

(D) $\Delta H = \Delta E$

10. For the reaction of one mole of zinc dust with one mole of sulphuric acid in a bomb calorimeter, ΔU and w correspond to

(A) $\Delta U < 0, w = 0$ **(B)** $\Delta U = 0, w < 0$

(C) $\Delta U > 0, w = 0$ **(D)** $\Delta U < 0, w > 0$

11. Which is not the correct relation between enthalpy (ΔH) and intrinsic energy (ΔE)

(A) $\Delta H = \Delta E + P\Delta V$ **(B)** $\Delta H = \Delta E + nRT$

(C) $\Delta H = \Delta E - P\Delta V$ **(D)** $\Delta E = \Delta H - P\Delta V$

12. The law of Lavoisier and Laplace illustrates

(A) The principle of conservation of energy

(B) Equivalence of mechanical and thermal energy

(C) The principle of conservation of matter

(D) Equivalence of mechanical and chemical energy

13. For the reaction $N_2 + 3H_2 \square 2NH_3; \Delta H =$

(A) $\Delta E - RT$ **(B)** $\Delta E - 2RT$

(C) $\Delta E + RT$ **(D)** $\Delta E + 2RT$

14. If ΔH is the change in enthalpy and ΔE the change in internal energy accompanying a gaseous reaction

(A) ΔH is always greater than ΔE

(B) $\Delta H < \Delta E$ only if the number of moles of the products is greater than the number of the reactants

(C) ΔH is always less than ΔE

(D) $\Delta H < \Delta E$ only if the number of moles of the products is less than the number of moles of the reactants

15. "The resultant heat change in a reaction is the same whether it takes place in one or several stages." This statement is called

(A) Lavoisier and Laplace law

(B) Hess's law

(C) Joule's law

(D) Le-chatelier's principle

Exercise # 2

SINGLE OBJECTIVE

AIIMS LEVEL

1. A system containing real gas changes it's state form state-1 to state-2.

State-1 (2 atm, 3L, 300 K)

State-2 (5 atm, 4L, 500 K)

If change in internal energy = 30 L atm then calculate change in enthalpy.

(A) 44 L atm **(B)** 35 L atm
(C) 40L atm **(D)** None of these

2. Mixing of non-reacting gases is generally accompanied by

(A) Decrease in entropy
(B) Increase in entropy
(C) Change in enthalpy
(D) Change in freeenergy

3. Which of the following reactions is associated with the most negative change in entropy ?

(A) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$
(B) $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$
(C) $C\ (s,\ graphite) + O_2 \longrightarrow CO_2(g)$
(D) $3C_2H_2(g) \longrightarrow C_6H_6(\ell)$

4. Predict which of the following reaction (s) has a positive entropy change ?

I. $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl\ (s)$
II. $NH_4Cl\ (s) \longrightarrow NH_3(g) + HCl(g)$
III. $2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$

(A) I and II **(B)** III
(C) II and III **(D)** II

5. Which one of the following has ΔS^0 greater than zero

(A) $CaO\ (s) + CO_2(g) \rightleftharpoons CaCO_3\ (s)$
(B) $NaCl\ (aq) \rightleftharpoons NaCl\ (s)$
(C) $NaNO_3\ (s) \rightleftharpoons Na^+\ (aq) + NO_3^-(aq)$
(D) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

6. For the gas - phase decomposition, $PCl_5(g) \overset{\Delta}{\rightleftharpoons} PCl_3(g) + Cl_2(g)$:

(A) $\Delta H < 0, \Delta S < 0$ **(B)** $\Delta H > 0, \Delta S > 0$
(C) $\Delta H > 0, \Delta S < 0$ **(D)** $\Delta H < 0, \Delta S > 0$

7. When 2 moles of an ideal gas $\left(C_{p,m}\ \frac{5}{2}R\right)$ heated from 300 K to 600 K at constant volume, the change in entropy of gas ΔS_{gas} is :

(A) 5R ln 2 **(B)** $\frac{3}{2}$ Rln 2
(C) 3R ln 2 **(D)** –3R ln 2

8. When one mole of an ideal gas is comressed to half of its initial volume and simultaneously heated to twice its initial temperature, the change in entropy of gas (ΔS) is :

(A) $C_{p,m}$ ln 2 **(B)** $C_{v,m}$ ln 2
(C) R ln 2 **(D)** $(C_{v,m} - R)$ ln 2

9. When two mole of an ideal gas $\left(C_{p,m} = \frac{5}{2}R\right)$ heated from 300 K to 600 K at constant pressure. The change in entropy of gas (ΔS) is :

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

10. If one mole of an ideal gas $\left(C_{p,m} = \frac{5}{2}R\right)$ is expanded isothermally at 300 K until it's volume is tripled, then change in entropy of gas is :

(A) zero **(B)** infinity
(C) $\frac{5}{2}$ R ln 3 **(D)** R ln 3

11. The entropy change when two moles of ideal monoatomic gas is heated from 200 to 300ºC reversibly and isochorically?

(A) $\frac{3}{2}$ R $\ln\left(\frac{300}{200}\right)$ **(B)** $\frac{5}{2}$R $\ln\left(\frac{573}{273}\right)$
(C) 3R $\ln\left(\frac{573}{473}\right)$ **(D)** $\frac{3}{2}$R $\ln\left(\frac{573}{473}\right)$

12. 1 mole of an ideal gas at 25°C is subjected to expand reversibly and adiabatically to ten times of its initial volume. Calculate the change in entropy during expansion (in $J k^{-1} mol^{-1}$)

(A) 19.15 **(B)** – 19.15
(C) 4.7 **(D)** zero

13. What is the change in entropy when 2.5 mole of water is heated from 27ºC to 87ºC ? Assume that the heat capacity is constant. ($C_{p,m}(H_2O)$ = 4.2 J/g-K ln (1.2) = 0.18)

(A) 16.6 J/K **(B)** 9 J/K
(C) 34.02 J/K **(D)** 1.89J/K

Exercise # 3

PART - 1

MATRIX MATCH COLUMN

1.

Columm-I	**Columm-II**
(A) Reversible isothermal expansion of an ideal gas	**(p)** $w = -2.303\, nRT \log\left(\frac{V_2}{V_1}\right)$
(B) Reversible adiabatic compression of an ideal gas	**(q)** PV^{γ} = constant
(C) Irreversible adiabatic expansion of an ideal gas	**(r)** $w = \frac{nR}{(\gamma - 1)}(T_2 - T_1)$
(D) Irreversible isothermal compression of an ideal gas	**(s)** $\Delta H = 0$

2.

Column I	**Column II**
(A) A process carried out infinitesimally slowly	**(p)** Adiabatic
(B) A process in which no heat enters or leaves the system	**(q)** $\Delta G = 0$
(C) A process carried out at constant temperature	**(r)** Sublimation
(D) A process in equilibrium	**(s)** $\Delta E = 0, \Delta H = 0$
(E) $A(\mathbf{s}) \longrightarrow A(g)$	**(t)** Reversible
(F) Cyclic process	**(u)** Isothermal

3.

Columm - I	**Columm - II**
(A) $(\Delta G_{system})_{T,P} = 0$	**(p)** Process is in equilibrium
(B) $\Delta S_{system} + \Delta S_{surrounding} > 0$	**(q)** Process is nonspontaneous
(C) $\Delta S_{system} + \Delta S_{surrounding} < 0$	**(r)** Process is spontaneous
(D) $(\Delta G_{system})_{T,P} > 0$	**(s)** System is unable to do useful work

4.

Columm - I	**Columm - II**
(A) Reversible adiabatic compression	**(p)** $\Delta S_{system} > 0$
(B) Reversible vaporisation of liquid	**(q)** $\Delta S_{system} < 0$
(C) $2N(g) \longrightarrow N_2(g)$	**(r)** $\Delta S_{surrounding} < 0$
(D) $MgCO_3(s) \xrightarrow{\Delta} MgO(s) + CO_2(g)$	**(s)** $\Delta S_{surrounding} = 0$

5.

Columm - I	**Columm - II**
(A) $C(s, graphite) + O_2(g) \longrightarrow CO_2(g)$	**(p)** $\Delta H^o_{combustion}$
(B) $C(s, graphite) \longrightarrow C(g)$	**(q)** $\Delta H^o_{formation}$
(C) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$	**(r)** $\Delta H^o_{atomization}$
(D) $CH_4(g) \longrightarrow C(g) + 4H(g)$	**(s)** $\Delta H^o_{sublimation}$

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. If Δ E is the heat of reaction for
$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
at constnat volume, the ΔH (heat of reaction at constant pressure), then the correct relation is **[CBSE AIPMT 2000]**

(A) $\Delta H = \Delta E + RT$ **(B)** $\Delta H = \Delta E - RT$
(C) $\Delta H = \Delta E - 2RT$ **(D)** $\Delta H = \Delta E + 2RT$

2. The entropy change in the fusion of one mole of solid melting at 27°C (latent heat of fusion is 2930 J mol^{-1}) is **[CBSE AIPMT 2000]**

(A) 9.77 $JK^{-1} mol^{-1}$ **(B)** 10.73 $JK^{-1} mol^{-1}$
(C) 2930 $JK^{-1} mol^{-1}$ **(D)** 108.5 $JK^{-1} mol^{-1}$

3. The factor of ΔG values is important in metallurgy. The ΔG values for the following reactions at 800°C are given as **[CBSE AIPMT 2000]**
$S_2(s) + 2O_2(g) \rightarrow 2SO_2(g), \Delta G = -544\ kJ$
$2Zn(s) + S_2(s) \rightarrow 2ZnS(s), \Delta G = -293\ kJ$
$2Zn(s) + O_2(g) \rightarrow 2ZnO(s), \Delta G = -480\ kJ$
the ΔG for the reaction,
$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$ will be

(A) –357 kJ **(B)** – 731 kJ
(C) –773 kJ **(D)** – 229 kJ

4. $PbO_2 \rightarrow PbO, \Delta G_{298} < 0$
$SnO_2 \rightarrow SnO, \Delta G_{298} > 0$
Most probable oxidation state of Pb and Sn will be **[CBSE AIPMT 2001]**

(A) Pb^{4+}, Sn^{4+} **(B)** Pb^{4+}, Sn^{2+}
(C) Pb^{2+}, Sn^{2+} **(D)** Pb^{2+}, Sn^{4+}

5. Change in enthalpy for reaction,
$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$
if heat of formation of $H_2O_2(l)$ and $H_2O(l)$ are –188 and –286 kJ/mol respectively is **[CBSE AIPMT 2001]**

(A) – 196 kJ/mol **(B)** + 196 kJ / mol
(C) + 948 kJ / mol **(D)** – 948 kJ /mol

6. When 1 mole gas is heated at constant voluem, temperature is raised from 298 to 308 K. Heat supplied to the gas is 500 J. Then, which statement is correct? **[CBSE AIPMT 2001]**

(A) $q = W = 500J, \Delta E = 0$
(B) $q = \Delta E = 500\ J, W = 0$
(C) $q = -W = 500\ J, \Delta E = 0$
(D) $\Delta E = 0, q = w = -500\ J$

7. Enthalpy of the reaction $CH_4 + \frac{1}{2}O_2 \rightarrow CH_3OH$, is negative. If enthalpy of combustion of CH_4 and CH_3OH are x and y respectively, then whcih relation is correct ? **[CBSE AIPMT 2001]**

(A) x > y **(B)** x < y
(C) x = y **(D)** x ≥ y

8. Unit of entropy is **[CBSE AIPMT 2002]**

(A) $JK^{-1} mol^{-1}$ **(B)** $J mol^{-1}$
(C) $J^{-1} K^{-1} mol^{-1}$ **(D)** $JK mol^{-1}$

9. In a closed insulated container a liquid is stirred with a paddle to increase the temperature, which of the following is true? **[CBSE AIPMT 2002]**

(A) $\Delta E = W \neq 0, q = 0$
(B) $\Delta E = W = 0, q \neq 0$
(C) $\Delta E = 0, W = q, q \neq 0$
(D) $W = 0, \Delta E = q, q \neq 0$

10. 2 moles of an ideal gas at 27°C temperature is expanded reversibly from 2 L to 20 L. Find entropy change (R = 2 cal/mol K). **[CBSE AIPMT 2002]**

(A) 92.1 **(B)** 0
(C) 4 **(D)** 9.2

11. Heat of combustion ΔH° for C(s), $H_2(g)$ and $CH_4(g)$ are –94, –68 and –213 kcal/mol. Then, ΔH° for $C(s) + 2H_2(g) \rightarrow CH_4(g)$ is **[CBSE AIPMT 2002]**

(A) –17 kcal/mol **(B)** –111 kcal/mol
(C) –170 kcal/mol **(D)** –85 kcal/mol

12. The denisties of graphite and diamond at 298 K are 2.25 and 3.31 g cm^{-3}, respectively. If the standard free energy difference (ΔG°) is equal to 1895 J mol^{-1}, the pressure at which graphite will be transformed into diamond at 298 K is **[CBSE AIPMT 2003]**

(A) 9.92×10^6 pa **(B)** 9.92×10^5 pa
(C) 9.92×10^8 pa **(D)** 9.92×10^7 Pa

13. What is the entropy change (in J $K^{-1} mol^{-1}$) when one mole of ice is converted into water at 0°C? (The enthalpy change for the converstion of ice to liquid water is 6.0 kJ mol^{-1} at 0°C) **[CBSE AIPMT 2003]**

(A) 2.198 $JK^{-1} mol^{-1}$ **(B)** 21.98 $JK^{-1} mol^{-1}$
(C) 20.13 $JK^{-1} mol^{-1}$ **(D)** 2.013 $JK^{-1} mol^{-1}$

14. For which one of the following equestions ΔH°_r equal to ΔH°_f for the product? **[CBSE AIPMT 2003]**

(A) $Xe(g) + 2F_2(g) \rightarrow XeF_4(g)$
(B) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
(C) $N_2(g) + O_3(g) \rightarrow N_2O_3(g)$

MOCK TEST

1. In an isobaric process, the ratio of heat supplied to the system (dQ) and work done by the system (dW) for diatomic gas is

(A) 1 : 1 **(B)** 7 : 2 **(C)** 7 : 5 **(D)** 5 : 7

2. The enthalpy change for the reaction of 50.00 ml of ethylene with 50.00 ml of H_2 at 1.5 atm pressure is $\Delta H = -0.31 kJ$. The value of ΔE will be

(A) -0.3024 kJ **(B)** 0.3024 kJ **(C)** 2.567 kJ **(D)** -0.0076kJ

3. Enthalpy of solution of NaOH (solid) in water is $-41.6\, kJ\, mol^{-1}$. When NaOH is dissolved in water, the temperature of water

(A) Increase **(B)** Decreases **(C)** Does not change **(D)** Fluctuates indefinitely

4. In which of the following entropy decreases ?

(A) Crystallization of sucrose from solution **(B)** Rusting of iron

(C) Melting of ice **(D)** Vaporization of camphor

5. For conversion C (graphite) $\rightarrow$ C (diamond) the ΔS is

(A) Zero **(B)** Positive **(C)** Negative **(D)** Unknown

6. For a reaction $\Delta H = 9.08$ kJ mol^{-1} and $\Delta S = 35.7 JK^{-1} mol^{-1}$

Which of the following statements is correct for the reaction

(A) Reversible and Isothermal **(B)** Reversible and Exothermic

(C) Spontaneous and Endothermic **(D)** Spontaneous and Exothermic

7. For a reaction to occur spontaneously

(A) $(\Delta H - T\Delta S)$ must be negative **(B)** $(\Delta H + T\Delta S)$ must be negative

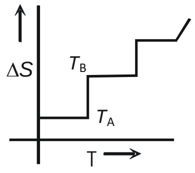
(C) ΔH must be negative **(D)** ΔS must be negative

8. The total amount of energy in the universe is fixed, but

(A) Disorder is increasing **(B)** Lightning is increasing

(C) Matter is increasing **(D)** Gravitation is decreasing

9. If for a given substance melting point is T_B and freezing point is T_A, then correct variation shown by graph between entropy change and temperature is

(A)


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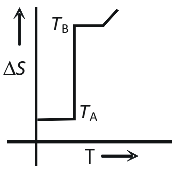

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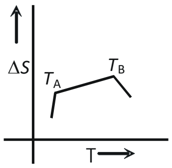

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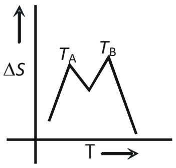


10. Which of the following would be expected to have the largest antropy per mole

(A) SO_2Cl_2 (s) **(B)** SO_2Cl_2 (g) **(C)** SO_2Cl_2 (l) **(D)** SO_2(g)

11. The enthalpies of formation of Al_2O_3 and Cr_2O_3 are –1596 kJ and –1134 kJ respectively. ΔH for the reaction $2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$ is

(A) –2730 kJ **(B)** –462 kJ **(C)** –1365 kJ **(D)** +2730kJ

CHAPTER 11

ALCOHOL, PHENOL AND ETHER

Organic compounds exist in which a hydrogen atom, joined to the carbon, acquires acid properties as a result of the proximity of certain functional groupings.

''VICTORGRIGNARD''

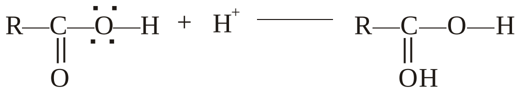
INTRODUCTION

Alcohols and phenols are formed when a hydrogen atom in a hydrocarbon, aliphatic and aromatic respectively, is replaced by –OH group. These classes of compounds find wide applications in industry as well as in day-to-day life. For instance, ordinary spirit used for polishing wooden furniture is chiefly a compound containing hydroxyl group, ethanol. The sugar we eat, the cotton used for fabrics, the paper we use for writing, are all made up of compounds containing –OH groups.

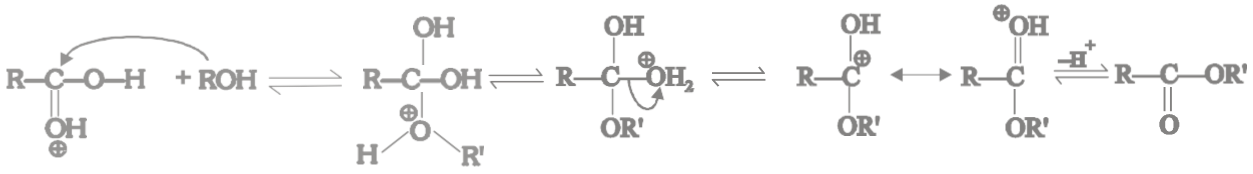
The substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group (R–O/Ar–O) yields another class of compounds known as 'ethers', for example, CH_3OCH_3 (dimethyl ether). Ethers as compounds formed by substituting the hydrogen atom of hydroxyl group of an alcohol or phenol by an alkyl or aryl group.

Mechanism :

$H_2SO_4 \longrightarrow H^+ + HSO_4^-$



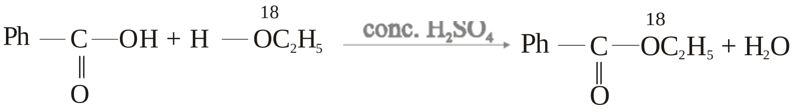
$R-\underset{\underset{O}{\|}}{C}-\ddot{\underset{..}{O}}-H + H^+ \longrightarrow R-\underset{\underset{OH}{\|}}{C}-O-H$



Note : This is a laboratory method to prepare ester.

Ex. 

$CH_3-\underset{\underset{O}{\|}}{C}-OH + H-OC_2H_5 \xrightarrow{\text{conc. } H_2SO_4} CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5 + H_2O$

Ex. 

$Ph-\underset{\underset{O}{\|}}{C}-OH + H-\overset{18}{O}C_2H_5 \xrightarrow{\text{conc. } H_2SO_4} Ph-\underset{\underset{O}{\|}}{C}-\overset{18}{O}C_2H_5 + H_2O$

Dry HCl can be used as dehydrating agent.

Ex. 

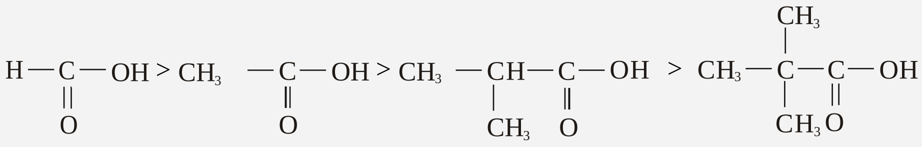
$CH_3-\underset{\underset{O}{\|}}{C}-OH + H-OC_2H_5 \xrightarrow{\text{Dry HCl}} CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5 + H_2O$

ETOOS KEY POINTS

(a) **Reactivity for esterification** $\propto \dfrac{1}{\textbf{Steric hinderence}}$.

(b) Reactivity of R – OH [If acid is same] : $CH_3-OH > 1° > 2° > 3°$ alcohol

(c) Reactivity of RCOOH [If alcohol is same] :



$H-\underset{\underset{O}{\|}}{C}-OH > CH_3-\underset{\underset{O}{\|}}{C}-OH > CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OH > CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{O}{\|}}{C}-OH$

(vii) **Reaction with CH ≡ CH :**

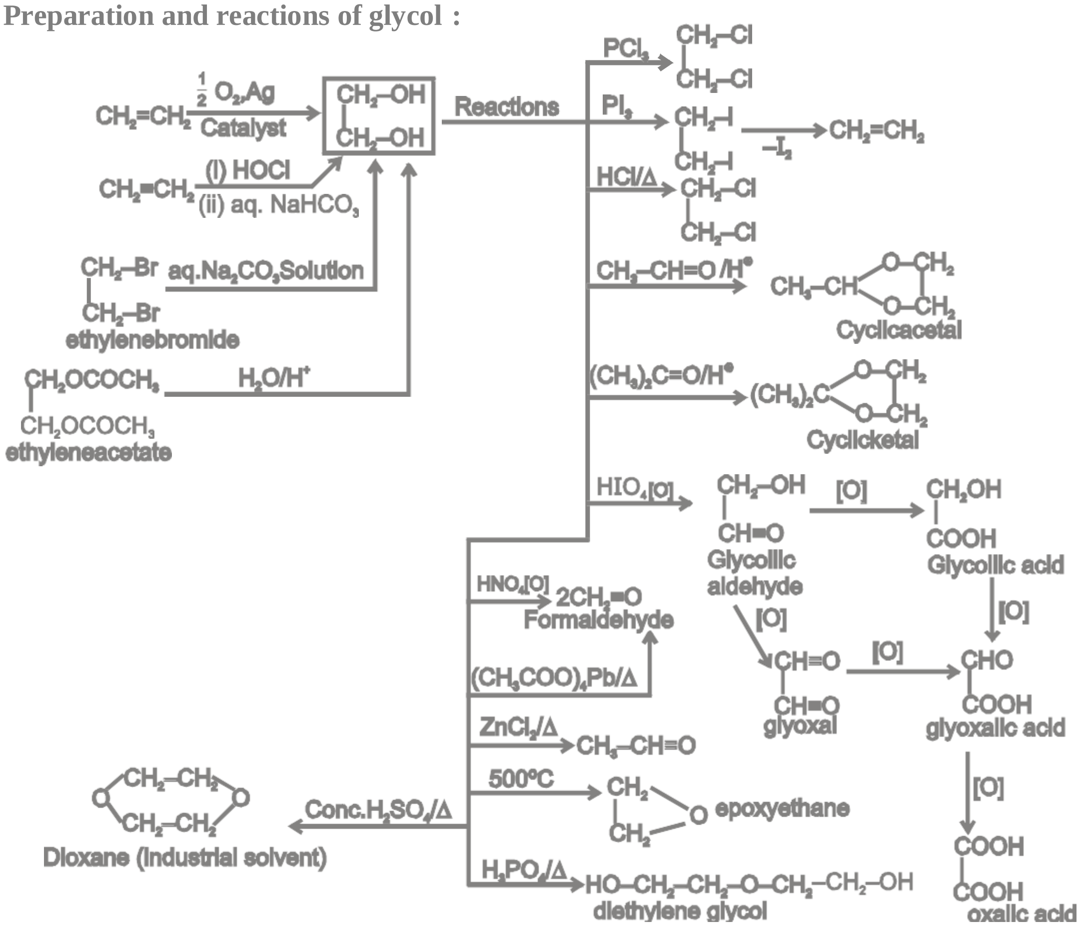
$CH\equiv CH + 2CH_3-OH \xrightarrow{BF_3/HgO} CH_3CH\left\langle\begin{matrix}OCH_3\\OCH_3\end{matrix}\right.$

Methylal

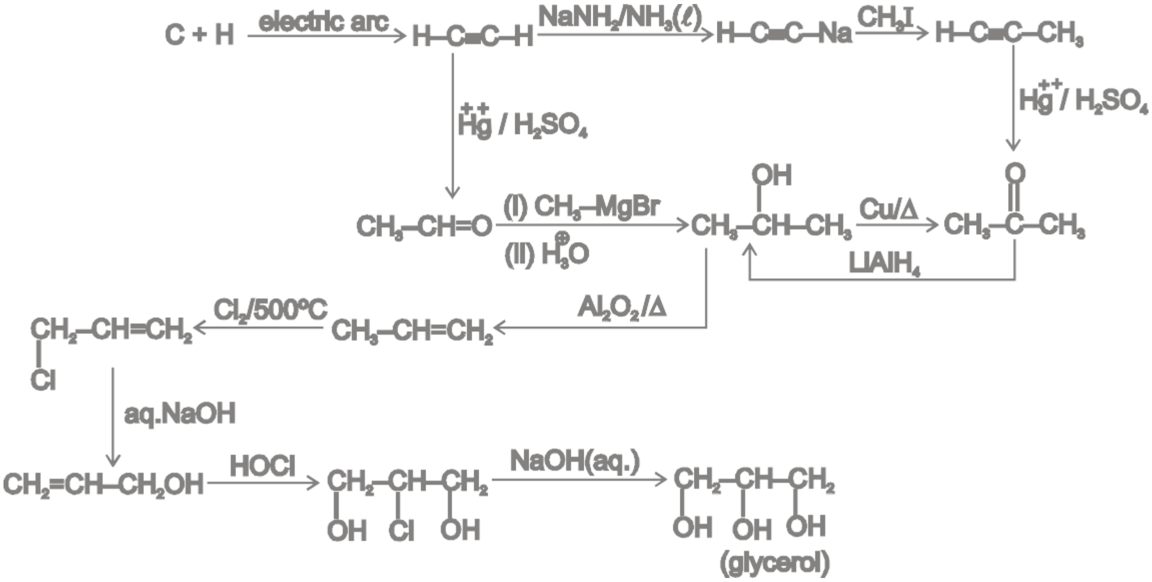
$CH\equiv CH + 2CH_3CH_2-OH \xrightarrow{BF_3/HgO} CH_3CH\left\langle\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right.$

Ethylal

1. Preparation and reactions of glycol :

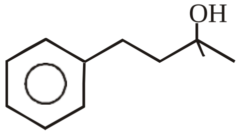


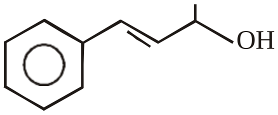
2. General Reactions of Glycerol :

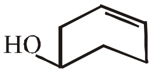


SOLVED EXAMPLE

Ex. 1 Give the IUPAC names for the following compounds. Chiral descriptions are not required.

(A) 

(B) 

(C) 

OH

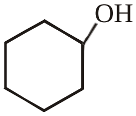
(D) Br

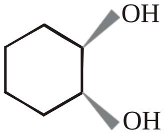
Sol. **(A)** 2-Methyl-4-phenylbutan-2-ol ; **(B)** **trans**-4-phenylbut-3-en-2-ol ;
(C) Cyclohex - 3-enol ; **(D)** 1-(**cis**-3-Bromocyclohexyl)propan-2-ol

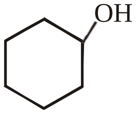
Ex. 2 How will you carry out the following conversions ? You may use other organic compounds if necessary.

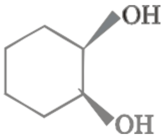
(A) CH_3OH to CH_3CH_2OH **(B)** CH_3CH_2OH to CH_3OH
(C) CH_3CH_2OH to $HOCH_2CH_2OH$ **(D)** $CH_3CH_2CH_2CH_2OH$ to $CH_3CH_2CHOHCH_3$
(E) CH_3CH_2OH to $CH_3CH_2CHOHCH_3$ **(F)** $C_6H_5COCH_3$ to $C_6H_5CH_2CH_2OH$

(G) CH_3CH_2OH to $(C_2H_5)_2CHOHCH_3$

(H) 

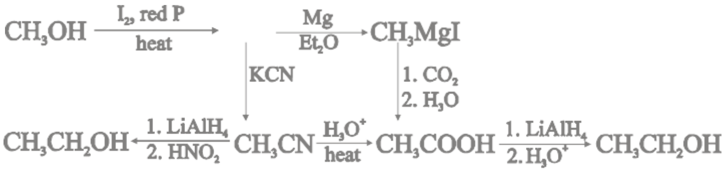
to 

(I) 

to 

(J) $CH_2 = CHCH_2OH$ to $CH_2OHCHOHCHO$

Sol. **(A)**



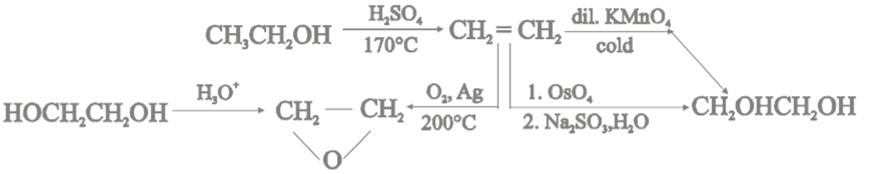
Alternatively, $CH_3OH \xrightarrow{PCC} HCHO \xrightarrow[2.\ H_3O^+]{1.\ CH_3MgI} CH_3CH_2OH$

(B)

$$CH_3CH_2OH \xrightarrow[H_2SO_4,\ heat]{K_2Cr_2O_7} CH_3COOH \xrightarrow{AgOH} CH_3COOAg \xrightarrow[CCl_4,\ heat]{Br_2} CH_3Br \xrightarrow{AgOH} CH_3OH$$

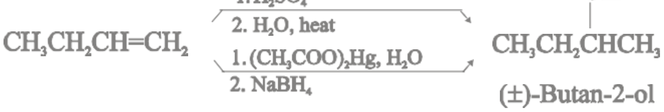
Alternatively, $CH_3CH_2OH \xrightarrow[170°C]{H_2SO_4} CH_2 = CH_2 \xrightarrow[2.\ Zn/H_2O]{1.\ O_3} HCHO \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4} CH_3OH$

(C)



(D)

$$CH_3CH_2CH_2CH_2OH \xrightarrow{PBr_3} CH_3CH_2CH_2CH_2Br \xrightarrow[heat]{alc.\ KOH} CH_3CH_2CH{=}CH_2$$



(±)-Butan-2-ol

(E) $CH_3CH_2OH \xrightarrow{PBr_3} CH_3CH_2Br \xrightarrow[Et_2O,\ heat]{Mg} CH_3CH_2MgBr$

$$CH_3CH_2OH \xrightarrow{PPC} CH_3CHO \xrightarrow[2.\ H_3O^+]{1.\ CH_3CH_2MgBr} CH_3CHOHCH_2CH_3$$

(±)-Butan-2-ol

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. Butane-2-ol is
(A) Primary alcohol **(B)** Secondary alcohol
(C) Tertiary alcohol **(D)** Aldehyde

2. Picric acid is
(A) Trinitroaniline **(B)** Trinitrotoluene
(C) A volatile liquid **(D)** 2, 4, 6 trinitrophenol

3. 3- pentanol is a
(A) Primary alcohol **(B)** Secondary alcohol
(C) Tertiary alcohol **(D)** None of these

4. Glycerol is a
(A) Primary alcohol
(B) Monohydric alcohol
(C) Secondary alcohol
(D) Trihydric alcohol

5. Cresols are
(A) Hydroxy toluenes **(B)** Dihydric phenols
(C) Trihydric phenols **(D)** Trihydric alcohols

6. Ethanol is prepared industrially by
(A) Hydration of ethylene
(B) Fermentation of sugars
(C) Both the above
(D) None of these

7. Ethyl alcohol is industrially prepared from ethylene by
(A) Permanganate oxidation
(B) Catalytic reduction
(C) Absorbing in H_2SO_4 followed by hydrolysis
(D) Fermentation

8. Propene, $CH_3 - CH = CH_2$ can be converted to 1-propanol by oxidation. Which set of reagents among the following is ideal to effect the conversion
(A) Alkaline $KMnO_4$
(B) B_2H_6 and alkalien H_2O_2
(C) O_3 / Zn dust
(D) OsO_4 / CH_4, Cl_2

9. Which one of the following will produce a primary alcohol by reacting with CH_3MgI
(A) Acetone **(B)** Methyl cyanide
(C) Ethylene oxide **(D)** Ethyl acetate

10. The fermentation of startch to give alcohol occurs mainly with the help of
(A) O_2 **(B)** Air
(C) CO_2 **(D)** Enzymes

11. Coconut oil upon alkaline hydrolysis gives
(A) Glycol **(B)** Alcohol
(C) Glycerol **(D)** Ethylene oxide

12. Which enzyme converts glucose and fructose both into ethanol
(A) Diatase **(B)** Invertase
(C) Zymase **(D)** Maltase

13. Chlorination of toluene in the presence of light and heat followed by treatment iwth aqueous NaOH gives
(A) o-cresol
(B) p-cresol
(C) 2, 4-dihydroxytolueone
(D) Benzyle alcohol

14. In the commercial manufacture of ethyl alcohol from starchy substances by fermentatio method, which enzymes stepwise complete the fermentation reaction
(A) Diastase, maltase and zymase
(B) Maltase, zymase and invertase
(C) Diastase, zymase and lactase

15. Primary alcohols can be obtained from the reaction of the $RMgX$ with
(A) CO_2 **(B)** $HCHO$
(C) CH_3CHO **(D)** H_2O

16. On heating aqueous solution of benzene diazonium chloride, which is formed
(A) Benzene **(B)** Chlorobenzene
(C) Phenol **(D)** Aniline

17. $LiAlH_4$ converts acetic acid into
(A) Acetaldehyde **(B)** Methane
(C) Ethyl alcohol **(D)** Methyl alcohol

18. Formaldehyde gives an additive product with methyl magnesium iodide which on aqueous hydrolysis gives
(A) Isopropyl alcohol **(B)** Ethyl alcohol
(C) Methyl alcohol **(D)** Propyl alcohol

19. Benzyl alcohol is obtained from benzaldehyde by
(A) Fittig's reaction **(B)** Cannizaro's reaction
(C) Kolbe's reaction **(D)** Wurtz's reaction

20. Benzene diazonium chloride on boiling with dilute sulphuric acid gives
(A) Toluene **(B)** Benzoic acid
(C) Benzene **(D)** Phenol

21. The reaction given below is known as
$C_2H_5ONa + IC_2H_5 \rightarrow C_2H_5OC_2H_5 + NaI$
(A) Kolbe's synthesis
(B) Wurtz's synthesis
(C) Williamson's synthesis
(D) Grignard's synthesis

22. Salicylaldehyde can be prepared from
(A) Phenol and chloroform
(B) Phenol, chloroform and sodium hydroxide
(C) Phenol, carbon tetrachloride and $NaOH$
(D) None of these

Exercise # 2

SINGLE OBJECTIVE

AIIMS LEVEL

1. In the following reaction sequence

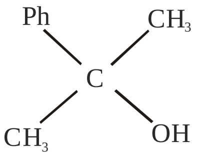
$Ph - C \equiv CH \xrightarrow[Hg^{2+}]{aq.H_2SO_4} A \xrightarrow[2.\ H_2O]{1.CH_3MgI} B$

the product **(B)** is :

(A) $PhCOCH_3$

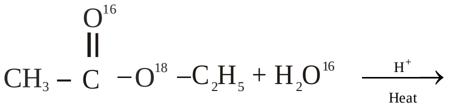
(B) $PhCH_2CHOHCH_3$

(C)



(D) $PhCH_2COCH_3$

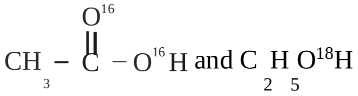
2. Consider the following reaction.



$CH_3 - \overset{\overset{O^{16}}{\|}}{C} - O^{18} - C_2H_5 + H_2O^{16} \xrightarrow[Heat]{H^+}$

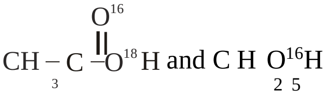
The products formed in the reaction are

(A)



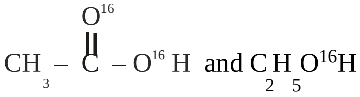
$CH_3 - \overset{\overset{O^{16}}{\|}}{C} - O^{16}H$ and $C_2H_5O^{18}H$

(B)



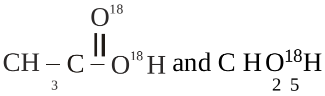
$CH_3 - \overset{\overset{O^{16}}{\|}}{C} - O^{18}H$ and $C_2H_5O^{16}H$

(C)



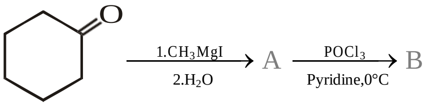
$CH_3 - \overset{\overset{O^{16}}{\|}}{C} - O^{16}H$ and $C_2H_5O^{16}H$

(D)



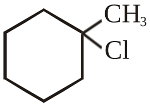
$CH_3 - \overset{\overset{O^{18}}{\|}}{C} - O^{18}H$ and $C_2H_5O^{18}H$

3. Consider the following reaction sequence,

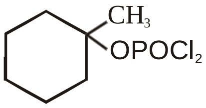


The product **(B)** is-

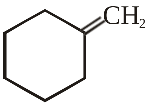
(A)



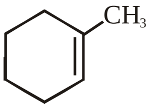
(B)



(C)



(D)



4. Consider the following reaction sequence

$CH_2 = CH_2 \xrightarrow[cold]{dil.KMnO_4} A \xrightarrow[excess]{PCl_5} B$

The products **(A)** and **(B)** are, respectively :

(A) CH_3CH_2OH and CH_3CH_2Cl

(B) CH_3CHO and CH_3CHCl_2

(C) $CH_2OH\ CH_2OH$ and CH_2ClCH_2Cl

(D) CH_2OHCH_2OH and CH_2OHCH_2Cl

5. Consider the following reaction sequence,

$CH_3C \equiv CH \xrightarrow[2\ mole]{HCl} A \xrightarrow[Heat]{aq.KOH} B$

The products **(A)** and **(B)** are, respectively,

(A) $CH_3CH_2CHCl_2$ and CH_3CH_2CHO

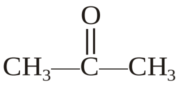
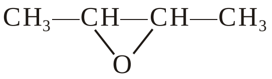
(B) $CH_3CCl_2CH_3$ and CH_3COCH_3

(C) $CH_3CCl_2CH_3$ and $CH_3C \equiv CH$

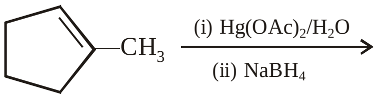
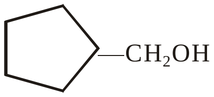
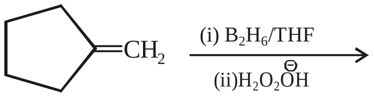
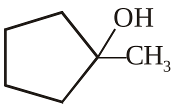
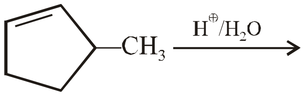
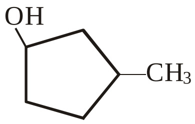
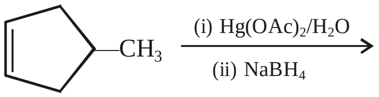
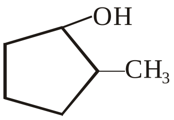
(D) $CH_3CHClCH_2Cl$ and $CH_3CHOHCH_2OH$

Exercise # 3 PART - 1 MATRIX MATCHCOLUMN

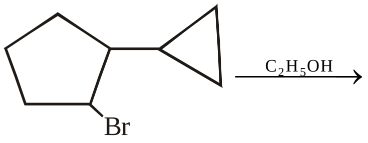
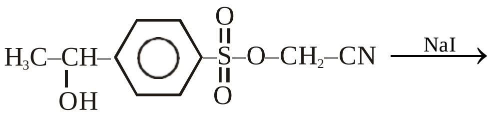
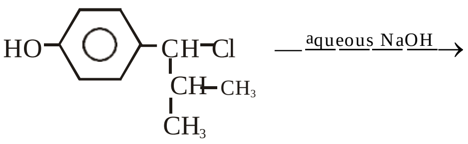
1. Match the column I with column II.

Column-I **(substrate + RMgX)**	**Column-II** **(Product)**
(A) HCHO	**(p)** Tertiaryalcohol
(B)  $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_3$	**(q)** First ketone then 3° alcohol
(C) 	**(r)** Secondary alcohol
(D) Ester	**(s)** Primaryalcohol

2. Match the column I with column II.

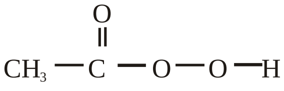
Column-I (Reaction)	**Column-II (Possible products)**
(A) 	**(p)** 
(B) 	**(q)** 
(C) 	**(r)** 
(D) 	**(s)** 

3. Match the characteristics mentioned in Column –II with the reactions given in Column –I

Column–I	**Column–II**
(A) 	**(p)** S_N2
(B) 	**(q)** Rearrangement
(C) 	**(r)** S_N1
(D) 	**(s)** Walden Inversion

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. Propan-1-ol may be prepared by reaction of propene with **[CBSE AIPMT 2000]**

(A) 
$CH_3-\overset{\overset{O}{\|}}{C}-O-O-H$

(B) H_3BO_3

(C) B_2H_6/NaOH-H_2O_2

(D) H_2SO_4 / H_2O

2. The ionisation conisation constant of phenol is higher than than that of ethanol because **[CBSE AIPMT 2000]**

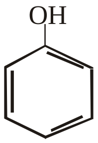
(A) Phenoxide ion is bulkier than ethoxide

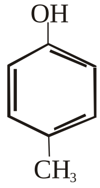
(B) phenoxide ion is stronger base than ethoxide

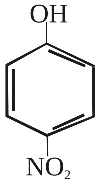
(C) phenoxide ion is stabilised through delocalisation

(D) phenoxide ion is less than ethoxide

3. The correct acidic order of following is **[CBSE AIPMT 2001]**

(I) 

(II) 

(III) 

(A) I>II>III **(B)** III>I>II

(C) II>III>I **(D)** I>III>II

4. Which on eof the following is correct? **[CBSE AIPMT 2001]**

(A) Reduction of any aldehyde gives secondary alcohol

(B) Reaction of vegetable oil with H_2SO_4 gives glycerine

(C) Alcoholic iodine with NaOH gives iodoform

(D) Sucrose on reaction with NaCl gives invert sugar

5. Which of the following is correct? **[CBSE AIPMT 2001]**

(A) Cycloheptane is an aromatic compound

(B) Diastase is an enzyme

(C) Acetophenone is an ether

(D) All of the above

6. In preparation of alkene from alcohol using Al_2O_3, which is effective factor **[CBSE AIPMT 2001]**

(A) Porosity of Al_2O_3

(B) Temperature

(C) Concentration

(D) Surface area of Al_2O_3

7. n-propyl alcohol and iso-propyl alcohol can be chemically distinguished by which reagent? **[CBSE AIPMT 2000]**

(A) PCI_5

(B) reduction

(C) Oxidation with potassium dichomate

(D) ozonolysis

8. The — OH group of an alcohol or the — COOH group of a carboxylic acid can be replaced by — CL using **[CBSE AIPMT 2004]**

(A) phosphorus pentachloride

(B) hypochlorous acid

(C) chlorine

(D) hydrochloric acid

9. Which of the following will not form a yellow precipitate on heating with an alkaline solution of iodine **[CBSE AIPMT 2004]**

(A) $CH_3CH(OH)CH_3$

(B) $CH_3CH_2CH(OH)CH_3$

(C) CH_3OH

(D) CH_3CH_2OH

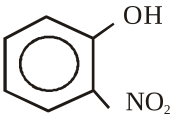
10. The enzyme which hydrolysis triglycerides into fatty acids and glycerol is called **[CBSE AIPMT 2004]**

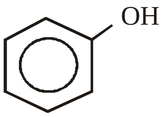
(A) maltase **(B)** lipase

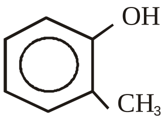
(C) zymase **(D)** pepsin

11. Which one of the following compounds is most acidic ? **[CBSE AIPMT 2005]**

(A) $ClCH_2—CH_2OH$

(B) 

(C) 

(D) 

MOCK TEST

STRAIGHT OBJECTIVE TYPE

1. Consider the following reaction sequence,

$CH_3C\equiv CH \xrightarrow[2\text{ mole}]{HCl} A \xrightarrow[Heat]{aq.KOH} B$

The products **(A)** and **(B)** are, respectively,

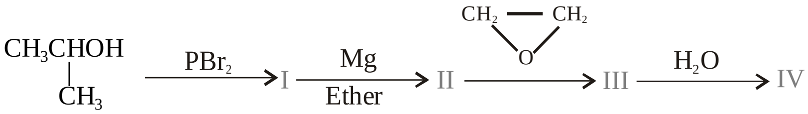
(A) $CH_3CH_2CHCl_2$ and CH_3CH_2CHO

(B) $CH_3CCl_2CH_3$ and CH_3COCH_3

(C) $CH_3CCl_2CH_3$ and $CH_3C\equiv CH$

(D) $CH_3CHClCH_2Cl$ and $CH_3CHOHCH_2OH$

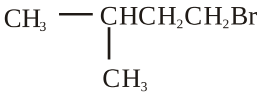
2. The final product **(IV)** in the sequence of reactions is :



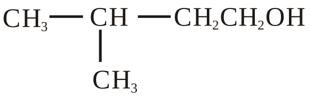
$\underset{\underset{CH_3}{|}}{CH_3CHOH} \xrightarrow{PBr_2} I \xrightarrow[Ether]{Mg} II \xrightarrow{\text{ethylene oxide}} III \xrightarrow{H_2O} IV$

(A) 

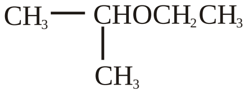
$CH_3-\underset{\underset{CH_3}{|}}{C}HOCH_2CH_2OH$

(B) 

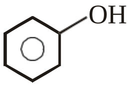
$CH_3-\underset{\underset{CH_3}{|}}{C}HCH_2CH_2Br$

(C) 

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2CH_2OH$

(D) 

$CH_3-\underset{\underset{CH_3}{|}}{C}HOCH_2CH_3$

3.  $\xrightarrow{CHCl_3 + KOH}$ Product :

about above reaction the incorrect statement is

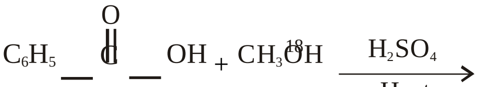
(A) The name of reaction is Reimer tiemann's reaction

(B) The intermediate in the reaction is dichloro carbene

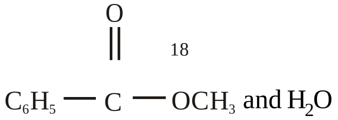
(C) The final product is o-hydroxy benzaldehyde

(D) the final product is benzyl chloride

4. The products formed in the reaction are :



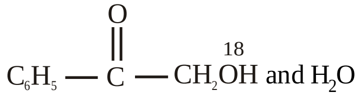
$C_6H_5-\overset{\overset{O}{\|}}{C}-OH + CH_3\overset{18}{O}H \xrightarrow[Heat]{H_2SO_4}$

(A) 

$C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{18}{O}CH_3$ and H_2O

(B) 

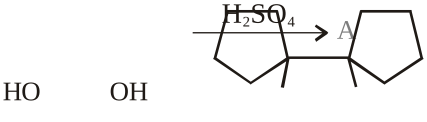
$C_6H_5-\overset{\overset{O}{\|}}{C}-OCH_3$ and $H_2\overset{18}{O}$

(C) 

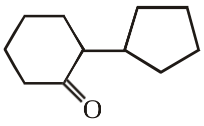
$C_6H_5-\overset{\overset{O}{\|}}{C}-CH_2\overset{18}{O}H$ and H_2O

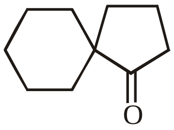
(D) $C_6H_5\overset{18}{O}CH_3$, CO and H_2O

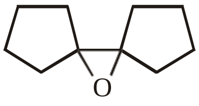
5. The major product **(A)** formed in the reaction

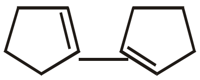


is :

(A) 

(B) 

(C) 

(D) 

CHAPTER 02

CHEMICAL KINETICS

Your life is a reflection of how effectively you balance potential and kinetic energy

''STEVE MARABOLI''

INTRODUCTION

Thermodynamics tells only about the feasibility of a reaction whereas chemical kinetics tells about the rate of reaction.

IN a spontaneous chemical reaction following questions arises.

How fast do the chemical reaction go?

How can the speed of a reaction change?

What is the mechanism of a reaction?

To answer the above question we study chemical kinetics.

So, chemical kinetics is the branch of physical chemistry which deals with study of rates of reactions, the mechanism by which the reactions proceed and factors affecting rate of reaction.

Ex. The rate of change in concentration of R in the reaction, $2P + Q \longrightarrow 2R + 3S$, was reported as 1.0 mol L^{-1} sec^{-1}. Calculate the reaction rate as well as rate of change of concentration of P, Q and S.

Sol. $$\frac{-1}{2}\frac{d[P]}{dt} = -\frac{d[Q]}{dt} = \frac{1}{2}\frac{d[R]}{dt} = \frac{1}{3}\frac{d[S]}{dt} = \text{Rate of reaction}$$

$$\because \quad \frac{d[R]}{dt} = 1.0\ \text{mol}L^{-1}s^{-1}$$

$$\therefore \quad -\frac{d[P]}{dt} = \frac{d[R]}{dt} = 1.0\ \text{mol}\ L^{-1}s^{-1}$$

$$\frac{-d[Q]}{dt} = \frac{1}{2}\frac{d[R]}{dt} = \frac{1}{2} = 0.5\ \text{mol}L^{-1}\ s^{-1}$$

$$\frac{-d[S]}{dt} = \frac{3}{2}\frac{d[R]}{dt} = \frac{3}{2} \times 1 = 1.5\ \text{mol}L^{-1}\ s^{-1}$$

$$\text{Rate of reaction} = \frac{1}{2}\frac{d[C]}{dt} = \frac{1}{2} \times 1 = 0.5\ \text{mol}\ L^{-1}s^{-1}$$

ETOOS KEY POINTS

Rate law for reversible reaction :

$$2NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4$$

$$\text{Rate} = \frac{1}{2}\frac{d[NO_2]}{dt} = K_1[NO_2]^2 - K_2[N_2O_4]$$

Rate Law

The experimental expression of rate of reaction in terms of concentration of reactions 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 a power or exponent that has to be found experimentaly.

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

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

The values of exponents x and y are found experimentaly 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.

Order of Reaction

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

For the reaction $aA + bB \rightarrow$ Product

Rate law is rate $= k[A]^x[B]^y$

Here x = order of reaction with respect to A

y = order of reaction with respect to B

$x + y = n$ (overall order of reaction)

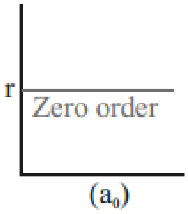
Order of reaction may be zero, positive, negative or fractional.

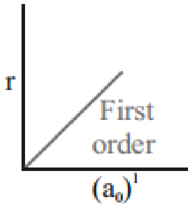
1. Expression for rate constants for reaction of different orders

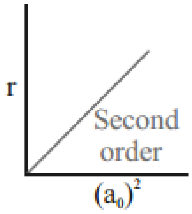
Type of reaction	Integrated rate equation	Unit of rate constant	Half-life period	$t^{3/4}$ life period
Zero order reaction	$-\frac{d[A]}{dt} = k_0[A]^0$ Differentiation form $\frac{dx}{dt} = k$	Concentration/time–1	$t_{\frac{1}{2}} = \frac{a}{2k_0}$	--
First order reaction	$k_1 \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$	$time^{-1}$	$t_{\frac{1}{2}} = \frac{0.693}{K_1}$	$t_{\frac{3}{4}} = 2 \times \frac{0.693}{k_1} = \frac{1.382}{k_1}$
Second order reaction	$k_2 = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$ Differential form $\frac{dx}{dt} = k(a-x)^2$	$Mole^{-1} litre\ time^{-1}$	$t_{\frac{1}{2}} = \frac{1}{k_2 a}$	$t_{\frac{3}{4}} = \frac{3}{k_2 a}$
Third order reaction	$k_3 = \frac{x \times (2a-x)}{t2a^2(a-x)^2}$ Differential form $\frac{dx}{dt} = k(a-x)^3$	$Litre^2 mole^{-2} time^{-1}$	$t_{\frac{1}{2}} = \frac{3}{2k_3 a^2}$	--

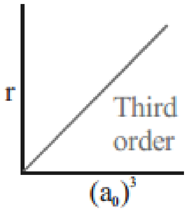
2. Some typical linear plots for reactions of different orders :

(i)

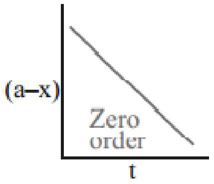


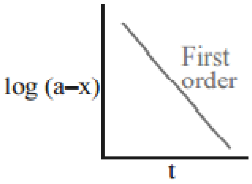


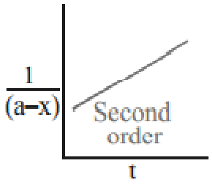


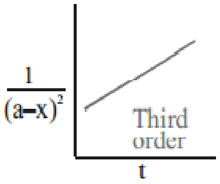


(ii)

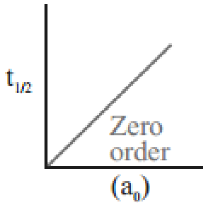


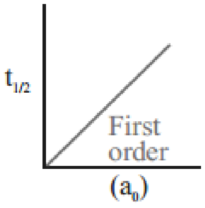


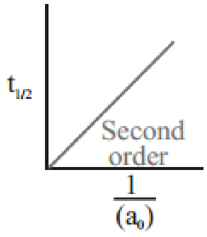


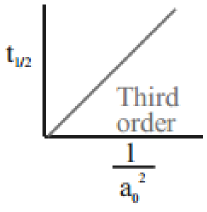


(iii)









SOLVED EXAMPLE

Ex.1 Which of the following statement is not correct about order of a reaction

(A) The order of a reaction can be a fractional number

(B) Order of a reaction is experimentally determined quantity

(C) The order of a reaction is alaway equalt to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction

(D) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression

Sol. (C) Order of reaction is equal to the sum of power of concentration of the reactants in rate law expression.

For any chmical reaction

xA + yB → Product

Rate = $k[A]^x[B]^y$

Order of reactino can be a fraction also, Order of reaction is not always equal to sum of the stoichiometric coefficients of reactants in the balanced chmical equation. For a reaction it may or may hnot be equal to sum of stoichiometiric coeffients of reactants.

Ex.2 Which of the following statements is correct

(A) The rate of a reaction decreases with passage of time as the concentration of reactants decreases

(B) The rate of a reaction is same at any time during the reaction

(C) The rate of a reaction is independent of temperature change

(D) The rate of a reaction decreses with increses in concentration of reactants (s)

Sol. (A) Rate of reaction defined as rate of decrease of concentration of any one of reactant with passage of time

$$\text{Rate of reaction} = \frac{\text{Rateof disappearance of rac tan t}}{\text{Time taken}}$$

$$r = \frac{-dx}{dt}$$

Thus, as the concentration of reactant decreases with passage of time, rate of reaction decreases.

Ex.3 Which of the following expressions is correct for the rate of reaction given below

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

(A) $\frac{\Delta[Br^-]}{\Delta t} = 5\frac{\Delta[H^+]}{\Delta t}$ **(B)** $\frac{\Delta[Br^-]}{\Delta t} = \frac{6}{5}\frac{\Delta[H^+]}{\Delta t}$

(C) $\frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}$ **(D)** $\frac{\Delta[Br^-]}{\Delta t} = 6\frac{\Delta[H^+]}{\Delta t}$

Sol. **(C)** Given, chimcal reaction is

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

Rate law expression for the above equation can be written as

$$-\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = \frac{-1}{6}\frac{\Delta[H^+]}{\Delta r} = \frac{+1}{3}\frac{\Delta[Br_2]}{\Delta t}$$

$$\Rightarrow \frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = \frac{-5}{6}\frac{\Delta[H^+]}{\Delta t}$$

$$\Rightarrow \frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}.$$

Ex.4 Rate law for reaction A + 2 B → C is found to be

Rate = k[A][B]

Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be ....

(A) The same **(B)** Doubled

(C) Quadrupled **(D)** Halved

Sol. (B) Rate law can be written as

Rate = k[A][B]

Rate of reaction w.r.t. B is of first order.

$R_1 = k\,[A]\,[B]$

when concentration of reactant 'B' is doubled then rate (R_2)

$R_2 = k[A][2B]$

$R_2 = 2k\,[A][B]$

$R_2 = 2R_1$

Therefore; as concentration of B is doubled keeping the concentration of A constant rate of reaction doubles.

Exercise # 1 SINGLE OBJECTIVE NEET LEVEL

1. The rate of a chemical reaction
(A) Increases as the reaction proceeds
(B) Decreases as the reaction proceeds
(C) May increase or decrease during the reaction
(D) Remains constant as the reaction proceeds

2. The rate of a reaction that not involve gases is not dependent on
(A) Pressure (B) Temperature
(C) Concentration (D) Catalyst

3. The rate at which a substance reacts depends on its
(A) Atomic weight (B) Equivalent weight
(C) Molecular weight (D) Active mass

4. The rate law for the reaction
RCl + NaOH(aq) ® ROH + NaCl is given by Rate . The rate of the reaction will be
(A) Doubled on doubling the concentration of sodium hydroxide
(B) Halved on reducing the concentration of alkyl halide to one half
(C) Decreased on increasing the temperature of the reaction
(D) Unaffected by increasing the temperature of the reaction

5. If doubling the concentration of a reactant `A' increases the rate 4 times and tripling the concentration of `A' increases the rate 9 times, the rate is proportional to
(A) Concentration of `A'
(B) Square of concentration of `A'
(C) Under root of the concentration of `A'
(D) Cube of concentration of `A'

6. The rate of chemical reaction at constant temperature is proportional to
(A) The amount of products formed
(B) The product of masses of the reactants
(C) The product of the molar concentration of the reactants
(D) The mean free path of the reaction

7. The concentration of a reactant decreases from 0.2 M to 0.1 M in 10 minutes. The rate of the reaction is
(A) 0.01 M (B) 10^{-2}
(C) 0.01 mol dm^{-3}min^{-1} (D) 1 mol dm^{-3}min^{-1}

8. When a reaction is progressing
(A) The rate of the reaction goes on increasing
(B) The concentration of the products goes on decreasing
(C) The concentration of the reactants goes on decreasing
(D) The reaction rate always remains constant

9. In a catalytic conversion of N_2 to NH_3 by Haber's process, the rate of reaction was expressed as change in the concentration of ammonia per time is 40×10^{-3} mol litre^{-1}s^{-1} . If there are no side reaction, the rate of the reaction as expressed in terms of hydrogen is (in mol litre^{-1}s^{-1})
(A) 60×10^{-3} (B) 20×10^{-3}
(C) 1.200 (D) 10.3×10^{-3}

10. If the concentration of the reactants is increased, the rate of reaction
(A) Remains unaffected
(B) Increases
(C) Decreases
(D) May increase or decrease

11. Time required for completion of ionic reactions in comparison to molecular reactions is
(A) Maximum (B) Minimum
(C) Equal (D) None

12. For reaction $2A + B \rightarrow$ products, the active mass of B is kept constant and that of A is doubled. The rate of reaction will then
(A) Increase 2 times (B) Increase 4 times
(C) Decrease 2 times (D) Decrease 4 times

13. In a reaction $2A + B \rightarrow A_2B$, the reactant A will disappear at
(A) Half the rate that B will decrease
(B) The same rate that B will decrease
(C) Twice the rate that B will decrease
(D) The same rate that A_2B will form

14. The rate of a gaseous reaction is given by the expression K[A][B]. If the volume of the reaction vessel is suddenly reduced to 1/4th of the initial volume, the reaction rate relating to original rate will be
(A) 1/10 (B) 1/8
(C) 8 (D) 16

15. A catalyst increases the rate of reaction because it
(A) Increases the activation energy
(B) Decreases the energy barrier for reaction
(C) Decreases the collision diameter
(D) Increases the temperature coefficient

16. Which of these does not influence the rate of reaction
(A) Nature of the reactants
(B) Concentration of the reactants
(C) Temperature of the reaction
(D) Molecularity of the reaction

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. $aA + bB \longrightarrow$ Product, $dx/dt = k\,[A]^a\,[B]^b$. If concentration of A is doubled, rate is four times. If concentration of B is made four times, rate is doubled. What is relation between rate of disappearance of A and that of B ?

(A) $-\{d\,[A] / dt\} = -\{d\,[B] / dt\}$
(B) $-\{d\,[A] / dt\} = -\{4\,d\,[B] / dt\}$
(C) $-\{4\,d\,[A] / dt\} = -\{d\,[B]/ dt\}$
(D) None of these

2. For the reaction,

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$$

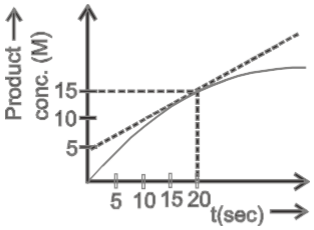
the rate expression can be written in the following ways:

$\{d\,[N_2] / dt\} = k_1\,[NO][H_2]$; $\{d[H_2O] / dt\}$
$= k[NO][H_2]$; $\{-\,d[NO] / dt\}$
$= k'_1\,[NO]\,[H_2]$; $\{-d[H_2] / dt\} = k''_1\,[NO][H_2]$

The relationship between k, k_1 , k'_1 and k''_1. is :

(A) $k = k_1 = k'_1 = k''_1$ **(B)** $k = 2k_1 = k'_1 = k''_1$
(C) $k = 2k'_1 = k_1 = k''_1$ **(D)** $k = k_1 = k'_1 = 2\,k''_1$

3. Rate of formation of product at t = 20 seconds is



(A) $0.5\,MS^{-1}$ **(B)** $1\,M\,S^{-1}$
(C) $1.5\,M\,S^{-1}$ **(D)** $2MS^{-1}$

4. In the following reaction : $xA \longrightarrow yB$

$$\log\left[-\frac{d[A]}{dt}\right] = \log\left[\frac{d[B]}{dt}\right] + 0.3$$

where –ve sign indicates rate of disappearance of the reactant. Thus, x : y is :

(A) 1 : 2 **(B)** 2 : 1
(C) 3 : 1 **(D)** 3 : 10

5. Rate of formation of SO_3 in the following reaction $2SO_2 + O_2 \rightarrow 2SO_3$ is 100 g min^{-1}. Hence rate of disappearance of O_2 is :

(A) 50 g min^{-1} **(B)** 40 g min^{-1}
(C) 200g min^{-1} **(D)** 20 g min^{-1}

6. For a reaction $pA + qB \rightarrow$ products, the rate law expression is $r = k[A]^1\,[B]^m$, then :

(A) $(p+1) < (1+ m)$
(B) $(p + q) > (1 + m)$
(C) $(p + q)$ may or may not be equal to $(1+ m)$
(D) $(p + q) = (1 + m)$

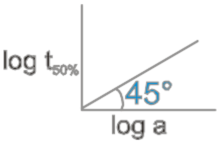
7. If rate constant is numerically the same for the three reactions of first, second and third order respectively. Assume all the reactions of the kind $A \rightarrow$ products. Which of the following is correct :

(A) if $[A] = 1$ then $r_1 = r_2 = r_3$
(B) if $[A] < 1$ then $r_1 > r_2 > r_3$
(C) if $[A] > 1$ then $r_3 > r_2 > r_1$
(D) All

8. For the irreversible process, $A + B \longrightarrow$ products, the rate is first–order w.r.t. A and second–order w.r.t. B. If 1.0 mol each of A and B introduced into a 1.0 L vessel, and the initial rate was 1.0×10^{-2} mol $L^{-1}\,s^{-1}$, rate when half reactants have been turned into products is :

(A) 1.25×10^{-3} mol $L^{-1}\,s^{-1}$
(B) 1.0×10^{-2} mol $L^{-1}\,s^{-1}$
(C) 2.50×10^{-3} mol $L^{-1}\,s^{-1}$
(D) 2.0×10^{-2} mol $L^{-1}\,s^{-1}$

9. What will be the order of reaction and rate constant for a chemical change having log $t_{50\%}$ vs log concentration of **(A)** curves as :



(A) 0, 1/2 **(B)** 1,1
(C) 2, 2 **(D)** 3,1

10. For a reaction $2A + B \rightarrow$ product, rate law is $-\frac{d[A]}{dt} = k[A]$. At a time when $t = \frac{1}{k}$, concentration of the reactant is

(C_0 = initial concentration)

(A) $\frac{C_0}{e}$ **(B)** $C_0\,e$
(C) $\frac{C_0}{e^2}$ **(D)** $\frac{1}{C}$

Exercise # 3 PART - 1 MATRIX MATCHCOLUMN

1. Match the following:

Column-I	Column-II
(A) $A + B \longrightarrow C + D$ $r = k_1[A][B]$	**(p)** Unit of rate constant possess concentration unit
(B) $A + B \longrightarrow C + D$ $r = k_2[A][B]^o$	**(q)** Rate constant for the reaction of both the reactants are equal
(C) $A + B \longrightarrow C + D$ $r = k_3[A]^o[B]^o$	**(r)** Rate of consumption of at least one of the reactants is equal to rate of production of at least one of the products
(D) $2A + B \longrightarrow 2C + 3D$ $r = k_3[A]^o[B]^o$	**(s)** If both reactants are taken in stoichiometric ratio, half life for both reactants are equal.

2. Match the following:

Column-I	Column-II
(Graph)	(Slope)
(A) C Vs t (abscissa) for zero order	**(p)** unity
(B) log C Vs t (abscissa) for first order	**(q)** zero
(C) $\left(\frac{-dc}{dt}\right)$ Vs c for zero order	**(r)** $-k$
(D) $\ln\left(\frac{-dc}{dt}\right)$ Vs ℓnc for first order	**(s)** $-\frac{k}{2.303}$

3. Match the following:

Column-I	Column-II
(A) If the activation energy is 65 kJ then how much time faster a reaction proceed at 25°C than at 0°C	**(p)** 2
(B) Rate constant of a first - order reaction is $0.0693\ \text{min}^{-1}$. If we start with $20\ \text{mol L}^{-1}$, it is reduced to $2.5\ \text{mol L}^{-1}$ in how many minutes	**(q)** Zero
(C) Half - lives of first - order and zero order reactions are same. Ratio of rates at the start of reaction is how many times of 0.693 Assume initial concentration to be same for the both.	**(r)** 11
(D) the half-life periods are given , $[A]_0$ (M) 0.0677 0.136 0.272 $t_{1/2}$ (sec) 240 480 960 order of the reaction is	**(s)** 30

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. For the reaction **[CBSE AIPMT 2001]**
$2N_2O_5 \rightarrow 4NO_2 + O_2$, rate and rate constant are 1.02×10^{-4} and 3.4×10^{-5} s^{-1} respectively, then concentration of N_2O_5 at that time will be

(A) 1.732
(B) 3
(C) 1.02×10^{-4}
(D) 3.4×10^{5}

2. When a biochemical reaction is carrid out in laboratory from outside of human body in the absence of enzyme, the rate of reaction obtained is 10^{-6} then activation energy of the reaction in the presence of enzyme is **[CBSE AIPMT 2001]**

(A) $\frac{6}{RT}$
(B) P is required
(C) different from E_a obtained in laboratory
(D) cannot say any hings

3. $3A\rightarrow 2B$, rate of reaction $+\frac{d[B]}{dt}$ is equal to **[CBSE AIPMT 2002]**

(A) $-\frac{3}{2}\frac{d[A]}{dt}$
(B) $-\frac{2}{3}\frac{d[A]}{dt}$
(C) $-\frac{1}{3}\frac{d[A]}{dt}$
(D) $+2\frac{d[A]}{dt}$

4. $3A\rightarrow B+C$ It would ba a zero order reaction, when **[CBSE AIPMT 2002]**

(A) the rate of reaction is proportional to square of concentration of A
(B) the rate of reaction remains same at any concentration of A
(C) the rate remains unchanged at any concentration of B and C
(D) the rate of reaction doubles if concentration of B is increased to double

5. The reaction, $A\rightarrow B$ follows first order kinetics. The time taken for 0.8 mole of A to produce 0.6 mole of B is 1h. what is the time taken for the conversion of 0.9 mole of A to 0.675 mole of B? **[CBSE AIPMT 2003]**

(A) 0.25h
(B) 2h
(C) 1 h
(D) 0.5h

6. The temperature dependence of rate constant (k) of a chemical eaction is written in terms of Arrhenius equation, $k=Ae^{-E^*/RT}$, Activation energy (E*) of the reaction can be calculated by plotting **[CBSE AIPMT 2003]**

(A) $\log k$ vs $\frac{1}{T}$
(B) $\log k$ vs $\frac{1}{\log T}$
(C) k vs T
(D) k vs $\frac{1}{\log T}$

7. If the rate of a reaction is equal to the rate constant, the order of the reaction is **[CBSE AIPMT 2003]**

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

8. The activation energy for a simple chemical reaction, $A\rightarrow B$ is E_α in forward direction. The activation energy for reverse reaction. **[CBSE AIPMT 2003]**

(A) can be less than or more than E_a
(B) is always double of E_a
(C) is negative of E_a
(D) is always less than E_a

9. The rate of first order reaction is 1.5×10^{-2} mol L^{-1} min^{-1} at 0.5 M concentration of the reactant. The half-life on the reaction is. **[CBSE AIPMT 2004]**

(A) 0.383 min
(B) 23.1min
(C) 8.73 min
(D) 7.53 min

10. For a fistt order reaction, $A \rightarrow B$, the reaction rate at reactant concentration of 0.01 M is found to be 2.0×10^{-5} mol L^{-1} s^{-1}. The half-life period of the reaction is **[CBSE AIPMT 2005]**

(A) 220s
(B) 30s
(C) 300s
(D) 347s

11. The rate of reaction between two reactants A and B decreases by a factor of4, if the concentration of reactant B is doubled. The order of this reaction with respect to reactant B is **[CBSE AIPMT 2005]**

(A) -1
(B) -2
(C) 1
(D) 2

MOCK TEST

STRAIGHT OBJECTIVE TYPE

1. For the reaction $2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$, if concentration of NO_2 in 100 seconds is increased by 5.2×10^{-3}m. Then rate of reaction will be

(A) $1.3\times10^{-5}ms^{-1}$ **(B)** $5\times10^{-4}ms^{-1}$ **(C)** $7.6\times10^{-4}ms^{-1}$ **(D)** $2\times10^{-3}ms^{-1}$

(E) $2.5\times10^{-5}ms^{-1}$

2. A first order reaction complete its 10% in 20 minutes then time required to complete its 19% is

(A) 30 minutes **(B)** 40 minutes **(C)** 50 minutes **(D)** 38 minutes

(E) 45 minutes

3. If a substance with half life 3 days is taken at other place in 12 days. What amount of substance is left now

(A) 1/4 **(B)** 1/8 **(C)** 1/16 **(D)** 1/32

4. The half-life of a first order reaction having rate constant $K = 1.7 \times 10^{-5}\ s^{-1}$ is

(A) 12.1 h **(B)** 9.7 h **(C)** 11.3 h **(D)** 1.8h

5. For the reaction $A + B \rightarrow C$, it is found that doubling the concentration of A increases the rate by 4 times, and doubling the concentration of B doubles the reaction rate. What is the overal order of the reaction.

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

6. Which of the following reactions end in finite time

(A) 0 order **(B)** 1st order **(C)** 2nd order **(D)** 3rd order

7. The rate constant of a reaction at temperature 200K is 10 times less than the rate constant at 400 K. What is the activation energy (E_a) of the reaction (R = gas constant)

(A) 1842.4 R **(B)** 921.2 R **(C)** 460.6 R **(D)** 230.3R

8. In respect of the equation $k = Ae^{-E_a/RT}$ in chemical kinetics, which one of the following statement is correct

(A) k is equilibrium constant **(B)** A is adsorption factor

(C) E_a is energy of activation **(D)** R is Rydberg's constant

9. The rate constant is doubled when temperature increases from 27°C to 37°C. Activation energy in kJ is

(A) 34 **(B)** 54 **(C)** 100 **(D)** 50

10. The activation energy of a reaction is zero. The rate constant of this reaction

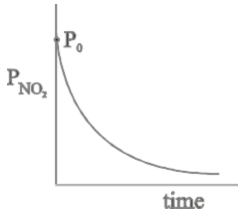
(A) Increases with increase of temperature **(B)** Decreases with an increase of temperature

(C) Decreases with decrease of temperature **(D)** Is independent of temperature

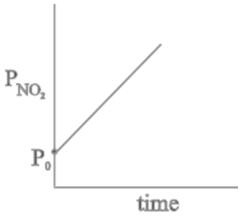
11. $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$

When N_2O_5 decompose, its $t_{1/2}$ does not change with its changing pressure during the reaction. So which one is the correct representation for "pressure of NO_2" vs "time" during the reaction when initial $P_{N_2O_5}$ is equals to P_0.

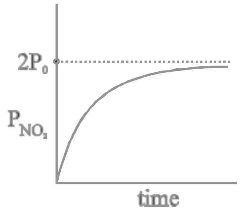
(A)



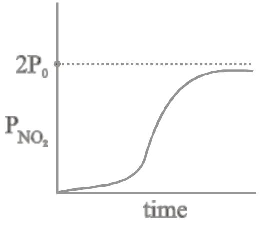
(B)



(C)



(D)



12. Choose the correct option :

(A) Antineutrino can be detected during the emission of :

(i) α-rays **(ii)** β-particles **(iii)** Protons **(iv)** X-rays

(B) Which has magic number of neutrons :

(i) ${}^{27}_{13}Al$ **(ii)** ${}^{209}_{83}Bi$ **(iii)** ${}^{238}_{92}U$ **(iv)** ${}^{56}_{26}Fe$

CHAPTER 08

COORDINATION COMPOUNDS

Coordination is critical to any large scale event. That's the lesson we are learning.

''LYNETTEMILLER''

INTRODUCTION

Compounds formed due to combination of two or more simple stable salts, which retain their identity is solid as well as in dissolved state, are called coordination compounds. These are backbone of modern inorganic and bio-inorganic chemistry and chemical industry. The concept of co-ordination compounds arises from the complex formation tendency of transition elements. These compounds play a vital role in our lives, as chlorophyll of plants, vitamin B_{12} and haemoglobin of animal blood are the co-ordination compounds of Mg, Co and Fe respectively. The co-ordination compounds play important role in analytical chemistry , polymerisation reactions, metallurgy and refining of metals, photography, water purification etc. Co-ordination compounds also find many applications in electroplating, textile dyeing and medicinal chemistry.

T TS

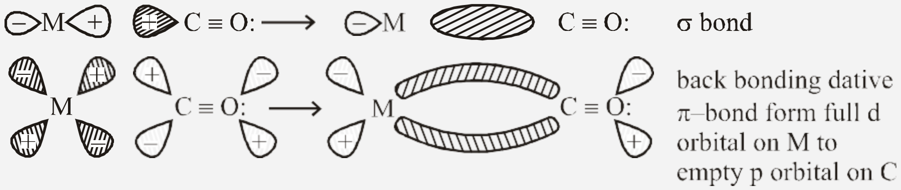
(1) Synergic Bonding :

Ligand which donate electron pair to central metal ion & form coordinate σ bond but simulataneously 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 atomn can donate its electron pair of a transition metal atom (M), forming OC→M coordinate bond.

Since the metal atom in metal carbonyl is in zero oxidation state, the formation of M → 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 M → CO π bond by the overlap between an appropriate filled orbital on the metal atom and empty π_y^* or π_2^* 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

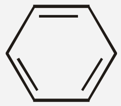
(a) M–C bond strength increases; M–C bond length decreases; because double bond character increases

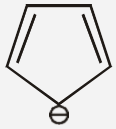
(b) C–O bond strength decreases; C–O bond length increases; because bond order of C–O decreases, electron density in ABMO of CO increases.

(2) □-donor and □-acceptor ligands :

ligands w2hich donote π electron to central metal ion & also accept electron density from central metal ion through synergic bonding.

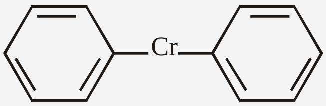
(i) $H_2C{=}CH_2$ (η^2 - ethylene) : it is a 2π electron donor

(ii)  (η^6 - benzene) : it is a 6π electron donor

(iii)  / $[C_5H_5]^-$ (η^5 - cyclopentadienyl) : it is a 6π electron donor

For Example

(a) $[Cr(\eta^6–C_6H_6)_2]$



sandwich compound

(b) $[Fe(\eta^5–C_5H_5)_2]$ ferrocene (sandwich compound)

(c) $K[PtCl_3(\eta^2–C_2H_4)]$ (Zeise salt)

ISOMERISM IN COMPLEXES

Complex compounds that have the same molecular formula but have different structural /spacial arrangements of ligands are called isomers. These are of two types, namely structural and stereo isomers.

Type of isomerism

Structural isomerism
- Ionisation isomerism
- Hydrate isomerism
- Linkage isomerism
- Coordination isomerism
- Coordination position isomerism

Space / stereo isomerism
- Geometrical isomerism
- Optical isomerism

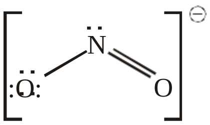
STRUCTURAL ISOMERISM

(i) **Ionisation Isomerism :** This type of isomerism is due to the exchange of groups between the complex ion and ions outside it. $[Co(NH_3)_5Br]SO_4$ is red -violet. An aqueous solution of it gives a white precipitate of $BaSO_4$ with $BaCl_2$ solution, thus confirming the presence of free SO_4^{2-} ions. In contrast $[Co(NH_3)_5SO_4]Br$ is red. A solution of this complex does not give a positive sulphate test with $BaCl_2$. It does give a cream coloured precipitate of AgBr with $AgNO_3$, thus confirming the presence of free Br^- ions. Other examples of ionisation isomerism are $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$ and $[Co(en)_2NO_2.Cl]SCN$, $[Co(en)_2NO_2.SCN]Cl$ and $[Co(en)_2Cl.SCN]NO_2$.

(ii) **Hydrate isomerism :** These isomers arise by the exchange of groups in the complex ion with water. Three isomers of $CrCl_3.6\ H_2O$ are known. From conductivity measurements and quantitative precipitation of the ionised Cl^-, they have been given the following

$[Cr(H_2O)_6]Cl_3$	Violet
$[Cr(H_2O)_5Cl]Cl_2.H_2O$	Green
$[Cr(H_2O)_4Cl_2]Cl.2H_2O$	Dark Green

(iii) **Linkage Isomerism :** This type of isomerism arises when the ligand attached to the central metal ion of a complex in different ways. Such ligands are called ambident ligands. Nitrite ion has electron pairs available for co-ordination both on N and O atoms.



Ex.

(a)	$[Co(NH_3)_5ONO]Cl_2$ pentaamminenitrito-o-cobalt(III) chloride **(red)**	and	$[Co(NH_3)_5NO_2]Cl_2$ pentaamminenitrito-N-cobalt-(III)-chloride **(yellow)**
(b)	$[Mn(CO_5).SCN]^+$ pentacarbonylthiocyanto –S-manganese (II) ion	and	$[Mn(CO_5)(NCS]^+$ pentacarbonylthiocyanato –N-manganese (II) ion

1. $CH_3B(OCH_3)$ is an organometallic compound but $B(OCH_3)$ is not.

2. The closed ring complexes formed by polydenatate ligands are called Chelates. Chelation leads to stability.

3. Estimation of nickel (II) is done by complexing with dimethyl glyoxime (DMG) whereas that of Ca^{+2} and Mg^{2+} ions is done by titrating against EDTA.

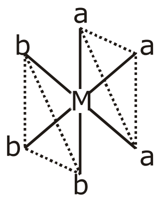
4. Complex in which ligands can be substituted by other ligands are called labile complexes. For example $[Cu(NH_3)_4]^{2+}$ is a labile complex because NH_3 ligands can be substituted by CN^- ligands.

$$[Cu(NH_3)_4]^{2+} + 4\,CN^- \rightarrow [Cu(CN)_4]_2 + 4NH_3$$

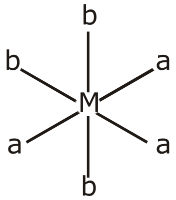
(less stable) (more stable)

5. Another type of geometrical isomerism is also shown by octahedral complexes of the type Ma_3b_3.

if each trio of donor atoms occupy adjacent positions at the corner of an octahedral face, then it is called facial (fac) isomer and when the position are around the meridian of the octahedron, then it is called meridional (mer) isomer.



fac-form



Mer-form

6. Haemoglobin is a complex of Fe, chlorophyll is a complex of Mg, vitamin B_{12} is a complex of Co.

7. σ-bond organometallic compounds generally contains a non-transition metal linked to carbon atom of alkyl group by σ bond. For example eg. R-MgX.

8. p-bonded organometallics are formed by donation of p-electrons of double bond to the metal atom. For example Zeise's salt $K[PtCl_3\,\eta^2 C_2H_4]$ and Ferrocene $Fe(\eta^5\text{-}C_5H_5)_2$

9. Grignard's reagent is one of the most useful organometallic compounds. Due to the high polarity of $(C^{\delta}–Mg^{\delta+})$ bond, it can be used to synthesise many organic compounds.

SOLVED EXAMPLE

Ex. 1 A solution containing 0.319 gm of complex $CrCl_3 \cdot 6H_2O$ was passed through cation exchanger and the solution given out was neutralised by 28.5 ml of 0.125 M NaOH. The correct formula of the complex will be: [molecular weight of complex = 266.5]

(A) $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$
(B) $[Cr(H_2O)_6]Cl_3$
(C) $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$
(D) All are correct

Ans. **(B)**

Sol. $Cl^- = HCl = NaOH$

$$nCl^- + nH^+ \longrightarrow nHCl$$

Thus 1 mol of complex will form n mol of HCl
1 mole of complex = n mol of HCl = n mole of NaOH

mole of complex $= \dfrac{0.319}{266.5} = 0.0012$; mole of NaOH

used $= \dfrac{28.5 \times 0.125}{1000} = 0.0036$

So 0.0012 mole of complex = 0.0036 mole of NaOH = 0.0036 mole of HCl

1 mole of complex $= \dfrac{0.0036}{0.0012} = 3$ mole of HCl

$\therefore$ n = 3

So complex is $[Cr(H_2O)_6]Cl_3$.

Ex. 2 Calculate the effective atomic number of the metal atoms in the following complexes / complex ions.

(A) $[Cr(CO)_6]$ **(B)** $[Fe(CN)_6]^{3-}$
(C) $[Co(CN)_6]^{4-}$ **(D)** $[Ni(NH_3)_6]^{2+}$

[Cr = 24 ; Fe = 26; Co = 27 and Ni = 28 as atomic numbers]

Ans. **(A)** 36 **(B)** 35
(C) 37 **(D)** 38

Sol. EAN = Number of electrons in metal atom or ion + Number of electrons donated by ligands to metal.

(A) $[Cr^0(CO)_6]$; EAN = 24 + 12 = 36 ;
(B) $[Fe^{III}(CN)_6]^{3-}$; EAN = 23 + 12 = 35
(C) $[Co^{II}(CN)_6]^{4-}$; EAN = 25 + 12 = 37 ;
(D) $[Ni^{II}(NH_3)_6]^{2+}$; EAN = 26 + 12 = 38

Ex. 3 Consider the following complexes :

(i) K_2PtCl_6 **(ii)** $PtCl_4 \cdot 2NH_3$
(iii) $PtCl_4 \cdot 3NH_3$ **(iv)** $PtCl_4 \cdot 5NH_3$

their electrical conductance in aqueous solutions are :

(A) 256, 0, 97, 404 **(B)** 404, 0, 97, 256
(C) 256, 97, 0, 404 **(D)** 404, 97, 256, 0

Ans. **(A)**

Sol. The electrical conductance of the complexes depend upon the number of ions given by them in the aqueous solutions.

(i) $K_2[PtCl_6] \xrightleftharpoons{aq} 2K^+(aq) + [PtCl_6]^{2-}(aq)$

(ii) $[Pt(NH_3)_2Cl_4] \xrightleftharpoons{aq} [Pt(NH_3)_2Cl_4](aq)$

(iii) $[Pt(NH_3)_3Cl_3]Cl \xrightleftharpoons{aq} [Pt(NH_3)_3Cl_3]^+(aq) + Cl^-(aq)$

(iv) $[Pt(NH_3)_5Cl]Cl_3 \xrightleftharpoons{aq} [Pt(NH_3)_5Cl]^{3+} + 3Cl^-$

Complex	**Number of ions**	**Expected electrical conductance**
(i) $K_2[PtCl_6]$	3	256
(ii) $[Pt(NH_3)_2Cl_4]$	0	0
(iii) $[Pt(NH_3)_3Cl_3]Cl$	2	97
(iv) $[Pt(NH_3)_5Cl]Cl_3$	4	404

So, the correct option is **(A)**.

Ex. 4 Give the order of chelating effect of following ligands.

(i) $C_2O_4^{2-}$ **(ii)** EDTA
(iii) dien

(A) iii > ii > i **(B)** i > ii > iii
(C) ii > iii > i **(D)** i > iii > ii

Ans. **(C)**

Sol. As number of donor atoms increases the number of bonds increase. So the chelating effect of ligands increase as oxalato, dien and EDTA has two, three and six donor atoms respectively.

Ex. 5 Write the structural formula corresponding to each of the following IUPAC names :

(A) potassium tetracyanidozincate (II)
(B) tetracarbonyl nickel (0)
(C) potassium tetracyanonickelate (0)
(D) potassium tris(oxalato)aluminate (III)

Ans. **(A)** $K_2[Zn^{II}(CN)_4]$ **(B)** $[Ni^0(CO)_4]$
(C) $K_4[Ni^0(CN)_4]$ **(D)** $K_3[Al^{III}(C_2O_4)_3]$

Sol. Refer IUPAC rule.

Exercise # 1 SINGLE OBJECTIVE NEET LEVEL

1. In $K_4Fe(CN)_6$

(A) (CN) are linked with primary valency
(B) (CN) are linked with secondary valency
(C) K are linked with secondary valency
(D) K are linked with non-ionic valency

2. The co-ordination number of copper in cuprammonium sulphate is

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

3. Which of the following acts as a bidentate ligand in complex formation

(A) Acetate
(B) Oxalate
(C) Thiocyanate
(D) EDTA

4. The co-ordination number of cobalt in the complex $[Co(en)_2Br_2]Cl_2$ is

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

5. Which of the following ligands forms a chelate

(A) Acetate
(B) Oxalate
(C) Cyanide
(D) Ammonia

6. According to Werner's theory

(A) Primary valency can be ionized
(B) Secondary valency can be ionized
(C) Primary and secondary valencies both cannot be ionized
(D) Only primary valency cannot be ionized

7. Which of the following is not true for ligand-metal complex

(A) Larger the ligand, the more stable is the metal-ligand bond
(B) Highly charged ligand forms strong bond
(C) Larger the permanent dipole moment of ligand, the more stable is the bond
(D) Greater the ionization potential of central metal, the stronger is the bond

8. What is the co-ordination number of the metal in $[Co(en)_2Cl_2]^+$

(A) 4
(B) 5
(C) 6
(D) 3

9. Bidentate ligand is

(A) CN^-
(B) Ethylene diammine (en)
(C) SCN^-
(D) EDTA

10. The coordination number of Pt in $[Pt(NH_3)_4Cl_2]^+$ ion is

(A) 2
(B) 4
(C) 6
(D) 8

11. Which is the example of hexadentate ligand

(A) 2, 2-dipyridyl
(B) Dimethyl glyoxime
(C) Aminodiacetate ion
(D) Ethylene diammine tetra acetate ion [EDTA]

12. The coordination number of a metal in coordination compounds is

(A) Same as primary valency
(B) Sum of primary and secondary valencies
(C) Same as secondary valency
(D) None of these

13. Ligand in a complex salt are

(A) Anions linked by coordinate bonds to a central metal atom or ion
(B) Cations linked by coordinate bonds to a central metal atom or ion
(C) Molecules linked by coordinate bonds to a central metal atom or ion
(D) Ions or molecules linked by coordinate bonds to a central metal atom or ion

14. A group of atoms can function as a ligand only when

(A) It is a small molecule
(B) It has an unshared electron pair
(C) It is a negatively charged ion
(D) It is a positively charged ion

15. Which of the following complexes show six coordination number

(A) $[Zn(CN)_4]^{2-}$
(B) $[Cr(H_2O)_6]^{3+}$
(C) $[Cu(CN)_4]^{2-}$
(D) $[Ni((NH_3)_4]^{2+}$

16. How many ions are produced in aqueous solution of $[Co(H_2O)_6]Cl_2$

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

17. IUPAC name of $[Pt(NH_3)_3(Br)(NO_2)Cl]Cl$ is

(A) Triamminechlorobromonitroplatinum (IV) chloride
(B) Triamminebromonitrochloroplatinum (IV) chloride
(C) Triamminebromochloronitroplatinum (IV) chloride
(D) Triamminenitrochlorobromoplatinum (IV) chloride

Exercise # 2

SINGLE OBJECTIVE

AIIMS LEVEL

1. Which of the following is not correctly matched ?

(A) $[Fe(en)_3]^{3+}$ - sp^3d^2 and paramagnetic

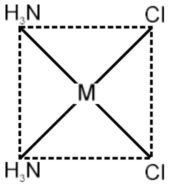
(B) $[FeCl_4]^{2-}$ - sp^3 and paramagnetic

(C) $[Fe(CN)_6]^{3-}$ - d^2sp^3 and paramagnetic

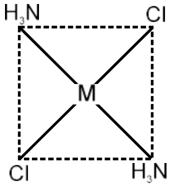
(D) $[Fe(CO)_2(NO^+)_2]$ - sp^3 and diamagnetic

2. Which of the following isomers of $[M(NH_3)_2Cl_2]$ would react with silver oxalate ($Ag_2C_2O_4$) to give a coordination compound ?

(A)



(B)



(C) Both **(D)** None

3. The complex $K_4[Zn(CN)_4(O_2)_2]$ is oxidised into $K_2[Zn(CN)_4(O_2)_2]$, then which of the following is correct ?

(A) Zn (II) is oxidised into Zn (IV)

(B) Paramagnetic moment decreases

(C) O – O bond length increases

(D) Paramagnetic moment increases

4. The hybridisation of $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ are :

(A) both sp^3d^2

(B) both d^2sp^3

(C) sp^3d^2 and d^2sp^3 respectively

(D) d^2sp^3 and sp^3d^2 respectively

5. Consider the following statements ;

S1 : The $[Co(ox)_3]^{3-}$ complex is diamagnetic and gains stability through chelation.

S2 : The $[Co(NO_2)_6]^{4-}$ is inner orbital complex involving d^2sp^3 hybridisation and is paramagnetic.

S3 : The complex $[PtCl_4]^{2-}$ is square planar and diamagnetic.

and arrange in the order of true / false

(A) T T T **(B)** F F T
(C) T F T **(D)** T T F

6. Select the correct statement ;

(A) Potassium ferrocyanide and potassium ferricyanide can be differentiated by measuring the solid state magnetic moment.

(B) The complex $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ can be differentiated by adding aqueous solution of barium chloride

(C) The complex $[Co(NH_3)_5Cl]Br$ and $[Co(NH_3)_5Br]Cl$ can be differentiated by adding aqueous solution of silver nitrate.

(D) All of these

7. All the following complexes show decrease in their weights when placed in a magnetic balance then the group of complexes having tetrahedral geometry is :

I $Ni(CO)_4$
II $K[AgF_4]$
III $Na_2[Zn(CN)_4]$
IV $K_2[PtCl_4]$
V $[RhCl(PPh_3)_3]$

(A) II , III , V **(B)** I , II , III
(C) I , III, IV **(D)** none of these

8. The complex $[Fe(H_2O)_5NO]^{2+}$ is formed in the brown ring test for nitrates when freshly prepared $FeSO_4$ solution is added to aqueous solution of NO_3^- ions followed by addition of conc. H_2SO_4. Select correct statement about this complex.

(A) Hybridisation of iron is sp^3d^2.

(B) Iron has +1 oxidation state.

(C) It has magnetic moment of 3.87 B. M. confirming three unpaired electrons in Fe.

(D) All the above are correct statements.

9. Which of the following has dsp^2 hybridisation and is diamagnetic in nature ?

(I) $Na_4[Cr(CO)_4]$ **(II)** $[Ni(DMGH)_2]$
(III) $[PtHBr(PEt_3)_2]$ **(IV)** $[Ag(SCN)_4]^{3-}$
(V) $[AuBr_4]^-$

(A) I, II, IV only **(B)** I, III, IV, V only
(C) II, III, V only **(D)** III, V only

10. Of the following complex ions, one exhibits isomerism. That is:

(A) $[Ag(NH_3)_2]^+$ **(B)** $[Co(NH_3)_5NO_2]^{2+}$
(C) $[Pt(en)Cl_2]$ **(D)** $[Co(NH_3)_5Cl]^{2+}$

Exercise # 3 PART - 1 MATRIX MATCHCOLUMN

1. Match the complexes given in column-I and the characteristic(s) given in column-II.

Column – I	**Column –II**
(Complexes)	**(characteristics)**
(A) [Ni (CO)$_4$]	**(p)** sp^3 hybridisation
(B) [AgF$_4$]$^-$	**(q)** Diamagnetic
(C) [Zn (CN)$_4$]$^{2-}$	**(r)** dsp^2
(D) [RhCl(PPh$_3$)$_3$]	**(s)** Unidentate ligand.
	(t) + 3 oxidation state of metal ion

2. Match the complexes given in column-I and the magnetic properties given in column-II.

Column I	**Column II**
(Complexes)	**(Magnetic properties)**
(A) [NiCl$_2$(PPh$_3$)$_2$]	**(p)** Paramagnetic with 1 unpaired electrons
(B) V(CO)$_6$	**(q)** Paramagnetic with 2 unpaired electrons
(C) [Cr(CN)$_6$]$^{4-}$	**(r)** Paramagnetic with 3 unpaired electrons
(D) Ni(CO)$_4$	**(s)** Diamagnetic

3. Match the complexes listed in column-I with type of hybridisation listed in column-II.

Column I	**Column II**
(A) [Au F$_4$]$^-$	**(p)** dsp^2 hybridisation
(B) [Cu(CN)$_4$]$^{3-}$	**(q)** sp^3 hybridisation
(C) [Co(NH$_3$)$_6$]$^{3+}$	**(r)** sp^{3}d^2 hybridisation
(D) [Fe(H$_2$O)$_5$ NO]$^{2+}$	**(s)** d^{2}sp^3 hybridisation

4. Match the pair of complexes given in column-I and the characteristic(s) given in column-II.

Column - I	**Column- II**
(A) (NH$_4$)$_2$[NiCl$_4$] and (NH$_4$)$_2$[Ni(CN)$_4$]	**(p)** Both show same electrical conductance.
(B) CoCl$_3$.6NH$_3$ and PtCl$_4$.5NH$_3$	**(q)** Both show same effective atomic number.
(C) [Pt(NH$_3$)$_2$Cl$_2$] and (NH$_4$)$_2$[PtCl$_4$]	**(r)** Both show same primary valencies.
(D) K$_2$[Fe(H$_2$O)$_6$] and K$_4$[FeCl$_6$]	**(s)** Both gives white participate with AgNO$_3$ solution.

5. Match the complexes given in column-I and the characteristic(s) given in column-II.

Column – I	**Column – II**
(Complexes)	**(characteristics)**
(A) [Ni (CO)$_4$]	**(p)** Tetrahedral
(B) [Fe(NO)$_2$(CO)$_2$]	**(q)** π back bonding
(C) [Ni(PF$_3$)$_4$]	**(r)** diamagnetic
(D) [PtCl$_3$(C$_2$H$_4$)]$^-$	**(s)** One of the ligand is three electron donor.

6. Match the complexes given in column-I and the characteristic(s) given in column-II.

Column – I	**Column –II**
(Complexes)	**(characteristics)**
(A) [Co(H$_2$O)$_6$]$^{3+}$	**(p)** d^{2}sp^3
(B) [CoF$_6$]$^{3-}$	**(q)** sp^{3}d^2
(C) [Co(NO$_2$)$_6$]$^{3-}$	**(r)** diamagnetic
(D) [Co(ox)$_3$]$^{3-}$	**(s)** paramagnetic

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. Shape of $Fe(CO)_5$ is **[CBSE AIPMT 2000]**
(A) Octahedral **(B)** square planar
(C) trigonl bipyramidal **(D)** square pyramidal

2. In the separation of Cu^{2+} and Cd^{2+} of IInd group in qualitative analysis of cations, tetrammine copper (II) sulphate and tetrammine copper (II) sulphate and tetrammine cadmium (II) sulphate react with KCN tofrom the corresponding cyano complexes, which one of the following pairs of the complexes and their relative stability enables the separation of Cu^{2+} and Cd^{2+} ? **[CBSE AIPMT 2001]**
(A) $K_3[Cu(CN)_4]$: less stable and $K_2[Cd(CN)_4]$: more stable
(B) $K_3[Cu(CN)_4]$: more stable and $K_2[Cd(CN)_4]$: less stable
(C) $K_2[Cu(CN)_4]$: less stable and $K_2[Cd(CN)_4]$: more stable
(D) $K_2[Cu(CN)_4]$: more stable and $K_2[Cd(CN)_4]$: less stable

3. Which one of the following complexes will have four isomers **[CBSE AIPMT 2001]**
(A) $[Co(en)_3]Cl_3$
(B) $[Co(en)_2Cl_2]Cl$
(C) $[Co(PPh_3)_2(NH_3)Cl_2]Cl$
(D) $[Co(PPh_3)_3CI]Cl_2$

4. Which of the following will exhibit maximum ionic conductivity ? **[CBSE AIPMT 2001]**
(A) $K_4[Fe(CN)_6]$ **(B)** $[Co(NH_3)_6]Cl_3$
(C) $[Cu(NH_3)_4]Cl_2$ **(D)** $[Ni(CO)_4]$

5. Which statement is incorrect ? **[CBSE AIPMT 2001]**
(A) $Ni(CO)_4$ - tetrahedral, paramagnetic
(B) $[Ni(CN_4]^{2-}$ square planar, diamagnetic
(C) $Ni(CO)^4$- tetrahedral, diamagnetic
(D) $[Ni(Cl)_4]^{2-}$ tetrahedral, paramagnetic

6. Coordination number of Ni in $[Ni(C_2O_4)_3]^{4-}$ is **[CBSE AIPMT 2000]**
(A) 3 **(B)** 6
(C) 4 **(D)** 2

7. Which of the following organometallic compounds is σ and π - bonded ? **[CBSE AIPMT 2001]**
(A) $[Fe(\eta^5\text{-}C\ H\ )\ ]$ **(B)** $K[PtCl(\eta^2\text{-}C\ H\ )]$

8. Which of the following will give maximum number of isomers?
(A) $[Co(NH_3)_4Cl_2]$ **(B)** $[Ni(en)(NH_3)_4]^{2+}$
(C) $[Ni(C_2O_4)(en)_2]^{2-}$ **(D)** $[Cr(SCN)_2(NH_3)_4]^{+}$

9. Atomic number of Cr and Fe are respectively 24 and 26, which of the following is paramagnetic with the spin of electron? **[CBSE AIPMT 2002]**
(A) $[Cr(CO)_6]$ **(B)** $[Fe(CO)_5]$
(C) $[Fe(CN)_6]4^{-}$ **(D)** $[Cr(NH_3)_6]^{3+}$

10. The hypothetical complex chloro diaquatriammine cobalt (III) chloride can be represented as **[CBSE AIPMT 2002]**
(A) $[CoCl(NH_3)_3(H_2O)_2]Cl_2$
(B) $[Co(NH_3)_3(H_2O)_2]Cl_2$
(C) $[Co(NH_2)_3(H_2O)_2]Cl$
(D) $[Co(NH_3)_3(H_2O)_3]Cl_3$

11. Which one of the folloiwng octahedral complexes will not show geemetrical isomerism? (A and B are monodentate ligands) **[CBSE AIPMT 2003]**
(A) $[MA_4B_2]$ **(B)** $[MA_5B]$
(C) $[MA_2B_4]$ **(D)** $[MA_3B_3]$

12. According to IUPAC nomenclature sodium nitroprusside is named as **[CBSE AIPMT 2003]**
(A) sodium pentacyanonitrosyl ferrate (II)
(B) sodium pentacyanonitrosyl ferrate (III)
(C) sodium nitoferricyanide
(D) sodium nitroferrocyanide

13. The number of unpaired electrons in the complex ion $[COF_6]^{3-}$ is (At.no.of Co =27) **[CBSE AIPMT 2003]**
(A) 3 **(B)** 2
(C) 2 **(D)** 0

14. Among the following which is not the π– bonded organometallic compound ? **[CBSE AIPMT 2003]**
(A) $K[PtCl_3(\eta^2\text{-}C_2H_4)]$ **(B)** $Fe(\eta^5\text{-}C^5H_5)_2$
(C) $Cr(\eta^6\text{-}C_6H_6)_2$ **(D)** $(CH_3)_4Sn$

15. Which of the following coordination compounds would exhibit optical isomerism?
(A) Pentaamminenitrocobalt (III) iodide
(B) Diamminedichloroplatinum (ii)
(C) Trans-Dicyanobis (ethylenediamine) chromium (III) chloride

(C) $[Co(CO)_5NH_3]^{2+}$ **(D)** $Fe(CH_3)_3$ **(D)** Tris- (ethylenediamine) cobalt (III) bromide

MOCK TEST

STRAIGHT OBJECTIVE TYPE

1. All the following complex ions are found to be paramagnetic

$P : [FeF_6]^{3-}$; $Q : [CoF_6]^{3-}$; $R : [V(H_2O)_6]^{3+}$; $S : [Ti(H_2O)_6]^{3+}$

The correct order of their paramagnetic moment (spin only) is

(A) $P > Q > R > S$ **(B)** $P < Q < R < S$ **(C)** $P = Q = R = S$ **(D)** $P > R > Q > S$

2. Which of the following statement(s) most likely to be incorrect?

(A) $Ti(NO_3)_4$ is a colourless compound **(B)** $[Cu(NCCH_3)_4]^+ BF_4^-$ is a colourless compound

(C) $[Cr(NH_3)_6]^{3+} 3Cl^-$ is a colourless compound **(D)** $K_3[VF_6]$ is colourless compound

3. Amongst the following, the species with tetrahedral geometry is :

(A) $[Pd(CN)_4]^{2-}$ **(B)** $[Ni(CN)_4]^{2-}$ **(C)** $[PdCl_4]^{2-}$ **(D)** $[NiCl_4]^{2-}$

4. Which of the following statements is correct?

(A) Potassium ferrocyanide is diamagnetic where as potassium ferricyanide is paramagnetic.

(B) Crystal field splitting in ferrocyanide ion is greater than that of ferricyanide ion.

(C) The geometry of $Ni(CO)_4$ and $[NiCl_2(PPh_3)_2]$ are tetrahedral.

(D) **(A)** & **(C)** both

5. Amongst $[Co(ox)_3]^{3-}$, $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$:

(A) $[Co(ox)_3]^{3-}$ and $[CoF_6]^{3-}$ are paramagnetic and $[Co(NH_3)_6]^{3-}$ is diamagnetic.

(B) $[Co(ox)_3]^{3-}$ and $[Co(NH_3)_6]^{3+}$ are paramagnetic and $[CoF_6]^{3-}$ is diamagnetic.

(C) $[Co(ox)_3]^{3-}$ and $[Co(NH_3)_6]^{3+}$ are diamagnetic and $[CoF_6]^{3-}$ is paramagnetic.

(D) $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$ are paramagnetic and $[Co(ox)_3]^{3-}$ is diamagnetic.

6. All the following complex show decreases in their weights when placed in a magnetic balance then the group of complexes having tetrahedral geometry is :

(i) $Ni(CO)_4$ **(ii)** $K[AgF_4]$ **(iii)** $Na_2[Zn(CN)_4]$ **(iv)** $K_2[PtCl_4]$

(v) $[RhCl(PPh_3)_3]$

(A) (ii), (iii), (v) **(B)** (i), (ii), (iii) **(C)** (i), (iii), (iv) **(D)** None of these

7. $[Fe(en)_2(H_2O)_2]^{2+} + en \rightarrow complex(X)$. The correct statement about the complex (X) is :

(A) It is a low spin complex **(B)** It is diamagnetic

(C) It shows geometrical isomerism **(D)** **(A)** and **(B)** both

8. On treatment of $[Ni(NH_3)_4]^{2+}$ with concentrated HCl, two compounds I and II having the same formula, $[Ni(NH_3)_2Cl_2]$ are obtained, I can be converted into II by boiling with dilute HCl. A solution of I reacts with oxalix acid to form $[Ni(NH_3)_2(C_2O_4)]$ where as II does not react. Point out the correct statement from the following.

(A) I cis, II trans; both tetrahedral **(B)** I cis, II trans; both square planar

(C) I trans, II cis; both tetrahedral **(D)** I trans, II cis; both square planar

9. The total number of isomers shown by $[Co(NH_3)_4(NO_2)_2]$ (NO_3) complex is :

(A) 10 **(B)** 6 **(C)** 4 **(D)** 12

10. In which of the following complex ion, the metal ion will never have t_{2g}^6, e_g^0 configuration according to CFT?

(A) $[FF_6]^{3-}$ **(B)** $[Fe(CN)_6]^{3-}$ **(C)** $[Fe(CN)_6]^{4-}$ **(D)** None of these

11. Which of the following polymerisation isomers of the compound having empirical formula $[Cr(NH_3)_3(NO_2)_3]$ has the lowest molecular mass?

(A) $[Cr(NH_3)_4(NO_2)_2]^+ [Cr(NH_3)_2(NO_2)_4]^-$ **(B)** $[Cr(NH_3)_6]^{3+}[Cr(NO_2)_6]^{3-}$

(C) $[Cr(NH_3)_5(NO_2)]^{2+}[Cr(NH_3)(NO_2)_5]^{2-}$ **(D)** All

CHAPTER 01

SOLID STATE

It seems probable to me that God, in the beginning, formed matter in solid, massy, hard, impenetrable, moveable particles.

''ISAAC NEWTON''

INTRODUCTION

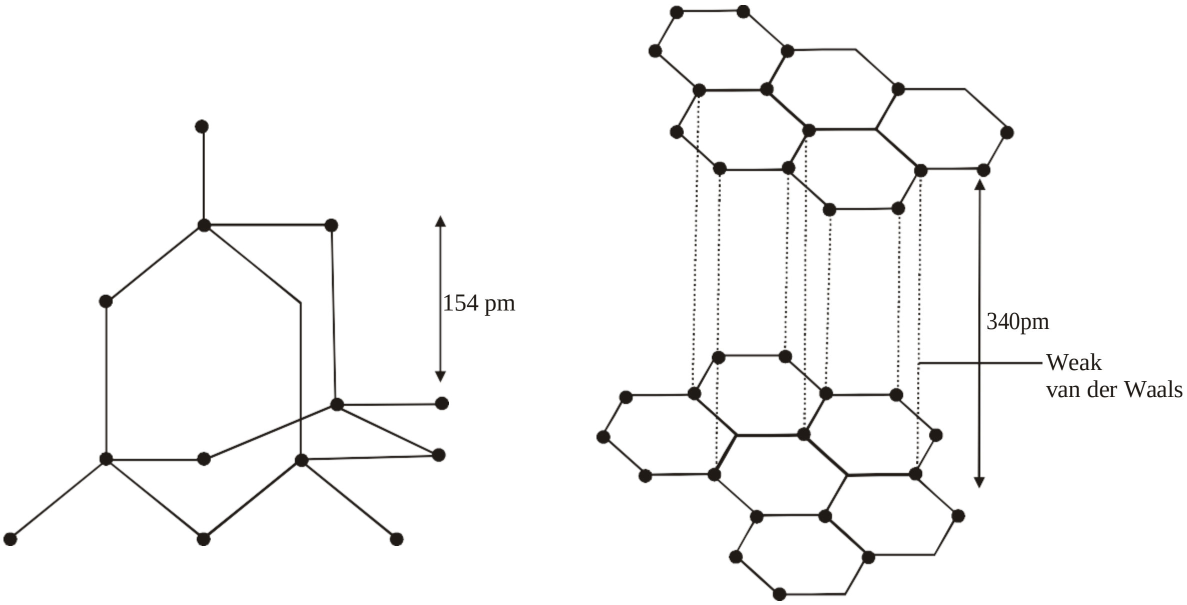
Matter can exist in three physical states namely ; solid, liquid and gas. Matter consists of tiny particles (atoms, ions or molecules). If the particles are very far off from one another, they behave like gases; nearer, they behave like liquids, and nearest, like solids. The three states of matter are thus known as the three states of aggregation from Latin word meaning **''Flacking together''**.

This chapter includes knowledge about

1. Most organised state of matter which includes study of various types of solids based upon arrangement of constituent particles in the bulk and different types of forces responsbile to bind the particles together.
2. Arrangement of unit cells in lattice and packing of lattice points in different arrangements.
3. Calculation of density of unit cell and unit cell dimension.
4. Calculation of packing efficiency of solids.
5. Types of voids, their locations and number of voids in different types of arrangements.
6. Imperfections or common defects in solids state.
7. Electrical and magnetic properties of solids.

3. **Covalent Solids (networks Solids) :** In these atoms are bonded together by covalent bond formation throughout the crystal. It means there is a continuous network of covalent bonds forming a giant three dimensional structure or giant molecule. Covalent bonds are strong and directional in nature. These solids are very hard, brittle and very high melting point. Due to absence of any free electrons or ions they are insulators. Their enthalpies of fusion are very high.

Example : Diamond, Graphite, Boron Nitride (BN), Silicon Carbide (SiC), SiO_2 (quartz) etc. are common examples of these solids.



(a) Diamond (b) Graphite

Structure of (a) Diamond & (b) Graphite

(a) Diamond : It has a three dimensional network of large number of sp^3 hybridised carbon atoms each bonded tetrahedrally to four more carbon atoms by single covalent bonds. It makes diamond extremely hard crystal with very high mp = 3843 K. Diamond does not conduct electricity at all.

(b) Graphite : Each carbon atom is sp2 hydridised and covalently bonded to three other carbon atoms of same layer by single bonds, forming a layer of hexagonal rings. At each carbon atom the fourth valence electron is available free, which moves among different layers and provides good electrical and thermal conducting nature to graphite. Different layers connect by van der wals forces. As the forces are quite weak, the layers can slide over each other and make graphite a soft, lubricating solid.

4. **Molecular Solids :** Their molecules are held together by dispersion forces, London forces, dipole-dipole forces or hydrogen bonds. On the basis of type of interactive forces these solids are studied under the following sub-headings.

(a) Non-Polar Molecular Solids : Either atoms (e.g., He, Ne, Ar) or molecules (e.g., H_2, I_2 and Cl_2) are bonded together by weak dispersion forces or London forces. These are non-conductor soft solids with low m.p. and low enthalpies of vaporisation. They are volatile in nature hence, at room temperature and pressure they are available in liquid or gaseous state.

e.g., Iodine, Solid H_2 and CO_2 (dry ice). naphthalene, Camphor etc.

(b) Polar Molecular Solids : Polar covalent molecules are held together by strong dipole-dipole forces. These are soft non-conducting solids with low Melting point and Boiling Points, which are still higher than non-polar molecular solids. They have high enthalpy of vaporisation.

Example : Solid HCl, NH_3 and SO_2 etc.

(c) Hydrogen Bonded Molecular Solids : Polar covalent molecules containing "H' atom as positive pole and N, O or F atom as negative pole are held together by intermolecular H-bonding. Under room temperature and pressure conditions they are generally volatile liquids or soft solids and non conductors ofelectricity.

Example : Ice

ETOOS KEY POINTS

(A) Super Cooled Liquid : like liquids amorphous solids have a tendency to flow, hence they are also called as pseudo solids or super cooled liquids. If we notice glass window pane of old buildings, we find them slightly thicker at the bottom than at the top. hence, glass is also called as super cooled liquid. Super cooled liquids can flow slowly under their own weight and lose shape and can be easily distorted.

(B) Isomorphous and Polymorphous Solids : Two or more solid substances existing in same crystalline form or structure are isomorphous to each other.

e.g., (i) $MfSO_4.\ 7H_2O$, $FeSO_4.\ 7H_2O$ and $ZnSO_4.\ 7H_2O$ are isomorphs

(ii) Na_2S and Ag_2S also show isomorphism

Existence of a substance in two or more crystalline forms having similar chemical composition but different arrangement of constituent particles is polymorphism.

e.g., ZnS in the form of zinc blende and wurtzite.

In case of elements polymorphism is also called allotropy and all crystalline allotropes are polymorphs to each other.

Ex. Identify molecular solid, covalent solid, ionic solid : $P_4(s)$, $S_8(s)$, SiC(s), $Al_2O_3(s)$, He (s), $Al_2Cl_6(s)$.

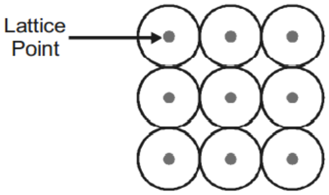
Sol. Molecular solid → P_4 (s), S_8 (s), He (s), Al_2Cl_6 (s)

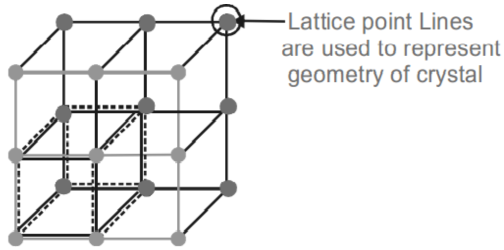
Covalent solid → SiC

Ionic solid → Al_2O_3(s).

Space Lattice/Crystalline Lattice/3–D Lattice

Space lattice is a regular arrangement of lattice points (atoms or ions or molecules showing how the particles are arranged at different sites in 3D -view.)





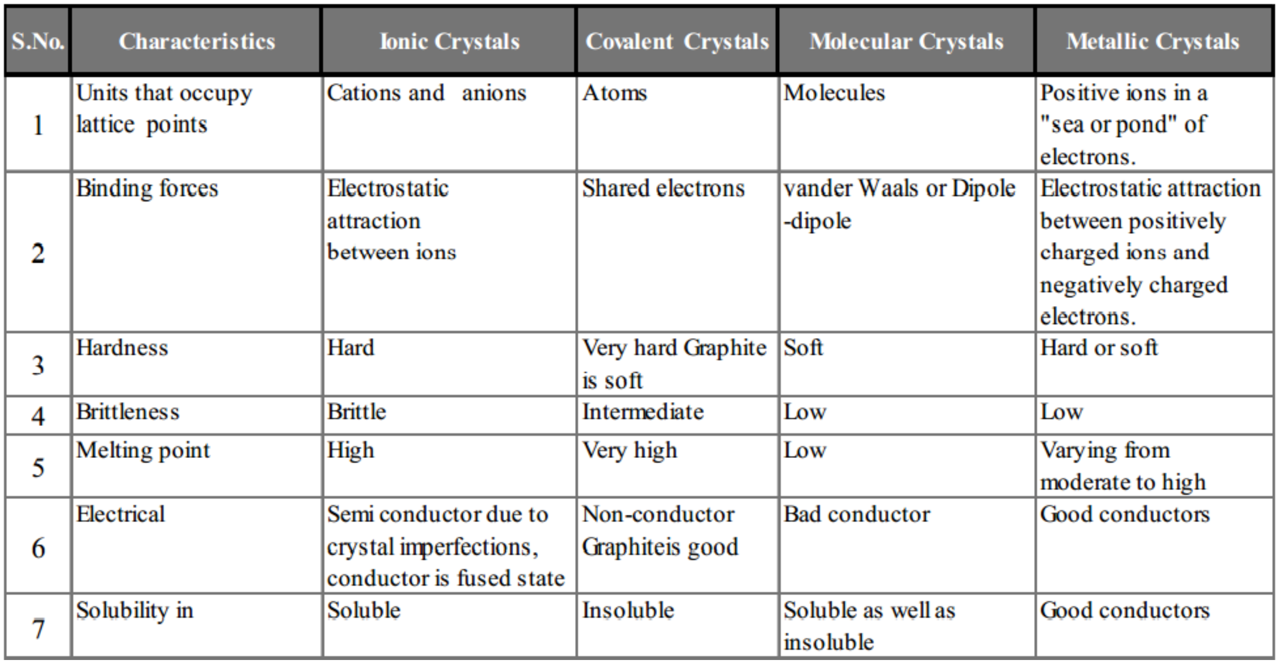
1. The three dimensional distribution of component particles in a crystal can be found by X-ray diffraction of different faces of the crystal.
2. On the basis of the classification of symmetry , the crystals have been divided into seven systems. These seven systems with the characteristics of their axes (Interfacial angles and intercepts) where some examples of each are given in the following table.

The crystal systems differ in length of unit cell edges (a, b and c) and the angles between the unit cell edges.

In cubic and trigonal (rhombohedral) systems, the three unit edges are of equal lengths but for the rest five systems it is not so. The interfacial angles are all 90º in the cubic, tetragonal and orthorhombic systems but it is not so for the rest four systems.

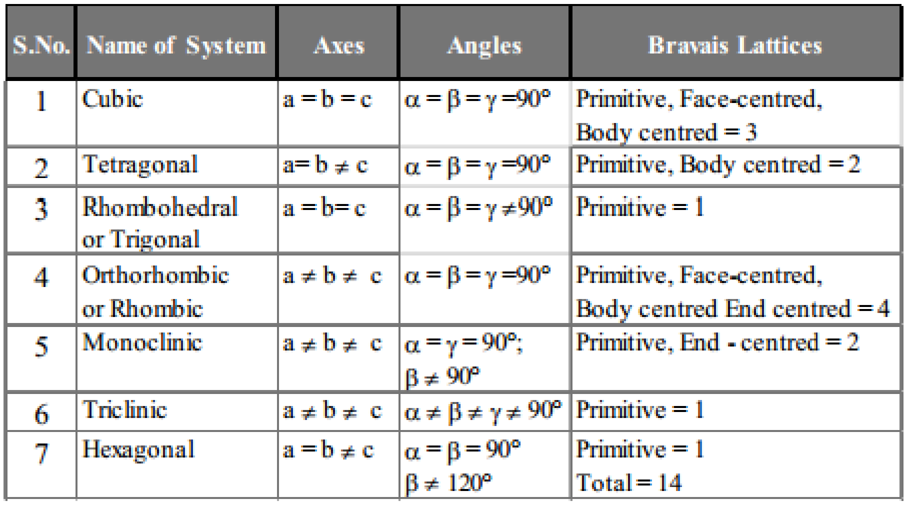
1. Various type of Criptals

Some Important Characteristics of Various types of Crystals



S.No.	Characteristics	Ionic Crystals	Covalent Crystals	Molecular Crystals	Metallic Crystals
1	Units that occupy lattice points	Cations and anions	Atoms	Molecules	Positive ions in a "sea or pond" of electrons.
2	Binding forces	Electrostatic attraction between ions	Shared electrons	vander Waals or Dipole -dipole	Electrostatic attraction between positively charged ions and negatively charged electrons.
3	Hardness	Hard	Very hard Graphite is soft	Soft	Hard or soft
4	Brittleness	Brittle	Intermediate	Low	Low
5	Melting point	High	Very high	Low	Varying from moderate to high
6	Electrical	Semi conductor due to crystal imperfections, conductor is fused state	Non-conductor Graphiteis good	Bad conductor	Good conductors
7	Solubility in	Soluble	Insoluble	Soluble as well as insoluble	Good conductors

The Seven Crystal Systems



S.No.	Name of System	Axes	Angles	Bravais Lattices
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Primitive, Face-centred, Body centred = 3
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, Body centred = 2
3	Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Primitive = 1
4	Orthorhombic or Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, Face-centred, Body centred End centred = 4
5	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$; $\beta \neq 90°$	Primitive, End - centred = 2
6	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	Primitive = 1
7	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ $\beta \neq 120°$	Primitive = 1 Total = 14

SOLVED EXAMPLE

Ex. 1 Titanium metal has a density of 4.54 g/cm^3 and an edge length of 412.6 pm. In what cubic unit cell does titanium crystallise? (Ti = 48)

Sol. Density $d = \frac{zM}{a^3 N_0}$

$d = 4.54$ g/cm^3, $M = 48$g mol^{-1}, $Z = ?$

$N_0 = 6.023 \times 10^{23}$ mol^{-1}

If value of z is known, structure can be decided

$$z = \frac{dN_0a^3}{M}$$

$$= \frac{4.54 \times 6.023 \times 10^{23} \times (412.6 \times 10^{-10})^3}{48} = 4$$

Thus, titanium has **face-centred cubic** structure.

Ex. 2 MgO has a structure of NaCl and TiCl has the structure of CsCl. What are the coordination numbers of ions in each (MgO and TiCl).

Sol. C.N. of Na$^+$ in NaCl = 6

C.N. of Cl$^-$ in NaCl = 6

hence C.N. of Mg^{2+} is also = **6**

and that of O^{--} or O^{2-} = **6 in MgO**

We know in CsCl

C.N. of Cs$^+$ = 8

C.N. of Cl$^-$ = 8

Hence, **Ti+ and Cl$^-$, in TiCl, have also C.N. 8 each.**

Ex. 3 A solid AB has the NaCl structure, If radius of cation A$^+$ is 120 pm, calculate the maximum possible value of the radius of the anion B$^-$.

Sol. We know for the NaCl structure, for maximum of radius of B$^-$, the ratio r$^+$ / r$^-$ should be minimum for octahedral void i.e. 0.414.

radius of cation/radius of anion = 0.414

$$\frac{r_{A^+}}{r_{B^-}} = 0.414$$

$$r_{B^-} = \frac{r_{A^+}}{0.414} = \frac{120}{0.414} = \textbf{290 pm.}$$

Ex. 4 Calculate the number of formula units in each of the following types of unit cells :

(A) MgO in a rock salt type unit cell

(B) ZnS in zinc blende structure

(C) platinum in a face-centred cubic unit cell.

Sol. **(A)** 4 (the same as in NaCl)

(B) 4

(C) 4 (1 at the corner, 3 at the face-centres)

Ex. 5 A mineral having the formula AB$_2$ crystallises in the cubic close-packed lattice, with the A atoms occupying the lattice points. What is the coordination number of the A atoms and B atoms ? What percentage fraction of the tetrahedral sites is occupied by B atoms ?

Sol. C.N. of A atom = 8

C.N. of B atom = 4

tetrahedral sites occupied by atoms B = 100% (all tetrahedral voids are occupied).

Ex. 6 (A) What is the C.N. of Cr atom in bcc structure ?

(B) Cobalt metal crystallises in a hexagonal closest packed structure. What is the C.N. of cobalt atom ?

(C) Describe the crystal structure of Pt, which crystallises with four equivalent atoms in a cubic unit cell.

Sol. (A) 8, **(B)** 12, **(C)** fcc or cubic close packed.

Ex. 7 The C.N. of the barium ion Ba^{2+}, in BaF$_2$ is 8. What must be the C.N. of F$^-$ ion ?

Sol. C.N. of barium ion tells us that it is surrounded by eight fluoride ions (charge 8 × (–1) = – 8). In order to balance out the eight negative charges, we need four barium ion (charge 4 × (+2) = +8). Hence, the C.N. of F$^-$ ions must be **4.**

Ex. 8 The radius of calcium ion is 94 pm and of oxide ion is 146 pm. Predict the crystal structure of calcium oxide.

Sol. The ratio $\frac{r_+}{r_-} = \frac{94}{146} = 0.644$

The prediction is an octahedral arrangement of the oxide ions around the calcium. Because the ions have equal but opposite charges, there must also be an octahedral arrangement of calcium ions around oxide ions. Thus CaO structure is similar to Rock Salt(NaCI) structure.

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. The three states of matter are solid, liquid and gas. Which of the following statement is/are true about them

(A) Gases and liquids have viscosity as a common property

(B) The molecules in all the three states possess random translational motion

(C) Gases cannot be converted into solids without passing through the liquid phase

(D) Solids and liquids have vapour pressure as a common property

2. A pure crystalline substance, on being heated gradually, first forms a turbid looking liquid and then the turbidity completely disappears. This behaviour is the characteristic of substances forming

(A) Isomeric crystals

(B) Liquid crystals

(C) Isomorphous crystals

(D) Allotropic crystals

3. Which of the following is ferroelectric compound

(A) $BaTiO_3$ **(B)** $K_4[Fe(CN)_6]$

(C) Pb_2O_3 **(D)** $PbZrO_3$

4. Solid is an example of

(A) Molecular crystal **(B)** Ionic crystal

(C) Covalent crystal **(D)** Metallic crystal

5. Value of heat of fusion of is

(A) Very low

(B) Very high

(C) Not very low and not very high

(D) None of the above

6. Piezoelectric crystals are used in

(A) TV **(B)** Radio

(C) Record player **(D)** Freeze

7. Which of the following is true for diamond

(A) Diamond is a good conductor of electricity

(B) Diamond is soft

(C) Diamond is a bad conductor of heat

(D) Diamond is made up of and

8. NaCl is an example of

(A) Covalent solid **(B)** Ionic solid

(C) Molecular solid **(D)** Metallic solid

9. Amorphous substances show

(a) Short and long range order

(b) Short range order

(c) Long range order

(d) Have no sharp M.P.

(A) a and c are correct

(B) b and c are correct

(C) c and d are correct

(D) b and d are correct

10. The characteristic features of solids are

(A) Definite shape

(B) Definite size

(C) Definite shape and size

(D) Definite shape, size and rigidity

11. Which one of the following is a good conductor of electricity

(A) Diamond **(B)** Graphite

(C) Silicon **(D)** Amorphous carbon

12. A crystalline solid

(A) Changes abruptly from solid to liquid when heated

(B) Has no definite melting point

(C) Undergoes deformation of its geometry easily

(D) Has an irregular 3-dimensional arrangements

(E) Softens slowly

13. Diamond is an example of

(A) Solid with hydrogen bonding

(B) Electrovalent solid

(C) Covalent solid

(D) Glass

14. The solid is a bad conductor of electricity since

(A) In solid there are no ions

(B) Solid is covalent

(C) In solid there is no velocity of ions

(D) In solid there are no electrons

15. The existence of a substance in more than one solid modifications is known as or Any compound having more than two crystal structures is called

(A) Polymorphism **(B)** Isomorphism

(C) Allotropy **(D)** Enantiomorphism

16. The correct statement in the following is

(A) The ionic crystal of AgBr has Schottky defect

(B) The unit cell having crystal parameters, $a=b\neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$ is hexagonal

(C) In ionic compounds having Frenkel defect the ratio $\frac{\gamma_+}{\gamma_-}$ is high

(D) The coordination number of Na^+ ion in NaCl is 4

Exercise # 2

SINGLE OBJECTIVE

AIIMS LEVEL

1. The smallest repeating pattern which when repeated in three dimensions results in the crystal of the substance is called

(A) Space lattice
(B) Crystal lattice
(C) Unit cell
(D) coordination number

2. The crystal system for which $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^0$ is said to be :

(A) triclinic
(B) tetragonal
(C) cubic
(D) orthorhombic

3. Choose the correct statements

(A) equivalent points in unit cells of a periodic lattice lie on a Bravais lattice
(B) equivalent points in unit cells of a periodic lattice do not lie on a Bravais lattice
(C) There are four Bravais lattices in two dimensions
(D) There are five Bravais lattices in three dimensions

4. Which of the following are the correct axial distance and axial angles for rhombohedral system?

(A) $a = b = c, \alpha = \beta = \gamma \neq 90^0$
(B) $a = b \neq c, \alpha = \beta = \gamma = 90^0$
(C) $a \neq b \neq c, \alpha = \beta = \gamma = 90^0$
(D) $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^0$

5. A metal crystallizes in a body centered cubic lattice (bcc) with the edge of the unit cell 5.2Å. The distance between the two nearest neighbour is

(A) 10.4 Å
(B) 4.5Å
(C) 5.2Å
(D) 9.0Å

6. Body centred cubic lattice has co–ordination number of :

(A) 8
(B) 12
(C) 6
(D) 4

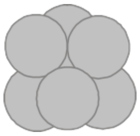
7. Consider a Body Centered Cubic(bcc) arrangement, let d_e, d_{fd}, d_{bd} be the distances between successive atoms located along the edge, the face-diagonal, the body diagonal respectively in a unit cell.Their order is given by:

(A) $d_e < d_{fd} < d_{bd}$
(B) $d_{fd} > d_{bd} > d_e$
(C) $d_{fd} > d_e > d_{bd}$
(D) $d_{bd} > d_e > d_{fd}$,

8. Lithium crystallizes in a body centered cubic lattice. How many next–nearest neighbors does each Li have?

(A) 6
(B) 8
(C) 12
(D) 4

9. The empty space between the shaded balls and hollow balls as shown in the diagram is called



(A) hexagonal void
(B) octahedral void
(C) tetrahedral void
(D) double triangular void

10. You are given 4 identical balls. What is the maximum number of square voids and triangular voids (in separate arrangements) that can be created ?

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

11. Which one of the following schemes of ordering closed packed sheets of equal sized spheres does not generate close packed lattice.

(A) ABCABC
(B) ABACABAC
(C) ABBAABBA
(D) ABCBCABCBC

12. Copper crystallises in a structure of face centerd cubic unit cell. The atomic radius of copper is 1.28 Å. What is axial length on an edge of copper.

(A) 2.16 Å
(B) 3.62 Å
(C) 3.94 Å
(D) 4.15 Å

13. The maximum percentage of available volume that can be filled in a face centred cubic system by atoms is-

(A) 74%
(B) 68%
(C) 34%
(D) 26%

14. In a face centred cubic lattice the number of nearest neighbours for a given lattice point are :

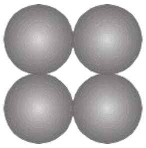
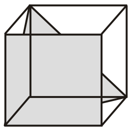
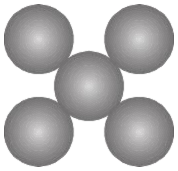
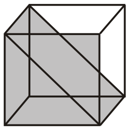
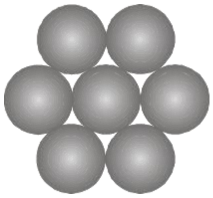
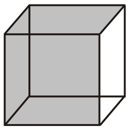
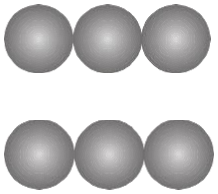
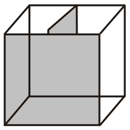
(A) 6
(B) 8
(C) 12
(D) 14

15. In a ccp structure, the (according to cubic 3D arrangement) :

(A) first and third layers are repeated
(B) first and fourth layers are repeated
(C) second and fourth layers are repeated
(D) first, third and sixth layers are repeated.

Exercise # 3 PART - 1 MATRIX MATCHCOLUMN

1.

Column I (Arrangement of the atoms/ions)		Column II (Planes in fcc lattice)	
(A)		(p)	
(B)		(q)	
(C)		(r)	
(D)		(s)	

2.

Column I	Column II
(A) ZnS crystal	(p) fcc
(B) CaF_2 crystal	(q) hcp
(C) NaCl crystal	(r) Distance between closest particles is $\frac{\sqrt{3}}{4}$ a.
(D) Diamond crystal	(s) Only one type of voids are occupied

3.

Column-I	Column-II
(A) 68% occupy of space	(p) Simple cubic lattice
(B) CsCl	(q) Diamond
(C) Hexagonal close packing in three dimensions	(r) Na_2O
(D) Antifluorite structure	(s) AB AB type of close packing
(E) Covalent crystal	(t) Body centred cubic lattice.

4.

Column-I	Column-II
(A) Spinel structure	(p) Framework silicate
(B) Glass	(q) $ZnFe_2O_4$
(C) Quartz	(r) NaCl crystal
(D) Metallic crystal	(s) Pseudo solid
(E) Co-ordination number 6	(t) Melleable and ductile

Exercise # 4

PART - 1

PREVIOUS YEAR (NEET/AIPMT)

1. A molecule contains atoms x and y so that x occurs at the corners of the cube while y at the face centres. The formula of the molecule can be

(A) xy_3 **(B)** x_3y
(C) xy_2 **(D)** x_2y **[2000]**

2. The edge length of face centred cubic unit cell is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is

(A) 288 pm **(B)** 398 pm
(C) 144 pm **(D)** 618 pm **[2000]**

3. A solid AB has NaCl type structure. The radius of A^+ is 100 pm. What is the radius of B^-?

(A) 190.47 **(B)** 540.13
(C) 525 **(D)** 78.12 **[2000]**

4. Crystalline solids have

(A) short range order **(B)** long range order
(C) anisotropic distribution **(D)** all of these

[2001]

5. Schottky defect defines imperfection in the lattice structure of a

(A) solid **(B)** gas
(C) liquid **(D)** plasma **[2002]**

6. An AB_2 type structure is found in

(A) NaCl **(B)** CaF_2
(C) Al_2O_3 **(D)** N_2O **[2002]**

7. An element (atomic mass 100 g/mol) having bcc structure has unit cell edge 400 pm. The density of element is (No. of atoms in bcc (Z) = 2).

(A) 2.144 g/cm^3 **(B)** 7.289 g/cm^3
(C) 5.188 g/cm^3 **(D)** 10.379 g/cm^3

[2002]

8. The crystal system of a compound with unit cell dimensions a = 0.387, b = 0.387 and c = 0.504 nm and $\alpha = \beta = 90°$ and $\gamma = 120°$ is

(A) cubic **(B)** hexagonal
(C) orthorhombic **(D)** rhombohedral

[2004]

9. If Z is the number of atoms in the unit cell that represents the closest packing sequence ...ABCABC..., the number of tetrahedral voids in the unit cell is equal to

(A) Z **(B)** 2Z
(C) Z/2 **(C)** Z/4 **[2005]**

10. Ca^{2+} and F^- are located in CaF_2 crystal, respectively at face centred cubic lattice points and in

(A) tetrahedral voids
(B) half of tetrahedral voids
(C) octahedral voids
(D) half of octahedral voids **[2006,2015]**

11. The energy gasps (E_g) between valence band and conduction band for diamond, silicon and germanium are in the order

(A) E_g (diamond) > E_g (silicon) > E_g (germanium)
(B) E_g(diamond) < E_g(silicon) < E_g(germanium)
(C) E_g(diamond) = E_g(silicon) = E_g(germanium)
(D) E_g(diamond) > E_g(germanium) > E_g(silicon)

[2006]

12. The coordination number in hcp is

(A) 6 **(B)** 12
(C) 18 **(D)** 24 **[2007]**

13. The flame colours of metal ions are due to

(A) Frenkel defect
(B) Schottky defect
(C) metal deficiency defect
(D) metal excess defect **[2008]**

14. A unit cell of sodium chloride has four formula units. the edge length of the unit cell is 0.564 nm. What is the density of sodium chloride ?

(A) 1.2 g/cm^3 **(B)** 2.165 g/cm^3
(C) 3.64 g/cm^3 **(D)** 4.56 g/cm^3

[2008]

15. Schottky defect in crystals is observed when

(A) unequal number of cations and anions are missing from the lattice
(B) equal number of cations and anions are missing from the lattice
(C) an ion leaves its normal site and occupies an interstitial site
(D) density of the crystal is increased **[2009]**

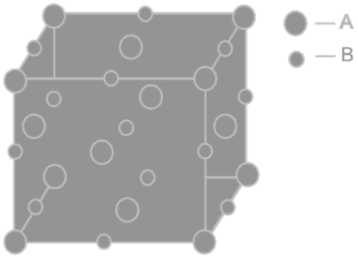
16. In tetragonal crystal system, which of the following is not true ?

(A) All axial lengths and all axial angles are equal.
(B) All three axial lengths are equal
(C) All three axial angles are equal
(D) Two axial angles are equal but the third is different. **[2010]**

MOCK TEST

STRAIGHT OBJECTIVE TYPE

1. A crystal is made of particles A and B. A forms FCC packing and B occupies all the octahedral voids. If all the particles along the plane as shown in figure are removed. Then, the formula of the crystal would be :

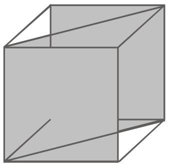


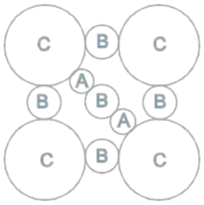
(A) AB **(B)** A_5B_7 **(C)** A_7B_5 **(D)** None of these

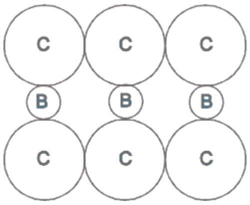
2. A crystal is made of particle X, Y & Z. X forms FCC packing, Y occupies all octahedral voids of X and Z occupies all tetrahedral voids of X, if all the particles along one body diagonal are removed then the formula of the crystal would be –

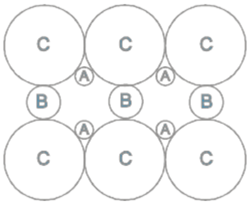
(A) XYZ_2 **(B)** X_2YZ_2 **(C)** $X_8Y_4Z_5$ **(D)** $X_5Y_4Z_8$

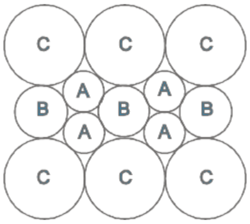
3. In a hypothetical solid C atoms are found to from cubical close packed lattice. A atoms occupy all tetrahedral voids & B atoms occupy all octahedral voids. A and B atoms are of appropriate size, so that there is no distortion in CCP lattice of C atoms. Now if a plane as shown in the following figure is cut. Then the cross section of this plane will look like.



(A)


(B)


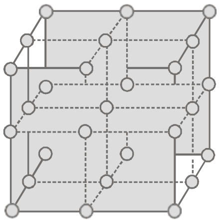
(C)


(D)


4. Diamond has face-centred cubic lattice. There are two atoms at (0, 0, 0) and $\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$ coordinates. The ratio other carbon-carbon bond distance to the edge of the unit cell is

(A) $\sqrt{\frac{3}{16}}$ **(B)** $\sqrt{\frac{1}{4}}$ **(C)** $\frac{1}{4}$ **(D)** $\frac{1}{\sqrt{2}}$

5 The following diagram shows arrangement of lattice point with a = b = c and $\alpha = \beta = \gamma = 90°$. Choose the correct options.



(A) The arrangement is SCwith each lattice point surrounded by 6 nearest neighbours.
(B) the arrangement is SC with each
(C) The arrangement is FCC with each lattice point surrounded by 12 nearest neighbours.
(D) The arrangement in BCC with each lattice point surrounded by 8 nearest neighbours.

CHAPTER 11

S-BLOCK

When the elements are arranged in vertical columns according to increasing atomic weight, so that the horizontal lines contain analogous elements again according to increasing atomic weight, an arrangement results from which several general conclusions may be drawn.

" DMITRYIVANOVICH MENDELEEV"

INTRODUCTION

The s-block elements of the Periodic Talbe are those in which the last eletron enters the outermost s-orbital. As the s-orbital can accommodate only two electrons, two groups (1 & 2) belong to the s-block of the periodic Table. Group 1 of the Periodic table. Group 1 of the Periodic Table consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are collectively known as the alkali metals. These are so called because they form hydroxides on reaction with water which are strongly alkaline in nature. The elements of Group 2 include beryllium, magnesium, calcium, strontium, barium and radium. These elements with the exception of beryllium are commonly known as the alkaline earth metals. These are so called because theiroxides and hydroxides are alkaline in nature and these metal oxides are found in the earth's crust.

The elements in which the last electron enters the outer most s - orbital are called s-block elements. The group I and II of periodic table belongs to the s-block.

ALKALIMETAL

PHYSICALPROPERTIES :

(i) Physical State

- (a) One electron in outermost sheel & General formula ns^1.
- (b) Francium is radioactive element.
- (c) All are silverywhite
- (d) Light soft, malleable and dutile metals with metallic lustre.
- (e) Alkali metal are paramagnetic, diamagnetic and colourless in form of ions.

(ii) Atomic Size

- (a) Biggest in their repective period
  (except noble gaselement)
- (b) Size increases from Li to Fr due to addition of an extra shell.
  $Li < Na < K < Rb < Cs < Fr$

(iii) Softness

- (a) Alkali metals are soft because of
  - (i) Large atomic size
  - (ii) BCC crystal structure (HCP in Li)
  - (iii) Loose packing (68 % packing efficiency)
  - (iv) Weak metallic bond
- (b) Cs is the softest metal in s-block

$$\text{Atomic size} \propto \frac{1}{\text{strength of metallic bond}} \propto \text{softness} \propto \frac{1}{\text{Melting \& Boiling point}}$$

(iv) Melting point and boiling point

- (a) Weak interatomic bonds are due to their large atomic radil and presence of only one valence electron hence melting point and boiling point are low.
- (b) Decreasing order of melting point and biling point is
  $Li > Na > K > Rb > Cs$
- (c) With the increase in the size of metal atom, the repulsion of the non-bonding electrons increases and therefore melting point and boiling point decreases from Li to Cs.

(v) Electro positive character or metallic character

Electropositive $\propto$ 1/Ionisation Potentical

Due to their larger sixe electron can easily be removed to form M^+ ion. Electro positive property increases from Li to Cs.

(vi) Flame Test

Alkali metals and their salts gives characteristic colour to bunsen flame. The flame energy causes an excitation of the outer most electron which on dropping back to ground state emits absorbed energy as visible light

Ex. Li-Crimson red Na-Golden yellowK-Violet
Rb-Red violet Cs-Blue

(vii) Photo Electric Effect

- (a) Atomic size of K, Rb and Cs is quite large, so their ionisation potential is very low
- (b) Due to very low ionisation potential their valuence shell electrons gets excited even by absorbing visible light. That's why Cs is used in photo cells.

1.	Active nitrogen	:	N(atomic nitrogen)
2.	Alums	:	$M_2'SO_4.M_2'''(SO_4)_3.24H_2O$ $M' = K^+$, NH_4^+ , Na^+etc. $M''' = Cr^{+3}, Al^{+3}, Fe^{+3}$etc.
3.	Asbestos	:	$CaMg_3(SiO_3)_4$
4.	Arsine	:	AsH_3
5.	Aquaregia	:	Conc. HNO_3 + Conc. HCl (1 : 3 part)
6.	Anhydrone	:	$Mg(CLO_4)_2$
7.	Argentoferrous galena	:	$PbS + Ag_2S$
8.	Borax	:	$Na_2B_4O_7.\ 10H_2O$
9.	Blue vitriol	:	$CuSO_4, 5H_2O$
10.	Barytes	:	$BaSO_4$
11.	Baryta water	:	$Ba(OH)_2$ solution
12.	Baryta	:	BaO
13.	Baking soda	:	$NaHCO_3$
14.	Bleaching powder	:	$CaOCl_2$
15.	Boranes	:	Hydride of borone
16.	Brine	:	NaCl solution
17.	Calgon	:	$Na_2[Na_4(PO_3)_6]$
18.	Coinage metals	:	Cu, Ag and Au
19.	Carborundum	:	SiC
20.	Cementite	:	FeC
21.	Caliche	:	$NaNO_3 + NaIO_3$
22.	Caustic soda	:	NaOH
23.	Caustic potash	:	KOH
24.	Calomel	:	Hg_2Cl_2
25.	Corrosive sublimate	:	$HgCl_2$
26.	Deuterium	:	$_1H^2$ of D
27.	D.D.T.	:	p-dichloro, diphenyl, trichloroethane
28.	Dry ice	:	Solid CO_2
29.	Freon	:	CF_2Cl_2
30.	Ferric Alum	:	$K_2SO_4.\ Fe_2(SO_4)_3.24H_2O$
31.	Fenton's reagent	:	H_2O_2 + few drops of $FeSO_4$
32.	Fusion's mixutre	:	$Na_2CO_3 + K_2CO_3$
33.	Fluid magnesia	:	12% solution of Mg $(HCO)_2$
34.	Fehling solution	:	$CuSO_4.\ 5H_2O$ + NaOH + Na,K tartarate

SOLVED EXAMPLE

Ex. 1 Li has the maximum value of ionisation potential among alkali metals i.e.e lithium has the minimum tendency to ionise to give Li^+ ion. lithium is –

(A) Strongest reducing

(B) Poorest reducing agent

(C) Strongest oxidisting agent

(D) Poorest oxidising agent

Sol. (A) The ionisation potential value of LIthium is maximum among alkali metals i.e., its tendency to ionise to give Li^+ ions should be the minimum i.e. Li should be the poorest reducing agent. But, lithium is the strongest reducing agent. This is due to the largest value of hydration energy of Li^+ ions.

Ex. 2 The highest melting point among alkali metal of –

(A) Li **(B)** Na

(C) K **(D)** Rb

Sol. **(A)** Li has highest melting point among alkali metals. All alkali metals have low M.P. The M.P. decrease down the group. The low M.P. are attributed to their larger atomic size due to which the binding energies of their atoms in the crystal lattice are low.

Ex. 3 Commercial common salt becomes slightly damp on keeping. This is due to the fact that –

(A) Common salt is hygroscopic

(B) Common salt contains some impurity which is hygroscopic

(C) Salt is efflorescent

(D) Salt is crystalline

Sol. **(B)** Commercial common salt commonly becomes slightly damp on keeping because common salt contains some impurity $MgCl_2$ and $CaCl_2$ which is hygroscopic in nature and absorbs moisture from the atmosphere.

Ex. 4 CO_2 gas along with solid (Y) is obtained when sodium salt (X) is heated. (X) is again obtained when CO_2 gas is passed into (Y). X & Y are –

(A) Na_2CO_3, Na_2O **(B)** Na_2CO_3, NaOH

(C) $NaHCO_3$, Na_2CO_3 **(D)** Na_2CO_3, $NaHCO_3$

Sol. **(C)** $\underset{(X)}{2NaHCO_3} \xrightarrow{\text{Heat}} \underset{(Y)}{Na_2CO_3} + H_2O + CO_2$

$\underset{(Y)}{Na_2CO_3} + H_2O + CO_2 \longrightarrow \underset{(X)}{2NaHCO_3}$

Ex. 5 The highest NaOH gives disproportionation reaction with

(A) S **(B)** CO_2

(C) SO_2 **(D)** SO_3

Sol. **(A)** $4S + 6NaOH \xrightarrow{\Delta} Na_2S_2O_3 + 2Na_2S + 3H_2O$

with excess pentasulfide forms

$Na_2S + 4S \longrightarrow Na_2S_5$

Ex. 6 Metallic magnesium is prepared by

(A) Reduction of MgO by coke

(B) Electrolysis of aqueous solution of $Mg(NO_3)$

(C) Displacement of Mg by ion from $MgSO_4$ solution

(D) Electrolysis of molten $MgCl_2$

Sol. **(D)** $\underset{\text{(Molten)}}{MgCl_2} \xrightarrow{\text{Electrolysis}} \underset{\text{Cation}}{Mg^{+2}} + \underset{\text{Anion}}{2Cl}$

Anode : $2Cl^- \longrightarrow 2Cl + 2e^-$, $Cl + Cl \longrightarrow Cl_3$

Cathode : $Mg^{+2} + 2e^- \longrightarrow Mg$

Ex. 7 The first ionization potential of Mg is

(A) Less than Al **(B)** More than Al

(C) Equal to Al **(D)** Zero

Sol. **(B)** The first ionization potential of Mg is more than Al sice the electron has to be removed from completely filled svalence shell of Mg.

Ex. 8 Portland cement is manufactured by using–

(A) Lime stone, clay and sand

(B) Lime stone, gypsum and sand

(C) Lime stone, gypsum and alumina

(D) Lime stone, clay and gypsum

Sol. **(D)** Lime stone – $CaCO_3$

Clay – silica and alumina

Gypsum – $CaSO_4.2H_2O$

Ex. 9 Gypsum $CaSO_4 2H_2O$ on heating to about 120°C forms a compound which has the chemical composition represented by

(A) $CaSO_4$ **(B)** $2CaSO_4.H_2O$

(C) $CaSO_4.H_2O$ **(D)** $2CaSO_4.3H_2O$

Sol. **(B)**

$\underset{\text{Gypsum}}{2(CaSO_4.2H_2O)} \xrightarrow[\text{Dehydration}]{120°} \underset{\text{Plaster of paris}}{2CaSO_4.\ H_2O + 3H_2O}$

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. As compared to potassium, sodium has

(A) Lower electronegativity

(B) Higher ionization potential

(C) Greater atomic radius

(D) Lower melting point

2. Potassium is kept in

(A) Alcohol
(B) Water
(C) Kerosene
(D) Liquid ammonia

3. The product obtained on fusion of $BaSO_4$ and Na_2CO_3 is

(A) $BaCO_3$
(B) BaO
(C) $Ba(OH)_2$
(D) $BaHSO_4$

4. Which of the following statement is correct regarding alkali metals

(A) Cation is less stable than the atom

(B) Cation is smaller than the atom

(C) Size of cation and atom is the same

(D) Cation is greater in size than the atom

5. Valency electrons in alkali metals are

(A) 1
(B) 7
(C) 4
(D) 2

6. Magnitude of which of the following property of alkali metals increases with the increase of atomic number

(A) Electronegativity **(B)** Ionic radius

(C) First ionization energy **(D)** Melting point

7. As compared to lithium, sodium reacts quickly with water because

(A) Its molecular weight is less

(B) It is stronger electronegative

(C) It is stronger electropositive

(D) It is a metal

8. Which is an ore of potassium

(A) Carnellite
(B) Cryolite
(C) Bauxite
(D) Dolomite

9. Na_2CO_3 can be manufactured by Solvey's process but K_2CO_3 cannot be prepared because

(A) K_2CO_3 is more soluble

(B) K_2CO_3 is less soluble

(C) $KHCO_3$ is more soluble than $NaHCO_3$

(D) $KHCO_3$ is less soluble than $NaHCO_3$

10. Which of the following alkali metals is smallest in size

(A) Rb
(B) K
(C) Na
(D) Li

11. When potassium dichromate crystal are heated with conc. HCl

(A) O_2 is evolved

(B) Chromyl chloride vapours are evolved

(C) Cl_2 is evolved

(D) No reaction takes place

12. Which of the following does not illustrate the anomalous properties of lithium

(A) The melting point and boiling point of Li are comparatively high

(B) Li is much softer than the other group I metals

(C) Li forms a nitride Li_3N unlike group I metals

(D) The ion of and its compounds are more heavily hydrated than those of the rest of the group

13. Correct order of increasing activity is

(A) Cu, Mg, Na
(B) Na, Mg, Cu
(C) Mg, Na, Cu
(D) Cu, Na, Mg

14. On heating anhydrous Na_2CO_3, ... is evolved

(A) CO_2
(B) Water vapour
(C) CO
(D) No gas

15. Chile saltpetre is

(A) $NaNO_3$
(B) Na_2SO_4
(C) KNO_3
(D) Na_2SO_3

16. A mixture of KCl and KF is added to sodium chloride

(A) To increase the conductivity of NaCl

(B) To decrease the melting point of NaCl

(C) To supress the degree of dissociation of NaCl

(D) To decrease the volatility of NaCl

Exercise # 2

SINGLE OBJECTIVE

AIIMS LEVEL

1. $CsBr_3$ contains
(A) Cs-Br covalent bonds
(B) Cs^{3+} and Br^- ions
(C) Cs^+ and Br_3^- ions
(D) Cs^{3+} and Br_3^{3-} ions

2. The golden yellow colour associated with NaCl to Bunsen flame can be explained on the basis of
(A) low ionisation potential of sodium
(B) emission spectrum
(C) photosensitivity of sodium
(D) sublimation of metallic sodium of yellow vapours

3. Incorrect statement regsrding the dissolution of alkali & alkaline earth metals in liq. NH_3 is
(A) Due to high L.E. and I.E. Be and Mg do not dissolve in liquid NH_3.
(B) Deep biue collour is due to absorption spectrum of solvated electron.
(B) Solution conducts electricity at all concentration.
(C) Solution remains paramagnetic at all concentration.

4. Which of the following carbide produces propyne on reaction with water.
(A) CaC_2 **(B)** Be_2C
(C) Al_4C_3 **(D)** Mg_2C_3

5. (Yellowppt)

$$T \xleftarrow{k_2CrO_4 / H^+} X \xrightarrow{dil.HCl} Y \text{ (Yellowppt)} + Z \uparrow$$

(pungent smelling gas) If X gives green flame test. Then, X is
(A) $MgSO_4$ **(B)** BaS_2O_3
(C) $CuSO_4$ **(D)** PbS_2O_3

6. Which of the following carbide does not release any hydrocarbon on reaction with water.
(A) SiC **(B)** Be_2C
(C) CaC_2 **(D)** Mg_2C_3

7. The salt which finds uses in qualitative inorganic analysis is
(A) $CuSO_4.5H_2O$ 0r $ZnSO_4.5H_2O$
(B) $K_2SO_4.Al_2(SO_4)_3.24H_2O$
(C) $Na(NH_4)HPO_4.4H_2O$
(D) $FeSO_4.(NH_4)_2SO_4.6H_2O$

(C)

8. (i) $A + Na_2CO_3 \rightarrow B + C$
(ii) $A \xrightarrow{CO_2}$ (Milky) C
The chemical formula of A and B are respectively
(A) NaOH & $Ca(OH)_2$
(B) $Ca(OH)_2$ and NaOH
(C) NaOH and CaO
(D) CaO & $Ca(OH)_2$

9. Which of the following statement is false
(A) The milk of magnesia used as antacid is chemically MgO + $MgCl_2$
(B) Stability of alkali metal peroxides increases with increase in atomic number.
(C) Hydration energy of AgF is higher than its lattice energy.
(D) Anhydrous $MgCl_2$ cannot be prepared by direct heating of $MgCl_2.6H_2O$.

10. $a + Al_2O_3 \xrightarrow{\text{High temperature}} X \xrightarrow[\text{water}]{CO_2 \text{in}} Y$;
Compound Y is
(A) $NaAlO_2$ **(B)** $NaHCO_3$
(C) Na_2CO_3 **(D)** Na_2O_2

11. Mg_2C_3 reacts with water forming propyne. C_3^{4-} has
(A) Two sigma and two pi bonds
(B) Three sigma and one pi bond
(C) Two sigma and one pi bond
(D) Two sigma and three pi bonds

12. (White ppt)

$$D \xleftarrow{Na_2CO_3} A \xrightarrow[\text{(in acetic acid)}]{K_2CrO_4} B\text{(Yellowppt)}$$

dil.$H_2SO_4 \downarrow$ C(Whiteppt)

if is the metallic salt, then the white ppt. of D must be of
(A) stronsium carbonate
(B) red lead
(C) barium carbonate
(D) calcium carbonate

13. Calcium imide on hydrolysis will give gas **(B)** which on oxidation by bleaching powder gives gas **(C)** gas **(C)** on reaction with magnesium give compound **(D).(D)** on hydrolysis gives again gas **(B).(B),(C)** and **(D)** are
(A) NH_3, N_2, Mg_3N_2
(B) N_2, NH_3, MgNH
N_2, N_2O_5, $Mg(NO_3)_2$
(D) NH_3, NO_2, $Mg(NO_2)_2$

Exercise # 3 PART - 1 MATRIX MATCHCOLUMN

1. Match the column-

Column - I	**Column - II**
(A) Ba	**(p)** Golden yellow
(B) Ca	**(q)** Apple green
(C) Na	**(r)** Brickred
(D) Rb	**(s)** violet

2. Match the column-

Column I	**Column II**
For the production of H_2O_2	
(A) Down process	**(p)** K_2CO_3
(B) Solvay process	**(q)** Manufacture of Na
(C) Leblance process	**(r)** Manufacture of NaOH
(D) Castner- Kellner cell	**(s)** Na_2CO_3

3. Match the column-

Column - I	**Column - II**
(A) $NaOH + SO_2 \rightarrow$	**(p)** $NaNO_3$
(B) $NaOH + CO_2 \rightarrow$	**(q)** Na_2SO_3
(C) $NaOH + NO_2 \rightarrow$	**(r)** Na_2CO_3
(D) $NaOH + HNO_3 \rightarrow$	**(s)** $NaNO_2$

4. Match the column-

Column-I	**Column-II**
(A) Metal sulphate $\xrightarrow{\Delta}$ metal oxide + SO2 + O_2	**(p)** Ba
(B) Metal cation + $K_2CrO_4 \rightarrow$ yellow ppt	**(q)** Sr
(C) Metal + $NH_3 \xrightarrow{\text{(liquid)}}$ blue solution	**(r)** Na
(D) MCl_2 + conc. $H_2SO_4 \rightarrow$ white ppt.	**(s)** Mg

5. Match the column-

Column-I	**Column - II**
(A) $Rb_2CO_3 > K_2CO_3 > Na_2CO_3$	**(p)** solubility of salts in water
(B) $SrSO_4 > CaSO_4 > MgSO_4$	**(q)** Thermal stability of salts
(C) Rb > K > Na	**(r)** Softness of metals
(D) Be > Mg > Ca	**(s)** Hydration energy of metals

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. The correct order of the mobility of the alkali metal ions in aqueous solution is **[CBSE AIPMT 2006]**

(A) $Li^+ > Na^+ > K^+ > Rb^+$

(B) $Na^+ > K^+ > Rb^+ > Li^+$

(C) $K^+ > Rb^+ > Na^+ > Li^+$

(D) $Rb^+ > K^+ > Na^+ > LI^+$

2. The correct order of increasing thermal stability of K_2CO_3, $MgCO_3$, $CaCO_3$ and $BeCO_3$ is **[CBSE AIPMT 2007]**

(A) $BeCO_3 < MgCO_3 < K_2CO_3 < CaCO_3$

(B) $BeCO_3 < MgCO_3 < CaCO_3 < K_2CO_3$

(C) $MgCO_3 < BeCO_3 < CaCO_3 < K_2CO_3$

(D) $K_2CO_3 < MgCO_3 < CaCO_3 < BeCO_3$

3. In which of the following the hydration energy is higher than the lattice energy? **[CBSE AIPMT 2007]**

(A) $BaSO_4$ **(B)** $MgSO_4$

(C) $RaSO_4$ **(D)** $SrSO_4$

4. The sequence of ionic mobility in aqueous solution is **[CBSE AIPMT 2008]**

(A) $K^+ > Na^+ > Rb^+ > Cs^+$

(B) $Cs^+ > Rb^+ > K^+ > Na^+$

(C) $Rb^+ > K^+ > Cs^+ > Na^+$

(D) $Na^+ > K^+ > Rb^+ > Cs^+$

5. Equimolar solution of the following were prepared in water separately. Which one of the solution will record the highest pH ? **[CBSE AIPMT 2008]**

(A) $SrCl_2$ **(B)** $BaCl_2$

(C) $MgCl_2$ **(D)** $CaCl_2$

6. Which one of the following is present as an active ingredient in bleaching powder for bleaching **[CBSE AIPMT 2011]**

(A) $Ca(OCl)_2$ **(B)** CaO_2Cl_2

(C) $CaCl_2$ **(D)** $CaOCl_2$

7. On heating which of the following releases CO_2 most easily ? **[CBSE AIPMT 2015]**

(A) K_2CO_3 **(B)** Na_2CO_3

(C) $MgCO_3$ **(D)** $CaCO_3$

8. Solubility of the alkaline earth's metal sulphates in water decreases in the sequence **[CBSE AIPMT 2015]**

(A) Mg > Ca > Sr > Ba

(B) Ca > Sr > Ba > Mg

(C) Sr > Ca > Mg > Ba

(D) Ba > Mg > Sr > Ca

9. "Metals are usually not found as nitrates in their ores". **[CBSE AIPMT 2015]**
Out of the following two (I and II) reasons which is/are true for the above observation ?

I. Metal nitrates are highly unstable.

II. Metal nitrates are highly soluble in water.

(A) I and II are true **(B)** I and II are false

(C) I is false but II is true **(D)** I is true but II is false

10. In context with beryllium, which one of the following statements is incorrect ? **[NEET 2016, Phase II]**

(A) It is rendered passive by nitric acid

(B) It forms Be_2C

(C) Its salts rarely hydrolyse

(D) Its hydride is electron-deficient and polymeric

11. Which of the following statement about hydrogen is incorrect ? **[NEET 2016, Phase I]**

(A) Hydrogen never acts as cation in ionic salts

(B) Hydronium ion, H_3O^+ exists freely in solution

(C) Dihydrogen does not act as a reducing agent

(D) Hydrogen has three isotopes of which tritium is the most common

12. The product obtained as a result of a reaction of nitrogen with CaC_2 is **[NEET 2016, Phase I]**

(A) CaCN **(B)** $CaCN_3$

(C) Ca_2CN **(D)** $Ca(CN)_2$

13. Ionic mobility of which of the following alkali metal ions is lowest when aqueous solution of their salts are put under an electric field ? **[NEET 2017]**

(A) Na **(B)** K

(C) Rb **(D)** Li

MOCK TEST

1. Philospher's wool when heated with BaO at 1100° C gives a compound. Identify the compound

(A) $BaZnO_2$ **(B)** $Ba + ZnO_2$ **(C)** $BaCdO_2$ **(D)** $BaO_2 + Zn$

2. The number of electron and proton in the third alkaline earth metal ion will be

(A) $\frac{e}{20}, \frac{p}{20}$ **(B)** $\frac{e}{18}, \frac{p}{20}$ **(C)** $\frac{e}{18}, \frac{p}{18}$ **(D)** $\frac{e}{19}, \frac{p}{20}$

3. The compounds of alkaline earth metals have the following magnetic nature

(A) Diamagnetic **(B)** Paramagnetic **(C)** Ferromagnetic **(D)** Diaferromagnetic

4. Which of the following is in the increasing order of the ionic character

(A) $PbCl_4 < PbCl_2 < CaCl_2 < NaCl$ **(B)** $PbCl_2 < PbCl_4 < CaCl_2 < NaCl$

(C) $PbCl_2 < PbCl_4 < NaCl < CaCl_2$ **(D)** $PbCl_4 < PbCl_2 < NaCl < CaCl_2$

5. KO_2 (potassium superoxide) is used in oxygen cylinders in space and submarines because it

(A) Absorbs CO_2 and increases O_2 content **(B)** Eliminates moisture

(C) Absorbs CO_2 **(D)** Produces ozone

6. Fire extinguishers contain H_2SO_4 and

(A) $CaCO_3$ **(B)** Na_2CO_3

(C) $NaHCO_3$ **(D)** $NaHCO_3$ and Na_2CO_3

7. The stability of the following alkali metal chlorides follows the order

(A) $LiCl > KCl > NaCl > CsCl$ **(B)** $CsCl > KCl > NaCl > LiCl$

(C) $NaCl > KCl > LiCl > CsCl$ **(D)** $KCl > CsCl > NaCl > LiCl$

8. The reaction of $Na_2S_2O_3$ with iodine gives

(A) Sodium sulphide **(B)** Sodium sulphite **(C)** Sodium sulphate **(D)** Sodium tetrathionate

9. Lithium aluminium hydride acts as

(A) Oxidising agent **(B)** Reducing agent **(C)** Both the above **(D)** None of these

10. Four reactions are given below

(i) $2Li + 2H_2O \rightarrow 2LiOH + H_2$ (ii) $2Na + 2H_2O \rightarrow 2NaOH + H_2$

(iii) $2LiNO_3 \xrightarrow{Heat} 2LiNO_2 + O_2$ (iv) $2NaNO_3 \xrightarrow{Heat} 2NaNO_2 + O_2$

Which of the above, if any, is wrong

(A) (iv) **(B)** (iii) **(C)** (i) **(D)** None of these

11. Increasing order of solubility is

(A) $CaCO_3, KHCO_3, NaHCO_3$ **(B)** $NaHCO_3, KHCO_3, CaCO_3$

(C) $KHCO_3, NaHCO_3, CaCO_3$ **(D)** $CaCO_3, NaHCO_3, KHCO_3$

CHAPTER 15

CHEMISTRY IN EVERYDAY LIFE

Science and everyday life cannot and should not be saperated.

''ROSALINDFRANKLIN''

INTRODUCTION

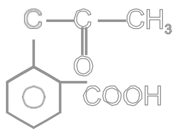
Chemistry in Everyday life helps us to have a look that where chemistry is used in our day to day life's routine. Medicines, Drugs, Chemical messangers in our body (hormones & neurotransmitters), Rocket propellants, chemicals in food, cleansing agents such as soaps & detergents, petrol the most important thing in the world in the present scenario, all types of cosmetics can be explained with the help of chemistry.

Thus advancement in chemistry helps us to synthesize & manufacture all these products economically and improve our standard of living. With the further enhancement of chemistry scientist are trying to delve into other fields as well so that further improvisation can be done.

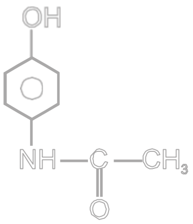
(D) Antipyretics :

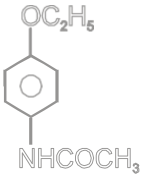
To bring down the body temp. in high fever are called antipyretics.

e.g - (a) Aspirin, (b) Analgin (Novalgin), (c) Paracetamol, (d) Phenacetin



Aspirin





p– Ethoxy acetanilide
(Phenacetin)

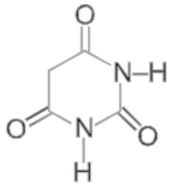
(E) Antimalarials :

To bring down the body temperature during malarial fever.

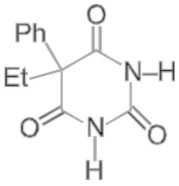
e.g. Quinine, Chloroquine, Paraquine and Primaquine etc.

(F) Tranquilizers :

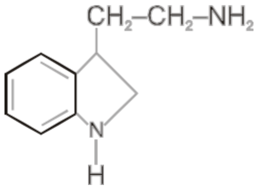
The chemical substances which acts on the central nervous system and has a calming effect. Since these are used for mental diseases so are known as psychotherapeutic drugs.



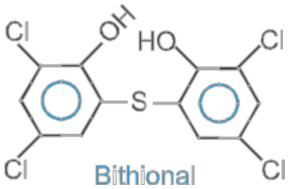
Barbituric acid



Luminal



Serotonin



Bithional

Reserpine, an alkanoid, is a powerful tranquilizer. It is obtained from a plant, Rauwolfia serpentina (common name - Sarpagandha) which grows in India.

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.

(b) **Mood elevators or Antidepressants :** A drug used for treatment of highly depressed patient, who has lost his confidence.

Example : Benzedrine (amphetamine)

(G) Anaesthetics :

These are chemical substances helping 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.

Example : Gaseous form → Nitrous oxide, ethylene, cyclopropane etc.

Liquid form → Chloroform, divinyl ether and sodium pentothal etc.

Liquid dish washing detergents are non ionic type. Main problem that appears in the use of this type of detergents. is that if their hydrocarbon chain is highly branched then bacteria cannot degrade this easily, they pollute rivers and other water sources. If hydrocarbon chain is unbranched then they are decomposed by microorganism and thus no pollution occur from them.

Difference between soap and detergents

Although the action of soap and detergents is similar but there are following differences between them :

(1) Soaps are salts of weak acid and strong base whereas detergents are salts of strong acid and strong base.

(2) Aqueous solution of soap is basic where as aqueous solution of detergents is neutral.

$$\text{R–COONa} + H_2O \longrightarrow \text{R–COOH} + \text{NaOH}$$

Soap Weak acid strong base

$$\text{ArSO}_3\text{Na} + H_2O \longrightarrow \text{ArSO}_3\text{H} + \text{NaOH}$$

Detergent Strong acid strong base

(3) Woolen and silk cloths in which soft fibres are present cannot be washed with soap whereas all type of fabrics can be washed with detergents

(4) Soap cannot work in hard water because soaps are precipitated as insoluble salt by reaction with Ca^{2+} and Mg^{2+} ions. Thus more soap is used for removing dust and grease from the clothes where as detergents are not precipitated by Ca^{2+} and Mg^{2+} ions. Thus detergents can be used in hard water also.

EDOS KEY POINTS

(i) Aspirin is used to prevent heart attacks besides being antipyretic and analgesic agents.

(ii) Soaps, detergents and phospholipids are called surfactants since they lower the surface tension of water.

(iii) Sodium soaps are hard while potassium soaps are soft. Therefore, whashing soaps are mostly sodium soaps while liquid soaps having creams and toilet soaps are potassium salts.

(iv) Unlike soaps, detergents can be used in hard water. The reson being that magnesium and calcium salts of detergents are soluble in water while those of soaps are insoluble in water.

(v) Aspirin is a non-narcotic analgesic but is toxic to liver. It also undergoes hydrolysis in the stomach producing salicyclic acid which causes bleeding from the stomach wall. Therefore, other non-narcotic analagesics such as naproxen, ibuprofen and diclofenac sodium or potassium are preferred to aspirin.

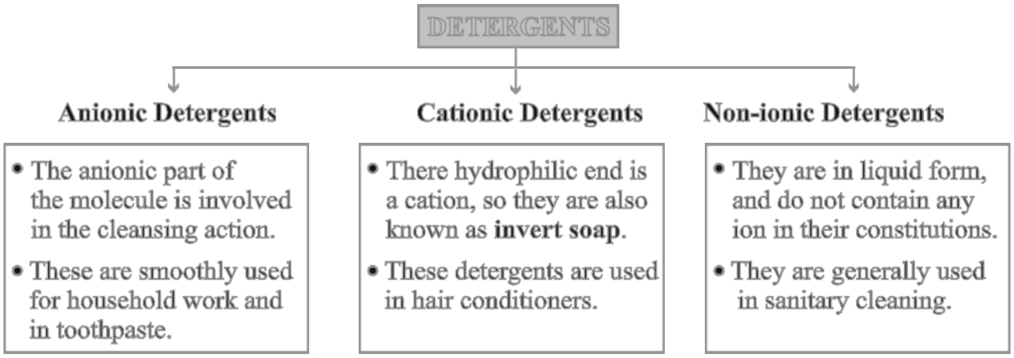
(vi) Sulpha drugs areeffective against bacterial infections.

(vii) Artificial sweetners have no caloric value and hence are useful for diabetic persons.

1. **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.

2.



DETERGENTS

Anionic Detergents

- The anionic part of the molecule is involved in the cleansing action.
- These are smoothly used for household work and in toothpaste.

Cationic Detergents

- There hydrophilic end is a cation, so they are also known as **invert soap**.
- These detergents are used in hair conditioners.

Non-ionic Detergents

- They are in liquid form, and do not contain any ion in their constitutions.
- They are generally used in sanitary cleaning.

SOLVED EXAMPLE

Ex.1 Which of the following statements is not correct ?

(A) Some antiseptics can be added to soaps

(B) Dilute solutions of some disinfectants can be used as antiseptic

(C) Disinfectants are antimicrobial drugs

(D) Antiseptic medicines can be ingested

Sol. (D) An antiseptic is an antimicrobal drug. It tends to destroy/ prevent development or inhibit the pathogenic action of microbes. Antiseptics are applied to the living tissues such as wounds, cuts, ulcers and diseased skin surfaces e.g., soframicine.

Bithinol the compound is also called bithional is added to soaps to impart antiseptic properties Dilute solutions of some disinfectants can be used as antiseptic e.g., 0.2 percent solution of pehnol is an antiseptic while its one percent solution is disinfectant. But, antiseptic medicines can not be ingested like antibiotics.

Ex.2 The most useful classification of drugs for medicinal chemists is...........

(A) On the basis of chemical structure

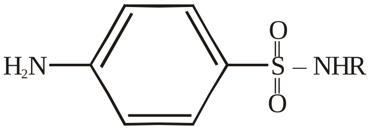
(B) On the basis of drug action

(C) ON the basis of molecular targets

(D) On the basis of pharmacological effect

Sol. (C) Drugs can be classified in the following ways

(A) on the basis of chemical structure : Drugs have been classified on the basis of their chemical structures have similar pharmacological activity. e.g., all sulphonamides having the common structural feature as given below are mostly antibacterial.



Structural feature of sulphonamide

(B) On the basis of drug action : This classification is based on the action of a drug on a particular biochemical process.

(C) On the basis of molecular target : Drugs usually interact with the biomolecules or biological macromolecules such as proteins, nucleic acids and lipids. These are called drug targets.

Drugs possessing some common structural features may have the same mechanism of action on a specific drug target. This classificationis most useful for the medicinal chemists

(D) On the basis of pharmacological effect : This classification is based upon the pharmacological effects of the drugs. It is more useful for the doctors because it provides them the whole range of drugs available for the treatment of a particular disease, e.g., analgesics reduce or kill pain while antiseptic either kill or arrest the growth of microorganisms.

Ex.3 Compound which is added to soap to impart antiseptic properties is ....

(A) Soldium laurylsulphate

(B) Sodium dodecylbenzenesulphonate

(C) Rosin

(D) Bithional

Sol. (D) Basically, all soaps are made by boiling fats or oils with suitable hydroxide. Variations are made by adding different raw materials. Sodium laurylsulphate and sodium dodecylbenzenesulphonate are anionic detergents

A gum rosin added to soap to make it lather well. Bithional is added to soaps to impart antiseptic properties to soap.

Ex.4 Glycerol is added to soap. It functions ....

(A) As a filler

(B) To increases leathering

(C) To prevent rapid drying

(D) To make soap granules

Sol. (C) Glycerol is added to shaving soap to prevent rapid drying while to enhance the leathering property of soap, a gum called rosin is added to them. It forms sodium rosinate which lathers well. Soap granules are dried miniature soap bubbles

Builders/ fillers make the soap act more rapidly. Builder or filter (e.g. sodium tripolyphosphate) is added to detergent powder. Its main function is to act as water softener by removing Mg^{2+} and Ca^{2+} ion from hard water by forming stable souble complexes.

Ex.5 Photochemical smog occurs in warm, dry and sunny climate. One of the following is not amongst the components of photochemical smog, identify it

(A) NO_2

(B) O_3

(C) SO_2

(D) Unsaturated hydrocarbon

Sol. (C) The smog which is formed in presence of sunligh is called photochemical smog. This occurs in the moths of summer when NO_2 and hydrocarbons are presents in large amounts in atmosphere.

Concentration of O_3, PAN, aldehydes and ketones builds up in the atmosphere.

SO_2 is not responsible for photochemical smog.

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. An antibiotic with a broad spectrum
(A) Kills the antibodies
(B) Acts on a specific antigen
(C) Acts on different antigens
(D) Acts on both the antigens and antibodies

2. Penifillin was first discovered by
(A) A. Fleming (B) Tence and Salke
(C) S.A. Waksna (D) Lewis Pasteur

3. A medicine which promotes the secretion of unrine is called
(A) Uretic (B) Monouretic
(C) Diuretic (D) Triuretic

4. An example of a psychedilic agent is
(A) DNA (B) LSD
(C) DDT (D) TNT

5. Versonal, a barbiturate drug is used as
(A) Anaesthetic (B) Sedative
(C) Antiseptic (D) None of these

6. Acetoxy benzoic acid is
(A) Antiseptic (B) Aspirin
(C) Antibiotic (D) Mordant dye

7. Antiseptic chloroxylenol is
(A) 4-chloro-3, 50dimethylphenol
(B) 3-chloro-4, 5-dimethylphenol
(C) 4-chloro-2, 5-dimethylphenol
(D) 5-chloro-3, 4-dimethylphenol

8. Which of the following is an insecticide
(A) Bakelite (B) TNT
(C) BHC (D) Aspirin

9. Which of the following drugs is an analgesic
(A) Sulphaguanidine (B) Paludrin
(C) Analgin (D) Iodex

10. Aspirin is
(A) Antibiotic (B) Antipyretic
(C) Sedative (D) Psychedelic

11. Which of the following drugs is a tranquilizer and sedative
(A) Sulphadiazine (B) Papaverine
(C) Equanil (D) Mescaline

12. Which of the following is a hypnotic drug
(A) Luminal (B) Salol
(C) Catechol (D) Chemisol

13. An antipyretic is
(A) Quinine (B) Paracetamol
(C) Luminal (D) Piperazine

14. The drug used as an antidepressant is
(A) Luminol (B) Tofranil
(C) Mescaline (D) Sulphadiazine

15. Chloramine-T is a
(A) Disinfectant (B) Antiseptic
(C) Analgesic (D) Antipyretic

16. Streptomycin is effective in the treatment of
(A) Tuberculosis (B) Malaria
(C) Typhoid (D) Cholera

17. Which of the following is not an antiseptic drug
(A) Iodoform (B) Dettol
(C) Gammexane (D) Genatian violet

18. Which is used for sterilization of water in water supply system of cities
(A) Chlorine
(B) Sulphurdioxide
(C) Potassium permanganate
(D) DDT

19. A drug effective in the treatment of pneumonia, bronchitis, etc, is
(A) Streptomycin (B) Chloramphenicol
(C) Penicillin (D) Sulphaguanidine

20. Aspirin is obtained by the reaction of CH_3COCl with
(A) Phenol (B) Benzoic acid
(C) Salicylic acid (D) Benzaldehyde

21. Salol can be used as
(A) Antiseptic (B) Antipyretic
(C) Analgesic (D) None of these

22. The drug which is effective in curing malaria is
(A) Quinine (B) Aspirin
(C) Analgin (D) Equanil

23. Morphine is
(A) Anaesthetic (B) Analgesic
(C) Antiseptic (D) Antibiotics

24. Which of the following is a hallucinogenic drug
(A) Methedrine (B) Calmpose
(C) LSD (D) Seconal

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. Which of the following is a basic dye –
(A) Alizarin **(B)** Phthalein **(C)** Aniline yellow **(D)** Orange-I

2. Diazo coupling is useful to prepare some –
(A) Pesticides **(B)** Dyes **(C)** Proteins **(D)** Vitamins

3. Which of the following is an azo dye –
(A) Methyl orange **(B)** Phenolphthalein **(C)** Malachite green **(D)** Methylene blue

4. An antipyretic is –
(A) Quinine **(B)** Paracetamol **(C)** Luminal **(D)** Piperazine

5. Medicine which is an antibiotic is –
(A) Ampicillin **(B)** Aspirin **(C)** Chloroquine **(D)** None of these

6. Alizarin belongs to the class of –
(A) Vat dyes **(B)** Mordant dyes **(C)** Substantive dyes **(D)** Reactive dyes

7. Paracetamol is a/an –
(A) Both antipyretic and analgesic **(B)** Analgesic
(C) Antipyretic **(D)** Antimalarial

8. Which of the following compounds is aspirin –
(A) Methyl salicylate **(B)** Acetylsalicylic acid **(C)** Phenyl salicylate **(D)** Salicylic acid

9. Sulpha drugs are derivatives of –
(A) Benzene sulphonic acid **(B)** Sulphanilic acid **(C)** Sulphanilamide **(D)** p - aminobenzoic acid

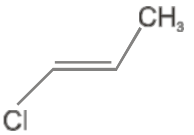
10. Which of the following is a natural dye –
(A) Phenolphthalein **(B)** Alizarin **(C)** Martius yellow **(D)** Malachite green

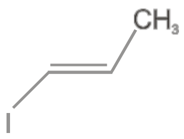
11. Octane number is zero for -
(A) Isoheptane **(B)** n-heptane **(C)** Isooctane **(D)** n-octane

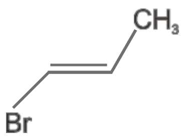
12. Petroleum is obtained from water gas, name of the reaction involved is -
(A) Fischer-tropsch **(B)** Bergius **(C)** Dow's **(D)** Kjeldahl's

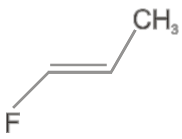
13. Which of the following represents a double base propellant ?
(A) Nitromethane **(B)** Nitrocellulose + nitroglycerine
(C) N_2O_4 + monomethylhydrazine **(D)** Liquid H_2 + liquid O_2

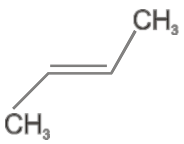
14. Which of the following represents a biliquid propellant ?
(A) Liquid N_2O_4 + unsymmetrical dimethylhydrazine (UDMH)
(B) Liquid N_2O_4 + acrylic rubber
(C) Nitroglycerine + nitrocellulose
(D) Polybutadiene + ammonium perchlorate

15. Which will have higher dipole moment than  ?

(A) 

(B) 

(C) 

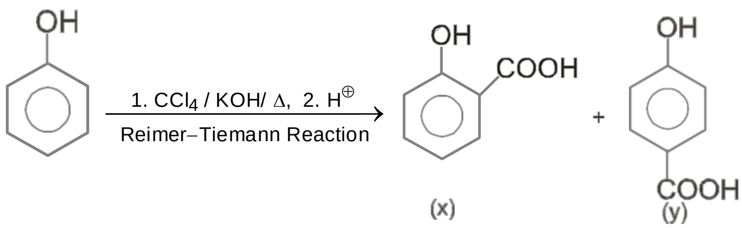
(D) 

Exercise # 3

PART - 1

MATRIX MATCHCOLUMN

1. Compare the properties of two isomeric products x and y formed in the following reaction.



Match the following :

Column-I	**Column-II**
(A) Dipole moment	**(p)** X > Y
(B) H_2O solubility	**(q)** Y = X
(C) Boiling point	**(r)** Y > X
(D) Melting point	**(s)** Can't say

Exercise # 4

PART - 1

PREVIOUS YEAR (NEET/AIPMT)

1. Green chemistry means such reactions which **[CBSE AIPMT 2008]**
(A) produce colour during reactions
(B) reduce the use and production of hazardous chemicals
(C) are related to the depletion of ozone layer
(D) study the reactions in plants

2. Which one of the following is employed as a tranquiliser ? **[CBSE AIPMT 2009]**
(A) Equanil (B) Naproxen
(C) tetracycline (D) Chloropheninamine

3. Whhich one of the following is employed as a tranquiliser drug ? **[CBSE AIPMT 2010]**
(A) Promethazine (B) Valium
(C) Naproxen (D) Mitepristone

4. Which one of the following is employed as antihistamine ? **[CBSE AIPMT 2011]**
(A) Diphenyl hydramine (B) Norethindrone
(C) Omeprazole (D) Chloroamphenicol

5. Which one of the following statements regarding photochemical smog is not correct ? **[CBSE AIPMT 2012]**
(A) Carbon monoxide does not play any role in photochemical smog formation
(B) Photochemical smog is an oxidising agent in character
(C) Photochemical smog is formed through photochemical reaction involving solar energy
(D) PHotochemical smog does not cause irritation in eyes and throat

6. Antiseptics and disinfectant either kill or prevent growth of microoranisms. Identify which of the following is not true. **[NEET 2013]**
(A) A 0.2% solution of phenol is an antiseptic while 1% solution acts as a disinfectant
(B) Chlorine and iodine are used as strong disinfectants
(C) Dilute solutions of boric acid and hydrogen, peroxide are strong antiseptics
(D) Disinfectants harm the living tissues

7. Which one of the following is not a common component of photochemical smog ? **[CBSE AIPMT 2014]**
(A) Ozone
(B) Acrolein
(C) Peroxyacetyl nitrate
(D) Chlorofluorocarbons

8. Bithional is generally added to the soaps as an additive to function as a/an **[CBSE AIPMT 2015]**
(A) softener (B) dryer
(C) buffering agent (D) antiseptic

9. Which of the following is an analgesic ? **[NEET 2016, Phase I]**
(A) Penicillin (B) Streptomycin
(C) Chloromycetin (D) Novalgin

10. Mixture of chloroxylenol and terpineol acts as **[NEET 2017]**
(A) analgesic (B) antiseptic
(C) antipyretic (D) antibiotic

11. Which of the following is a sink for CO ? **[NEET 2017]**
(A) Haemoglobin
(B) Microorganisms present in the soil
(C) Oceans
(D) Plants

MOCK TEST

STRAIGHT OBJECTIVE TYPE

1. Aspirin is
(A) Antibiotic (B) Antipyretic (C) Sedative (D) Psychedelic

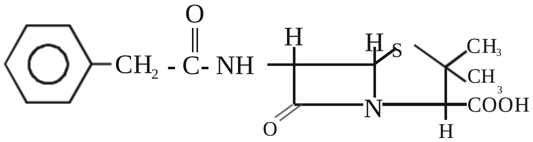
2. Which of the following drugs is a tranquilizer and sedative
(A) Sulphadiazine (B) Papaverine (C) Equanil (D) Mescaline

3. Which of the following is a hypnotic drug
(A) Luminal (B) Salol (C) Catechol (D) Chemisol

4. An antipyretic is
(A) Quinine (B) Paracetamol (C) Luminal (D) Piperazine

5. The drug used as an antidepressant is
(A) Luminol (B) Tofranil (C) Mescaline (D) Sulphadiazine

6. The structure given below is known as



(A) Penicilline F (B) Penicillin G (C) Penicillin K (D) Ampicillin
(E) Sulphadiazine

7. Aspirin is chemically
(A) Methyl salicylate (B) Ethyl salicylate (C) Acetyl salicylic acid (D) o-hydroxy benzoic acid

8. Which of the following can possibly be used as analgesic without causing addiction and any modification
(A) Morphine (B) N-acetylparaaminophenol
(C) Diazepam (D) Tetra hydrocatenol

9. Further growth of cancerous cells in the body is arrested by
(A) Physiotherapy (B) Chemotherapy (C) Electrotherapy (D) Psychotherapy

10. Which one of the following is known as broad spectrum antibiotics
(A) Streptomycine (B) Ampicillin (C) Chloramphenicol (D) Penicillin G

11. Which of the following is a local anaesthetic
(A) Diazepam (B) Procaine (C) Mescaline (D) None of the above

12. Which of the following is molecular disease
(A) Allergy (B) Cancer (C) German measeles (D) Sickel-cell-anaemia

13. Which statement is false
(A) Some disinfectants can be used antiseptics at low concentration
(B) Sulphadiazine is a synthetic antibacterial
(C) Ampicillin is a natural antibiotic
(D) Aspirin is analgesic and antipyratic both

14. Tranquilisers are substances used for the treatment of
(A) Cancer (B) AIDS (C) Mental diseases (D) Physical disorders
(E) Blood infection

CHAPTER 08

PERIODIC TABLE

If you memorize the periodic table it will speed you up if you're a chemist, but by and large, the reason you have a periodic table is so that you can store that information outside of your body. That way it frees up some part of your brain to do something else.

"BILLNYE"

INTRODUCTION

The chapter gives an insight to the contribution made by different scientists to arrange the known elements in a manner which could be smooth and informative and the elements properties could justify its position. Thus what we see in the form of modern periodic table today follow a logical sequence of electronic configuration capable enough to explain the trend in physical and chemical properties of the elements.

At present 118 elements are known. of them, the recently discovered elements are man made. Efforts to synthesise new elements are continuing. With such a large number of elements it is very difficult to study individually the chemistry of all these elements and their innumerable compounds individually. To ease out this problem, scientists searched for a systematic way to organise their knowledge by classifying the elements.

(a) Along a period acidic nature increases.

(b) Down the group basic nature increases

Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl

$\longleftarrow\!\!\!\!\longrightarrow$

$X_A - X_O > 2.3$	$X_A - X_O = 2.3$	$X_A - X_O < 2.3$
Basic	Amphoteric	Acidic

ie. when in periodic table the distance between the element and oxygen increases, basic character increases.

$$\underset{\xrightarrow{\hspace{6em}}}{NO_2 > ZnO > K_2O}$$

acidic character decreases

ED OS KEY POINTS

Note: BeO, Al_2O_3, ZnO, SnO, PbO, SnO_2, PbO_2, Sb_2O_3 etc. are amphoteric oxides.
CO, H_2O, NO, N_2O etc. are neutral oxides.

$\boxed{\text{Acidic strength of oxide and oxyacid} \propto \text{Electronegativity}}$

B_2O_3 $\quad CO_2$ $\quad N_2O_5$

$\xrightarrow{\hspace{10em}}$

EN increase, acidic nature increasse.

$SO_3 > SeO_3 > TeO_3$	$HNO_3 > H_2CO_3 > H_3BO_3$	$HClO_4 > HBrO_4 > HIO_4$
$H_2SO_4 > H_2SeO_4 > H_2TeO_4$	$H_3PO_4 > H_3AsO_4 > H_3SbO_4$	$N_2O_5 > P_2O_5 > As_2O_5$
$H_2SO_3 > H_2SeO_3 > H_2TeO_3$	$HOF > HOCl > HOBr > HOI$	$N_2O_3 > P_2O_3 > As_2O_3 > Sb_2O_3$

$\boxed{\text{Acidic nature oxidation state}}$

Acidic properties increases with increasing oxidation state of an element

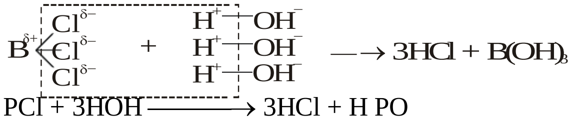
$HClO_4 > HClO_3 > HClO_2 > HClO$	$HNO_3 > HNO_2$
$H_2SO_4 > H_2SO_3$	$N_2O_5 > N_2O_3$
$SO_3 > SO_2$	$Sb_2O_5 > Sb_2O_3$

(I) Hydrolysis of AX :

Where A = Other element and X = Halogen

(a) If electronegativity of X > Electronegativity of A then on hydrolysis product will be HX.

Ex. (BCl_3), Electronegativity of Cl > Electronegativity of B

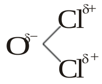


$PCl_3 + 3HOH \longrightarrow 3HCl + H_3PO_3$

$PCl_3 . Cl_2 + H_2O \longrightarrow 2HCl + POCl_3$

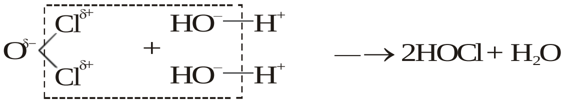
$POCl_3 + 3HOH \longrightarrow 3HCl + H_3PO_4$

(b) If electronegativity of X < electronegativity of A then on hydrolysis product will be HOX (hypohalous acid)

Ex. Cl_2O 

Here electronegativity of O > Cl

So On hydrolysis –



important facts to remember

1. Lowest electronegativity : Cs
2. Highest electronegativity : F
3. Highest ionisation potential : He
4. Lowest ionisation potential : Cs
5. Lowest electron affinity : Noble gases
6. Highest electron affinity : Chlorine
7. Least electropositive element : F
8. Lowest m. pt. metal : Hg
9. Highest m. pt. and b. pt. metal : W (Tungsten)
10. Lowest m. pt. and b. pt. non metal : He
11. Notorious element : Hydrogen
12. Lightest element : Hydrogen
13. Smallest atomic size : H
14. Largest atomic size : Cs
15. Largest anionic size : I^-
16. Smallest cation : H^+
17. Most electropositive element : Cs
18. Element with electronegativity next to Fluorine : Oxygen
19. Group containing maximum no. of gaseous elements in periodic table : Zero group
20. Total number of gaseous elements : in periodic table : 11 (H, N, O, F, Cl, He, Ne, Ar, Kr, Xe, Rn)
21. Total number of liquid elements in periodic table : 6 (Ga, Br, Cs, Hg, Fr, Uub)
22. Liquid element of radioactive nature : Fr
23. Total number of radioactive elements in periodic table : 25
24. Volatile d block elements : Zn, Cd, Hg, Uub
25. Element containing no neutron : H
26. Most abundant element on earth : Oxygen
27. Most abundant metal on earth : Al
28. Element having maximum tendency for catenation : Carbon
29. Non metal having highest m. pt., b.pt. : Carbon (dimond)
30. Metals showing highest oxidation number : Os (+8), Ru
31. Most electrovalent compound : CsF
32. Most stable carbonate : Cs_2CO_3

SOLVED EXAMPLE

Ex. 1 Following are the valence shell electronic configurations of some elements.

(i) $3s^2\,3p^5$ **(ii)** $3d^{10}\,4s^2$

(iii) $2s^2\,3p^6\,4s^1$ **(iv)** $1s^2\,2s^2$

Find out the blocks to which they belong in the periodic table ?

Ans. **(i)** p-block **(ii)** d-block

(iii) s-block **(iv)** s-block

Sol. The block of the elements depend on the type of sub-shell which receive the last electron. In case of

(i) it enters in 3p-subshell,

(ii) z it enters 3d-subshell,

(iii) it enters 4s-subshell and

(iv) it enters 2s-subshell.

Ex. 2. A M^{2+} ion derived from a metal in the first transition metal series has four electrons in 3d subshell. What element might M be ?

Ans. Chromium

Sol. Electron configuration of M^{2+} is

$[Ar]^{18}\,4s^0\,3d^4$

□ Electron configuration of M is

$[Ar]^{18}\,4s^1\,3d^5$ (and not $4s^2\,3d^4$)

So total number of electrons = 24.

Hence, metal M is chromium (Cr).

Ex. 3 Find out the group of the element having the electronic configuration, $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6\,4s^2$.

Ans. As last electron enters in d-subshell, therefore this belongs to d-block. For d-block element the group number is equal to the number of valence shell electrons + number of electrons in (n-1) d-subshell.

So, group number = 6 + 2 = 8.

Ex. 4 Arrange the following ions in the increasing order of their size : Be^{2+}, Cl^-, S^{2-}, Na^+, Mg^{2+}, Br^- ?

Ans. $Be^{2+} < Mg^{2+} < Na^+ < Cl^- < S^{2-} < Br^-$

Sol. Be^{2+} is smaller than Mg^{2+} as Be^{2+} has one shell where as Mg^{2+} has two shells.

Mg^{2+} and Na^+ are isoelectronic species : Ionic radius $\propto$ 1/nuclear charge.

Cl^- and S^{2-} are isoelectronic species : Ionic radius $\propto$ 1/nuclear charge.

Cl^- is smaller than Br^- as Cl^- has three shells where as Br^- has four shells.

Ex. 5 In Column- I , there are given electronic configurations of some elements. Match these with the correct metals given in Column-II :

Column-I	**Column-II**
(A) ns^2, np^5	**(p)** Chromium
(B) $(n-1)\,d^{10}$, ns^1	**(q)** Copper
(C) $(n-1)\,d^5$, ns^1	**(r)** Krypton
(D) $(n-1)\,d^{10}$, ns^2, np^6	**(s)** Bromine

Ans. **(A)** → (s) ; **(B)** → (q) ; **(C)** → (p) ; **(D)** → (r).

Sol. **(A)** ns^2np^5 is general valence shell electron configuration of halogens. So this configuration belongs to bromine.

(B) $(n-1)\,d^{1\text{-}10}\,ns^{1\text{-}2}$; This is electron configuration of d-block elements. As it contains $(n-1)\,d^{10}ns^1$ configuration it belongs to copper.

(C) $(n-1)\,d^{1\text{-}10}\,ns^{1\text{-}2}$; This is electron configuration of d-block elements. As it contains $(n-1)\,d^5\,ns^1$ configuration it belongs to chromium.

(D) Noble gases has valence shell electron configuration $ns^2\,np^6$, so it belongs to krypton.

Ex. 6 Match the metals given in Column-II with their type given in Column-I :

Column-I	**Column-II**
(A) Metalloid	**(p)** Sulphur
(B) Radioactive	**(q)** Gold
(C) Transition metal	**(r)** Arsenic
(D) Chalcogen	**(s)** Uranium

Ans. **(A)** → (r) ; **(B)** → (s) ; **(C)** → (q) ; **(D)** → (p)

Sol. **(A)** Arsenic is a metalloid because it behaves as metal (forming cation, As^{3+} -$AsCl_3$) as well as nonmetal (forming anion, As^{3-}-AsH_3).

(B) Uranium is a radioactive element.

(C) Those elements which in their neutral atoms or in most common oxidation state have partially filled d-orbitals are called as transition elements. Gold in its +3 oxidation state has electron configuration $[Xe]^{54}$, $5d^8 6s^0$.

(D) 16th group elements like oxygen and sulphur are ore forming elements and therefore are called as chalcogens.

Exercise # 1

SINGLE OBJECTIVE | NEET LEVEL

1. Which of the following statement is not correct for the element having electronic configuration

$1s^2$, $2s^2p^6$, $3s^1$

(A) It is a monovalent electropositive
(B) It forms basic oxide
(C) It is a non-metal
(D) It has low electron affinity

2. Which of these dose not reflect the periodicity of the elements
(A) Bonding behaviour **(B)** Electronegativity
(C) Ionization energy **(D)** Neutron/proton ratio

3. If an atom has electronic configuration

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$, it will be placed in

(A) Second group **(B)** Third group
(C) Fifth group **(D)** Sixth group

4. All the s-block elements of the periodic table are placed in the groups …
(A) IA and IIA **(B)** IIIA and IVA
(C) B sub groups **(D)** VA to VIIA

5. The electronic configuration of halogen is
(A) ns^2np^6 **(B)** ns^2np^3
(C) ns^2np^5 **(D)** ns^2

6. The ratio between radii of He^+ ion and H atom is
(A) $\frac{1}{2}$ **(B)** 1
(C) $\frac{3}{2}$ **(D)** 2

7. The smallest among the following ions is
(A) Na^+ **(B)** Mg^{2+}
(C) Ba^{2+} **(D)** Al^{3+}

8. Which is smallest in size
(A) O^{2-} **(B)** C^{4-}
(C) F^- **(D)** N^{3-}

9. Which of the following has largest size
(A) Al **(B)** Al^+
(C) Al^{+2} **(D)** Al^{+3}

10. Of the following, the one with largest size is
(A) Cl^- **(B)** Ar
(C) K^+ **(D)** Ca^{2+}

11. Which cation has smallest radius
(A) K^+ **(B)** Na^+
(C) Li^+ **(D)** Be^{2+}

12. The radii of F, F^-, O and O^{-2} are in the order of
(A) $O^{2-} > F^- > O > F$ **(B)** $O^{2-} > F^- > F > O$
(C) $F^- > O^{2-} > F > O$ **(D)** $O^{2-} > O > F^- > F$

13. Which of the following has the smallest size
(A) Na^+ **(B)** Mg^{+2}
(C) Cl^- **(D)** F^-

14. Which of the following is largest
(A) Cl^- **(B)** S^{2-}
(C) Na^+ **(D)** F^-

15. Which of the following property displays progressive increase down a group in the Bohr's periodic table
(A) Electronegativity **(B)** Electron affinity
(C) Ionization potential **(D)** Size of the atom

16. Atomic radii of fluorine and neon in angstrom units are respectively given by
(A) 0.762, 1.60
(B) 1.60, 1.60
(C) 0.72, 0.72
(D) None of these values

17. Which ion has greatest radius in the following
(A) H^- **(B)** F^-
(C) Br^- **(D)** I^-

18. Which has the maximum atomic radius
(A) Al **(B)** Si
(C) P **(D)** Mg

19. Which one of the following ions has the highest value of ionic radius
(A) O^{2-} **(B)** B^{3+}
(C) Li^+ **(D)** F^-

20. On going down a main sub-group in the periodic table (example Li to Cs in IA or Be to Ra in IIA), the expected trend of changes in atomic radius is a
(A) Continuous increase
(B) Continuous decrease
(C) Periodic one, an increase followed by a decrease
(D) A decrease followed by increase

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. Atomic number of Ag is 47. In the same group, the atomic numbers of elements placed above and below Ag in Long form of periodic table will be :
(A) 29, 65 (B) 39, 79
(C) 29, 79 (D) 39, 65

2. Element with electronic configuration as [Ar] $3d^5$ $4s^1$ is placed in____in Modern periodic table :
(A) IA (1st group), s-block
(B) IB (7th group), d-block
(C) VIB (8th group), d-block
(D) VIB (6th group), d-block

3. In modern periodic table, the element with atomic number Z = 118 will be :
(A) Uuo ; Ununoctium ; alkaline earth metal
(B) Uno ; Unniloctium ; transition metal
(C) Uno ; Unniloctium ; alkali metal
(D) Uuo ; Ununoctium ; noble gas

4. Which of the following is not an actinoid :
(A) Curium (Z = 96) (B) Californium (Z = 98)
(C) Uranium (Z = 92) (D) Terbium (Z = 65)

5. Which of the following statements is not correct regarding hydrogen :
(A) It resembles halogens in some properties.
(B) It resembles alkali metals in some properties.
(C) It can be placed in 17th group of Modern periodic table.
(D) It cannot be placed in 1st group of Modern periodic table.

6. The order of screening effect of electrons of s, p, d and f orbitals of a given shell of an atom on its outer shell electrons is
(A) $s > p > d > f$ (B) $f > d > p > s$
(C) $p < d < s > f$ (D) $f > p > s > d$

7. Which of the following is/are generally true regarding effective nuclear charge (Z_{eff}) :
(A) It increases on moving left to right in a period.
(B) It remains almost constant on moving top to bottom in a group.
(C) For isoelectronic species, as Z increases, Z_{eff} decreases.
(D) Both (A) and (B).

8. Which of the following is the correct order of size of the given species :
(A) $I > I^- > I^+$ (B) $I^+ > I^- > I$
(C) $I > I^+ > I^-$ (D) $I^- > I > I^+$

9. Match the correct atomic radius with the element :

S.No.	Element	Code	Atomic radius (pm)
(i)	Be	(p)	74
(ii)	C	(q)	88
(iii)	O	(r)	111
(iv)	B	(s)	77
(v)	N	(t)	66

(A) (i) – r, (ii) – q, (iii) – t, (iv) – s, (v) – p
(B) (i) – t, (ii) – s, (iii) – r, (iv) – p, (v) – q
(C) (i) – r, (ii) – s, (iii) – t, (iv) – q, (v) – p
(D) (i) – t, (ii) – p, (iii) – r, (iv) – s, (v) – q

10. Select correct statement(s) about radius of an atom:
(A) Values of Vander waal's radii are larger than those of covalent radii because the Vander waal's forces are much weaker than the forces operating between atoms in a covalently bonded molecule.
(B) The metallic radii are smaller than the Vander waal's radii, since the bonding forces in the metallic crystal lattice are much stronger than the Vander waal's forces.
(C) Both (A) & (B)
(D) None of these

11. Which of the following order of atomic / ionic radius is not correct ?
(A) $F < Cl < Br < I$ (B) $Y^{3+} > Sr^{2+} > Rb^+$
(C) $Nb \approx Ta$ (D) $Li > Be > B$

12. The size of isoelectronic species F^-, Ne and Na^+ is affected by :
(A) nuclear charge (Z)
(B) valence principal quantum number (n)
(C) electron-electron interaction in the outer orbitals
(D) none of the factors because their size is the same.

13. Which of the following order of radii is correct :
(A) $Li < Be < Mg$ (B) $H^+ < Li^+ < H^-$
(C) $O < F < Ne$ (D) $Li < Na < K < Cs < Rb$

14. Which one of the following statements is incorrect in relation to ionisation enthalpy ?
(A) Ionization enthalpy increases for each successive electron.
(B) The greatest increase in ionization enthalpy is experienced on removal of electron from core of noble gas configuration.
(C) End of valence electrons is marked by a big jump in ionization enthalpy.
(D) Removal of electron from orbitals bearing lower n value is easier than from orbitals having higher n value.

Exercise # 3

PART - 1

MATRIX MATCHCOLUMN

1. Match the electronic configurations of the elements given in **column-(I)** with their correct characteristic**(s)** (i.e. properties for given configuration) given in **column-(II)**.

Column-I	**Column-II**
(A) $1s^2$	**(p)** Element shows highest negative oxidation state.
(B) $1s^2\ 2s^2\ 2p^5$	**(q)** Element shows highest first ionisation enthalpy.
(C) $1s^2\ 2s^2 2p^6\ 3s^2 3p^5$	**(r)** Element shows highest electronegativity on Pauling scale.
(D) $1s^2\ 2s^2\ 2p^2$	**(s)** Element shows maximum electron gain enthalpy (most exothermic).

2. Match Column–I (atomic number of elements) withColumn–II (position of element in periodic table) and select the correct answer using the codes given below :

Column-I	**Column-II**
(A) 19	**(p)** p-block
(B) 22	**(q)** f-block
(C) 32	**(r)** d-block
(D) 64	**(s)** s-block

3. Match the species/elements listed in column I with their characteristic listed in column II.

Column I	**Column II**
(A) SO_2, NO^{-3}, CO_3^{-2}	**(p)** Semi-metals
(B) Ge, As, Sb	**(q)** Inert gases
(C) Ar, Kr, Xe	**(r)** Isoelectronic species
(D) Ca, Sr, Ba	**(s)** Alkaline earth metals

4. Match the values of ionization energy and electron gain enthalpi listed in column I with characteristic(s) of elements listed in column II.

Column I			**Column II**
$\Delta_1 H_1$,	$\Delta_1 H_2$,	$\Delta_{eg}H$(in kJ mol^{-1}) ,	
(A) 2372	5251	+48	**(p)** Elements which acts as a strong reducing agent
(B) 419	3051	-48	**(q)** Elements which exists as a monoatomic molecule
(C) 1681	3374	-333	**(r)** Least reactive non-metal
(D) 1008	1846	-295	**(s)** Elements which acts as a strong oxidising agent
			(t) Element which oxide is a stronger basic in nature

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. Correct order of Ist ionisation potential (IP) among following elements Be, B, C, N, O is

[CBSE AIPMT 2001]

(A) B < Be < C < O < N
(B) B < Be < C < N < O
(C) Be < B < C < N < O
(D) Be < B < C < O < N

2. An atom has electronic configuration $1s^2$, $2s^2 2p^6$, $3s^2 3p^6 3d^3$, $4s^2$, you will place it in

[CBSE AIPMT 2002]

(A) fifth group
(B) fifteenth group
(C) second group
(D) third group

3. Which of the following order is wrong ?

[CBSE AIPMT 2002]

(A) $NH_3 < PH_3 < AsH_3$ – Acidic
(B) Li < Be < B < C – 1st Ionisation potential
(C) $Al_2O_3 < MgO < Na_2O < K_2O$ – Baisc
(D) $Li^+ < Na^+ < K^+ < Cs^+$ – Ionic radius

4. The ions O^{2-}, F^-, Na^+ Mg^{2+} and Al^{3+} are isoelectronic. Their ionic radii show

[CBSE AIPMT 2003]

(A) an increase from O^{2-} to F^- and then decrease from Na^+ to Al^{3+}
(B) a decrease from O^{2-} to F^- and then increase from Na^+ to Al^{3+}
(C) a significant increase from O^{2-} to Al^{3+}
(D) a significant decrease from O^{2-} to Al^{3+}

5. Ionic radii are **[CBSE AIPMT 2004]**

(A) inversely proportional to effective nuclear charge
(B) inversely proportional to square of effective nuclear charge
(C) directly proportional to effective nuclear charge
(D) directly proportional to square of effective nuclear charge

6. Identify the correct order of the size of the following.

[CBSE AIPMT 2007]

(A) $Ca^{2+} < K^+ < Ar < S^{2-} < Cl^-$
(B) $Ca^{2+} < K^+ < Ar < Cl^- < S^{2-}$
(C) $Ar < Ca^{2+} < K^+ < Cl^- < S^{2-}$
(D) $Ca^{2+} < Ar < K^+ < Cl^- < S^{2-}$

7. Which of the following electronic configuration of an atom has the lowest ionisation enthalpy ?

[CBSE AIPMT 2007]

(A) $1s^2, 2s^2 2p^5$ **(B)** $1s^2, 2s^2 2p^3$
(C) $1s^2, 2s^2 2p^5, 3s^1$ **(D)** $1s^2, 2s^2 2p^6$

8. The correct order of decreasing second ionisation enthalpy of Ti(22), Cr(24) and Mn(25) is

[CBSE AIPMT 2008]

(A) Cr > Mn > V > Ti
(B) V > Mn > Cr > Ti
(C) Mn > Cr > Ti > V
(D) Ti > V > Cr > Mn

9. Which of the following oxides is not expected to react with sodium hydroxide?

[CBSE AIPMT 2009]

(A) B_2O_3 **(B)** CaO
(C) SiO_2 **(D)** BaO

10. Which one of the elements with the following outer orbital configurations may exhibit the largest number of oxidation states? **[CBSE AIPMT 2009]**

(A) $3d^3, 4s^2$ **(B)** $3d^5, 4s^1$
(C) $3d^5, 4s^2$ **(D)** $3d^2, 4s^2$

11. Amongst the elements with following electronic configurations, which one may have the highest ionisation energy ? **[CBSE AIPMT 2009]**

(A) [Ne] $3s^2 3p^3$ **(B)** [Ne] $3s^2 3p^2$
(C) [Ar] $3d^{10}, 4s^2 4p^3$ **(D)** [Ne] $3s^2 3p^1$

12. Which of the following represents the correct order of increasing electron gain enthalpy with negative sign for the elements O, S, F and Cl?

[CBSE AIPMT 2010]

(A) Cl < F < O < S
(B) O < S < F < Cl
(C) F < S < O < Cl
(D) S < O < Cl < F

13. The correct order of the decreasing ionic radii among the following isoelectronic species is

[CBSE AIPMT 2010]

(A) $Ca^{2+} > K^+ > S^{2-} > Cl^-$
(B) $Cl^- > S^{2-} > Ca^{2+} > K^+$
(C) $S^{2-} > Cl^- > K^+ > Ca^{2+}$
(D) $K^+ > Ca^{2+} > Cl^- > S^{2-}$

MOCK TEST

STRAIGHT OBJECTIVE TYPE

1. Consider the following statements;

(I) Rutherford name was associated with the developement of periodictable.

(II) A metal M having electronic configuration $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$ is d-block element.

(III) Diamond is not an element.

(IV) The electronic configuration of the most electronegative element is $1s^2, 2s^2, 2p^5$, and select the correct one from the given codes.

(A) I, II, IV **(B)** I, II, III, IV **(C)** II, IV **(D)** I, III, IV

2. The correct order of second ionisation potential of carbon, nitrogen, oxygen and flourine is :

(A) $C > N > O > F$ **(B)** $O > N > F > C$ **(C)** $O > F > N > C$ **(D)** $F > O > N > C$

3. The electron gain enthalpies of halogens in kJ/mol are as given below.

$F = –332, Cl = –349, Br = –324, I = –295$

The less negative value for F as compared to that of Cl is due to :

(A) strong electron-electron repulsions in the compact 2p-subshell of F.

(B) weak electron-electron repulsions in the compact 2p- subshell of Cl

(C) smaller electronegativity value of F than Cl

(D) **(A)** and **(B)** both

4. Which of the following statement is not correct ?

(A) The first ionisation energies (in kJ/mol) of carbon, silicon, germaniu, tin and lead are 1086, 786, 761, 708 and 715 respectively.

(B) Down the group, electronegativity decreases from B to Tl in boron family.

(C) Among oxides of the elements of carbon family, CO is neutraql, GeO is acidic and SnO is amphoteric.

(D) The 4f- and 5f- inner transition elements are placed separately at the bottom of the periodic table to maintain its structure.

5. Which of the following order is correct ?

(A) $F > N > C > Si > Ga$ – non-metallic character. **(B)** $F > Cl > O > N$ – oxidising property.

(C) $C < Si > P > N$ – electron affinity value. **(D)** All of these.

6. If the same element is forming oxides in different oxidation state then :

(A) that oxide will be neutral in nature in which element will be in its highest oxidation state.

(B) that oxide will be highest acidic in nature in which element will be in the highest oxidation state.

(C) that oxide will be amphoteric in nature in which element will be in the highest oxidation state.

(D) that oxide will be higly basic in nature in which element will be in the highest oxidation state.

7. What will be the order of Ist ionisation energy

(A) $Li > Na > K$ **(B)** $K > Li > Na$ **(C)** $Na > Li > K$ **(D)** $Li > K > Na$

8. Which of the following configurations represents atoms of the elements having the highest second ionization energy

(A) $1s^2 2s^2 2p^4$ **(B)** $1s^2 2s^2 2p^6$ **(C)** $1s^2 2s^2 2p^6 3s^1$ **(D)** $1s^2 2s^2 2p^6 3s^2$

9. The first ionization potentials in electron volts of nitrogen and oxygen atoms are respectively given by

(A) 14.6, 13.6 **(B)** 13.6, 14.6 **(C)** 13.6, 13.6 **(D)** 14.6, 14.6

10. The elements which occupy the peaks of ionisation energy curve, are

(A) Na, K, Rb, Cs **(B)** Na, Mg, Cl, I **(C)** Cl, Br, I, F **(D)** He, Ne, Ar, Kr

CHAPTER 09

CHEMICAL BONDING

The nature of the chemical bond is the problem at the heart of all chemistry.

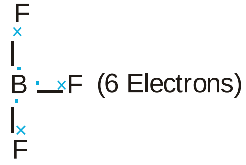
"BRYCE CRAWFORD"

INTRODUCTION

The attractive force which holds various constituents (atoms, ions, etc,) together in different chemical species is called a chemical bond. Since the formation of chemical compounds takes place as a result of combination of atoms of various elements in different ways, it raises many questions. why do atoms combine? Why are only certain cmbinations possible? Why do molecules possess definite shapes? To answer such questions different theories and concepts have been put forward from time to time. These are kossel-Lewls approach, valence Shell Electron Pair Repulsion (VSEPR) Theory, Valence Bond (VB) Theory and Molecular orbital and the interpretation of the nature of chemical bonds have closely been related to the developments in the understanding of the structure of atom, the electronic configuration of elements and the periodic table. Every system tends to be more stable and bonding is nature's way of lowering the energy of the system to attain stability .

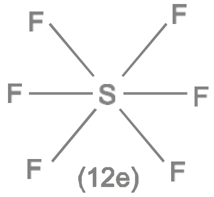
Contraction of Octet (Incomplete Octet)

BeF_2	BF_3	$AlCl_3$	BCl_3
(4e)	(6e)	(6e)	(6e)



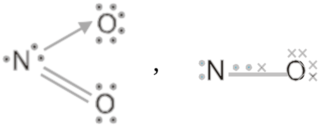
Expansion of Octet (Due to Empty d-Orbitals)

PCl_5	SF_6	ClF_3	ICl_5	IF_7
↓	↓	↓	↓	↓
($10e^-$)	($12e^-$)	($10e^-$)	($12e^-$)	($14e^-$)



Odd Electron Species

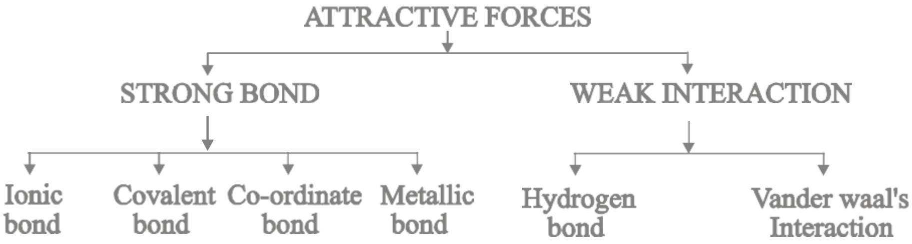
Ex. NO, NO_2, ClO_2 etc.



Compounds of Noble Gases

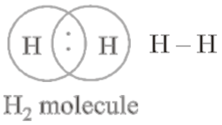
Noble gases which have already completed their octets (or douplet in case of He.) should not form compounds. However, their compounds like XeF_2, XeF_6 & KrF_2 etc., have been actually prepared.

CLASSIFICATION OFBONDS



Covalent Bond

(a) A covalent bond is formed by the mutual sharing of electrons between two atoms of electronegativity elements to complete their octet.(Except H which completes its duplet)

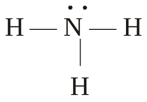


H_2 molecule

(b) The shared pair of electrons should have opposite spins, and are localised between two atoms concerned.

(c) Shairing of electrons may occurs in three ways –

No. of electrons shared between two atoms	Bonded Electron pair	Bond
2	1	Single bond (–)
4	2	Double bond (=)
6	3	Triple bond (≡)

Ex. 

$$H - \overset{\cdot\cdot}{\underset{|}{N}} - H \quad (\text{H below N})$$

{Three single bonds (not triple bond}

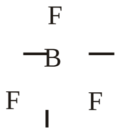
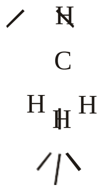
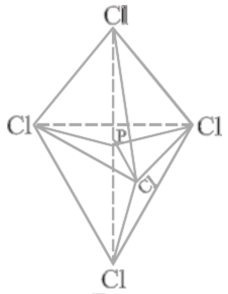
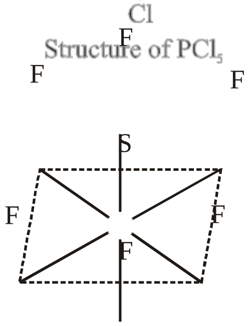
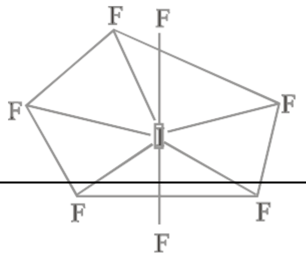
N ≡ N Triple bond. (not three single bond) O = O (Double bond) H – O – H (Two single bonds.)

Co-ordinate Bond

(a) It is a covalent bond in which the shared electron pair come from one atom is called coordinate bond.

(b) Necessary conditions for the formation of co-ordinate bond are -

(i) Octet of donor atom should be complete and should have atleast one lone pair of electron.

Sr. No.	Hybridisation	Structure	Bond Angle	Examples
1.	sp	Linear F Be F	180°	BeF_2
2.	sp^2	Triagonal planar 	120°	BF_3
3.	sp^3	Tetrahedral 	109°28'	CH_4
4.	sp^3d	Trigonal bipyramidal  Structure of PCl_5	3 orbitals-120° 2 perpendicular orbitals	PCl_5
5.	sp^3d^2	Octahedral 	90° between all hybrid orbitals	SF_6
6.	sp^3d^3	pentagonalbipiramidal 	5 bondangle 72° and 10 bond angles 90°	IF_7

SOLVED EXAMPLE

Ex.1 Which of the following will be strongest Lewis base ?

(A) CH_3CN **(B)** CH_3NH_2

(C) N_2 **(D)** None of these

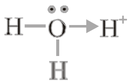
Sol. **(B)** In CH_3NH_2 hybridisation of N is sp^3 while in CH_3 CN hybridisation of N is sp. N_2 is also sp hybridised.

We know that in hybridisation, as s-character increases the electronegativity of atom also increases. Due to this tendency the release of lone pair of electrons becomes some what difficult. In methyl amine the nitrogen is in sp^3 hybridisation and therefore the donation of the lone pair of electron will be quite easier; so it is strongest Lewis base.

Ex.2 Which type of hybridisation is found in H_3O^+ ?

Sol. According to steric no. rule

Steric number = Number of bond pair(s) + number of lone pair(s) at central atom



So, steric number = 3 + 1 = 4.

Thus the hybridisation of oxygen in H_3O^+ is sp^3.

Ex.3 Classify the following bonds as ionic, polar covalent or covalent and give your reasons :

(A) SiSi bond in $Cl_3SiSiCl_3$

(B) SiCl bond in $Cl_3SiSiCl_3$

(C) CaF bond in CaF_2

(D) NH bond in NH_3

Sol. **(A)** Covalent, due to identical electronegativity.

(B) Covalent, due to less electronegativity difference.

(C) Ionic, due to more electronegativity difference.

(D)) Covalent, due to nearly similar electronegativity.

Ex.4 **(A)** Which one has highest and lowest melting point and why ?

NaCl KCl RbCl CsCl

(B) Why melting points of cesium halide (CsX) decrease in the order given below ?

CsF > CsCl > CsBr > CsI.

Sol. **(A)** NaCl will have highest lattice energy on account of the smaller Na^+ while CsCl has lowest lattice energy on account of the larger Cs^+. Hence NaCl has highest melting point and CsCl has lowest melting point .

(B) As size of anions increase their polarisability increases thus their covalent character increases and melting point decrease.

Ex.5 Which is **incorrect** statement?

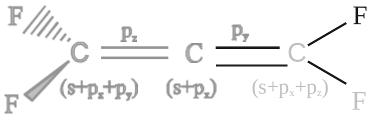
(A) In $CF_2=C=CF_2$ molecule all the four fluorine atoms are not in the same plane.

(B) Ka_2 of fumaric acid is more than Ka_2 of maleic acid due to intra molecular hydrogen bonding in maleic acid.

(C) The O–O bond length in $O_2[AsF_4]$ is longer than KO_2.

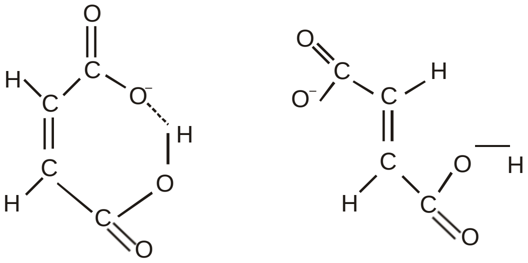
(D) The bond angle order in halogen – S – halogen is $OSF_2 < OSCl_2 \leq OSBr_2$

Ans. **(C)**

Sol. **(A)** 

As both carbon atoms are in different planes, all the four fluorine atoms are not in the same plane.

(B) maleic acid fumaric acid



Due to intramolecular hydrogen bonding the maleate ion gets stabilized and thus removal of second hydrogen becomes quite difficult.

(C) $O_2[AsF_4] = O_2^+$ B.O = 2.5

$KO_2 = O_2^-$ B.O = 1.5

Bond order $\propto \frac{1}{\text{bond length}}$; so O_2^+ has smaller bond length than O_2^-

(D) Greater the size of the halogen atoms greater will be the steric repulsions and thus larger will be the bond angles.

Ex.6 Which of the compounds $MgCO_3$ and $ZnCO_3$ is thermally more stable ? Explain.

Sol. Mg^{+2} has less polarising power due to inert gas configuration while Zn^{+2} has higher polarising power due to pseudo inert gas configuration. A cation i.e. Zn^{2+} with a greater, polarising power exercise a

Exercise # 1

SINGLE OBJECTIVE **NEET LEVEL**

1. Which forms a crystal of NaCl
(A) NaCl molecules **(B)** Na^+ and Cl^- ions
(C) Na and Cl atoms **(D)** None of the above

2. When sodium and chlorine reacts then
(A) Energy is released and ionic bond is formed
(B) Energy is released and a covalent bond is formed
(C) Energy is absorbed and ionic bond is formed
(D) Energy is absorbed and covalent bond is formed

3. Which one is least ionic in the following compounds
(A) AgCl **(B)** KCl
(C) $BaCl_2$ **(D)** $CaCl_2$

4. The valency of sulphur in sulphuric acid is
(A) 2 **(B)** 4
(C) 6 **(D)** 8

5. The number of electrons involved in the bond formation of N_2 molecule
(A) 2 **(B)** 4
(C) 6 **(D)** 10

6. The electronic configuration of four elements are given in brackets

$$L\left(1s^2,\ 2s^2\,2p^1\right);\ M\left(1s^2,\ 2s^2\,2p^5\right)$$

$$Q\left(1s^2,\ 2s^2\,2p^6,\ 3s^1\right);\ R\left(1s^2,\ 2s^2\,2p^2\right)$$

The element that would most readily form a diatomic molecule is
(A) Q **(B)** M
(C) R **(D)** L

7. Which species has the maximum number of lone pair of electrons on the central atom?
(A) $[ClO_3]^-$ **(B)** XeF_4
(C) SF_4 **(D)** $[I_3]^-$

8. A simple example of a coordinate covalent bond is exhibited by
(A) C_2H_2 **(B)** H_2SO_4
(C) NH_3 **(D)** HCl

9. The bond that exists between NH_3 and BF_3 is called
(A) Electrovalent **(B)** Covalent
(C) Coordinate **(D)** Hydrogen

10. Which of the following does not have a coordinate bond
(A) SO_3 **(B)** HNO_3
(C) H_2SO_4 **(D)** HNO_2

11. Which molecules has zero dipole moment
(A) H_2O **(B)** CO_2
(C) HF **(D)** HBr

12. In the following which one have zero dipole moment
(A) BF_3 **(B)** CCl_4
(C) $BeCl_2$ **(D)** All of these

13. Which molecule has the largest dipole moment
(A) HCl **(B)** HI
(C) HBr **(D)** HF

14. The unequal sharing of bonded pair of electrons between two atoms in a molecule causes
(A) Dipole
(B) Radical formation
(C) Covalent bond
(D) Decomposition of molecule

15. Which one in the following is not the resonance structure of
(A) $O = C = O$ **(B)** $^{-}O - C \equiv O^{+}$
(C) $^{+}O \equiv C - O^{-}$ **(D)** $O \equiv C = O$

16. Which of the following molecule contains one pair of non-bonding electrons
(A) CH_4 **(B)** NH_3
(A) H_2O **(D)** HF

17. Resonance is due to
(A) Delocalization of sigma electrons
(B) Delocalization of pi electrons
(C) Migration of H atoms
(D) Migration of protons

18. Resonating structures have different
(A) Atomic arrangements
(B) Electronic arrangements
(C) Functional groups
(D) Alkyl groups

19. The structure of $\left[Cu\left(H_2O\right)_4\right]^{++}$ ion is
(A) Square planar **(B)** Tetrahedral
(C) Distorted rectangle **(D)** Octahedral

20. The bond angle in PH_3 would be expected to be close to
(A) 90° **(B)** 105°
(C) 109° **(D)** 120°

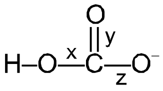
21. In which molecule are all atoms coplanar
(A) CH_4 **(B)** BF_3
(C) PF_3 **(D)** NH_3

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. Pick out among the following species isoelectronic with CO_2.
(A) N_3^- (B) $(CNO)^-$
(C) $(NCN)^{2-}$ (D) All of these

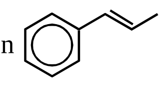
2. The correct order of increasing C-O bond length of CO, CO_3^{2-}, CO_2 is :
(A) $CO_3^{2-} < CO_2 < CO$ (B) $CO_2 < CO_3^{2-} < CO$
(C) $CO < CO_3^{2-} < CO_2$ (D) $CO < CO_2 < CO_3^{2-}$

3. The average charge on each O atom and average bond order of I–O bond in IO_6^{5-} is :
(A) –1 and 1.67 (B) – 5/6 and 1.67
(C) –5/6 and 1.33 (D) –5/6 and 1.167

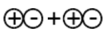
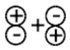
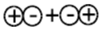
4. 
$H-O\overset{x}{-}\overset{\overset{O}{\|\,y}}{C}\underset{z}{-}O^-$ The relation between x, y and z in bicarbonate ion with respect to bond length is :
(A) x > y > z (B) x > z > y
(C) z = y > x (D) x > y = z

5. Indicate the wrong statement :
(A) A sigma bond is stronger then π - bond
(B) p-orbitals always have only sidewise overlapping
(C) s-orbitals never form π - bonds
(D) There can be only one sigma bond between two atoms

6. C_3^{4-} has
(A) two σ and two π bond
(B) three σ and one π bond
(C) two σ and one π bond
(D) two σ and three π bond

7. How many bonds are there in  ?
(A) 13 (B) 23
(C) 20 (D) 26

8. Which of the following overlaps is **incorrect** [assuming z-axis to be the internuclear axis] ?
(A) $2\,p_y + 2\,p_y \rightarrow \pi\,2\,p_y$
(B) $2\,p_z + 2\,p_z \rightarrow \sigma\,2p_z$
(C) $2\,p_x + 2\,p_x \rightarrow \pi\,2\,p_x$
(D) $1\,s + 2\,p_y \rightarrow \pi\,(1\,s\text{-}2\,p_y)$
(A) ‘a’ & ‘b’ (B) ‘b’ & ‘d’
(C) only ‘d’ (D) None of these

9. Effective overlapping will be shown by :
(A)  (B) 
(C)  (D) All the above

10. The covalency of nitrogen in HNO_3 is
(A) 0 (B) 3
(C) 4 (D) 5

11. What is covalency of I in IF_7 ?
(A) 5 (B) 3
(C) 7 (D) 1

12. In which of the following N is in the sp^2 hybridisation state
(A) $(CH_3)_3N$ (B) CH_3CONH_2
(C) CH_3CN (D) NO_2^+

13. In pent-3-en-1-yne the terminal carbon-atoms have following hybridisation
(A) sp & sp^2 (B) sp^2 & sp^3
(C) sp^2 & sp (D) sp & sp^3

14. Identify the correct match.

(i) XeF_2
(A) Central atom has sp^3 hybridisation and bent geometry.
(ii) N_3^-
(B) Central atom has sp $d^{3\ 2}$ hybridisation and octahedral.
(iii) PCl_6^- (PCl_5 (s) anion)
(C) Central atom has sp hybridisation and linear geometry.

(iv) ICl_2^+ (I_2Cl_6 (ℓ) cation)
(D) Central atom has sp^3d hybridisation and linear geometry.

(A) (i – a), (ii – b), (iii – c), (iv – d)
(B) (i – d), (ii – b), (iii – d), (iv – c)
(C) (i – b), (ii – c), (iii – a), (iv – d)
(D) (i – d), (ii – c), (iii – b), (iv – a)

Exercise # 3 PART - 1 MATRIX MATCHCOLUMN

1.

Column-I	Column-II
(A) $H_3P_3O_9$	(p) S–O–S bond is present
(B) $H_2S_2O_7$	(q) Di-basic acid
(C) $H_2S_4O_6$	(r) P–O–P bond is present
(D) $H_4P_2O_5$	(s) Central atom (S or P) in maximum oxidation state.

2.

Column-I	Column-II
(A) N_2^+ is stable than N_2^-	(p) due to one have greater number of electrons in antibonding molecular orbitals than other
(B) NO can easily lose its electron than N_2	(q) one has B.O. 3 and other has 2.5
(C) NO have large bond length than NO^+	(r) both are paramagnetic with same bond order
(D) He_2^+ exists, but is less stable than H_2^+	(s) one is paramagnetic and other diamagnetic

3.

Column – I	Column – II
(A) SO_3 (gas)	(p) Polar with $p\pi$–$d\pi$ bonds and identical S–O bond, lengths.
(B) OSF_4	(q) One lone pair and $p\pi – d\pi$ bond.
(C) SO_3F^-	(r) Non–polar with $p\pi – p\pi$ and $p\pi – d\pi$ bonds. Identical S–O bond lengths.
(D) $ClOF_3$	(s) Polar with $p\pi – d\pi$ bond.

4.

Column – I	Column –II
(A) IF_2^-	(p) sp^3d
(B) ClF_3	(q) polar
(C) XeO_3F_2	(r) one of the bond angles is 180^0.
(D) SF_4	(s) one lone pair

5.

Column-I	Column-II
(A) Blue vitriol	(p) Ionic bond
(B) Gypsum	(q) Covalent bond
(C) Pure orthophosphoric acid	(r) Hydrogen bond
(D) Chloral hydrate	(s) Resonance stabilisation

Exercise # 4

PART - 1

PREVIOUS YEAR (NEET/AIPMT)

1. Which one of the following molecules will form a linear polymeric structure due to hydrogen bonding ? **[CBSEAIPMT 2000]**

(A) NH_3 **(B)** H_2O
(C) HCl **(D)** HF

2. Which one of the following is planar ? **[CBSE AIPMT 2000]**

(A) XeF_4 **(B)** XeO_4
(C) XeO_3F **(D)** XeO_3F_2

3. The relationship between the dissociation energy of N_2 and N_2^+ is **[CBSEAIPMT 2000]**

(A) dissociation energy of $N_2^{\square}$ $\square$ dissociation energy of N_2
(B) dissociation energy of N_2 = dissociation energy of N_2^+
(C) dissociation energy N_2 > dissociation energy of N_2^+
(D) dissociation energy of N_2 can either be lower or higher than the dissociation energy of N_2^+

4. Which one of the following is not paramagnetic ? **[CBSE AIPMT2000]**

(A) NO **(B)** N_2^+
(C) CO **(D)** O_2^-

5. Among the following group which represents the collection of isoelectronic species ? **[CBSE AIPMT 2000]**

(A) $NO, CN^{\square}, N_2, O_2^{\square}$
(B) $NO^{\square}, CO_2^{2\square}, O_2^{\square}, CO$
(C) $N_2, C_2^{2\square}, CO, NO$
(D) $CO, NO^{\square}, CH^{\square}, C_2^{2\square}$

6. Among the following group which represents the collection of isoelectronic species ? **[CBSE AIPMT 2000]**

(A) $NO_2^{\square}$ **(B)** $NO_3^{\square}$
(C) $PO_4^{3\square}$ **(D)** $CO_3^{2\square}$

7. A compound contains atoms of three elements A, B and C. If the oxidation number of A is +2, B is +5 and that of C is –2, the possible formula of the compound is **[CBSEAIPMT 2000]**

(A) $A_2(BC_3)_2$ **(B)** $A_3(BC_4)_2$
(C) $A_3(B_4C)_2$ **(D)** ABC_2

8. Which of the following two are isostructural ? **[CBSE AIPMT 2001]**

(A) XeF_2, and lF_2^- **(B)** NH_3, and BF_3
(C) CO_3^{2-}, and SO_3^{2-} **(D)** PCl_5, and lcl_5

9. In which of the following, bond angle is maximu ? **[CBSE AIPMT 2001]**

(A) NH_3 **(B)** NH_4^+
(C) PCl_3 **(D)** SCl_2

10. In X–H - - - Y, X and Y both are electronegative elements, then **[CBSEAIPMT 2001]**

(A) electron density on X will increase and on H will decrease
(B) in both electron density will increase
(C) in both electron density will decrease
(D) on X electron density will decrease and on H increase

11. Main axis of a diatomic molecule is z molecular orbital, p_x and p_y overlaps to form which of the following orbitals ? **[CBSE AIPMT2001]**

(A) π-molecular orbital **(B)** σ-molecular orbital
(C) δ-molecular orbital **(D)** NO bond will form

12. Which of the following is isoelectronic ? **[CBSE AIPMT 2002]**

(A) CO , NO **(B)** NO^-, CO
(C) CN^2, Co^2 **(D)** SO_2^2, CO_2^2

13. Which of the following has pπ - dπ bonding ? **[CBSE AIPMT 2002]**

(A) $NO_3^{\square}$ **(B)** $SO_3^{2\square}$
(C) $BO_3^{3\square}$ **(D)** $CO_3^{2\square}$

14. In NO_3^- ion number of bond pair and lone pair of electrons on nitrogen atom are **[CBSE AIPMT 2002]**

(A) 2, 2 **(B)** 3, 1
(C) 1, 3 **(D)** 4, 0

15. Which of the following statement is not correct for sigma and pi-bonds formed between two carbon atoms ? **[CBSEAIPMT 2003]**

(A) Free rotation of atoms about a sigma bond is allowed but not in case of a pi-bond
(B) Sigma bond determines the direction between carbon atoms but a pi-bond has no primary effect in this regard
(C) Sigma bond is stronger than a pi-bond
(D) Bond energyies of sigma and pi-bonds are of the order of 264 kJ/mol and 347 kJ/mol. respectively

MOCK TEST

1. Among the following species, identify the isostructural pairs, NF_3, NO_3^-, BF_3, H_3O^+, HN_3

(A) $[NF_3,\ NO_3^-]$ and $[BF_3,\ H_3O^+]$ **(B)** $[NF_3,\ HN_3]$ and $[NO_3^-,\ BF_3]$

(C) $[NF_3,\ H_3O^+]$ and $[NO_3^-,\ BF_3]$ **(D)** $[NF_3,\ H_3O^+]$ and $[HN_3,\ BF_3]$

2. In the compound $CH_2 = CH - CH_2 - CH_2 - C \equiv CH$, the $C_2 - C_3$ bond is of the type

(A) $sp - sp^2$ **(B)** $sp^3 - sp^3$ **(C)** $sp - sp^3$ **(D)** $sp^2 - sp^3$

3. The correct order of increasing C – O bond length of CO, CO_3^{2-}, CO_2 is

(A) $CO_3^{2-} < CO_2 < CO$ **(B)** $CO < CO^{2-} < CO$ **(C)** $CO < CO^{2-} < CO$ **(D)** $CO < CO < CO^{2-}$

2 3 3 2 2 3

4. In the dichromate dianion

(A) 4 Cr – O bonds are equivalent **(B)** 6 Cr – O bonds are equivalent

(C) All Cr – O bonds are equivalent **(D)** All Cr – O bonds are non-equivalent

5. Hybridisation state of chlorine in ClF_3 is

(A) sp^3 **(B)** sp^3d **(C)** sp^3d^2 **(D)** sp^3d^3

6. In which of the following the central atom does not use sp^3 hybrid orbitals in its bonding

(A) BeF_3^- **(B)** OH_3^+ **(C)** NH_2^- **(D)** NF_3

7. The magnetic moment of $K_3[Fe(CN)_6]$ is found to be 1.7 B.M. How many unpaired electron (s) is/are present per molecule

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

8. N_2 and O_2 are converted into monocations N_2^+ and O_2^+ respectively. Which is wrong

(A) In N_2 the N – N bond weakens **(B)** In O_2 the O – O bond order increases

(C) In O_2 paramagnetism decreases **(D)** N_2^+ becomes diamagnetic

9. The common features among the species CN^-, CO and NO+ are

(A) Bond order three and isoelectronic **(B)** Bond order three and weak field ligands

(C) Bond order two and -acceptors **(D)** Isoelectronic and weak field ligands

10. The number of S – S bonds in sulphur trioxide trimer S_3O_9 is

(A) Three **(B)** Two **(C)** One **(D)** Zero

11. Select the most ionic and most covalent compounds respectively from the following.

CrO_5, Mn_2O_7, PbO, P_4O_{10}, SnO_2

(A) CrO_5, Mn_2O_7 **(B)** Mn_2O_7, PbO **(C)** CrO_5, P_4O_{10} **(D)** CrO_5, SnO_2

12. In which of the following sets central atom of each member involves sp^3 hybridisation ?

(A) IO_4^-, ICl_4^-, IF_4^+ **(B)** XeO_3, XeO_4, XeF_4

(B) SO_3, SO_3^{2-}, SO_4^{2-} **(D)** PCl_4^+, BF_4^-, ClO_4^-

CHAPTER 13

NITROGEN AND ITS DERIVATIVES

Many years ago it was taught that plants and animals were composed of different materials: Plants, of a chemical substance of three elements- Carbon, Hydrogen and Oxygen; animals of one of four elements, nitrogen being added to the other three.

''ASAGRAY''

INTRODUCTION

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl group(s). In nature, they occur among protein, vitamins, alkaloids and hormones. The chief commerical use of amines is as intermediates in the synthesis of medicines and fibres. Synthetic examples include polymers, dyestuffs and drugs. Two biologically active compounds, namely adrenaline and ephedrine, both containing secondary amino group, are used to increase blood pressure. Novocain, a synthetic amino compound, is used as an anaesthetic in dentistry. Benadryl, a well known antihistaminic drug also contains tertiary amino group. Quaternary ammonium salts are used as surfactants. Diazonium salts are intermediates in the preparation of a variety of aromatic compounds including dyes. In this Unit, you will learn about amines, cyanide, isocyanide and diazonium salts.

AMINES

Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by alkyl groups(s).Amines are classified as primary, secondary and tertiary depanding on the number of alkyl groups attached to nitrogen atom.

General formula

1° amine
$C_nH_{2n+1}NH_2$ or $C_nH_{2n+3}N$

2° amine
$(C_nH_{2n+1})_2NH$

3° amine
$(C_nH_{2n+1})_3N$

GENERALMETHODOFPREPARATION :

(I) AMMONOLYSISOFALKYLHALIDESANDALCOHOL:

(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.

$$R{-}X \xrightarrow[-\,HX]{NH_3} R{-}NH_2 \xrightarrow[-\,HX]{R{-}X} R_2{-}NH \xrightarrow[-\,HX]{R{-}X} R_3N \xrightarrow{R{-}X} R_4\overset{\oplus}{N}\overset{\cdot}{X}$$

(Quaternaryammonium salt)

If ammonia is taken in excess, 1° amine is the main product.

(b) Ammonolysis of alcohols :

When ROH and NH_3 are passed over Al_2O_3 or ThO_2 at 350° C all the three types of amines are formed.

$$R{-}OH \xrightarrow[Al_2O_3/\ 400°C]{NH_3} R{-}NH_2 \xrightarrow[Al_2O_3]{R{-}OH} R_2{-}NH \xrightarrow[Al_2O_3]{R{-}OH} R_3N$$

Note : (i) Quaternary ammonium hydroxide is not formed due to steric hindrance.

(ii) If excess of ammonia is used, then main product will be primary amine.

(II) BY REDUCTION:

(a) With $RCONH_2$: $RCONH_2 \xrightarrow[\text{or } Na/C_2H_5OH]{LiAlH_4} RCH_2NH_2$

(b) With RCN : $RCN + 4H \xrightarrow{Na/C_2H_5OH} RCH_2NH_2$

This reaction is called mendius reaction.

The reduction of alkyl isocynides with sodium and ethanol gives secondary amines.

$$R{-}NC + 4H \xrightarrow{Na/C_2H_5OH} RNHCH_3$$

(c) With Oximes : $R{-}CH{=}N{-}OH + 4H \xrightarrow[Na/C_2H_5OH]{LiAlH_4} RCH_2{-}NH_2 + H_2O$

(d) With RNO_2 : $RNO_2 + 6H \xrightarrow[\Delta]{Sn/HCl} RNH_2 + 2H_2O$

In lab method we use Sn/HCl while in industrial method we use Fe / HCl.

(III) BYHYDROLYSISOF:

(a) R—NC : Alkyl isocyanide undergoes hydrolysis with mineral acid and forms alkyl amine.

$$R{-}NC + 2H_2O \xrightarrow{HCl} RNH_2 + HCOOH$$

General formula

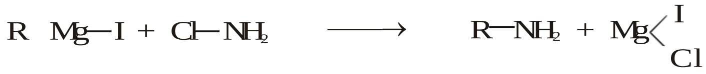
- 1° amine: $C_nH_{2n+1}NH_2$ or $C_nH_{2n+3}N$
- 2° amine: $(C_nH_{2n+1})_2NH$
- 3° amine: $(C_nH_{2n+1})_3N$

Genral method of prepratiomn :

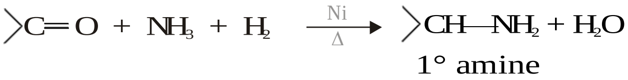
1. $R{-}OH \xrightarrow[Al_2O_3/\ 400°C]{NH_3} R{-}NH_2 \xrightarrow[Al_2O_3]{R-OH} R_2{-}NH \xrightarrow[Al_2O_3]{R-OH} R_3N$

2. $RCONH_2 \xrightarrow[\text{or } Na/C_2H_5OH]{LiAlH_4} RCH_2NH_2$

3. $RCN + 4H \xrightarrow{Na/C_2H_5OH} RCH_2NH_2$

4. 

$R\ Mg{-}I + Cl{-}NH_2 \longrightarrow R{-}NH_2 + Mg\langle^{I}_{Cl}$

5. 

$\rangle C{=}O + NH_3 + H_2 \xrightarrow[\Delta]{Ni} \rangle CH{-}NH_2 + H_2O$

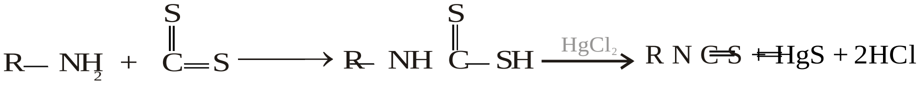
1° amine

6. $C_6H_5CONH_2 + Br_2 + 4KOH \longrightarrow C_6H_5NH_2 + K_2CO_3 + 2KBr + 2H_2O$

7. $C_6H_5COOH + N_3H \xrightarrow[H_2SO_4]{conc.} C_6H_5NH_2 + N_2\uparrow + CO_2\uparrow$

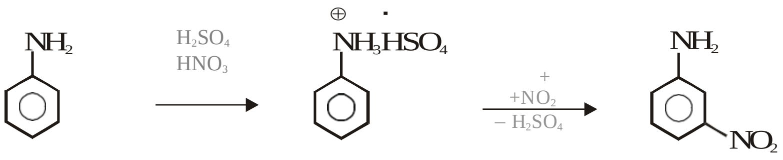
Chemical reaction :

1. $RNH_2 + HCl \longrightarrow [RNH_3]^{\oplus}Cl \xrightarrow[\text{High temp.}]{\Delta} R{-}Cl + NH_3$

2. 

$R{-}NH_2 + S{=}C{=}S \longrightarrow R{-}NH{-}\overset{S}{\overset{\|}{C}}{-}SH \xrightarrow{HgCl_2} R\ N\ C{=}S + HgS + 2HCl$

3. $R{-}NH_2 + HONO \longrightarrow R{-}OH + N_2\uparrow + H_2O$

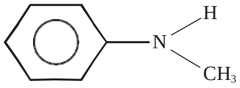
4. 

SOLVED EXAMPLE

Ex. 1 Amongst the following, the strongest base in aqueous medium is ....

(A) CH_3NH_2 **(B)** $NCCH_2NH_2$ **(C)** $(CH_3)_2NH$ **(D)** $C_6H_5NHCH_3$

Sol. **(C)**

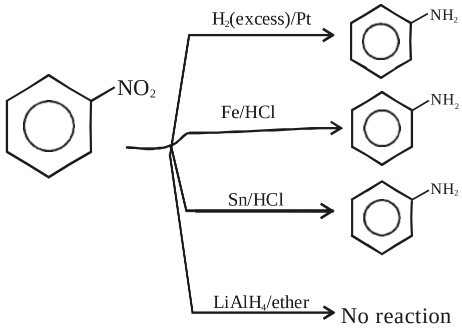
Compound	**Factors responsible for basic character are**
(A) $Ch_3 - NH_2$	Inductive effect (+I)
(B) $NC - CH_2 - NH_2$	Inductive effect (–I)
(C) $(CH_3)_2NH$	Inductive effect (+I) and Solvation
(D) 	–I effect and resonance

Since, +I effect and solvation increases basic character while –I effect and resonance decreases basic character.

Ex. 2 Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine

(A) H_2(excess)/ Pt **(B)** $LiAlH_4$ in ether **(C)** Fe and HCl **(D)** Sn and HCl

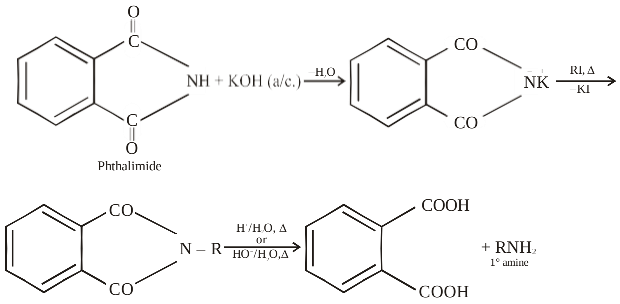
Sol. **(B)** Aryl nitro compound can't be converted into amine using $LiAlH_4$ in ether.



Ex. 3 The source of nitrogen in Gabriel synthesis of amines is ......

(A) Sodium azide, NaN_3 **(B)** Sodium nitrite, $NaNO_3$
(C) Potassium cyanide, KCN **(D)** Potassium phthalimide $C_6H_4(CO_2)N^-K^+$

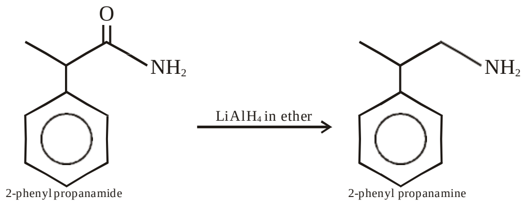
Sol. **(D)** Source of nitrogen in Gabriel phthalimide synthesis is potassium phthalimide



Ex. 4 The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is ....

(A) Excess H_2 **(B)** Br_2 in aqueous NaOH
(C) Iodine in the presence of red phosphorus **(D)** $LiAlH_4$ in ether

Sol. **(D)** The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is $LiAlH_4$ in ether. Reaction is as given below



Exercise # 1 SINGLE OBJECTIVE NEET LEVEL

1. Cyanide ion is

(A) Nucleophilic

(B) Electrophilic

(C) Strongly acidic

(D) Non-reactive and neutral

2. Compounds containing both amino and COOH groups are known as

(A) Diamines (B) Unknown

(C) Amino acids (D) Enzymes

3. Which of the following is 1° amine

(A) Ethylene diamine (B) Dimethylamine

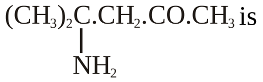
(C) Trimethyl amine (D) N-methyl aniline

4. C_3H_9N represents

(A) Primary amine (B) Secondary amine

(C) Tertiary amine (D) All of these

5.



$(CH_3)_2\underset{\underset{NH_2}{|}}{C}.CH_2.CO.CH_3$ is

(A) Diacetone (B) Acetoneamine

(C) Diacetoneamine (D) Aminoacetone

6. Amides may be converted into amines by reaction named after

(A) Perkin (B) Claisen

(C) Hoffmann (D) Kolbe

7. Reaction $CH_3CONH_2 \xrightarrow{NaOBr}$ gives

(A) CH_3Br (B) CH_4

(C) CH_3COBr (D) CH_3NH_2

8. Acetamide is treated separately with the following reagents. Which would give methyl amine

(A) PCl_5 (B) $NaOH + Br_2$

(A) Sodalime (D) Hot conc. H_2SO_4

9. The amine formed from an amide by means of bromine and alkali has

(A) Same number of C atoms as that of amide

(B) One less C atom than that of amide

(C) One more C atom than that of amide

(D) Two more C atoms than that of amide

10. $CH_3CN \xrightarrow{Na+C_2H_5OH} X$

The compound X is

(A) CH_3CONH_2 (B) $CH_3CH_2NH_2$

(C) C_2H_6 (D) CH_3NHCH_3

11. Ethylamine can be prepared by the action of bromine and caustic potash on

(A) Acetamide (B) Propionamide

(C) Formamide (D) Methyl cyanide

12. Ethylamine can be obtained by the

(A) Action of NH_3 on ethyl iodide

(B) Actio of NH_3 on ethyl alcohol

(C) Both (A) and (B)

(D) None of these

13. Aniline is usually purified by

(A) Steam distillation

(B) Simple distillation

(C) Vacuum distillation

(D) Extraction with a solvent

14. Reduction of nitroalkanes yields

(A) Acid (B) Alcohol

(C) Amine (D) Diazo compounds

15. Acetamide changes into methylamine by

(A) Hofmann bromamide reaction

(B) Hofmann reaction

(C) Friedel-Craft's reaction

(D) Hinsberg reaction

16. When methyl iodide is heated with ammonia, the product obtained is

(A) Methylamine

(B) Dimethylamine

(C) Trimethylamine

(D) A mixture of the above three amines

17. Acetanilide can be prepared from aniline and which of the following

(A) Ethanol (B) Acetaldehyde

(C) Acetone (D) Acetic anhydride

18. Reduction of nitroalkanes in neutral medium (e.g. Zn / NH_4Cl) forms mainly

(A) $R-NH_2$ (B) $R-NHOH$

(C) $R-N=N-Cl$ (D) All of these

19. Nitrosobenzene can be prepared by oxidizing aniline from

(A) H_2SO_4 (B) H_2SO_5

(C) H_2SO_3 (D) $K_2Cr_2O_7$

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. A secondaryamine is
(A) An organic compound with two $-NH_2$ groups
(B) A compound with two carbon atoms and an $-NH_2$ group
(C) A compound with an $-NH_2$ group on the carbon atom in number 2 position
(D) A compound in which two of the hydrogens of $-NH_3$ have been replaced by organic groups

2. The structural formula of methyl aminomethane is
(A) $(CH_3)_2CHNH_2$ **(B)** $(CH_3)_3N$
(C) $(CH_3)_2NH$ **(D)** CH_3NH_2

3. Allyl isocyanide has
(A) 9 sigma bonds and 4 pi bonds
(B) 8 sigma bonds and 5 pi bonds
(C) 8 sigma bonds, 3 pi bonds and 4 non-bonding electrons
(D) 9 sigma bonds, 3 pi bonds and 2 non-bonding electrons

4. Reduction of nitroalkanes yields
(A) Acid **(B)** Alcohol
(C) Amine **(D)** Diazo compounds

5. Acetamide changes into methylamine by
(A) Hofmann bromamide reaction
(B) Hofmann reaction
(C) Friedel-Craft's reaction
(D) Hinsberg reaction

6. When methyl iodide is heated with ammonia, the product obtained is
(A) Methylamine
(B) Dimethylamine
(C) Trimethylamine
(D) A mixture of the above three amines

7. Acetanilide can be prepared from aniline and which of the following
(A) Ethanol **(B)** Acetaldehyde
(C) Acetone **(D)** Acetic anhydride

8. Reduction of nitroalkanes in neutral medium (e.g. Zn / NH_4Cl) forms mainly
(A) $R-NH_2$ **(B)** $R-NHOH$
(C) $R-N=N-Cl$ **(D)** All of these

9. Nitrosobenzene can be prepared by oxidizing aniline from
(A) H_2SO_4 **(B)** H_2SO_5
(C) H_2SO_3 **(D)** $K_2Cr_2O_7$

10. The Hinsberg's method is used for
(A) Preparation of primary amines
(B) Preparation of secondaryamines
(C) Preparation of tertiary amines
(D) Separation of amine mixtures

11. Reaction of primary amines with aldehyde yields
(A) Amides **(B)** Aldimines
(C) Nitriles **(D)** Nitro compounds

12. When acetamide is treated with HNO_2, the gas is evolved
(A) H_2 **(B)** O_2
(C) N_2 **(D)** CH_4

13. Nitrobenzene on nitration gives
(A) o-dinitrobenzene
(B) p-dinitrobenzene
(C) m-dinitrobenzene
(D) o- and p-nitrobenzene

14. Reduction of alkyl nitrites yields
(A) Alcohol **(B)** Base
(C) Amine **(D)** Acid

15. When primary amines are treated with HCl, the product obtained is
(A) An alcohol **(B)** A cyanide
(C) An amide **(D)** Ammonium salt

16. Which one is weakest base
(A) Ammonia **(B)** Methylamine
(C) Dimethylamine **(D)** Trimethylamine

17. Chloroform when treated with aniline and alcoholic KOH gives
(A) Phenyl cyanide **(B)** Phenyl isocyanide
(C) Chlorobenzene **(D)** Phenol

18. Which of following do not react with HNO_2
(A) Primary nitroalkanes
(B) Secondary nitroalkanes
(C) Tertiary nitroalkanes
(D) All of these

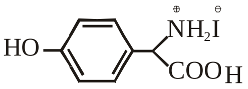
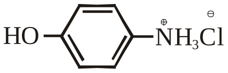
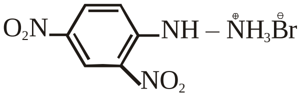
19. Primary amines can be distinguished from secondary and tertiary amines by reacting with
(A) Chloroform and alcoholic KOH
(B) Methyl iodide
(C) Chloroform alone
(D) Zinc dust

Exercise # 3 PART - 1 MATRIX MATCH COLUMN

1. Match each of the compunds in Column I with its characteristic reaction(s) in Column II.

Column - I	**Column - II**
(A) $CH_3CH_2CH_2CN$	**(p)** Reduction with Pd – C/H_2
(B) $CH_3CH_2OCOCH_3$	**(q)** Reduction with $SnCl_2/HCl$
(C) $CH_3-CH=CH-CH_2OH$	**(r)** Development of foul smell on treatment with chloroform and alcoholic KOH
(D) $CH_3CH_2CH_2CH_2NH_2$	**(s)** Reduction with diisobutylaluminium hydride (DIBAL–H)
	(d) Alkaline hydrolysis

2. Match the entries in Column I with the correctly related entries in Column II.

Column - I	**Column - II**
(A) $H_2N-\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$	**(p)** sodium fusion extract of the compound gives Prussian blue colour with $FeSO_4$
(B) 	**(q)** gives positive $FeCl_3$ test
(C) 	**(r)** gives white precipitate with $AgNO_3$
(D) 	**(s)** reacts with aldehydes to form the corresponding hydrozone derivative

3. Match the entries listed in Column I with appropriate entries listed in Column II.

Column - I **(Amines)**	**Column - II** **(Distinguish by)**
(A) $C_2H_5NH_2$ and $C_6H_5NH_2$	**(p)** Carbylamine test
(B) $(C_2H_5)_3$ N and $(C_2H_5)_2$ NH	**(q)** Azo dye test
(C) $C_2H_5NH_2$ and $(C_2H_5)_3$ N	**(r)** Hinsberg's reagent test
(D) $(C_2H_5)_3$ N and $C_6H_5NH_2$	**(s)** Liebermann nitroso reaction

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. An organic compound A on reduction gives compound B which on reduction with chloroform and potassium hydroxide forms C. The compound C on catalytic reduction gives N-methylaniline. The compound A is **[CBSE AIPMT 2000]**

(A) nitrobenzene **(B)** nitromethane

(C) methylamine **(D)** aniline

2. Intermediates formed during reaction of

$\underset{\underset{O}{\|}}{RCNH_2}$ with Br_2 and KOH are **[CBSE AIPMT 2001]**

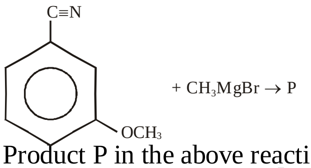
(A) RCONHBr and RNCO

(B) RNHCOBr and RNCO

(C) RNHBr and RCONHBr

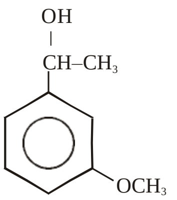
(D) $RCONBr_2$

3.

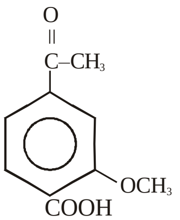


Product P in the above reaction is **[CBSE AIPMT 2002]**

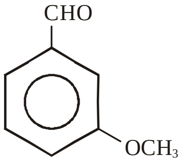
(A)



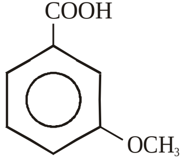
(B)



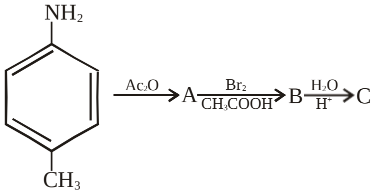
(C)



(D)

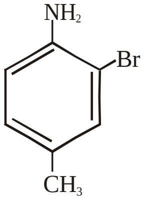


4. The final product C, obtained in this reaction

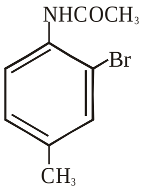


Would be **[CBSE AIPMT 2003]**

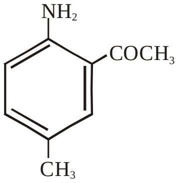
(A)



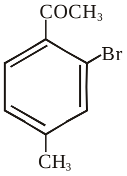
(B)



(C)

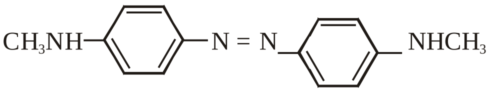


(D)

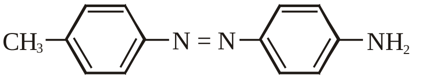


5. Aniline when diazotised in cold and then treated with dimethyl aniline, gives a coloured proeduct. Its structure would be **[CBSE AIPMT 2004]**

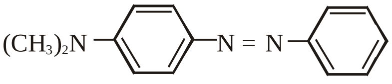
(A)



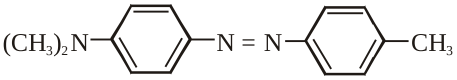
(B)



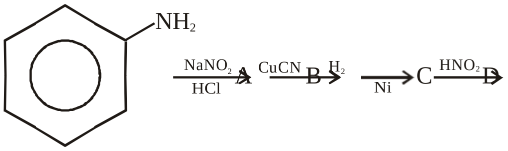
(C)



(D)



6. Aniline in a set of reactions yielded a product



The structure of the product D would be **[CBSE AIPMT 2005]**

(A) $C_6H_5CH_2NH_2$ **(B)** $C_6H_5CH_2NHCH_2CH_3$

(C) C_6H_5NHOH **(D)** $C_6H_5CH_2OH$

7. Electrolytic reduction of nitrobenzene in weakly acidic medium gives **[CBSE AIPMT 2005]**

(A) aniline

(B) nitrosobenzene

(C) N-phenyl hydroxylamine

(D) p-hydroxyaniline

8. Which of the following is mroe basic than aniline ? **[CBSE AIPMT 2006]**

(A) Diphenylamine **(B)** Triphenylamine

(C) p-nitroaniline **(D)** Benzylamine

9. Which one of the following on reduction with $LiAlH_4$ yields a secondary amine ? **[CBSE AIPMT 2007]**

(A) Methyl isocyanide **(B)** Acetamide

(C) Methyl cyanide **(D)** Nitroethane

10. Nitrobenzene on reaction with conc. HNO_3/H_2SO_4 at 80-100°C forms which one of the following products ? **[NEET 2007]**

(A) 1, 2-dinitrobenzene **(B)** 1, 3-dinitrobenzene

(C) 1, 4-dinitrobenzene **(D)** 1, 2, 4-trinitrobenzene

MOCK TEST

STRAIGHT OBJECTIVE TYPE

1. Acetonitrile is:

(A) C_2H_5CN **(B)** CH_3CN **(C)** CH_3COCN **(D)** $C_6H_5CH_2CN$

2. In alkyl cyanide alkyl group attached with

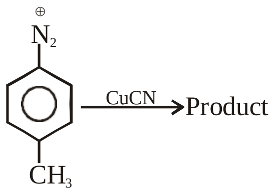
(A) C of CN group **(B)** N of CN group

(C) Either C or N of CN group **(D)** Both C and N of CN group

3. Number of isomeric primary amines obtained from $C_4H_{11}N$ are

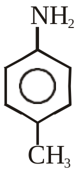
(A) 3 **(B)** 4 **(C)** 5 **(D)** 6

4.

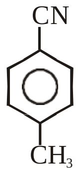


The product is

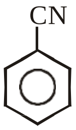
(A)



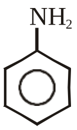
(B)



(C)



(D)



5. Ethyl amine on heating with CS_2 in presence of $HgCl_2$ forms

(A) C_2H_5NCS **(B)** $(C_2H_5)_2S$ **(C)** $(C_2H_5)_2CS$ **(D)** $C_2H_5(CS)_2$

6. Which of the following reacts with $NaNO_2$ + HCl to give phenol

(A) $C_6H_5CH_2NHCH_3$ **(B)** $(CH_3)_2NH$ **(C)** CH_3NH_2 **(D)** $C_6H_5NH_2$

7. When chlorobenzene is treated with NH_3 in presence of Cu_2O in xylene at 570 K. The product obtained is

(A) Benzylamine **(B)** Diazonium salt **(C)** Schiff's base **(D)** Aniline

8. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc.H_2SO_4. In the nitrating mixture, HNO_3 acts as a

(A) Base **(B)** Acid **(C)** Catalyst **(D)** Reducing agent

9. The rate determining step for the preparation of nitrobenzene from benzene is

(A) Removal of $\overset{+}{NO_2}$ **(B)** Removal of $\overset{+}{NO_2}$ **(C)** Formation of $\overset{+}{NO_2}$ **(D)** Formation of $\overset{+}{NO_2}$

10. In this reaction

$C_6H_5NH_2 + HCl + NaNO_2 \rightarrow X$. Product X is

(A) Aniline hydrochloride **(B)** Nitroaniline

(C) Benzenediazonium chloride **(D)** None of these

11. The end product of the reactions is

$$C_2H_5NH_2 \xrightarrow{HNO_2} A \xrightarrow{PCl_5} B \xrightarrow{H.NH_2} C$$

(A) Ethyl cyanide **(B)** Ethyl amine **(C)** Methyl amine **(D)** Acetamide

12. Primary and secondary amines are distinguished by

(A) Br_2/KOH **(B)** $HClO_4$ **(C)** HNO_2 **(D)** NH_3

CHAPTER 16

HYDROCARBONS

> *In organic chemistry, we have learnt to derive from compounds containing only carbon and hydrogen, i.e. from the hydrocarbons, all other types of combinations such as alcohols, aldehydes, ketones, acids, etc.*
>
> **"OTTO WALLACH"**

INTRODUCTION

The term hydrocarbon is self-explanatory which means compounds of carbon and hydrogen only. Hydrocarbons play a key role in our daily life. We must be familiar with the terms LPG and CNG used as fuels. LPG is the abbreviated form of liquified petroleum gas whereas CNG stands for compressed natural gas. Another term LNG (liquified natural gas) is also in news these days. This is also a fuel and is obtained by liquifaction of natural gas. Petrol, diesel and kerosene oil are obtained by the fractional distillation of petroleum found under the earth's crust. Coal gas is obtained by the destructive distillation of coal, Natural gas is found in upper strata during drilling of oil wells. The gas after compression is known as compressed natural gas. LPG is used as a domestic fuel with the least pollution. Kerosence oil is also used as a domestiofuel but it causes some pollution. Automobiles need fuels like petrol, diesel and CNG. petrol and CNG operated automobiles cause less pollution. All these fuels contain mixture of hydrocarbons, which are sources of energy. Hydrocarbons are also used for the manufacture of polymers like polythene, polypropene, polystyrene etc. Higher hydrocarbons are used as solvents for paints. They are also used as the starting materials for manufacture of many dyes and drugs. Thus , we can well understand the importance of hydrocarbons in our daily life. In this unit, we will learn more about hydrocarbons.

$CH_3^{\bullet} + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$

(iii) Chain terminating (third)step

$CH_3^{\bullet} + {}^{\bullet}Cl \longrightarrow H_3Cl$

$CH_3^{\bullet} + {}^{\bullet}CH_3 \longrightarrow CH_3 - CH_3$

$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$

Ex. $\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow{h\nu} \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$

(excess)

When chlorine is in excess, carbon tetrachloride will be the major product.

Ex. $\underset{\text{Methane}}{CH_4} + \underset{\text{(excess)}}{Cl_2} \xrightarrow{h\nu} \underset{\text{(Main)}}{CCl_4}$

Bromination : Bromination of alkanes is similar to chlorination but not so vigrous.

Iodination : Iodination of alkanes is slow and reversible.

$CH_4 + I_2 \overset{\Delta}{\rightleftharpoons} CH_3 - I + HI$

$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$

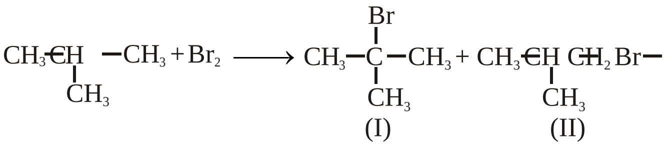
Iodisation is very slow because energy of activation of the reaction is very large.

ED OS KEY POINTS

Halogenation is inhibited in presence of oxygen because oxygen reacts with alkyl free radicals to form less reactive peroxy alkyl radical R–O–O° which can not propagate the chain.

Ex. What is the percentage of products obtained from monobromination of isobutane?

Sol.



$$\underset{\underset{CH_3}{|}}{CH_3-CH}-CH_3 + Br_2 \longrightarrow \underset{\text{(I)}}{CH_3-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3} + \underset{\text{(II)}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2Br}$$

$$\frac{\text{Product (I)}}{\text{Product (II)}} = \frac{\text{No.of primary H}}{\text{No.of tertiary H}} \times \frac{\text{reactivity of primary H}}{\text{reactivity of tertiary H}} = \frac{9}{1} \times \frac{1}{1600} = \frac{9}{1600}$$

$$\text{\% of product (I)} = \frac{9}{1600+9} \times 100 = 0.56\%$$

$$\text{\% of product (II)} = \frac{1600}{1600+9} \times 100 = 99.44\%$$

(b) **Nitration :** When a mixture of vapour of alkane nitric acid is heated at high temperature (400°C – 450°C) a mixture of all possible nitroalkanes is obtained (The reaction involves both C–C and C–H bond cleavage).

$R-\boxed{H + HO}-NO_2 \xrightarrow{\text{high temp.}} R-NO_2 + H_2O$

REACTION CHART FOR ALKANES

GMP

(1) $R{-}C\equiv CH$ or $R{-}CH{=}CH_2$ $\xrightarrow[200\text{-}300^\circ C]{H_2,\ Ni}$ Sabatier senderens reaction

(2) $R{-}X$ $\xrightarrow[\text{Red P-HI, }LiAlH_4]{\text{Zn-Cu+HCl}}$

(3) RX $\xrightarrow[\text{Wurtz reaction}]{\text{Na, dry ether}}$

(4) RX $\xrightarrow[\text{Frankland's reaction}]{Zn}$

(5) RX $\xrightarrow[\text{(Corey-House reaction)}]{R_2CuLi}$ $\boxed{\begin{matrix}R{-}H\\ \text{or}\\ R{-}R\\ \text{or}\\ C_nH_{2n+2}\end{matrix}}$

(6) $R{-}Mg{-}X$ $\xrightarrow[\text{Or }NH_3\text{ or }RNH_2]{\text{+HOH or ROH}}$

(7) $R{-}OH$, $R{-}CHO$, $R{-}\underset{\underset{O}{\|}}{C}{-}R$, $RCOCl$, $RCOOH$ $\xrightarrow{\text{RedP/HI}}$

(8) $R{-}\underset{\underset{O}{\|}}{C}{-}R$ $\xrightarrow[\text{Clemensor's reduction}]{\text{Zn-Hg/Conc. HCl}}$

(9) $R{-}\underset{\underset{O}{\|}}{C}{-}R$ $\xrightarrow[\text{Wolf/Kishner reduction}]{H_2N\text{-}NH_2}$

or

$(RCH_2CH_2)_3B$ $\xrightarrow{\_H_2O}$

(10) $RCOONa$ $\xrightarrow{\text{NaOH+Cao}}$

(11) $RCOONa$ $\xrightarrow{\text{Kolbe's Selectrolytic synthesis}}$

GR

(1) $\xrightarrow{X_2,hv\text{ or UV light or }400^\circ C}$ RX

(2) $\xrightarrow{\text{Nitration}}$ $R{-}N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$

(3) $\xrightarrow{\text{Sulphonation }H_2S_2O_7}$ Alkyl Sulphonic acid

(4) $SO_2 + Cl_2$ $\xrightarrow[hv]{\text{Reed reaction}}$ RSO_2Cl

(5) $\xrightarrow[\text{Isomerisation}]{AlCl_3/HCl}$ branched alkanes

(6) $\xrightarrow[500\text{-}700^\circ C]{\text{Pyrolysis}}$ Alkenes + CH_4 or C_2H_6

(7) $\xrightarrow[+Al_2O_3\ 500^\circ C]{\text{Cr or Mo or V oxide}}$ Aromatic compound

(8) $\xrightarrow[\text{step up reaction}]{CH_2N_2}$ Higher alkane

(9) $\xrightarrow{O_2}$ $CO_2 + H_2O$

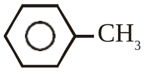
Combustion

SOLVED EXAMPLE

Ex.1 n-Heptane when heated to a temperature of about 800 K under high pressure in the presence of Cr_2O_3/Al_2O_3 catalyst gives

(A) 1-heptene **(B)** 2-Methylhexane **(C)** Toluene **(D)** Xylene

Sol. **(C)** $CH_3 – (CH_2)_5 – CH_3 \xrightarrow{-4H_2}$



Toluene

Ex.2 The reaction conditions leading to the best yield of C_2H_5Cl are –

(A) C_2H_5 (excess) + Cl_2 $\xrightarrow{\text{UV light}}$

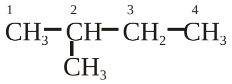
(B) $C_2H_6 + Cl_2$ $\xrightarrow[\text{room temperature}]{\text{Dark}}$

(C) $C_2H_6 + Cl_2$ (excess) $\xrightarrow{\text{UV light}}$

(D) $C_2H_6 + Cl_2$ $\xrightarrow{\text{UV light}}$

Sol. **(D)** C_2H_6 should be used in excess, otherwise polychlorination will take place

Ex.3 In iso-pentane, the H atom that can be most easily substituted is on –



$$\overset{1}{C}H_3-\underset{\displaystyle CH_3}{\overset{2}{C}H}-\overset{3}{C}H_2-\overset{4}{C}H_3$$

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

Sol. **(B)** Ease of substitutation of various types of H atom is 3° > 2° > 1°.

Ex.4 8 c.c. of gaseous hydrocarbon requires 40 c.c. of O2 for complete combustion. Identify hydrocarbon.

Sol. Volume of hydrocarbon = 8 c.c. ; Volume of O_2 = 40 c.c.

Formula No.1, $\frac{8}{40} = \frac{2}{3n+1}$ (For alkane)

$\frac{1}{5} = \frac{2}{3n+1}$ or 3n + 1 = 10 or 3n = 10 – 1 = 9, n = 2

The value of n comes in whole number from 1st formula it means hydrocarbon is Alkane and it is of 3C atom.

∴ Hydrocarbon is C_3H_8 (Propane)

Ex.5 10 mL of a mixture of CH_4 and C_3H_8 requires 41 mL of oxygen for complete combustion. What is the volume of CH_4 and C_3H_8 in the mixture.

Sol. Suppose the volume of CH_4 in (CH_4 + C_3H_8) mix = x c.c.

= Volume of C_3H_8 will be = 10 – x c.c.

For CH_4 $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

∵ 1 vol. of CH_4 requires 2 vol. of O_2 for complete combustion

∴ x c.c. of CH_4, 2x c.c. of O_2

For C_3H_8 $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

∵ 1 volume of C_3H_8 requires 5 ml of O_2 for complete combustion

∴ (10 – x) c.c. of C_3H_8 requires 5(10 – x) c.c. of O_2

Total Volume of O_2 = 2 x + 5 (10 – x) it is equivalent to 41

(according to question)

∵ 2x + (10 – x) = 41

∴ x = 3 c.c.

Volume of CH_4 is 3 c.c. and volume of C_3H_8 is 7 c.c.

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. Which of the following will have least hindered rotation about carbon-carbon bond?

(A) Ethane
(B) Ethylene
(C) Acetylene
(D) Hexachloroethane

2. Alkanes are readily attacked by–

(A) Electrophiles
(B) Nucleophiles
(C) Free radicals
(D) bases

3. Isopropyl bromide undergoes Wurtz reaction to form –

(A) Hexane
(B) 2, 3-Dimethyl butane
(C) Propane
(D) Neohexane

4. Alkanes can be prepared from Grignard reagents by reacting with –

(A) Alcohols
(B) Primary amines
(C) Alkynes
(D) All of them

5. Which reducing agent is used in Clemmensen reduction –

(A) Zn/ HCl
(B) $LiAlH_4$
(C) Zn-Hg/HCl
(D) Na/C_2H_5OH

6. Isomerisation in alkane may be brought about by using

(A) Al_2O_3
(B) Fe_2O_3
(C) $AlCl_3$ and HCl
(D) concentrated H_2SO_4

7. Formatio of alkane by the action of Zn on alkyl halide is called –

(A) Frankland reaction
(B) Wurtz reaction
(C) Cannizzaro's reaction
(D) Kolbe's reaction

8. The hydrocarbon which is a liquid at room temperature is –

(A) butane
(B) propane
(C) decane
(D) neopentane

9. The most important method of preparation of hydrocarbons of lower carbon number is –

(A) Pyrolysis of higher carbon number hydrocarbons
(B) Electrolysis of salts of fatty acids
(C) Sabatier Senderen's reaction
(D) Direct synthesis

10. Which of the following will not produce ethane

(A) Reduction of CH_3COOH with HI/P_4
(B) Reduction of CH_3COCH_3 with HI/P_4
(C) Decarboxylation of sodium propionate with soda lime
(D) Hydrogenation of ethene in the presence of Ni.

11. The thermal decomposition of alkanes in the absence of air is known as –

(A) oxidation
(B) Combustion
(C) Hydrogenation
(D) pyrolysis

12. Methane can be prepared by :

(A) Wurtz reactions
(B) hydrogenation
(C) decarboxylation
(D) dehydrohalogenation

13. Whihc of the following alkyl halides is not suitable for Corey-House synthesis of alkanes –

(A) CH_3l
(B) C_2H_5Br
(C) $CH_3CH_2CH_2CH_2l$
(D) $(CH_3)_3CBr$

14. An alknae is most likely to react with –

(A) A free radical
(B) An alkali
(C) An electrophilic
(D) A nucleophile

15. The most volatile alkane is :

(A) n-pentane
(B) isopentane
(C) neopentane
(D) n-hexane

16. Which of the following reactions does not involved a C–C bond formation?

(A) Hydrolysis of a Grignard reagent
(B) Combination of two alkyl free radicals
(C) Corey-House synthesis of alkanes
(D) $RNa + R-Br \rightarrow R-R + NaBr$

17. Wurtz reaction on a mixture of ethyl halide and isobutyl halide gives –

(A) Butane and isobutane
(B) Butane and 2, 5-dimethylhexane
(C) Butane,2,5-dimethylhexane and isohexane
(D) Butane and isohexane

18. Which reducing agent is used in Clemmensen reduction ?

(A) Zn/HCl
(B) $LiAlH_4$
(C) Zn-Hg/HCl
(D) Na/C_2H_5OH

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. Alcohols undergo dehydration in the following sequence –

(A) 1° > 2° > 3° **(B)** 3° > 2° > 1°
(C) 1° > 3° > 2° **(D)** 3° > 1° > 2°

2. The reaction : $CH_2 = CHCH_3 + HBr \longrightarrow CH_3CHBrCH_3$ is –

(A) Nucleophilic additon
(B) Electrophilic additon
(C) Electrophilic substitution
(D) Free radical addition

3. The ozonolysis of an olefin gives only propanone. The olefin is :

(A) propene
(B) but-1-ene
(C) but-2-ene
(D) 2,3-dimethylbut-2-ene

4. Aqueous sulphuric acid reacts with 2-methyl-1-butene to give predominantly –

(A) Isobutyl hydrogen sulphate
(B) 2-methyl-2-butanol
(C) 2-methyl-1-butanol
(D) Secondary butyl hydrogen sulphate

5. Olefines can be converted to paraffins by –

(A) Halogenation **(B)** Hydrolysis
(C) Hydration **(D)** Hydrogenation

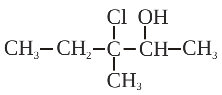
6. Anti-Markownikoff addition of HBr is not observed in

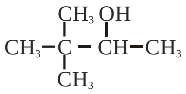
(A) propene **(B)** butene
(C) 2-butene **(D)** 2-pentene

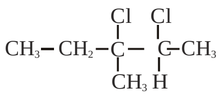
7. The addition of HCl in the presence of peroxide does not follow anti-Markownikoffs rule because

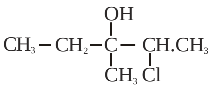
(A) HCl bond is too strong to be broken homolytically
(B) Cl atom is not reactive enough to add on to a double bond
(C) Cl combines with H to give back HCl
(D) HC is a reducing agent

8. 3-Methyl-2-penten on reaction with HOCl gives –

(A)

$CH_3-CH_2-\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{OH}{|}}{CH}-CH_3$

(B)

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{OH}{|}}{CH}-CH_3$

(C)

$CH_3-CH_2-\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{Cl}{|}}{\underset{\underset{H}{|}}{C}}-CH_3$

(D)

$CH_3-CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{Cl}{|}}{CH}.CH_3$

9. The addition of Br_2 to trans-2-butene produces

(A) (+) 2,3-dibromobutane
(B) (–) 2,3-dibromobutane
(C) rac-2,3-dibromobutane
(D) meso-2,3-dibromobutane

10. $CH_2 = CH_2 \xrightarrow{Cl_2} A \xrightarrow{AgOH}$? the product is a –

(A) Glycol **(B)** Dial
(C) Dioic acid **(D)** None of these

11. The olefin which on ozonolysis gives CH_3CH_2CHO and CH_3CHO is –

(A) 1-butene **(B)** 2-butene
(C) 1-pentene **(D)** 2-pentene

12. Alkene $\xrightarrow{B_2H_5} \xrightarrow{H_2O_2/OH^-}$ 2° alcohol. The alkene would be –

(A) $CH_3 - CH = CH_2$
(B) $CH_3CH_2 - CH = CH_2$
(C) $(CH_3)_2C = CH_2$
(D) $CH_3 - CH = CH - CH_3$

13. Ethylene reacts with alkaline $KMnO_4$ to form –

(A) Oxalic acid **(B)** HCHO
(C) Ethyl alcohol **(D)** Glycol

14. Which order is correct for bond length –

(A) ≡ C – H > – C – H > = C – H
(B) – C – H < ≡ C – H < = C – H
(C) ≡ C – H < = C – H < – C – H
(D) None of these

15. Which one of these will react with sodium metal –

(A) Ethyne **(B)** Ethene
(C) Ethane **(D)** Ether

16. Ethyne adds on HCl to first give a –

(A) Carbanion **(B)** A free radical
(C) A vinylic cation **(D)** A biradical

17. The relative acidity of ethyne, ethene and ethane follows the order –

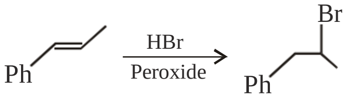
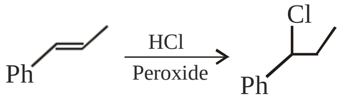
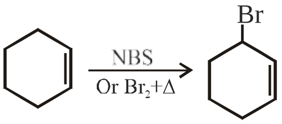
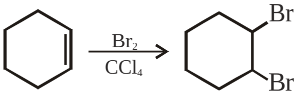
(A) Ethane > Ethyne < Ethene
(B) Ethyne > Ethene > Ethane
(C) Ethyne < Ethene < Ethane
(D) Ethene < Ethane < Ethyne

Exercise # 3

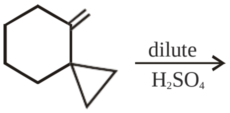
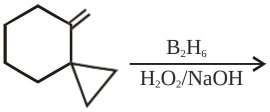
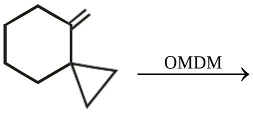
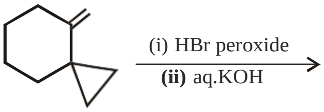
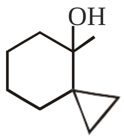
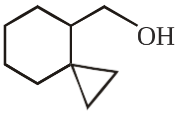
PART - 1

MATRIX MATCHCOLUMN

1.

Column I (Reactions) **(Reactant) (Major Product)**	**Column - II** **(Intermediate involve)**
(A) 	**(p)** Free Radical
(B) 	**(q)** Carbanion
(C) 	**(r)** Carbocation
(D) 	**(s)** Two isomers are formed

2. Match the column :

Column I	**Column - II**
(A) 	**(p)** Over all reaction involves Markowinkof's addition of water molecule on alkene.
(B) 	**(q)** Over all reaction involves Anti-Markownikof's addition of water molecule on alkene.
(C) 	**(r)** Reaction involves carbocation rearrangement.
(D) 	**(s)**  is major product
	(t)  is major product

Exercise # 4

PART - 1

PREVIOUS YEAR (NEET/AIPMT)

1. In Friedel-Craft's synthesis of toluene, the reactants in addition to anhydrous $AlCl_3$ are- **[CBSE AIPMT- 2000]**

(A) $C_6H_5Cl + CH_4$ **(B)** $C_6H_5Cl + CH_3Cl$

(C) $C_6H_6 + CH_4$ **(D)** $C_6H_6 + CH_3Cl$

2. Among the following alkenes

1- butene cis-2-butene trans-2butene

I II III

the decreasing order of stability is

[CBSE AIPMT-2000]

(A) II > I > III **(B)** III > II > I

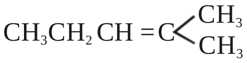
(C) III > I > II **(D)** I > II > III

3. Which alkene on ozonolysis gives

CH_3CH_2CHO and

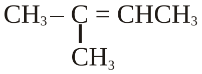

$CH_3\underset{\underset{O}{\|}}{C}CH_3$

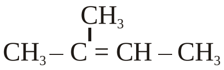
[CBSE AIPMT- 2001]

(A)

$CH_3CH_2CH=C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$

(B) $CH_3CH_2CH=CHCH_2CH_3$

(C) $CH_3CH_2CH=CHCH_3$

(D)

$CH_3-\underset{\underset{CH_3}{|}}{C}=CHCH_3$

4. The compound,

$CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_3$
on reaction with $NaIO_4$ in the presence of $KMnO_4$ gives

[CBSE AIPMT - 2003]

(A) $CH_3COCH_3 + CH_3CHO$

(B) $CH_3CHO + CO_2$

(C) CH_3COCH_3

(D) $CH_3COCH_3 + CH_3COOH$

5. Reaction of HBr with propene in the presence of peroxide gives **[CBSE AIPMT - 2004]**

(A) iso-propyl bromide **(B)** 3-bromo propane

(C) allyl bromide **(D)** n-propyl bromide

6. Using anhy. $AlCl_3$ as catalyst, which one of the folowing reactions produce ethylbenzene (PhEt)?

[CBSE AIPMT-2004]

(A) $H_3C-CH_2OH + C_6H_6$

(B) $CH_3-CH=CH_2 + C_6H_6$

(C) $H_2C=CH_2=C_6H_6$

(D) $H_3C-CH_3 + C_6H_6$

7. Products of the following reaction-

[CBSE AIPMT - 2005]

$CH_3C{\equiv}C.CH_2CH_3 \xrightarrow[\text{(ii) hydrolysis}]{\text{(i) } O_3}$ ...... are

(A) $CH_3CHO + CH_3CH_2CHO$

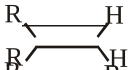
(B) $CH_3COOH + CH_3COCH_3$

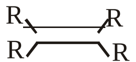
(C) $CH_3COOH + HOOC.CH_2CH_3$

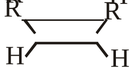
(D) $CH_3COOH + CO_2$

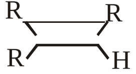
8. Which one of the following alkenes will react faster with H_2 under catalytic hydrogenation conditions?

[CBSE AIPMT - 2005]

(A)


(B)


(C)


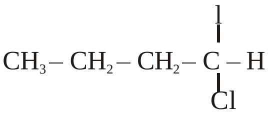
(D)


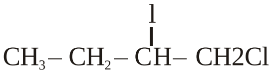
9. Predict the product C obtained in the following reaction of butyne - 1. **[CBSE AIPMT - 2007]**

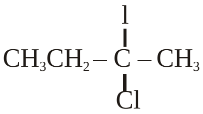
$CH_3CH_2-C\equiv CH + HCl \longrightarrow B \xrightarrow{HI} C$

(A)

$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2CH_2l$

(B)

$CH_3-CH_2-CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{l}{|}}{C}}-H$

(C)

$CH_3-CH_2-\overset{\overset{l}{|}}{CH}-CH2Cl$

(D)

$CH_3CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{l}{|}}{C}}-CH_3$

10. Which of the following compounds with molecular formula, C_5H_{10} yields acetone on ozonolysis ?

[CBSE AIPMT - 2007]

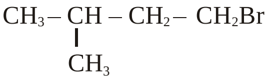
(A) 2- methyl-2buten **(B)** 3-methyl-1-butene

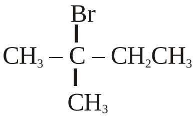
(C) Cyclopentane **(D)** 2-methyl-1-butene

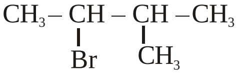
11.

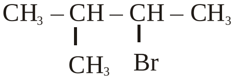
$H_3C-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2 + HBr \rightarrow A$

A (predominantly) is - **[CBSE AIPMT - 2008]**

(A)

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2Br$

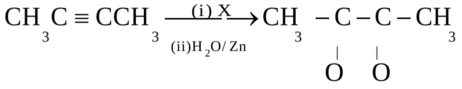
(B)

$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}-CH_2CH_3$

(C)

$CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

(D)

$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{Br}{|}}{CH}-CH_3$

MOCK TEST

1.



$$CH_3C \equiv CCH_3 \xrightarrow[(ii) H_2O/Zn]{(i) X} CH_3 - \underset{O}{\underset{|}{C}} - \underset{O}{\underset{|}{C}} - CH_3$$

X in the above reaction is

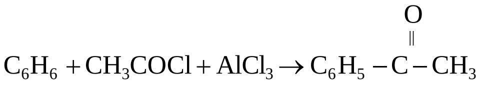
(A) HNO_3 (B) O_2 (C) O_3 (D) $KMnO_4$

2. Which of the following is Friedel-Craft's reaction

(A) $C_6H_6 + FeCl_3 + Cl_2 \rightarrow C_6H_5Cl$

(B) $C_6H_5CHO + CH_3CHO + KOH \rightarrow C_6H_5CH = CH - CHO$

(C)



$C_6H_6 + CH_3COCl + AlCl_3 \rightarrow C_6H_5 - \overset{O}{\overset{\|}{C}} - CH_3$

(D) $C_6H_5OH + CHCl_3 + KOH \longrightarrow$ Salicylaldehyde

3. Condition for maximum yield of C_2H_5Cl is

(A) C_2H_6 (excess) $+ Cl_2 \xrightarrow{\text{UV Light}}$

(B) $C_2H_6 + Cl_2 \xrightarrow[\text{Room temp.}]{\text{Dark}}$

(C) $C_2H + Cl$ (excess) $\xrightarrow{\text{UV Light}}$

(D) $C_2H_6 + Cl_2 \xrightarrow{\text{UV Light}}$

4. When ethyl alcohol is heated with red phosphorus and HI, then which of the following is formed

(A) C_2H_6 (B) CH_4 (C) C_3H_8 (D) C_2H_4

5. In the Fischer-Tropsch synthesis of petrol..... and....... are used as the raw materials

(A) H_2; CO (B) CH_4 ; H_2 (C) CH_4; CH_3OH (D) CH_3OH; CO

6. Which one of the following reactions is most suitable for the preparation of n-propyl benzene

(A) Friedel-Craft's reaction (B) Wurtz reaction (C) Wurtz-Fittig reaction (D) Grignard reaction

7. Propane cannot be prepared from which reaction

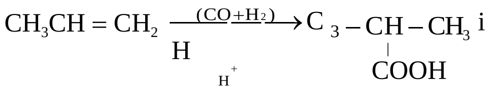
(A) $CH_3 - CH = CH_2 \xrightarrow[OH^-]{B_2H_6}$

(B) $CH_3CH_2CH_2I \xrightarrow[P]{HI}$

(C) $CH_3CH_2CH_2Cl \xrightarrow{Na}$

(D) None of these

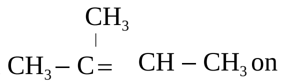
8. The reaction



$$CH_3CH = CH_2 \xrightarrow[H \quad H^+]{(CO+H_2)} C_3 - \underset{COOH}{\underset{|}{CH}} - CH_3$$ is known as

(A) Wurtz reaction (B) Koch reaction (C) Clemmensen reduction (D) Kolbe's reaction

9. The compound



$CH_3 - \overset{CH_3}{\overset{|}{C}} = CH - CH_3$ on reaction with $NaIO_4$ in the presence of $KMnO_4$ gives

(A) $CH_3CHO + CO_2$

(B) CH_3COCH_3

(C) $CH_3COCH_3 + CH_3COOH$

(D) $CH_3COCH_3 + CH_3CHO$

10. In the reaction :

$$HC \equiv CH + 2AgNO_3 \xrightarrow{NH_4OH} X + 2NH_4NO_3 + 2H_2O$$

'X' is

(A) Ag_2C (B) Ag_2C_2 (C) AgC (D) AgOH

CHAPTER 14

ECOSYSTEM

"We must trust to nothing but facts: These are presented to us by Nature, and cannot deceive. We ought, in every instance, to submit our reasoning to the test of experiment, and never to search for truth but by the natural road of experiment and observation."

"ANTOINE LAVOISIER (1743-1794)"

INTRODUCTION

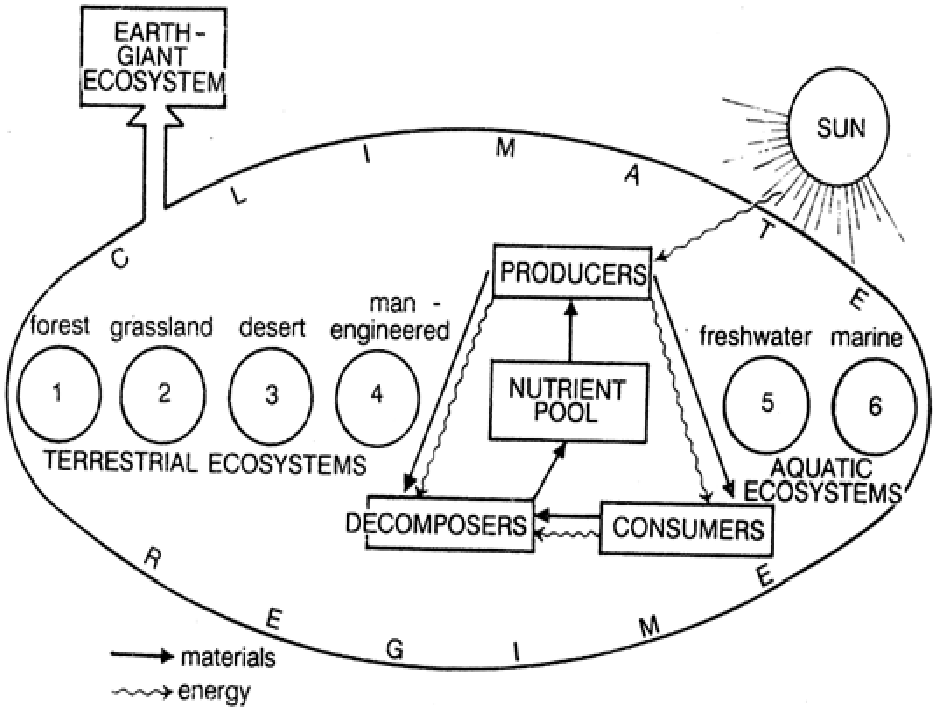
Ecosystem can be visualized as a functional unit of nature which varies greatly in size from a small pong to a large forest or a sea. Many ecologists regarding the entire biosphere as a global ecosystem, as a composite of all local ecosystems on earth. Wise range of living organisms ar present on earth surface. All living organisms such as plants, animals and microorganisms interact among themselves and also with the surrounding physical environment and maintains a balance in nature.
This forms a self sustaining or funtional unit of the living world known as **Ecosystem.** This sytem is too muc big so that is why it is divided into two parts: terrestial and aquatic. Forest,vgrasslands and desert are examples of terrestial ecosystems ; pond lake , wetland, river and estuary are examples of aquatic ecosystems.

This chapter gives us an overview of different types of ecosystems, structural as well as functional aspects related to productivity, energy flow, decomposition, ecological efficiencies nutrient cycling.

Ecosystem

Introduction

- **A.G.Tansley -** The term **"Ecosystem"** first of all coined by A.G. Tansley.
  According to Tansley - Ecosystem is **symbol** of **structure and function** of nature.
- **E.P.Odum -** Father of ecosystem ecology.
  According to E.P.Odum - Ecosystem is the **smallest structural and functional unit of nature** or environment.
- **Karl Mobius -** Used term **Biocoenosis** for ecosystem.
- **Thienmann -** Used term **Biosystem** for ecosystem.
- **Sukhachov -** Used term **Biogeocoenosis** for ecology.
- **Misra -** Used term **Ecosom** for ecosystem.
- **Forbes -** Used term **Microcosom** for ecosystem. For artificial ecosystem in laboratory.



- **Definition -** Total living (biotic) and non living (aboitic) componants of the environment present in a particular area is called ecosystem.
- In any ecosystem, communities or living organisms interact with their physical environment in such a way that there is a well defined flow of energy forming clear **trophic** (food) **levels** and **material cycles** within this ecosystem.
- Ecosystem is normally an open system because there is a continuous and variable entry and loss of **energy** and **materials**.
- An ecosystem may be small like a drop (microsystem) of water and as large as sea or tract of forest.
- An ecosystem may be temporary as a fresh water pool or a field or permanent like a forest or sea.
- Thus any area of nature that includes living organisms and nonliving substances interacting, so that a **flow of energy** leads to characteristic **trophic structures** and **cycling of materials** makes the ecosystem.

ETOOS KEY POINTS

(i) Ecological efficiency - The percentage of energy transferred from one trophic level to the next is called ecological efficiency or food chain efficiency.

$$\text{E.E} = \frac{\text{Energy in biomass production at a trophic level}}{\text{Energy in biomass production at previous trophic level}} \times 100$$

(ii) Assimilation efficiency - It is the production of consumed energy that is assimilated.

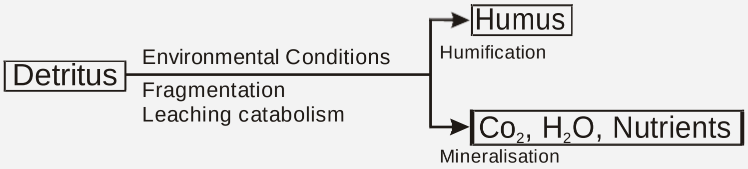
$$\text{A.E.} = \frac{\text{Food energy assimilated}}{\text{Food energy ingested}} \times 100$$

(iii) Net production efficiency -

$$\text{N.P.E.} = \frac{\text{Net primary productivity}}{\text{G.P.P.}} \times 100$$

(iv) Photosynthetic efficiency -

$$\text{P.E.} = \frac{\text{G.P.P.}}{\text{Incident total solar radiation}} \times 100$$

⇒ 

→ Ecology is a subject which studies the interactions among organisms and between the organism and its physical (abiotic) environment.

→ Key elements that lead to so much variation in the physical and chemical conditions of different habitats are temperature, water, light and soil.

→ The productivity and distrubution of plants is also heavily dependent on water.

→ The salt concentration (measured as salinity in parts per thousand) is less than 5 percent in inland water 30-35 percent in the sea water and > 100 percent in some hypersaline lagoons)Some organisms are tolerant of a wide range of salinities (euryhaline) but other are restricted to a narrow range (stenohaline).

→ Regulate : Some organisms are able to maintain homeostasis by physiological (sometimes behavioural also) means which ensures constant body temperature, constant osmotic concentration.

→ Conform : An overwhelming majority (99 percent) of animals and nearly all plants cannot maintain a constant internal environment. Their body temperature changes with the ambient temperature. In aquatic animals, the osmotic concentration of the body fluids changes with that of the ambient water osmotic concentration.

→ Heat loss or heat gain is a function of surface area. Since small animals have a larger surface area relative to their volume, they tend to lose body heat very fast when it is cold outside then they have to expend much energy to generate body heat through metabolism. This is the main reason why very small animals are rarely found in polar regions.

→ If the stressful external conditions are localised or remain only for a short duration, the organism has two other alternatives. (i) Migration (ii) Suspention

→ Under unfavourable conditions many zooplankton species in lakes and ponds are known to enter diapause, a stage of suspended development.

→ Adaptation is any attribute of the organism (morphological, physioloical, behavioural) that enables the organism to survive and reproduce in its habitat.

→ Mammals from colder climates generally have shorter ears and limbs to minimise heat loss. (This is called the Allen's Rule).

→ The body compensates low oxygen availability by increasing red blood cell production decreasing the binding capacity of haemoglobin and by increasing breathing rate.

→ Some organism show behavioural responses to cope with variations in their environment.

→ Desert lizards bask in the sun and absorb heat when their body temperature drops below the comfort zone but move into shade when temperature rise above the comfort zone.

→ Some organisms breed only once in their lifetime (Pacific salmon fish, bamboo) while others breed many times during their lifetime (most birds and mammals). Some produce a large number of small-sized offsprings (Oysters, pelagic fishes) while others produce a small number of large-sized offsprings (birds, mammals).

→ Life history traits of organisms have evolved in relation to the constraints imposed by the a biotic and biotic components of the habitat in which they live.

→ Predator acting as contents for energy transfer across tropic level.

→ Since the invaded land does not have its natural predators. The prickly pear cactus introduced into Australia in the early 1920's caused havoc by spreading rapidly into millions of hectares of rangeland.

→ Biological control methods adopted in agricultural pest control are based on the ability of the predator to regulate prey population. Predators are also help the in maintaining species diversity in a community by reducing the intensity of competition among competing prey species.

→ Nearly 25 percent of all insects are known to be phytophagous (feeding on plant sap and other parts of plants) Thorns (Acacia, Cactus) are the most common morphological means of defence .

→ Calotropis grow in abandoned fields. The plant produces highly poisonous cardiac glycosides and that is why you will never see any cattle or goat browsing on the plant.

→ Competition : Competition occurs when closely related species compete for the same resources that are limiting.

→ Resources need not be limiting for competition to occur, in interference competition, the feeding efficiency of one

SOLVED EXAMPLE

Ex.1 In an aquatic ecosystem, the trophical level equivalent to cows in grassland is

(A) Phytoplankton (B) Zooplankton

(C) Nekton (D) Benthos

Sol. (B)

Ex.2 When peacock eats snakes which eat insects thriving on green plants, the peacock is

(A) A primary consumer

(B) A primary decomposer

(C) Final decomposer

(D) The apex of food pyramid

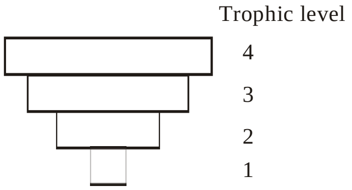
Sol. (D) : Because Peacock is the top consumer

Ex.3 Two food chains are given below

Tree → aphid → insectivorous bird → bird of prey → carnivorous fish

Which diagram is a pyramid of energy representing both food chains

(A)



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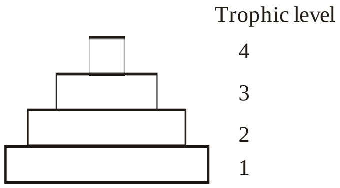
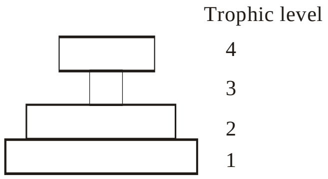
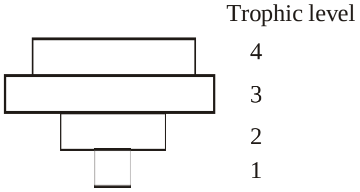


(C)



(D)

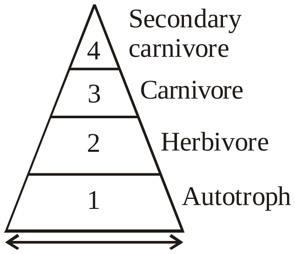


Sol. (B)

Ex.4 Using the figure, determine which animals would be found in the same trophic level

A. Trophic level Trophic level	**Feeding strategy**	**Grazing food chain**	**Decomposer food chain**
4	Secondary carnivore	Cooper's hawk	Owl
3	Carnivore	Robin	Shrew
2	Herbivore	Cricket	Earthworm
1	Autotrophs	Maple tree leaves	Dead maple leaves

B. Pyramid of productivity



(A) Humans and horses

(B) Eagles and blue jays

(C) Pine trees and garden snakes

(D) Cricket and cows

Sol. (D)

Ex.5 In a food chain herbivores are

(A) Primary producers

(B) Primary consumers

(C) Secondary consumers

(D) Decomposers

Sol. (B) : Primary consumers or harbivores of first order are depend upon producers or green plants for their food.

Ex.6 Of the total incident solar radiation the proportion of PAR is

(A) Morethan 80 % (B) About 70 %

(C) About 60 % (D) Less than 50 %

Sol. (D) : Plants capture 2-10 % of PAR

Ex.7 Plants growing on sandstone are

(A) Psammophytes (B) Oxylophytes

(C) Lithophytes (D) Phanerophytes

Sol. (C)

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. In a pond if there is too much wastage, then the BOD of pond will

(A) Increase **(B)** Decrease
(C) Remain same **(D)** **(A)** and **(B)** both

2. Which of the following abundantly occurs in pond ecosystem

(A) Producer **(B)** Consumer
(C) Top consumer **(D)** Decomposers

3. If all decomposers are removed from an ecosystem, what will happen

(A) All consumers will die
(B) Energy cycle will be affected
(C) Balance of biogeochemical cycle will be disturbed
(D) Only herbivores will die

4. Which of the following is the most stable ecosystem

(A) Mountain **(B)** Desert
(C) Forest **(D)** Ocean

5. In a biotic community, primary consumers are

(A) Omnivores **(B)** Carnivores
(C) Detritivores **(D)** Herbivores

6. Which of the following does not effect the forest ecosystem

(A) Deforestation **(B)** Soil erosion
(C) Climatic variation **(D)** None of these

7. The pyramid of energy in a forest ecosystem is

(A) Always upright
(B) Always inverted
(C) Both upright and inverted
(D) None of the above

8. In an ecosystem, there is flow of energy at different trophic levels. This is as follows :

(A) Primary consumers - Tertiary consumers - Secondary consumers - Decomposers - Producers
(B) Producers - Primary consumers - Secondary consumers - Tertiary consumers - Decomposers
(C) Producers - Decomposers - Primary consumers - Tertiary consumers - Secondary consumers
(D) Producers - Primary consumers - Tertiary consumers - Secondary consumers - Decomposers

9. We refer to the following as the food chain

(A) Large number of animals near a source of food
(B) Transfer of food energy from the green plants through a series of consumer organisms
(C) Large number of human beings forming a human chain near a source of food
(D) None of these

10. In a food chain, lion is a

(A) Secondary consumer **(B)** Primary consumer
(C) Tertiary consumer **(D)** Secondary producer

11. In a pond ecosystem, benthos means

(A) Primary consumers in the depth of a pond
(B) Zooplankton on the water surface
(C) Periphyton
(D) Epineuston

12. Transfer of energy from one trophic level to other trophic level is according to the second law of thermodynamics. The efficiency of energy transfer from herbivorous to carnivorous is

(A) 25% **(B)** 50%
(C) 10% **(D)** 5%

13. In a food chain, which of the following produces in the largest amount

(A) Producers **(B)** Decomposers
(C) Tertiary consumers **(D)** Primary consumers

14. If forest area is reduced to half, which one of the following will be a long term effect

(A) The natives (tribals) of that area will die on account of hunger
(B) Cattles of that area will die due to scarcity of fodder
(C) To diversity in germplasm will effect the crop breeding
(D) It will be converted into large desert

15. The first link in any food chain is always a green plant because

(A) They are widely distributed
(B) They are firmly fixed to the soil
(C) They alone have a capacity to fix atmospheric CO2 in the presence of sunlight
(D) All of the above

16. Food levels in an ecosystem are called

(A) Trophic levels **(B)** Consumer levels
(C) Producer levels **(D)** Herbivore levels

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. Food chain consists of
(A) Producer, consumer and decomposer
(B) Producer, carnivore and decomposer
(C) Producer and primary consumer
(D) Producer, herbivore and carnivore

2. Animals which live at the bottom of sea are
(A) Nekton (B) Diatom
(C) Banthos (D) Plankton

3. Green plants are
(A) Autotrophs (B) Heterotrophs
(C) Chemotrophs (D) None of these\

4. Pyramid of energy is
(A) Upright (B) Inverted
(C) Oblique (D) None of these

5. The flora and fauna in lakes or ponds are
(A) Lentic biota (B) Lotic biota
(C) Abiotic biota (D) Field layer

6. During food chain the maximum energy is stored in
(A) Producers (B) Decomposers
(C) Herbivores (D) Carnivores

7. Transition zone between two ecosystems or vegetational regions is termed
(A) Ecocline (B) Ecotone
(C) Ecad (D) Barrier

8. The ecosystem consists of
(A) Producers (B) Consumers
(C) Decomposers (D) All of these

9. In a food chain, the total amount of living material is depicted by
(A) Pyramid of energy (B) Pyramid of numbers
(C) Pyramid of biomass (D) All of these

10. The biotic part of ecosystem includes
(A) Producers (B) Consumers
(C) Decomposers (D) All of these

11. When the number of organisms at successive levels are plotted, they assume the shape of a pyramid. This is called the pyramid of
(A) Energy (B) Number
(C) Biomass (D) Both (A) and (C)

12. The two vegetation of ecosystem are separated by
(A) Ecotone (B) Ecoline
(C) Ecosystem (D) Ecesis

13. Energy enters into the ecosystem through
(A) Herbivores (B) Carnivores
(C) Producers (D) Decomposers

14. Which of the following is an artificial ecosystem
(A) Rice-field (B) Forest
(C) Grassland (D) Lake

15. Which are the biotic components of forest ecosystem
(A) Producers (B) Decomposers
(C) Consumers (D) All of the above

16. Which of the following is most important abiotic factor in pond ecosystem
(A) Water (B) Phytoplankton
(C) Zooplankton (D) Temperature

17. The bacteria that attack dead organic matter are
(A) Producer (B) Herbivore
(C) Carnivores (D) Decomposers

18. 10% law of flow of energy in ecosystem was proposed by
(A) Lindemann (B) Carl Mobius
(C) Tensely (D) Darwin

19. A plant being eaten by a herbivorous which in turn is eaten by a carnivorous makes
(A) Food chain (B) Food web
(C) Omnivorous (D) Interdependent

20. When peacock eats snakes which eat insects thriving on green plants, the peacock is
(A) A primary consumer
(B) A primary decomposer
(C) Final decomposer
(D) The apex of food pyramid

21. Acacia arabica is a
(A) Mesophyte (B) Hydrophyte
(C) Xerophyte (D) Halophyte

22. Casuarina equisetifolia is a
(A) Mesophyte (B) Xerophyte
(C) Halophyte (D) Forest epiphyte

23. The plants in which vascular tissues are absent and well developed aerenchyma is present, are
(A) Xerophytes (B) Halophytes
(C) Hydrophytes (D) Mesophytes

Exercise # 3 PART - 1 MATRIX MATCH COLUMN

1. Match Column - I (Indian forest types) with Column - II (dominant tree genera) and choose the correct option

Column - I	**Column - II**
(A) Tropical rain forest	**(1)** Hopea
(B) Tropical deciduous	**(2)** Shoera
(C) Temperate broad leaf forest	**(3)** Quercus
(D) Temperate coniferous forest	**(4)** Picea

(A) A - 1, B - 2, C - 3, D - 4
(B) A - 2, B - 1, C - 4, D - 3
(C) A - 3, B - 2, C - 1, D - 4
(D) A - 1, B - 2, C - 4, D - 3
(E) A- 4, B - 3, C - 2, D - 1

2. Match Column - I with Column - II and choose the correct answer from the code given below.

Column - I	**Column - II**
(A) Population	**(i)** Part of the earth consisting of all the ecosystems of the world
(B) Community	**(ii)** Assemblage of all the individuals belonging to different species occuring in an are**(A)**
(C) Ecosystem	**(iii)** Group of similar individuals belonging
(D) Ecosphere	**(iv)** Interaction between the living organisms and their physical environment
	(v) Classification of organisms based on the type of environment

(A) A- (iii), B - (ii), C - (i), D - (v)
(B) A- (iv), B - (v), C - (iii), D - (i)
(C) A- (ii), B - (iii), C - (i), D - (iv)
(D) A- (iii), B - (ii), C - (iv), D - (i)

3. Match Column - I with Column - II and choose the correct answer from the code given below.

Column - I	**Column - II**
(A) Gross primary productivity	**(i)** Self-sustainable ecosystem
(B) Net primary productivity	**(ii)** Aquatic
(C) Pond	**(iii)** O_2 requiring process
(D) Aquarium	**(iv)** Photosynthetic production
(E) Decomposition	**(v)** Available to secondary consumers

(A) A - (iv), B - (ii), C - (i), D - (iii), E - (v)
(B) A - (iv), B - (v), C - (i), D - (ii), E - (iii)
(C) A - (i), B - (iii), C - (ii), D - (iv), E - (v)
(D) A - (ii), B - (i), C - (iii), D - (v), E - (iv)

4. Match Column - I with Column - II and choose the correct answer from the code given below.

Column - I	**Column - II**
(A) Gross primary products	**(i)** Green plants
(B) Secondary productivity	**(ii)** Rate of synthesis of organic matter by consumers
(C) Transducers	**(iii)** Total organic matter produced from solar energy
(D) Food web	**(iv)** Interlocking pattern

(A) A- (i), B - (ii), C - (iii), D - (iv)
(B) A- (iii), B - (ii), C - (i), D - (iv)
(C) A- (iii), B - (iv), C - (i), D - (ii)
(D) A- (ii), B - (i), C - (iv), D - (iii)

Exercise # 4

PART - 1

PREVIOUS YEAR (NEET/AIPMT)

1. The greatest biomass of autotrophs in the world’s oceans is that of

(A) Benthic brown algae, coastal red algae and dephnids
(B) Benthic diatoms and marine viruses
(C) Sea grasses anmd slime molds
(D) Free-floating micro-algae, cyanobaceria and nanoplankton

2. Bamboo plant is growing in a far forest then what will be the trophic level of it : -

(A) First trophic level (T1)
(B) Second trophic level (T2)
(C) Third trophic level (T3)
(D) Fourth trophic level (T4)

3. Choose the correct match Bladderwert, sundew, venus flytrap : -

(A) Nepanthese, Dionea, Drosera
(B) Nepanthese, Utricularia, Vanda
(C) Utricularia, Drosera, Dionea
(D) Dionea, Trapa, Vanda

4. An ecosystem which can be easily damaged but can recover after some time if damaging effect stops will be having -

(A) Low stability and high resilience
(B) High stability and low resilience
(C) Low stability and low resilience
(D) High stability and high resilience

5. If by radiation all nitrogenase enzyme are inactivated, then there will be no :-

(A) Fixation of nitrogen in legumes
(B) Fixation of atmospheric nitrogen
(C) Conversion from nitrate to nitrite in legumes
(D) Conversion from ammonium to nitrate in soil

6. Which of the following is expected to have the highest value (gm/m^2/yr) in a grassland ecosystem : -

(A) Secondary production (SP)
(B) Tertiary production (TP)
(C) Gross production (GP)
(D) Net production (NP)

7. Which one of the following pairs in mismatched-

(A) Biomass burning – Release of CO_2
(B) Nuclear power – Radioactive wastes
(C) Solar energy – Green house effect
(D) Fossil fuel burning – Release of CO_2

8. More than 70% of world's fresh water is contained in –

(A) Antarctica
(B) Glaciers and Mountains
(C) Greenland **(D)** Polar ice

9. Prolonged liberal irrigation of agricultural fields is likely to create the problem of -

(A) Acidity **(B)** Aridity
(C) Metal toxicity **(D)** salinity

10. Which one of the following is not used for construction of ecological pyramids ?

(A) Dry weight
(B) Number of individuals
(C) Rate of energy flow **(D)** Fresh weight

11. Which one of the following ecosystem types has the highest annual net primary productivity?

(A) Tropical rain forest
(B) Tropical deciduous forest
(C) Temperate evergreen forest.
(D) Temperate deciduous forest

12. A lake near a village suffered heavy mortality of fishes within a few days. Consider the following reasons for this?

(I) Lots of urea and phosphate fertilizer were used in the crops in the vicinity
(II) The area was sprayed with DDT by an aircraft
(III) The lake water turned green and stinky
(IV) Phytoplankton populations in the lake declined initially thereby greatly reducing photosynthesis

Which two of the above were the main causes of fish mortality in the lake?

(A) II and III **(B)** III and IV
(C) I and III **(D)** I and II

13. The slow rate of decomposition of fallen logs in nature is due to their:

(A) Low moisture content
(B) poor nitrogen content
(C) anaerobic environment around them
(D) low cellulose content

14. About 70% of total global carbon is found in:

(A) Grasslands **(B)** Agroecosystems
(C) Oceans **(D)** Forests

MOCK TEST

1. The primary producers of the deep-sea hydrothermal vent ecosystem are

(A) Green algae (B) Chemosynthetic bacteria
(C) Blue- green algae (D) Coral reefs

2. The rate of formation of new organic matter by deer in a forest ecosystem is called

(A) Standing crop (B) primary productivity
(C) Net primary productivity (D) Secondary productivity

3. Identify the ecologist from the given hints.

(i) He carried out long-terrn ecosystem experiments using outdoor plots
(ii) In his experiments he showed that " increased diversity contributed to higher productivity"
(A) Ahmed Khan (B) David Tilman (C) Stanley Cohen (D) Ernest Chain

4. Which one of the following is a characteristic feature of cropland ecosystem ?

(A) Absence of weds (B) Ecological succession
(C) Absence of soil organisms (D) Least genetic diversity

5. Which of the following relations is correct regarding GPP and NPP of an ecosystem ?

(A) NPP = GPP - Animal consumption (B) NPP = GPP + Plant respiration
(C) NPP =GPP - Plant respiration (D) NPP = GPP+ Animal consumption

6. Which of the following statements about productivity is true

(A) Primary productivity of all ecosystems is a constant.
(B) The annual net primary productivity of the whole of the biosphere is 17 billion tons (dry weight) of organic matter.
(C) Net primary productivity is the amount of biomass available for consumption by carnivores.
(D) Secondary productivity is defined as the rate of formation of new organic matter by decomposers.
(E) Primary productivity depends on the plant species inhabiting a particular area.

7. The biomass available for consumption to heterotophs and the rate of formation of new organic matter by consumers are defined as

(A) Gross primary productivity and net primary productivity respectively
(B) Net primary productivity and gross primary productivity respectively
(C) Gross primary productivity and secondary productivity respectively
(D) Net primary productivity and secondary productivity respectively
(E) Secondary productivity and net primary productivity respectively.

8. The breakdown of detritus into small particles by detritivores is called

(A) Leaching (B) Humification (C) Fragmentation (D) Catabolism

9. Lindeman for the first time gave energy transfer law, which states that

(A) only 20% of the energy is transferred to each trophic level
(B) only 10% of the energy is transferred to each trophic level
(C) only 30% of the energy is transferred to each trophic level
(D) only 50 of the energy is transferred to each trophic level.

10. The gross primary productivity of an ecosystem is 170 tons of organic matter and amount used in respiration in 50 tons Calculate the net primary productivity of the ecosystme

(A) 120 tons (B) 100 tons (C) 70 tons (D) 12 tons
(E) 17 tons

CHAPTER 10

HALOALKANES AND HALOARENES

The reactions of organic magnesium compounds are of two kinds - reactions of substitution and reactions of addition.

''VICTORGRIGNARD''

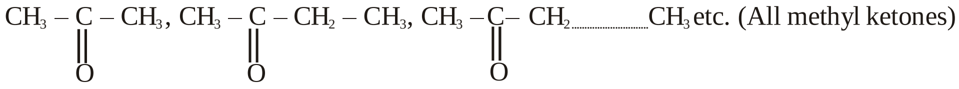
INTRODUCTION

Compounds derived from hydrocarbons by replacement of one or more H-atoms by corresponding no. of halogen atoms are known as **halogen derivatives**.

There are three major classes of organohalogen compounds; alkyl halides, vinyl halides, and aryl halides.

An **alkyl halide** simply has a halogen atoms bonded to one of the sp^3 hybrid carbon atoms of an alkyl group. A **vinyl halide** or **Aryl halide** has a halogen atom bonded to one of the sp^2 hybrid carbon atoms or an aromatic ring. They are different from alkyl halides because their bonding and hybridization are different.

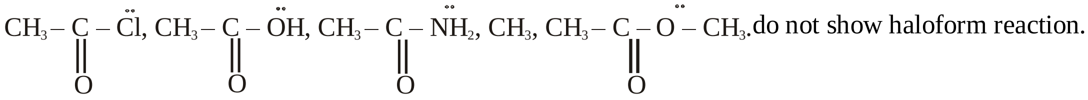
Ex.



$CH_3-\underset{\underset{O}{\|}}{C}-CH_3$, $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$, $CH_3-\underset{\underset{O}{\|}}{C}-CH_2$……$CH_3$ etc. (All methyl ketones)

$CH_3-\underset{\underset{O}{\|}}{C}-COOH$, $CH_3-\underset{\underset{O}{\|}}{C}-CHO$ Also show haloform reaction.

(–) ve haloform reaction : Reaction in which haloforms are not formed with X_2 and alkali.



$CH_3-\underset{\underset{O}{\|}}{C}-\ddot{C}l$, $CH_3-\underset{\underset{O}{\|}}{C}-\ddot{O}H$, $CH_3-\underset{\underset{O}{\|}}{C}-\ddot{N}H_2$, CH_3, $CH_3-\underset{\underset{O}{\|}}{C}-\ddot{O}-CH_3$. do not show haloform reaction.

(iii) Preparation of pure $CHCl_3$:

$$\underset{\text{Chloral hydrate}}{CCl_3CHO.\ 2H_2O} \xrightarrow[\Delta]{NaOH} \underset{\text{(Pure Chloroform)}}{CHCl_3} + HCOONa + 2H_2O$$

(iv) Industrial Preparation :

$$\begin{matrix} CH_3CH_2-OH \\ \text{or} \\ CH_3COCH_3 \end{matrix} \xrightarrow{\text{aq. NaCl/electrolysis}} CHCl_3 + \begin{matrix} HCOONa \\ \text{or} \\ CH_3COONa \end{matrix}$$

Physical Properties :

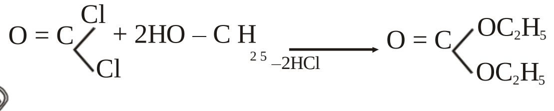
$CHCl_3$ is colourless and sweet smelling liquid. it's B.P. is 61ºC and it is insoluble in H_2O and have density more than H_2O. Chloroform is used as Anaesthetic.

Chemical Properties :

(i) Oxidation : $CHCl_3 + [O] \xrightarrow{\text{Air and light}} COCl_2 + HCl$

Phosgene gas or
Carbonyl Chloride
(Poisonous gas)

$CHCl_3$ is stored in dark coloured bottles which are filled upto the brim to prevent oxidation of $CHCl_3$ into $COCl_2$ and 1% ethanol is also added to chloroform.

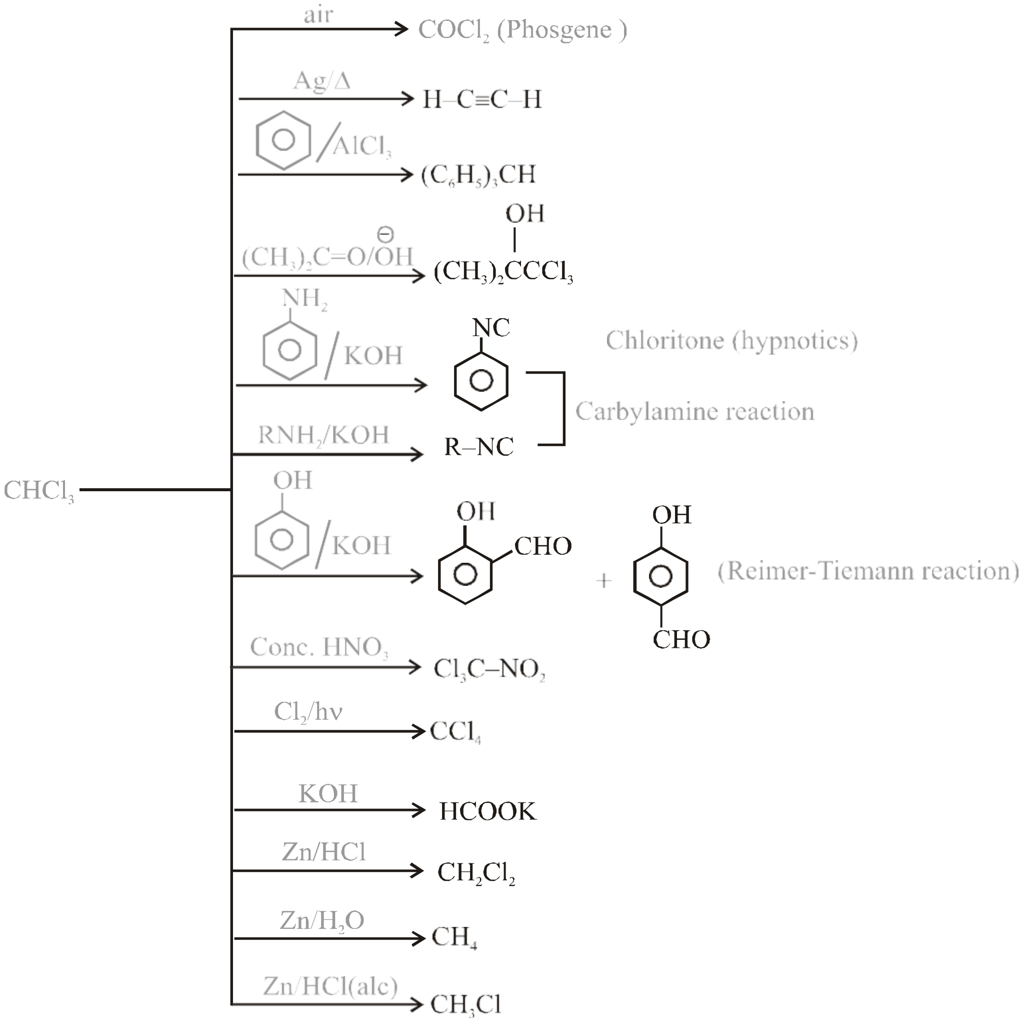


$$O=C\begin{matrix} Cl \\ Cl \end{matrix} + 2HO-C_2H_5 \xrightarrow[-2HCl]{} O=C\begin{matrix} OC_2H_5 \\ OC_2H_5 \end{matrix}$$

ED OS KEY POINTS

Reagent	Pure $CHCl_3$	Impure $CHCl_3(COCl_2 + HCl)$
Blue litmus	No Change	turns into red
$AgNO_3$	No reaction	White ppt of AgCl
Conc. H_2SO_4	No reaction	Yellow solution

Reactions of chloroform :



- Purity of chloroform (presence of phosgene) can be tested before use as anaesthetic by treating with aqueous solution of AgNO$_3$ because the presence of COCl$_2$ may cause cardiac failure.
- Chloroform is stored in dark colour bottle containing small amount of ethyl alcohol. (It converts phosgene into diethylcarbonate).

SOLVED EXAMPLE

Ex. 1 Which of the following is used as insecticide :

(A) D.D.T.
(B) Chloritone
(C) Chloropicrin
(D) **(A)** and **(C)** both

Sol. **(D)**

Ex. 2 The product in the following reaction is :

$\text{Ph} - \text{Cl} + \text{Fe} / \text{Br}_2 \longrightarrow \text{Product}$

(A) o– bromo-chloro benzene
(B) p– bromo-chloro benzene
(C) **(A)** and **(B)** both
(D) 2, 4, 6-tribromo chloro benzene

Sol. **(C)** Since – Cl group is deactivating and o/p directing group so only o– and p– products are formed.

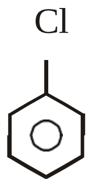
Ex. 3 The most reactive towards SN^1 is :

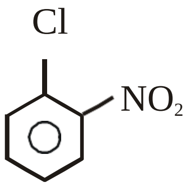
(A) $PhCH_2Cl$
(B) Ph–Cl
(C) $CH_3CHCl(CH_3)$
(D) p–NO_2—Ph—CH_2—Cl

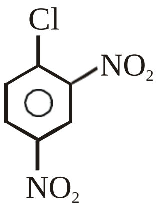
Sol. **(A)** S_{N^1} the intermediate carbocation is formed.

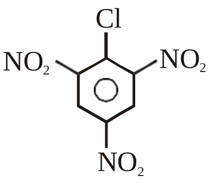
$C_6H_5—CH_2Cl \longrightarrow C_6H_5\overset{\oplus}{C}H_2$ is maximum stable due to resonance.

Ex. 4 Which of the following undergoes Hydrolysis most easily :

(A)


(B)


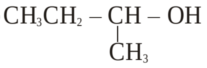
(C)


(D)


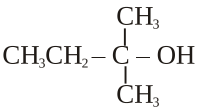
Sol. **(D)** If there is more m-directing group then there will be more nuclephilic substitution reaction.

Ex. 5 The order of reactivity of following alcohols with halogen acids is ....

(i) $CH_3CH_2 - CH_2 - OH$

(ii)


$CH_3CH_2 - \underset{|}{\underset{CH_3}{CH}} - OH$

(iii)


$CH_3CH_2 - \overset{CH_3}{\underset{CH_3}{C}} - OH$

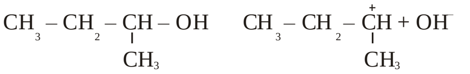
(A) (i) > (ii) > (iii)
(B) (iii) > (ii) > (i)
(C) (ii) > (i) > (iii)
(D) (i) > (iii) > (ii)

Sol. **(B)** Reaction between alcohols and halogen acid follows $S_N{}^1$ mechanism. In $S_N{}^1$ mechanism carbocations are formed as intermediates.

Let us consider the formation of carbocations with the given three alcohols

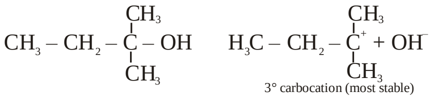
$CH_3 - CH_2 - CH_2 - OH \quad CH_3 - CH_2 - \overset{+}{C}H + OH^-$

In this case, 1° carbocation is formed. It is least stable. So, here $S_N{}^2$ mechanism is followed. In this $S_N{}^2$ mechanism a transitory state is observed in α-carbon is linked with two nucleophiles.



$CH_3 - CH_2 - \underset{CH_3}{CH} - OH \quad CH_3 - CH_2 - \underset{CH_3}{\overset{+}{C}H} + OH^-$

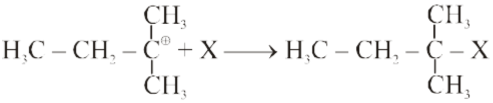
2° carbocation (more stable than 1° carbocation)



$CH_3 - CH_2 - \overset{CH_3}{\underset{CH_3}{C}} - OH \quad H_3C - CH_2 - \overset{CH_3}{\underset{CH_3}{C^+}} + OH^-$

3° carbocation (most stable)

The raction proceeded with stable carbocatio. Higher the stability of carbocation, higher will be the possibilities of attack of X^- ion to the carbocation. As, the tertiary carbocation is most stable so the possibilities of attack of X^- ion are more prominent in case of tertiary carbocations. Thus, attack of X^- ion to carbocation is proceeded with tertiary carbocation as follows



$H_3C - CH_2 - \overset{CH_3}{\underset{CH_3}{C^{\oplus}}} + X \longrightarrow H_3C - CH_2 - \overset{CH_3}{\underset{CH_3}{C}} - X$

3° carbocation

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. How many structural isomers are possible for a compound with molecular formula C_3H_7Cl

(A) 2 **(B)** 5
(C) 7 **(D)** 9

2. In CH_3CH_2Br, % of Br is

(A) 80 **(B)** 75
(C) 70 **(D)** 7

3. Gem- dibromide is

(A) $CH_3CH(Br)OH(Br)CH_3$
(B) $CH_3CBr_2CH_3$
(C) $CH_2(Br)CH_2CH_2$
(D) CH_2BrCH_2Br

4. Ethylidene dibromide is

(A) CH_3-CH_2-Br
(B) $Br-CH_2-CH_2-Br$
(C) CH_3-CHBr_2
(D) $CH_2=CBr_2$

5. Benzylidene chloride is

(A) $C_6H_5CH_2Cl$ **(B)** $C_6H_5CHCl_2$
(C) $C_6H_4ClCH_2Cl$ **(D)** $C_6H_5CCl_3$

6. Which of the following halide is 2^o

(A) Isopropyl chloride **(B)** Isobutyl chloride
(C) *n*-propyl chloride **(D)** *n*-butyl chloride

7. Haloforms are trihalogen derivatives of

(A) Ethane **(B)** Methane
(C) Propane **(D)** Benzene

8. Benzene hexachloride is

(A) 1, 2, 3, 4, 5, 6-hexachlorocyclohexane
(B) 1, 1, 1, 6, 6, 6-hexachlorocyclohexane
(C) 1, 6-phenyl-1, 6-chlorohexane
(D) 1, 1-phenyl-6, 6-chlorohexane

9. Number of ▯ – bonds present in *B.H.C.* (Benzene hexachloride) are

(A) 6 **(B)** Zero
(C) 3 **(D)** 12

10. The general formula for alkyl halides is

(A) $C_nH_{2n+1}X$ *(B)* $C_nH_{2n+2}X$
(C) $C_nH_{n+1}X$ **(D)** $C_nH_{2n}X$

11. The following reaction is known as

$C_2H_5OH + SOCl_2 \xrightarrow{\text{Pyridine}} C_2H_5Cl + SO_2 + HCl$

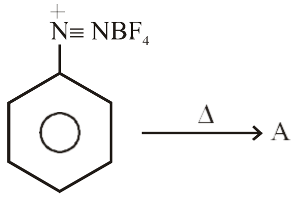
(A) Kharasch effect
(B) Darzen's procedure
(C) Williamson's synthesis
(D) Hunsdiecker synthesis reaction

12. What is the main product of the reaction between 2-methyl propene with HBr

(A) 1-bromo butane
(B) 1-bromo-2 methyl propane
(C) 2-bromo butane
(D) 2-bromo-2 methyl propane

13. Halogenation of alkanes is

(A) A reductive process
(B) An oxidative process
(C) An isothermal process
(D) An indothermal process

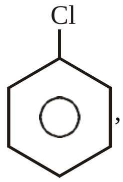
14. 

In the above process product *A* is

(A) Fluorobenzene
(B) Benzene
(C) 1, 4-difluorobenzene
(D) 1, 3-difluorobenzene

15. Silver acetate $+ Br_2 \xrightarrow{CS_2}$. The main product of this reaction is

(A) CH_3-Br **(B)** CH_3COI
(C) CH_3COOH **(D)** None of these

16. Diazonium salts + Cu_2Cl_2 + HCl → ,

the reaction is known as

(A) Chlorination
(B) Sandmeyer's reaction
(C) Perkin reaction
(D) Substitution reaction

Exercise # 2

SINGLE OBJECTIVE AIIMS LEVEL

1. Consider the following reaction sequence,

$CH_3C\equiv CH \xrightarrow[HgSO_4]{aq.H_2SO_4} A \xrightarrow[Heat]{PCl_5} B.$

The products **(A)** and **(B)** are, respectively,

(A) CH_3COCH_3 and $CH_3CCl_2CH_3$

(B) CH_3CH_2CHO and $CH_3CH_2CHCl_2$

(C) $CH_3CHOHCH_3$ and $CH_3CHClCH_3$

(D) $CH_3CH_2CH_2OH$ and $CH_3CH_2CH_2Cl$

2. Which of the following has highest dipole moment:

(A) CH_3Cl **(B)** CH_3F

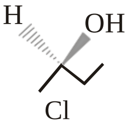
(C) CH_3Br **(D)** CH_3I

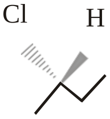
3. In S_{N^1} the first step involves the formation of

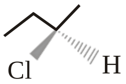
(A) free radical **(B)** carbanion

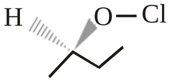
(C) carbocation **(D)** final product

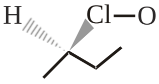
4. The product formed in the reaction

 + $SOCl_2 \rightarrow$ is-

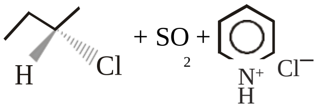
(A) 

(B) 

(C) 

(D) 

5. The reaction 



proceeds by the mechanism

(A) S_{N^1} **(B)** S_{N^2}

(C) S_Ni **(D)** S_E2

6. 1, 3- Dibromopropane reacts with metallic zinc to form

(A) propene **(B)** cyclopropane

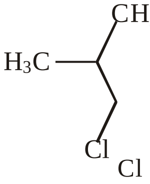
(C) propane **(D)** hexane

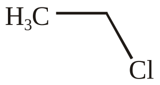
7. To form alkane isonitrile, alkyl halide is reacted with:

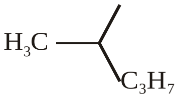
(A) KCN **(B)** AgCN

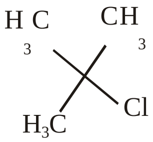
(C) HCN **(D)** NH_4CN

8. Which one of the following compounds most readily undergoes substitution by S_N2 mechanism ?

(A) 

(B) 

(C) 

(D) 

9. Sec. Butyl chloride undergo alkaline hydrolysis in the polar solvent by

(A) S_{N^2} **(B)** S_{N^1}

(C) S_{N^1} and S_{N^2} **(D)** none of these

10. The products of reaction of alcoholic silver nitrite with ethyl bromide are

(A) Ethane **(B)** Ethene

(C) Ethyl alcohol **(D)** Nitro ethane

11. The reaction ,$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$ obeys the mechanism

(A) S_{N^1} **(B)** S_{N^2}

(C) E_1 **(D)** E_2

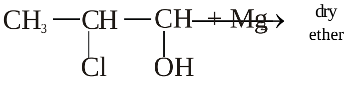
12. Ethylidene chloride can be prepared by the reaction of HCl and

(A) Ethane **(B)** Ethylene

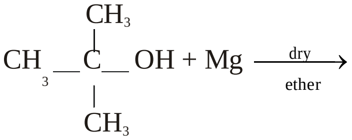
(C) Acetylene **(D)** Ethylene glycol

13. Grignard reagent can be prepared by

(A) $CH_3—CH_2—Cl + Mg \xrightarrow[ether]{dry}$

(B) 

$CH_3—\underset{Cl}{CH}—\underset{OH}{CH} + Mg \rightarrow$ dry ether

(C) 

$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—OH + Mg \xrightarrow[ether]{dry}$

(D) All of them

14. Most stable carbocation formed from $(CH_3)_3C–Br$, $(C_6H_5)_3CBr$, $(C_6H_5)_2CHBr$ and $C_6H_5CH_2Br$ would be

(A) $C_6H_5\overset{\oplus}{C}H_2$ **(B)** $(CH_3)_3\overset{\oplus}{C}$

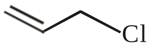
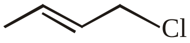
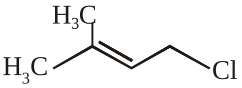
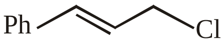
(C) $(C_6H_5)_3\overset{\oplus}{C}$ **(D)** $(C_6H_5)_2\overset{\oplus}{C}H$

Exercise # 3

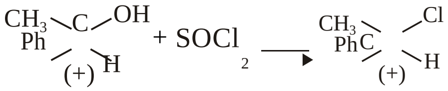
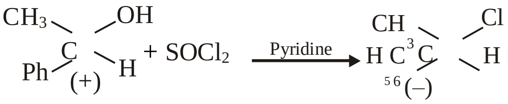
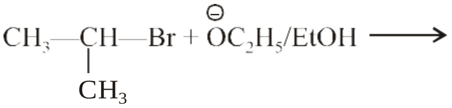
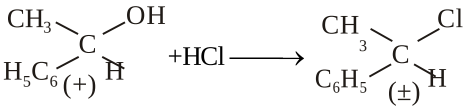
PART - 1

MATRIX MATCH COLUMN

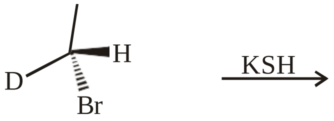
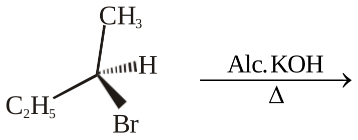
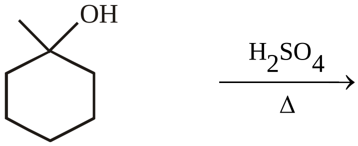
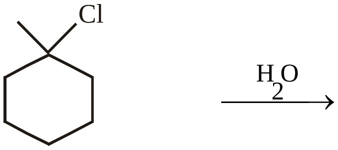
1. Match the column I with column II.

Column-I (Substrate)	**Column-II** (Relative rate of solvolysis in 50% aqueous ethanol at 45°C)
(A) 	**(p)** 7700
(B) 	**(q)** 1
(C) 	**(r)** 91
(D) 	**(s)** 1,30,000

2. Match the column I with column II.

Column-I (reaction)	**Column-II (Mechanism)**
(A) 	**(p)** S_N1
(B) 	**(q)** S_N2
(C)  $CH_3-\underset{\underset{CH_3}{\mid}}{CH}-Br + \overset{\ominus}{O}C_2H_5/EtOH \longrightarrow$	**(r)** S_Ni
(D) 	**(s)** E_2

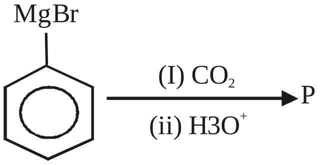
3. Match the column I and II.

Column I Reaction	**Column II** Type of reaction
(A) 	**(p)** S_N1
(B) 	**(q)** S_N2
(C) 	**(r)** E1
(D) 	**(s)** E2

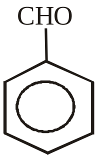
Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

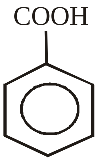
1. An organic compound A (C_4H_9Cl) on reactiion with Na/diethly gives a hydrocarbon which on monochlorination gives only one chlora derivative, then A is **[CBSE AIPMT 2001]**
(A) t-butyl chloride **(B)** s-butyl chloride
(C) iso-butyl chioride **(D)** n-butyl chloride

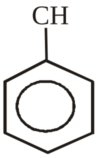
2. Reactivity order of halides for dehydrohalogenation is **[CBSE AIPMT 2002]**
(A) R—F > R—CI > R—Br > R—I
(B) R—I >R—Br > R—Cl>R—F
(C) R—I >RCI>R—Br>R—F
(D) R—F > R—I > R—Br > R—CI

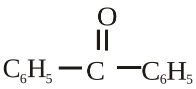
3. 

In the above reaction product 'P' is **[CBSE AIPMT 2002]**

(A) 

(B) 

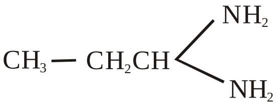
(C) 

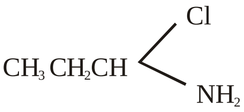
(D) 
$C_6H_5 - \overset{\overset{O}{||}}{C} - C_6H_5$

4. $CH_3CH_2Cl \xrightarrow{NaCN} X \xrightarrow{Ni/H_2} Y \xrightarrow{Aceticanhydride} Z$
In above reaction sequence, Z is **[CBSE AIPMT 2002]**
(A) $CH_3CH_2CH_2NHCOCH_3$
(B) $CH_3CH_2CH_2NH_2$
(C) $CH_3CH_2CH_2CONHCH_3$
(D) $CH_3CH_2CH_2CONHCOCH_3$

5. When phenol is treated with $CHCl_3$ and NaOH, the product formed is **[CBSE AIPMT 2000]**
(A) benzaldehyde **(B)** salicylaldehyde
(C) salicylic acid **(D)** benzoic acid

6. When $CH_3CH_2CHCl_2$ is treated with $NaNH_2$, the product formed is **[CBSE AIPMT 2002]**
(A) $CH_3 - CH = CH_2$
(B) $CH_3 - C \equiv Ch_2$

(C) 

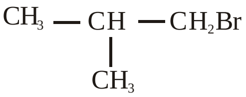
(D) 

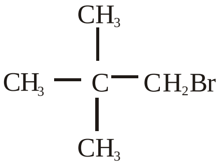
7. Which of the following is responsible for depletion of the ozone layer in the upper strate of the atmosphere? **[CBSE AIPMT 2004]**
(A) Polyhalogens **(B)** Ferrocenes
(C) Fullerenes **(D)** Freons

8. Chloropicrin is obtained by the reaction of **[CBSE AIPMT 2004]**
(A) steam on carbon tetrachloride
(B) nitric acid on chlorobenzene
(C) chlorine on picric acid
(D) nitric acid on chloroform

9. Which of the following undergoes nucleophilic substitution exclusivery by S_N1 mechanism **[CBSE AIPMT 2005]**
(A) Benzyl chloride **(B)** Ethyl chloride
(C) Chlorobenzene **(D)** Isoproply chloride

10. In a S_N2 substitution reaction of the type **[CBSE AIPMT 2008]**
$R - Br - Cl^{-} \xrightarrow{DMF} R - Cl + Br^{-}$
Which one of the following has the highest relative rate ?
(A) $CH_3 - CH_2 - CH_2Br$

(B) 
$CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2Br$

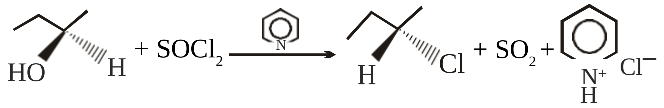
(C) 
$CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_2Br$

(D) CH_3CH_2Br

MOCK TEST

STRAIGHT OBJECTIVE TYPE

1. The reaction



proceeds by the mechanism

(A) S_{N^1} (B) S_{N^2} (C) S_Ni (D) S_{E^2}

2. The products of reaction of alcoholic silver nitrite with ethyl bromide are

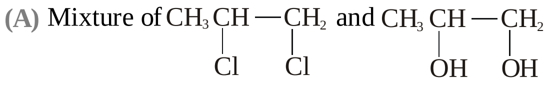
(A) Ethane (B) Ethene (C) Ethyl alcohol (D) Nitro ethane

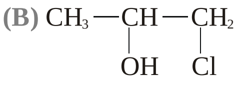
3. For the reaction

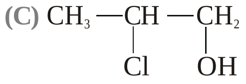
$$CH_3CH(X)CH_2CH_3 \xrightarrow{\text{alc. KOH}} \begin{cases} CH_3—CH=CH—CH_3 \\ CH_2=CH—CH_2—CH_3 \end{cases}$$

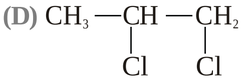
(A) $CH_3—CH=CH—CH_3$ predominates
(B) $CH_2=CH—CH_2—CH_3$ predominates
(C) Both are formed in equal amounts
(D) The product ratio depends on the halogen

4. Identify 'Z' in the following reaction series, $CH_3.CH_2CH_2Br \xrightarrow{\text{aq.NaOH}} (X) \xrightarrow[\text{Heat}]{Al_2O_3} (Y) \xrightarrow{HOCl} (Z)$:


(A) Mixture of $CH_3CH(Cl)—CH_2(Cl)$ and $CH_3CH(OH)—CH_2(OH)$


(B) $CH_3—CH(OH)—CH_2(Cl)$

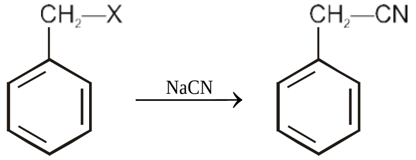

(C) $CH_3—CH(Cl)—CH_2(OH)$


(D) $CH_3—CH(Cl)—CH_2(Cl)$

5. Ethyl alcohol reacts at a faster rate with HI than with HCl in forming the corresponding ethyl halides under identical conditions mainly because -

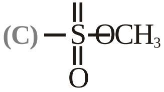
(A) HI, being a stronger acid, protonates ethyl alcohol at oxygen much better and helps substitution
(B) the bond length in HI is much shorter than that in HCl
(C) I^- is a much better leaving group
(D) I^- is a much better nucleophile than Cl^-

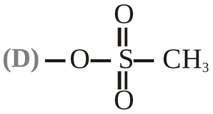
6.



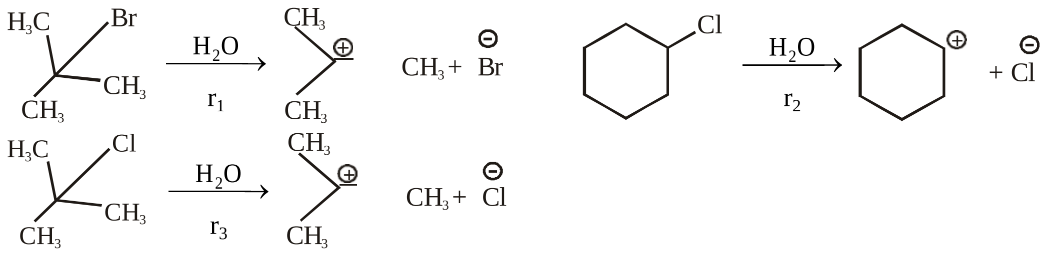
In the given reaction rate is fastest, when (X) is :

(A) –OH (B) $–NH_2$


(C) $-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-OCH_3$


(D) $-O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-CH_3$

7.



the rates r_1 , r_2 and r_3 are in the order :

(A) $r_1 > r_2 > r_3$ (B) $r_3 > r_1 > r_2$ (C) $r_1 > r_3 > r_2$ (D) $r_2 > r_1 > r_3$

CHAPTER 09

METALLURGY

All parts of the material universe are in constant motion and though some of the changes may appear to be cyclical, nothing ever exactly returns, so far as human experience extends, to precisely the same condition.

''JOSEPH HENRY''

INTRODUCTION

The branch of chemistry which deals with the method of extraction of metals from their ores. A few elements like carbon, sulphur, gold and noble gases, occur in free state while others in combined forms in the earth's crust. The extraction and isolation of an element from its combined form involves various principles of chemistry. A particular element may occur in a variety of compounds. The process of metallurgy and isolation should be such that it is chemically feasible and commericially viable. Still, some general principles are common to all the extraction processes of metals. For obtaining a particular metal, first we look for minerals which are naturally occurring chemical substances in the earth's crust obtainable by mining. Out of many minerals in which a metal may be found, only a few are viable to be used as sources of that metal. Such minerals are known as ores.

Rarely, an ore contains only a desired substance. It is usually contaminated with earthly or undesired materials known as gangue. The extractin and isolation of metals from ores involve the following major steps:

- Concentration of the ore,
- Isolation of the metal from its concentrated ore, and
- Purification of the metal.

  The entire scientific and technological process used for isolation of the metal from its ores is known as metallurgy.

Advantages of Roasting

- Excess of sulphur is removed as volatile oxide.

  $$S + \underset{\text{(air)}}{O_2} \rightarrow SO_2 \uparrow$$

- The metal sulphide is converted into metal oxide.
- Impurities of arsenic and antimony are removed as their volatile oxides.

  $Sb_4 + 3O_2 \rightarrow 2Sb_2O_3$

  $As_4 + 3O_2 \rightarrow 2As_2O_3$

(III) Reduction of Ore to the Metal

The calcined or roasted ore is then reduced to the metallic state in either of the following ways.

(A) Reduction by Carbon (Smelting) : (This is common method of reduction)

"Reduction of the oxide with carbon at high temperature is known as smelting".

The oxides of less electropositive metals like Pb, Zn, Fe, Sn, Cu etc. are reduced by strongly heating them with coal or coke, in the blast furnace.

Slag : Fusible metarial during reduction process.

Slag : Gangue + substance (for remove gangue)

Flux : Substance used to convert non fusible impurities into fusible one.

ETD OS KEY POINTS

Three types of flux :

(a) **Acidic Flux :** Substance used to remove basic impurities (metal oxide)

For example $\underset{\text{(basic impurity)}}{CaO} + \underset{\text{(acidic flux)}}{SiO_2} \rightarrow \underset{\text{(Slag)}}{CaSiO_3}$

Acidic flux are non metal oxide (SiO_2, P_2O_5 etc.)

(b) **Basic flux :** Substance used to remove acidic impurities (non metal oxide)

From example $\underset{\text{(basic flux)}}{\underset{\downarrow}{CaO}} + \underset{\text{(acidic impurities)}}{\underset{\downarrow}{SiO_2}} \longrightarrow \underset{\text{Slag}}{\underset{\downarrow}{CaSiO_3}}$

Basic flux are metal oxide. (CaO, MgO, etc.)

(c) **Neutral flux :** Substance used in electrolytic reduction to decrease the fusion temperature and to increase the conductivity of the solution by providing free ions.

For example $(\underset{\text{Cryolite}}{Na_3AlF_6} + \underset{\text{Flourspar}}{CaF_2})$, $CaCl_2$ etc.

Smelting :

- Concentrate ore (ore + gangue) + RA (carbon) + Flux (RA ⇒ Reducing agent)

  $$\downarrow$$

  Metal + Slag + gases

- $$\left.\begin{matrix} Cr_2O_3 \\ Mn_3O_4 \\ MnO_2 \end{matrix}\right\} \longrightarrow \text{Carbon is not used for reduction}$$

- Coke is not used for reduction of s-block oxide Al_2O_3 (due to formation of metal carbides)

  $CaO + 2C \longrightarrow CaC_2 + CO$

Mettallurgy at a Glance

FLOW SHEET FOR THE EXTRACTION OF ALUMINIUM

Aluminium ore, $Al_2O_3 \cdot 2H_2O$ (Bauxite)

↓

REFINING OF BAUXITE

(a) Baeyer's process :

$$\text{Bauxite ore} \xrightarrow{\text{Roasted}} \text{as to convert FeO into } Fe_2O_3$$

$$\underset{\text{ore}}{\text{Roasted}} + \underset{\text{Solution}}{NaOH} \xrightarrow[80\text{ atm.}]{150°C} NaAlO_2 \xrightarrow[\text{in presence of little } Al(OH)_3]{\text{Hydrolysis}} \underset{\text{ppt.}}{Al(OH)_3} + NaOH$$

(b) Hall's Process :

$$\underset{\text{ore}}{\text{Bauxite}} + Na_2CO_3 \xrightarrow{\text{Fused}} NaAlO_2$$

↓ extracted with water

Solution

↓ warmed 50°–60°C

CO_2 is circulated

↓

$\underset{\text{ppt.}}{Al(OH)_3} + Na_2CO_3$

(c) Serpeck's process :

$$\text{Bauxite ore} + \underset{\text{nitrogen}}{\text{Coke}} \xrightarrow{1800°C} AlN \xrightarrow{H_2O} \underset{\text{ppt.}}{Al(OH)_3} + \underset{\text{by product}}{NH_3}$$

↓

CALCINATION

$$Al(OH)_3 \xrightarrow{1500°C} \underset{\text{Anhydrous alumina}}{Al_2O_3}$$

↓

ELECTROLYTIC REDUCTION

Electrolyte Al_2O_3 dissolved in Na_3AlF_6 and CaF_2

Cathode—Carbon lining **Anode**—Graphite rods

$$Al_2O_3 \xrightarrow[950°C]{\text{Electrolysis}} \underset{99.8\%\text{ pure}}{Al} + O_2$$

↓

ELECTROLYTIC REFINING

(Hoope's process)

↓

Pure Al (99.98% pure)

SOLVED EXAMPLE

Ex. 1 Using data given below, predict whether the reduction of MgO with C is spontaneous or not at 1500°C.

$$2\,C + O_2 \longrightarrow 2\,CO \qquad \Delta G_o \approx -530\ kJ$$

$$2\,MgO \longrightarrow 2\,Mg + O_2 \qquad \Delta G^o \approx +730\ kJ$$

Sol. The positive value of ΔG^o indicates that the reduction of MgO with C dose not occur to a significant extent at 1500°C

$$2\,C + O_2 \longrightarrow 2\,CO \qquad \Delta G_o \approx -530\ kJ$$

$$2\,MgO \longrightarrow 2\,Mg + O_2 \qquad \Delta G^o \approx +730\ kJ$$

$$2\,MgO + 2C \longrightarrow 2Mg + 2CO$$

or $MgO + C \longrightarrow Mg + CO \qquad \Delta G^o$ positive value.

Ex. 2 Sea water $\xrightarrow{(A)} Mg(OH)_2 \xrightarrow{(B)} Mg\,Cl_2.\,6H_2O \xrightarrow{(C)} MgCl_2 \xrightarrow{(D)} Mg + Cl\uparrow_2$

Identify the reagents and processes (A) to (D) and give the name of this process.

Sol. $MgCl_2$(from sea water) + $Ca(OH)_2$ (A) $\rightarrow Mg(OH)_2\downarrow + CaCl_2$; $Mg(OH)_2 + 2HCl$ (B) $\rightarrow MgCl_2(aq.) + 2H_2O$

Crystallisation of $MgCl_2(aq)$ yields $MgCl_2.6H_2O$

$$MgCl_2\,6H_2O \xrightarrow[\text{Dry HCl}]{\text{Calcination (C)}} MgCl_2 + 6H_2O$$

$$MgCl_2(\ell) \xrightarrow{\text{Electrolysis is (D)}} \underset{\substack{\downarrow +2e^- \\ Mg \\ \text{(cathode)}}}{Mg^{2+}} + \underset{\substack{\downarrow Cl_2 \\ Cl_2 \\ \text{(anode)}}}{2Cl^-}$$

Name of the process is Dow's process.

Ex. 3 Convert magnesite into anhydrous $MgCl_2$.

Sol. $Mg\,CO_3 \xrightarrow{\Delta} MgO + CO_2$.

$$MgO + C + Cl_2 \longrightarrow MgCl_2 + CO$$

Ex. 4 At a site, low grade copper ores are available and zinc and iron scraps are also available. Which of the two scraps would be more suitable for reducing the leached copper ore and why?

Sol. Since zinc lies above iron in electrochemical series, it is more reactive than iron. As a result, if zinc scraps are used the reduction will be faster. However, zinc is a costlier metal than iron. Therefore, it will be advisable and advantageous to use iron scraps.

Ex. 5 A metal is extracted from its sulphide ore and the process of extraction involves the following steps.

Metal sulphide $\xrightarrow{(A)}$ Concentrated ore $\xrightarrow{(B)}$ Matte $\xrightarrow{(C)}$ Impure metal $\xrightarrow{(D)}$ Pure metal

Identify the steps (A), (B), (C) and (D).

Sol. (A) Froth floatation process. Sulphide ores are concentrated by froth-floatation process.

(B) Roasting. Metal sulphides are roasted to convert into metal oxide and to remove impurities.

In roasting ; $2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$.

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2.$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2.$$

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

(C) Bessemerisation / self reduction. Reduction of metal oxide by its sulphide takes place in Bessemer converter.

In Bessemerisation ; $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$ (self - reduction)

(D) Electro-refining. Pure metal is obtained at cathode.

$$M^{n+} + n\,e^- \longrightarrow m$$

Ex. 6 Write chemical equations for metallurgical processes to represent :

(i) roasting of galena (PbS) in limited supply of air at moderate temperature.

(ii) reduction of Cu_2O using coke as a reducing agent.

(iii) deposition of pure silver from an aqueous solution of Ag^+.

Sol. (i) $2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$

$$PbS + 2O_2 \longrightarrow PbSO_4$$

(ii) $Cu_2O + C \longrightarrow 2Cu + CO$

(iii) $Ag^+ + e^- \xrightarrow{\text{Electrolysis}} Ag\downarrow$ (at cathode)

Ex. 7 Which is not the correct process-mineral matching in metallurgical extraction.

(A) Leaching : silver
(B) Zone refining : lead.
(C) Liquation : tin
(D) Van Arkel : Zr

Sol. Lead is purified by Electro-refining. Zone refining is used for the purification of Si and Ge.

Therefore, (B) option is correct.

Exercise # 1 SINGLE OBJECTIVE NEET LEVEL

1. The most abundant element on earth crust is
(A) Hydrogen **(B)** Oxygen
(C) Silicon **(D)** Carbon

2. Naturally occurring substances from which a metal can be profitably (or economically) extracted are called
(A) Minerals **(B)** Ores
(C) Gangue **(D)** Salts

3. Titanium containing mineral found in our country is
(A) Bauxite **(B)** Dolomite
(C) Chalcopyrites **(D)** Elmanite

4. Silicon is main constituent of
(A) Alloys **(B)** Rocks
(C) Animals **(D)** Vegetables

5. Which of ore is metalloid
(A) As **(B)** Na
(C) Au **(D)** Fe

6. A mineral is called an ore if
(A) Metal present in mineral is precious
(B) Metal can be extracted from it
(C) Metal can be extracted profitably from it
(D) Metal cannot be extracted from it

7. The highest quantity present in the atmosphere is of
(A) Oxygen **(B)** Hydrogen
(C) Nitrogen **(D)** Ozone

8. Which of the following statement is correct
(A) Bauxite is an ore of aluminium
(B) Magnetite is an ore of manganese
(C) Haematite is an ore of mercury
(D) Pyrites is an ore of phosphorus

9. Carnellite is a mineral of
(A) Ca **(B)** Na
(C) Mg **(D)** Zn

10. The salt which is least likely to be found in minerals is
(A) Chloride **(B)** Sulphate
(C) Sulphide **(D)** Nitrate

11. Metal which can be extracted from all the three dolomite, magnesite and carnallite is
(A) Na **(B)** K
(C) Mg **(D)** Ca

12. Cinnabar is an ore of
(A) Hg **(B)** Cu
(C) Pb **(D)** Zn

13. Metallurgy is the process of
(A) Concentrating the ore
(B) Roasting the ore
(C) Extracting the metal from the ore
(D) Adding carbon to the ore in blast furnace

14. What is believed to be the second most common element in the universe
(A) Helium **(B)** Hydrogen
(C) Nitrogen **(D)** Silicon

15. Which of the following substances consists of only one element
(A) Marble **(B)** Sand
(C) Diamond **(D)** Glass

16. Which of the following minerals is not an ore of aluminum
(A) Bauxite **(B)** Gypsum
(C) Cryolite **(D)** Corundum

17. An example of halide ore is
(A) Galena **(B)** Bauxite
(C) Cinnabar **(D)** Cryolite

18. Which of the following is not an ore
(A) Bauxite **(B)** Malachite
(C) Zinc blende **(D)** Pig iron

19. "Chile saltpetre" is an ore of
(A) Iodine **(B)** Sodium
(C) Bromine **(D)** Magnesium

20. Sulphide ores are generally concentrated by
(A) Froth floatation process
(B) Magnetic separation
(C) Gravity separation
(D) By hand picking

21. Froth floatation process is used for the concentration of
(A) Oxide ores **(B)** Sulphide ores
(C) Chloride ores **(D)** Amalgams

22. A process used for the concentration of ore is
(A) Froth floatation **(B)** Roasting
(C) Electrolysis **(D)** Bessemerization

Exercise # 2

SINGLE OBJECTIVE

AIIMS LEVEL

1. Bauxite is leached with :

(A) KCl (B) NaCN
(C) NaOH (D) Na_2SO_4

2. Froth floatation process for the concentration of sulphide ores is an illustration of the practical application of:

(A) adsorption (B) absorption
(C) sedimentation (D) coagulation

3. Which one of the following is not a method of concentration of ore ?

(A) electromagnetic separation
(B) smelting
(C) gravity separation
(D) froth floatation process

4. The formula of carnallite is :

(A) $LiAl(Si_2O_5)_2$ (B) $KCl.MgCl_2.6H_2O$
(C) $K_2O.Al_2O_3.6SiO_2$ (D) $KCl.MgCl_2.2H_2O$

5. Dolomite is mineral whose formula is :

(A) $CaMg(CO_3)_2$ (B) $MgCO_3$
(C) $CaCO_3.MgCO_3$ (D) (A) & (C) both

6. Magnetic separation process may be used for the concentration of :

(A) chalcopyrite (B) bauxite
(C) haematite (D) calamine

7. The metal which mainly occurs as oxide ore in nature is :

(A) gold (B) lead
(C) aluminium (D) magnesium

8. The reason, for floating of ore particles in concentration by froth floatation process is that :

(A) they are light
(B) they are insoluble
(C) they are charged
(D) they are hydrophobic

9. Choose the correct option using the code regarding roasting process.

(I) It is the process of heating the ore in air in a reverberatory furnace to obtain the oxide.
(II) It is an exothermic process.
(III) It is used for the concentration of sulphide ore.
(IV) It removes easily oxidisable volatile impurities present in the concentrated ore.

(A) I, II and III (B) I, II and IV
(C) I, III and IV (D) I, II, III and IV

10. The slag consists of molten impurities, generally, in the form of:

(A) metal carbonate (B) metal silicate
(C) metal oxide (D) metal nitrate

11. The process of the isolation of a metal by dissolving the ore in a suitable chemical reagent followed by precipitation of the metal by a more electropositive metal is called :

(A) hydrometallurgy (B) electrometallurgy
(C) zone refining (D) electro-refining

12. In the metallurgy of iron, the upper layer obtained in the bottom of blast furnace mainly contains :

(A) $CaSiO_3$ (B) spongy iron
(C) Fe_2O_3 (D) $FeSiO_3$

13. Ellingham diagram represents:

(A) change of ΔG with temperature.
(B) change of ΔH with temperature.
(C) change of ΔG with pressure.
(D) change of $(\Delta G - T\Delta S)$ with temperature.

14. A sulphide ore like ZnS is first roasted into its oxide prior to reduction by carbon because :

(A) a sulphide ore cannot be reduced to metal at all
(B) no reducing agent is found suitable for reducing a sulphide ore.
(C) the Gibb's free energy of formation of most sulphides are greater than that for CS_2.
(D) a metal oxide is generally less stable than the metal sulphide.

15. Which of the following statements is correct regarding the slag obtained during the extraction of a metal like copper or iron ?

(A) The slag is lighter and has lower melting point than the metal
(B) The slag is heavier and has lower melting point than the metal
(C) The slag is lighter and has higher melting point than the metal
(D) The slag is heavier and has higher melting point than the metal

16. Which one of the following reactions occurs during smelting in the reduction zone at lower temperature (in iron metallurgy)?

(A) $CaO + SiO_2 \longrightarrow CaSiO_3$ (slag)
(B) $Fe_2O_3 + 3C \longrightarrow 2Fe + CO$

(C) $3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$
(D) $CO_2 + C \longrightarrow 2CO$

Exercise # 3 PART - 1 MATRIX MATCHCOLUMN

1.

Column-I (Ore)	Column-II
(A) Iron	(p) Carbon reduction method
(B) Lead	(q) Self reduction
(C) Copper	(r) Thermite process
(D) Chromium	(s) Hydrometallurgical process

2. Match the ores given in column-I with typ(s) of processes given in column-II.

Column – I	Column – II
(A) Haematite	(p) Slag formation during roasting/smelting and bessemerisation.
(B) Copper pyrites	(q) Reduction by carbon monoxide / carbon at different temperatures.
(C) Carnallite	(r) Electrolytic reduction.
(D) Bauxite	(s) Calcination.

3. Match the type of processes involved in the extraction of metal given in column-I with the given ores in column-II.

Column – I	Column – II
(A) Slag formation	(p) Extraction of copper from copper pyrites.
(B) Froth – floatation	(q) Extraction of aluminium form bauxite.
(C) Leaching	(r) Extraction of iron from haematite.
(D) Roasting	(s) Extraction of tin from cassiterite
	(t) Extraction of lead from galena.

4. Match the name of the processes given in column-I with type(s) of metallurgical methods given in column-II.

Column – I	Column – II
(A) Hall – Heroult process	(p) Molten $Al_2O_3 + Na_3AlF_6$ electrolysis.
(B) Dow's sea water process	(q) Molten $MgCl_2 + CaCl_2 + NaCl$ electrolysis.
(C) Hoop's process	(r) Molten impure aluminium + fluorides of Na^+, Ba^{2+} and Al^{3+} electrolysis.
(D) Mac-Arthur Forrest process	(s) Complex formation and displacement method.

Exercise # 4

PART - 1

PREVIOUS YEAR (NEET/AIPMT)

1. The method of zone refining of metals is based on the principle of **[CBSE AlPMT 2003]**

(A) Greater noble character of the solid metal than that of the impurity

(B) Greater solubility of the impurity in the molten state than in the solid

(C) Greater mobility of the pure metal than that of impurity

(D) Higher melting point of the impurity than that of the pure metal

2. A solid compount X on heating gives CO_2 gas and a residue mixed with water forms Y. On passing an excess of CO_2 through Y in water, a clear solution Z is obtained. On boiling Z, compound X is reformed. The compound X is **[CBSE AlPMT 2004]**

(A) $Ca(HCO_3)_2$ **(B)** $CaCO_3$

(C) Na_2CO_3 **(D)** $K2CO_3$

3. Which of the following statements, about the advantage of roasting of sulphide ore before reduction is not true? **[CBSE AlPMT 2007]**

(A) Carbon and hydrogen are suitable reducing agents for metal sulphides

(B) The $\Delta_f G^0$ of the sulphide is greater than those for CS_2 and H_2S

(C) The $\Delta_f G^0$ is negative for roasting of sulphide ore to oxide

(D) Roasting of the sulphide to the oxide is thermodynamically feasible

4. Sulphide ores of metals are usually concentrated by froth floatation process. Which one of the following sulphide ores offers an exception and is concentrated by chemical leaching **[CBSE AlPMT 2007]**

(A) Argentite **(B)** Galena

(C) Copper pyrite **(D)** Sphalerite

5. Which of the following pairs of metals is purified by van Arkel method ? **[CBSE AlPMT 2011]**

(A) Zr and Ti **(B)** Ag and Au

(C) Ag and Au **(D)** Ni and Fe

6. Which of the following elements is present as the impurity to the maximum extent in the pig iron? **[CBSE AlPMT 2011]**

(A) Carbon **(B)** Silion

(C) Phosphorus **(D)** Manganese

7. In the extraction of copper from its sulphide ore, the metal is finally obtained by the reduction of cuprus oxide with **[CBSE AlPMT 2012]**

(A) copper (I) sulphide (Cu_2S)

(B) Sulphur dioxide

(C) Iron sulphide(FeS)

(D) Carbon Monoxide (CO)

8. Which one of the following is a mineral of iron? **[CBSE AlPMT 2012]**

(A) Malachite **(B)** Cassiterite

(C) Pyrolusite **(D)** Magnetite

9. Aluminium is extracted from alumina (Al_2O_3) by electrolysis of a molten mixture of **[CBSE AlPMT 2012]**

(A) $Al^2O^3+HF+NaAIF_4$

(B) $Al_2O_3+CaF_2+NaAIF_4$

(C) $Al_2O_3+Na_3AIF_6+CaF_2$ d

(D) $Al_2O_3+KF+Na_3AIF_6$

10. Roasting of sulphides gives the gas X as a by-product. This is a 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 acideic acts as a reducing agent and its acid has never been insolated. The gas X is **[NEET 2013]**

(A) H_2S **(B)** SO_2

(C) CO_2 **(D)** SO_3

11. In the extraction of copper from its sulphide ore, the metal finally obtained by the reduction of cuprous oxide with **[CBSE AlPMT 2015]**

(A) iron (II) sulphide **(B)** carbon monoxide

(C) copper (I) sulphide **(D)** sulphur dioxide

12. Match items of Column I with the items of Column II and assign the correct code. **[NEET 2016, Phase I]**

Column I	**Column II**
(A) Cyanide process	**(1)** Ultrapure Ge
(B) Froth floatation process	**(2)** Dressing of ZnS
(C) Electrolytic reduction	**(3)** Extraction of Al
(D) Zone refining	**(4)** Extraction of Au
	(5) Purification of Ni

Codes

	a	**b**	**c**	**d**
(A)	2	3	1	5
(B)	1	2	3	4
(C)	3	4	5	1
(D)	4	2	3	1

13. Extraction of gold and silver involves leaching with CN^- ion. Silver is later recovered by **[NEET 2017]**

(A) liquation **(B)** distillation

(C) zone refining **(D)** displacement with Zn

MOCK TEST

STRAIGHT OBJECTIVE TYPE

1. Match the column (I) and (II) and select the correct answer using the codes given below.

Column - I	**Column - II**
(A) Argentite	**(1)** Halide ore
(B) Cuprite	**(2)** Carbonate one
(C) Siderite	**(3)** Oxide ore
(D) Carnallite	**(4)** Sulphide ore

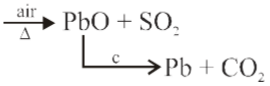
Codes :–

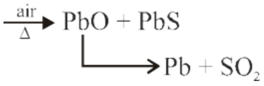
	a	b	c	d
(A)	4	3	2	1
(B)	1	2	3	4
(C)	2	3	4	1
(D)	3	4	1	2

2. NaCN is sometimes added in the froth floatation process as a depressant when mineral contains ZnS and PbS because,

(A) $Pb(CN)_2$ is precipitated while there is no effect on ZnS.
(B) ZnS forms soluble complex $Na_2[Sn(CN)_4]$ while PbS forms froth
(C) PbS forms soluble complex $Na_2[Pb(CN)_4]$ while ZnS forms froth.
(D) silicious impurities settle down on the bottom.

3. Main source of lead is galena (PbS). It is converted to Pb by :

(A) : PbS 

(B) : PbS 

Self-reduction process is :

(A) A　**(B)** B　**(C)** both　**(D)** none

4. The chemical composition of "slag" formed during the smelting process in the extraction of copper is :

(A) $Cu_2O + FeS$　**(B)** $FeSiO_3$　**(C)** $CuFS_2$　**(D)** $Cu_2S + FeO$

5. Which of the following statement is incorrect about the extractive metallurgy of copper?

(A) Matte chiefly consists of cuprous sulphide and some ferrous sulphide
(B) Most of the impurity of iron sulphide is removed as fusible slag during roasting.
(C) The copper pyrites is concentrated by froth floatation process.
(D) The copper obtained from Bessemer converter is called as blister copper

6. Roasted silver ore + $CN^-_{(aq)} + O_2 \rightarrow [X]_{(aq)} + OH^-_{(aq)}$; $[X]_{(aq)} + Zn \rightarrow [Y]_{(aq)} + Ag\downarrow$

The [X] and [Y] are respectively :

(A) $[Ag(CN)_2]^-$, $[Zn(CN)_6]^{-4}$　**(B)** AgCN, $[Zn(CN)_4]^{-2}$
(C) $[Ag(CN)_4]^{-3}$, $[Zn(CN)_4]^{-2}$　**(D)** $[Ag(CN)_2]^-$, $[Zn(CN)_4]^{-2}$

7. Match column (I) with column (II) and select the correct answer using codes given below in the lists.

Column - I	**Column - II**
(i) Cyanide process	**(A)** Extraction of Al
(ii) Self reduction	**(B)** Extraction of Ag
(iii) Electrolytic reduction	**(C)** Extraction of Cu
(iv) Carbon reduction	**(D)** Extraction of Sn

(A) (i) - (b), (ii) - (c), (iii) - (a), (iv) - (d)　**(B)** (i) - (b), (ii) - (d), (iii) - (a), (iv) - (c)
(C) (i) - (d), (ii) - (a), (iii) - (c), (iv) - (b)　**(D)** (i) - (c), (b) - (ii) - (d), (iv) - (a)

CHAPTER 04

ELECTRO CHEMISTRY

The removal of an electron from the surface of an atom - that is, the ionization of the atom - means a fundamental structural change in its surface layer.

''JOHANNES STARK''

INTRODUCTION

Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations. The subject is of importance both for theoritical and practical considerations. A large number of metals, sodium hydroxide, chlorine, fluorine and many other chemicals are produced by electrochemical methods. Batteris and fuel cells convert chemical energy into electrical energy and are used on a large scale in various instruments and devices. The reactions carried out electrochemically can be energy efficient and less polluting. Therefore, study of electrochemistry is important for creating new technologies that are ecofriendly. The transmission of sensory signals through cells to brain and vice versa and communication between the cells are known to have electrochemical origin. Electrochemistry, is therefore, a very vast and interdisciplinary subject. In this Unit, we will cover only some of its important elementary aspects.

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 following(I).

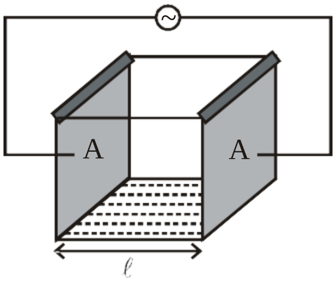
$R = \frac{V}{I}$ • R is expressed in ohms.

(b) **Conductance (C) :** The conductance of a conductor is equal to reciprocal of resistance

$C = \frac{1}{R}$ • C is expressed in mho or Siemens(S) or Ω^{-1}

(c) **Specific resistance /Resistivity(□) :** The resistance (R) of a conductor of uniform cross section is directly proportional to its length(ℓ) and inversely proportional to its area of cross section (A)

$R \propto \frac{\ell}{A}$; $R = \rho \frac{\ell}{A}$



where ρ is a constant and called resistivity or specific resistance.

When $\ell = 1$, $A = 1$, then $\rho = R$

Thus the specific resistance may be defined as the resistance of a conductor of unit length and unit area of cross section.

or

Therefore resistance offered by 1 cm^3 elecrolytic solution is known as resistivity.

- Unit of $\rho \rightarrow$ ohm .cm elecrolyte

(d) **Specific conductance / Conductivity(□) :**

It is defined as the reciprocal of specific resistance

$\kappa = \frac{1}{\rho}$

The above definitions apply to metallic conductors and electrolytes.

- In the case of solution of electrolytes, the resistance offered by the solution to the flow of current is –
- Directly proportional to the distance between the electrodes

  $R \propto \ell$
- Inversely proportional to the area of cross section of the electrodes

$R \propto \frac{1}{A}$ $R = \rho \frac{\ell}{A}$

The conductance $C = \frac{A}{\rho\ell}$

$\because \frac{1}{\rho} = \kappa$ so $\kappa = \frac{C\ell}{A}$

If $\ell = 1$ cm and $A = 1$ cm^2 then

$\kappa = C$

Hence specific conductivity of a solution is defined as the conductance of one centimeter cube of the solution of the electrolyte.

Ex. A current of 2 A was passed for 1.5 hours through a solution of $CuSO_4$ when 1.6 g of copper was deposited. Calculate percentage current efficiency.

Sol. Amount of current required to deposit 1 mole Cu (63.5 g) = 2 × 96500 C

Current required to deposit 1.6g of copper $= \frac{2 \times 96500}{63.5} = 4862.99$ C

Current actually passed through = 2 × 1.5 × 60 × 60 = 10800

Current efficiency $= \frac{4862.99}{10800} \times 100 = 45.03\%$

ED OS KEY POINTS

(i) The electric current consists of flow of electrons and the current enters the electrolyte through anode and leaves through the cathode and electrons are being forced into the cell.

(ii) During the electrolysis of aqueous electrolytic solutions, redox processes become complicated because of the formation of ions from water which also take part in the electrolysis.

(iii) Cations arranged in the series of standard reductin electrode potentials in the order Mn^{2+}, Zn^{2+}, Cr^{3+}, Fe^{2+}, Ni^{2+}, Pb^{2+} and H^+ are reduced along with the water molecules during the electrolysis of solutions.

(iv) Anions of hydracids and those of salts of these acids (F^-, Cl^-, Br^-, I^-, S^{2-}, CN^- etc.) hold their electrons less tightly than does the OH^- ion from water. This is the reason why during the electrolysis of aqueous solutions of salts of hydracids, the acid anions are oxidised.

(v) Anions of oxyacids sucha s NO_3^-, SO_3^{2-}, PO_4^{3-} etc. hold their electrons more tightly than the OH^- ions. Hence, during the electrolysis of aqueous solutions of salts of oxyacids, water molecule is oxidised. [$2H_2O - 4e^- \rightarrow O_2 + 4H^+$], while the salt ions (anions) remain unchanged.

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 cell anode and cathode are same so $E^0_{cell} = 0$.

eg. Pt, $H_2(g)$ (P_1 atm) | $H^+(C_1)$ || $H^+(C_2)$ | $H_2(g)$ (P_2 atm), Pt

Anode Reaction : $H_2(P_1) \longrightarrow 2H^+(C_1) + 2e^-$

Cathode Reaction : $2H^+(C_2) + 2e^- \longrightarrow H_2(P_2)$

Cell Reaction : $H_2(P_1) + 2H^+(C_2) \longrightarrow 2H^+(C_1) + H_2(P_2)$

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log\frac{[P]}{[R]}$$

So, $$E_{cell} = 0 - \frac{0.0591}{2}\log\left[\frac{C_1}{C_2}\right]^2\frac{P_2}{P_1}$$

Case 1 : If $P_1 = P_2 = 1$ atm $E_{cell} = -\frac{0.059}{2}\log\left[\frac{C_1}{C_2}\right]^2$

(10) KOHLRAUSEH'SLAW:

$$\Lambda^{\infty}_{m} (A_x B_y) = x\lambda^{\infty}_{+} + y\lambda^{\infty}_{-}$$

$$\Lambda^{\infty}_{m} (K_2 SO_4) = 2\lambda^{\infty}_{+} + \lambda^{\infty}_{-}$$

$$\Lambda^{\infty}_{m} (Na_3PO_4) = 3\lambda^{\infty}_{+} + \lambda^{\infty}_{-}$$

$$\Lambda^{\infty}_{m} [Fe_2(SO_4)_3] = 2\lambda^{\infty}_{+} + 3\lambda^{\infty}_{-}$$

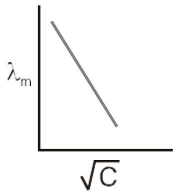
(11) FORMULA

(1) $R = \rho \times \frac{\ell}{A}$

(2) $\lambda_m = k \times \frac{1000}{M}$

(3) $\lambda_{eq.} = k \times \frac{1000}{N}$

(4) for strong electrolyte $\lambda_m = \lambda m_{\infty} - b\sqrt{C}$



12. The reduction of cations is based on the standard reduction potential provided all ons have 1 M concentration, which follows the order

Li+ < K+ < Ba+2 < Ca+2 < Na+ < Mg+2 < Al+3 < $Zn^{+2} < Fe^{+2} < Ni^{+2} < Sn^{+2} < Pb^{+2} < H^{+} < Cu^{+2} < Ag^{+} < Au^{3+}$

13. From anions the oxidation is based on standard oxidation potentials provided they are at 1 M concentration which follows the order $SO_4^{-2} < NO_3^{-} < OH^{-} < Cl^{-} < Br^{-} < I^{-}$

14. A | A^{n+} | B^{n+} | B

$$E_{cell} = E^0_{B^{n+1}/B} - E^0_{A^{n+}/A} - \frac{0.059}{n} \log \frac{[A^{n+}]}{[B^{n+}]}$$

15. For non-redox reaction EMF is not defined.

16. For a half cell of the type Cl^- (C) | AgCl | Ag, its half cell potential is equal tothe half cell potential of Ag^+ ($K_{SP}/[Cl^-]$) + Ag but the E° of the two half cells are not same.

17. Concentration cells are those whose E^{o}_{cell} is zero. They are categorized as electrode and electrolyte concentrations cells.

SOLVED EXAMPLE

Ex. 1 Which cell will measure standard electrode potential of copper electrode

(A) $Pt(s)|H_2(g, 0.1\,bar)|H^+(aq., 1\,M)||Cu^{2+}(aq, 1\,M)|Cu$

(B) $Pt(s)|H_2(g, 1\,bar)|H^+(aq., 1\,M)||Cu^{2+}(aq, 2\,M)|Cu$

(C) $Pt(s)|H_2(g, 1\,bar)|H^+(aq., 1\,M)||Cu^{2+}(aq, 1\,M)|Cu$

(D) $Pt(s)|H_2(g, 0.1\,bar)|H^+(aq., 0.1\,M)||Cu^{2+}(aq, 1\,M)|Cu$

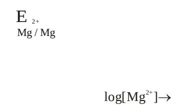
Sol. **(C)** Standard electrode potential of copper electrode can be calculated by constructing a concentration cell composed of two half cell reactions in which concentration of species on left hand and right hand side are unity. In such case cell potential is equal to standard electrode potential.

$$\underbrace{Pt(s)\,|\,H_2(g,1bar)\,||\,H^+(aq,1M)}_{\text{Oxidation half cellreaction}}\,||\,\underbrace{Cu^{2+}(aq,\,1M)\,|Cu}_{\text{Re duction half cellreaction}}$$

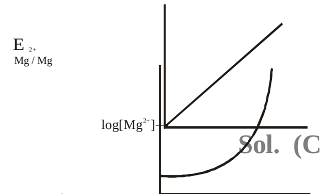
Ex. 2 Electrode potential for Mg electrode varies according to the equation

$$E_{Mg^{2+}/Mg} = E^{\ominus}_{Mg^{2+}/Mg} - \frac{0.059}{2}\log\frac{1}{[Mg^{2+}]}$$. The graph of $E_{Mg^{2+}/Mg}$ vs $\log[Mg^{2+}]$ is

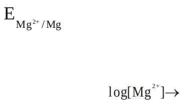
(A)



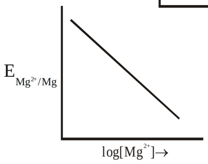
(B)



(C)



(D)



Sol. **(B)** Electrode potential for Mg electrode varies according to the equation

$$E_{Mg^{2+}/Mg} = E^{\circ}_{Mg^{2+}/Mg} - \frac{0.059}{2}\log\frac{1}{[Mg^{2+}]}$$

$$E_{Mg^{2+}/Mg} = E^{\circ}_{Mg^{2+}/Mg} + \frac{0.059}{2}\log[Mg^{2+}]$$

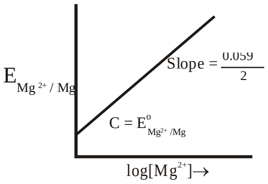
$$E_{Mg^{2+}/Mg} = \frac{0.059}{2}\log[Mg^{2+}] + E^{o}_{Mg^{2+}/Mg}$$

The equation represents equation of straight line. It can be correlated as

$$\underset{Y}{\underset{\uparrow}{E_{Mg^{2+}/Mg}}} = \underset{M}{\underset{\uparrow}{\left(\frac{0.059}{2}\right)}}\underset{X}{\underset{\uparrow}{\log[Mg^{2+}]}} + \underset{+C}{\underset{\uparrow}{E^{o}_{Mg^{2+}/Mg}}}$$

So intercept **(C)**= $E^{o}_{Mg^{2+}/Mg}$

Thus equation can be diagrammatically represented as.



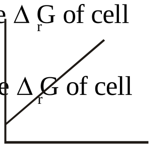
Ex. 3 Which of the following statement is correct

(A) E_{cell} and Δ_rG of cell reaction both are extensive properties

(B) E_{cell} and Δ_rG of cell reaction both are intensive properties

(C) E_{cell} is an intensive property while Δ_rG of cell reaction is an extensive property

(D) E_{cell} is an extensive property while Δ_rG of cell reaction is an intensive property



Sol. **(C)** E_{cell} is an intensive property as it does not depend upon mass of species (number of particles) but Δ_rG of the cell reaction is an extensive property because this depends upon mass of species (number of particles).

Ex. 4 Which of the following statement is not correct about an inert electrode in a cell

(A) It does not participate in the cell reaction

(B) It provides surface either for oxidation or for reduction reaction

(C) It provides surface for conduction of electrons

(D) It provides surface for redox reaction

Sol. **(D)** An inert electrode in a cell provide surface for either oxidation or for reduction reaction by conduction of electrons through its surface but does not praticipate in the cell reaction.

It does not provide surface for redox reaction.

Exercise # 1 SINGLE OBJECTIVE NEET LEVEL

1. Which of the following will not conduct electricity in aqueous solution

(A) Copper sulphate **(B)** Sugar
(C) Common salt **(D)** None of these

2. Strong electrolytes are those which

(A) Dissolve readily in water
(B) Conduct electricity
(C) Dissociate into ions at high dilution
(D) Completely dissociate into ions at all dilutions

3. In aqueous solution, strong electrolytes

(A) Are partially ionized
(B) Do not ionise
(C) Ionise almost completely
(D) Form polymers

4. An electrolyte

(A) Forms complex ions in solution
(B) Gives ions only when electricity is passed
(C) Possesses ions even in solid state
(D) Gives ions only when dissolved in water

5. Electrolytes when dissolved in water dissociates into ions because

(A) They are unstable
(B) The water dissolves it
(C) The force of repulsion increases
(D) The forces of electrostatic attraction are broken down by water

6. Electrolyte can conduct electricity because

(A) Their molecules contain unpaired electrons, which are mobile
(B) Their molecules contain loosely held electrons which get free under the influence of voltage
(C) The molecules break up into ions when a voltage is applied
(D) The molecules are broken up into ions when the electrolyte is fused or is dissolved in the solvent

7. Which one of the following metals could not be obtained on electrolysis of aqueous solution of its salts

(A) Ag **(B)** Mg **(C)** Cu **(D)** Cr

8. Which of the following aqueous solution will conduct an electric current quite well

(A) Glycerol **(B)** HCl
(C) Sugar **(D)** Pure water

9. On the electrolysis of aqueous solution of sodium sulphate, on cathode we get

(A) Na **(B)** H_2
(C) SO_2 **(D)** SO_3

10. Electrolysis involves oxidation and reduction respectively at

(A) Anode and cathode **(B)** Cathode and anode
(C) At both the electrodes **(D)** None of the above

11. Which of the following compounds will not undergo decomposition on passing electricity through aqueous solution

(A) Sugar **(B)** Sodium Chloride
(C) Sodium Bromide **(D)** Sodium Acetate

12. During the electrolysis of an electrolyte, the number of ions produced, is directly proportional to the

(A) Time consumed
(B) Electro chemical equivalent of electrolysis
(C) Quantity of electricity passed
(D) Mass of electrons

13. When the sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrodes are

Cathode	Anode
(A) Pure zinc	Pure copper
(B) Impure sample	Pure copper
(C) Impure zinc	Impure sample
(D) Pure copper	Impure sample

14. In the electrolytic cell, flow of electrons is from

(A) Cathode to anode in solution
(B) Cathode to anode through external supply
(C) Cathode to anode through internal supply
(D) Anode to cathode through internal supply

15. An electric current is passed through an aqueous solution of the following. Which one shall decompose

(A) Urea **(B)** Glucose
(C) $AgNO_3$ **(D)** Ethyl alcohol

16. Amount of electricity that can deposit 108 gm of silver from $AgNO_3$ solution is

(A) 1 ampere **(B)** 1 coulomb
(C) 1 faraday **(D)** None of the above

Exercise # 2

SINGLE OBJECTIVE

AIIMS LEVEL

1. The standard reduction potentials E° of the following systems are

System	**E° (volts)**
(i) $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	1.51
(ii) $Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	0.15
(iii) $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	1.33
(iv) $Ce^{4+} + e^- \longrightarrow Ce^{3+}$	1.61

The oxidising power of the various species decreases in the order

(A) $Ce^{4+} > Cr_2O_7^{2-} > Sn^{4+} > MnO_4^-$

(B) $Ce^{4+} > MnO_4^- > Cr_2O_7^{2-} > Sn^{4+}$

(C) $Cr_2O_7^{2-} > Sn^{4+} > Ce^{4+} > MnO_4^-$

(D) $MnO_4^- > Ce^{4+} > Sn^{4+} > Cr_2O_7^{2-}$

2. Consider the reaction : (T = 298 K)

$Cl_2(g) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq.)$

The emf of the cell, when $[Cl^-] = [Br_2] = [Br^-] = 0.01M$ and Cl_2 gas is at 1 atm pressure, will be :

(E° for the above reaction is = 0.29 volt)

(A) 0.54 volt **(B)** 0.35 volt
(C) 0.24 volt **(D)** –0.29 volt

3. $2Ce^{4+} + Co \longrightarrow 2Ce^{3+} + Co^{2+}$ $E^o_{cell} = 1.89$ V, $E^o_{Co^{2+}/Co} = -0.277$ V hence, $E^o_{Ce^{4+}/Ce^{3+}}$ is :

(A) 0.805 V **(B)** 1.62 V
(C) –0.805 V **(D)** – 1.61 V

4. Given : $E^o(Cu^{2+} | Cu) = 0.337$ V and $E^o(Sn^{2+} | Sn) = -0.136$ V. Which of the following statements is correct?

(A) Cu^{2+} ions can be reduced by $H_2(g)$

(B) Cu can be oxidized by H^+

(C) Sn^{2+} ions can be reduced by $H_2(g)$

(D) Cu can reduce Sn^{2+}

5. Red hot carbon will remove oxygen from the oxide AO and BO but not from MO, while B will remove oxygen from AO. The activity of metals A, B and M in decreasing order is

(A) A > B > M **(B)** B > A > M
(C) M > B > A **(D)** M > A > B

6. What is the emf at 25° C for the cell, $Ag \left| \begin{matrix} AgBr(s), Br^- \\ a = 0.34 \end{matrix} \right|, \left| \begin{matrix} Fe^{3+}, & Fe^{2+} \\ a = 0.1 & a = 0.02 \end{matrix} \right| Pt$

The standard reduction potentials for the half-reactions

$AgBr + e^- \rightarrow Ag + Br^-$ and $Fe^{3+} + e^- \rightarrow Fe^{2+}$ are + 0.0713 V and + 0.770 V respectively.

(A) 0.474 volt **(B)** 0.529 volt
(C) 0.356 volt **(D)** 0.713 volt

7. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$; $E^o = 1.51$ V ; $\Delta G_1^0 = -5 \times 1.51 \times F$

$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$; $E^o = 1.23$ V; $\Delta G_2^0 = -2 \times 1.23 \times F$ $E^o_{MnO_4^-|MnO_2}$ is

(A) 1.70 V **(B)** 0.91 V
(C) 1.37 V **(D)** 0.548 V

8. A hydrogen electrode placed in a buffer solution of CH_3COONa and CH_3COOH in the ratios of x : y and y : x has electrode potential values E_1 volts and E_2 volts, respectively at 25ºC. The pK_a values of acetic acid is (E_1 and E_2 are oxidation potentials)

(A) $\frac{E_1 + E_2}{0.118}$ **(B)** $\frac{E_2 - E_1}{0.118}$
(C) $-\frac{E_1 + E_2}{0.118}$ **(D)** $\frac{E_1 - E_2}{0.118}$

9. The electrode potential of electrode

M (s) ☐☐ M^{n+} (aq) (2M) + ne^-.

at 298 K is E_1. When temperature is doubled and concentration is made half, then the electrode potential becomes E_2. Which of the following represents the correct relationship between E_1 and E_2 ?

(A) $E_1 > E_2$ **(B)** $E_1 < E_2$
(C) $E_1 = E_2$ **(D)** Can't be predicted

10. During the preparation of $H_2S_2O_8$ (per disulphuric acid) O_2 gas also releases at anode as byproduct, When 9.72 L of H_2 releases at cathode and 2.35 L O_2 at anode at STP, the weight of $H_2S_2O_8$ produced in gram is

(A) 87.12 **(B)** 43.56
(C) 83.42 **(D)** 51.74

Exercise # 3 PART - 1 MATRIX MATCHCOLUMN

1. Match Matrix ($E^0_{Ag^+/Ag} = 0.8$, $K_{SP}(AgCl) = 10^{10}$).

Column – I	Column – II
(A) Pt | H_2 (0.1 bar) | H^+ (0.1 M) ‖ H^+ (1 M) | H_2 (0.01 bar) | Pt	**(p)** Concentration cell
(B) Ag | AgCl (KCl, 0.1M) ‖ Ag^+ (0.01M) | Ag	**(q)** $E_{cell} > 0$
(C) Cu | Cu^{2+} (0.1 M) ‖ Cu^{2+} (0.01 M) | Cu	**(r)** $E^o_{cell} = 0$ but cell is working.
(D) Pt | Cl_2 (1bar) | HCl (0.1 M) ‖ NaCl (0.1M) | Cl_2 | Pt (1 bar)	**(s)** non working condition

2. Match the column

Column I	Column II
(A) Zn / Zn^{+2} | | Mg^{2+} / Mg c_1 c_2 ($c_1 = c_2$)	**(p)** $E_{cell} = 0$
(B) Zn / Zn^{+2} | | Ag^+ / Ag at. equilibrium	**(q)** $E^0_{cell} = 0$
(C) Ag / Ag^+ | | Ag^+ / Ag c_1 c_2 ($c_1 = c_2$)	**(r)** $E^0_{cell} = +ve$
(D) Fe / Fe^{+2} | | Ag/ Ag^+ c_1 c_2 ($c_1 = c_2$)	**(s)** $E^0_{cell} = -ve$

3. **Column-I** and **Column-II** contains four entries each. Entries of **Column-I** are to be matched with some entries of **Column-II**. One or more than one entries of **Column-I** may have the matching with the same entries of **Column-II**.

Column-I	Column-II
(A) Very dilute solution of HCl	**(p)** O_2 evolved at anode
(B) Very dilute solution of NaCl	**(q)** H_2 evolved at cathode
(C) Concentrate solution of NaCl	**(r)** Cl_2 evolved at anode
(D) Fairly concentrate solution of $AgNO_3$	**(s)** Ag deposition at cathode

4.

Column-I	Column-II
(A) Cathode	**(p)** Primary cell
(B) 1 Coulomb	**(q)** Secondary cell
(C) Dry cell	**(r)** 6.24 × 10^{18} electrones
(D) Lead strong cell	**(s)** Concentration cell
(E) Zn|Zn^{2+}(0.01M)‖Zn^{2+}(0.1M)|Zn	**(t)** Positive terminal of electrochemical cell

5.

Column-I	Column-II
(A) Cell constant	**(p)** $E^0_{cathode} + E^0_{anode}$
(B) Anode	**(q)** ℓ/A
(C) Conductance	**(r)** Mass of product deposited by 1 coulomb of electricity.
(D) Electrochemical equivalent	**(s)** $(\text{Resistance})^{-1}$
(E) E^0_{cell}	**(t)** Involve oxidation

6.

Column-I	Column-II
(A) Conductance	**(p)** Cm^{-1}
(B) Specific conductance	**(q)** $Ohm^{-1}cm^2mol^{-1}$
(C) Cell constant	**(r)** Ohm^{-1}
(D) Equivalent conductance	**(s)** $Ohm^{-1}cm^{-1}$

Exercise # 4

PART - 1

PREVIOUS YEAR (NEET/AIPMT)

1. The equivalent conductances of Ba^{2+} and Cl^- are 127 76 Ω^{-1} cm^{-1} eq^{-1} respectively at infinite dilution. The equivalent conductance of $Bacl_2$ at infinite dilution will be **[CBSE AIPMT 2000]**

(A) 139.52 **(B)** 203

(C) 279 **(D)** 101.5

2. Cu^+ (aq) is unstable in solution and undergoes simultaneous oxidation and reduction according to the reaction

$2Cu^+ (aq)$ □ $Cu^{2+} (aq) + Cu(s)$

Choose the correct E^0 for above reaction if d

$E^0_{cu^{2+}/cu} = 0.34$ V and $E^0_{cu^{2+}/cu^+} = 0.15$ V

[CBSE AIPMT 2000]

(A) -0.38 V **(B)** + 0.49 V

(C) +0.38 V **(D)** -0.19 V

3. Cell reaction in spontaneous when **[CBSE AIPMT 2000]**

(A) E^0_{red} is negative **(B)** E^0_{red} is positive

(C) ΔG^0 is negative **(D)** ΔG^0 is positive

4. The most convenient method to protect the bottom of the ship made of iron is **[CBSE AIPMT 2000]**

(A) Coating it with red lead oxide

(B) white tin plating

(C) connecting it with Mg block

(D) connecting it with Pb block

5. Standard electrode potentials are

Fe^{2+} / Fe, E^0 = - 0.4 V

Fe^{3+} / Fe,$^{2+}$,E^0 = 0.77 V

Fe^{2+} ,Fe^{3+} and Fe block are kept together, then **[CBSE AIPMT 2001]**

(A) Fe^{3+} increases

(B) Fe^{3+} decreases

(C) $\frac{Fe^{2+}}{Fe^{3+}}$ remains unchanged

(D) Fe^{2+} decreases

6. In electrolysis of NaCl when Pt electrode is taken then H_2 is liberated at cathode while with Hg cathode it forms sodium amalgam because **[CBSE AIPMT 2002]**

(A) Hg is more inert than Pt

(B) more voltage is required to reduce H^+ at Hg than at Pt

(C) Na is dissolved in Hg while it does not dissolved in Pt

(D) Concentration of H^+ ions is larger when Pt electrode is taken

7. On the basis of the information available from the reaction. **[CBSE AIPMT 2003]**

$\frac{4}{3}Al + O_2 \rightarrow \frac{2}{3}Al_2, \Delta G = -827\, kmol^{-1}$ of O_2, the minimum EMF required to carry out the electrolysis of Al^2O^3 is (F=96500 C mol-1)

(A) 2.14 V **(B)** 4.28 V

(C) 6.42 V **(D)** 8.56 V

8. The standard EMF of a galvanic cell involving cell reaction with n-2 is found to be 0.295 V at 25^0C. The equilibrium constant of the reaction would be (Given F = 96500 C mol^{-1}. **[CBSE AIPMT 2004]**

(A) 2.0×10^{11} **(B)** 4.0×10^{12}

(C) 10×10^{2} **(D)** 10×10^{10}

9. 4.5 g of aluminium (atomic mass 27u) 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. **[CBSE AIPMT 2005]**

(A) 44.8 L **(B)** 22. 4L

(C) 11.2 L **(D)** 5.6L

10. A hypothetical electrochemical cell is shown below

A |A^+ (xM)|| B^+(yM)| B **[CBSE AIPMT 2006]**

(A) $A+B^+ \longrightarrow A^+ +B$

(B) $A^+ +B \longrightarrow A+B^+$

(C) $A^+ +e^- \longrightarrow A, B^+ +e^- \longrightarrow B$

(D) the celll reaction cannot be predicted

11. $E^0_{Fe^{2+}/Fe} = -0.441$ V and $E^0_{Fe^{3+}/Fe^{2+}} = 0.771$V the standard emf of the reaction $Fe+2Fe^{3+} \longrightarrow 3Fe^{2+}$ will be **[CBSE AIPMT 2006]**

(A) 0.111 V **(B)** 0.330 V

(C) 1.653 V **(D)** 1.212 V

12. The equilibrium constant of the reaction,

$Cu(s) + 2Ag^+ (aq) \longrightarrow Cu^{2+} (aq) + 2Ag(s)$m

E^0 =0.46 V at 298 K is **[CBSE AIPMT 2007]**

(A) 2.0×10^{10} **(B)** 4.0×10^{10}

(C) 4.0×10^{15} **(D)** 2.4×10^{10}

13. The efficiency of a fule cell is given by **[CBSE AIPMT 2007]**

(A) $\Delta G/\Delta S$ **(B)** $\Delta G/\Delta H$

(C) $\Delta S/\Delta G$ **(D)** $\Delta H/\Delta G$

MOCK TEST

STRAIGHT OBJECTIVE TYPE

1. If the standard electrode potential of Cu^{2+}/Cu electrode is 0.34V, what is the electrode potential of 0.01M concentration of Cu^{2+} (T = 298 K)

(A) 0.399 V **(B)** 0.281 V **(C)** 0.222 V **(D)** 0.176 V

2. Calculate the electrode potential at 298°K for Zn/Zn^{2+} electrode in which the activity of zinc ions is 0.001 M and $E^o_{Zn/Zn^{2+}}$ is -0.74 volts

(A) 0. 38 volts **(B)** 0.83 volts **(C)** 0.40 volts **(D)** 0.45 volts

3. Which of the following expression is correct

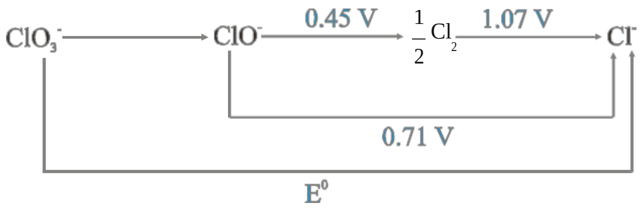
(A) $\Delta G^o = -nFE^o_{cell}$ **(B)** $\Delta G^o = +nFE^o_{cell}$

(C) $\Delta G^o = -2.303RT\ nFE^o_{cell}$ **(D)** $\Delta G^o = -nF\log K_C$

4. For the feasibility of a redox reaction in a cell, the e.m.f. should be

(A) Positive **(B)** Fixed **(C)** Zero **(D)** Negative

5.



The E^0 in the given diagram is,

(A) 0.5 **(B)** 0.6 **(C)** 0.7 **(D)** 0.8

6. What is cell entropy change of the following cell ?

$Pt(s)\ |\ H_2(g)\ |\ CH_3COOH, HCl\ ||KCl\ (aq)\ |\ Hg_2Cl_2\ (s)\ |\ Hg$

P = 1 atm 0.1 M 0.1 M

Emf of the cell ius found to be 0.045 V at 298 K and temperature coefficient is 3.4×10^{-4} V K^{-1}

Given $K_{a\,(CH_3COOH)} = 10^{-5}M$

(A) 60 **(B)** 65.2 **(C)** 69.2 **(D)** 63.5

7. Following cell has EMF 0.7995 V.

$Pt\ |\ H_2\ (1\ atm)\ |\ HNO_3\ (1M)\ |\ |AgNO_3\ (1M)\ |\ Ag$

If we add enough KCl to the Ag cell so that the final Cl^- is 1M. Now the measured emf of the cell is 0.222 V. The Ksp of AgCl would be :

(A) $1 \times 10^{-9.8}$ **(B)** $1 \times 10^{-19.6}$ **(C)** 2×10^{-10} **(D)** 2.64×10^{-14}

8. The solubility of $[Co(NH_3)_4Cl_2]\ ClO_4$ if the $\lambda_{Co(NH_3)_4Cl_2^+} = 50$, $\lambda_{ClO_4^-} = 70$ and the measured resistance was 33.5 Ω in a cell with cell constant of 0.20 is ___________

(A) 59.7 mmol/L **(B)** 49.7 mmol/L **(C)** 39.7 mmol/L **(D)** 29.7 mmol/L

CHAPTER 12

ALDEHYDE, KETONE AND CARBOXYLIC ACID

> *In organic chemistry, we have learnt to derive from compounds containing only carbon and hydrogen i.e. from the hydrocarbons, all other types of combinations such as alcohol, aldehyde, ketones, acids etc.*
>
> **''OTTO WALLACH''**

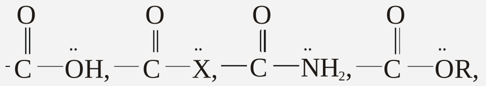
INTRODUCTION

Organic Compounds having $>C=O$ group are called carbonyl compounds and $>C=O$ group is known as carbonyl or oxo group. It's general formula is $C_n H_{2n}O$ ($n = 1, 2, 3$) Carbonyl compounds are grouped into two categories.

In aldihydes,the carbonyl group is bonded to a carbon and hydrogen while in ketones, it is bonded to two carbon atoms.The carbonyl compounds in which carbonyl group is bonded to oxygen are known as carboxylic acids, and their derivatives (e.g. esters, anhydrides) while in compounds where carbon is attached to nitrogen and to halogens are called amides and acyl halides respectively.

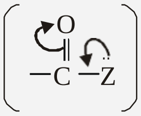
Aldehydes, ketones and carboxylic acids are play an important role in biochemical processes, add fragrance and flavour to many food products and pharmaceuticals.

ETOOS KEY POINTS



$$-\overset{O}{\overset{\|}{C}}-\ddot{O}H,\ -\overset{O}{\overset{\|}{C}}-\ddot{X},\ -\overset{O}{\overset{\|}{C}}-\ddot{N}H_2,\ -\overset{O}{\overset{\|}{C}}-\ddot{O}R,$$

In all the compounds given above, lone pair of electrons and double bond are conjugate.



so resonance occurs. These compounds have $-\overset{O}{\overset{\|}{C}}-$ group still they are not carbonyl compounds because carbonyl group takes parts in resonance with the lone pair of electrons.

General Methods of Preparation :

(A) For both Aldehydes and Ketones

By Oxidation of Alcohols :

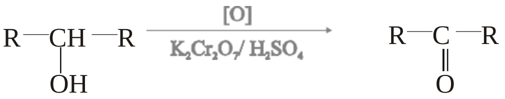
Primary alcohols $\xrightarrow{[O]}$ Aldehydes

Secondary alcohols $\xrightarrow{[O]}$ Ketones

By $K_2Cr_2O_7$ / H_2SO_4 :

Oxidation of primary alcohols gives aldehyde and oxidation of secondary alcohols gives Ketones. Here, ($K_2Cr_2O_7$ / H_2SO_4) is a strong oxidising agent.

$$RCH_2OH \xrightarrow[K_2Cr_2O_7/\,H_2SO_4]{[O]} RCHO \quad \text{(Aldehyde)}$$



$$R-\underset{OH}{\underset{|}{C}H}-R \xrightarrow[K_2Cr_2O_7/\,H_2SO_4]{[O]} R-\underset{O}{\underset{\|}{C}}-R \quad \text{(Ketone)}$$

Aldehydes are quite susceptible to further oxidation to acids -

$$RCH_2OH \xrightarrow{[O]} R-CHO \xrightarrow{[O]} R-COOH$$

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.

Note : Aldehydes can be prepared from 1° alcohol, secondary alcohols can be oxidized to ketones, by oxidation with pyridinium chlorochromate (PCC) in CH_2Cl_2 solvent, pyridinium dichromate (PDC) and with Jones reagent (CrO_3+H_2SO_4) in acetone.

Oppenauer Oxidation :

The oxidation of secondary alcohols to ketones by heating them with specific reagent : $[(CH_3)_3CO]_3Al$ (Aluminium-t-butoxide) in presence of acetone. Primary alcohols may also be oxidized to aldehydes if ketones is replaced by a better hydrogen acceptor, e.g. p-benzoquinone. The equilibrium can be controlled by the amount of acetone, an excess of which favours the oxidation of the alcohol.

2^O Alcohol — Acetone — Ketone — Isopropyl alcohol

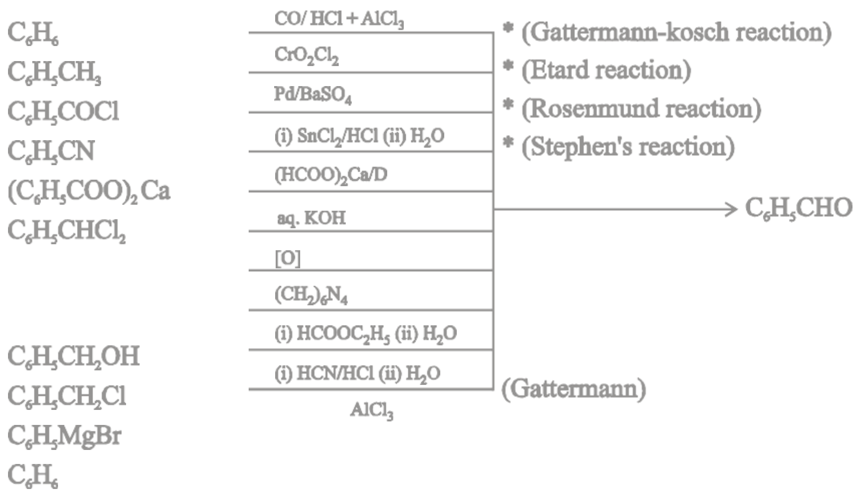
1^0 Alcohol — Quinone — Aldehyde — Quinol

Note : The reaction is the reverse of **Meerwein-Ponndorf -verley reduction**.

BENZALDEHYDE (C_6H_5CHO)

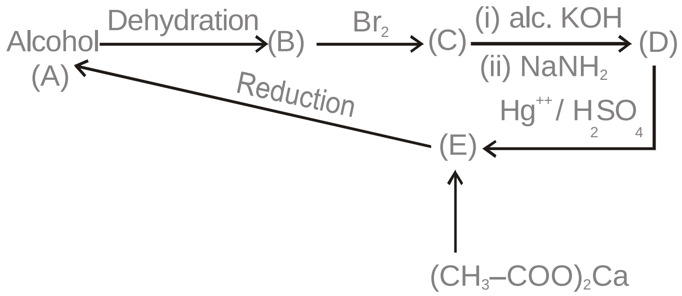
Oil of bitter almonds

General Method of Preparation :

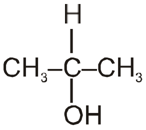


SOLVED EXAMPLE

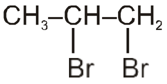
Ex. 1 Find out unknown in following reactions.



Sol. Since E is obtained on dry distillation of calcium salt of acetic acid hence E will be $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$. Thus other unknowns are

A = 
$CH_3-\underset{OH}{\overset{H}{C}}-CH_3$

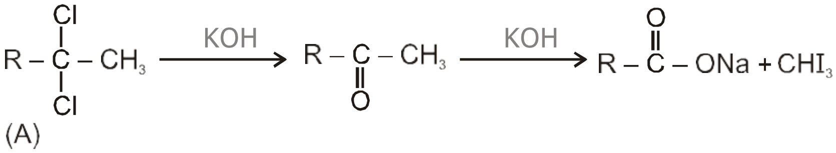
$B = CH_3-CH=CH_2$

C = 
$CH_3-\underset{Br}{CH}-\underset{Br}{CH_2}$

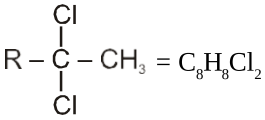
$D = CH_3-C\equiv C-H$

Ex. 2 What will be structure of aromatic $C_8H_8Cl_2$ **(A)**, which on aqueous alkalihydrolysis gives product **(B)**. **(B)** gives positive iodoform test.

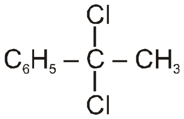
Sol. Since **(B)** is showing iodoform test hence it will be methylketone only as it is obtained on aqueous alkali hydrolysis of **(A)** which will be non-terminal gem dihalides as –


$$\underset{(A)}{R-\underset{Cl}{\overset{Cl}{C}}-CH_3} \xrightarrow{KOH} R-\underset{O}{\underset{\|}{C}}-CH_3 \xrightarrow{KOH} R-\overset{O}{\overset{\|}{C}}-ONa+CHI_3$$

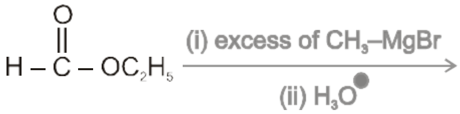
Now unknown 'R' can be known as :

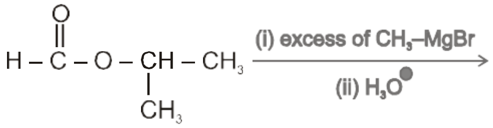

$$R-\underset{Cl}{\overset{Cl}{C}}-CH_3 = C_8H_8Cl_2$$

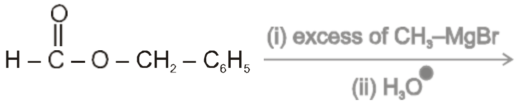
$R = C_8H_8Cl_2 - C_2H_3Cl_2 = C_6H_5$

Hence 'A' is 
$C_6H_5-\underset{Cl}{\overset{Cl}{C}}-CH_3$

Ex. 3 Write the products of the following reactions.

(A) 
$H-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i) excess of } CH_3-MgBr}$

(B) 
$H-\overset{O}{\overset{\|}{C}}-O-\underset{CH_3}{CH}-CH_3 \xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i) excess of } CH_3-MgBr}$

(C) 
$H-\overset{O}{\overset{\|}{C}}-O-CH_2-C_6H_5 \xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i) excess of } CH_3-MgBr}$

(D) 
$H-\overset{O}{\overset{\|}{C}}-O-C_6H_5 \xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i) excess of } CH_3-MgBr}$

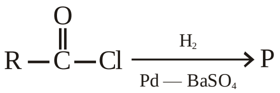
Exercise # 1 SINGLE OBJECTIVE NEET LEVEL

1. The end product in the following sequecne of reaction is

$HC \equiv CH \xrightarrow[20\%H_2SO_4]{1\%HgSO_4} A \xrightarrow{CH_3MgX} B \xrightarrow{[O]}$

(A) Acetic acid (B) Isopropyl alcohol (C) Acetone (D) Ethanol

2. In the following reaction, product P is



$R-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[Pd - BaSO_4]{H_2} P$

(A) RCH_2OH (B) $RCOOH$ (C) $RCHO$ (D) RCH_3

3. Acetophenone is prepared from

(A) Rosenmund reaction (B) Sandmayer reaction (C) Wurtz reaction (D) Friedel craft reaction

4. Compound which gives acetone on ozonolysis

(A) $CH_3-CH=CH-CH_3$ (B) $(CH_3)_2C=C(CH_3)_2$ (C) $C_6H_5CH=CH_2$ (D) $CH_3CH=CH_2$

5. Identify the reaction X and the product Y

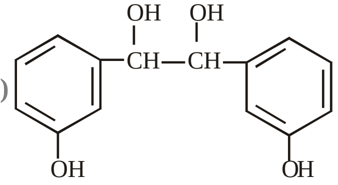
$CH_3-OH-CH_3+X \rightarrow (CH_3)_3C-OMg-Cl \xrightarrow{Hydrolysis} Y+Mg(OH)Cl$

(A) $X=MgCl_2$; $Y=CH_3CH=CH_2$ (B) $X=CH_3MgCl$; $Y=C_2H_5COCH_3$

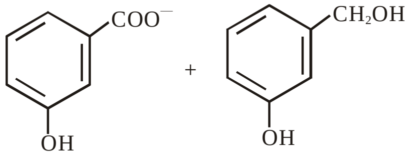
(C) $X=CH_3MgCl$; $Y=(CH_3)_3C-OH$ (D) $X=C_2H_5MgCl$; $Y=(CH_3)_3C-OH$

6. When m-chlorobenzaldehyde is treated with 50% KOH solution, the product (s) obtained is (are)

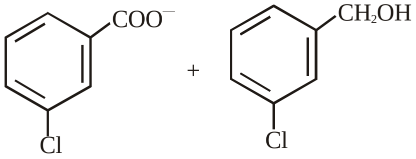
(A)



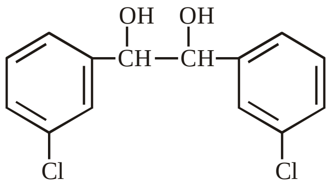
(B)



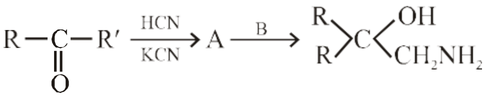
(C)



(D)

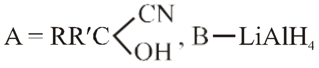


7. A and B in the following are



$R-\underset{\underset{O}{\|}}{C}-R' \xrightarrow[KCN]{HCN} A \xrightarrow{B} \underset{R}{\overset{R}{>}}C\underset{CH_2NH_2}{\overset{OH}{<}}$

(A)

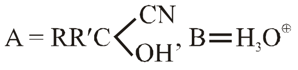


$A = RR'C\underset{OH}{\overset{CN}{<}}$, $B-LiAlH_4$

(B)

$A = RR'C\underset{COOH}{\overset{OH}{<}}$, $B-NH_3$

(C)



$A = RR'C\underset{OH}{\overset{CN}{<}}$, $B=H_3O^{\oplus}$

(D) $A=RR'CH_2CN$, $B=NaOH$

8. Reduction of Aldehydes and Ketones to hydrocarbon take place in the presence of

(A) Zn amalgam and HCl acid (B) $Pd/BaSO_4$

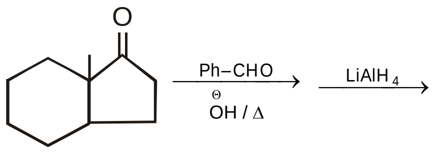
(C) Anhydrous $AlCl_3$ (D) Ni / Pt

9. Reduction of $>C=O$ to CH_2 can be carried out with

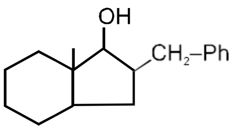
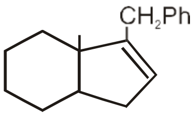
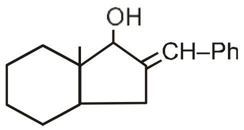
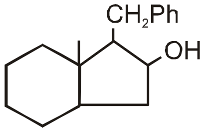
(A) Catalytic reduction (B) Na/C_2H_5OH

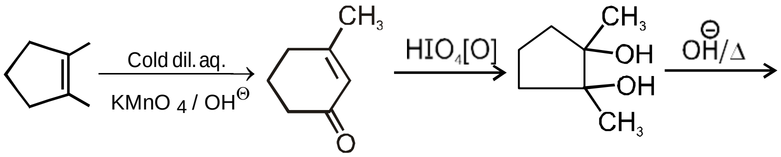
(C) Wolf-Kishmer reduction (D) $LiAlH_4$

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. 

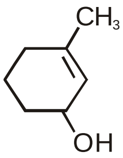
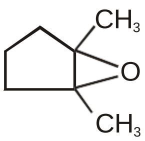
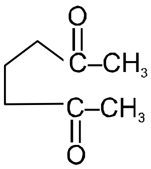
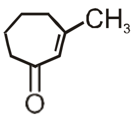
[X], Product (X) in this reaction is :

(A) 
(B) 
(C) 
(D) 

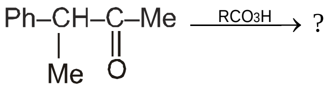
2. 

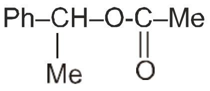
(Z)

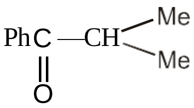
The products of the above reaction is / are :

(A) 
(B) 
(C) 
(D) 

3. What will be the product of the following reaction

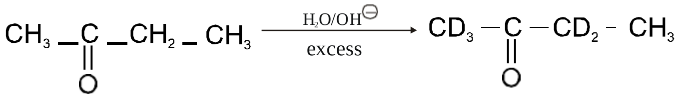

$\text{Ph}-\underset{\text{Me}}{\underset{|}{\text{CH}}}-\underset{\text{O}}{\underset{\|}{\text{C}}}-\text{Me} \xrightarrow{\text{RCO}_3\text{H}} ?$

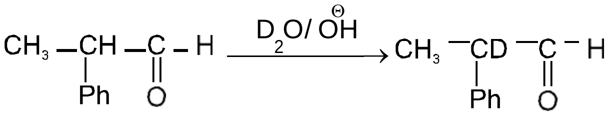
(A) 
$\text{Ph}-\underset{\text{Me}}{\underset{|}{\text{CH}}}-\text{O}-\underset{\text{O}}{\underset{\|}{\text{C}}}-\text{Me}$

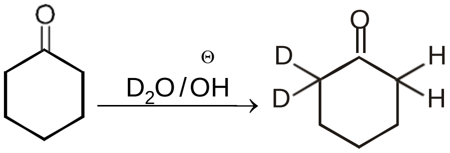
(B) 
$\text{Ph}\underset{\text{O}}{\underset{\|}{\text{C}}}-\text{CH}\begin{matrix}\text{Me}\\ \text{Me}\end{matrix}$

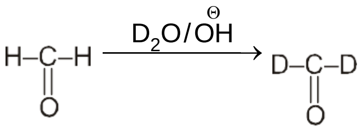
(C) PhCH(Me)OCOOMe **(D)** None of these

4. In which of the following reaction deuterium exchange is observed ?

(A) 
$\text{CH}_3-\underset{\text{O}}{\underset{\|}{\text{C}}}-\text{CH}_2-\text{CH}_3 \xrightarrow[\text{excess}]{\text{H}_2\text{O/OH}^\ominus} \text{CD}_3-\underset{\text{O}}{\underset{\|}{\text{C}}}-\text{CD}_2-\text{CH}_3$

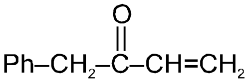
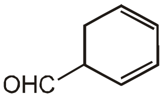
(B) 
$\text{CH}_3-\underset{\text{Ph}}{\underset{|}{\text{CH}}}-\underset{\text{O}}{\underset{\|}{\text{C}}}-\text{H} \xrightarrow{\text{D}_2\text{O/}\overset{\ominus}{\text{OH}}} \text{CH}_3-\underset{\text{Ph}}{\underset{|}{\text{CD}}}-\underset{\text{O}}{\underset{\|}{\text{C}}}-\text{H}$

(C) 

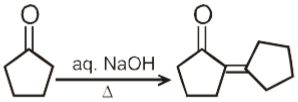
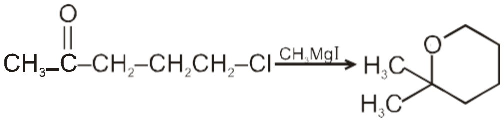
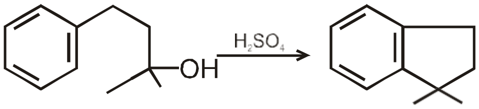
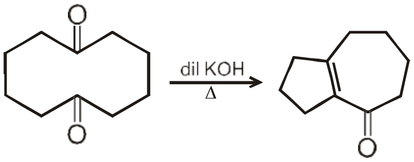
(D) 
$\text{H}-\underset{\text{O}}{\underset{\|}{\text{C}}}-\text{H} \xrightarrow{\text{D}_2\text{O/}\overset{\ominus}{\text{OH}}} \text{D}-\underset{\text{O}}{\underset{\|}{\text{C}}}-\text{D}$

Exercise # 3 PART - 1 MATRIX MATCH COLUMN

1.

Column-I	Column-II
(A)  $Ph{-}CH_2{-}\overset{O}{\overset{\parallel}{C}}{-}CH{=}CH_2$	**(p)** 1, 4-addition
(B) 	**(q)** Tautomerism
(C) $CH_3{-}CH{=}CH{-}CH{=}CH_2$	**(r)** $AgNO_3/NH_4OH$

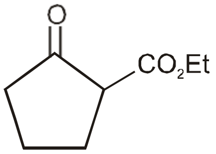
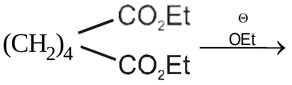
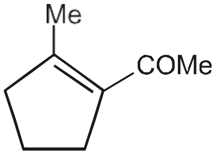
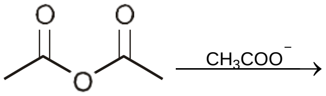
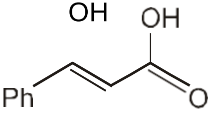
2.

Column-I	Column-II
(A) 	**(p)** Nucleophilic substitution
(B) 	**(q)** electrophilic substitution
(C) 	**(r)** Dehydration
(D) 	**(s)** Nucleophilic addition

3. Match the product of **Column- II** with the reaction given in **Column- I.**

Column- I	Column- II
(A) RMgI + Acetonitrile ($CH_3C \equiv N$)	**(p)** Alkanone
(B) RMgI + Carbon disulphide	**(q)** Ester
(C) RMgI.(1eq) + Ethyl chloroformate	**(r)** 1° Alcohol
(D) RMgI + Oxirane	**(s)** Dithionic acid

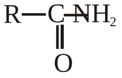
4. Match the column

Column I	Column II
(A) $MeCO(CH_2)_4COMe \xrightarrow[\text{(ii) } H^+/\Delta]{\text{(i) } OH^{\ominus}}$	**(p)** 
(B) 	**(q)** 
(C) PhCHO + 	**(r)** $(Ph)_2\underset{OH}{\underset{\mid}{C}}{-}COO^-$
(D) $PhCOCOPh \xrightarrow{OH^{\ominus}}$	**(s)** 

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. During reduction of aldehydes with hydrazine and potassium hydroxide, the first is the formation of **[CBSE AIPMT 2000]**

(A) $R - CH = N - NH_2$ **(B)** $R - C \;\; N =$

(C) 
$R - \underset{\underset{O}{\|}}{C} - NH_2$

(D) $R - CH = NH$

2. Polarisation of electrons in acrolein may be written as **[CBSE AIPMT2000]**

(A) $\overset{\delta+}{CH_2} - CH \quad CH - \overset{\delta-}{O}$

(B) $\overset{\delta+}{CH_2} - \overset{\delta+}{CH} \quad CH - O$

(C) $\overset{\delta+}{CH_2} - CH \quad CH - \overset{\delta+}{O}$

(D) $\overset{\delta-}{CH_2} - \overset{\delta+}{CH} \quad CH - O$

3. Reduction by $LiAlH_4$ of hydrolysed product of an ester gives **[CBSE AIPMT 2000]**

(A) two acids

(B) two aldehydes

(C) One molecule of alcohol and another of carboxlic acid

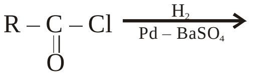
(D) two alcohols

4. Benzoic acid may be converted into ethyl benzoate by reaction with **[CBSE AIPMT2002]**

(A) sodium ethoxide **(B)** ethyl chloride

(C) dry HCl, C_2H_5OH **(D)** ethanol

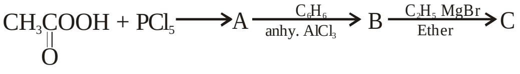
5. In the following reaction, product P is **[CBSE AIPMT 2002]**


$R - \underset{\underset{O}{\|}}{C} - Cl \xrightarrow[Pd - BaSO_4]{H_2} P$

(A) RCH_2OH **(B)** RCOOH

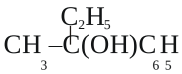
(C) RCHO **(D)** RCH_3

6. In a set of the given reactions, acetic acid yielded a product C.


$CH_3\underset{\underset{O}{\|}}{C}OOH + PCl_5 \longrightarrow A \xrightarrow[\text{anhy. } AlCl_3]{C_6H_6} B \xrightarrow[\text{Ether}]{C_2H_5\,MgBr} C$

Product C would be **[CBSE AIPMT 2003]**

(A) $CH_3CH(OH)C_6H_5$

(B) 
$CH_3 - \overset{\overset{C_2H_5}{|}}{C}(OH)C_6H_5$

(C) $CH_3CH(OH)C_2H_5$ **(D)** $CH_3COC_6H_5$

7. Which one of the following orders of acidic strength is correct ? **[CBSE AIPMT 2003]**

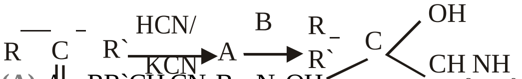
(A) $RCOOH > HOH > HC \equiv CH > ROH$

(B) $RCOOH > HC \equiv CH > HOH > ROH$

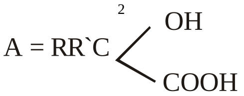
(C) $RCOOH > ROH > HOH > HC \equiv CH$

(D) $RCOOH > HOH > ROH > HC \equiv CH$

8. A and B in the following reactions are **[CBSE AIPMT 2003]**



(A) A = RR`CH CN, B = NaOH
$_2$

(B) 
A = RR`C(OH)(COOH) B=CH_3

(C) 
A = RR`C(CN)(COOH) B=CH_3

(D) 
A = RR`C(CN)(OH) B=$LiAlH_4$

9. Which one of the following can be oxidised to the corresponding carbonyl compound? **[CBSE AIPMT 2004]**

(A) 2-hydroxy propane

(B) Ortho-nitro phenol

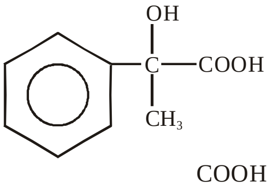
(C) Phenol

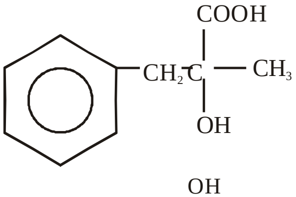
(D) 2-methyl -2 hydroxypropane

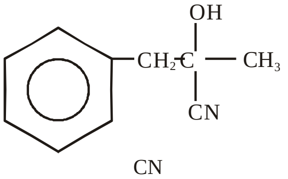
10. In a set of reactions, acitic acid yielded a product D.

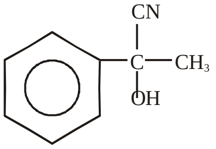
$CH_3COOH \xrightarrow{SOCl_2} A \xrightarrow[\text{anhy. } AlCl_3]{\text{Benzene}} B \xrightarrow{HCN} C \xrightarrow{HOH} D$

The structure of D would be **[CBSE AIPMT 2005]**

(A) 

(B) 

(C) 

(D) 

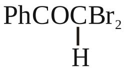
MOCK TEST

STRAIGHT OBJECTIVE TYPE

1. $PhCoCHBr_2 \xrightarrow{OH^-} A \xrightarrow{OH^-} B \xrightarrow{H^+} C$

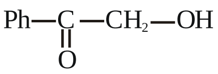
The compound 'C' is

(A) PhCH(OH)CHO **(B)** PhCH(OH)COOH **(C)**



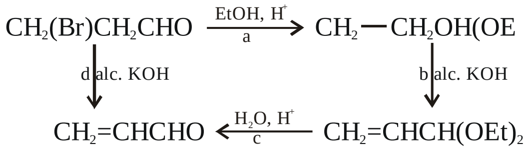
$PhCO\underset{H}{\underset{|}{C}}Br_2$

(D)



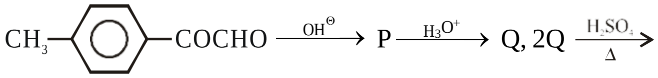
$Ph-\underset{O}{\underset{\|}{C}}-CH_2-OH$

2. Which stepis not fresh in the following loop?



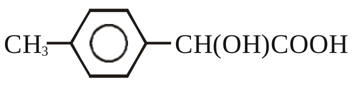
(A) step - a **(B)** step - b **(C)** step - c **(D)** step - d

3.

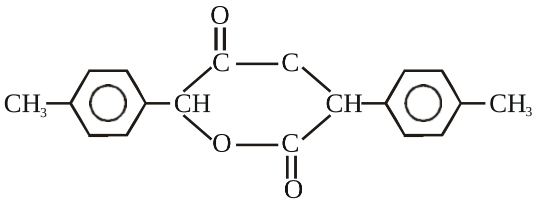


R, The product R is

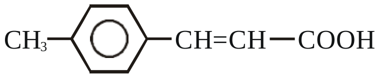
(A)



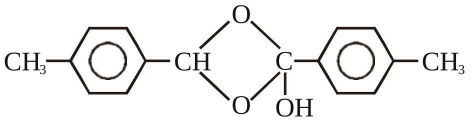
(B)



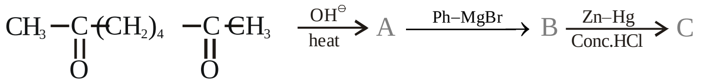
(C)



(D)



4.

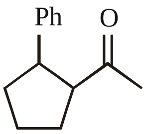


$CH_3-\underset{O}{\underset{\|}{C}}-(CH_2)_4-\underset{O}{\underset{\|}{C}}-CH_3 \xrightarrow[heat]{OH^\ominus} A \xrightarrow{Ph-MgBr} B \xrightarrow[Conc.HCl]{Zn-Hg} C$

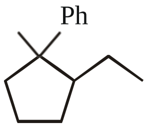
The product 'C' is

(A)

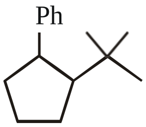
(B)



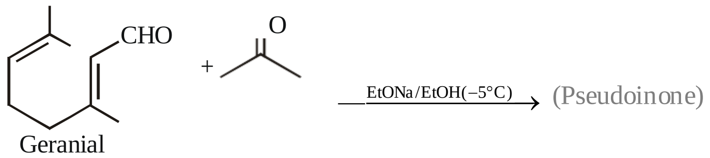
(C)



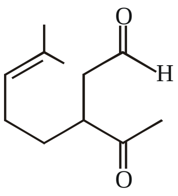
(D)



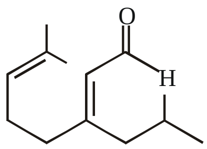
5. The structure of major proeduct (pseudoionone) is,



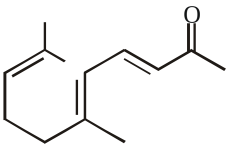
(A)



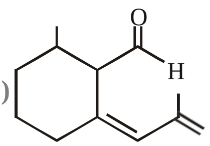
(B)



(C)



(D)



CHAPTER 06

REDOX REACTION

The meeting of two personalities is like the contact of two chemical substances; if there is any reaction, both are transformed

"CARL JUNG"

INTRODUCTION

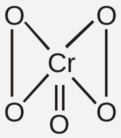
A number of phenomena, both phtysical as well as biological, are concerned with redox reaction. These reactions find extensive use in pharmaceutical, biological, industrial, metallurgical and agricultural areas. The importance of these reactions is apparent from the fact that burning of different types of fuels for obtaining energy for domestic, transport and other commercial purposes, electrochemical processes for extraction of highly reactive metals and non-metals, manufacturing of chemical compounds like caustic soda, operation of dry and wet batteries and corrosion of metals fall within the purview of redox processes. Of late, environmental issues like Hydrogen Economy (use of liquid hydrogen as fuel) and development of 'Ozone Hole' have started figuring under redox phenomenon.

ED OS KEY POINTS

Miscellaneous Examples

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

(I) The structure of CrO_5 is

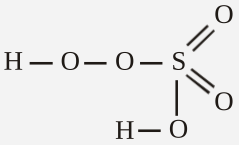


From the structure, it is evident that in CrO_5 there are two peroxide linkages and one double bond. The contribution of each peroxide linkage is –2. Let the oxidation number of Cr is x.

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

$\therefore$ Oxidation number of Cr = + 6.

(II) The structure of H_2SO_5 is



From the structure, it is evident that in H_2SO_5, there is one peroxide linkage, two sulphur-oxygen double bonds and one OH group. Let the oxidation number of S = x.

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

or $x + 2 - 8 = 0$ or $x - 6 = 0$ or $x = 6$

$\therefore$ Oxidation number of S in H_2SO_5 is + 6 .

Oxidation State as a periodic property :

Oxidation state of an atom depends upon the electronic configuration of an atom i.e. why it is periodic properties.

(a) I A group of alkali metals show +1 oxidation state.

(b) II A group or alkaline earth metals show +2 oxidation state

(c) The maximum normal oxidation state, show by III A group elements is +3. These elements also show +2 to +1 oxidation states also.

(d) Elements of IV A group show their maximum and minimum oxidation states +4 and –4 respectively.

(e) Non metals shows number of oxidation states, the relation between maximum and minimum oxidation states for non metals is equal to (maximum oxidation state – minimum oxidation state = 8).

For example sulphur has maximum oxidation number +6 as being in VI A group element.

Paradox of fractional oxidation number :

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

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

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

Structure of C_3O_2
(Carbon suboxide)

Etoos Tips & Formulas

Oxidation :

(i) Addition of Oxygen
(ii) Removal of Hydrogen
(iii) Addition of Electronegative element
(iv) Removal of Electropositive element
(v) Increment in oxidation state of Electropositive element
(vi) increase in (+) ve valency or decrease in (–) ve valency of a substance takes place called oxidation.

Reduction :

(i) Removal of Oxygen:
(ii) Addition of Hydrogen
(iii) Removal of Electronegative element
(iv) Addition of Electropositive element
(v) Decrement in oxidation state of Electropositive element
(vi) decrease in (+) ve valency or increase in (–) ve valency of a substance is called reduction.

Oxidising agent (oxidant) and reducing agent (Reductant)

Oxidising agent or Oxidant

Oxidising agents are those compounds which can oxidise others and reduce itself during the chemical reaction. Those reagents in which for an element, oxidation number decreases or which undergoes gain of electrons in a redox reaction are termed as oxidants.

Reducing agent or Reductant

Reducing agents are those compounds which can reduce other and oxidise itself during the chemical reaction. Those reagents in which for an element, oxidation number increases or which undergoes loss of electrons in a redox reaction are termed as reductants.

Ex. KI , $Na_2S_2O_3$ etc are the powerful reducing agents.

Oxidation number change method :-(method of balancing redox equation)

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

The general procedure involves the following steps :-

(i) Select the atom in oxidising agent whose oxidation number decreases and indicate the gain of electrons.
(ii) Select the atom in reducing agent whose oxidation number increases and write the loss of electrons.
(iii) Now cross multiply i.e.multiply oxidising agent by the number of loss of electrons and reducing agent by number of gain of electrons.
(iv) Balance the number of atoms on both sides whose oxidation numbers change in the reaction.
(v) In order to balance oxygen atoms, add H_2O molecules to the side deficient in oxygen. Then balance the number of H atoms by adding H^+ ions in the hydrogen.

SOLVED EXAMPLE

Ex. 1 The weight of sodium bromate required to prepare 55.5 mL of 0.672 N solution for cell reaction, $BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$, is

(A) 1.56 g (B) 0.9386 g
(C) 1.23 g (D) 1.32 g

Sol. Meq. of $NaBrO_3 = 55.5 \times 0.672 = 37.296$

Let weight of $NaBrO_3$ = W

□ $\frac{W}{M_{NaBrO_3}} \times 6 \times 1000 = 37.296$ (equivalent weight = M/6) of n-factor = 6

□ $\frac{M}{151} \times 6 \times 1000 = 37.296$

□ W = 0.9386 g

Hence, **(B)** is the correct answer.

Ex. 2 $NaIO_3$ reacts with $NaHSO_3$ according to equation

$IO_3^- + 3HSO_3^- \longrightarrow I^- + 3H^+ + 3SO_4^{2-}$

The weight of $NaHSO_3$ required to react with 100 mL of solution containing 0.68 g of $NaIO_3$ is

(A) 5.2 g (B) 0.2143 g
(C) 2.3 g (D) none of the above

Sol. Meq. of $NaHSO_3$ = Meq. of $NaIO_3$ = N × V = $\frac{0.68}{198} \times 6 \times 1000$ $(I^{5+} + 6e^- \rightarrow I^-)$

□ $\frac{W_{NaHSO_3}}{M_{NaHSO_3}} \times 2 \times 1000 = \frac{0.68}{198} \times 6 \times 100$

$W_{NaHSO_3} = \frac{0.68 \times 6 \times 100 \times 104}{198 \times 1000} = 0.2143$

Hence **(B)** is the correct answer.

Ex. 3 If 0.5 moles of $BaCl_2$ is mixed with 0.1 moles of Na_3PO_4, the maximum amount of $Ba_3(PO_4)_2$ that can be formed is

(A) 0.7 mol (B) 0.5 mol
(C) 0.2 mol (D) 0.05 mol

Sol. Let us first solve this problem by writing the complete balanced reaction.

$3BaCl_2 + 2Na_3PO_4 \longrightarrow Ba_3(PO_4)_2\downarrow + 6NaCl$

We can see that the moles of $BaCl_2$ used are $\frac{3}{2}$ times the moles of Na_3PO_4. Therefore, to react with 0.1 mol of Na_3PO_4, the moles of $BaCl_2$ required would be $0.1 \times \frac{3}{2} = 0.15$. Since $BaCl_2$ is 0.5 mol, we can conclude that Na_3PO_4 is the limiting reagent.

Therefore, moles of $Ba_3(PO_4)_2$ formed is $0.1 \times \frac{3}{2}$ = 0.05 mol.

Hence, **(D)** is the correct answer.

Ex. 4 A 0.1097 g sample of As_2O_3 required 36.10 mL of $KMnO_4$ solution for its titration. The molarity of $KMnO_4$ solution is.

(A) 0.02 (B) 0.04
(C) 0.0122 (D) 0.3

Sol.

n-factor = 5

$As_2O_3 + MnO_4^- \qquad 2AsO_4^{3-} + Mn^{2+}$

n-factor = 4

Let, molarity of $KMnO_4$ solution be M

□ Eq. of As_2O_3 = Eq. of $KMnO_4$ solution

$\frac{0.1097}{198} \times 4 = \frac{36.10 \times M \times 5}{1000}$ (Equivalent weight $As_2O_3 = \frac{198}{4}$)

Molarity = 0.0122 M

Hence, **(C)** is the correct answer.

Ex. 5 In basic medium, CrO_4^{2-} oxidize $S_2O_3^{2-}$ to form SO_4^{2-} and itself changes to $Cr(OH)_4^-$. How many mL of 0.154 M CrO_4^{2-} are required to react with 40 mL of 0.246 M $S_2O_3^{2-}$?

(A) 200 mL (B) 156.4 mL
(C) 170.4 mL (D) 190.4 mL

Sol. 40 × 0.246 × 8 = V × 0.154 × 3 (Meq. of $S_2O_3^{2-}$ = Meq. of CrO_4^{2-})

□ V = 170.4 mL

Hence, **(C)** is the correct answer.

Ex. 6 10 mL of 0.4 M $Al_2(SO_4)_3$ is mixed with 20 mL of 0.6 M $BaCl_2$. Concentration of Al^{3+} ion in the solution will be.

(A) 0.266 M (B) 10.3 M
(C) 0.1 M (D) 0.25 M

Sol.

	$Al_2(SO_4)_3$	+ $BaCl_2$	$\longrightarrow BaSO_4\downarrow$	+ $AlCl_3$
Initial Meq.	10 × 0.4 × 6 = 24	20 × 0.6 × 2 = 24	0	0
Final Meq.	0	0	24	24

$[Al^{3+}] = \frac{24}{30 \times 3} = 0.266$ M

Hence **(A)** is the correct answer.

Ex. 7 0.52 g of a dibasic acid required 100 mL of 0.2 N NaOH for complete neutralization. The equivalent weight of acid is

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

Sol. Meq. of Acid = Meq. of NaOH

$\frac{0.52}{E} \times 1000 = 100 \times 0.2$

□ E = 26

Hence **(A)** is the correct answer.

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. H_2O_2 reduces MnO_4^- ion to

(A) Mn^+ (B) Mn^{2+}

(C) Mn^{3+} (D) Mn^-

2. When a sulphur atom becomes a sulphide ion

(A) There is no change in the composition of atom

(B) It gains two electrons

(C) The mass number changes

(D) None of these

3. The ultimate products of oxidation of most of hydrogen and carbon in food stuffs are

(A) H_2O alone (B) CO_2 alone

(C) H_2O and CO_2 (D) None of these

4. When P reacts with caustic soda, the products are PH_3 and NaH_2PO_2. This reaction is an example of

(A) Oxidation

(B) Reduction

(C) Oxidation and reduction (Redox)

(D) Neutralization

5. Which one of the following does not get oxidised by bromine water

(A) Fe^{2+} to Fe^{3+} (B) Cu^+ to Cu^{2+}

(C) Mn^{2+} to MnO_4^- (D) Sn^{3+} to Sn^{+4}

6. In the reaction $H_2S + NO_2 \rightarrow H_2O + NO + S$. H_2S is

(A) Oxidised (B) Reduced

(C) Precipitated (D) None of these

7. The conversion of PbO_2 to $Pb(NO_3)_2$ is

(A) Oxidation

(B) Reduction

(C) Neither oxidation nor reduction

(D) Both oxidation and reduction

8. In the course of a chemical reaction an oxidant

(A) Loses electrons

(B) Gains electrons

(C) Both loses and gains electron

(D) Electron change takes place

9. $2CuI \rightarrow Cu + CuI_2$, the reaction is

(A) Redox (B) Neutralisation

(C) Oxidation (D) Reduction

10. H_2S reacts with halogens, the halogens

(A) Form sulphur halides (B) Are oxidised

(C) Are reduced (D) None of these

11. Equation $H_2S + H_2O_2 \rightarrow S + 2H_2O$ represents

(A) Acidic nature of H_2O_2

(B) Basic nature of H_2O_2

(C) Oxidising nature of H_2O_2

(D) Reducing nature of H_2O_2

12. In the reaction

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

the reductant is

(A) $C_2O_4^{2-}$ (B) MnO_4^-

(C) Mn^{2+} (D) H^+

13. A reducing agent is a substance which can

(A) Accept electron (B) Donate electrons

(C) Accept protons (D) Donate protons

14. Which of the following is the most powerful oxidizing agent

(A) F_2 (B) Cl_2

(C) Br_2 (D) I_2

15. Of the four oxyacids of chlorine the strongest oxidising agent in dilute aqueous solution is

(A) $HClO_4$ (B) $HClO_3$

(C) $HClO_2$ (D) $HOCl$

16. Identify the correct statement about H_2O_2

(A) It acts as reducing agent only

(B) It acts as both oxidising and reducing agent

(C) It is neither an oxidiser nor reducer

(D) It acts as oxidising agent only

17. Several blocks of magnesium are fixed to the bottom of a ship to

(A) Keep away the sharks

(B) Make the ship lighter

(C) Prevent action of water and salt

(D) Prevent puncturing by under-sea rocks

18. Which of the following behaves as both oxidising and reducing agents

(A) H_2SO_4 (B) SO_2

(C) H_2S (D) HNO_3

Exercise # 2

SINGLE OBJECTIVE | AIIMS LEVEL

1. In which of the following acid, which acid has oxidation reduction and complex formation properties

(A) HNO_3 (B) H_2SO_4
(C) HCl (D) HNO_2

2. The compound which could not act both as oxidising as well as reducing agent is

(A) SO_2 (B) MnO_2
(C) Al_2O_3 (D) CrO

3. Of all the three common mineral acids, only sulphuric acid is found to be suitable for making the solution acidic because

(A) It does not react with $KMnO_4$ or the reducing agent
(B) Hydrochloric acid reacts with $KMnO_4$
(C) Nitric acid is an oxidising agent which reacts with reducing agent
(D) All of the above are correct

4. For H_3PO_3 and H_3PO_4 the correct choice is

(A) H_3PO_3 is dibasic and reducing
(B) H_3PO_3 is dibasic and non-reducing
(C) H_3PO_4 is tribasic and reducing
(D) H_3PO_3 is tribasic and non-reducing

5. Match List I with List II and select the correct answer using the codes given below the lists

List I (Compound)	List II (Oxidation state of N)
(A) NO_2	(1) +5
(B) HNO	(2) -3
(C) NH_3	(3) + 4
(D) N_2O_5	(4) +1

Codes :

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

6. M^{3+} ion loses $3e^-$. Its oxidation number will be

(A) 0 (B) +3
(C) + 6 (D) -3

7. Oxidation number of oxygen in potassium super oxide (KO_2) is

(A) - 2 (B) -1
(C) - 1/2 (D) - 1/4

8. One mole of N_2H_4 loses 10 mol of electrons to form a new compound Y. Assuming that all nitrogen appear in the new compound, what is the oxidation state of N_2 in Y ? (There is no change in the oxidation state of hydrogen)

(A) + 3 (B) - 3
(C) - 1 (D) +5

9. An element A in a compound ABD has oxidation number A^{n-}. It is oxidised by $Cr_2O_7^{2-}$ in acid medium. In the experiment 1.68×10^{-3} moles of $K_2Cr_2O_7$ were used for 3.26×10^{-3} moles of ABD. The new oxidation number of A after oxidation is

(A) 3 (B) 3 –n
(C) n – 3 (D) +n

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

(A) $H_2S_2O_7 > Na_2S_4O_6 > Na_2S_2O_3 > S_8$
(B) $H_2SO_5 > H_2SO_3 > SCl_2 > H_2S$
(C) $SO_3 > SO_2 > H_2S > S_8$
(D) $H_2SO_4 > SO_2 > H_2S > H_2S_2O_8$

11. In which of the following reaction is there a change in the oxidation number of nitrogen atoms :-

(A) $2\,NO_2 \rightarrow N_2O_4$
(B) $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$
(C) $N_2O_5 + H_2O \rightarrow 2HNO_3$
(D) none

12. For the redox reaction :

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

the correct stoichiometric coefficients of MnO_4^-, $C_2O_4^{2-}$ and H^+ are respectively

(A) 2,5,16 (B) 16,5,2
(C) 5,16,2 (D) 2,16,5

13. A certain weight of pure $CaCO_3$ is made to react completely with 200 mL of an HCl solution to give 224 mL of CO_2 gas at STP. The normality of the HCl is :-

(A) 0.05 N (B) 0.1N
(C) 1.0 N (D) 0.2 N

14. The volume of 1.5 M H_3PO_4 solution required to neutralize exactly 90 mL of a 0.5 M $Ba(OH)_2$ solution is :-

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

Exercise # 3 PART - 1 MATRIX MATCHCOLUMN

1.

Column-I	Column-II
(A) Molarity	**(p)** Dependent on temperature
(B) Molality	**(q)** $\frac{M_A \times n_A}{n_AM_A + n_BM_B}$ x 100
(C) Mole fraction	**(r)** Independent of temperature
(D) Mass %	**(s)** $\frac{X_A}{X_BM_B} \times 1000$

Where M_A, M_B are molar masses, n_A, n_B are no of moles & X_A, X_B are mole fractions of solute and solvent respectively.

2.

Column-I	Column-II
(A) 100 ml of 0.2 M $AlCl_3$ solution + 400 ml	**(p)** Total concentration of cation**(s)** = 0.12 M of 0.1 M HCl solution
(B) 50 ml of 0.4 M KCl + 50 ml H_2O	**(q)** $[SO_4^{2-}] = 0.06$ M
(C) 30 ml of 0.2 M K_2SO_4 + 70 ml H_2O	**(r)** $[SO_4^{2-}] = 2.5$ M
(D) 200 ml 24.5% (w/v) H_2SO_4	**(s)** $[Cl^-] = 0.2$ M

3.

Column-I	Column-II
(A) 4.1 g H_2SO_3	**(p)** 200 mL of 0.5 N base is used for complete neutralization
(B) 4.9 g H_3PO_4	**(q)** 200 millimoles of oxygen atoms
(C) 4.5 g oxalic acid ($H_2C_2O_4$)	**(r)** Central atom is in its highest oxidation number
(D) 5.3 g Na_2CO_3	**(s)** May react with an oxidising agent

4.

Column-I	Column-II
(A) Sn^{+2} + MnO_4^- (acidic) 3.5 mole 1.2 mole	**(p)** Amount of oxidant available decides the number of electrons transfer
(B) $H_2C_2O_4$ + MnO_4^- (acidic) 8.4 mole 3.6 mole	**(q)** Amount of reductant available decides the number of electrons transfer
(C) $S_2O_3^{-2}$ + I_2 7.2 mole 3.6 mole	**(r)** Number of electrons involved per mole of oxidant > Number of electrons involved per mole of reductant
(D) Fe^{+2} + $Cr_2O_7^{-2}$ (acidic) 9.2 mole 1.6 mole	**(s)** Number of electrons involved per mole of oxidant < Number of electrons involved per mole of reductant.

Exercise # 4

PART - 1

PREVIOUS YEAR (NEET/AIPMT)

1. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ion in acidic solution **[AIPMT (Prelims)–2007]**

(A) 1 **(B)** $\frac{3}{5}$

(C) $\frac{4}{5}$ **(D)** $\frac{2}{5}$

2. Oxidations numbers of P in PO_4^{3-}, of S in SO_4^{2-} and that of Cr in $Cr_2O_7^{2-}$, are respectively **[AIPMT (Prelims)–2009]**

(A) +3 , +6 and +5 **(B)** +5 , +3 and +6

(C) –3 , +6 and +6 **(D)** +5 , +6 and +6

3. Oxidation states of P in $H_4P_2O_5$, $H_4P_2O_6$, $H_4P_2O_7$ are respectively **[AIPMT (Prelims)–2010]**

(A) +3 , +5 ,+4 **(B)** +5 ,+3, +4

(C) +5, +4, +3 **(D)** +3 , +4,+5

4. How much amount of $CuSO_4.5H_2O$ required for liberation of 2.54 g I_2 when titrated with KI **[AIIMS-2011]**

(A) 2.5 gm **(B)** 4.99 gm

(C) 2.4 gm **(D)** 1.2 gm

5. A solution contains Fe^{2+}, Fe^{3+} and I^- ions. This solution was treated with iodine at 35°C. E° for Fe^{3+}/Fe^{2+} is 0.77 V and E° for $I_2/2I^-$ = 0.536 V. The favourable redox reaction is **[AIPMT (Mains)–2011]**

(A) I^- will be oxidised to I_2

(B) Fe^{2+} will be oxidised to Fe^{3+}

(C) I_2 will be reduced to I^-

(D) There will be no redox reaction

6. In which of the following compounds, nitrogen exhibits highest oxidation state ? **[AIPMT (Prelims) –2012]**

(A) N_3H **(B)** NH_2OH

(C) N_2H_4 **(D)** NH_3

7. (a) $H_2O_2 + O_3 \rightarrow H_2O + 2O_2$ **[AIPMT - 2014]**

(b) $H_2O_2 + Ag_2O \rightarrow 2Ag + H_2O + O_2$

Role of hydrogen peroxide in the above reactions is respectively

(A) Oxidizing in (a) and reducing in (b)

(B) Reducing in (a) and oxidising in (b)

(C) Reducing in (a) and (b)

(D) Oxidising in (a) and (b)

8. Which of the following processes does not involve oxidation of iron ? **[AIPMT - 2015]**

(A) Liberation of H_2 from steam by iron at high temperature

(B) Rusting of iron sheets

(C) Decolourization of blue $CuSO_4$ solution by iron

(D) Formation of $Fe(CO)_5$ from Fe

9. Assuming complete ionization, same moles of which of the following compounds will require the least amount of acidified $KMnO_4$ for complete oxidation ? **[Re -AIPMT - 2015]**

(A) FeC_2O_4 **(B)** $Fe(NO_2)_2$

(C) $FeSO_4$ **(D)** $FeSO_3$

MOCK TEST

1. Amongst the following identify the species with an atom in + 6 oxidation state

(A) MnO_4^- **(B)** $Cr(CN)_6^{3-}$ **(C)** NiF_6^{2-} **(D)** CrO_2Cl_2

2. In which of the following compounds, is the oxidation number of iodine is fractional

(A) IF_3 **(B)** IF_2 **(C)** I_3^- **(D)** IF_7

3. The compound $YBa_2Cu_3O_7$ which shows superconductivity has copper in oxidation state..........Assume that the rare earth element Yttrium is in its usual +3 oxidation state

(A) 3/7 **(B)** 7/3 **(C)** 3 **(D)** 7

4. The oxidation number of sulphur in S_8, S_2F_2, H_2S respectively, are

(A) 0, +1 and - 2 **(B)** + 2, +1 and - 2 **(C)** 0, + 1 and + 2 **(D)** - 2, + 1 and - 2

5. Which one of the following reactions is not an example of redox reaction

(A) $Cl_2 + 2H_2O + SO_2 \rightarrow 4H^+ + SO^{4-} + 2Cl^-$ **(B)** $Cu^{++} + Zn \rightarrow Zn^{++} + Cu$

(C) $2H_2 + O_2 \rightarrow 2H_2O$ **(D)** $HCl + H_2O \rightarrow H_3O^- + Cl^-$

6. For the reactions, $C + O_2 \rightarrow CO_2$; $\Delta H = -393J$

$2\,Zn + O_2 \rightarrow 2\,ZnO$; $\Delta H = -412J$

(A) Carbon can oxidise Zn **(B)** Oxidation of carbon is not feasible

(C) Oxidation of Zn is not feasible **(D)** Zn can oxidise carbon

7. In the reaction $B_2H_6 + 2KOH + 2X \rightarrow 2Y + 6H_2$, X and Y are respectively

(A) H_2, H_3BO_3 **(B)** HCl, KBO_3 **(C)** H_2O, KBO_3 **(D)** H_2O, KBO_2

8. In a balanced equation $H_2SO_4 + x\,HI \rightarrow H_2S + y\,I_2 + z\,H_2O$, the values of x, y, z are

(A) x = 3, y = 5, z = 2 **(B)** x = 4, y = 8, z = 5 **(C)** x = 8, y = 4, z = 4 **(D)** x = 5, y = 3, z = 4

9. Which of the following can act as an acid and as a base

(A) $HClO_3^-$ **(B)** $H_2PO_4^-$ **(C)** HS^- **(D)** All of these

10. MnO_4^{2-} (1 mole) in neutral aqueous medium is disproportionate to

(A) 2/3 mole of MnO_4^- and 1/3 mole of MnO_2 **(B)** 1/3 mole of MnO_4^- and 2/3 mole of MnO_2

(C) 1/3 mole of Mn_2O_7 and 1/3 mole of MnO_2 **(D)** 2/3 mole of Mn_2O_7 and 1/3 mole of MnO_2

11. The conductivity of a saturated solution of $BaSO_4$ is $3.06 \times 10^{-6}\,ohm^{-1}\,cm^{-1}$ and its equivalent conductance is $1.53 ohm^{-1}\,cm^{-1}\,equivalent^{-1}$. The K_{sp} of the $BaSO_4$ will be

(A) 4×10^{-12} **(B)** 2.5×10^{-9} **(C)** 2.5×10^{-13} **(D)** 4×10^{-6}

12. When MnO_2 is fused with KOH, a coloured compound is formed, the product and its colour is

(A) K_2MnO_4, purple green **(B)** $KMnO_4$, purple

(C) Mn_2O_3, brown **(D)** Mn_3O_4 black

13. In the following reaction,

$3Br_2 + 6CO_3^{2-} + 3H_2O = 5Br^- + BrO_3^- + 6HCO_3$

(A) Bromine is oxidised and carbonate is reduced **(B)** Bromine is reduced and water is oxidised

(C) Bromine is neither reduced nor oxidised **(D)** Bromine is both reduced and oxidised

CHAPTER 07

LOCK ELEMENTS

> *if all the elements are arranged in the order of atomic weights, a periodic repitition is obtained. This is expressed by the law of periodicity.*

'' DMITRIMENDELEEV''

INTRODUCTION

The elements is which last electron enters into p-subshell are called as p-block elements. The number of p-orbitals are three and, therefore, the maximum number of electrons that can be accommodated in a set of p-orbitals is six, hence p-block contains six groups. The general electronic configuration of these elements is ns^2np^{1-6} **(except forHe)**.

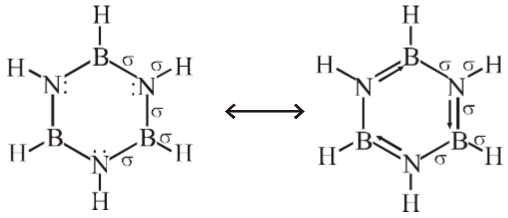
p-block elements can be either metals, metalloids or non-metals. Maximum oxidation state shown by p-block elements is equal to the sum of valence electrons (i.e., sum of s-and p-electrons) or the group number minus 10 known as group oxidation state.

Absence of d-orbitals in the elements of second period and presence of d- and f-orbitals in rest of elements have significant effects on the properties as a result lower oxidation state will be more stable. This effect is known as **inert pair effect**.

(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

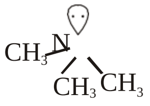
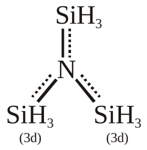
(2) pπ-dπ back bonding :

$$\underset{\substack{\text{2nd period}\\\text{with lp}}}{p} \xrightarrow{\hspace{1cm}} \underset{\substack{\text{3rd period}\\\text{empty}}}{d}$$

it is used to explain following observations :

(a) Hybridisation

Ex.

Trimethyl amine	**Trisilyl amine**
$(CH_3)_3N$	$(SiH_3)_3N$
	
• sp^3 hybrid (N)	• sp^2 hybrid (N)
• trigonal pyramidal	• trigonal planar
• Lewis base (due to presence of lp)	• Not Lewis base
	• Bond angle increases

(b) Acidic strength

$CH_3 - \ddot{O} - H$ Methyl alcohol	$SiH_3 - \ddot{O} - H$ Silyl alcohol
• No back bonding	• Back bonding present in conjugate base
• Less acidic	• More acidic

(II) Dimerisation / Polymerisation

Types of Dimerisation

3C—2e	3C—4e
B_2H_6	$(BeCl_2)_2$
$(BeH_2)_2$	$(BeCl_2)_n$
$(BeH_2)_n$	$(AlCl_3)_2$
$Al_2(CH_3)_6$	$(ICl_3)_2$
$Ga_2(CH_3)_6$	

ED OS KEY POINTS

Reactivity towards halogen :

Element in pure state	Type of bonding	Meling Point
C	Covalenet	4100°C
Si	Covalent	1420°C
Ge	Covalnet	945°C
Sn	Metallic	232°C
Pb	Metallic	327°C

On moving down the group from carbon to lead stability of +4 oxidation state decreases while stability of +2 oxidation state increases andd hence decreases oxidising power decreases down the group due to inert pair effect.

These elements form two types of hallides – MX_2 and MX_4. Most of the MX_4 are covalent. SnF_4 and PbF_4 are ionic in nature.

Thermal stability decreases with increasing atomic size of molecular mass of tetrahalide or due to decreasing polarity.

$CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$ and

$CF_4 > CCl_4 > CBr_4 > Cl_4$

In these compounds :

Hybridisation → sp^3

Geometry → Regular tetrahedral

Polarity → NON-POLAR

Bond angle → 109° 28′

PbI_4 is not stable as I^- is strong reducing agent which reduces Pb^{+4} to Pb^{+2} and also stability of +4 oxidation state of Pb is lesser than +2 state.

Sodium Zeolite [$Na_2Al_2Si_2O_8$] / [$Na_2O.Al_2O_3.2SiO_2$]

(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.

BORON FAMILY

(1) Amorphous boron of low purity (called moissan boron) is obtained by reducing B_2O_3 with Mg or Na at a high temperature. It is 95–98% pure (being contaminated with metal borides), and is black in colour.

$$Na_2[B_4O_5(OH)_4].8H_2O \xrightarrow{\text{acid}} H_3BO_3 \xrightarrow{\text{heat}} B_2O_3 \xrightarrow{\text{Mg or Na}} 2B + 3MgO$$

(2) BORANES

Boranes are boron hydrogen compounds with general molecular formula B_nH_{n+4} or $B_n\ H_{n+6}$.They are electron deficient compounds.

(3) ALUM

Alums are double sulphates with their general formula $R_2SO_4.M_2(SO_4)_3.24H_2O$ where R = monovalent radical like Na^+ , K^+, NH_4^+ and M = Trivalent radical like Al^{+3}, Cr^{+3}. Fe^{+3}.

CARBON FAMILY

(1) Carbon is found in nature in various allotropic forms which are:

(i) Crystalline Form : Diamond, Graphite, Fullerenes

(ii) Amorphous Form : Coal

(2) SILICON (Si)

Silicon is the second most abundant (27.2%) element after oxygen (45.5%) in the earth's crust. It does not occur free in nature but in the combined state, it occurs widely in form of silica and silicates. All mineral rocks, clays and soils are built of silicates of magnesium, aluminium, potassium or iron. Aluminium silicate is however the most common constituent of rocks and clays.

Silica is found in the free state in sand, flint and quartz and in the combined state as silicates like

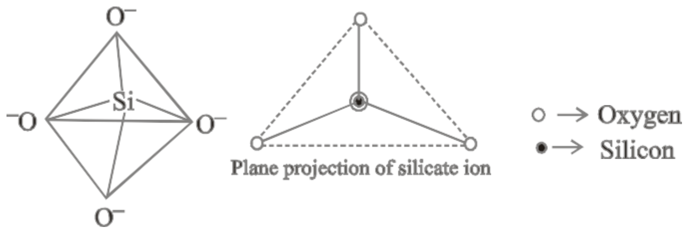
(a) Feldspar – $K_2O.Al_2O_3.6SiO_2$

(b) Kaolinite – Al_2O_3. 2 SiO_2. $2H_2O$

(c) Asbestos – CaO. 3MgO.4SiO_2

Silicates are also important :

Silicates have basic unit of SiO_4^{4-}, each silicon atom is bonded with four oxide ions tetrahedrally.



SOLVED EXAMPLE

Ex.1 By adding gypsum to cement

(A) Setting time of cement becomes less

(B) Setting time of cement increases

(C) Colour of cement becomes light

(D) Shining surface is obtained

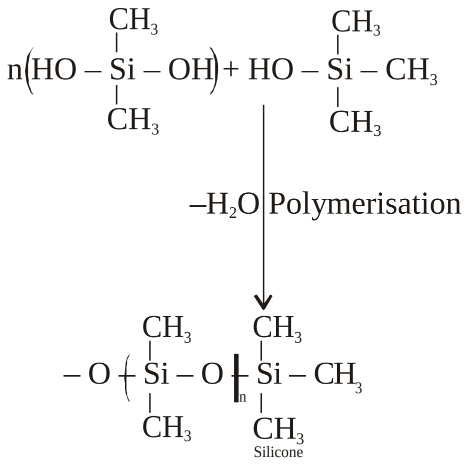
Ans. **(B)** Raw materials for cement-limestone, clay, gypsum, Cement is a dirty greyish heavy powder containing calcium aluminates and silicated.

Gypsum ($CaSO_4.5H_2O$) is added to the components to increases the setting time of cement to that it gets sufficiently hardened. Setting of cement is an exothermic process and involves hydration of calcium aluminated and silicates.

Ex. 2 Silcon has a strong tendency to form polymers like silicones. The chain length of silicon polymer can be controlled by adding

(A) $MeSiCl_3$	**(B)** Me_2SiCl_2
(C) Me_3SiCl	**(D)** Me_4Si

Ans. **(C)** Silicon has a strong tendency to form polymers like silicones. The chain length of silicon polymer can be controlled by adding Me_3SiCl which block the ends as shown below



Ex. 3 Quartz is extensively used as a piezoelectric material. it contains......

(A) Pb	**(B)** Si
(C) Ti	**(D)** Sn

Ans. **(B)** Quartz, cristobalite and tridymite are some of the crystalline forms of silica and they are intercovertable at suitable temperature. Quartz is edxtensively used as a piezoelectric material.

Ex.4 The most commonly used reducing agent is

(A) $AlCl_3$	**(B)** $PbCl_2$
(C) $SnCl_4$	**(D)** $SnCl_2$

Ans. **(D)** Reducing agents are those substance which resduced other subastance and it self oxidises

In $SnCl_2$, Sn exists in +2 oxidation state, thus, acts as a strong reducing agent i.e.,

$$SnCl_2 + 2FeCl_3 \longrightarrow 2FeCl_2 + SnCl_4$$

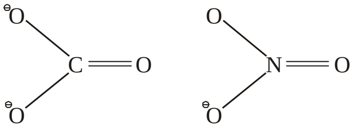
$$SnCl_2 + 2CuCl_2 \longrightarrow 2CuCl + SnCl_4$$

Ex.5 Which of the following piars of ions are isolectonic and isostructural

(A) CO_3^{2-}, NO_3^-	**(B)** ClO_3^-, CO_3^{2-}
(C) SO_3^{2-}, NO_3^-	**(D)** ClO_3^-, SO_3^{2-}

Ans. **(A)** Compounds having same value of total number of electrons are known as isolectronic.

For CO_3^{2-}	For NO_3^-
Total number of electons	Total number of electrons
$= 6 + 8 \times 3 + 2$	$= 7 + 8 \times 3 + 1$
$= 6 + 24 + 2$	$= 7 + 25$
$= 32$	$= 32$



Hence, CO_3^{2-} and NO_3^- are isolectronic. These two ions have similar structure so they are isostructural. Both have triangular planar structure as in both the species carbon and nitrogen are sp^2 hybridised.

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. The most acidic of the following compounds is

(A) P_2O_3 **(B)** Sb_2O_3
(C) B_2O_3 **(D)** As_2O_3

2. Identify the statement that is not correct as far as structure of diborane is concerned

(A) There are two bridging hydrogen atoms in diborane
(B) Each boron atom forms four bonds in diborane
(C) The hydrogen atoms are not in the same plane in diborane
(D) All B - H bonds in diborane are similar

3. Soft heavy metal melts at and is used in making heat sensitive thermometers the metal is

(A) Galium **(B)** Sodium
(C) Potassium **(D)** Caesium

4. Which of the following is formed when aluminium oxide and carbon is strongly heated in dry chlorine gas

(A) Aluminium chloride
(B) Hydrate aluminium chloride
(C) Anhydrous aluminium chloride
(D) None of these

5. Which metal burn in air at high temperature with the evolution of much heat

(A) Cu **(B)** Hg
(C) Pb **(D)** Al

6. Aluminium hydroxide is soluble in excess of sodium hydroxide forming the ion

(A) AlO_2^{+3} **(B)** AlO_2^{-3}
(C) AlO_2^{-} **(D)** AlO_3^{-}

7. Boron form covalent compound due to

(A) Higher ionization energy
(B) Lower ionization energy
(C) Small size
(D) Both **(A)** and **(C)**

8. In diborane, the two H–B–H angles are nearly

(A) 60°, 120° **(B)** 95°,120°
(C) 95°,150° **(D)** 120°,180°

9. Which of the following is a non-metal

(A) Gallium **(B)** Indium
(C) Boron **(D)** Aluminium

10. Which of the following is most acidic

(A) Na_2O **(B)** MgO
(C) Al_2O_3 **(D)** CaO

11. When orthoboric acid (H_3BO_3) is heated, the residue left is

(A) Metaboric acid **(B)** Boron
(C) Boric anhydride **(D)** Borax

12. Silicon dioxide is formed by the reaction of

(A) $SiCl_4 + 2H_2O$ **(B)** $SiO_2 + 4HF$
(C) $SiO_2 + NaOH$ **(D)** $SiCl_4 + NaOH$

13. Which alkali metal carbonate decomposes on heating to liberate CO_2 gas

(A) Li_2CO_3 **(B)** $CaCO_3$
(C) Na_2CO_3 **(D)** Al_2CO_3

14. Which of the following gives propyne on hydrolysis

(A) Al_4C_3 **(B)** Mg_2C_3 **(C)** B_4C **(D)** La_4C_3

15. Which one of the following statements is not correct

(A) Zinc dissolves in sodium hydroxide solution
(B) Carbon monoxide reduces iron (III) oxide to iron
(C) Mercury (II) iodide dissolves in excess of potassium iodide solution
(D) Tin (IV) chloride is made by dissolving tin solution in concentrated hydrochloric acid

16. In laboratory silicon can be prepared by the reaction

(A) By heating carbon in electric furnace
(B) By heating potassium with potassium dichromate
(C) Silica with magnesium
(D) None of these

17. Which of the following is the correct statement for red lead

(A) It is an active form of lead
(B) Its molecular formula is Pb_2O_3
(C) It decomposes into Pb andm CO_2
(D) It decomposes into PbO and O_2

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. Boric acid polymerizes due to –
(A) The presence of hydrogen bonds
(B) Its acidic nature
(C) Its geometry
(D) Its monobasic nautre

2. Aluminium is obtained by–
(A) Reduction of Al_2O_3 with coke
(B) Electrolysis of Al_2O_3 dissolved in Na_3AlF_6
(C) Reduction of Al_2O_3 with chromium
(D) Heating cryolite and alumina

3. In thermite welding, aluminium acts as –
(A) A solder
(B) A flux
(C) An oxidising agent
(D) A reducing agent

4. The final product obtained when boric acid is heated to red heat is –
(A) Metaboric acid
(B) Tetraboric acid
(C) Boron oxide
(D) Pyroboric acid

5. Which of the following can be detected by the borax-bead test ?
(A) Ni^{2+}
(B) Co^{2+}
(C) Pb^{+2}
(D) Both (A) & (B)

6. The hydrides of boron are called
(A) Boron hydrogen compounds
(B) Hydrogen borides
(C) Boranes
(D) Hydroboric acids

7. Which one of the following mixed sulphates is not an alum ?
(A) $K_2SO_4.Al_2(SO_4)_3.24H_2O$
(B) $K_2SO_4.Cr_2(SO_4)_3.24H_2O$
(C) $Na_2SO_4.Fe(SO_4)_3.24H_2O$
(D) $CuSO_4.Al_2(SO_4)_3.24H_2O$

8. Higher percentage of carbon is found in –
(A) Anthracite
(B) Lignite
(C) Bituminous
(D) Peat

9. From B_2H_6, all the following can be prepared except –
(A) B_2O_3
(B) H_3BO_3
(C) $B_2(CH_3)_6$
(D) $NaBH_4$

10. The product formed in the reaction,
$BCl_3 + H_2O \longrightarrow$ Product is –
(A) $H_3BO_3 + HCl$
(B) $B_2O_3 + HOCl$
(C) $B_2H_6 + HCl$
(D) No reaction

11. Silicones have the general formula –
(A) SiO_4^{4-}
(B) $Si_2O_7^{6-}$
(C) $(R_2SiO)_n$
(D) $(SiO_3)_n^{2-}$

12. In which of the following there exists a $p\pi - d\pi$ bonding –
(A) Diamond
(B) Graphite
(C) Dimethylamine
(D) Trisilylamines

13. Glass or silica soluble in –
(A) $HClO_4$
(B) HF
(C) Aqua-regia
(D) H_2SO_4

14. The species present in solution when CO_2 is dissolved in water are –
(A) $CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}$
(B) H_2CO_3, CO_3^{2-}
(C) CO_3^{2-}, HCO_3^-
(D) CO_2, H_2CO_3

15. P_2O_5 is used extensively as a –
(A) Dehydrating agent
(B) Catalytic agent
(C) Reducing agent
(D) Preservative

16. The number of molecules of water needed to convert one molecules of P_2O_5 into orthophosphoric acid is –
(A) 2
(B) 3
(C) 4
(D) 5

17. Producer gas is a mixture of –
(A) CO and N_2
(B) CO_2 and H_2
(C) CO and H_2
(D) CO_2 and N_2

18. Which variety of glass is used for manufacture of optical glasses ?
(A) Sodium glass
(B) Flint glass
(C) Ground glass
(D) Quartz

19. The colour imparted by Co(II) compounds to glass is –
(A) Green
(B) Deep–Blue
(C) Yellow
(D) Red

20. In warfare smoke screens are prepared from –
(A) PH_3
(B) CaC_2
(C) P_2O_5
(D) $COCl_2$

21. In Haber's process for the manufacture of ammonia, the catalyst used is –
(A) Finely divided nickel
(B) Finely divided molybdenum
(C) Finely divided iron
(D) Finely divided platinum

Exercise # 3 PART - 1 MATRIX MATCHCOLUMN

1. Match the reactions listed in column-I with characteristic(s) / type of reactions listed in column-II.

Column-I	Column-II
(A) $BBr_3 + H_2 \longrightarrow B$	(p) Borax bead test
(B) $Na_2B_4O_7.\ 10\ H_2O + CuSO_4 \rightarrow Cu(BO_2)_2$	(q) Reduction
(C) $AlCl_3 + H_2O \longrightarrow HCl$	(r) White fumes
(D) $Cr_2O_3 + Al \longrightarrow Cr$	(s) Hydrolysis

2. Match the reactions listed in column-I with characteristic(s) / type of reactions listed in column-II.

Column-I	Column-II
(A) $Al_2(C_2)_3 + H_2O \longrightarrow$	(p) One of the products contains both σ and π bonds
(B) $CH_2(COOH)_2 + P_4O_{10} \longrightarrow$	(q) Hydrolysis
(C) $CH_3SiCl_3 + H_2O \longrightarrow$	(r) Dehydration
(D) $SnCl_2.2H_2O \xrightarrow[\text{standing}]{\text{on}}$	(s) complex crosslinked polymer

3. Match the reactions listed in column-**I** with the product(s) listed in column-**II**.

Column–I	Column–II
(A) $B_2O_3 + H_2O$	(p) H_3BO_3
(B) $B_2H_6 + H_2O$	(q) H_2
(C) $B_3N_3H_6 + H_2O$	(r) HCl
(D) $BCl_3 + H_2O$	(s) NH_3
	(t) N_2

4. Match the type of silicates listed in column-I with characteristic(s) listed in column-II.

Column–I	Column–II
(A) Cyclic silicates	(p) Tetrahedral hybridisation.
(B) Single chain silicates	(q) Si–O bonds are 50% ionic and 50% covalent.
(C) Pyro silicates	(r) General formula is $(SiO_3)_n^{2n-}$
(D) Sheet silicates (two dimensional)	(s) Two oxygen atoms per tetrahedron are shared.

5. Match the materials listed in column-I with type of silicates listed in column-II.

Column–I	Column–II
(A) Spondumene	(p) Two dimensional sheet silicates
(B) Thorteveitite	(q) Pyrosilicates
(C) Kaolin	(r) Chain silicates
(D) Quartz	(s) Three dimensional sheet silicates.

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. Which one of the following arrangements does not truly represent the property indicated against it? **[CBSE AIPMT 2000]**

(A) $Br_2 < Cl_2 < F_2$ Oxidising power
(B) $Br_2 < Cl_2 < F_2$ Electronegativity
(C) $Br_2 < F_2 < Cl_2$ Electron affinity
(D) $Br_2 < Cl_2 < F_2$ Bond energy

2. Among the following the electron deficient compound is **[CBSE AIPMT 2000]**

(A) BCl_3 **(B)** CCl_4
(C) PCl_5 **(D)** $BeCl_2$

3. Nitogen forms N_2, but phosphorus when form P_2 readily converted into P_4 reason is **[CBSE AIPMT 2001]**

(A) triple bond present between phosphorus atom
(B) pπ -pπ bonding is weak
(C) pπ – bonding is strong
(D) multiple bond form easily

4. Which reaction is not feasible ? **[CBSE AIPMT 2002]**

(A) $2KI + Br_2 \longrightarrow 3KBr + I_2$
(B) $2KBr + I_2 \longrightarrow 2KCl + Br_2$
(C) $2KBr + Cl_2 \longrightarrow 2KCl + Br_2$
(D) $2H_2O + 2F_2 \longrightarrow 4HF + O_2$

5. Which of the following statements is true? **[CBSE AIPMT 2002]**

(A) Silicon exhibits 4 coordination number in its compounds
(B) Bond energy of F_2 is less than Cl_2
(C) Mn(III) oxidation state is more stable than Mn(II) in aqueous state
(D) Elements of 15th group shows only +3 and +5 oxidation states

6. In borax bead test which compound is formed? **[CBSE AIPMT 2002]**

(A) Ortho borate **(B)** Meta borate
(C) Double oxide **(D)** Tetra Borate

7. Zn gives H_2 gas with H_2SO_4 and HCl but not with HNO_3 because **[CBSE AIPMT 2002]**

(A) Zn act as oxidising agent when react with HNO_3
(B) HNO_3 is weaker acid than H_2SO_4 and HCl
(C) In electrochemical series Zn is placed above hydrogen
(D) NO_3^- is reduced in preference to hydronium ion

8. The oxidation states of sulphur in the anious SO_3^{2-}, $S_2O_6^{2-}$ and $S_2O_6^{2-}$ follows the order **[CBSE AIPMT 2003]**

(A) $S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$
(B) $S_2O_6^{2-} < S_2O_4^{2-} < SO_3^{2-}$
(C) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$
(D) $SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$

9. Which one of the following compounds is not a protonic acid **[CBSE AIPMT 2003]**

(A) HOCl is a stronger acid than HOBr
(B) HF is a stronger acid than HCl
(C) Among hailde ions. iodide is the most powerful reducing agent
(D) Fluorine is the only halogen that does not show a variable oxidation state

10. Which one of the following compounds is not a protonic acid? **[CBSE AIPMT 2003]**

(A) $SO(OH)_2$ **(B)** $SO_2(OH)_2$
(C) $B(OH)_3$ **(D)** $PO(OH)_3$

11. Which one of the following statements about the zeolites is false ? **[CBSE AIPMT 2004]**

(A) They are used as cation exchangers
(B) They have open structure which enables them to take up small molecules
(C) Zeolites are aluminosilcates having three dimensional network
(D) Some of the SiO_4^{4-} units are replaced by AlO_4^{5-} and AlO_6^{9-} ions in zeolites

12. Which is the best description of behaviour of bromine in the reaction given below?

$H_2O + Br_2 \longrightarrow HBr + HoBr$ **[CBSE AIPMT 2004]**

(A) Only oxidised
(B) Only reduced
(C) Both oxidised and reduced
(D) Only proton accepted

MOCK TEST

STRAIGHT OBJECTIVE TYPE

1. Ozone with KI solution produces
(A) Cl_2 (B) I_2 (C) HI (D) IO_3

2. The gases respectively absorbed by alkaline pyrogallol and oil of cinnamon is
(A) O_3, CH_4 (B) O_2, O_3 (C) SO_2, CH_4 (D) N_2O, O_3

3. Ozone turns trimethyl paper
(A) Green (B) Violet (C) Red (D) Black

4. Ozone is obtained from oxygen
(A) By oxidation at high temperature (B) By oxidation using a catalyst
(C) By silent electric discharge (D) By conversion at high pressure

5. Which of the following statement is true about ozone layer
(A) It is harmful because ozone is dangerous to living organism
(B) It is beneficial because oxidation reaction can proceed faster in the presence of ozone
(C) It is beneficial because ozone cuts out the ultraviolet radiation of the sun
(D) It is harmful because ozone cuts out the important radiation of the sun which are vital for photosynthesis

6. The correct order of the thermal stability of hydrogen halides (H -X) is
(A) $HI > HBr > HCl > HF$ (B) $HF > HCl > HBr > HI$
(C) $HCl < HF < HBr < HI$ (D) $HI > HCl < HF < HBr$

7. Phosgene is the common name of
(A) Carbonyl chloride (B) Phosphine
(C) Phosphorus oxychloride (D) Phosphorus trichloride

8. The solubility of iodine in water increases in the presence of
(A) Alcohol (B) Chloroform (C) Sodium hydroxide (D) Potassium iodide

9. When thiosulphate ion is oxidised by iodine, which one of the following ion is produced
(A) SO_3^{2-} (B) SO_4^{2-} (C) $S_4O_6^{2-}$ (Tetrathionate) (D) $S_2O_6^{2-}$

10. Which one of the following noble gases is the least polarizable
(A) Xe (B) Ar (C) Ne (D) He

11. Which one of the following noble gases is not found in the atmosphere
(A) Rn (B) Kr (C) Ne (D) Ar

12. Helium is added to the oxygen supply used by deep sea divers because
(A) It is less soluble in blood than nitrogen at high pressure
(B) It is lighter than nitrogen
(C) It is readily miscible with oxygen
(D) It is less poisonous than nitrogen

13. Which of the following statements is not correct for a noble gas
(A) Ar is used in electric bulbs (B) Kr is obtained during radioactive disintegration
(C) Half life of Rn is only 3.8 days (D) He is used in producing very low temperature

14. Aqueous solution of orthoboric acid can be titrated against sodium hydroxide using phenolphthalein indicator only in the presence of :
(A) trans-glycerol (B) catechol (C) cis-glycerol (D) both (B) and (C)

CHAPTER 07

TRANSITION ELEMENTS (D & F - BLOCK)

I've always believed there are moments in our lives which can be defined as a transition between the before and after, between the cause and the effect.

''BENJAMINX. WRETLIND''

INTRODUCTION

The d-block of the periodic table contains the elements of the groups 3-12 in which the d orbitals are progressively filled in each of the four long periods. The elements constituting the f-block are those in which the 4 f and 5 f orbitals are progressively filled in the latter two long periods; these elements are formal members of group 3 from which they have been taken out to form a separate f-block of the periodic table. The names transition metals and inner transition metals are often used to refer to the elements of d-and f-blocks respectively.

There are mainly three series of the transition metals, 3d series (Sc to Zn), 4d series (Y to Cd) and 5d series (La to Hg, omitting Ce to Lu). The fourth 6d series which begins with Ac is still incomplete. The two series of the inner transition metals, (4f and 5f) are known as lanthanoids and actinoids respectively.

The presence of partially filled d or f orbitals in their atoms sets the study of the transition elements and their compounds apart from that of the main group elements. However, the usual theory of valence as applicable to the main group elements can also be applied successfully to the transition elements.

TRANSITION ELEMENTS (D & F BLOCK)

(a) The element lying between s- and p-block element of the periodic table are collectively known as transition or transitional elements. (T.E'.S.)

(b) Their properties are transitional between the highly electropositive s- block element to least electropositive p- block element.

(c) In d- block elements, the last differentiating electron is accommodated to the penultimate shell.

(d) The general electronic configuration of transition element is **(n-1)d1-10 ns0, 1 or 2**

(e) These elements either in their atomic state or in any of their common oxidation state have partly filled (n-1)d orbitals of (n-1)th main shell.

(f) The transition elements have an incompletely filled d-level. Since Zn, Cd, Hg elements have d^{10} configuration and are not considered as transition elements but they are d-block elements.

Electronic Configuration

Ist Transition Series

Symbol	Sc	Ti	V	**Cr**	Mn	Fe	Co	Ni	**Cu**	Zn
Atomic No.	21	22	23	**24**	25	26	27	28	**29**	30
3d electrons	1	2	3	**5**	5	6	7	8	**10**	10
4s electrons	2	2	2	**1**	2	2	2	2	**1**	2

Irregular electronic configuration Cr, Cu

IInd Transition Series

Symbol	Y	Zr	**Nb**	**Mo**	Tc	**Ru**	**Rh**	**Pd**	**Ag**	Cd
Atomic No.	39	40	**41**	**42**	43	**44**	**45**	**46**	**47**	48
4d electrons	1	2	**4**	**5**	5	**7**	**8**	**10**	**10**	10
5s electrons	2	2	**1**	**1**	2	**1**	**1**	**0**	**1**	2

Irregular electronic configuration Nb, Mo, Ru, Rh, Pd, Ag

IIIrd Transition Series

Symbol	La	Hf	Ta	**W**	Re	Os	Ir	**Pt**	**Au**	Hg
Atomic No.	57	72	73	**74**	75	76	77	**78**	**79**	80
5d electrons	1	2	3	**4**	5	6	7	**9**	**10**	10
6s electrons	2	2	2	**2**	2	2	2	**1**	**1**	2

ED OS KEY POINTS

Irregular electronic configuration W, Pt, Au

The irregularities in the observed configuration of Cr ($3d^5\ 4s^1$ instead of $3d^4\ 4s^2$), Cu ($3d^{10}\ 4s^1$), Mo ($4d^5\ 5s^1$), Pd ([Kr] $4d^{10}\ 5s^0$), Au ([Xe] $4f^{14}\ 5d^{10}\ 6s^1$), Ag ([Kr] $4d^{10}\ 5s^1$) are explained on the basis of the concept that half-filled and completely filled d-orbitals are relatively more stable than other d-orbitals.

d-block

1. The f-blocks elements differ from those of d-blocks elements in that they have unstable electroconfiguration in the outer shells in comparison to that of d-blocks element.

d-block elements	electronic configuration
	$(n-1)d^{1-10}ns^{1-2}$

Most common oxidation state +2

2. The colour in d-block elements is due to d-excitation while in f-block element, it is due to f-f transitions.

3. They show variable oxidation state due to less energy difference between ns and (n-1) d sub shell.

4. Most of the d-block compounds act as catalyst due to their variable oxidation state or complex formation tendency or adsorption on their surface. Example :

contact proecess = V_2O_5

Ostwald process = Pt/Rh

Haber process = $Fe_2O_3 + Al_2O_3 + K_2O$

Zeigter Natta = $TiCl_4 + (C_2H_5)_3Al$

Phenton reagent = $FeSO_4 + H_2O_2$

Hydrogenation of Alkene = Ni/Pd

Decomposition of $KClO_3$ = MnO_2

Wilkinsion catalyst = RhCl +PPh_3

5. Action of heat on copper sulphate

$$CuSO_4.5H_2O \xrightarrow{\text{Exposure}} CuSO_4.\,3H_2O \xrightarrow{\text{373K}} CuSO_4.H_2O \xrightarrow{\text{500K}} CuSO_4$$

Bluish green White

6. **Chemical volcano**. When crystals of red coloured ammonium dichromate are heated, a violent action takes place accompained by flashes of light and nitrogen is liberated leaving behind a dark green residue of chromium sesquioxide (Cr_2O_3)

$$(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3$$

Ammonium dichromate Chromium sesquioxide

SOLVED EXAMPLE

Ex. 1 Amongst $[TiF_6]^{2-}$, $[CoF_6]^{3-}$, Cu_2Cl_2 and $[NiCl_4]^{2-}$ [Atomic number ; Ti = 22, Co = 27, Cu = 29, Ni = 28] the colourless species are :

(A) $[TiF_6]^{2-}$ and $[Cu_2Cl_2]$ (B) Cu_2Cl_2 and $[NiCl_4]^{2-}$
(C) $[TiF_6]^{2-}$ and $[CoF_6]^{3-}$ (D) $[CoF_6]^{3-}$ and $[NiCl_4]^{2-}$

Ans. (A)

Sol. In $[TiF_6]^{2-}$ the titanium is in +4 oxidation state having the electronic configuration $[Ar]^{18} 3d^0 4s^0$. Similarly in Cu_2Cl_2 the copper is in +1 oxidation state having the electronic configuration $[Ar]^{18} 3d^{10} 4s^0$. As they do not have any unpaired electrons for d-d transition, they are therefore colourless.

In $[NiCl_4]^{2-}$ the nickel is in +2 oxidation state and electronic configuration is $[Ar]^{18} 3d^8 4s^0$. As it has two unpaired electrons, so the complex is coloured. In $[CoF_6]^{3-}$, the cobalt is in +3 oxidation state having electron configuration $[Ar]\ 3d^6 4s^0$. As it has four unpaired electrons, so the complex is coloured.

Ex. 2 On the basis of trends in the properties of the 3d-series elements, suggests possible M^{2+} aqua ions for use as reducing agents, and write a balanced chemical equation for the reaction of one of these ions with O_2 in acidic solution.

Sol. Because oxidation state +2 is most stable for the later elements of 3d-series elements, strong reducing agents include ions of the metals on the left of the series: such ions include V^{2+} (aq) and Cr^{2+} (aq) The Fe^{2+} (aq) ion is only weakly reducing. The Co^{2+} (aq), Ni^{2+} (aq), and Cu^{2+} (aq) ions are not oxidized in water.

$$Fe^{3+} \xrightarrow{+0.77} Fe^{2+} \xrightarrow{-0.44} Fe$$

The chemical equation for the oxidation is then

$$4\,Fe^{2+}(aq) + O_2(g) + 4H^+(aq) \longrightarrow 4Fe^{3+}(aq) + 2H_2O(\ell).$$

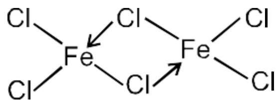
Ex. 3 Match the reactions given in column-I with the characteristic(s) of the reaction products given in column-II.

Column-I	Column-II
(A) $TiCl_4 \xrightarrow{Zn}$	(p) One of the products is bright orange coloured but diamagnetic.
(B) $FeCl_3 \xrightarrow{573K}$	(q) One of the products is green coloured and paramagnetic.
(C) $KMnO_4 \xrightarrow{750K}$	(r) One of the products is violet and paramagnetic.
(D) $K_2Cr_2O_7 + H_2SO_4$ (cold & conc.)	(s) One of the products exists as dimer.

Ans. [A – r] ; [B – s ; [C – q] ; [D – p].

Sol. (A) $TiCl_4 \xrightarrow{Zn} TiCl_3$, violet (one unpaired electron so d-d transition is possible).

(B) $2FeCl_3 \xrightarrow{573K}$



gas dimer.

(C) $2KMnO_4 \xrightarrow{750K} K_2MnO_4$ green (one unpaired electron so d-d transition is possible) + MnO_2 + O_2.

(D) $K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2CrO_3$ bright orange (diamagnetic) + $2KHSO_4$ + H_2O.

Ex. 4 Among the following statements choose the true or false statement(s).

(A) $K_2Cr_2O_7$ on heating with charcoal gives metallic potassium and Cr_2O_3.

(B) On heating in current of H_2 the crystalline $KMnO_4$ is converted into KOH and Mn_3O_4.

(C) Hydrated ferric chloride on treatment with 2, 2–dimethoxypropane gives anhydrous ferric chloride.

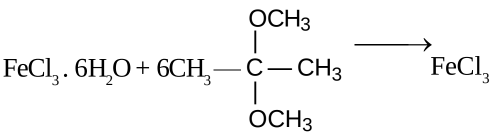
Ans. (A) False (B) False

(C) True

Sol. (A) $K_2Cr_2O_7 + 2C\text{ (charcoal)} \xrightarrow{\Delta} Cr_2O_3 + K_2CO_3 + CO\uparrow$.

(B) $2KMnO_4 + 5H_2 \xrightarrow{\Delta} 2\,KOH + 2MnO + 4H_2O$.

(C)



$$FeCl_3 . 6H_2O + 6CH_3—C(OCH_3)_2—CH_3 \longrightarrow FeCl_3$$

(anhydrous) + $12CH_3OH$ + $6CH_3COCH_3$.

Ex. 5 A compound (A) is used in paints instead of salts of

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. The number of unpaired electrons Cr^{+} in will be
(A) 3 (B) 4
(C) 5 (D) 6

2. The highest oxidation state of Cr will be
(A) 2 (B) 3
(C) 4 (D) 6

3. Which statement is true about the transitional elements
(A) They are highly reactive
(B) They show variable oxidation states
(C) They have low M.P.
(D) They are highly electropositive

4. The transitional metal which form green compound in +3 oxidation state and yellow orange compound in +6 oxidation state is
(A) Fe (B) Ni
(C) Cr (D) CO

5. Highest (+7) oxidation state is shown by
(A) Co (B) Cr
(C) V (D) Mn

6. Transitional elements are
(A) All metals
(B) Few metals and few non-metals
(C) All solids
(D) All highly reactive

7. Which of the following has highest ionic radii
(A) Cr^{+3} (B) Mn^{+3}
(C) Fe^{+3} (D) Co^{+3}

8. In a reaction the ferrous iron is oxidised to ferric ion. The equivalent weight of the ion in the above reaction is equal to
(A) Half of the atomic weight
(B) 1/5 of the atomic weight
(C) The atomic weight
(D) Twice the atomic weight

9. Which of the following element has maximum density
(A) Hg (B) Au
(C) Os (D) Pb

10. Which is heaviest among the following
(A) Iron (B) Copper
(C) Gold (D) Silver

11. Transitional elements exhibit variable valencies because they release electrons from the following orbits
(A) ns orbit (B) ns and np orbits
(C) (n - 1)d and ns orbits (D) (n - 1)d orbit

12. The tendency towards complex formation is maximum in
(A) s - block elements (B) p - block elements
(C) d - block elements (D) f - block elements

13. Which forms coloured salts
(A) Metals
(B) Non-metals
(C) p - block elements
(D) Transitional elements

14. Which element belongs to d - block
(A) Na (B) Ca
(C) Cu (D) Ar

15. Variable valency is shown by
(A) Na (B) Cu
(C) Mg (D) Al

16. The element with a atomic number 26 is
(A) A non-metal (B) Krypton
(C) Iron (D) Manganese

17. One of the following metals forms a volatile carbonyl compound and this property is taken advantage of for its extraction. This metal is
(A) Iron (B) Nickel
(C) Cobalt (D) Tungston

18. The coinage metals are
(A) Iron, Cobalt, Nickel
(B) Copper and Zinc
(C) Copper, Silver and Gold
(D) Gold and Platinum

19. Which of the following structure is that of a coinage metal
(A) 2, 8, 1 (B) 2, 8, 18, 1
(C) 2, 8, 8 (D) 2, 18, 8, 3

20. An elements in+3 oxidation state has the electronic configuration $(Ar)3d^{3}$. Its atomic number is
(A) 24 (B) 23
(C) 22 (D) 21

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. The atomic volumes of the transition elements are low compared with elements in neighboring group 1 and 2 because

(A) the nuclear charge is poorly screened and so attracts all the electrons more strongly.

(B) the extra electrons added occupy inner orbitals.

(C) **(A)** and **(B)** both.

(D) none.

2. The transition elements have a general electronic configuration :

(A) $ns^2np^6nd^{1-10}$

(B) $(n-1)\,d^{1-10}ns^{0-2}np^{0-6}$

(C) $(n-1)\,d^{1-10}ns^{1-2}$

(D) none.

3. The wrong statement regarding transition metals among the following is :

(A) 4s electrons penetrate towards the nucleus more than 3d electrons

(B) atomic radii of transition metals increase rapidly with increase in atomic number because of poor shielding of nuclear attraction by (n – 1)d electrons

(C) second and third transition series elements have nearly the same size

(D) their densities are higher and densities of the 5d series elements are higher than those of 4d series elements.

4. Which of the following statements is correct?

(A) The lesser number of oxidation states in 3d-series in the beginning of the series is due to the presence of too few electrons to loose or share

(B) The lesser number of oxidation states in 3d-series towards the end of the series is due to the presence of too many electrons and thus fewer empty orbitals to share electrons with the ligands

(C) **(A)** and **(B)** both

(D) None is correct

5. First IE of 5d series elements are higher than those of 3d and 4d series elements. This is due to :

(A) bigger size of atoms of 5d-series elements than 3d-series elements.

(B) greater effective nuclear charge is experienced by valence electrons because of the weak shielding of the nucleus by 4*f*-electrons in 5d series.

(C) **(A)** and **(B)** both.

(D) None of these.

6. Maximum oxidation sate is shown by :

(A) Os **(B)** Mn
(C) Cr **(D)** Co

7. Ionisation energies of Ni and Pt in kJ mol^{-1} are given below.

	$\underbrace{(IE)_1 + (IE)_2}$	$\underbrace{(IE)_3 + (IE)_4}$
Ni	2.49	8.80
Pt	2.60	6.70

So, (select the correct statement)

(A) nickel (II) compounds tend to be thermodynamically more stable than platinum (II)

(B) platinum (IV) compounds tend to be more stable than nickel (IV)

(C) **(A)** & **(B)** both

(D) none is correct

8. Which of the following statement is false ?

(A) Of the d^4 species, manganese (III) is strongly reducing while Cr^{2+} is strongly oxidising.

(B) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.

(C) The d^1 configuration is very unstable in ions.

(D) None of these

9. Magnetic moment of Cr^{+2} (Z =24), Mn^{+2} (Z = 25) and Fe^{2+} (Z = 26) are x,y,z. They are in order :

(A) $x < y < z$ **(B)** $x > y > z$
(C) $z < x = y$ **(D)** $x = z < y$

10. The magnetic moment of $_{25}Mn$ in ionic state is $\sqrt{15}$ B.M, then Mn is in :

(A) +2 state **(B)** +3 state
(C) +4 state **(D)** +5 state

11. Which of the following group of ions is paramagnetic in nature :

(A) Cu^+, Zn^{2+}, Sc^{3+} **(B)** $Mn^{2+}, Fe^{3+}, Ni^{2+}$
(C) $Cr^{2+}, Mn^{3+}, Sc^{3+}$ **(D)** $Cu^{2+}, Ni^{2+}, Ti^{4+}$

12. Which of the following has the maximum number of unpaired d-electron?

(A) Zn^{2+} **(B)** Fe^{2+}
(C) Ni^{2+} **(D)** Cu^{2+}

13. The highest magnetic moment is shown by the transition metal ion with the outermost electronic configuration is :

(A) $3d^5$ **(B)** $3d^2$
(C) $3d^7$ **(D)** $3d^9$

Exercise # 3

PART - 1

MATRIX MATCHCOLUMN

1. Match the reactions listed in Column (I) with the characteristic(s) of the products/type of reactions listed in Column (II).

Column - I	Column - II
(A) $MnO_4^{2-} + CO_2 \longrightarrow$	(p) Two pungent smelling gases are liberated.
(B) $CrO_4^{2-} + H^+ \longrightarrow$	(q) Show disproportionation reaction.
(C) $FeSO_4 \xrightarrow{\Delta}$	(r) Dimeric bridged tetrahedral metal ion.
(D) $CuCI_2\ 2H_2O \xrightarrow{\Delta}$	(s) One of the products has central metal in its highest stable oxidation state.

2. Match the salts/mixtures listed in Column (I) with their respective name listed in Column (II).

Column - I	Column - II
(A) $ZnS + BaSO_4$ mixture	(p) Lunar caustic
(B) $FeSO_4\ (NH_4)_2SO_4.\ 6H_2O$	(q) Schwitzer`s regent.
(C) $AgNO_3$	(r) Lithopone
(D) $[Cu(NH_3)_4]SO_4$	(s) Mohr's salt

3. Match the pairs of complexes/compounds listed in Column (I) with the characteristic(s) of the reaction products listed in Column (II).

Column - I	Column - II
(A) Cu(I) and Zn (II) complexes	(p) Pair of compounds having similar colour and some magnetic moment but equal.
(B) $KMnO_4$ and $K_2Cr_2O_7$	(q) Pair of compounds which are diamagnetic but coloured.
(C) Cu_2O and HgI_2	(r) Pair of compounds having metals in the highest stable oxidation states.
(D) $VOCI_2$ and $CuCI_2$	(s) Pair of compounds which show diamagnetism and are colourless.

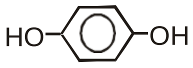
4.

Column-I (Metals)	Column-II (Ores)
(A) Zn	(p) Cyanide process
(B) Cu	(q) hydrometallurgical process
(C) Ag	(r) roasting
(D) Pt	(s) brass.

5.

Column-I (Alloys)	Column-II (Constituents)
(A) $TiCl_4$	(p) Adams catalyst in reduction
(B) $PdCl_2$	(q) In preparation of $(CH_3)_2SiCl_2$
(C) Pt/PtO	(r) Used as the Natta catalyst in polythene production
(D) Cu	(s) Wake process for converting C_2H_4 to CH_3CHO

6. Match the reactions in Column I with the types of products / the use of products in Column II.

Column - I	Column - II
(A)  + AgBr(s) $\rightarrow$	(p) Turnbull's blue pigment
(B) $BaCl_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow$	(q) Schwitzer's reagent
(C) $FeSO_4 + K_3[Fe(CN)_6] \rightarrow$	(r) Rinmann's green pigment
(D) $Cu(OH)_2 + NH_4OH + (NH_4)_2SO_4 \rightarrow$	(s) Chromyl chloride test
(E) $ZnO + Co(NO_3)_2 \xrightarrow{\Delta}$	(t) Photography

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. Which one of the following forms a colourless solution in aqueous medium ?
(At.No. Sc=21, Ti =22, V=23, Cr=24)
[CBSE AIPMT 2000]

(A) V^{3+}
(B) Cr^{3+}
(C) Ti^{3+}
(D) Sc^{3+}

2. Which of the folloiwng statements is not correct ?
[CBSE AIPMT 2001]

(A) La (OH)$_3$ is less basic than Li (OH) ion^{3+} decreases
(B) In lanthanide series, ionic radius of Ln^{+3} ion decreases
(C) La is actually an element of transition series rather lanthanide
(D) Atomic radium of Zr and Hf are same because of lanthanide contraction

3. In the following transition metals, the maximum number of oxidation states are exhibited by
[CBSE AIPMT 2002]

(A) chromium (Z=24)
(B) manganese (Z=25)
(C) iron (Z=26)
(D) titanium (Z=22)

4. General electronic configuration of lanthanides are
[CBSE AIPMT 2002]

(A) (n-2) f$^{1-14}$ (n-1) s^{2}p^{6}d$^{0-1}$ns^2
(B) (n-2) f$^{10-14}$ (n-1) d $^{0-1}$ns^2
(C) (n-2) f$^{0-14}$ (n-1)d^{10} ns^2
(D) (n-2)d$^{0-1}$ (n-1)f$^{1-14}$ns^2

5. In the silver plating of coper, K[Ag(CN)$_2$] is used instead of AgNo$_3$. The reason is
[CBSE AIPMT 2002]

(A) a thin layer of Ag is formed on Cu
(B) more voltage is required
(C) Ag$^+$ ions are completely removed from solution
(D) less availability of Ag$^+$ ions, as Cu cannot displace Ag from [Ag from [Ag(CN)$_2$]$^-$ ion

6. CuSO$_4$ when reacts with KCN forms CuCN which is insoluble in water. If is soluble in water. It is soluble in excess of KCN due to the formation of the complex
[CBSE AIPMT 2002]

(A) K$_2$[Cu(CN)$_4$]
(B) K$_3$[Cu (CN)$_4$]
(C) Cu (CN)$_2$
(D) Cu [KCu(CN)$_4$]

7. The basic character of the transition metal monoxides follows the order
(At. no. Ti=22, V=23, Cr= 24, Fe=26)
[CBSE AIPMT 2003]

(A) TiO > FeO > VO > CrO
(B) TiO > VO > CrO > FeO
(C) VO > CrO> TiO> FeO
(D) CrO > VO > FeO > TiO

8. The correct order of ionic redil of Y^{3+}, La^{3+}, Eu^{3+} and Lu^{3+} is **[CBSE AIPMT 2003]**
At.No.Y=39,La=57, Eu=63,Lu=71

(A) Lu^{3+} < Eu^{3+} <La^{3+} < Y^{3+}
(B) La^{3+} < Eu^{3+} <Lu^{3+} < Y^{3+}
(C) Y^{3+} < La^{3+} <Eu^{3+} < Lu^{3+}
(D) Y^{3+} < LU^{3+} <Eu^{3+} < Lu^{3+}

9. Which one of the following characteristics of the transition metals is associated with their catalytic activity? **[CBSE AIPMT 2003]**

(A) Colour of hydrated ions
(B) Variable oxidation states
(C) High enthalpy of atomisation
(D) Paramagnetic behaviour

10. Lanthanides are **[CBSE AIPMT 2004]**

(A) 14 elements in the sixth period (At. no. = 90 to 103) that are filling 4f sub-level
(B) 14 elements in the seventh period (At. no. = 90 to 103) that are filling 5f sub-level
(C) 14 elements in the sixth period (At. no. = 58 to 71) that are filling 4f sub-level
(D) 14 elements in the seventh period (At. no. = 58 to 41) that are filling 4f sub-level

11. Among the following series of transition metal ions, the one in which all metal ions have 3d^2 electronic configurations is **[CBSE AIPMT 2004]**
(At.No Ti=22, V=23,Cr=24, Mn=25

(A) Ti^{3+}, V^{2+},Cr^{3+}Mn^{4+}
(B) Ti$^+$, V^{4+}, Cr^{6+}, Mn7$^+$
(C) Ti^{4+},V^{3+},Cr^{2+},Mn^{3+}
(D) Ti^{2+},V^{3+} ,Cr^{4+},Mn^{5+}

12. Four successive members of the first row transition elements are listed below with their atomic numbers. which one of them is expected to have the highest third ionisation enthalpy? **[CBSE AIPMT 2005]**

(A) Vanadium (Z=23)
(B) Chromium (Z=24)
(C) Iron (Z=26)
(D) Managanese (Z=25)

MOCK TEST

STRAIGHTOBJECTIVE TYPE

1. Zn and Hg belong to the same group, they differ in many of their properties. The property that is shared by both is
(A) They form oxide readily **(B)** They react with steam readily
(C) They react with hot concentrated sulphuric acid **(D)** They react with hot sodium hydroxide

2. Which of the following ionic species will impart colour to an aqueous solution
(A) Ti^{4+} **(B)** Cu^{+} **(C)** Zn^{2+} **(D)** Cr^{3+}

3. The number of electrons in the outermost shell of the 3d-transition elements generally remains
(A) $(n-1)d^n$ **(B)** nd^n **(C)** ns^2 **(D)** $(n-1)s^2$

4. The 3d-elements show variable oxidation states. What is the maximum oxidation state shown by the element Mn
(A) + 4 **(B)** + 5 **(C)** + 6 **(D)** + 7

5. Which of the following ions gives coloured solution
(A) Cu^{+} **(B)** Zn^{2+} **(C)** Ag^{+} **(D)** Fe^{2+}

6. Which metal represents more than one oxidation state
(A) Al **(B)** Na **(C)** Mg **(D)** Fe

7. A reduction in atomic size with increase in atomic number is a characteristic of elements of
(A) High atomic masses **(B)** d-block **(C)** f -block **(D)** Radioactive series

8. Colourless solutions of the following four salts are placed separately in four different test tubes and a strip of copper is dipped in each one of these. Which solution will turn Blue
(A) KNO_3 **(B)** $AgNO_3$ **(C)** $Zn(NO_3)_2$ **(D)** $ZnSO_4$

9. Zinc when reacted with excess of NaOH gives
(A) Zinc hydroxide **(B)** Zinc oxide **(C)** Di sodium zincate **(D)** Sodium zincate

10. Pair of metals which dissolves in NaOH solution
(A) Al, Cu **(B)** Zn, Hg **(C)** Zn, Cu **(D)** Zn, Al

11. Lucas reagent is
(A) Anhydrous $ZnCl_2$ + conc.HCl **(B)** Hydrous $ZnCl_2$ + dil.HCl
(C) Conc. HNO_3 + anhydrous $ZnCl_2$ **(D)** Conc. HNO_3 + anhydrous $MgCl_2$

12. What is the effect of shaking dil. H_2SO_4 with small quantity of anhydrous $CuSO_4$
(A) The white solid dissolves to form a colourless solution
(B) The white solid dissolves to form a green solution
(C) The white solid turns blue but does not dissolve
(D) The white solid dissolves to form a blue solution

13. Which metal is electro-deposited on iron surface to prevent rusting
(A) Cu **(B)** Zn **(C)** Mg **(D)** Pb

14. To prevent corrosion, iron pipes carrying drinking water are covered with zinc. The process involved is
(A) Photoelectrolysis **(B)** Electroplating **(C)** Galvanization **(D)** Cathodic protection

CHAPTER 03

SOLUTION AND COLLIGATIVE PROPERTIES

I was captured for life by chemistry and by crystals.

''DOROTHYHODGKIN''

INTRODUCTION

Solution is a mixture of more than one pure substances. A dilute aqueous solution of sugar revives the size of partially dried resins while a concentrated aqueous solution of sugar decreases the size of fresh resins by dehydration. Dysentery and dehydration is treated by aqueous solution of salt, ORS. A "kulfi" vendor uses aqueous solution of salt as freezing mixture to freeze kulfis as this solution provides sub zero temperature.

When two or more chemically non-reacting substances are mixed and form homogeneous mixture is called **solution**.

When the solution is composed of only two chemical substances, it is termed a binary solution, similarly, it is called tertiary and quaternary if it is composed of three and four components respectively.

Solution = solute + solvent

Ex. 1 mole heptane (V.P. = 92 mm of hg) is mixed with 4 mol. Octance (V.P. = 31 mm of Hg), form an ideal solution. Find out the vapour pressure of solution

Sol. Total mole = 1 + 4 = 5

Mole fraction of heptane $X_A = 1/5$

Mole fraction of octane $X_B = 4/5$

$$P_S = X_A P^0_A + X_B P^0_B = \frac{1}{2} \times 92 + \frac{4}{5} \times 32 = 43.2 \text{ mm of Hg}$$

Ex. At 88ºC benzene has a vapour pressure of 900 torr and toluene has a vapour pressure of 360 torr. What is the mole fraction of benzene in the mixture with toluene that will be boil at 88ºC. at 1 atm pressure, benzene – toluene form an ideal solution.

Sol. P_s = 760 torr, because solution boils at 88ºC

$\therefore P_s = P^0_B X_B + P^0_t X_t$

760 = 900a + 360 – 360 a

a = 0.74 where ‘a’ is mole fraction of $C_6H_6(X_B)$

EDOS KEY POINTS

Konowaloff’s rule

(i) **Konowaloff’s rule : -** At any fixed temperature, the vapour phase is always richer in the more volatile component as compared to the solution phase. In other words, mole fraction of the more volatile component is always greater in the vapour phase than in the solution phase. Alternatively, vapour phase is relatively richer in the component whose addition to the liquid mixture results in an increase in the total vapour pressure.

(ii) **Mole fraction of component in the vapour phase**

$$= \frac{\text{Partial pressure of that component}}{\text{Total vapour pressure}} = \frac{p^0_A \chi_A}{p^0_A \chi_A + p^0_B \chi_B}$$

where p^0_A = vapour pressure of A

χ_A = Mole fraction of A

p^0_B = Vapour pressure of B

χ_B = Mole fraction of GB

AZEOTROPICMIXTURES

This type of liquid mixture, having a definite composition and boiling like a pure liquid is called azeotropic mixture or constant boiling mixture. The azeotropic mixture cannot be separated by fractional distillation, such solutions are called azeotropic solutions and this phenomenon is known as azeotropy. In azeotropic conditions combination of solute and solvent (solution) starts behaving like one single molecule (with reference to boiling point). This happens due to certain inter-molecular pattern of attractive forces leaving no molecule out of this network, so no component is free to show it’s own boiling point but solution behaves like one single entity and therefore boils at a particular boiling point and therefore solution becomes inseperable by fractional distillation method as this method is only helpful when components differ in their boiling points. Two type of non-ideal solution form two different azeotropes.

1. **Vapour Pressure :** Pressure of any volatile substance at any given temperature.

T ↑ ⇒ V.P.↑

Attractive forces ↑ ⇒ V.P. ↓

2. **Raoult's law**

Non volatile solute and volatile solvent solution.

$$\text{If } \begin{cases} B = \text{Non volatile solid} \\ P_B = 0 \end{cases}$$

$$P_A = P_A^\circ X_A$$

3. **Colligative Properties :** Properties depends on no. of particles of Non volatile solute in solution.

No. of particle of Non volatile solute ↑ Colligative Properties ↑

(1) **Relative lowering of V.P.**

$$\frac{P_A^\circ - P_A}{P_A^\circ} = i\frac{n_B}{n_A + n_B} \approx i\frac{n_B}{n_A}$$

Where n_B = mole of Non-volatile solute.

i = Vant Hoff's factor.

(2) **Elevation in B.P.**

$$\Delta T_b = (T_b' - T_b) = i.\ k_b \times m.$$

$$\text{where } K_b = \frac{RT_b^2}{1000 \times \ell_v}$$

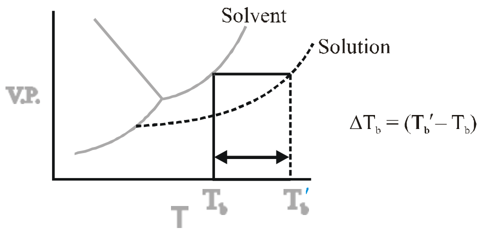
where T_b = B.P. of pure solvent.

ℓ_v = Latent heat of vapourization per gm

K_b = molal elevation constant

M = molar mass

$$\text{where } \ell_v = \left(\frac{\Delta H_{vap}}{M}\right)$$



(3) **Depression** in FP.

$$\Delta T_f = T_f - T_f' = i\ k_f \times m$$

$$\text{where } k_f = \frac{RT_f^2}{1000 \times \ell_f}$$

T_f = f.p. of pure solvent

k_f = molal depression contsant

ℓ_f = latent heat of fusion per gm.

SOLVED EXAMPLE

Ex.1 Which of the following units is useful in relating concentration of solution with its vapoup pressure

(A) Mole fraction **(B)** Parts per million

(C) Mass percentage **(D)** Molality

Sol. **(A)** According to Henry's law partial pressure of gas in the solution is proportional to the mole fraction of gas in the solution.

$$p = K_H X$$

where, K_H = Henry's constant.

Ex.2 On dissolving sugar in water at room temperature solution feels cool to touch. Under which of the following cases dissolution of sugar will be most rapid

(A) Sugar crystals in cold water

(B) Sugar crystals in hot water

(C) Powdered sugar in cold water

(D) Powdered sugar in hot water

Sol. **(D)** Dissolution of sugar in water will be most rapid when powdered sugar is dissolved in hot water because powder from can easily insert in the vacancies of liquid particles. Further dissolution of sugar in water is an endothermic process. Hence, high temperature will favour the dissolution of sugar in water.

Ex.3 At equilibrium the rate of dissolution of a solid solute in a volatile liquid is .....

(A) Less than the rate of crystallisation

(B) Greater than the rate of crystallisation

(C) Equal to the rate of crystallisation

(D) Zero

Sol. **(C)** At equilibrium the rate of dissolution of solid in a volatile liquid solvent is equal to the rate of crystallization.

Ex.4 A beaker contains a solution of substance 'A' Precipitation of substance 'A' takes place when small amount of 'A' is added to the solution. The solution is ......

(A) Saturated **(B)** Supersaturated

(C) Unsaturated **(D)** Concentrated

Sol. **(D)** When solute is added to the solution three cases may arise

(i) It dissolves into solution then solution is unsaturated.

(ii) It does not dissolve in the solution then solution is known as saturated.

(iii) When solute get precipitated solution is known as supersaturated solution.

Ex.5 Maximum amount of a solid that can be dissolved in a specified amount of a given liquid solvent does not depend upon ......

(A) Temperature **(B)** Nature of solute

(C) Pressure **(D)** Nature of solvent

Sol. **(C)** Maximum amount of solid that can be dissolved in a specified amount of a given solvent does not depend upon pressure. This is because solid and liquid are highly incompressible is because solid and liquid are highly incompressible and practically remain unaffected by change in pressure.

Ex.6 Low concentration of oxygen in the blood and tissues of people living at high altitude is due to .....

(A) Low temperature

(B) Low atmospheric pressure

(C) High atmospheric pressure

(D) Both low temperature and high atmospheric pressure

Sol. **(B)** Low concentration of oxygen in the blood and tissues of people living at high altitude is due to low atmospheric pressure. Because at high altitiude, the partial pressure of oxygen is less than at the ground level. This decreased atmospheric pressure causes release of oxygen from blood.

Ex.7 Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixtures will show a positive deviation from Raoult's law

(A) Methanol and acetone

(B) Chloroform and acetone

(C) Nitric acid and water

(D) Phenol and aniline

Sol. **(A)** In pure methanol, molecules are hydrogen bonded. One adding acetone, its molecules get in between the host molecules and break some of the hydrogen bonds between them.

Therefore, the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules.

ON the other hand, other three remaining options will show negative deviation from Raoult's law where the intermolecular attractive forces between the solute -solvent molecules are stronger than those between the solute-solute and solvent-solvent molecules.

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. The solubility of a gas in water depends on

(A) Nature of the gas **(B)** Temperature

(C) Pressure of the gas **(D)** All of the above

2. Which of the following is not correct for D_2O

(A) Boiling point is higher than H_2O

(B) D_2O reacts slowly than H_2O

(C) Viscosity is higher than H_2O at 25°

(D) Solubility of NaCl in it is more than H_2O

3. The statement " The mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent" is

(A) Dalton's Law of Partial Pressures

(B) Law of Mass Action

(C) Henry's Law

(D) None of these

4. Which is correct about Henry's law

(A) The gas in contact with the liquid should behave as an ideal gas

(B) There should not be any chemical interaction between the gas and liquid

(C) The pressure applied should be high

(D) All of these

5. The statement "If 0.003 moles of a gas are dissolved in 900 g of water under a pressure of 1 atmosphere, 0.006 moles will be dissolved under a pressure of 2 atmospheres", illustrates

(A) Dalton's law of partial pressure

(B) Graham's law

(C) Raoult's law

(D) Henry's law

6. The solution of sugar in water contains

(A) Free atoms

(B) Free ions

(C) Free molecules

(D) Free atom and molecules

7. 25 ml of 3.0 M HNO_3 are mixed with 75 ml of 4.0 M HNO_3. If the volumes are additive, the molarity of the final mixture would be

(A) 3.25 M **(B)** 4.0 M

(C) 3.75 M **(D)** 3.50M

8. The amount of anhydrous Na_2CO_3 present in 250 ml of 0.25 M solution is

(A) 6.225 g **(B)** 66.25g

(C) 6.0 g **(D)** 6.625g

9. Dilute one litre 1 molar solution by 5 litre water, the normality of that solution is

(A) 0.2 N **(B)** 5N

(C) 10 N **(D)** 0.33N

10. If 5.85 gms of NaCl are dissolved in 90 gms of water, the mole fraction of NaCl is

(A) 0.1 **(B)** 0.2

(C) 0.3 **(D)** 0.01

(e) 0.0196

11. The molarity of 0.006 mole of NaCl in solution is

(A) 0.6 **(B)** 0.06

(C) 0.006 **(D)** 0.066

(e) None of these

12. 9.8 g of H_2SO_4 is present in 2 litres of a solution. The molarity of the solution is

(A) 0.1 M **(B)** 0.05 M

(C) 0.2 M **(D)** 0.01M

13. What will be the molarity of a solution containing 5g of sodium hydroxide in 250 ml solution

(A) 0.5 **(B)** 1.0

(C) 2.0 **(D)** 0.1

14. The normality of 0.3 M phosphorus acid (H_3PO_3) is

(A) 0.1 **(B)** 0.9

(C) 0.3 **(D)** 0.6

15. Which of the following has maximum number of molecules

(A) 16gm of O_2 **(B)** 16 gm of NO_2

(C) 7 gm of N_2 **(D)** 2 gm of H_2

16. Molarity is expressed as

(A) Gram/litre **(B)** Moles/litre

(C) Litre/mole **(D)** Moles/1000 gms

17. 200 ml of HCl solution requires 19.85 ml of 0.01M NaOH solution for complete neutralization. The molarity of HCl solution is

(A) 0.0099 **(B)** 0.099

(C) 0.99 **(D)** 9.9

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. Persons are medically considered to have lead poisoning if they have a concentration greater than 10 micrograms of lead per decilitre of blood. Concentration in parts per billion is :

(A) 1000 **(B)** 100
(C) 10 **(D)** 1

2. Which statement best explains the meaning of the phrase "like dissolves like " ?

(A) A Solute will easily dissolve a solute of similar mass
(B) A solvent and solute with similar intermolecular forces will readily form a solution
(C) The only true solutions are formed when water dissolves a non-polar solute
(D) The only true solutions are formed when water dissolves a polar solute

3. An ionic compound that attracts atmospheric water so strongly that a hydrate is formed is said to be :

(A) Dilute **(B)** Hygroscopic
(C) Immiscible **(D)** Miscible

4. The vapour pressure of water depends upon :

(A) Surface area of container
(B) Volume of container
(C) Temperature
(D) All

5. A liquid is kept in a closed vessel. If a glass plate (negligible mass) with a small hole is kept on top of the liquid surface, then the vapour pressure of the liquid in the vessel is:

(A) More than what would be if the glass plate were removed
(B) Same as what would be if the glass plate were removed
(C) Less than what would be if the glass plate were removed
(D) Cannot be predicted

6. At higher altitudes, water boils at temperature < 100ºC because

(A) temperature of higher altitudes is low
(B) atmospheric pressure is low
(C) the proportion of heavy water increases
(D) atmospheric pressure becomes more.

7. Among the following substances, the lowest vapour pressure is exerted by:

(A) Water **(B)** Mercury
(C) Kerosene **(D)** Rectified spirit

8. When a liquid that is immiscible with water was steam distilled at 952ºC at a total pressure of 748 torr, the distillate contained 1.25 g of the liquid per gram of water. The vapour pressure of water is 648 torr at 95.2ºC, what is the molar mass of liquid?

(A) 7.975 g/mol **(B)** 166 g/mol
(C) 145.8 g/mol **(D)** None of these

9. Two liquids X and Y are perfectly immiscible. If X and Y have molecular masses in ratio 1 : 2, the total vapour pressure of a mixture of X and Y prepared in weight ratio 2 : 3 should be (P_x^0 = 400 torr, P_y^0 = 200 torr)

(A) 600 torr **(B)** 400 torr
(C) 800 torr **(D)** 1000 torr

10. An ideal solution contains two volatile liquids A (p^o = 100 torr) and B (p^o = 200 torr). If mixture contain 1 mole of A and 4 mole of B then total vapour pressure of the distillate is:

(A) 150 **(B)** 180
(C) 188.88 **(D)** 198.88

11.. The vapour pressure of two pure liquids A and B, that form an ideal solution are 100 and 900 torr respectively at temperature T. This liquid solution of A and B is composed of 1 mole of A and 1 mole of B. What will be the pressure, when 1 mole of mixture has been vaporized ?

(A) 800 torr **(B)** 500 torr
(C) 300 torr **(D)** None of these

12. For a binary ideal liquid solution, the total pressure of the solution is given as :

(A) $P_{total} = P^o_A + (P^o_A - P^o_B)\,X_B$
(B) $P_{total} = P^o_B + (P^o_A - P^o_B)\,X_A$
(C) $P_{total} = P^o_B + (P^o_B - P^o_A)\,X_A$
(D) $P_{total} = P^o_B + (P^o_B - P^o_A)\,X_B$

13. Given at 350 K $p_A°$ = 300 torr and $p_B°$ = 800 torr, the composition of the mixture having a normal boiling point of 350 K is

(A) $X_A = 0.08$ **(B)** $X_A = 0.06$
(C) $X_A = 0.04$ **(D)** $X_A = 0.02$

Exercise # 3 PART - 1 MATRIX MATCHCOLUMN

1. Assuming all the solutes are non volatile and all solutions are ideal and neglect the hydrolysis of cation and anion.

Column – I	Column – II
(A) 10 ml 0.1 M NaOH aqueous solution is added to 10 ml 0.1 M HCl aqueous solution	**(p)** Osmotic pressure of solution increases
(B) 10 ml 0.1 M NaOH aqueous solution is added to 10 ml 0.1 M CH_3COOH aqueous solution	**(q)** Vapour pressure of solution increases
(C) 10 ml 0.1 M HCl aqueous solution is added to 10 ml 0.1 M NH_3 aqueous solution	**(r)** Boiling point of solution increases
(D) 10 ml 0.1 M HCl aqueous solution is added to 10 ml 0.1 M KOH aqueous solution	**(s)** Freezing point of solution increases

2.

Column I	Column II
(A) Acetone + $CHCl_3$	**(p)** $\Delta S_{mix.} > 0$
(B) Ethanol + Water	**(q)** $\Delta V_{mix.} > 0$
(C) $C_2H_5Br + C_2H_5I$	**(r)** $\Delta H_{mix.} < 0$
(D) Acetone + Benzene	**(s)** Maximum boiling azeotropes
	(t) Minimum boiling azeotropes

3.

Column-I (Properties)	Column-II (Affecting factors)
(A) Relative lowering of vapour pressure	**(p)** Directly proportional to van't Hoff factor, i
(B) Elevation in boiling point	**(q)** Directly proportional to molality
(C) Freezing point	**(r)** Directly proportional to molarity
(D) Osmotic pressure	**(s)** Indirectly proportional to lowering of vapour pressure

4. Match the entries listed in Column I with appropriate entries listed in Column II.

Column-I	Column-II
(A) 0.1 M $BaCl_2$ solution	**(p)** 271 K
(B) 0.1 M NaCl solution	**(q)** 270 K
(C) 0.1 M $K_3[Fe(CN)_6]$	**(r)** 268 K
(D) 0.1 M $Al_2(SO_4)_3$ solution	**(s)** 269 K

Given : Freezing point of 0.1 M sucrose solution = 272 K

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. Which of the following colligative property can provide molar mass of proteins (or polymers or colloids) with greatest precision? **[CBSE AIPMT 2000]**

(A) Osmotic pressure
(B) Elevation in boiling point
(C) Depression in freezing point
(D) Relative lowering of vapour pressure

2. Molarity of liquid HCl, if density of solution is 1.17 g/cc is **[CBSE AIPMT 2001]**

(A) 36.5 **(B)** 18.25
(C) 32.05 **(D)** 42.10

3. Pure water can be obtained from sea water by **[CBSE AIPMT 2001]**

(A) centrifugation **(B)** plasmolysis
(C) reverse osmosis **(D)** sedimentation

4. 1 M and 2.5 L NaOH solution is mixed with another 0.5 M and 3 L NaOH solution. Then, find out the molarity of resultant solution. **[CBSE AIPMT 2002]**

(A) 0.80 M **(B)** 1.0 M
(C) 0.73 M **(D)** 0.50 M

5. A solution contains non-volatile solute of molecular mass, M_2. Which of the following can be used to calculate the molecular mass of solute in terms of osmotic pressure? **[CBSE AIPMT 2002]**

(A) $M_2 = \left(\frac{m_2}{\pi}\right)VRT$ **(B)** $M_2 = \left(\frac{m_2}{V}\right)\frac{RT}{\pi}$

(C) $M_2 = \left(\frac{m_2}{V}\right)\pi RT$ **(D)** $M_2 = \left(\frac{m_2}{V}\right)\frac{\pi}{RT}$

6. A solution containing components A and B follows Raoult's law, when **[CBSE AIPMT 2002]**

(A) A - B attraction force is greater than A-A and B-B
(B) A - B attraction force is less than A - A and B - B
(C) A - B attraction force remains same as A - A and B - B
(D) volume of solution is different from sum of volumes of solute and solvent

7. Formation of a solution from two components can be considered as **[CBSE AIPMT 2003]**

I. pure solvent → separated solvent molecules, ΔH_1
II. pure solute → separated solute molecules, ΔH_2
III. separated solvent and solute molecules → solution, ΔH_3

Solution so formed will be ideal, if

(A) $\Delta H_{sol.} = \Delta H_1 - \Delta H_2 - \Delta H_3$
(A) $\Delta H_{sol.} = \Delta H_1 - \Delta H_2 - \Delta H_3$
(A) $\Delta H_{sol.} = \Delta H_1 + \Delta H_2 + \Delta H_3$
(A) $\Delta H_{sol.} = \Delta H_1 + \Delta H_2 - \Delta H_3$

8. The vapour pressure of two liquids P and Q are 80 and 60 torr, respectively, The total vapour pressure of solution obtained by mixing 3 moles of P and 2 moles of Q would be **[CBSE AIPMT 2005]**

(A) 140 torr **(B)** 20 torr
(C) 68 torr **(D)** 72 torr

9. A solution of urea (mol. mass 56 g mol^{-1}) boils at 100.18°C at the atmospheric pressure. If k_f and k_b for water are 1.86 and 0.512 K kg mol^{-1} respectively, the above solution will freeze at **[CBSE AIPMT 2005]**

(A) – 6.54°C **(B)** 6.54°C
(C) 0.654°C **(D)** –0.654°C

10. A solution has 1 : 4 mole ratio of pentane to hexane. The vapour pressure of the pure hydrocarbons at 20°C are 440 mm of Hg for pentane and 120 mm of Hg for hexane. The mole fraction of pentane in the vapour phase would be **[CBSE AIPMT 2005]**

(A) 0.549 **(B)** 0.200
(C) 0.786 **(D)** 0.478

11. The mole fraction of the solute in one molal aqueous solution is **[CBSE AIPMT 2005]**

(A) 0.027 **(B)** 0.036
(C) 0.018 **(D)** 0.009

12. A solution containing 10 g per dm^3 of urea (molecular mass = 60 g mol^{-1}) is isotonic with a 5 % solution of a non-volatile solute. The molecular mass of this non-volatile solute is **[CBSE AIPMT 2006]**

(A) 250 g mol^{-1} **(B)** 300 g mol^{-1}
(C) 350 g mol^{-1} **(D)** 200 g mol^{-1}

MOCK TEST

STRAIGHT OBJECTIVE TYPE

1. When ethanol mixes in cyclohexane; cyclohexane reduces the intermolecular forces between ethanol molecule. In this, liquid pair shows

(A) Positive deviation by Raoult's law **(B)** Negative deviation by Raoult's law
(C) No deviation by Raoult's law **(D)** Decrease in volume

2. Liquids A and B form an ideal solution

(A) The enthalpy of mixing is zero
(B) The entropy of mixing is zero
(C) The free energy of mixing is zero
(D) The free energy as well as the entropy of mixing are each zero

3. As a result of osmosis the volume of solution

(A) Increases **(B)** Decreases **(C)** Remains constant **(D)** Increases or decreases

4. A solution of urea contain 8.6 gm/litre (mol. wt. 60.0). It is isotonic with a 5% solution of a non-volatile solute. The molecular weight of the solute will be

(A) 348.9 **(B)** 34.89 **(C)** 3489 **(D)** 861.2

5. One mole each of urea, glucose and sodium chloride were dissolved in one litre of water Equal osmotic pressure will be produced by solutions of

(A) Glucose and sodium chloride **(B)** Urea and glucose
(C) Sodium chloride and urea **(D)** None of these

6. A solution of 1 molal concentration of a solute will have maximum boiling point elevation when the solvent is

(A) Ethyl alcohol **(B)** Acetone **(C)** Benzene **(D)** Chloroform

7. Mark the correct relationship between the boiling points of very dilute solutions of $BaCl_2 (t_1)$ and $KCl(t_2)$, having the same molarity

(A) $t_1 = t_2$ **(B)** $t_1 > t_2$ **(C)** $t_2 > t_1$ **(D)** t_2 is approximately equal to t_1

8. What should be the freezing point of aqueous solution containing 17 gm of C_2H_5OH in 1000 gm of water (water $K_f = 1.86$ deg– kg mol^{-1})

(A) -0.69^o C **(B)** -0.34^o C **(C)** 0.0^o C **(D)** 0.34^o C

9. For 0.1 M solution, the colligative property will follow the order

(A) $NaCl > Na_2SO_4 > Na_3PO_4$ **(B)** $NaCl < Na_2SO_4 < Na_3PO_4$
(C) $NaCl > Na_2SO_4 \approx Na_3PO_4$ **(D)** $NaCl < Na_2SO_4 = Na_3PO_4$

10. Which of the following will have the lowest vapour pressure

(A) 0.1M KCl solution **(B)** 0.1 M urea solution
(C) 0.1M Na_2SO_4 solution **(D)** 0.1M $K_4 Fe(CN)_6$ solution

11. The Van't Hoff factor for sodium phosphate would be

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

12. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to

(A) Ionization of benzoic acid **(B)** Dimerization of benzoic acid
(C) Trimerization of benzoic acid **(D)** Solvation of benzoic acid

CHAPTER 17

ENVIRONMENTAL CHEMISTRY & ANALYSIS OF ORGANIC COMPOUNDS

We won't have a society if we destroy the environment.

''MARGARETMEAD''

INTRODUCTION

The branch of science which deals with the chemical phenomena occuring in the environment is called as environmental chemistry.

Environmental studies deal with the sum of all social, economical, biological, physical and chemical interrelations with our surroundings. In this unit of the focus will be on environmental chemistry. Environmental chemistry deals with wth study of the origin, transport, reactions, effects and fates of chemical species in the environment.

The environment means surroundings. It has 4 following component.

(i) Atmosphere

(A) Function of the atmosphere

- It contain all the gases which are essential for the life on the earth.
- It is a carrier of water vapour which are needed for all life.
- O_3 is present in it which absorbs harmful U.V. radiations.
- It maintain heat balance of the earth by absorbing infrared radiation coming from the sun and remitted from the earth.

(B) Pressure, weight and temp of the atmosphere

- Pressure of atm = $10^5 N/m^2$
- Mass of atm = 5×10^{15} tonnes.
- Temp. of atm = – 100° C to 1200° C
- Increases in altitude of 5 km, the pressure and the density of air decrease by one half.

(C) Composition of air (or atmosphere)

- It is divided in 3 categories.
- Major component = N_2, O_2, water vapour.
- Minor component = Ar, CO_2
- Traces component = He, Ne, Ar, Kr, CH_4, H_2, CO, N_2O, SO_2, NO, NO_2, HCHO, NH_3, O_3.

(D) Regions (or structure) of the atmosphere :- It has 4 region. These regions are defined by the temp.

Region	Altitude from earth's surface	Temp. range	Species present or gasses present
Troposphere	0 - 11 km	decrease from 15 to – 56°C	N_2, O_2, CO_2, H_2O vapour
Stratosphere or coroyones sphere	11 - 50 km	increase from – 56° to – 2°C	N_2, O_2, O_3, 0-atm
Mesosphere	50 – 85 km ionosphere	decrease from – 2° to – 92°C	N_2, O_2, NO^+, O_2^+
Thermosphere	85 – 500 km ionosphere	increase from – 92° to 1200°C	O_{2+}, O_{+}, NO_{+}, $_{-}$e

(ii) Hydro sphere (75% of earth) : The part in which contain water in the form of sea, oceans, rivers, lakes, ponds.

(iii) Lithosphere : It is solid component of the earth consisting of soil, rocks, mountains.

(iv) Biosphere : It is the part of the lithosphere, hydrosphere and atm. Where living organism interact with these parts and lived together. **Ex.** Green plants.

ACID RAIN : The rain containing H_2SO_4, HNO_3 (and small amount of HCl) which are formed from the oxide of S and N_2 present in the air is called as acid rain. The pH of acid rain is 4-5.

GREENHOUSEEFFECT

The warming of earth due to remission of sun's energy absorbed by the earth. The remission of earth's energy is absorbed by CO_2 molecules and H_2O vapour present near the earth's surface and then its radiation back to the earth, is called as green house effect. So the temp. of the earth is increased is called as global warming.

Calculation of % of C

% of C in W gm organic substance = % of C = $\frac{12}{44} \times \frac{m}{W} \times 100$

Calculation of % of N

% of Nitrogen in W gm organic substance = % of N = $\frac{28}{22400} \times \frac{V}{W} \times 100$

Calculation of % of Halogen

% of halogen = $\frac{\text{Atomic mass of X}}{\text{Molar mass of AgX}} \times \frac{m}{W} \times 100$

Calculation of % of Sulphur

% of S = $\frac{32}{233} \times \frac{m}{W} \times 100$

Calculation of % of Phosphorous

% of P = $\frac{62}{222} \times \frac{m}{W} \times 100$

SOLVED EXAMPLE

Ex. 1 How can domestic waste be used as manure ?

Sol. Domestic waste comprises of two types of materials, biodegradable such as leaves, rotten food, etc., and non-biodegradable such as plastics, glass metal, scrap, etc. The non-biodegradable waste is sent to industry for recycling The biodegradable waste should be deposited in the land fills. With the passage of time, it is converted into compost manure.

Ex. 2 For your agricultural field or garden, you have developed a compost producing pit. Discuss the process in the light of bad odour, files and recycling of wastes for a good produce.

Sol. The compost producing pit should be set up at a suitable place or in a tin to protect ourselves from bad odour and files. It should be kept covered so that files cannot make entry into it and the bad odour is minimized. The recyclable material like plastics, glass, newspapers, etc.. should be sold to the vendor who further sells it to the dealer. The dealer further supplies it to the industry involved in recycling process.

Ex. 3 A large number of fish are suddenly found floating dead on a lake. There is no evidence of toxic dumping but you find an abundance of phytoplankton. Suggest a reason for the fish kill.

Sol. Excessive phytoplankton (organic pollutants such as leaves, grass, trash, etc.) present in water is biodegradable. A large population of bacteria decomposes this organic matter in water. During this process they consume the oxygen dissolved in water. Water has already limited dissolved oxygen (= 10 ppm) which gets is further depleted. When the level of dissolved oxygen falls below 6 ppm, the fish cannot survive. Hence, they die and float dead in water.

Ex. 4 What would have happened if the greenhouse gases were totally missing in the earth's atmosphere ? Discuss.

Sol. The solar energy radiated back from the earth surface is absorbed by the greenhouse gases (i.e. CO_2, CH_4, O_3, CFC's and water vapour) present near the earth's surface. They heat up the atmosphere near the earth's surface and keep it warm. As a result, they keep the temperature of the earth constant and help in the growth of plants and existence of life on the earth. If there were no greenhouse gases, there would have no vegetation and life on the earth.

Ex. 5 **(i)** Name two important sinks of CO_2.

(ii) What is marine pollution

(iii) What is humification?

(iv) What are viable and non-viable particulates ?

Sol. **(i)** Oceans (which dissolve it) and plants (which use it for photosynthesis)

(ii) Pollution of sea water due to discharge of wastes into it is called marine pollution.

(iii) The decomposition of organic material (leaves, root etc.) in the soil by microorganism to produce humus is called humification.

(iv) Viable particulates are small size living organisms such as bacteria, fungi, moulds, algae, etc. Non-viable particulates are formed by disintegration of large size materials or condensation of small size particles or droplets e.g. mist, smoke, fume and dust.

Ex. 6 Answer the following subparts

(i) What is loam soil ?

(ii) What are asbestosis and silicosis ?

(iii) What are particulates and what is their approximatesize ?

(iv) Name three natural source of air pollution

(v) How are flue gases from industries feed from oxides of nitrogen and sulphur ?

Sol. **(i)** Soil containing 34% air, 66% water along with humus is called loam soil is best for crops.

(ii) Asbestosis and silicosis is lung disease caused by particulates.

(iii) Particulates are finely divided solid or liquid particles suspended in air. Their size varies from $2 \times 10^{-4}\ \mu$ to $500\ \mu$

(iv) Volcanic erruptions, forest fires and pollen grains of flowers.

(v) The flue gases are subjected to scrubbing with conc. H_2SO_4 or with alkaline solutions such as $Ca(OH)_2$ or $Mg(OH)_2$ etc.

Ex. 7 **(i)** Why does rain water normally have a pH of about 5.6 / When does it become acid rain ?

(ii) Why is acid rain considered as a threat to Taj mahal ?

(iii) Explain giving reason " The presence of CO reduces the amount of haemoglobin available in the blood for carrying oxygen to the body cells."

(iv) State briefly the reactions causing ozone layer depletion in the stratosphere.

Exercise # 1 SINGLE OBJECTIVE NEET LEVEL

1. Air pollutants that produce photochemical oxidants include :
(A) CO_2, CO and SO_2 (B) N_2O, NO and HNO_3
(C) O_2, Cl_2 and HNO_3. (D) O_3, Cl_2 and SO_2

2. Atmosphere of big/metropolitian cities are polluted most by :
(A) automobile exhausts. (B) pesticide residue.
(C) household waste. (D) radio-active fall out.

3. Ozone layer of upper atmosphere is being destroyed by :
(A) chlorofluorocarbon
(B) SO_2
(C) photochemical oxidants/O_2 & CO_2
(D) smog

4. Carbon monooxide is pollutant as it :
(A) inactivates nerves
(B) inhibits glycolysis
(C) combines with oxygen
(D) combines with haemoglobin

5. Pollution is :
(A) removal of top soil
(B) release of toxic/undesirable materials in environment
(C) conservation of energy
(D) all of above

6. Burning of fossil fuels is the main source of, which of the following pollutants ?
(A) Nitrogen oxide (B) Nitric oxide
(C) Nitrous oxide (D) Sulphur dioxide

7. SO_2 and NO_2 produce pollution by increasing :
(A) alkalinity (B) acidity
(C) neutrality (D) buffer action

8. The aromatic compounds present as particulates are :
(A) benzene
(B) toluene
(C) nitrobenzene
(D) polycyclic hydrocarbons

9. Classical smog occurs in places of :
(A) excess CO_2 (B) cool and humid
(C) warm, dry and sunny (D) excess NH_3

10. Acid rains are produced by:
(A) excess NO_2 and SO_2 from burning fossil fuels
(B) excess production of NH_3 by industry and coal gas
(C) excess release of carbon monoxide by incomplete combustion
(D) excess formation of CO_2 by combustion and animal respiration.

11. Spraying of DDT produces pollution of the type:
(A) air (B) air and water
(C) air and soil (D) air, water and soil

12. Most hazardous metal pollutant of automobile exhausts is :
(A) mercury (B) cadmium
(C) lead (D) copper

13. Chlorofluorocarbon releases which of the following chemical harmful to ozone :
(A) fluorine (B) chlorine
(C) nitrogen peroxide (D) sulphur dioxide

14. Which of the following statements is true about photochemical smog ?
(A) It is reducing in nature.
(B) it is formed in winter.
(C) It is a sulphurous smog.
(D) Components of the smog, NO and O_3, irritate the nose and throat and their high concentration causes headache, chest pain, dryness of the throat, cough and difficulty in breathing.

15. Which of the following is not a part of green chemistry ?
(A) Photochemistry (B) Sonochemistry
(C) Nuclear chemistry (D) Biochemistry

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. Ultraviolet radiation from sun causes a reaction that produces :

(A) fluorides **(B)** carbon monooxide
(C) sulphur dioxide **(D)** ozone

2. Ozone depletion in stratosphere shall result in :

(A) forest fires
(B) increased incidence of skin burns and skin cancer
(C) increase in biological oxygen demand
(D) global warming

3. Incomplete combustion of petrol or diesel oil in automobile engines can be best detected by testing the fuel gases for the presence of?

(A) CO and water vapour **(B)** CO
(C) NO_2 **(D)** SO_2

4. Which of the following statements is true about ozone layer ?

(A) It is harmful because ozone is dangerous to living organism.
(B) It is beneficial because oxidation reaction can proceed faster in the presence of ozone.
(C) It is beneficial because ozone cuts off the ultra violet radiation of the sun.
(D) It is harmful because ozone cuts out the important radiation of the sun which are vital for photosynthesis.

5. Besides CO_2, the other green house gas is :

(A) CH_4 **(B)** N_2
(C) Ar **(D)** O_2

6. Which of the following statements is true?

(A) London smog is oxidising in nature.
(B) London smog contains H_2SO_4 droplets.
(C) London smog is mixture of smoke, fog and SO_2.
(D) London smog causes bronchitis.

7. Which of the following processes does not increase the amount of CO_2 in atmosphere ?

(A) Decay of animals **(B)** Breathing
(C) Photosynthesis **(D)** Burning of petrol

8. Consider the following statement and select the correct option :

S_1 : Dust is the non-viable particle.
S_2 : Particulates acquire negative charge and are attracted by the positive electrode.
S_3 : O_2 is a green house gas.
S_4 : Algae is a viable particulate.

(A) S_1 and S_2 only **(B)** S_1, S_2 and S_3 only
(C) S_1, S_2 and S_4 only **(D)** S_2, S_3 and S_4

9. Drained sewage has biological oxygen demand (BOD):

(A) more than that of water
(B) less than that of water
(C) equal to that of water
(D) none of the above

10. Eutrophication causes reduction in :

(A) dissolved hydrogen **(B)** dissolved oxygen
(C) dissolved salts **(D)** all the above

11. Sewage water is purified by:

(A) microorganism **(B)** light
(C) fishes **(D)** aquatic plants

12. Which of the following will increase the BOD of water supply ?

(A) CO_2 **(B)** O_3
(C) H_2O **(D)** C_2H_5OH

13. Which causes water pollution ?

(A) Pathogens
(B) Automobile exhausts
(C) PCBs
(D) (A) and (C)

14. Water pollution is less if BOD is :

(A) less than 5 ppm **(B)** less than 15 ppm
(C) less than 50 ppm **(D)** less than 100 ppm

15. Most abundant water pollutant is :

(A) detergents **(B)** pesticides
(C) industrial wastes **(D)** ammonia

Exercise # 3

PART - 1

MATRIX MATCHCOLUMN

1. Match the entries of column-I with appropriate entries of column-II. Each entry in column-I may have one or more than one correct option(s) from column-II.

Column-I	Column-II
(A) Classical smog	**(p)** SO_2
(B) Photochemical smog	**(q)** NO_2
(C) Particulate Pollutants	**(r)**) bacteria
(D) Gaseous pollutants	**(s)** smoke
	(t) Fe_3O_4

2. Match the entries of column-I with appropriate enteries of column-II. Each entry in column-I may have one or more than one correct option(s) from column-II.

Column-I	Column-II
(A) Acid rain	**(p)** Oxides of nitrogen
(B) Green house effect	**(q)** Oxides of sulphur
(C) Ozone hole	**(r)** Carbon dioxide
(D) Eutrophication	**(s)** Phosphate fertilizer i.e. plant nutrient (excess).
	(t) Chlorofluorocarbon (CFCs)

Exercise # 4

PART - 1

PREVIOUS YEAR (NEET/AIPMT)

1. Green chemistry means such reactions which

[CBSE AIPMT 2008]

(A) produce colour during reactions
(B) reduce the use and production of hazardous chemicals
(C) are related to the depletion of ozone layer
(D) study the reaction in plants

2. Which one of the following statements regarding photochemical smog is not correct ?

[CBSE AIPMT 2012]

(A) Carbon monoxide does not play any role in photochemical smog formation
(B) Photochemical smog is an oxidising agent in character
(C) Photochemical smog is formed through photochemical reaction involving solar energy
(D) Photochemical smog does not cause irritation in eyes and throat

MOCK TEST

1. Domestic waste mostly constitutes :
(A) non-biodegradable pollution **(B)** biodegradable pollution
(C) effluents **(D)** air pollution

2. Measurement of rate oxygen utilisation by a unit volume of water over a period of time is to measure :
(A) fermentation **(B)** biogas generation
(C) biosynthetic pathway **(D)** biological oxygen demand.

3. Fishes die in water bodies polluted by sewage due to :
(A) pathogens **(B)** clogging of gills by silt **(C)** reduction in oxygen **(D)** foul smell

4. Phosphate pollution is caused by :
(A) weathering of phosphate rock only **(B)** agriculture fertilizers only
(C) phosphate rocks and sewage **(D)** sewage and agricultural fertilizers.

5. Which of the following statements is false ?
(A) The lower the concentration of dissolved oxygen, the more polluted is the water sample.
(B) The tolerable limit of lead in drinking water is 50 ppm.
(C) Water is considered pure if it has BOD less than 5 ppm.
(D) None of the above

6. Which of the following statements is false ?
(A) The industrial and domestic sewage discharge is the main reason for river water pollution.
(B) Surface water contains a lot of organic matter and mineral nutrients.
(C) Oil spill in sea water causes heavy damage to fishery.
(D) Oil slick in sea water increases dissolved oxygen.

7. Modes of controlliing pollution in large cities includes :
(A) cleanliness and less use of insecticides
(B) proper disposal of organic wastes, sewage and industrial effluents.
(C) use of liquefied carbondioxide with a suitable detergent in place of tetrachloroethene for dry cleaning.
(D) all the above

8. Which of the following is not a herbicide ?
(A) Sodium chlorate **(B)** Sodium arsenate **(C)** Phosphate **(D)** Triazines

9. DDT is :
(A) green house gas **(B)** biodegradable pollutant
(C) non-biodegradable pollutant **(D)** none of above

10. In stratosphere, which of the following radical retards the formation of O_3 ?
(A) $\dot{C}H_3$ **(B)** $\dot{C}l$ **(C)** $\dot{F}$ **(D)** Cl_2

11. Which of the following helps in creating ozone over antractia ?
(A) Radioactive clouds **(B)** Polar stratospheric clouds
(C) Spring clouds **(D)** Smoke clouds

12. Which are natural sinks for $\dot{C}lO$ radicals in other parts of stratosphere ?
(A) SO_2 and NO_2 **(B)** NO and NO_2 **(C)** CH_4 and NO_2 **(D)** Cl_2 and F_2

CHAPTER 07

STATES OF MATTER (GASEOUS AND LIQUID)

If molecules can be structurally identical and yet possess dissimilar properties, this can be explained only on the ground that the difference is due to a different arrangement of the atoms in space.

" JOHANNESWISLICENUS"

INTRODUCTION

Matter is made up of atoms or molecules. The arrangement of these molecules determines the state of matter. There are three recognised state of matter : Solid, Liquid and Gas. Matter can change between states when the temperature or pressure is changed. State changes of matter are physical rather than chemical.

For example Water can exist as ice, which is a solid; it can exist as liquid; or it can exist in the gaseous state as water vapour or steam.Physical properties of ice, water and steam are very different,In all the three states of water chemical composition of water remain the same. Charecteristics of the three states of water depands on the energies of molecules and on the manner in which water molecules aggregate.

Chemical properties of a substance do not change with the change of its physical state; but rate of chemical reactions depands upon the physical state.

DIFFERENCEBETWEENSTATESOFMATTER

	Gas	Liquid	Solid
i.	Assumes the shape and volume of its container.	Assumes the shape of the part of the container which it occupies	Retains a fixed volume and shape.
ii.	Particles can move past one another.	Particles can move/slide past one another.	Rigid-particles locked into place.
iii.	Compressible, lots of free space between particles	Not easily compressible, little space between particles.	Not easily compressible, little free space between particles.
iv.	Flows easily, particles can move past one another.	Flows easily, particles can move/slide past one another	Does not flow easily, rigid-particles cannot move/slide one past another
v.	Low density.	Intermediate density.	High density.
vi.	Very small intermolecular attraction but high kinetic energies.	Considerable intermolecular attraction, kinetic energy is less.	Intermolecular forces are high, vibrational motion only.

GASEOUSSTATE

Important Properties of Gases :

(a) **Mass :** Mass in gm = Moles × Molecular mass.

(b) **Volume :** Volume of the gas is the volume of container in which they are filled in.

(c) **Temperature :** Temperature of a gas is the measure of kinetic energy of gas.
Kinetic energy $\propto$ Temperature

(d) **Pressure :** Pressure of gas is defined as the force exerted by the gas on the walls of its container. It is often assumed that pressure is isotropic, i.e. it is the same in all the three directions.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}},$$

$$P = \frac{Mg}{A} = \frac{v \times d \times g}{A} = \frac{A \times h \times d \times g}{A}$$

P = hdg

Where.... h = height of the mercury column supported by the barometer.
d = density of mercury.
g = acceleration due to gravity.

Units and Determination of Pressure of Gas :

(a) In SI unit the unit of pressure is the pascal (N/m^2) instead, the unit bar, kPa or MPa is used.
$1\ \text{bar} = 10^5\ N/m^2 = 100\ kN/m^2 = 100\ kPa$

(b) Pressure are also stated in mm or cm of mercury.
$1\ \text{atm} = 760\ \text{mm Hg} = 1.01325\ \text{bar} = 1.01325 \times 10^5\ \text{Pa} = 101.325\ KN/m^2 = 1.0332\ Kgf/cm^2$
$1\ Pa = 1\ Nm^{-2} = 1\ Kgm^{-1}\ S^{-1}$
$1L = 1dm^3 = 10^{-3}\ m^3$ (SI unit)
1L atm = 101.325 J

$$1\ \frac{KN}{m^2} = 1 \times 10^3\ \frac{N}{m^2} = \frac{1 \times 10^3 \times kg}{9.8 \times 10^4\ cm^2} = \frac{1}{98}\ kgf/cm^2$$

$$1\text{Torr} = \frac{101325}{760}\ \text{Pa} = 133.322\ \text{Pa}$$

$$= \frac{(\text{Force / Area}) \times (\text{Area} \times \text{Length})}{\text{Mole} \times \text{Degree(K)}}$$

$$= \frac{\text{Force} \times \text{Length}}{\text{Mole} \times \text{Degree(K)}} = \frac{\text{Work or energy}}{\text{Mole} \times \text{Degree (K)}}$$

Physical Significance of R

The dimentions of R are energy per mole per kelvin and hence it represents the amount of work (or energy) that can be obtained from one mole of a gas when its temperature is raised by 1K.

ETOOS KEY POINTS

Units of R

(i) In lit-atmR = $\frac{1 \text{ atm} \times 22.4 \text{ lit}}{273 \text{ K}}$ = 0.0821 lit-atm $\text{mol}^{-1}\text{K}^{-1}$

(ii) In C.G.S system R = $\frac{1 \times 76 \times 13.6 \times 980 \text{ dyne cm}^{-2} \times 22400 \text{ cm}^3}{273 \text{ K}}$

= 8.314×10^7 erg $\text{mole}^{-1}\text{K}^{-1}$.

(iii) In M.K.S. system R = 8.314 Joule $\text{mole}^{-1}\text{K}^{-1}$. [$10^7$ erg = 1 joule]

(iv) In calories R = $\frac{8.314 \times 10^7 \text{ erg mole}^{-1}\text{K}^{-1}}{4.184 \times 10^7 \text{ erg}}$

= 1.987 ≈ 2 calorie $\text{mol}^{-1}\text{K}^{-1}$.

Ex. Some spherical balloons each of volume 2 litre are to be filled with hydrogen gas at one atm & 27°C from a cylinder of volume 4 litres. The pressure of the H_2 gas inside the cylinder is 20 atm at 127°C. Find number of balloons which can be filled using this cylinder. Assume that temperature of the cylinder is 27°C.

Sol. No. of moles of gas taken initially = $\frac{20 \times 4}{R \times 400}$ = 2.43 L

No. of moles of gas left in cylinder = $\frac{1 \times 4}{R \times 300}$ = 0.162L

No. of moles of gas to be filled in balloons = 2.43 – 0.162 = 2.268

Let we have 'n' balloons that we can fill

No. of moles of gas that can be filled in 1 balloon = $\frac{1 \times 2}{0.082 \times 300}$ = 0.081

$\therefore$ 0.081 × n = 2.268

n = 28 balloons.

Ex. At room temperature following reaction goes to completion

$2NO + O_2 \xrightarrow{} 2NO_2 \xrightarrow{} N_2O_4$

Dimer N_2O_4 at 262 K is solid. A 250 ml flask and a 100 ml flask are separated by a stop cock. At 300 K, the nitric oxide in the large flask exerts a pressure of 1.053 atm and the smaller on contains O_2 at 0.789 atm. The gases are mixed by opening the stop cock and after the end of the reaction, the flasks are cooled to 220 K.

Neglecting the vapour pressure of dimer. Find out the pressure and composition of gas remaining at 220 K (Assume gases behave ideally).

1. GAS LAW

(I) Boyle's Law

$$V \propto \frac{1}{P} (n, T = \text{const})$$

$P_1V_1 = P_2V_2$

(II) Charle's Law

$V \propto T$ (n, P = const)

$$\frac{V_2}{V_1} = \frac{T_2}{T_1}$$

(III) Gay lussac's Law

$P \propto T$ (n, V = const)

$$\frac{P_2}{P_1} = \frac{T_2}{T_1}$$

(IV) Avogadro's Law

$V \propto$ moles $\propto$ number of molecules (P, T = cosnt)

Ideal gas equation $PV = nRT$

$R = 0.0821$ lit atm $mol^{-1} K^{-1}$

$R = 8.314$ J $K^{-1} mol^{-1}$ or 8.314 N × $K^{-1} mol^{-1}$

$R = 2$ cal $K^{-1} mol^{-1}$

$R = 8.314 \times 10^7$ erg $K^{-1} mol^{-1}$

2. GRAHAM'S DIFFUSION LAW

It is applicable for non reacting gases

$$r \propto \frac{1}{\sqrt{d}}$$

$$r \propto \frac{1}{\sqrt{VD}}$$

$$r \propto \frac{1}{\sqrt{Mw}} \qquad (P, T = \text{const})$$

$$VD = \frac{d_{gas}}{dH_2} = \frac{Mw}{2}$$

rate of diffusion $r = \frac{\ell_{\text{diffused gas}}}{t_{\text{time taken}}}$

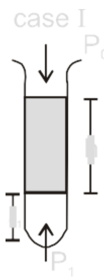
(Where, ℓ = distance travelled by differed gas)

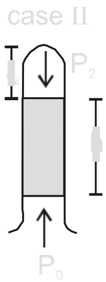
$$r = \frac{V_{\text{diffused gas}}}{t_{\text{time taken}}}$$

$$r = \frac{n_{\text{diffused gas}}}{t_{\text{time taken}}}$$

SOLVED EXAMPLE

Ex. 1 A gas column is trapped between closed end of a tube and a mercury column of length (h) when this tube is placed with its open end upwards the length of gas column is (ℓ_1), the length of gas column becomes (ℓ_2) when open end of tube is held downwards. Find atmospheric pressure in terms of height of Hg column.





Sol. for gas $P_1 = (P_O + h)$ $\quad P_2 = (P_O - h)$

$V_1 = \pi r^2 \ell_1$ $\quad V_2 = \pi r^2 \ell_2$

at const T. and moles.

$P_1V_1 = P_2V_2$; $(P_O + h)\pi r^2\ell_1 = (P_O - h)\pi r^2\ell_2$

$P_O\ell_2 + h\ell_1 = P_O\ell_2 - h\ell_2$

$P_O\ell_2 - P_o\ell_1 = h\ell, + h\ell_2$

$$P_0 = \frac{h(\ell_1 + \ell_2)}{(\ell_2 - \ell_1)}$$ cm of Hg column **Ans.**

Ex. 2 The diameter of a bubble at the surface of a lake is 4 mm and at the bottom of the lake is 1 mm. If atmospheric pressure is 1 atm and the temperature of the lake water and the atmosphere are equal. what is the depth of the lake ?

(The density of the lake water and mercury are 1 g/ml and 13.6 g/ml respectively. Also neglect the contribution of the pressure due to surface tension)

Sol. $P_1V_1 = P_2V_2$

□ $(760\text{ mm} \times 13.6 \times g)\frac{4}{3}\pi(4\text{ mm}/2)^3$

$= (760\text{ mm} \times 13.6 \times g + h \times 1 \times g)\ \frac{4}{3}\pi(1\text{ mm}/2)^3$

$760 \times 13.6 \times 64 = (760 \times 13.6 + h)$

$h = 64 \times 760 \times 13.6 - 760 \times 13.6$

$h = 63 \times 760 \times 13.6\text{ mm}$

$h = \frac{63 \times 760 \times 13.6}{1000 \times 1000}$ km = 0.6511 km = **651.1 m Ans.**

Ex. 3 A gas is initially at 1 atm pressure. To compress it to 1/4 th of initial volume, what will be the pressure required ?

Sol. $P_1 = 1$ atm $\quad V_1 = V$

$P_2 = ?$ $\quad V_2 = \frac{V}{4}$

$P_1V_1 = P_2V_2$ $\quad$ at const. T & n

$P_2 = \frac{P_1V_1}{V_2} = \frac{1\text{ atm} \times V}{\frac{V}{4}}$ **= 4 atm Ans.**

Ex. 4 Find the lifting power of a 100 litre balloon filled with He at 730 mm and 25°C. (Density of air = 1.25 g /L).

Sol. Since, $\quad PV = nRT$

$PV = \frac{W}{M}RT$ □$W = \frac{PVM}{RT} = \frac{730}{760} \times \frac{100 \times 4}{0.082 \times 298}$ g

i.e., Wt. of He = 15.72 g

Wt. of air displaced = 100 × 1.25 g/L = 125 g

□Lifting power of the balloon = 125 g – 15.72 g

= **109.28 g Ans.**

Ex. 5 A weather balloon filled with hydrogen at 1 atm and 300 K has volume equal to 12000 litres. On ascending it reaches a place where temperature is 250 K and pressure is 0.5 atm. The volume of the balloon is :

(A) 24000 litres $\quad$ **(B)** 20000 litres

(C) 10000 litres $\quad$ **(D)** 12000 litres

Sol. Using $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$; $\frac{1\text{ atm} \times 12000\text{ L}}{300\text{ K}}$

$= \frac{0.5\text{ atm} \times V_2}{250\text{ K}}$

□ $V_2 = 20,000$ L

Hence **Ans. (B)**

Ex. 6 If water is used in place of mercury then what should be minimum length of Barometer tube to measure normal atmospheric pressure.

Sol. $P_{Hg} = P_{H_2O} = P_{atm}$.

$0.76\text{ m} \times 13.6 \times g = h_{H_2O} \times 1 \times g$

$h_{H_2O} = 0.76 \times 13.6 =$ **10.336 m Ans.**

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. Which one of the following statements is not correct about the three states of matter i.e. solid, liquid and gaseous

(A) Molecules of a solid possess least energy whereas those of a gas possess highest energy

(B) The density of solid is highest whereas that of gases is lowest

(C) Gases like liquids possess definite volumes

(D) Molecules of a solid possess vibratory motion

2. The temperature and pressure at which ice, liquid water and water vapour can exist together are

(A) $0^o C, 1 atm$ **(B)** $2^o C, 4.7 atm$

(C) $0^o C, 4.7 mm$ **(D)** $-2^o C, 4.7 mm$

3. Which of the following is true about gaseous state

(A) Thermal energy = Molecular attraction

(B) Thermal energy >> Molecular attraction

(C) Thermal energy << Molecular attraction

(D) Molecular forces >> Those in liquids

4. Kinetic energy of molecules is highest in

(A) Gases **(B)** Solids

(C) Liquids **(D)** Solutions

5. Which of the following statement is correct

(A) In all the three states the molecules possess random translational motion

(B) Gases cannot be converted into solids without passing through liquid state

(C) One of the common property of liquids and gases is viscosity

(D) According to Boyle's law V/P is constant at constant T

6. If P, V, T represent pressure, volume and temperature of the gas, the correct representation of Boyle's law is

(A) $V \propto \frac{1}{T}$ (at constant P)

(B) $PV = RT$

(C) $V \propto 1/P$ (at constant T)

(D) $PV = nRT$

7. At constant temperature, in a given mass of an ideal gas

(A) The ratio of pressure and volume always remains constant

(B) Volume always remains constant

(C) Pressure always remains constant

(D) The product of pressure and volume always remains constant

8. Air at sea level is dense. This is a practical application of

(A) Boyle's law **(B)** Charle's law

(C) Avogadro's law **(D)** Dalton's law

9. If 20 cm^3 gas at 1 atm. is expanded to 50 cm^3 at constant T, then what is the final pressure

(A) $20 \times \frac{1}{50}$ **(B)** $50 \times \frac{1}{20}$

(C) $1 \times \frac{1}{20} \times 50$ **(D)** None of these

10. Which of the following statement is false

(A) The product of pressure and volume of fixed amount of a gas is independent of temperature

(B) Molecules of different gases have the same K.E. at a given temperature

(C) The gas equation is not valid at high pressure and low temperature

(D) The gas constant per molecule is known as Boltzmann constant

11. Densities of two gases are in the ratio 1 : 2 and their temperatures are in the ratio 2 : 1, then the ratio of their respective pressures is

(A) 1 : 1 **(B)** 1 : 2

(C) 2 : 1 **(D)** 4 : 1

12. At constant pressure, the volume of fixed mass of an ideal gas is directly proportional to

(A) Absolute temperature **(B)** Degree centigrade

(C) Degree Fahrenheit **(D)** None

13. Which of the following expression at constant pressure represents Charle's law

(A) $V \propto \frac{1}{T}$ **(B)** $V \propto \frac{1}{T^2}$

(C) $V \propto T$ **(D)** $V \propto d$

14. Use of hot air balloons in sports and meteorological obsevations is an application of

(A) Boyle's law **(B)** Newtonic law

(C) Kelvin's law **(D)** Charle's law

15. A 10 g of a gas at atmospheric pressure is cooled from 273°C to 0°C keeping the volume constant, its pressure would become

(A) 1/2 atm **(B)** 1/273 atm

(C) 2 atm **(D)** 273 atm

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. A and B are two identical vessels. A contains 15 g ethane at 1atm and 298 K. The vessel B contains 75 g of a gas X_2 at same temperature and pressure. The vapour density of X_2 is :

(A) 75 **(B)** 150
(C) 37.5 **(D)** 45

2. The density of neon will be highest at :

(A) STP **(B)** 0°C, 2 atm
(C) 273°C. 1 atm **(D)** 273°C. 2 atm

3. Equal weights of ethane & hydrogen are mixed in an empty container at 25° C, the fraction of the total pressure exerted by hydrogen is:

(A) 1 : 2 **(B)** 1 : 1
(C) 1 : 16 **(D)** 15 : 16

4. A mixture of hydrogen and oxygen at one bar pressure contains 20% by weight of hydrogen. Partial pressure of hydrogen will be

(A) 0.2 bar **(B)** 0.4 bar
(C) 0.6 bar **(D)** 0.8 bar

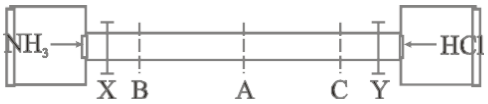
5. A compound exists in the gaseous phase both as monomer (A) and dimer (A_2). The atomic mass of A is 48 and molecular mass of A_2 is 96. In an experiment 96 g of the compound was confined in a vessel of volume 33.6 litre and heated to 273ºC. The pressure developed if the compound exists as dimer to the extent of 50 % by weight under these conditions will be :

(A) 1 atm **(B)** 2 atm
(C) 1.5 atm **(D)** 4 atm

6. 20 ℓ of SO_2 diffuses through a porous partition in 60 seconds. Volume of O_2 diffuse under similar conditions in 30 seconds will be :

(A) 12.14 ℓ **(B)** 14.14 ℓ
(C) 18.14 ℓ **(D)** 28.14 ℓ

7. See the figure-1 :



The valves of X and Y are opened simultaneously. The white fumes of NH_4Cl will first form at:

(A) A
(B) B
(C) C
(D) A,B and C simultaneously

8. X ml of H_2 gas effuses through a hole in a container in 5 sec. The time taken for the effusion of the same volume of the gas specified below under identical conditions is :

(A) 10 sec. He **(B)** 20 sec. O_2
(C) 25 sec. CO_2 **(D)** 55 sec. CO_2

9. Three identical footballs are respectively filled with nitrogen , hydrogen and helium at same pressure. If the leaking of the gas occurs with time from the filling hole, then the ratio of the rate of leaking of gases ($r_{N_2} : r_{H_2} : r_{He}$) from three footballs under identical conditions (in equal time interval) is :

(A) $\left(1 : \sqrt{14} : \sqrt{7}\right)$ **(B)** $\left(\sqrt{14} : \sqrt{7} : 1\right)$
(C) $\left(\sqrt{7} : 1 : \sqrt{14}\right)$ **(D)** $\left(1 : \sqrt{7} : \sqrt{14}\right)$

The rates of diffusion of SO_3, CO_2, PCl_3 and SO_2 are in the following order -

(A) $PCl_3 > SO_3 > SO_2 > CO_2$
(B) $CO_2 > SO_2 > PCl_3 > SO_3$
(C) $SO_2 > SO_3 > PCl_3 > CO_2$
(D) $CO_2 > SO_2 > SO_3 > PCl_3$

11. The kinetic energy of N molecules of O_2 is x joule at – 123ºC. Another sample of O_2 at 27ºC has a kinetic energy of 2 x. The latter sample contains ________ molecules of O_2.

(A) N **(B)** N/2
(C) 2 N **(D)** 3 N

12. The average kinetic energy (in joules of) molecules in 8.0 g of methane at 27° C is :

(A) 6.21×10^{-20} J/molecule
(B) 6.21×10^{-21} J/molecule
(C) 6.21×10^{-22} J/molecule
(D) 3.1×10^{-22} J/molecule

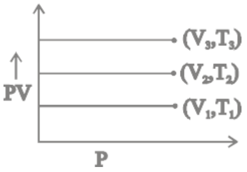
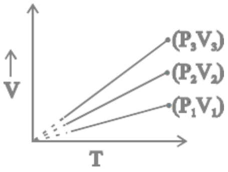
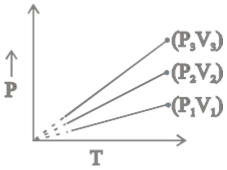
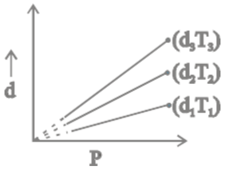
13. According to kinetic theory of gases, for a diatomic molecule :

(A) The pressure exerted by the gas is proportional to the mean velocity of the molecule.
(B) The pressure exerted by the gas is proportional to the r.m.s. velocity of the molecule.
(C) The r.m.s. velocity of the molecule is inversely proportional to the temperature.
(D) The mean translational K.E. of the molecule is proportional to the absolute temperature.

10.

Exercise # 3 PART - 1 MATRIX MATCHCOLUMN

1. For a fixed amount of the gas match the two column :

Column-I	Column-II
(A) 	**(p)** $T_1 > T_2 > T_3$
(B) 	**(q)** $P_1 > P_2 > P_3$
(C) 	**(r)** $V_1 > V_2 > V_3$
(D) 	**(s)** $d_1 > d_2 > d_3$

2.

Column-I	Column-II
(A) $P_1V_1 = P_2V_2 = P_3V_3 =$	**(1)** Dalton's law of partial pressures at constant temperature
(B) $\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3} =$ .... at constant pressure.	**(2)** Kinetic equation of ideal gases.
(C) $r \propto \sqrt{\frac{1}{d}}$	**(3)** 22.4 litre at STP
(D) $P = P_1 + P_2 + P_3 +$	**(4)** Isotherm
(E) $(V - b)\left(P + \frac{a}{V^2}\right) = RT$	**(5)** Isobar
(F) R/N	**(6)** Charles' law
(G) Molar volume	**(7)** Graham's law
(H) $PV = \frac{1}{3}mnc^2$	**(8)** Boyle's law
(I) Graph between P and V at constant temperature	**(9)** Equation for real gases.
(J) Graph between V and T at constant pressure	**(10).** Boltzmann's constant.

3.

Column – I	Column – II
(A) At low pressure	**(p)** $Z = 1 + \frac{pb}{RT}$
(B) At higher pressure	**(q)** $Z = 1 - \frac{a}{V_mRT}$
(C) At low density of gas	**(r)** gas is more compressible than ideal gas
(D) For H_2 and He at 0°C	**(s)** gas is less compressible than ideal gas

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. Which of the following expressions correctly represents the relationship between the average molar kinetic energy. $\overline{KE}$ of CO and N_2 molecules at the same temperature? **[CBSE AIPMT 2000]**

(A) $\overline{KE}_{CO} \square \overline{KE}_{N_2}$

(B) $\overline{KE}_{CO} \square \overline{KE}_{N_2}$

(C) $\overline{KE}_{CO} \square \overline{KE}_{N_2}$

(D) Cannot be predicited unless volumes of the gases are given

2. Acompound formed by elements Aand B crystallises in the cubic structure, where A atoms are present at the corners of a cube and B atoms are present at the face centres. The formula of the compound is **[CBSE AIPMT 2000]**

(A) A_2B_2 **(B)** AB_3
(C) AB **(D)** A3B

3. The beans are cooked earlier in pressure cooker, because **[CBSE AIPMT 2001]**

(A) boiling point increases with increasing pressure
(B) boiling point decreases with increasing pressure
(C) extra pressure of pressure cooker, softens the beans
(D) internal energy is not lost while cooking in pressure cooker

4. Zn converts from its melted state to its solid state, it is hcp structure, then find out the number of nearest atoms. **[CBSE AIPMT 2001]**

(A) 6 **(B)** 8
(C) 12 **(D)** 4

5. The der Waals'real gas, act as an ideal gas, at which condition? **[CBSE SIPMT 2002]**

(A) High temperature, low pressure
(B) Low temperature, high pressure
(C) High temperature, high pressure
(D) Low temperature, low pressure

6. The pyknometic density of sodium chloride crystal is 2.165×10^3 kg m^{-3} while its X-ray density is 2.178 $\times 10^3$ kg m^{-3}. The fraction of unoccupied sites in sodium chloride crystal is **[CBSE AIPMT 2003]**

(A) 5.96×10^{-1} **(B)** 5.96×10^{-3}
(C) 5.96 **(D)** 5.96×10^{-2}

7. A compound formed by elements X and Y crystallises in a cubic structure in which the X-atoms are at the corners of a cube and the Y-atoms are at the face centres. The formula of the compound is **[CBSE AIPMT 2004]**

(A) XY_3 **(B)** X_3Y
(C) XY **(D)** XY_2

8. The surface tension of which of the following liquids is maximum ? **[CBSE AIPMT 2005]**

(A) H_2O **(B)** C_6H_6
(C) CH_3OH **(D)** C_2H_5OH

9. In a face centred cubic (fcc) lattice, a unit cell is shared equally by how many unit cells ? **[CBSE AIPMT 2005]**

(A) 8 **(B)** 4
(C) 2 **(D)** 6

10. CsBr crystallises in a body centred cubic lattice. The unit cell length is 436.6 pm. Given that the atomic mass of Cs = 133 u and that of Br = 80 u and Avogadro number being 6.023×10^{23} mol^{-1}, the density of CsBr is **[CBSE AIPMT 2006]**

(A) 42.5 g/cm^3 **(B)** 0.425 g/cm^3
(C) 8.25 g/cm^3 **(D)** 4.25 g/cm^3

11. The appearance of colour in solid alkali metal halides is generally due to **[CBSE AIPMT 2006]**

(A) F - centres **(B)** Schottky defect
(C) Frenkel defect **(D)** Interstitial positions

12. The fraction of total volume occupied by the atoms present in a simple sube is **[CBSE AIPMT 2007]**

(A) $\frac{\pi}{6}$ **(B)** $\frac{\pi}{3\sqrt{2}}$
(C) $\frac{\pi}{4\sqrt{2}}$ **(D)** $\frac{\pi}{4}$

13. If NaCl is doped with 10^{-4} mol % of $SrCl_2$, the concentration of cation vacancies will be ($N_A = 6.023 \times 10^{23}$ mol^{-1}) **[CBSE AIPMT 2007]**

(A) 6.023×10^{15} mol^{-1} **(B)** 6.023×10^{16} mol^{-1}
(C) 6.023×10^{17} mol^{-1} **(D)** 6.023×10^{14} mol^{-1}

MOCK TEST

STRAIGHT OBJECTIVE TYPE

1. If some moles of O_2 diffuse in 18 sec and same moles of other gas diffuse in 45 sec then what is the molecular weight of the unknown gas

(A) $\frac{45^2}{18^2} \times 32$ **(B)** $\frac{18^2}{45^2} \times 32$ **(C)** $\frac{18^2}{45^2 \times 32}$ **(D)** $\frac{45^2}{18^2 \times 32}$

2. The ratio of rates of diffusion of SO_2, O_2 and CH_4 is

(A) $1 : \sqrt{2} : 2$ **(B)** $1 : 2 : 4$ **(C)** $2 : \sqrt{2} : 1$ **(D)** $1 : 2 : \sqrt{2}$

3. If C_1, C_2, C_3...... represent the speeds of n_1, n_2, n_3........... molecules, then the root mean square speed is

(A) $\left(\frac{n_1C_1^2 + n_2C_2^2 + n_3C_3^2 + \square}{n_1 + n_2 + n_3 + \square}\right)^{1/2}$

(B) $\frac{(n_1C_1^2 + n_2C_2^2 + n_3C_3^2 + \square)^{1/2}}{n_1 + n_2 + n_3 + ...}$

(C) $\frac{(n_1C_1^2)^{1/2}}{n_1} + \frac{(n_2C_2^2)^{1/2}}{n_2} + \frac{(n_3C_3^2)^{1/2}}{n_3} + ...$

(D) $\left[\frac{(n_1C_1 + n_2C_2 + n_3C_3 + ...)^2}{(n_1 + n_2 + n_3 + ...)}\right]^{1/2}$

4. 50 ml of hydrogen diffuses out through a small hole from a vessel in 20 minutes. The time needed for 40 ml of oxygen to diffuse out is

(A) 12 min **(B)** 64 min **(C)** 8 min **(D)** 32 min

5. At what temperature will the average speed of CH_4 molecules have the same value as O_2 has at 300 K

(A) 1200 K **(B)** 150 K **(C)** 600 K **(D)** 300K

6. A sample of O_2 gas is collected over water at 23°C at a barometric pressure of 751 mm Hg (vapour pressure of water at 23° C is 21 mm Hg). The partial pressure of O_2 gas in the sample collected is

(A) 21 mm Hg **(B)** 751mm Hg **(C)** 0.96 atm **(D)** 1.02atm

7. In an experiment during the analysis of a carbon compound, 145 l of H_2 was collected at 760 mm Hg pressure and 27° C temperature. The mass of H_2 is nearly

(A) 10 g **(B)** 12 g **(C)** 24 g **(D)** 6 g

8. The volume of 1 g each of methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}) was measured at 350 K and 1 atm. What is the volume of butane

(A) 495 **(B)** 600 **(C)** 900 **(D)** 1700

9. The ratio of the rate of diffusion of helium and methane under identical condition of pressure and temperature will be

(A) 4 **(B)** 2 **(C)** 1 **(D)** 0.5

10. At what temperature in the celsius scale, V (volume) of a certain mass of gas at 27° C will be doubled keeping the pressure constant

(A) 54° C **(B)** 327° C **(C)** 427° C **(D)** 527°C

11. If pressure becomes double at the same absolute temperature on 2 L CO_2, then the volume of CO_2 becomes

(A) 2 L **(B)** 4 L **(C)** 25 L **(D)** 1 L

12. If density of vapours of a substance of molar masss 18gm/mole at 1 atm pressureand 500K is 0.36 kg m^{-3}, then value of Z for the vapours is : (Take $R = 0.082$ L atm $mole^{-1}$ K^{-1})

(A) $\frac{41}{50}$ **(B)** $\frac{50}{41}$ **(C)** 1.1 **(D)** 0.9

CHAPTER 12

NOMENCLATURE OF ORGANIC COMPOUNDS

Organic compounds exist in which a hydrogen atom, joined to the carbon, acquires acid properties as a result of the proximity of certain functional groupings.

"VICTORGRIGNARD"

INTRODUCTION

The IUPAC of organic chemistry is a systematic method of naming organic chemical compounds as recommended by the International Union of Pure and Applied Chemistry (IUPAC) . It is published in the nomenclature of organic chemistry. Ideally, every possible organic compounds should have a name which an unambiguous structural formula can becreated.

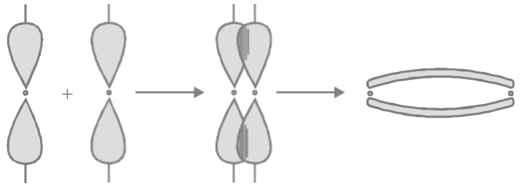
To avoid long and tedious names in normal communication the official IUPAC naming recommendations are not always followed in practice, except when it is necessary to give an unambiguous and absolute definition to a compound. IUPAC name can be simpler than older names, as with ethanol, instead of ethyl alcohal. For relatively simple molecules they can be more easily understood than non-systematic names, which must be learnt or looked up.

- (sigma) bonds : The molecular orbital formed by the overlapping of two-s atomic orbitals or one s and one p atomic orbitals or co-axial overlapping of p-orbitals is called a σ bond.

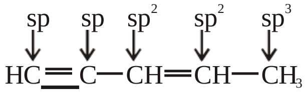
or

or

(Pi) bonds : π bond is formed by the lateral overlapping of two p-atomic orbitals. It is weaker than σ bond, as there is only partial overlapping.

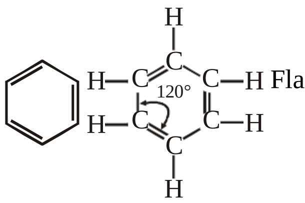


Ex.



$\overset{sp}{HC} \equiv \overset{sp}{C} - \overset{sp^2}{CH} = \overset{sp^2}{CH} - \overset{sp^3}{CH_3}$

Ex.



Flat hexagonal structural due to sp^2 hybridised

C-atom in benzene

ETOOS KEY POINTS

(i) Overlapping of hybrid orbitals also give σ bonds. σ bonds are stronger, as they are resulted from the effective axial overlapping.

(ii) More the directional character (p) in covalent bond more is the strength of the bond.

$$sp^3 - sp^3 > sp^3 - sp^2 > sp^2 - sp^2 > sp - sp$$

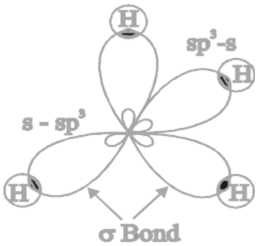
(iii) π electrons are mobile hence π bond is more reactive. π bond is formed by the collateral overlapping of sp^2 orbitals.

(iv) sp^2 hybridised orbitals overlap with each other and with s orbitals of six H-atoms forming C–C and C–H σ bonds.

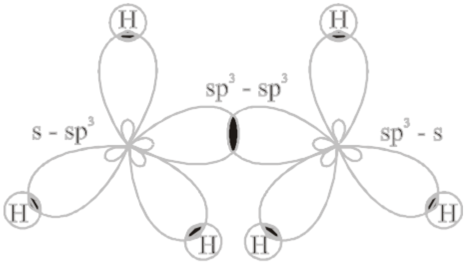
(v) Six 2p unhybridised orbitals of 6 C-atom in benzene form 3π bonds by lateral overlapping with each other. These six π electrons are free to move over all the six carbon atoms. Since delocalised electrons have lower energy than localised.

(vi) The relative sized of hybrid orbital follows the order $sp^3 > sp^2 > sp$

(vii) The electronegativity of hybrid orbitals follows the order $sp > sp^2 > sp^3$

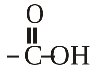
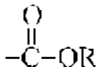
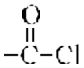
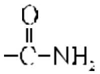
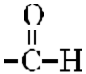
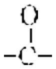
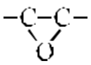


Methane



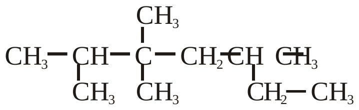
Ethane

The order of priority of functional groups used in IUPAC nomenclature of organic compounds.

Functional Group	Structure	Prefix	Suffix
Carboxylic acid	 $-\overset{O}{\overset{\|}{C}}-OH$	Carboxy	- oic acid
Sulphonic acid	$-SO_3H$	Sulpho	sulphonic acid
Ester	 $-\overset{O}{\overset{\|}{C}}-OR$	Alkoxy carbonyl	alkyl...oate
Acid chloride	 $-\overset{O}{\overset{\|}{C}}-Cl$	Chloroformyl or Chlorocarbonyl	- oyl chloride
Acid amide	 $-\overset{O}{\overset{\|}{C}}-NH_2$	Carbamoyl/Amido	- amide
Carbonitrile/Cyanide	$-C \equiv N$	Cyano	nitrile
Aldehyde	 $-\overset{O}{\overset{\|}{C}}-H$	Formyl or Oxo	- al
Ketone	 $-\overset{O}{\overset{|}{C}}-$	Keto or oxo	- one
Alcohol	$-OH$	Hydroxy	- ol
Thio alcohol	$-SH$	Mercapto	thiol
Amine	$-NH_2$	Amine	amine
Ether	$-O-R$	Alkoxy	-
Oxirane		Epoxy	-
Nitro derivative	$-NO_2$	Nitro	-
Nitroso derivative	$-NO$	Nitroso	-
Halide	$-X$	Halo	-
Double bond	$C = C$	-	ene
Triple bond	$C \equiv C$	-	yne

SOLVED EXAMPLE

Ex. 1 How may 1°, 2°, 3° and 4° carbon atoms are present in following molecule.

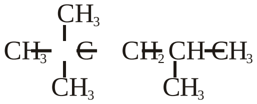


$$\mathrm{CH_3-\underset{CH_3}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\underset{CH_2-CH_3}{CH}-CH_3}$$

Sol. 1° Carbon atoms = 6, 2° Carbon atoms = 2,
3° Carbon atoms = 2, 4° Carbon atom = 1

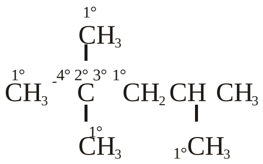
Note : Primary, secondary, tertiary & quaternary carbon atoms in a molecule are denoted by the letters p, s, t and q respectively.

Ex. 2 How many 1°, 2°, 3° and 4° carbon atoms are present in following molecule.



$$\mathrm{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\underset{CH_3}{CH}-CH_3}$$

Sol.

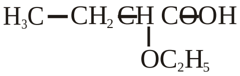


$$\mathrm{\overset{1°}{CH_3}-\overset{\overset{1°}{CH_3}}{\underset{\overset{1°}{CH_3}}{\overset{4°}{C}}}-\overset{2°}{CH_2}-\underset{1°\,CH_3}{\overset{3°}{CH}}-\overset{1°}{CH_3}}$$

1° Carbon atoms = 5, 2° Carbon atom = 1,
3° Carbon atom = 1, 4° Carbon atom = 1

Ex. 3 Write the IUPAC name of following compounds.

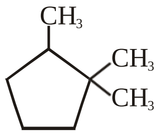
(i)



$$\mathrm{H_3C-CH_2-\underset{OC_2H_5}{CH}-COOH}$$

(ii) 3-Bromocyclohexane-1-sulphonic acid

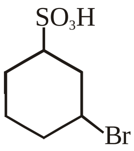
(iii)



(iv) 3-Cyano-3-ethoxy-4-nitropentanoyl bromide

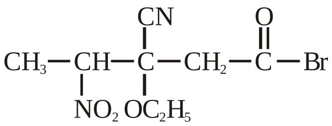
Sol. **(i)** 2-Ethoxybutanoic acid

(ii)



(iii) 1,1,2-Trimethylcyclopentane

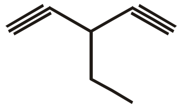
(iv)



$$\mathrm{CH_3-\underset{NO_2}{CH}-\overset{CN}{\underset{OC_2H_5}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-Br}$$

Ex. 4 Draw the structure of following IUPAC name.

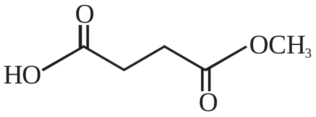
(i)



(ii) 3-Methoxycarbonylpropanoic acid

Sol. **(i)** 3-Ethypenta-1,4-diyne

(ii)

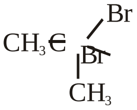


Ex. 5 Make the structure of following organic compounds

1. Isopropylidene Bromide
2. Active amylene Iodide
3. Isobutylene glycol
4. Isobutylene

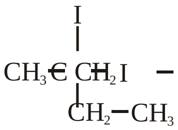
5. Trimethylene glycol

Sol. **1.**



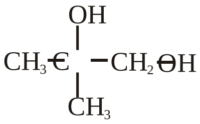
$$\mathrm{CH_3-\overset{Br}{\underset{CH_3}{C}}-Br}$$

2.



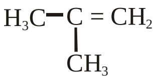
$$\mathrm{CH_3-\overset{I}{\underset{CH_2-CH_3}{C}}H_2I}$$

3.



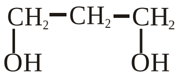
$$\mathrm{CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2-OH}$$

4.



$$\mathrm{H_3C-\underset{CH_3}{C}=CH_2}$$

5.



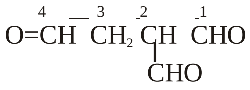
$$\mathrm{\underset{OH}{CH_2}-CH_2-\underset{OH}{CH_2}}$$

Ex. 6 The correct IUPAC name of the following compound is

$$\mathrm{O=CH-CH_2-\underset{H-C=O}{CH}-CHO}$$

(A) 1,1-diformyl propanal
(B) 3-formyl butanedial
(C) 2-formyl butanedial
(D) 1, 1,3-ethane tricarbaldehyde

Sol. **(C)** The principal functional group is – CHO.



$$\mathrm{O=\overset{4}{CH}-\overset{3}{CH_2}-\underset{CHO}{\overset{2}{CH}}-\overset{1}{CHO}}$$

2-formyl butanedial

Exercise # 1

SINGLE OBJECTIVE **NEET LEVEL**

1. The hybrid state of C-atoms which are attached to a single bond with each other in the following structure are :

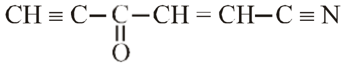
$CH_2 = CH–C \equiv CH$

(A) sp^2, sp (B) sp^3, sp
(C) sp^2, sp^2 (D) sp^2, sp^3

2. In the compound $HC \equiv C – CH_2 – CH = CH–CH_3$, the $C_2–C_3$ bond is the type of :

(A) $sp – sp^2$ (B) $sp^3 – sp^3$
(C) $sp – sp^3$ (D) $sp^2 – sp^2$

3. The number of acetynilic bond in the structure are :



$$CH \equiv C-\underset{\underset{O}{\|}}{C}-CH = CH-C \equiv N$$

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

4. The group of heterocyclic compound is :

(A) Phenol, Furane (B) Furane, Thiophene
(C) Thiophene, Phenol (D) Furane, Aniline

5. Which of the following is the first member of ester homologous series ?

(A) Ethyl ethanoate (B) Methyl ethanoate
(C) Methyl methanoate (D) Ethyl methanoate

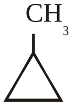
6. Which of the following compound's prefix 'iso' is not correct –

(A) Iso pentane (B) Iso Hexane
(C) Iso butane (D) Iso octane

7. A substance containing an equal number of primary, secondary and tertiary carbon atoms is :

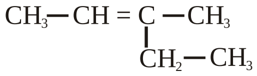
(A) Mesityl Oxide (B) Mesitylene
(C) Maleic acid (D) Malonic acid

8. How many secondary carbon atoms does methyl cyclopropane have ?



(A) Nine (B) One
(C) Two (D) Three

9. The IUPAC name of the compound



$$CH_3-CH = \underset{\underset{CH_2-CH_3}{|}}{C}-CH_3 \quad \text{is :}$$

(A) 2-Ethyl-2-butene (B) 3-Ethyl-2-butene
(C) 3-Ethyl-2-butene (D) 3-methyl-2-pentene

10. IUPAC name of $CH_2=CH – CH_2–CH_2– C \equiv CH$ is :

(A) 1, 4-Hexenyne (B) 1-Hexen-5-yne
(C) 1-Hexyne-5-ene (D) 1, 5-Hexyne

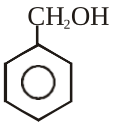
11. $(CH_3)_3 C – CH=CH_2$ has the IUPAC name :

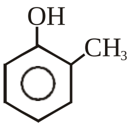
(A) 3,3 – Dimethyl-1-butene
(B) 2, 2-Dimethyl-1-butene
(C) 2, 2-Dimethyl-3-butene
(D) 1, 3-Dimehtyl-1-propene

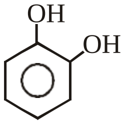
12. What is not true about homologous series ?

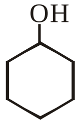
(A) All the members have similar chemical properties
(B) They have identical physical properties
(C) They can be represented by a general formula
(D) Adjacent members differ in molecular mass by 14

13. The homologue of phenol is –

(A)


(B)


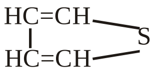
(C)


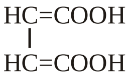
(D)


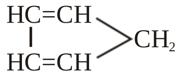
14. The IUPAC name of the following is $[CH_3CH(CH_3)]_2 C(CH_2CH_3)C(CH_3)C(CH_2CH_3)_2$

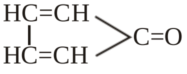
(A) 3,5-Diethyl-4,6-dimethyl-5-[1-methylethyl] hept-3-ene
(B) 3, 5-Diethyl-5-isopropyl-4, 6-dimethylhept-2-ene
(C) 3,5-Diethyl-5-propyl-4, 6-dimethylhept-3-ene
(D) None of these

15. Which of the following is a heterocyclic compound

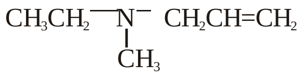
(A)


(B)


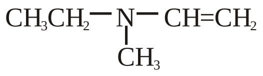
(C)


(D)


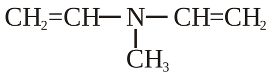
16. Ethyl methyl vinyl amine has the structure –

(A)


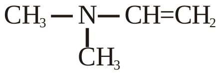
$$CH_3CH_2-\underset{\underset{CH_3}{|}}{N}-CH_2CH=CH_2$$

(B)


$$CH_3CH_2-\underset{\underset{CH_3}{|}}{N}-CH=CH_2$$

(C)


$$CH_2=CH-\underset{\underset{CH_3}{|}}{N}-CH=CH_2$$

(D)


$$CH_3-\underset{\underset{CH_3}{|}}{N}-CH=CH_2$$

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. The number of C-atoms in second member of an ester is/are :

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

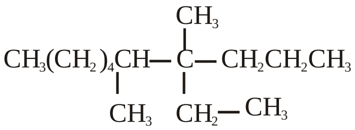
2. The number of primary, secondary and tertiary carbon atom in toluene is given by the set :

(A) 1, 6, 0 (B) 1, 5, 1
(C) 2, 5, 0 (D) 1, 6, 1

3. $C_3H_6Br_2$ can shows :

(A) Two gem dibromide
(B) Three vic dibromide
(C) Two tert. dibromo alkane
(D) Two sec. dibromo alkane

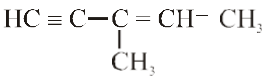
4. What is the correct IUPAC name for the following compound ?



$CH_3(CH_2)_4CH(CH_3)-C(CH_3)(CH_2-CH_3)-CH_2CH_2CH_3$

(A) 3, 4-Dimethyl-3-propyl nonane
(B) 6, 7-Dimethyl-2-propyl nonane
(C) 6, 7-Dimethyl-7-ethyl decane
(D) 4-Ethyl-4, 5-dimethyl decane

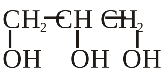
5. The IUPAC name for



$HC \equiv C-C(CH_3) = CH-CH_3$

(A) 3-methyl-2-pentene-4-yne
(B) 3-Methyl-3-pentene-1-yne
(C) 3-methyl-4-pentyne-1-ene
(D) 3-Methyl pentenyne

6. The IUPAC name of the compound Glycerine



$CH_2(OH)-CH(OH)-CH_2(OH)$

(A) 1, 2, 3-Tri hydroxy propane
(B) 3-Hydroxy pentane-1, 5-diol
(C) 1, 2, 3-Hydroxypropane
(D) Propane-1,2,3-triol

7. Which of the following is crotonic acid :

(A) $CH_2 = CH-COOH$
(B) $C_6H_5-CH = CH-COOH$
(C) $CH_3-CH = CHCOOH$
(D)

$CH-COOH \| CH\ COOH$

(A)

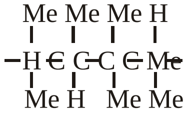
8. In which of the following species a carbon has sp-hybridization :

(A) CH_3COOH (B) CH_3COCH_3
(C) CH_3-CH_2-CN (D)

9. All the following IUPAC name are correct except :

(A) 1-Chloro-1-ethoxy propane
(B) 1-Amino-1-ethoxypropane
(C) 1-Ethoxy-2-propanol
(D) 1-Ethoxy-1-propanamine

10. Number of 3° carbon and 1° hydrogen respectively in the following structure are :



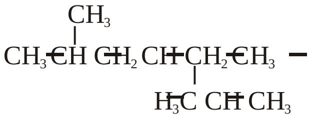
(A) 3, 21 (B) 3, 23
(C) 2, 18 (D) 3, 18

11. Which of the following are tertiary radicals :

(A) $(CH_3)_3\dot{C}$ (B) $(CH_3)_2\dot{C}H$

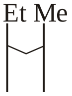
(C) $(CH_3)_2\dot{C}-C_2H_5$ (D) $(CH_3)_3C-\dot{C}H_2$

12. The correct IUPAC name for the given structure is :



3-Isopropyl-4-methylhexane
(B) 4-Isoprpyl-3-methylhexane
(C) 3-Ethyl-2, 5-dimethylhexane
(D) 2-Ethyl-3-isopropylpentane

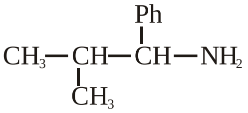
13. The IUPAC name of



is :

(A) 2, 3-Dimethyl hexane
(B) 2-Ethyl-4-methyl pentane
(C) 3-Ethyl-2-methyl pentane
(D) 2, 4-Dimethyl hexane

14. The IUPAC name of the compound is

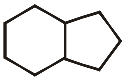
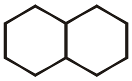
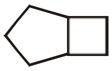
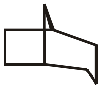


$CH_3-CH(CH_3)-CH(Ph)-NH_2$

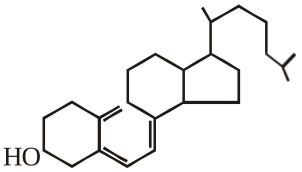
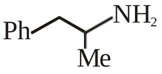
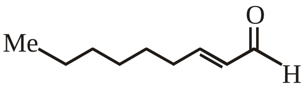
(A) 1-Amino-1-phenyl-2-methyl propane
(B) 2-Methyl-1-phenyl propane-1-amine
(C) 2-Methyl-1-amino-1-phenyl propane
(D) 2-Chloro-2-Methylpropane

Exercise # 3 PART - 1 MATRIX MATCHCOLUMN

1. Match column I with column II and select the correct answer from the given codes :

Column - I **(Compounds)**	**Column - II** **(number of carbons in the bridges)**
(A) 	**(p)** [3.2.1]
(B) 	**(q)** [4.3.0]
(C) 	**(r)** [4.4.0]
(D) 	**(s)** [3.2.0]

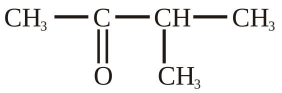
2. Match the column

Column - I **Compound**	**Column - II** **Containing all the functional groups**
(A)  Vitamin D_3	**(p)** 1°amine
(B)  Amphetamine	**(q)** 2° alcohol
(C)  A cockroach repellent found in cucumbers	**(r)** Triene
	(s) Aldehyde and ene

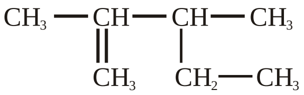
Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. The incorrect IUPAC name is

[CBSE AIPMT 2001]

(A) 
$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

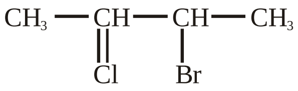
2-methyl-3-butanone

(B) 
$CH_3-\underset{\underset{CH_3}{\|}}{CH}-\underset{\underset{CH_2-CH_3}{|}}{CH}-CH_3$

2, 3-dimethyl pentane

(C) $CH_3-C\equiv CCH(CH_3)_2$

4-methyl-2pentyne

(D) 
$CH_3-\underset{\underset{Cl}{\|}}{CH}-\underset{\underset{Br}{|}}{CH}-CH_3$

2-bromo-3chloro butane

2. IUPAC name of the following is

[CBSE AIPMT 2002]

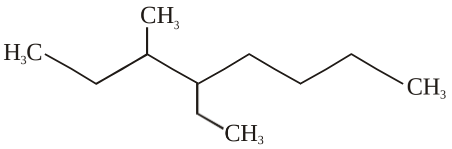
$CH_2=CH-CH_2-CH_2-C\equiv CH$

(A) 1, 5-hexenyne **(B)** 1-hexene-5-yne

(C) 1-hexyne-5-ene **(D)** 1, 5-hexynene

3. Name of the compound given below

[CBSE AIPMT 2003]



(A) 2, 3-diethylheptane

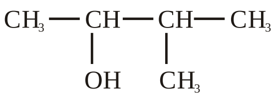
(B) 5-ethyl-6-methyloctane

(C) 4-ethyl-3-methylocatne

(D) 3-methyl-4-ethyloctane

4. Names of some compounds are given. Which one if not correct in IUPAC system?

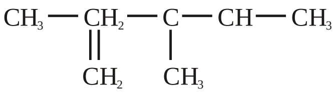
[CBSE AIPMT 2005]

(A) 
$CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

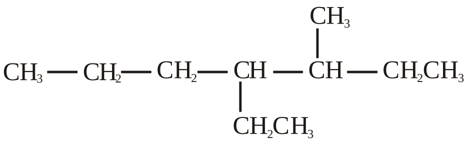
3-methyl-2-butanol

(B) $CH_3-C\equiv CH-CH(CH_3)_2$

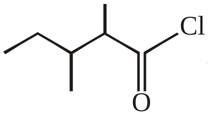
4-methyl-2-pentyne

(C) 
$CH_3-\underset{\underset{CH_2}{\|}}{CH_2}-\underset{\underset{CH_3}{|}}{C}-CH-CH_3$

2- enthyl-3-methylbut-ene

(D) 
$CH_3-CH_2-CH_2-\underset{\underset{CH_2CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_2CH_3$

3- methyl-4-ethyl heptane

5. The IUPAC name of  is

[CBSE AIPMT 2006]

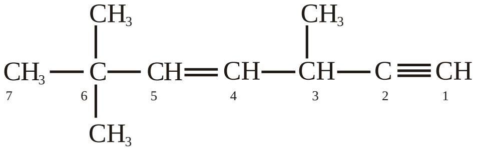
(A) 3, 4-dimethylpentanoyl chloride

(B) 1-chloro-1-oxo-2, 3-dimethylpentane

(C) 2-enthyl-3methylbutanoyl chloride

(D) 2, 3-dimethylpentanoyl chloride

6. The state of hybridisation of C_2, C_3, C_5 and C_6 of the hydrocarbon,


$\underset{7}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\underset{6}{C}}}-\underset{5}{CH}=\underset{4}{CH}-\overset{\overset{CH_3}{|}}{\underset{3}{CH}}-\underset{2}{C}\equiv\underset{1}{CH}$

is in the followng sequence **[CBSE AIPMT 2009]**

(A) sp, sp^3, sp^2 and sp^3

(B) sp^3, sp^2, sp^2 and sp

(C) sp, sp^2, sp^2 and sp^3

(D) sp, sp^2, sp^3 and sp^2

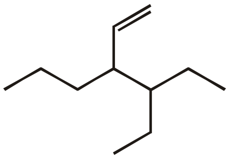
7. The IUPAC name of the compound having the formula $CH\equiv C-CH=CH_2$ is **[CBSE AIPMT 2009]**

(A) 3-butene-1-yne **(B)** 1-butyn-3-ene

but-1-yne-3-ene **(D)** 1-butene-3-yne

8. The correct IUPAC name of the compound

[CBSEAIPMT 2011]

 is

(A) 3-ethyl-4-ethenylheptane

(B) 3-ethyl-4-propylhex-5-ene

(C) 3-(1-ethyl propyl) hex-1-ene

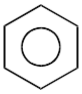
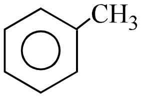
(D) 4-ethyl-3-propylhex-1-ene

MOCK TEST

1. How many carbons are in simplest alkyne having two side chains?
(A) 5 **(B)** 6 **(C)** 7 **(D)** 8

2. The commercial name of trichloroethene is:
(A) Westron **(B)** Perclene **(C)** Westrosol **(D)** Orlone

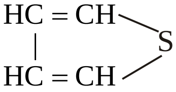
3. The compound which has one isopropyl group is:
(A) 2,2,3,3-Tetramethyl pentane **(B)** 2,2-Dimethyl pentane
(C) 2,2,3-Trimethyl pentane **(D)** 2-Methyl pentane

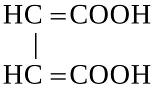
4  and 

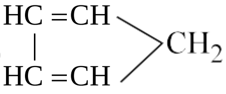
Number of secondary carbon atoms present in the above compounds are respectively:
(A) 6,4,5 **(B)** 4,5,6 **(C)** 5,4,6 **(D)** 6,2,1

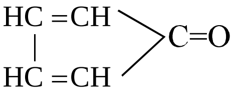
5 A substance containing an equal number of primary, secondary and tertiary carbon atoms is:
(A) Mesityl Oxide **(B)** Mesitylene
(C) Maleic acid **(D)** Malonic acid

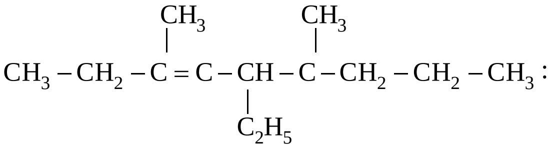
6 Which of the following is a heterocyclic compound

(A) 

(B) 

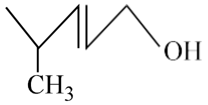
(C) 

(D) 

7 The correct IUPAC name of the compound 

$CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}=C-\underset{\underset{C_2H_5}{|}}{CH}-\overset{CH_3}{\overset{|}{C}}-CH_2-CH_2-CH_3$:

(A) 5-Ethyl-3, 6-dimethyl non-3-ene **(B)** 5-Ethyl-4, 7-dimethyl non-3-ene
(C) 4-Methyl-5, 7-diethyl oct-2-ene **(D)** 2,4-Ethyl-5-methyl oct-2-ene

8 IUPAC name of  is:

(A) 5-Methyl hexanol **(B)** 2-Methyl hexanol
(C) 2-Methyl hex-3-enol **(D)** 4-Methyl pent-2-enol

9 The IUPAC name of acetyl acetone is:
(A) Pentane-2,5- dione **(B)** Pentane -2,4-dione **(C)** Hexane-2,4-dione **(D)** Butane-2,4-dione

10 When vinyl & allyl are joined each other, we get
(A) Conjugated alkadiene **(B)** cumulative alkadiene
(C) Isolated alkadiene **(D)** Allenes

CHAPTER 14

BIOMOLECULES & POLYMERS

The beauty of Chemistry is that I can design my own molecular world.

"BENL. FERINGA"

INTRODUCTION

Complex organic compound which governs the comman activities of the living organism are called biomolecules.Living systems are made up of various complex biomolecules like carbohydrates, proteins, nuclic acids, lipids e.t.c. In addition, some simple molecules like vitamins and mineral salts also play an important role in the functions of organism.

Among biomolecule, **nucleic acids**, namely DNA and RNA have the unique function of storing of proteins, which are of critical importance to life on earth.**Carbohydrate**, which are made up of primarily of molecules containing atoms of carbon, hydrogen and oxygen are essential energy source and structural components of all life and they are among the most abundant biomolecule on earth.

Polymer is defined as a high molecular weight compound formed by the combination of large number of one or more types of small molecules(Monomers)

CARBOHYDRATES

Carbohydrates received their name because of their general formula $C_x(H_2O)_y$, according to which they appear to be hydrates of carbon.

$$xCO_2 + yH_2O \xrightarrow{\text{Sunlight, chlorophyll}} \underset{\text{Carbohydrate}}{C_x(H_2O)_y} + xO_2$$

A polyhydroxy compound that has an aldehyde or a ketone functional group present, either free or as hemiacetal or acetal are called carbohydrate.

Carbohydrates are substances with the general formula $C_x(H_2O)_y$, and were therefore called carbohydrates(hydrates of carbon) because they contained hydrogen and oxygen in the same proportion as in water.

However, a number of compounds have been discovered which are carbohydrates by chemical behaviour, but do not conform to the formula $C_x(H_2O)_y$, e.g., 2-deoxyribose, $C_5H_{10}O_4$.

ED OS KEY POINTS

It is also important to note that all compounds conforming to the formula $C_x(H_2O)_y$ are not necessarily carbohydrates, e.g., formaldehyde, CH_2O ; acetic acid, $C_2H_4O_2$; etc.

Carbohydrates are often referred to as Saccharides (Latin, Saccharum = sugar) because of the sweet taste of the simpler members of the class, the sugars.

Classification of Carbohydrate :

The carbohydrates are divided into three major classes depending on the number of simple sugar units present in their molecule.

(i) **Monosaccharide :** A carbohydrate that cannot be hydrolyzed to simpler compounds is called monosaccharide.

Monosaccharide which have six carbon are either aldohexoses or ketohexoses. **Ex.** glucose, fructose, ribose.

(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 monosaccharides units obtained on hydrolysis on 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) **Polysaccharide :** A carbohydrate that can be hydrolyzed to many monosaccharide molecules is called a polysaccharide. Example : Starch, Cellulose, etc.

The carbohydrates may also be classified as either reducing or non-reducing sugars. All those carbohydrates which reduce Fehling's solution and Tollen's reagent are referred to as reducing sugars. All monosaccharides whether aldose or ketose are reducing sugars.

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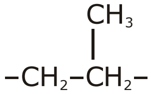
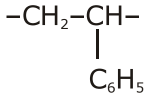
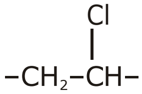
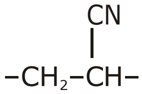
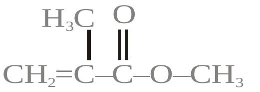
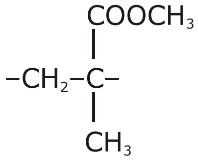
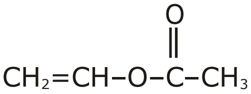
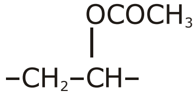
In disaccharides, if the reducing groups of monosaccharides i.e., aldehydric or ketonic groups are bonded, these are **non-reducing sugars e.g. sucrose.** On the other hand, sugars in which these functional groups are free, are called reducing sugars, for example, maltose and lactose.

COMMON POLYMERS

	Monomer	**Repeating unit**	**Polymer**
1.	$CH_2=CH_2$ Ethylene	$-CH_2-CH_2-$	Polyethylene
2.	$CH_3-CH=CH_2$ Propene	 $-CH_2-\overset{CH_3}{\overset{\vert}{CH_2}}-$	Polypropene
3.	$C_6H_5-CH=CH_2$ Styrene	 $-CH_2-\underset{C_6H_5}{\underset{\vert}{CH}}-$	Polystyrene
4.	$CF_2=CF_2$ Tetrafluoroethylene	$-CF_2-CF_2-$ ethylene (PTFE), Teflon	Polytetrafluoro
5.	$CH_2=CH-Cl$ Vinyl chloride	 $-CH_2-\overset{Cl}{\overset{\vert}{CH}}-$	Polyvinyl Chloride (PVC)
6.	$CH_2=CH-CN$ Vinyl cyanide or	 $-CH_2-\overset{CN}{\overset{\vert}{CH}}-$ polyacrylonitrile,	Polyvinyl cyanide, Acrylonitrile Orlon.
7.	 $CH_2=\overset{H_3C}{\overset{\vert}{C}}-\overset{O}{\overset{\Vert}{C}}-O-CH_3$ Methyl methacrylate	 $-CH_2-\underset{CH_3}{\underset{\vert}{\overset{COOCH_3}{\overset{\vert}{C}}}}-$ Plexiglas, Lucite	Polymethyl metha acrylate,
8.	 $CH_2=CH-O-\overset{O}{\overset{\Vert}{C}}-CH_3$ Vinyl acetate	 $-CH_2-\overset{OCOCH_3}{\overset{\vert}{CH}}-$	Polyvinyl Acetate
9.	$CH_2=CH-CH=CH_2$ 1, 3-butadiene	$-CH_2-CH-CH-CH_2-$ Buna rubber	Polybutadiene,

SOLVED EXAMPLE

Ex. 1 Sucrose on hydrolysis yields a mixture which is

(A) Optically inactive **(B)** Dextrorotatory **(C)** Laevorotatory **(D)** Racemic

Sol. **(C)** Sucrose on hydrolysis yields equimolar mixture of D-(—)-fructose and D-(+)glycose. Since specific rotation of (—)-fructose is greater than (+)-glucose D the mixture is laevorotatory.

Ex. 2 A high molecular weight molecule which does not contain repeating structural units is called a

(A) Polymer **(B)** Macromolecule **(C)** Both **(A)** and **(B)** **(D)** None of these

Sol. (B) A polymer has always repeating structural units derived from monomer. For example proteins and nucleic acid are regarded as macromolecules, but not polymers because their molecules do not contain repeating structural units. All polymers are macromolecules, but all macromolecules are not polymers.

Ex. 3 The force of attraction between the neighbouring peptide chains is

(A) van der Waal's force **(B)** Covalent bond **(C)** Hydrogen bond **(D)** Peptide linkage

Sol. **(C)** Neighbouring peptide chains are held by hydrogen bonds between —CO— and — NH—.

Ex. 4 Peptides on hydrolysis give

(A) Ammonia **(B)** Amines **(C)** Amino acids **(D)** Hydroxy acids

Sol. **(C)** Peptides are formed by condensation of α-amino acids. Therefore, on hydrolysis they yield α-amino acids.

Ex. 5 An example of a condensation polymer is

(A) PVC **(B)** terylene **(C)** polypropylene **(D)** polystyrene

Sol. (B) In condensation polymerization, a series of condensation reactions between the (generally two) monomers containing atleast two functional groups each occur with the loss of a small molecule such as H_2O, CH_3OH or HX (X = halogen). Terylene is a condensation polymer of ethylene glycol and terephthalic acid.

Ex. 6 Although both polymers are prepared by free radical processes, poly (vinyl chloride) is amorphous and poly (vinylidene chloride) (saran) is highly crystalline. How do you account for the different ? (vinylidene chloride is 1,1-dichloroethene).

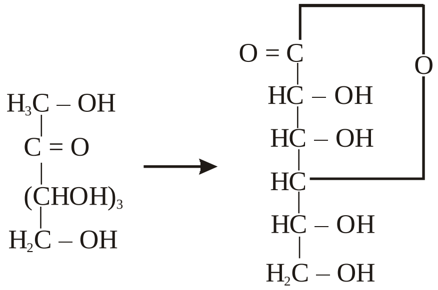
Sol. As poly (vinyl chloride) is able to show stereoisomerism and further it is formed by a free radical process, it is atactic (chlorine atoms (distributed randomly), the molecules fit together poorly.

Poly (vinylidene chloride) has two identical substituents on each carbon and the chains fit together well.

Ex. 7 Compound A $C_5H_{10}O_4$, is oxidized by $Br_2 - H_2O$ to the acid, $C_5H_{10}O_5$. (A) Forms a triacetate (Ac_2O) and is reduced by HI to n-pentane. Oxidation of (A) with HIO_4 gives, among other product, 1 molecule of CH_2O and 1 molecule of HCO_2H. What are the possible structures of (A) and how could you distinguish between them ?

Sol. (A) is an aldehyde, contains three hydroxyl groups and the carbon skeleton consists of five carbon atoms in a straight chain. Also, the formula $C_5H_{10}O_4$ therefore suggests that (A) is a deoxy-sugar. If we now try to work out the possibilities based directly on the periodic oxidation of (A), we shall find it.

Ex. 8 Convert



Exercise # 1

SINGLE OBJECTIVE **NEET LEVEL**

1. Which one among the following is athermosetting plastic

(A) PVC (B) PVA
(C) Bakelite (D) Perspex

2. The basis on the mode of their formation, the polymers can be classified

(A) As addition polymers only
(B) As condensation polymers only
(C) As copolymers
(D) Both as addition and condensation polymers

3. Theremoplastics are

(A) Linear polymers (B) Highlycross-linked
(C) Both (A) and (B) (D) Crystalline

4. 'Cis-1, 4-polyisoprene' is

(A) Thermoplastic
(B) Thermosetting plastic
(C) Elastic (rubber)
(D) Resin

5. 'Shellac' secreted by lac insects is

(A) Natural plastic (B) Natural resin
(C) Natural elastic (D) Any of these

6. Which of the following is a syndiotactic polymer in $-[-CH_2 - C(YZ)-]_z -$

(A) All Y group lie on one side of the chain and all Z groups on the other side
(B) The Y and Z groups lie altermately on each side of the chain
(C) The Y and Z groups are arranged in a random fashion
(D) Y and Z groups are same

7. Polymers of the type Z – Mn – Y, i.e. those which contain a foreign molecule in addition to the recurring unit are known as

(A) Semisynthetic polymers
(B) Atactic polymers
(C) Telomers
(D) Plasticiser

8. In the natural rubber 'Caoutchuc', the isoprene units are joined by

(A) Head-to-head (B) Tail-to-tail
(C) Heat-to-tail (D) All of these

9. The degree of crystallinity of which of the following is highest

(A) Atactic polyvinylchloride
(B) Isotactic polyvinylchloride
(C) Syndiotactic polyvinylchloride
(D) all of these

10. Monomers are converted to polymer by

(A) Hydrolysis of monomers
(B) Condensation reaction between monomers
(C) Protonation of monomers
(D) None of these

11. Polymer formation from monomers starts by

(A) Condensatin reaction between monomers
(B) Coordinate reaction between monomers
(C) Conversion of monomer to monomer ions by protons
(D) Hydrolysis of monomers

12. When condensation product of hexamethylenediamine and adipic acid is heated to 553 K (80°C) in an atmosphere of nitrogen for about 4-5 hours, the product obtained is

(A) Solid polymer of nylon 66
(B) Liquid polymer of nylon 66
(C) Gaseous polymer of nylon 66
(D) Liquid polymer of nylon 66

13. Polymerization of glycol with dicarboxylic acids is

(A) Addition polymerisation
(B) Condensation polymerisation
(C) Telomerisation
(D) Any of these

14. The 'mercerised cellulose' is chemically prepeared by

(A) Acetylation (B) Mercuriation
(C) Halogenation (D) Hydrolysis

15. The plastics if are hard, become soft and readily workable by addition of certain compounds called

(A) Catalysts (B) Telomers
(C) Plasticisers (D) Vulcaniser

16. Discovery of 'nylon' is associated with

(A) Newyork and London
(B) Newyork and Longuet
(C) Nyholm and London
(D) None of these

Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

1. Which of the following pairs form the same osazone ?
(A) Glucose and fructose (B) Glucose and galactose
(C) Glucose and arabinose (D) Lactose and maltose

2. The term inverted sugar refers to an equimolar mixture :
(A) D-Glucose and D-galactose (B) D-Glucose and D-fructose
(C) D-Glucose and D-mannose (D) D-Glucose and D-ribose

3. Cellulose on hydrolysis yields
(A) β-D-Fructose (B) α-D-Glucose (C) β-D-Glucose (D) α-D-Fructose

4. Glucose when treated with CH_3OH in presence of dry HCl gas gives α- and β- methylglucosides because it contains
(A) an aldehydic group (B) a $-CH_2OH$ group (C) a ring structure (D) five – OH group

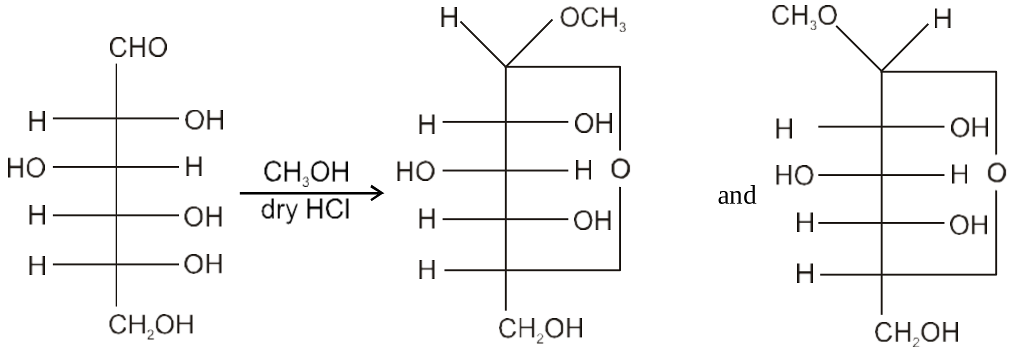
5. α-D glucose and β-D-glucose differ from each other due to the difference in one of the carbon atoms, with respect to its
(A) Number of OH groups (B) Configuration (C) Conformation (D) Size of hemiacetal ring

6. In Ketohexose the possible optical isomers are
(A) 12 (B) 4 (C) 16 (D) 8

7. Which of the following indicates the presence of 5 –OH groups in glucose
(A) Penta-acetyl derivative of glucose (B) Cyanohydrin formation of glucose
(C) Reaction with fehling's solution (D) Reaction with Tollen's reagent

8. Find true and False from the following statements regarding carbohydrates
S_1 : All monosaccharides whether aldoses or ketoses are reducing sugars.
S_2 : Bromine water can be used to differentiate between aldoses and ketoses
S_3 : A pair of diastereomeric aldoses which differ only in configuration at C-2 are anomers.
S_4 : Osazone formation destroys the configuration at C-2 of an aldose, but does not affect the configuration of the rest of the molecule.
(A) TTTT (B) TFTF (C) TTFT (D) FTTT

9. D-glucose, on treating with methanol in presence of dry HCl gives methyl glucosides according to the following reaction



D-Glucose (I) **Methyl-α-D-glucoside** (II) **Methyl-β-D-glucoside** (III)

Mention true (T) and False (F) from the following statements
S1 : The glucosides do not reduce fehling's solution
S2 : The glucosides do not react with hydrogen cyanide or hydroxylamine
S3 : Behaviour of glucosides as stated in S_1 and S_2 indicates the absence of free – CHO group.
S4 : The two forms of glucosides are enantiomers.
(A) TTFF (B) FTTT (C) TTTF (D) TFTF

Exercise # 3

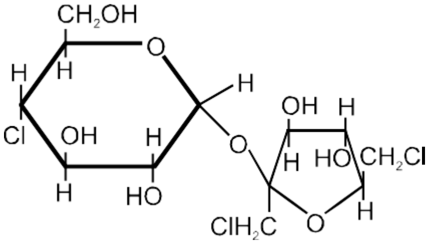
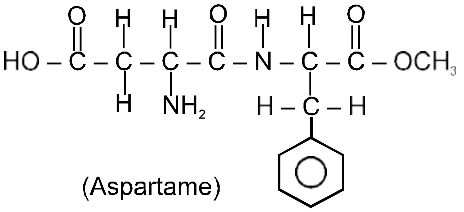
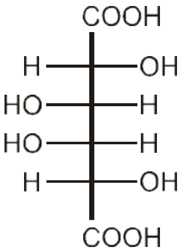
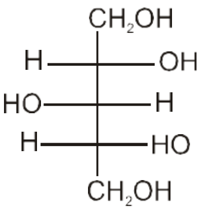
PART - 1

MATRIX MATCHCOLUMN

1. Match Column-I with Column-II.

Column-I **(polymer)**	**Column-II** **(monomer)**
(A) Bakelite	**(p)** ω- caprolactam
(B) Polypropylene	**(q)** Ethylene glycol + phthalic anhydride
(C) Glyptal	**(r)** propene
(D) Nylon-6	**(s)** Phenol + formaldehyde

2. Match the Following :

Column I **(Artificial sweeteners)**	**Column II** **(Characteristics)**
(A)  (Sucralose)	**(p)** A derivative of dipeptide
(B)  (Aspartame)	**(q)** A derivative of disaccharide
(C)  (Galactoric) (Aldaric acid)	**(r)** Reduction product of an aldopentose
(D)  (Xylitol)	**(s)** Oxidation product of aldohexose

Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

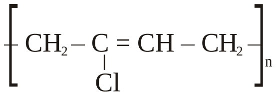
1. Which one of the following has magnesium ? **[CBSE AIPMT 2000]**
(A) Vitamin-B_{12} **(B)** Chlorophyll
(C) Haemocyanin **(D)** Carbonic anhydrase

2. α-D-(+)-glucose and β-D-(+)-glucose are **[CBSE AIPMT 2000]**
(A) anomers **(B)** epimers
(C) enantiomers **(D)** geometrical isomers

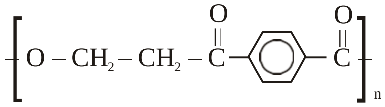
3. The hormone which controls the processes like burning of fats, proteins and carbohydrates to liberate energy in the body is **[CBSE AIPMT 2000]**
(A) cortisone **(B)** thyroxine
(C) adrenaline **(D)** insulin

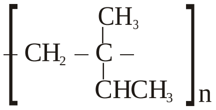
4. $CF_2 = CF_2$ is a monomer of **[CBSE AIPMT 2000]**
(A) Buna-S **(B)** teflon
(C) glyptal **(D)** nylon-6

5. Which one of the following is not correctly matched ? **[CBSE AIPMT 2001]**

(A) Neoprene 
$\left[CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2 \right]_n$

(B) Nylon - 66 $\left[NH-(CH_2)_6-NH-CO-(CH_2)_4-C-O \right]_n$

(C) Terylene 

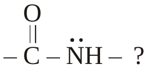
(D) PMMA 
$\left[CH_2-\underset{\underset{CHCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}- \right]_n$

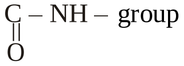
6. Which one of the following gives positive Fehling's solution test ? **[CBSE AIPMT 2001]**
(A) Sucrose **(B)** Glucose
(C) Fats **(D)** Protein

7. Which of the following is correct about H-bonding in nucleotide ? **[CBSE AIPMT 2001]**
(A) A-T, G-C **(B)** A-G, T-C
(C) G-T, A-C **(D)** A-A, T-T

8. Which of the following is correct statement ? **[CBSE AIPMT 2001]**
(A) Starch is a polymer of α-glucose
(B) Amylose ia a component of cellulose
(C) Proteins are composed of only one type of amino acid
(D) In cyclic structure of fructose, ther are four carbons and one oxygen atom

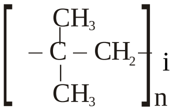
9. Which statement is incorrect about peptide bond


$-\overset{\overset{O}{||}}{C}-\ddot{N}H-$?

[CBSE AIPMT 2001]
(A) C–N bond length in proteins is longer than usual bond length of C–N bond
(B) Spectroscopic analysis show planar structure of  $-\underset{\underset{O}{||}}{C}-NH-$ group
(C) C–n bond length in proteins is smaller than usual bond length of C–N bond
(D) None of the above

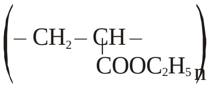
10. Enzymes are made up of **[CBSE AIPMT 2002]**
(A) edible proteins
(B) proteins with specific structure
(C) nitrogen conatining carbohydrates
(D) carbohydrates

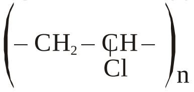
11. Which is not true statemen ? **[CBSE AIPMT 2002]**
(A) α-carbon of α-amino acid is asymmetric
(B) All proteins are found in L-form
(C) Human bond can synthesise all proteins they need
(D) At pH = 7 both amino and carboxylic groups exist in ionised form

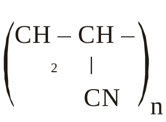
12. Monomer of  $\left[-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2- \right]_n$ is **[CBSE AIPMT 2002]**
(A) 2-methylpropene **(B)** styrene
(C) propylene **(D)** ethene

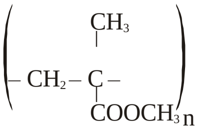
13. Cellulose is a polymer of **[CBSE AIPMT 2002]**
(A) glucose **(B)** fructose
(C) ribose **(D)** sucrose

14. Acrilan is a hard, horny and a high melting material. Which of the following represents its structure ? **[CBSE AIPMT 2003]**

(A) 
$\left(-CH_2-\underset{\underset{COOC_2H_5}{|}}{CH}- \right)_n$

(B) 
$\left(-CH_2-\underset{\underset{Cl}{|}}{CH}- \right)_n$

(C) 
$\left(CH_2-\underset{\underset{CN}{|}}{CH}- \right)_n$

(D) 
$\left(-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}- \right)_n$

MOCK TEST

STRAIGHT OBJECTIVE TYPE

1. Perlon is
(A) Rubber **(B)** Nylon-6 **(C)** Terelene **(D)** Oxlon

2. Styrene at room temparature is
(A) Solid **(B)** Liquid **(C)** Gas **(D)** Colloidal solution

3. Which one of the following can be used as monomer in a polymerisation reaction
(A) CH_3CH_2Cl **(B)** CH_3CH_2OH **(C)** C_6H_6 **(D)** C_3H_6

4. The Zieglar-Natta catalysts are
(A) Stereospecific **(B)** Non-metallic complexes
(C) Gaseous catalysts **(D)** Universal in all polymerisation reactions

5. Melamine is
(A) Gas **(B)** Yellow liquid **(C)** White crystalline solid **(D)** Colloidal solution

6. Insulin is a protein which plays the role of
(A) An antibody **(B)** A harmone **(C)** An enzyme **(D)** A transport agent

7. Proteins fulfil several functions in living systems. An example of a protein which acts as a hormone is
(A) Casein **(B)** Oxytocin **(C)** Trypsin **(D)** Keratin

8. Pick out the unsaturated fatty acid from the following
(A) Stearic acid **(B)** Lauric acid **(C)** Oleic acid **(D)** Palmitic acid

9. Vitamin B_{12} contains metal
(A) Ca (II) **(B)** Zn (II) **(C)** Fe (II) **(D)** Co (III)

10. The number of molecules of ATP produced in the lipid metabolism of a molecule of palmitic acid is
(A) 130 **(B)** 36 **(C)** 56 **(D)** 86

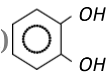
11. Protein can be most easily removed from
(A) Alkanes **(B)** Alkenes **(C)** Alkynes **(D)** Benzene

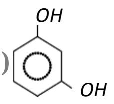
12. A raw material used in making nylon is
(A) Adipic acid **(B)** Butadiene **(C)** Ethylene **(D)** Methyl methacrylate

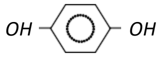
13. Nylon is formed when a dicarboxylic acid is treated with a
(A) Dihydric alcohol **(B)** Polyhydric alcohol **(C)** Diamine **(D)** Diester

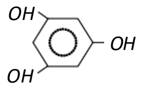
14. Vinyl chloride can be converted into PVC. In this reaction, the catalyst used is
(A) Peroxides **(B)** Cuprous chloride
(C) Anhydrous zinc chloride **(D)** Anhydrous $AlCl_3$

15. The monomeric units of terylene are glycol and which of the following

(A) 

(B) 

(C) 

(D) 

16. Neoprene, a synthetic rubber contains which of the following element besides C and H
(A) N **(B)** O **(C)** Cl **(D)** F

17. Hydrolysis of sucrose is called
(A) Esterification **(B)** Saponification **(C)** Inversion **(D)** Hydration

CHAPTER 01

SOME BASIC CONCEPTS OF CHEMISTRY

> *Consider Chemistry among the most useful of sciences, and big with future discoveries for the utility and safety of the human race*
>
> **“THOMAS JEFFERSON”**

INTRODUCTION

In this chapter we will study the basic concepts and techniques which will form the base of chemistry and will be useful in every chapter you are going to study. A you already know, chemistry is about the study of matter, so we will study the characteristics, classification and measurement of matter with international system of units and their inter conversions, and how to make precise and accurate scientific calculations. After this we will study about the laws of Chemical Combinations and Dalton’s atomic theory and how to deal with calculations involving atoms, molecules, **moles and molar mass**. Also how to determine molecular formula and what is Emperical formula will be discussed in this chapter.

Classification of universe

The whole universe consists of matter and energy. In a chemical reaction niether any mass is destroyed nor any energy is lost. Energy can only be trnsformed from one form to another and that we will study in detail later in this chapter. So basically Universe is classified into 2 categoies as follows:

(I) Matter

(II) Energy

(I) Matter

The thing which occupy space and having mass which is feel by our five senses is called as **matter**. It is mainly subdivided on the basis of two kinds of classifications :

(I) Physical classification

(II) Chemical classification

Physical Classification :

We see different things around us having different shaped, sizes and colors, mass and occupy space, all these things are composed of matter. Depending upon physcial and chemical properties matter is classified into following three ctaegories

(a) Solid

(b) Liquid

(c) Gas

(a) Solid

A substance is said to be solid if it possesses a definite volume and a definite shape. Constituent particles are tightly packed and usually there is a regu;lar pattern among the particles and they do not have much freedom to move or not easily compressible.

Ex. sugar, iron, gold, wood, NaCl etc.

(b) Liquid

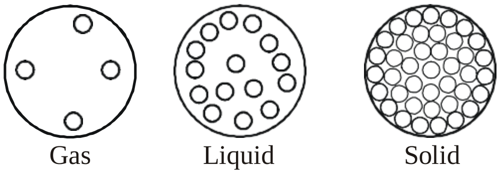
A substance is said to be liquid if it possesses a definite volume but not definite shape. They take up the shape of the vessel in which they are put. The intermolecular distance is high as compared to solids and thus they have the tendancy to flow but they are not much compressible due to little free space but can flow easily.

Ex. water, milk, oil, mercury, alcohol, Bromine etc.

(c) Gas

A substance is said to be gas if it neither possesses a definite volume nor a definite shape. This is because they fill up the whole vessel in which they are put. The intermolecular distance is highest in gases and are highly compressible.

Ex. hydrogen(H_2), oxygen(O_2), carbon dioxide(CO_2), etc.



Solid, Liquid and Gaseous states of matter are inter convertible by changing temperature and pressure.

$$\text{Solid} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \text{Liquid} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \text{Gas}$$

For example, water can be converted into ice and water vapour as follows :

$$\text{Ice} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \text{Water} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \text{Vapour}$$

EDOS KEY POINTS

Direct conversion of solid to gaseous state is called as **sublimation**. Champhor undergoes sublimation. Also further on applying pressure at a particular temperature gases can be liquified, this principle is applied to compress natural gas and petroleum gas which are available for our uses as CNG and LPG.

Chemical Classification :

At the macroscopic level depending upon the composition, matter can also be divided into two broad categories :

(a) Pure Substance

(b) Mixture

(a) Pure Substance

A material containing only one type of substance. They have fixed composition and their properties also do not vary. Pure Substance can not be seperated into simpler substance by physical method.

Ex. Element = Na, Mg, Ca .... etc.

Compound = HCl, H_2O, CO_2, HNO_3...................... etc.

2 Types

(i) Element

(ii) Compound

(i) Element : The pure substance containing only one kind of atoms .

3 Types (depend on physical and chemical property)

- Metal
- Non-metal
- Metalloids

(ii) Compound

It is defined as pure substance containing more than one kind of atoms which are combined together in a fixed ratio by weight and which can be decomposed into simpler substance by the suitable chemical method. The properties of a compound are differnt from those of its components.

Ex. H_2O , HCl, HNO_3........................ etc.

2 : 16

1 : 8 **by wt.**

Compounds are further classified into two categories :

- Organic Compound
- Inorganic Compound

(b) Mixture

A material which contain more than one type of substances and which is mixed any ratio by wt. i.e the components of a mixture have variable composition. The property of the mixture is the property of its components. The mixture can be seperated by simple physical method. Depending upon the composition mixtures are of two types :

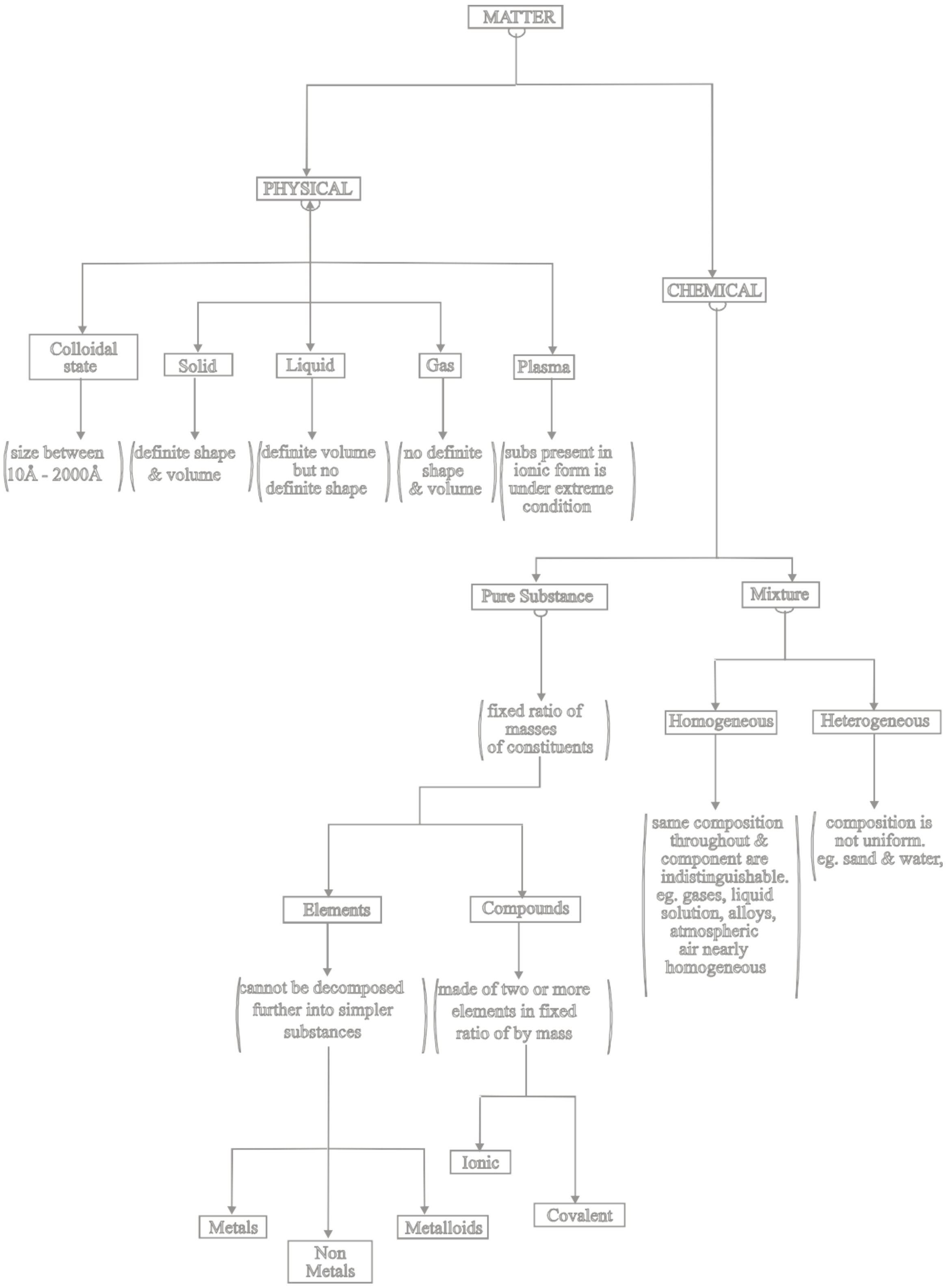
(i) Homogeneous mixture

(ii) Hetrogeneous mixture

(i) Homogeneous Mixture

The mixture, in which all the components are present in **uniform** is called as homogeneous mixture.

Ex. Water + Salt, Water + Sugar, Water + alcohol, Air gasoline, brass etc.


MATTER
PHYSICAL
CHEMICAL
Colloidal state
Solid
Liquid
Gas
Plasma
size between 10Å - 2000Å
definite shape & volume
definite volume but no definite shape
no definite shape & volume
subs present in ionic form is under extreme condition
Pure Substance
Mixture
fixed ratio of masses of constituents
Homogeneous
Heterogeneous
same composition throughout & component are indistinguishable. eg. gases, liquid solution, alloys, atmospheric air nearly homogeneous
composition is not uniform. eg. sand & water,
Elements
Compounds
cannot be decomposed further into simpler substances
made of two or more elements in fixed ratio of by mass
Ionic
Covalent
Metals
Non Metals
Metalloids

SOLVED EXAMPLE

Ex. 1 Show that in the reaction

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, mass is conserved.

Sol. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

moles before reaction	1	3	0
moles after reaction	0	0	2

Mass before reaction = mass of 1 mole $N_2(g)$ + mass of 3 mole $H_2(g)$

= 14 x 2 + 3 x 2 = 34 g

mass after reaction = mass of 2 mole NH_3

= 2 x 17 = 34 g.

Ex. 2 Find the density of $CO_2(g)$ with respect to $N_2O(g)$.

Sol. $\text{R.D.} = \frac{\text{M.wt.of } CO_2}{\text{M.wt.of } N_2O} = \frac{44}{44} = 1.$

Ex. 3 Find the vapour density of N_2O_5

Sol. $\text{V.D.} = \frac{\text{Mol. wt.of } N_2O_5}{2} = 54.$

Ex. 4 Write a balance chemical equation for following reaction :

When ammonia (NH_3) decompose into nitrogen (N_2) gas & hydrogen (H_2) gas.

Sol. $NH_3 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$ or $2NH_3 \rightarrow N_2 + 3H_2$.

Ex. 5 When 170 g NH_3(M =17) decomposes how many grams of N_2 & H_2 is produced.

Sol. $NH_3 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$

$$\frac{\text{moles of } NH_3}{1} = \frac{\text{molesof } N_2}{1/2} = \frac{\text{molesof } H_2}{3/2}.$$

So moles of $N_2 = \frac{1}{2} \times \frac{170}{17} = 5.$

So wt. of N_2 = 5 × 28 = 140 g.

Similarly moles of $H_2 = \frac{3}{2} \times \frac{170}{17} = 15.$

So wt. of H_2 = 15 × 2 = 30 g.

Ex. 6 When x gram of a certain metal brunt in 1.5 g oxygen to give 3.0 g of its oxide. 1.20 g of the same metal heated in a steam gave 2.40 g of its oxide. shows the these result illustrate the law of constant or definite proportion

Sol. Wt. of metal = 3.0 – 1.5 = 1.5 g

so wt. of metal : wt of oxygen = 1.5 : 1.5 = 1 : 1

similarly in second case ,

wt. of oxygen = 2.4 – 1.2 = 1.2 g

so wt. of metal : wt of oxygen = 1.2 : 1.2 = 1 : 1

so these results illustrate the law of constant proportion.

Ex. 7 Find out % of O & H in H_2O compound.

Sol. $\% \text{ of} O = \frac{16}{18} \times 100 = 88.89\%$

$\% \text{ of } H = \frac{2}{18} \times 100 = 11.11\%$

Ex. 8 Acetylene & butene have empirical formula CH & CH_2 respectively. The molecular mass of acetylene and butene are 26 & 56 respectively deduce their molecular formula.

Ans. C_2H_2 & C_4H_8

Sol. $n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$

For Acetylene :

$n = \frac{26}{13} = 2$

□ Molecular formula = C_2H_2

For Butene :

$n = \frac{56}{14} = 4$

□ Molecular formula = C_4H_8 .

Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

1. Which of the following pairs of substances illustrate the law of multiple proportions

(A) CO and CO_2 **(B)** H_2O and D_2O

(C) NaCl and NaBr **(D)** MgO and $Mg(OH)_2$

2. 1.0 g of an oxide of A contained 0.5 g of A. 4.0 g of another oxide of A contained 1.6 g of A. The data indicate the law of

(A) Reciprocal proportions

(B) Constant proportions

(C) Conservation of energy

(D) Multiple proportions

3. Among the following pairs of compounds, the one that illustrates the law of multiple proportions is

(A) NH_3 and NCl_3 **(B)** H_2S and SO_2

(C) CuO and Cu_2O **(D)** CS_2 and $FeSO_4$

4. The percentage of copper and oxygen in samples of CuO obtained by different methods were found to be the same. This illustrates the law of

(A) Constant proportions

(B) Conservation of mass

(C) Multiple proportions

(D) Reciprocal proportions

5. Two samples of lead oxide were separately reduced to metallic lead by heating in a current of hydrogen. The weight of lead from one oxide was half the weight of lead obtained from the other oxide. The data illustrates

(A) Law of reciprocal proportions

(B) Law of constant proportions

(C) Law of multiple proportions

(D) Law of equivalent proportions

6. Chemical equation is balanced according to the law of

(A) Multiple proportion

(B) Reciprocal proportion

(C) Conservation of mass

(D) Definite proportions

7. Avogadro number is

(A) Number of atoms in one gram of element

(B) Number of millilitres which one mole of a gaseous substances occupies at NTP

(C) Number of molecules present in one gram molecular mass of a substance

(D) All of these

9. Which one of the following properties of an element is not variable

(A) Valency **(B)** Atomic weight

(C) Equivalent weight **(D)** All of these

10. The modern atomic weight scale is based on

(A) C^{12} **(B)** O^{16}

(C) H^1 **(D)** C^{13}

11. 1 amu is equal to

(A) $\frac{1}{12}$ of C –12

(C) 1g of H_2

(B)

o
f
O
-
1
6
1
4
—

(D) 1.66×10^{-23} kg

8. Which property of an element is always a whole number

(A) Atomic weight **(B)** Equivalent weight

(C) Atomic number **(D)** Atomic volume

12.

Sulphur forms the chlorides S_2Cl_2 and SCl_2. The equivalent mass of sulphur in SCl_2 is

(A) 8 g/mole **(B)** 16g/mole

(C) 64.8 g/mole **(D)** 32 g/mole

13. The sulphate of a metal M contains 9.87% of M. This sulphate is isomorphous with $ZnSO_4.7H_2O$. The atomic weight of M is

(A)40.3 **(B)**36.3

(C)24.3 **(D)**11.3

14. When 100 ml of 1 M NaOH solution and 10 ml of 10 N H_2SO_4 solution are mixed together, the resulting solution will be

(A) Alkaline **(B)** Acidic

(C) Strongly acidic **(D)** Neutral

15. In chemical scale, the relative mass of the isotopic mixture of oxygen atoms (O^{16}, O^{17}, O^{18}) is assumed to be equal to

(A)16.002 **(B)**16.00

(C)17.00 **(D)**11.00

16. For preparing 0.1 N solution of a compound from its impure sample of which the percentage purity is known, the weight of the substance required will be

(A) More than the theoretical weight

(B) Less than the theoretical weight

(C) Same as the theoretical weight

(D) None of these

17. 1 mol of CH_4 contains

(A) 6.02×10^{23} atoms of H

(B) 4 g atom of Hydrogen

(C) 1.81×10^{23} molecules of CH

(D) 3.0 g of carbon

Exercise # 2

SINGLE OBJECTIVE

AIIMS LEVEL

1. Calculate the amount of Ni needed in the Mond's process given below

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

If CO used in this process is obtained through a process, in which 6 g of carbon is mixed with 44 g CO_2.

(A) 14.675 g **(B)** 29g

(C) 58 g **(D)** 28 g

2. The mass of 70% H_2SO_4 required for neutralisation of 1 mol of NaOH.

(A) 49 gm **(B)** 98gm

(C) 70 gm **(D)** 34.3gm

3. In a certain operation 358 g of $TiCl_4$ is reacted with 96 g of Mg. Calculate % yield of Ti if 32 g of Ti is actually obtained [At. wt. Ti = 48, Mg = 24]

[Hint : $\frac{358}{190} = 1.88$]

(A) 35.38 % **(B)** 66.6%

(C) 100 % **(D)** 60%

4. 0.5 mole of H_2SO_4 is mixed with 0.2 mole of Ca $(OH)_2$ The maximum number of moles of $CaSO_4$ formed is

(A) 0.2 **(B)** 0.5

(C) 0.4 **(D)** 1.5

5. Equal weight of 'X' (At. wt. = 36) and 'Y' (At. wt. = 24) are reacted to form the compound X_2Y_3. Then :

(A) X is the limiting reagent

(B) Y is the limiting reagent

(C) No reactant is left over and mass of X_2Y_3 formed is double the mass of 'X' taken

(D) none of these

6. 25.4 g of iodine and 14.2g of chlorine are made to react completely to yield a mixture of ICl and ICl_3. Calculate the number of moles of ICl and ICl_3 formed.

(A) 0.1 mole, 0.1 mole **(B)** 0.1 mole, 0.2 mole

(C) 0.5 mole, 0.5 mole **(D)** 0.2 mole, 0.2 mole

7. What weights of P_4O_6 and P_4O_{10} will be produced by the combustion of 31g of P_4 in 32g of oxygen leaving no P_4 and O_2.

(A) 2.75g, 219.5g **(B)** 27.5g, 35.5g

(C) 55g, 71g **(D)** 17.5g, 190.5g

8. What weight of $CaCO_3$ must be decomposed to produce the sufficient quantity of carbon dioxide to convert 21.2 kg of Na_2CO_3 completely in to $NaHCO_3$. [Atomic mass Na = 23, Ca = 40]

$CaCO_3 \longrightarrow CaO + CO_2$

$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$

(A) 100 Kg **(B)** 20Kg

(C) 120 Kg **(D)** 30Kg

9. NX is produced by the following step of reactions

$M + X_2 \longrightarrow MX_2$; $3MX_2 + X_2 \longrightarrow M_3X_8$; $M_3X_8 + N_2CO_3 \longrightarrow NX + CO_2 + M_3O_4$

How much M (metal) is consumed to produce 206 gm of NX. (Take at wt of M = 56, N=23, X = 80)

(A) 42 gm **(B)** 56gm

(C) $\frac{14}{3}$ gm **(D)** $\frac{7}{4}$ gm

10. 0.05 mole of $LiAlH_4$ in ether solution was placed in a flask containing 74g (1 mole) of t-butyl alcohol. The product $LiAlHC_{12}H_{27}O_3$ weighed 12.7 g. If Li atoms are conserved, the percentage yield is :

(Li = 7, Al = 27, H = 1, C = 12, O = 16).

(A) 25% **(B)** 75%

(C) 100% **(D)** 15%

11. A sample of a mixture of $CaCl_2$ and NaCl weighing 4.44 gm was treated to precipitate all the Ca as $CaCO_3$, which was then heated and quantitatively converted to 1.12g of CaO. (At . wt. Ca = 40, Na = 23, Cl = 35.5)

(A) Mixture contains 25% NaCl

(B) Mixture contains 60% $CaCl_2$

(C) Mass of $CaCl_2$ is 2.22 g

(D) Mass of $CaCl_2$ 1.11 g

12. The oxidation states of Sulphur in the anions SO_3^{2-}, $S_2O_4^{2-}$ and $S_2O_6^{2-}$ follow the order :

(A) $S_2O_6^{2-} < S_2O_4^{2} < SO_3^{2-}$

(B) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$

(C) $SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$

(D) $S_2O_4^{2} < S_2O_6^{2-} < SO_3^{2-}$

13. The oxidation number of Phosphorus in $Mg_2P_2O_7$ is :

(A) + 3 **(B)** +2

(C) + 5 **(D)** – 3

Exercise # 3

PART - 1

MATRIX MATCH COLUMN

1.

Column I	Column II
(A) $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(s) + H_2(g)$ above reaction is carried out by taking 2 moles each of Zn and HCl	(p) 50% of excess reagent left
(B) $AgNO_3(aq) + HCl(aq) \rightarrow AgCl(s) + HNO_3(g)$ above reaction is carried out by taking 170 g $AgNO_3$ and 18.25 g HCl (Ag = 108)	(q) 22.4 L of gas at STP is liberated
(C) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ 100 g $CaCO_3$ is decomposed]	(r) 1 moles of solid (product) obtained.
(D) $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$ 2/3 moles of $KClO_3$ decomposed	(s) HCl is the limiting reagent

2.

Column-I	Column-II
(A) 100 ml of 0.2 M $AlCl_3$ solution + 400 ml of 0.1 M HCl solution	(p) Total concentration of cation(s) = 0.12 M
(B) 50 ml of 0.4 M KCl + 50 ml H_2O	(q) $[SO_4^{2-}] = 0.06$ M
(C) 30 ml of 0.2 M K_2SO_4 + 70 ml H_2O	(r) $[SO_4^{2-}] = 2.5$ M
(D) 200 ml 24.5% (w/v) H_2SO_4	(s) $[Cl^-] = 0.2$ M

3.

Column-I	Column-II
(A) Molarity	(p) Dependent on temperature
(B) Molality	(q) $\frac{M_A \times n_A}{n_A M_A + n_B M_B} \times 100$
(C) Mole fraction	(r) Independent of temperature
(D) Mass %	(s) $\frac{X_A}{X_B M_B} \times 1000$

Where M_A, M_B are molar masses, n_A, n_B are no of moles & X_A, X_B are mole fractions of solute and solvent respectively.

4.

Column-I	Column-II
(A) Law of conservation of mass	(p) CH_4 has carbon and hydrogen in 3 : 1 mass ratio.
(B) Law of multiple proportion	(q) 10 mL N_2 combines with 30 mL of H_2 to form 20 mL of NH_3
(C) Law of definite proportion	(r) S and O_2 combine to form SO_2 and SO_3
(D) Law of reciprocal proportion	(s) In H_2S and SO_2 mass ratio of H and O w.r.t. sulphur is 1 : 16, hence in H_2O, mass ratio of H and O is 1 : 8.
(E) Gay Lussac's Law	(t) 4.2 g $MgCO_3$ gives 2.0 g residue on heating.

5.

Column-I	Column-II (mass of product)
(A) $\underset{1g}{2H_2} + \underset{1g}{O_2} \longrightarrow 2H_2O$	(p) 1.028 g
(B) $\underset{1g}{3H_2} + \underset{1g}{N_2} \longrightarrow 2NH_3$	(q) 1.333 g
(C) $\underset{1g}{H_2} + \underset{1g}{Cl_2} \longrightarrow 2HCl$	(r) 1.125 g
(D) $\underset{1g}{2H_2} + \underset{1g}{C} \longrightarrow CH_4$	(s) 1.214 g

Exercise # 4

PART - 1

PREVIOUS YEAR (NEET/AIPMT)

1. Assuming fully decomposed, the volume of CO_2 released at STP on heating 9.85 g of $BaCO_3$ (at. mass of Ba = 137) will be **[CBSE AIPMT 2000]**
(A) 1.12 L (B) 0.84L
(C) 2.24 L (D) 4.96L

2. percentage of Se in peroxidase anhydrase enzyme is 0.5% by weight (at. weight = 78.4), then minimum molecular weight of peroxidase anhydrase enzyme is **[CBSEAIPMT 2001]**
(A) 1.568×10^3 (B) 15.68
(C) 2.168×10^4 (D) 1.568×10^4

3. Specific volume of cylindrical virus particle is 6.02 × 10–2 cc/g, whose radius and length are 7Å and 10Å respectively. If $N_A = 6.023 \times 10^{23}$, find molecular weight of virus. **[CBSEAIPMT 2001]**
(A) 15.4 kg/mol (B) 1.54×10^4 kg/mol
(C) 3.08×10^4 kg/mol (D) 3.08×10^3 kg/mol

4. Which has maximum number of molecules ? **[CBSE AIPMT 2002]**
(A) 7 g N_2 (B) 2 gH_2
(C) 16g NO_2 (D) 16 g O_2

5. In Haber process 30 L of dihydrogen and 30L of dinitrogen were taken for reaction which yielded only 50% of the expected product. What will be the composition of gaseous mixture under the aforesaid condition in the end ? **[CBSE AIPMT 2003]**
(A) 20 L ammonia, 10 L nitrogen, 30 L hydrogen
(B) 20 L ammonia, 25 L nitrogen, 15 L hydrogen
(C) 20 L ammonia, 20 L nitrogen, 20 L hydrogen
(D) 10 L ammonia, 25 L nitrogen, 15 L hydrogen

6. The maximum number of molecules are present in **[CBSE AIPMT2004]**
(A) 15 L of H_2 gas at STP (B) 5 L of N_2 gas at STP
(C) 0.5 g of H_2 gas (D) 10 g of O_2 gas

7. The mass of carbon anode consumed (giving only carbon dioxide) in the production of 270 kg of aluminium metal from bausite by the Hall process is (at. mass of Al = 27) **[CBSEAIPMT 2005]**
(A) 180 kg (B) 270kg
(C) 540 kg (D) 90kg

8. The number of moles of $KMnO_4$ reduced by one mole of KI in alkaline medium is **[CBSE AIMPT 2005]**
(A) one fifth (B) five
(C) one (D) two

9. An element, X has the following isotopic composition :
^{200}X : 90%, ^{199}X : 8.0 %, ^{202}X : 2.0%
The weighted average atomic mass of the naturally occurring element X is closest to **[CBSE AIMPT 2007]**
(A) 201 u (B) 202u
(C) 199 u (D) 200u

10. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ion in acidic solution is **[CBSEAIPMT 2007]**
(A) 4/5 (B) 2/5
(C) 1 (D) 3/5

11. Number of moles of MnO_4^- required to oxidise one mole of ferrous oxalate completely in acidic medium will be **[CBSEAIPMT 2008]**
(A) 0.6 mole (B) 0.4mole
(C) 7.5 moles (D) 0.2mole

12. How many moles of lead (II) chloride will be formed from a reaction between 6.5 g of PbO and 3.2 g of HCl? **[CBSEAIPMT 2008]**
(A) 0.044 (B) 0.333
(C) 0.011 (D) 0.029

13. What volume of oxygen gas (O_2) measured at 0°C and 1 atm, is needed to burn completely 1L of propane gas (C_3H_8) measured under the same conditions ? **[CBSEAIPMT 2008]**
(A) 7 L (B) 6 L
(C) 5 L (D) 10L

14. Volume occupied by one molecule of water (density = 1 g cm^{-3}) is **[CBSE AIPMT2008]**
(A) 9.0×10^{-23} cm^3 (B) 6.023×10^{-23} cm^3
(C) 3.0×10^{-23} cm^3 (D) 5.5×10^{-23} cm^3

15. 10 g of hydrogen and 64 g of oxygen were filled in a steel vessel and exploded. Amount of water produced in this reaction will be **[CBSE AIMPT 2009]**
(A) 2 moles (B) 3 moles
(C) 4 moles (D) 1 mol

16. The number of atoms in 0.1 mole of a triatomic gas is ($NA = 6.023 \times 10^{23}$ mol^{-1}) **[CBSE AIPMT 2010]**
(A) 6.026×10^{22} (B) 1.806×10^{23}
(C) 3.600×10^{23} (D) 1.800×10^{22}

MOCK TEST

1. The charge on 1 gram ions of Al^{3+} is : (N_A = Avogadro number, e = charge on one electron)

(A) $\frac{1}{27} N_A e$ coulomb **(B)** $\frac{1}{3} \times N_A e$coulomb **(C)** $\frac{1}{9} \times N_A e$coulomb **(D)** $3 \times N_A e$coulomb

2. The weight of a molecule of the compound $C_{60}H_{22}$ is :
(A) 1.09×10^{-21}g **(B)** 1.24×10^{-21}g **(C)** 5.025×10^{-23}g **(D)** 16.023×10^{-23}g

3. 16 g of an ideal gas SO_X occupies 5.6 L. at STP. The value of x is
(A) x = 3 **(B)** x = 2 **(C)** x = 4 **(D)** none

4. Calculate the molecular formula of compound which contains 20% Ca and 80% Br (by wt.) if molecular weight of compound is 200. (Atomic wt. Ca = 40, Br = 80)
(A) $Ca_{1/2}Br$ **(B)** $CaBr_2$ **(C)** CaBr **(D)** Ca_2Br

5. A compound possess 8% sulphur by mass. The least molecular mass is :
(A) 200 **(B)** 400 **(C)** 155 **(D)** 355

6. Equal weight of 'X' (At. wt. = 36) and 'Y' (At. wt. = 24) are reacted to form the compound X_2Y_3. Then :
(A) X is the limiting reagent
(B) Y is the limiting reagent
(C) No reactant is left over and mass of X_2Y_3 formed is double the mass of 'X' taken
(D) none of these

7. The mass of 70% H_2SO_4 required for neutralisation of 1 mol of NaOH.
(A) 49 gm **(B)** 98 gm **(C)** 70 gm **(D)** 34.3gm

8. What weights of P_4O_6 and P_4O_{10} will be produced by the combustion of 31g of P_4 in 32g of oxygen leaving no P_4 and O_2.
(A) 2.75g, 219.5g **(B)** 27.5g, 35.5g **(C)** 55g, 71g **(D)** 17.5g, 190.5g

9. NX is produced by the following step of reactions

$M + X_2 \longrightarrow MX_2$; $3MX_2 + X_2 \longrightarrow M_3X_8$; $M_3X_8 + N_2CO_3 \longrightarrow NX + CO_2 + M_3O_4$
How much M (metal) is consumed to produce 206 gm of NX. (Take at wt of M = 56, N=23, X = 80)

(A) 42 gm **(B)** 56 gm **(C)** $\frac{14}{3}$ gm **(D)** $\frac{7}{4}$gm

10. In $FeCr_2O_4$, the oxidation numbers of Fe and Cr are :
(A) + 2 and + 3 **(B)** 0 and + 2 **(C)** + 2 and + 6 **(D)** + 3 and + 6

11. The average oxidation state of Fe in Fe_3O_4 is :
(A) 2 and 3 **(B)** 8/3 **(C)** 2 **(D)** 3

12. A solution of $FeCl_3$ is $\frac{M}{30}$ its molarity for Cl^- ion will be :

(A) $\frac{M}{90}$ **(B)** $\frac{M}{30}$ **(C)** $\frac{M}{10}$ **(D)** $\frac{M}{5}$

13. The molarity of Cl^- in an aqueous solution which was (w/V) 2% NaCl, 4% $CaCI_2$ and 6% NH_4Cl will be
(A) 0.342 **(B)** 0.721 **(C)** 1.12 **(D)** 2.18