HAND BOOK

FOR

INTERMEDIATE FIRST YEAR

CHEMISTRY

BOARD OF INTERMEDIATE EDUCATION

HAND BOOK PREPARED BY

Smt. K. Nagamani

Principal (Retd.),
Sri Durga Malleswara Siddhartha Mahila Jr Kalasala,
Vijayawada.

Dr.GJVSND Lakshmi
Principal,
Government Junior College,
Tiruvuru.

Dr. P. Reddi Rani
JL in Chemistry,
Government Junior College (G),
Chandragiri.

Sri T. K. Durga Prasad
JL in Chemistry,
SRR & CVR Government Junior College,
Vijayawada.

Dr. P. Trinadha Raja
JL in Chemistry,
Government Junior College,
Rajahmundry.

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CHEMISTRY - I

UNIT–I

SOME BASIC CONCEPTS OF CHEMISTRY

I. Multiple choice questions: (1 mark)

1. **The drug Azidothymidine (AZT) is used in the treatment of**

1) Cancer 2) AIDS 3) Bronchitis 4) Ulcer

Ans: 2

2. **Which one of the following pairs of the compounds illustrates the law of multiple proportions?**

1) H_2O & Na_2O 2) MgO & Na_2O 3) Na_2O & BaO 4) $SnCl_2$ & $SnCl_4$

Ans: 4

3. **Chemical equations is balanced according to the law of**

1) Multiple proportions 2) Reciprocal proportions

3) Conservations of mass 4) Definite proportion

Ans: 3

4. **If the abundances of isotopes of iron,** ^{54}Fe, ^{56}Fe **and** ^{57}Fe **are** $5\%, 90\%$ **and** 5% **respectively. The atomic mass of Fe can be**

1)55.85 2) 55.95 3)55.75 4) 56.05

Ans: 2

5. **The density of gas at STP is** $1.25\ gL^{-1}$ **.The molecular mass of the gas is**

1)$14U$ 2) $28U$ 3)$16U$ 4) $32\ U$

Ans: 2

6. 2.4×10^{22} **atoms of a diatomic element weights** $1.32\ g$ **. It's molecular mass is**

1)$33u$ 2) $16.5u$ 3)$66\ u$ 4) $40\ u$

Ans: 3

7. **Two elements X and Y form two compounds** X_2Y_3 **and** X_2Y **.0.5 mole of** X_2Y_3 **weight 38 g and 0.1 mole** X_2Y **weights 4.4 g. The atomic mass X and Y could be**

1)$20U$, $15U$ 2) $31U$, $16U$ 3)$14U$, $16U$ 4) $16U$, $27U$

Ans: 3

8. **Which of the following contain more number of molecules?**

1) 448 L of O_2 at STP 2)440 L of CO_2

3)22.4 L of water STP 4) 2.24 L of H_2 at STP

Ans: 3

9. **Which of the following will have the largest number of atoms?**

1)1g $Au_{(s)}$ 2)1g $Na_{(s)}$ 3)1g $Li_{(s)}$ 4) 1g $Cl_{2(g)}$

Ans: 3

10. **The empirical formula of an organic compound is** CH_2 **. The mass of 1 mole of it is 42 g. The molecular formula of the compound is**

1) C_4H_8 2) C_2H_4 3) C_3H_6 4) CH_2

Ans: 3

11. The volume (in litre) of CO_2 liberated at STP when 10 g of 90% pure limestone is heated completely is

1)22.4 2)2.24 3)20.16 4) 2.016

Ans: 4

12. The mole fraction of $NaCl$ in a solution containing 1 mole of $NaCl$ in 1000g of water is

1)0.0177 2)0.001 3)0.5 4) 0.244

Ans: 1

13. 3.42 g of a substance of molecular mass 342 U is present in 250 g of water. Molality of this solution is

1)0.4m 2)0.04m 3)0.8m 4) 4m

Ans: 2

14. The number of moles of $NaOH$ required to make a 0.2 M solution of 1 litre

1)1 2)0.5 3)0.2 4)2

Ans: 3

Note: In textbook option 1) read as <u>1</u> and option 3) read as <u>0.2</u>

15. At present "amu" has been replaced by

1) Molar mass 2) Atomic mass 3) Unified mass 4) Formula mass

Ans: 3

II. Fill in the blanks: (1 mark)

1. One amu is numerically equal to _____

Ans: 1.66×10^{-24}g

2. The numerical value of Avogadro number is_____

Ans: 6.02×10^{23}

3. The Number of atoms present in 64 g of sulphur (S_8) is_____

Ans: $2N_A = 1.204\times10^{24}$

4. The molar volume of any gas at STP is_____

Ans: 22.7 litres at P=1bar or 22.4 litres at P=1atm

5. When 20 grams of sugar $(C_{12}H_{22}O_{11})$ is dissolved in water to make a final volume of 2 Liters. The molarity of sugar solution is _____.

Ans: 0.0292 M

III .One word answer questions: (1 mark)

1) How many litres are present in 1 mL?

Ans: 0.001 L

2) What is the basicity of hypo phosphorous acid (H_3PO_2)?

Ans: 1

3) In the given reaction, $NaOH + H_2SO_4 \rightarrow NaHSO_4 + H_2O$: What is the equivalent weight of H_2SO_4?

Ans: 98

4) Write the relation between Kelvin scale and Celsius scale of temperature.

Ans: $K = {}^0C + 273.15$

5) How many molecules are present in 1 cc of N_2 gas at STP?

Ans: 2.65×10^{19} molecules

IV. Very short answer questions: (2 marks)

1) How many moles of glucose are present in 540 g of glucose?

Ans: No. of moles of Glucose = $\frac{wt.of\ Glu\cos e}{G.M.W\ of\ Glu\cos e}$

$$= \frac{540}{180} = 3$$

2) Calculate the weight of 0.1 mole of sodium carbonate.

Ans: Wt of Na_2CO_3 = no of moles of $Na_2CO_3 \times GMWt\ of\ Na_2CO_3$

$$= 0.1 \times 106\ gm$$

$$= 10.6\ gm$$

3) How many molecules of glucose are present in 5.23 g of glucose?

Ans: No. of molecules = $moles \times Avogadro's$ Number

$$= \frac{5.23}{180} \times 6.023 \times 10^{23}$$

$$= 1.75 \times 10^{22}\ molecules.$$

4) The empirical formula of a compound is CH_2O. It's molecular mass is 90. Calculate the molecular formula of the compound.

Ans: Molecular formula $= n \times Empirical$ formula

Where $n = \frac{M.f.wt}{E.f.wt} = \frac{90}{3} = 3.$

$\therefore$ Molecular formula $= (CH_2O)_3$

$$= C_3H_6O_3$$

5) Calculate the volume of O_2 at STP required to completely burn 100 mL of acetylene.

Ans: $2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$

2×22400ml 5×22400ml

2×22400 ml of C_2H_2 require 5×22400ml of O_2

100 ml of C_2H_2 requires

$$= \frac{100 \times 5 \times 22400}{2 \times 22400} = 250ml$$

6) Calculate the mass percent of the different elements present in sodium sulphate (Na_2SO_4).

Ans: Molecular weight of $Na_2SO_4 = 142$

142 gm of Na_2SO_4 contains 46 gm of sodium

$\therefore$ 100 gm of Na_2SO_4 contains $= \frac{100 \times 46}{142} = 32.38\%$

142 gm of Na_2SO_4 contains 32 gm of sulphur

$\therefore$ 100 gm of Na_2SO_4 contains $= \frac{100 \times 32}{142} = 22.54\%$

142 gm of Na_2SO_4 contains 64 gm of oxygen

$\therefore$ 100 gm of Na_2SO_4 contains $= \frac{100 \times 64}{142} = 45.08\%$

7) What do you mean by significant figures?

Ans: Significant figures are meaningful digits which are known with certainty plus one which is estimated or uncertain.

Example: If we write a result as11.2 mL, we say the 11 is certain and 2 is uncertain and the uncertaintly would be ± 1 in the last digit.

8) How many significant figures are present in the following?

(i) 0.0025 (ii) 208

Ans: (i) 0.0025 has two significant figures.

(ii) 208 has three significant figures.

9) Define and explain molar mass.

Ans: Molar mass: The mass of one mole of any substance in grams is called its molar mass.

Example: Molar mass of H_2SO_4 is 98 grams.

Mole: It is the mass of a substance which contains Avogadro's number of structural units $\left(N_A = 6.023\times10^{23}\right)$

One mole = 1 gram molecule

= gram molecular weight

= mass of 6.023×10^{23} molecules in grams

One mole = One gram atom

= One gram atomic weight

= mass of 6.023×10^{23} atoms in grams

10) What volume of CO_2 (in L) is obtained at STP by heating 4g of $CaCO_3$?

Ans: Decomposition of calcium carbonate on heating $\underset{100\,gm}{CaCO_3} \rightarrow CaO + \underset{22.4lit}{CO_2}$.

According to the reaction

1 mole of $CaCO_3$ decomposes give one mole of CO_2 gas

$\therefore$ 100 gm of $CaCO_3$ On heating gives 22.4 lit of CO_2.

4 gm of $CaCO_3$ heating gives? $= \dfrac{4\times22.4}{100}$ = 0.896 lit

V. SHORT ANSWER QUESTIONS: (4 marks)

1) How much minimum volume of CO at STP is needed to react completely with 0.112 L of O_2 at 1.5 atm pressure and 127^0C to give CO_2?

Ans: Reaction between CO and O_2 is

$2CO + O_2 \rightarrow 2CO_2$

From given data and using ideal gas equation

No. of moles of $O_2 = \dfrac{PV}{RT} = \dfrac{(1.5)(0.112)}{(0.0821)(400)}$

$= 5.11\times10^{-3}$

As per stoichiometric equation, one mole of O_2 react with two moles of CO.

$\therefore$ The minimum volume of CO required at STP is

$$= 2 \times 5.11 \times 10^{-3} \times 22,400$$

$$= 10.22 \times 10^{-3} \times 22,400$$

$$= 228.9 \text{ml}$$

2) Chemical analysis of a carbon compound give the following percentage composition by weight of the elements present, carbon=10.06%, hydrogen = 0.84% and chlorine = 89.1%. Calculate the empirical formula of the compound.

Ans:

Symbol of the element	% Composition	At.wt	Relative no of Atoms $= \frac{\%composition}{At.wt}$	Simple ratio
C	10.06	12	$\frac{10.06}{12} = 0.84$	$\frac{0.84}{0.84} = 1$
H	0.84	1	$\frac{0.84}{1} = 0.84$	$\frac{0.84}{0.84} = 1$
Cl	89.1	35.5	$\frac{89.1}{35.5} = 2.51$	$\frac{2.51}{0.84} = 3$

$\therefore$ Empirical formula of the compound is $CHCl_3$.

3) Dinitrogen and dihydrogen react with each other to produce ammonia according to the following chemical equation.

$N_{2\,(g)} + 3H_{2\,(g)} \rightarrow 2NH_{3\,(g)}$

(i) Calculate the mass of ammonia produced if 2.00×10^3 g of dinitrogen reacts with $1.00 \times 10^3 g$ of dihydrogen.

(ii)Will any of the two reactants remain unreacted?

Ans: i) The balanced equation for the reaction between di Nitrogen and di Hydrogen is

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$28\ gm \quad 3 \times 2\ gm \quad 2 \times 17\ gm$$

From above stoichiometric equation, 28 gm of N_2 react with 6 gm of H_2 produce 34 gm of NH_3.

By using given data,

No of moles of $N_2 = \frac{2 \times 10^3}{28} = 71.4\ moles$

No of moles of $H_2 = \frac{1 \times 10^3}{2} = 5 \times 10^2$ (or) 500 moles.

As per stochiometric equation.

1 mole of N_2 Can react with 3 moles of H_2

71.4 moles of N_2 can react $= \frac{71.4 \times 3}{1} = 214.2\ moles$ of H_2 (Excess regent)

Production formation depends on limiting reagent

$\therefore$ 1 moles of N_2 Can produce 34 gm of NH_3

71.4 moles of N_2 Can produce $= 71.4 \times 34 = 2427.6\ gm$

(ii) Yes i.e H_2.

4) Calculate the empirical formula of a compound having percentage composition potassium $(K) = 26.57$, chromium $(Cr) = 35.36$, oxygen (O) = 38.07 (Given the atomic weights of K,Cr and O as 39.52 , and 16 respectively).

Ans:

Symbol of the element	% Composition	At.wt	Relative number of Atoms	Simple ratio	Whole number ratio
K	26.57	39	$\frac{26.57}{39} = 0.67$	$\frac{0.67}{0.67} = 1$	$1 \times 2 = 2$
Cr	35.36	52	$\frac{35.36}{52} = 0.67$	$\frac{0.67}{0.67} = 1$	$1 \times 2 = 2$
O	38.07	16	$\frac{38.07}{16} = 2.38$	$\frac{2.38}{0.67} = 3.5$	$3.5 \times 2 = 7$

$\therefore$ Empirical formula of the compound is $K_2Cr_2O_7$

5) A carbon compound contains 12.8% carbon, 2.1% hydrogen and 85.1% bromine. The molecular mass of the compound is 187.9 u. Calculate its molecular formula.

Ans:

Symbol of the element	% Composition	At.wt	Relative number of Atoms	Simple ratio
C	12.8	12	$\frac{12.8}{12} = 1.067$	$\frac{1.067}{1.067} = 1$
H	2.1	1	$\frac{2.1}{1} = 2.1$	$\frac{2.1}{1.067} = 2$
Br	85.1	80	$\frac{85.1}{80} = 1.067$	$\frac{1.067}{1.067} = 1$

$\therefore$ Empirical formula is $C_1H_2Br_1$

Molecular weight = 188

Empirical formula weight $= 12 + 2 + 80 = 94$

$$n = \frac{M.F.\ weight}{E.F.\ weight} = \frac{188}{94} = 2$$

Molecular formula = n x empirical formula

$= 2 \times CH_2Br = C_2H_4Br_2$

6) Calculate the amount of 90 % H_2SO_4 required for the preparation of 450 kg HCl as per the given equation.

Ans: $2\,NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$

From the above reaction,

98 gm of H_2SO_4 gives $2 \times 36.5\ gm$ of HCl

Wt of $H_2SO_4\,(?)$ gives 420×10^3 gm of HCl

Weight of $H_2SO_4 = \frac{98 \times 420 \times 10^3}{2 \times 36.5}$

$= 563.8\ kg\ (i.e\ 100\%)$

But H_2SO_4 contains only 90 %

The weight (H_2SO_4) to be taken is

$= \frac{563.8 \times 100}{90} = 626.44\ kg$.

7) When 50 g of sample of sulphur was burnt in air 4% of the sample was left over. Calculate the volume of air required at STP containing 21% oxygen by volume.

Ans: Amount of sulphur taken = 50 gm

Amount of sample left = 2 gm

Amount of sulphur reacted = 50 - 2 = 48 gm

Sulphur burns with oxygen in air is

$S + O_2 \rightarrow SO_2$

No of moles of sulphur $= \frac{48}{32} = 1.5$

According to stoichiometric equation (reaction) no of moles of oxygen required is 1.5 moles.

Volume of oxygen required at STP $= 1.5 \times 22.4\ lit = 33.6\ lit$

21 lit of O_2 present in 100 lit of air

33.6 lit of O_2 required, then how much volume of air taken

$= \frac{33.6 \times 100}{21} = 160\ lit$

8) Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

What mass of $CaCO_3$ is required to react completely with 250ml of 0.75M HCl?

Ans: $CaCO_{3\,(s)} + 2\ HCl_{\,(aq)} \rightarrow CaCl_{2\,(aq)} + CO_{2\,(g)} + H_2O_{\,(l)}$

We know that $n = \frac{M \times V\ in\ ml}{1000}$

from given data, no of moles of $HCl = \frac{0.75 \times 25}{1000} = 0.01875$

As per stoichiometric equation (reaction) 2 moles of HCl react with 1 mole of $CaCO_3$.

Then 0.01875 moles of HCl react with how many moles of $CaCO_3$

$= \frac{0.01875 \times 1}{2} = 0.009375$

$\therefore$ Wt of $CaCO_3 = no\ of\ moles \times G.M.Wt = 0.009375 \times 100 = 0.9375\ gm$.

9) Calculate the volume of 0.1 M $KMnO_4$ required to react with 100 mL of 0.1 M $H_2C_2O_4.2H_2O$ solution in presence of H_2SO_4 .

Ans: Reaction between $KMnO_4$ within $H_2C_2O_4$ in Presence of H_2SO_4 is

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

$KMnO_4$ Solution	$H_2C_2O_4.2H_2O$ Solution
$M_1 = 0.1M$	$M_2 = 0.1M$
$V_1 = ?$	$V_2 = 100\ ml$
$n_1 = 2$	$n_2 = 5$

According to volumetric analysis principle

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

$$V_1 = \frac{M_2V_2}{n_2} \times \frac{n_1}{M_1}$$

$$= \frac{(0.1)(100)}{5} \times \frac{2}{0.1} = 40\ ml.$$

$\therefore$ Volume of $KMnO_4$ is required = 40 ml

10) Calculate the amount of carbon dioxide that could be produced when

I. 1 Mole of carbon is burnt in air

II. 1 mole of carbon is burnt in 16g of dioxygen.

Ans: (i) $\underset{1mole}{C} + \underset{1mole}{O_2} \rightarrow \underset{1mole}{CO_2}$

As Per stoichiometric equation (reaction),

1 mole of carbon burn with oxygen produce 44 gm of CO_2.

(ii) $\underset{12\ gm}{C} + \underset{32\ gm}{O_2} \rightarrow \underset{44\ gm}{CO_2}$

As Per stoichiometric equation,(reaction) 32 gm of oxygen react with 12 gm of carbon.

But 16 gm of oxygen is given .so 6 gm of carbon is sufficient

$\therefore 22\ gm\ of\ CO_2\ is\ produced.$

VI. Long answer questions: (8 marks)

1) The approximate production of sodium carbonate per months 424×10^6 g, while that of methyl alcohol is 320×10^6 g. Which is produced more in terms of moles?

Ans: Moles of sodium carbonate produced per month

$$= \frac{424 \times 10^6}{106} = 4 \times 10^6$$

Moles of $methyl\ Alcohol$ produced per month $= \frac{320 \times 10^6}{32} = 10^7$

So, methyl Alcohol produced in terms of moles is more.

2) 0.188g of an organic compound having an empirical formula CH_2Br displaced 24.2 cc. of air at 14^0C and 752 mm pressure. Calculate the molecular formula of the compound. (Aqueous tension at 14^0C is 12 mm)

Ans: Pressure of dry gas = Pressure of gas –Aqueous tension

$$= 752 - 12 \quad = 740\ mm$$

From given data

$w = 0.188\ gm$ $\qquad M.wt : ?$

$V = \frac{24.2}{1000}\ lit$ $\qquad P = \frac{740}{760}\ atm$

T= 273+14 $\qquad$ = 287K.

Substituting these values in ideal gas equation

$$\therefore PV = \frac{w}{M}RT$$

Molecular weight $= \frac{0.188 \times 0.0821 \times 287 \times 760 \times 1000}{740 \times 24.2} = 188\ gm$

Emperical formula of the compound = CH_2Br

Wt.of Emperical formula of the compound $= 12 + 2 + 80 = 84$

$\therefore n = \frac{M.F.W}{E.F.W} = \frac{188}{94} = 2.$

Molecular formula $= 2 \times E.F = C_2H_4Br_2$.

3) An astronaut receives the energy required in his body by the combustion of 34 g of sucrose per hour. How much oxygen he has to carry along with him for his energy requirement in a day?

Ans: Weight of sucrose required per day $= 34 \times 24 = 816\ gm$

Moles of sucrose = $\frac{wt}{M.wt} = \frac{816}{342} = 2.385$

Sucrose react with oxygen as follows

$C_{12}H_{22}O_{11} + 12\,O_2 \rightarrow 12CO_2 + 11\,H_2O$.

According to the above reaction

1 mole sucrose requires 12 moles of O_2.

2.385 moles of sucrose requires

$$= \frac{2.385 \times 12}{1} = 28.63$$

wt of oxygen = no of moles $\times$ M.wt

$= 28.63 \times 32 = 916.2\ gm$

4) Calculate the volume of H_2 liberated at 27^0C and 760 mm of Hg pressure by action 0.6g magnesium with excess of dil HCl.

Ans: Magnesium reacts with dilute hydrochloric acid as

$Mg + 2HCl \rightarrow MgCl_2 + H_2$.

No of moles of $Mg = \frac{0.6}{24} = 0.025$

As per stoichimetric equation, no of moles of hydrogen liberated is 0.025

From given data

P = 760 mm $\qquad$ T = 27+273

= 1 atm $\qquad$ = 300k.

V = ? $\qquad$ n = 0.025

R = 0.0821

Substituting these values in ideal gas equation, volume of H_2 is

$$V = \frac{nRT}{P} = \frac{0.025 \times 0.0821 \times 300}{1} = 0.615\ lit$$

5) Calculate the mass of sodium acetate (CH_3COONa) required to make 500 mL of 0.375 molar aqueous solution. Molar mass of sodium acetate is $82.0245\ gmol^{-1}$

Ans: Given data

Molarity (M) = 0.375

$$\text{Volume of solution} = \frac{500}{1000}\ \text{lit}$$

$$M.Wt\ of\ CH_3COONa = 82.0245\ gm\ mole^{-1}$$

We know that

$$M = \frac{wt}{M.wt} \times \frac{1000}{Volinml}$$

$\therefore$ wt of CH_3COONa Present in 500 ml solution is

$$= \frac{0.375 \times 82.0245 \times 500}{1000}$$

$$= 15.38 gm.$$

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UNIT-2
STRUCTURE OF ATOM

I. Multiple choice questions: (1mark)

1. **Which of the following statements are correct about cathode rays**

   I. They move from cathode to anode.

   II. These are visible rays.

   III. Television picture tubes are cathode ray tubes.

   IV. In the absence of electrical or magnetic field, these rays travel in a straight line.

   Choose the most appropriate answer from the options given below

   1) I, II and III 2) II, III and IV

   3) I, III and IV 4) I, II, III and IV

   Ans:3) I, III and IV

2. **Increasing order for the values of e/m for electron (e), proton(p), neutron (n) and α-particles is**

   1) $e<p<n<\alpha$ 2) $n<\alpha<p<e$ 3) $n<p<e<\alpha$ 4) $n<p<\alpha<$ e

   Ans: 2) $n<\alpha<p<e$

   Solution: charge/mass for n=0,α=2/4,p=1/1, e =1/1837

   So, order is n,α,p,e.

3. **Rutherford's experiment on the scattering of α-particles showed for the first time that the atom has**

   1) Electrons 2) Protons 3) Nucleus 4) Neutrons

   Ans: 3) Nucleus

4. **Thomson's model of the atom is also called**

   1) Plum pudding model 2) Raisin pudding model

   3) Watermelon model 4) All of the above

   Ans: 4) All of the above

5. **In photoelectric effect at which frequency electron will be ejected with certain kinetic energy (ν_0 = threshold frequency)**

   1) $\nu - \nu_0$ 2) $\nu_0 > \nu$ 3) $\nu_0 \geq \nu$ 4) $\nu > \nu_0$

   Ans: 4) $\nu > \nu_0$

6. **A 600 Watt mercury lamp emits monochromatic radiation of wave length 331.3 nm. How many photons are emitted from the lamp per second. (h= 6.626×10^{-34} Js, Velocity of light: 3×10^{8} m/s)**

   1) 1×10^{19} 2) 1×10^{20} 3) 1×10^{21} 4) 1×10^{23}

   Ans: 3) 1×10^{21}

   Solution: Here Power = 600 W

   $\Lambda = 331.3\text{nm} = 331.3 \times 10^{-9}$ m,h=6.626×10^{-34}J ,

   c=3×10^{8}ms^{-1} , t = 1sec

   $$Power = \frac{Energy}{Time} = \frac{nhc}{\lambda t}$$

$$600 = \frac{n \times 6.626 \times 10^{-34} \times 3 \times 10^{8}}{331.3 \times 10^{-9} \times 1}$$

$$n = \frac{600 \times 331.3 \times 10^{-9} \times 1}{6.626 \times 10^{--34} \times 3 \times 10^{8}}$$

$n = 1 \times 10^{21}$

7. Which of the following electronic transitions in the hydrogen atom will require highest energy?

1) n=4 to n=5 2) n=1 to n=2 3) n=3 to n=5 4) n=2 to n=3

Ans: 2) n=1 to n=2

Note: In hydrogen atom the energy levels are quantized, and as the value of n increases the energy levels get closer together

8. The ratio of radii of second orbit of hydrogen atom to 4th orbit of He^+ ion is

1) 1:4 2) 2:1 3) 1:2 4) 3:2

Ans: 3) 1:2

Solution: Radius of nth orbit is $= \frac{0.529 \times n^2}{z}$

$r_H = \frac{0.529 \times 2^2}{1}$, For Hydrogen n = 2, Z = 1

$r_{He^+} = \frac{0.529 \times 4^2}{2}$, For Helium n = 4, Z = 2

$$\frac{r_H}{r_{He^+}} = \frac{\frac{0.529 \times 2^2}{1}}{\frac{0.529 \times 4^2}{2}} = \frac{1}{2} = 1:2$$

Note: $\frac{r_H}{r_{He^+}} = \frac{n_H^2}{n_{He^+}^2} \times \frac{Z_{He^+}}{Z_H}$

9. The energies of an electron in first orbit of He^+ and 3rd orbit of Li^{2+} in J are respectively

1) -8.72×10^{-18} , -2.18×10^{-18} J
2) -8.72×10^{-18} , -1.96×10^{-17} J
3) -1.96×10^{-17} , -2.18×10^{-18} J
4) -8.72×10^{-17} , -1.96×10^{-17} J

Ans: 1) -8.72×10^{-18} J , -2.18×10^{-18} J

Solution: $E_n = -2.18 \times 10^{-18} \times \frac{Z^2}{n^2}$ J

where, E_n = energy of an electron in nth orbit,

Z = atomic number, n = orbit number

For helium ion (He^+),Z =2, n = 1

$\therefore E_n = -2.18 \times 10^{-18} \times \frac{2^2}{1^2}$ J

$= -8.72 \times 10^{-18}$J

For lithium ion (Li^{2+}), Z=3, n=3

$\therefore E_n = -2.18 \times 10^{-18} \times \frac{3^2}{3^2}$ J

$= -2.18 \times 10^{-18}$J

10. The value of Rydberg constant is

1)109777cm $^{-1}$ 2) 109977cm $^{-1}$ 3) 109677cm $^{-1}$ 4) 109277cm $^{-1}$

Ans: 3) 109677cm $^{-1}$

11. The velocity of a particle A is 0.1 m/s and that of particle B is 0.05 m/s. If the mass of the particle B is 5 times that of particle A. Then the ratio of de-Broglie wavelengths associated with the particles A and B is

1) 2:5 2) 3:4 3) 6:4 4) 5:2

Ans: 4) 5:2

Solution: $\boldsymbol{\lambda = \frac{h}{mv}}$

$\lambda_A = \frac{h}{m_A \times 0.1}$, $\lambda_B = \frac{h}{\mathbf{5 \times m_A \times 0.05}}$, $\frac{\lambda_A}{\lambda_B} = \frac{5 \times m_A \times 0.05}{m_B \times 0.1} = \frac{5}{2}$

Note : $\frac{\lambda_A}{\lambda_B} = \frac{m_B V_B}{m_{AV_A}}$

12. The number of radial nodes and angular nodes of a 4f orbital are respectively

1) 0,3 2) 1,2 3) 2,1 4) 2,0

Ans:1) 0,3

Solution: The number of radial nodes = n - l – 1

For 4f orbital Radial nodes = 4 – 3 - 1 =0

Angular nodes (nodal planes) = l (Azimuthal quantum number)

Angular nodes for 4f orbital = 3

13. Maximum number of electrons possible with spin quantum number +1/2 with principal quantum number n =4 is

1)16 2) 9 3) 4 4) 25

Ans: 1)16

Solutions: The number of orbitals = n^2 =4^2 =16 Total electrons = 32

The maximum number of electrons with spin + $\frac{1}{2}$. = 16

14. The wavelength of second line in the Lyman series of hydrogen atomic spectrum is (Rydberg constant = R cm^{-1})

1) $\frac{8R}{9}$ 2) $\frac{9}{8R}$ 3) $\frac{4}{3R}$ 4) $\frac{3R}{4}$

Ans: 2) $\frac{9}{8R}$

Solution: = $\frac{1}{\lambda}$ = R [$\frac{1}{n_1^2} - \frac{1}{n_2^2}$]

For second line in Lyman series

n_1 =1, n_2 = 3

$\frac{1}{\lambda}$ = R[$\frac{1}{1^2} - \frac{1}{3^2}$] = R[$\frac{1}{1} - \frac{1}{9}$] = $\frac{8R}{9}$

$\therefore \lambda = \frac{9}{8R}$

15. What is the correct orbital designation of an electron with the quantum numbers n = 4, l = 3, m = -2, s= +1/2 ?

1) 3s 2) 4f 3) 5p 4) 4d

Ans: 2) 4f

II Fill in the Blanks: (1mark)

1. Splitting of spectral lines in magnetic field is called_____

Ans: Zeeman effect

2. Splitting of spectral lines in electric field is called _____

Ans: Stark effect

3. The preference of three unpaired electrons in the nitrogen atom can explained by ____

Ans: Hund's Rule

4. The electronic configuration of copper is _____

Ans: $[Ar]4s^1 3d^{10}$

5. The electronic configuration of chromium is _____

Ans: $[Ar]4s^1 3d^5$_____

6. In potassium atom, the differentiating electrons enters 4s orbital instead of 3d orbital. This is according to_____

Ans: Aufbau principle

III One word answer questions:(1mark)

1. Define isotopes.

Ans: Isotopes are atoms of the same element that have the same atomic number, (Z) but a different mass number (A).

2. Write the difference between orbit and orbital?

Ans: A circular path around the nucleus in which electrons revolve is called as orbit.

In an atom, the region around the nucleus where the probability of finding the electron is maximum is known as atomic orbital.

3. How many nodal planes are present in d orbitals?

Ans: d orbital has two nodal planes.

4. How many 'P' electrons are present in Sulphur atom?

Ans: Sulphur has 10 'p' electrons.

(Sulphur has electronic configuration – $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$)

5. What are degenerate orbitals?

Ans: Degenerate orbitals are atomic orbitals within the same subshell that have the same energy level.

Eg: 2p orbitals (px, py, and pz) are degenerate.

IV Very Short Answer Questions:(2mark)

1. Calculate the charge of one mole of electrons.

Ans: One electron has charge – 1.602×10^{-19} coulombs.

One mole of electrons has charge $-6.023 \times 10^{23} \times 1.602 \times 10^{-19} = 9.648846 \times 10^4 = 96488.5$ coulombs (Approximately 96500C).

2. How many neutrons and electrons are present in the nuclei of ${}^{13}_{6}C, {}^{18}_{8}O, {}^{24}_{12}Mg, {}^{56}_{26}Fe$ **?**

Ans:

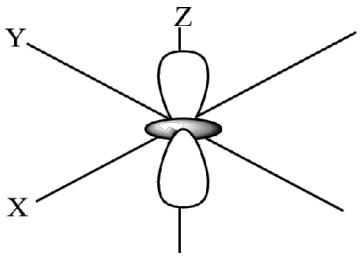
Nuclei	Number of electrons	No of Neutrons (A-Z)
${}^{13}_{6}C$	6	7
${}^{18}_{8}O$	8	10
${}^{24}_{12}Mg$	12	12
${}^{56}_{26}Fe$	26	30
Note: Number of protons = number of electrons = Z (neutral atom) Number of neutrons = Mass number (A) - number of protons (Z)		

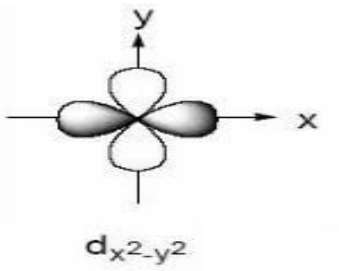
3. What is a black body?

Ans: The body which is perfect absorber and emitter of all type of radiations incident on it is called a black body.

4. Draw the shape of d_{Z^2} **and** $d_{X^2-Y^2}$ **orbital.**

Ans: d_{z^2} orbital





5. What is the frequency of radiation of wave length 600 nm?

Ans: $\upsilon = \frac{C}{\lambda}$

$\lambda = 600$ nm $= 600 \times 10^{-9}$ m $= 6 \times 10^{-7}$ m, $C = 3 \times 10^{8}$ m/sec.

$$\upsilon = \frac{3 \times 10^{8}}{6 \times 10^{-7}} = \frac{1}{2} \times 10^{15}$$

$= 0.5 \times 10^{15} = 5 \times 10^{14}$ sec^{-1}

6. How many subshells are associated with n=5?

Ans:

For n = 5

l values (n-1)= 0, 1, 2, 3, 4

l = 0 → s – orbital

l = 1 → p — orbital

l = 2 → d – orbital

l = 3 → f – orbital

l = 4 → g — orbital

→ Five subshells are associated with n = 5.

7. How many electrons in an atom may have n=4, $m_s = +\frac{1}{2}$?

Ans: For n = 4 → l values are 0, 1, 2, 3
l = 0 → s contains 1 electron with m_s = + 1/2
l = 1 → p contains 3 electron with m_s = + 1/2
l = 2 → d contains 5 electron with m_s = + 1/2
l = 3 → f contains 7 electron with m_s = + 1/2
∴ Total no.of electrons with m_s = +1/2 for n = 4
= 1 + 3 + 5 + 7 = 16.

8. Explain Pauli's exclusion principle.

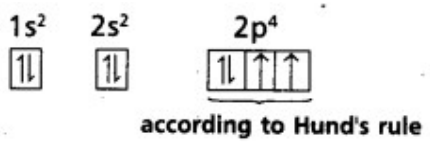
Ans:

Pauli's exclusion principle:

"No two electrons in an atom can have the same set of four quantum numbers".
This can also be stated as "only two electrons may exist in the same orbital and these electrons must have opposite spins".

9. What is Hund's rule?

Ans: Hund's rule: It states "Pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each (i.e.,) all the orbitals are singly occupied".
Ex : '$_8$O' electronic configuration is



10. What is Aufbau principle?

Ans: Aufbau's principle: "In the ground state of the atoms, the orbitals are filled in order of their increasing energies".
In other words electrons first occupy the lowest energy orbital available to them. The order in which the orbitals are filled as follows :
1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 4f < 5d < 6p < 7s

V Short Answer Questions: (4 marks)

1. Explain photo electric effect.

Ans: The ejection of electrons from a metal surface, when the radiations of suitable frequency strike the metal surface is called photoelectric effect.
Explanation using Einstein's quantum theory:

1) To explain photoelectric effect, Einstein utilized Quantum theory.
2) When a photon strikes metal surface, it uses some part of its energy to eject the electron from the metal atom. The remaining part of the total energy is given to the ejected electrons in the form of kinetic energy.

Hence we can write $h\upsilon = W + KE \Rightarrow h\upsilon = h\upsilon_0 + \frac{1}{2}m_e v^2$

where $h\upsilon$ = energy of photon,
υ = Threshold frequency,

m_e = mass of electron
W = energy required to overcome the attractive forces on the electron in the metal (work function)
KE = kinetic energy of ejected electron,
V = Velocity of ejected electron.

3) If a photon of sufficient energy strike the metal surface and could eject the electron. But if a photon has insufficient energy, it cannot eject the electron from the metal.
eg. : A photon of violet light [high frequency] can eject the electrons from the surface of potassium but a photon of red light [low frequency] cannot eject the electrons.

2. Which of the following sets of quantum numbers are not possible?

(a) n=0 ; l=0 ; m_l =0; m_s =+1/2 ;
(b) n=1 ; l=0 ; m_l=0 ;m_s= -1/2
(c) n=1, l=1 ; m_l =0 ;m_s =+1/2 ;
(d) n=2 ; l=1 ; m_l =0 m_s = +1/2

Ans: Following set of quantum numbers are not possible.

a) n = 0, l = 0, m_l = 0, m_s = +1/2

Reason:

'n' is principal quantum number, whose values are from 1 to n. The value of 'n' never equal to zero. But given n = 0.

c) n = 1, l = 1, m_l = 0, m_s = +1/2

Reason:

Values of 'l' are from 0 to (n – 1).
If n = 1 then the value of 'l' is zero not equal to '1'.

e) n = 3, l = 3, m_l = – 3, m_s = +1/2

Reason:

If n = 3, possible values of 'l' are 0, 1, 2, but not equal to '3'.

3. What is a nodal plane? How many nodal planes are possible for 2p, and 3dorbitals?

Ans: The plane at which the probability of finding the electron is zero is called as nodal plane.

- For 2p orbitals one nodal plane is possible for each 'p' orbital.
- For 3d orbitals two nodal planes are possible for each'd' orbital.

4. Explain the difference between orbit and orbital.

Ans: **Orbit**

1. A circular path which is present around the nucleus in which electrons revolve is called as orbit.
2. It represents two- dimensional planar motion of an electron.
3. Orbits are circular in shape and are non-directional paths.
4. The maximum no. of electrons in any orbit is given by the formula $2n^2$ (n = orbit number).

Orbital

1. The 3-dimensional space where the probability of finding the electron is maximum around the nucleus is called as orbital.
2. It represents three-dimensional planar motion of an electron.
3. These have definite shape and these are directional except' s orbital.
4. Each orbital can occupy a maximum of two electrons.

5. Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the de Broglie wavelength associated with the electron revolving around the orbit.

Ans:

1. Consider the Bohr's angular momentum equation.

$$mvr = \frac{nh}{2\pi}$$

i.e The angular momentum of an electron is integral multiple of 'h/2π'

$$mvr = \frac{nh}{2\pi}$$

2. $2\pi r = \frac{nh}{mv}$
3. According to de-Broglie's wavelength $\lambda = h/mv$

   $2\pi r = n\left(\frac{h}{mv}\right)$
4. $2\pi r = n\lambda$.

Thus the circumference of the Bohr orbit is integral multiple of de-Broglie's wave length.

VI Long Answer Questions: (8 marks)

1. Explain briefly the Planck's quantum theory.

Ans: The postulates of Planck's quantum theory are

a) The emission of radiation is due to vibrations of charged particles (electrons) in the body.

b) The emission is not continuous but in discrete packets of energy called quanta. This emitted radiation propagates in the form of waves.

c) The energy (E) associated with each quantum for a particular radiation of frequency V is given by E = hv, Here 'h' is Planck's constant.

d) A body can emit or absorb either one quantum (hv) of energy or some whole number multiple of it. Thus energy can be emitted or absorbed as hv, 2hv, 3hv etc., but not fractional values. This is called quantisation of energy.

e) The emitted radiant energy is propagated in the form of waves.

f) Values of Planck's constant in various units:

$h = 6.625 \times 10^{-27}$ erg.sec

$= 6.625 \times 10^{-34}$ J.s

Success of Planck's quantum theory: This theory successfully explains the black body radiations. A black body is a perfect absorber and also a perfect radiator of radiations.

2. What are the postulates of Bohr's model of hydrogen atom? Discuss the importance of this model to explain various series of line spectra in hydrogen atom.

Ans: The postulates of Bohr's model of hydrogen atom

1. The electrons in an atom revolve around the nucleus in fixed circular paths with definite velocity, radius and energy are called orbits.
2. The energy of the electron in an orbit does not change with time. The energy of the electron in an orbit remains constant. It neither emits nor absorbs energy. Hence these orbits are termed as stationary orbits or energy levels. They are indicated as 1,2,3,4……(or) K,L,M,N etc.
3. The energy of an electron changes when the electron moves from one orbit to another orbit.
   a) If electron jumps from lower energy orbit to higher energy orbit, it absorbs energy.

b) If electron jumps from higher energy orbit to lower energy orbit, it releases energy. The energy difference between these two orbits $\Delta E = E_2 - E_1 = hv$
Where E_2 = Higher energy orbit, E_1 = Lower energy orbit

4. The angular momentum of electron is always integral multiple of $\frac{h}{2\pi}$

it is given by $mvr = \frac{nh}{2\pi}$ where m= mass of electron
v = velocity of electron
r = radius of an orbit
h = Planck's constant

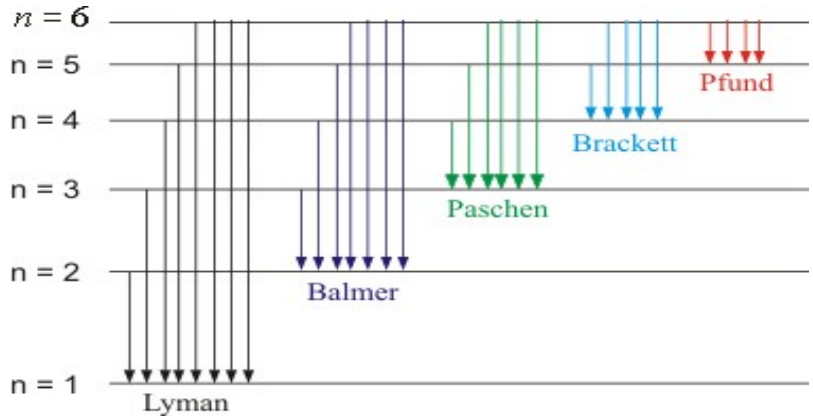
Hydrogen Spectrum:-

1. When H_2 gas is heated or subjected to silent electric discharge tube, the electrons in various hydrogen atoms absorb different amounts of energy and jump into various higher energy levels.
2. In higher energy levels energy is more but stability is less. Therefore, electrons return back to lower energy level in single or multiple steps.
3. Energy is released during this process and it appears as lines in hydrogen spectrum.
4. When electrons jump from higher energy level to lower energy levels 5 types of spectral lines are formed.

When an electron jumps from any higher energy level to
a) n=1 lines in Lymen series are produced in U.V. region.
b) n=2 lines in Balmer series are produced in Visible region.
c) n=3 lines in Paschen series are produced in near I.R. region.
d) n=4 lines in Brackett series are produced in middle I.R. region.
e) n=5 lines in Pfund series are produced in far I.R region

The hydrogen spectrum consists of the following series of lines.

Series	n_1	n_2	Region
Lyman series	1	2, 3, 4,.....	UV region
Balmer series	2	3, 4, 5,.....	Visible region
Paschen series	3	4, 5, 6,.....	Near I.R
Bracket series	4	5, 6, 7,.....	Middle I.R
Pfund series	5	6, 7, 8,.....	Far I.R



3. How are quantum numbers n,l and m_l arrived at ? Explain the significance of these quantum numbers.

Ans: The set of numbers which are useful to describe the state of the electron in an atom are called as quantum numbers. They are four types

1. Principal quantum number.
2. Azimuthal quantum number.
3. Magnetic quantum number.
4. Spin quantum number.

(1) Principal quantum number:

- It was proposed by Neil's Bohr.
- It is indicated by 'n'.
- 'n' values are1,2,3,…..(or)K,L,M,N,……
- The total number of electrons in an orbit $= 2n^2$.

Significance:It indicates the size and energy of the orbit.

(2) Azimuthal quantum number:

- It was proposed by Sommerfeld.
- It is indicated by '*l*'.
- '*l*' value are from 0,1,2to(n−1).

Significance: It indicates the shape of orbital.

Subshell	l	Shape of orbital
s	0	spherical
p	1	dumb-bell
d	2	double dumb-bell
f	3	Fourfold dumb-bell shape

(3) Magnetic quantum number:

- It was proposed by Lande.
- It is indicated by 'm'.
- 'm' values are ranging from−l to +l including 0.
- Total number of m values (2*l* +1)

Significance: It indicates the orientation of orbitals in space.

Subshell	l	m values -l to +l	Total m values (2l+1)
s	0	0	1
p	1	-1,0,+1	3
d	2	-2,-1,0,+1,+2	5
f	3	-3,-2,-1,0,+1,+2,+3	7

(4) Spin quantum number:

- It was proposed by Uhlenbeck and Goudsmith.
- It is indicated by's'.
- 's'values are $+\frac{1}{2}$(in clockwise direction) or -1/2 in anticlock wise direction)

Significance: It indicates the spin direction of the revolving electron.

4. What are various ranges of electromagnetic radiation? Explain the characteristics of electromagnetic radiation.

Ans: Electromagnetic radiation: When electrically charged particle is accelerated alternating electric and magnetic fields are produced and transmitted. These fields are transmitted in the form of waves called electromagnetic waves or electromagnetic radiation.

Important Characteristics of a wave:

1) These are produced by oscillating charged particles in a body.

2) These radiations can pass through vacuum also. So medium for transmission is not required.

3) Velocity (c): It is defined as the linear distance travelled by the wave in one second.

Units : cm sec^{-1} (or) m see^{-1}

All kinds of electromagnetic waves have the same velocity.(3×10^8 m sec^{-1})

4) Wavelength (λ): It is defined as the distance between any two successive crests or troughs of waves.

Units: A ; m ;cm ; nm or pm

1 A° = 10^{-10} m

1 nm = 10^{-9} m = 10^{-7} cm

1 pm = 10^{-12}m.

5) Frequency (v): It is defined as the number of waves passing through a point in one second.

Units: Hertz (Hz); cycles sec^{-1} or sec^{-1}.

$$\upsilon = \frac{c}{\lambda}$$

6) Wave number ($\bar{\upsilon}$): It is defined as the number of waves present in one unit length. It is equal to the reciprocal of the wavelength.

$\bar{\upsilon} = 1/\lambda = \upsilon \times c$

Relation between wavelength and frequency :

$c = \upsilon \times \lambda \Rightarrow \upsilon = c/\lambda$

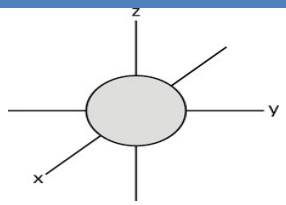
7. Amplitude: Amplitude (A) is the height of the crest (or) depth of trough of a wave, It determines intensity (or) brightness of the wave.

5. Define atomic orbital. Explain the shapes of s,p and d orbitals with the help of diagram.

Ans: Atomic orbital: In an atom, the region around the nucleus where the probability of finding the electron is maximum is known as atomic orbital.

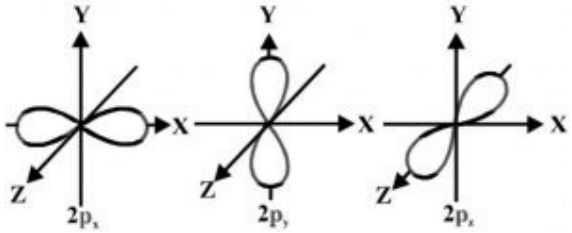
Shapes of s-Orbital:

1. When l = 0, then the orbital is known as s-orbital. The shape of s-orbital is spherical.
2. As the value of 'n' increases, the size of the orbital increases.
   That is, 1s < 2s < 3s < ....
3. s- orbital does not possess any directional property.
4. The number of nodal planes for s-orbital is 'zero'.
5. Various possible quantum numbers for s-orbitals are:
   n = 1, 2, 3, ... ; l = 0 ; m = 0.



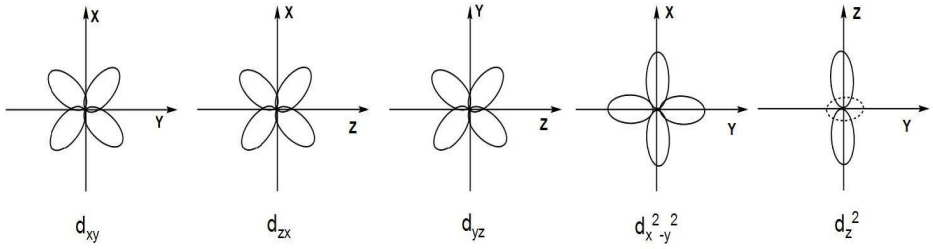
II) Shape of p-orbitals:

1. When l = 1, then the orbital is known as p-orbital. The shape of p-orbital is dumb-bell with 2 lobes.
2. The p-subshell contains 3 sub-orbitals. They are p_x, p_y, p_z degenerate orbitals.
3. All the 3 sub-orbitals are mutually perpendicular.
4. Each p-orbital has 1 nodal plane.
5. Various possible quantum numbers for p-orbital are:
   n = 2, 3, 4, ... ; l = 1 ; m = -1, 0, 1.



III) Shape of d- orbitals:

1. When l = 2, then the orbital is known as d-orbital. The shape of d-orbital is double dumb-bell with 4 lobes.
2. The d-subshell contains 5 sub-orbitals. They are d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, and d_{z^2}.
3. The shapes of the first 3 orbitals are similar and their lobes are in between their axes, and in the next two orbitals, lobes are present along the axes.
4. Each d-orbital has 2 nodal planes except dz^2.
5. Various possible quantum numbers for d-orbital are:
   n = 3, 4, 5, ... ; l = 2 ; m = -2, -1, 0, 1, 2.



Shapes of d-orbitals

6. Explain the emission and absorption spectra. Discuss the general description of line spectra in hydrogen atom.

Ans: Emission spectrum:

1. It is produced when the substance emits the radiations.
2. It consists of bright lines on dark background.
3. It is produced due to the emission of energy by electrons.
4. It is classified into 2 types

a. continuous spectrum b. Discontinuous spectrum

Absorption spectrum:

1. It is produced when substance absorb the certain radiations.
2. It consists of dark lines on bright background.
3. It is produced due to the absorption of energy by electrons.
4. It is not classified.

Line spectra of Hydrogen - Bohrs Theory:

In case of hydrogen atom line spectrum is observed and this can be explained by using Bohr's Theory.

1. When hydrogen gas is heated or subjected to silent electric discharge tube, the electrons in various hydrogen atoms absorb different amounts of energy and jump into various higher energy levels.
2. In higher energy levels energy is more but stability is less. Therefore, electrons return back to lower energy level in single or multiple steps.
3. Energy is released during this process and it appears as lines in hydrogen spectrum.
4. When electrons jump from higher energy level to lower energy levels 5 types of spectral lines are formed.
   a) When electron jumps from any higher energy level to n=1 lines in Lymen series are produced in U.V. region.
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   e) When electron jumps from any higher energy level to n=5 lines in Pfund series are produced in far I.R region.

The hydrogen spectrum consists of the following series of lines.

Series	n_1	n_2	Region
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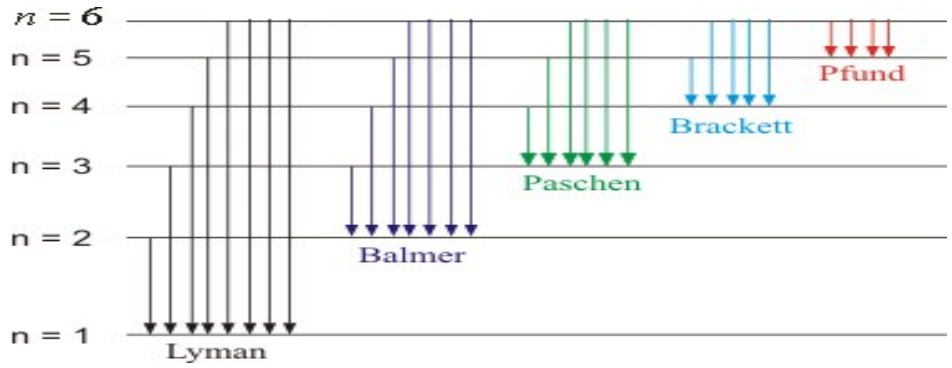
Bracket series	4	5,6,7,.....	Middle I.R
Pfund series	5	6,7,8,.....	Far I.R



7. Write the postulates and limitations of Bohr's model of an atom.

Ans:

Bohr 's Postulates:

1. The electrons are revolving around the nucleus in a fixed circular path is called orbits. These orbits are denoted by K, L, M, N… or 1, 2, 3, 4…….
2. As long as electron revolves in a particular orbit it does not lose or gain energy. These orbits are called Stationary orbits.
3. The energy difference between two levels $\Delta E = E_2 - E_1 = hv$
4. The angular momentum of electron is always integral multiple of $\frac{h}{2\pi}$ it is given by $mvr = \frac{nh}{2\pi}$.

Bohr's Limitations:

1. Spectra of multielectron atoms: Bohr's theory could explain the spectra of Hydrogen and single electron species like He^{+}, Li^{2+}, Be^{3+}, but it fails to explain the spectra of multielectron atoms.
2. Fine structure: It fails to explain this fine structure of Hydrogen atom.
3. Splitting up of spectral lines: This theory fails to explain Zeeman effect and Stark effect.
   (The splitting up of spectral lines when an atom is subjected to strong magnetic field is called Zeeman effect.
   The splitting up of spectral lines when an atom is subjected to strong electric field is called Stark effect.)
4. Flat model: Bohr's theory gives a flat model of the orbits. Bohr's theory cannot explain this dual nature of electronic both particle and wave nature.
5. It fails to support the uncertainty principle proposed by Heisenberg.
6. It could not explain the ability of atoms to form molecules by chemical bonds.

Note : Any four limitations

8. What are the consequences that lead to the development of quantum mechanical model of an atom?

Ans: Consequences that lead to development of quantum mechanical model of an atom are as follows.

1. Classical mechanics successfully explained the motion of macro scopic objects.
   Eg: Falling stone, Planets etc.,.
2. Classical mechanics failed to explain the motion of microscopic objects like electrons, atoms, molecules etc.
3. Classical mechanics ignores the concept of dual behaviour of matter and especially for sub atomic particles.
4. The Branch of science deals with the dual behaviour of matter is called quantum mechanics. this deals with the motions of microscopic objects like electron.

Important features of quantum mechanical model of atom:

1 The energy of electrons in an atom is quantized (it can only have certain specific values).

2. The existence of quantized electronic energy levels is a direct result of the wave like properties at electrons and are allowed solution at schrodinger wave equations.

3. All the information about the electron in an atom is contained in its orbital wave function 'Ψ' and quantum mechanics makes it possible to extract this information from 'Ψ'.

4. The path of the electron can never be determined accurately. Therefore, we find only the probability of the electron at different points in space, around an atom.
5. The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function i.e., |Ψ|2 at that point. $|\Psi|^2$ is known as probability density and is always positive. From the value of $|\Psi|^2$ at different points within the atom, it is possible to predict the region around the nucleus where electron will most probably be found.

9. Explain the following

a) debroglie's Concept b) Heisenberg's uncertainity principle

Ans: a) deBroglie's Concept

de Broglie's concept, also known as the de Broglie hypothesis, proposes that all matter exhibits wave-like properties, just as light exhibits both particle and wave characteristics. This means that particles like electrons and atoms have both a particle nature and a wave nature, and their wave nature.

$$\lambda = \frac{h}{mv} \qquad \therefore p = mv$$

so, the above equation becomes

$$\lambda = \frac{h}{p}$$

(Where λ is wavelength, h is Planck's constant, and p is momentum) is a key aspect of de Broglie's hypothesis.

b) Heisenberg uncertainty principle:

"Simultaneous and exact determination of the position and momentum of a sub-atomic particle, like electron moving with high speed is impossible."

If Δx and Δp represents the uncertainties in the position and momentum respectively. Then according to Heisenberg

$$\Delta x.\ \Delta p \geq \frac{h}{4\pi} \text{——- (1)}$$

The product of uncertainties in position (Δx) and momentum (Δp) of an electron cannot be less than h/4π. It can be equal or greater than h/4π.

Since momentum = mass x velocity, the equation (1) can be written as

$$\Delta x \times m\ (\Delta v) \geq \frac{h}{4\pi}$$

$$\Delta x \times \Delta v \geq \frac{h}{4\pi}$$

If the position is determined accurately Δx = 0 and Δv = ∝.

That means the inaccuracy in measuring the velocity is ∝.

If velocity is determined accurately Δv = 0 and Δx = ∝.

Significance of Uncertainty Principle:

1. This principle rules out the existence of definite paths or trajectories of electrons and other similar particles.
2. This principle is significant only for motion of microscopic objects, and is negligible for that of macroscopic objects.

UNIT-3
CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

I Multiple choice questions (1 mark)

1. Which of the following oxides, when dissolved in water form an acidic solution?

1) Na_2O 2) CO

3) Al_2O_3 4) Cl_2O_7

Ans: 4) Cl_2O_7

2. The maximum covalency of $[AlF_6]^{3-}$ and $[AlF_6]^{3-}$ are respectively

1) 4,6 2) 4,4 3) 6,4 4) 6,6

Ans: 1) 4,6

3. The increasing order of ionization enthalpy of 2nd period elements is___

1) $Li < B < Be < C < N < O < F < Ne$

2) $Li < Be < B < C < N < O < F < Ne$

3) $Li < B < Be < C < O < N < F < Ne$

4) $Li < Be < B < C < O < N < F < Ne$

Ans: 3) $Li < B < Be < C < O < N < F < Ne$

4. The difference in electro negativities of elements give information regarding

1) Bond length 2) Nature of bond

3) volume of anion 4) Volume of cation

Ans: 2) Nature of bond

5. The atomic radius of fluorine is 64 pm. What is the ionic radius of fluoride ion___?

1)64 pm 2) 136 pm 3) 32 pm 4) 60 pm

Ans: 2) 136 pm

6. The atomic number of the element unnilennium is

1)102 2)108 3)119 4)109

Ans:4) 109

7. Which one of the following sets of ions represents a collection of iso electronic species

1. Li^+, Na^+, Mg^{+2}, Ca^{+2}
2. Ba^{2+}, Sr^{2+}, K^+, Ca^{+2}
3. N^{3-}, O^{-2}, F^-, S^{-2}
4. K^+, Cl^-, Ca^{+2}, Sc^{+3}

Ans: 4) K^+, Cl^-, Ca^{+2}, Sc^{+3}

8. Three elements X,Y and Z are in the 3rd period of the periodic table. The oxides of X,Y and Z respectively are basic, amphoteric and acidic. The correct order of the atomic numbers of X,Y and Z is

1)X < Z <Y 2) Z<Y<X 3) X<Y <Z 4) Y<X<Z

Ans: X<Y <Z

9. In which of following are arranged in the decreasing order their metallic nature

1)Na > Mg> Be> Si>P 2)P>Si>Be>Mg>Na

3)Si>P>Be>Na>Mg 4) Be>Na>Mg>Si>P

Ans: Na > Mg> Be> Si>P

10. What is the atomic number of the element present in the 4th period and 17th group of the periodic table?

1) 29 2) 35 3) 37 4)30

Ans: 2) 35

11. If the formula of oxide of Eka aluminium is E_2O_3, its chloride can be

1) $AlCl_3$ 2) $GaCl_3$ 3) $GeCl_3$ 4) Ga_2Cl_3

Ans: 2) $GaCl_3$

12. To which group an element with atomic numbers 84 belongs to?

1) Group-12 2) Group-17 3) Group-16 4) Group-11

Ans: 3) Group-16

13. As we move from left to right across a period, the non-metallic character _____ and as we go down the group metallic character_____

1) Increases, Decreases 2) Decreases, Increases

3) Decreases, Increases 4) Increases, Increases

Ans: 4) Increases, Increases

14. The IUPAC official name of Unnilquadium

1) Seaborgium 2) Lawrencium

3) Dubnium 4) Rutherfordium

Ans: 4) Rutherfordium

II **Fill in the blanks (1 mark)**

1 **Among the alkali metals, the metal with the highest ionization enthalpy is _____**
Ans: Lithium

2 **The examples of neutral oxides_____**
Ans:CO,NO, N_2O

3 **Beryllium more closely resembles with ___**
Ans: Aluminium

4 **The element with highest electro negativity on Pauling scale is _____**
Ans: Electronegativity

5 **In an atom the decrease in the attraction between nucleus and outer most electrons by the core electrons is called _____**
Ans: Sheilding effect (or) screening effect.

III **One Word Answer questions (1 Mark)**

1 **State Medeleev's periodic law.**
Ans: Physical and chemical properties of elements are periodic functions of their atomic weights.

2 **State Mosley's modern periodic law.**
Ans: Physical and chemical properties of elements are periodic functions of their atomic numbers.

3 **What are the elements having highest electro negativity and electron gain enthalpy?**
Ans: Fluorine, Chlorine

4 **What is a diagonal relationship?**
Ans: Second period elements diagonally exhibits similar properties with third period elements

5 **What is an amphoteric oxide?**
Ans: Oxide having both acidic and basic nature

6 **What is iso electronic series?**
Ans: Atom and ions which contain the same number of electrons

7 **What are transuranic elements?**
Ans: Elements after uranium

8 **What is the starting element of fifth period?**
Ans: Rubidium

9 **What are the units of electron gain enthalpy?**
Ans: kilo Joules per mole

10 **For which group, valency and group number has no relation.**
Ans: Zero Group

IV Very short answer questions (2marks)

1. An element 'X' has atomic number 34. Give its position in the periodic table.
Ans: The element X with atomic no (z) = 34 has electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^4$. Hence the element is present in 4^{th} period and 16^{th} group (VIA group).

2. Mg^{2+} is smaller than O^{2-} in size. Why?
Ans: Mg^{2+} and O^{2-} ions are iso electronic species.
In case of iso electronic species nuclear charge increases size of ion decreases. So Mg^{2+} has small size than O^{2-}.

3. How does the nature of oxides change along third period from Na_2O to Cl_2O_7?
Ans: In 3^{rd} period from left to right the oxide nature varies from high basic nature to high acidic nature.

Basic nature gradually decreases and acidic nature gradually increases.

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
(basic)	(basic)	(amphoteric)	(acidic)	(acidic)	(acidic)	(acidic)

4. Consider the following species N^{3-}; O^{2-}, F^-, Na^+, Mg^{2+} and Al^{3+}
a. What is common in them?
b. Arrange them in the increasing order of their ionic radii?
Ans: Given ions are
N^{-3}, O^{-2}, F^-, Na^+, Mg^{+2} and Al^{+3}.
a) The above ions have same number of electrons (All have 10 electrons). So these are called iso electronic species.
b) The increasing order of ionic radii among above ions is
$Al^{+3} < Mg^{+2} < Na^+ < F^- < O^{-2} < N^{-3}$
Reason : – In case of iso electronic species as the nuclear charge increases ionic radii decreases.

5. Name any two bridge elements?
Ans.2nd period elements are called Bridge elements
Eg : Be, B.

6. Define metallic radius and covalent radius?

Ans: Metallic radius : The crystal radius is half the internuclear distance between two adjacent atoms in a metal.

Covalent radius : Covalent radius is half the equilibrium distance between the nuclei of two atoms with a covalent bond.

7. Why cation is smaller and anion is larger in radii than their parent atoms?

Ans: Cation has high effective nuclear charge and decrease in size is observed. Hence cation has smaller radii.

Anion has very low effective nuclear charge and increase in size observed. Hence anion has larger radii.

8. How are electronegativity, metallic & non-metallic characters related?

Ans: Greater the electronegativity values of an element indicates the non metallic nature and low metallic nature of that element.

Lower the electronegativity value of an element indicates that low non metallic nature and high metallic nature of that element.

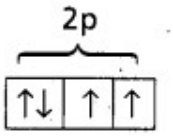
Electronegativity ∝ Non metallic nature

Electronegativity ∝ 1 / Metallic Nature

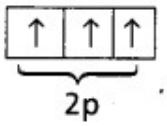
9. Ionisation enthalpy (IE_1) of O is less than N. why?

Ans:

- Oxygen has electronic configuration $1s^2\ 2s^2\ 2p^4$



- Nitrogen has electronic configuration $1s^2\ 2s^2\ 2p^3$



- Nitrogen has half filled shell and is stable so more amount of energy is required to remove an electron, than in oxygen.
  Hence IE, of 'O' is less than that of 'N'.

10. What are the oxidation state and covalency of Al in $[AlCl(H_2O)_5]^{2+}$?

Ans: The oxidation state of Al is +3 and the covalency is 6.

V. Short answers questions (4 marks)

1. Give any four characteristic properties of transition elements?

Ans: Characteristic properties of elements:

a) They exhibit more than one oxidation state.

b) Most of the elements and their ions exhibit colour.

c) These elements and their compounds act as good catalysts for various chemical processes.

d) They and their ions exhibit paramagnetic properties.

e) They form useful alloys.

2. Assign the position of the element having outer electronic configuration.

a. ns^2np^4 for n = 3

b. $(n-1)d^2ns^2$ for n = 4.

Ans : a) ns^2np^4 for n = 3.

- $3s^2 3p^4$ → element is sulphur
- Sulphur belongs to VIA group (Group – 16) and 3rd period in periodic table,

b) $(n-1)d^2\ ns^2$ for n = 4

- $3d^2\ 4s^2$ → element is Titanium
- Titanium belongs to IVB group (Group – 4) and 4th period in the periodic table.

3. Which of the following will have the most negative electron gain enthalpy and which is the least electronegative? P, S, Cl, F. Explain?

Ans: Electron gain enthalpy generally becomes more negative across a period as we move from left to right. Within a group, electron gain enthalpy becomes less negative down a group. However, adding an electron to the 2p-orbital leads to greater repulsion than adding an electron to the larger 3p-orbital. Hence the element with most negative electron gain enthalpy is chlorine; the one with the least negative electron gain enthalpy is phosphorous.

4. Arrange the following in the order of increasing:

1. EA O, S and Se
2. Radius Fe, Fe^{2+}, Fe^{3+}.
3. IE : Na, K and Rb
4. EN: $F, Cl, Br\ and$ I

Ans:

1. Increasing order of electron affinity is O < Se < S.
2. Increasing order of radius is $Fe^{3+} < Fe^{2+} <$ Fe.
3. Increasing order of IE is Rb < K < Na.
4. Increasing order of electronegativity is I < Br < Cl <F

5. Write a note on

1. **Atomic radius**
2. **Metallic radius**
3. **Covalent radius.**

Ans:

1. <u>Atomic radius:</u> The atomic radius decreases from left to right in a period. With an increase in the atomic number in a period the nuclear charge increase. As a result the effective nuclear charge over the outermost electrons increases, due to this the orbitals are pulled closer to the nucleus causing in a decrease in the atomic radius.

The atomic radius increases from top to the bottom in a group because – with an increase in the atomic number the electrons are added to new shells resulting an increase in the number of inner shells. Hence atomic radius increases from top to bottom in a group.

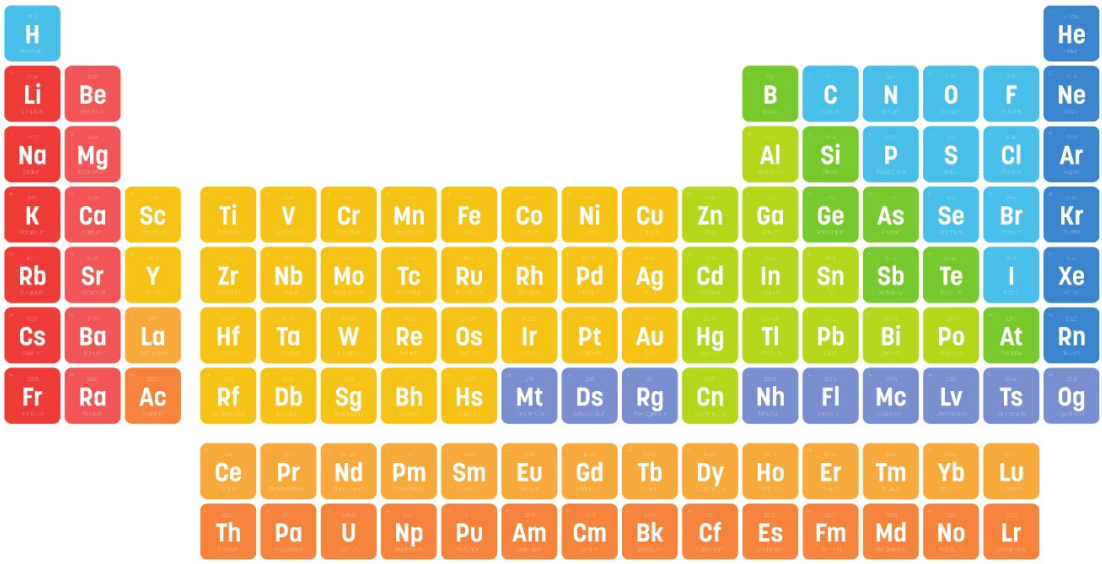
2. <u>Metallic radius:</u> The term is used for metal atoms. A metallic crystal contains metal atoms in close packing. These metal atoms are considered spherical. They are supposed to touch each other in the crystal.

The crystal radius is half the inter nuclear distance between two adjacent atoms of a solid metallic crystal.

e.g.: The inter nuclear distance between two adjacent sodium atoms in a crystal of sodium metal is 3.72 A. So crystal radius of sodium is 3.722 = 1.86 A
For potassium it is 2.31 A.

3. <u>Covalent radius:</u> It is used generally for non – metals. Covalent radius is half the equilibrium distance between the nuclei of two atoms held together by a covalent bond. Covalent radii of two atoms can be added to give inter nuclear distance between them. As the number of covalent bonds between the two atoms increases the inter atomic distance between carbon atoms decreases.

e.g. : Covalent radius of H is 0.37A and for chlorine it is 0.99A. Hence inter nulear distance between H and Cl in HCl is 1.36A.



Periodic Table of Elements

VI. Long answers questions (8 marks)

1. **Discuss the construction of long form of periodic table.**

Ans: 1) The elements are arranged in the long form of the periodic table in the increasing order of atomic numbers.

2) 'Neils Bohr' constructed the long form of the periodic table based on electronic configuration of elements.

The important features of the long form of the periodic table are :

It consists of seven horizontal rows called periods and 18 vertical columns which are classified into 16 groups only.

Periods : Every period starts with an alkali metal and ends with an inert gas. The first period consists of two elements only (H, He) and is called very short period.

Second period consists 8 elements (Li to Ne) and is called first short period. The third period consists (Na to Ar) 8 elements and is called second short period.

Fourth period contains 18 elements (K to Kr) and is called first long period. Fifth period is the second long period with 18 elements (Rb to Xe).

Sixth period is the longest period with 32 elements which starts with Cs and ends with Rn. This period includes 14 lanthanides.

Seventh period is an incomplete period with 20 radioactive elements.

Groups : There are 16 groups in the long form of the periodic table (in transition elements three vertical columns are fused and designated as VIII group). These groups are IA, IIA, IIIB, IVB, VB, VIB, VIIB, VIII, IB, IIB, IIIA, IVA, VA, VIA, VIIA and zero group.

The elements of IA, IIA, IIIA, IVA, VA, VIA, VIIA groups are called representative elements or normal elements.

Elements of IB, IIB, IIIB, IVB, VB, VIB, VIIB and VIII groups have their ultimate and penultimate shell incomplete. These are called transition elements.

IB elements have $(n-1)\,d^{10}\,ns^2$ outermost electronic configuration.

Zero group elements have stable electronic configuration. These elements are called inert gases, noble gases. These elements have been grouped at the extreme right of the periodic table.

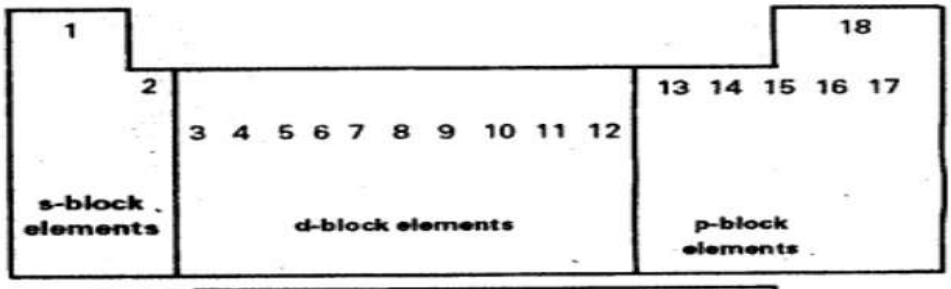
In this long periods have been expanded and short periods are broken to accommodate the transitional elements in the middle of the long period.

*Lanthanides and actinides have been grouped separately and placed at the bottom of the periodic table.

2. **Write an essay on s, p, d and f block elements?**

Ans: According to the electronic configuration of elements, the elements have been classified into four blocks. The basis for this classification is the entry of the differentiating electron into the subshell. They are classified into s, p, d and f blocks.

's' block elements : If the differentiating electron enters into 's' orbital, the elements belongs to 's' block.



s, p and f-block elements in the long form of periodic table

In every group there are two 's' block elements. As 's' orbital can accomodate a maximum of two electrons, 's' block has two groups IA and IIA.

'p' block elements : If the differentiating electron enters into 'p' orbital, the elements belongs to 'p' block.

'p' block contains six elements in each period. They are IIIA to VIIA and zero group elements. The electronic configuration of 'p' block elements varies from ns^2np^1 to ns^2np^6.

'd' block elements : If the differentiating electron enters into (n – 1) d – orbitals the elements belongs to'd' block.

These elements are in between's' and 'p' blocks. These elements are also known as transition elements. In these elements n and (n – 1) shells are incompletely filled. The general electronic configuration of'd' block elements is $(n-1)\,d^{1-10}\,ns^{1-2}$. This block consists of IIIB to VIIB, VIII, IB and IIB groups.

'f' block elements : If the differentiating electron enters into 'f' orbitals of antipenultimate shell (n – 2) of atoms of the elements belongs to 'f block. They are in sixth and seventh periods in the form of two series with 14 elements each. They are known as lanthanides and actinides and are arranged at the bottom of the periodic table.

The general electronic configuration is $(n-2)f^{1-14}\,(n-1)d^{0-1}\,ns^2$.

In these shells the last three shells (ultimate, penultimate and anti penultimate) are incompletely filled

Lanthanides belongs to 4f series. It contains Ce to Lu

Actinides belong to 5f series. It contains Th to Lr.

Advantages of this kind of classification :

As a result of this classification of elements were placed in correct positions in the periodic table. It shows a gradual gradation in physical and chemical properties of elements.

The metallic nature gradually decreases and non – metallic nature gradually increases from 's' block to 'p block. This classification gave a special place for radioactive elements.

3. Relate the electronic configuration of elements and their properties in the classification of elements.

Ans: The chemical properties of all elements depend upon the electronic configuration. Upon the basis of complete and incomplete electron shells and chemical properties, the elements are classified into four types. (Type -1, Type – II, Type – III and Type – IV).

Type – I(Inert gas elements): All the elements with an electronic configuration $ns^2\,np^6$ including He belongs to this type, nth shell of those elements are completely filled. The elements show chemical inertness due to completely filled shells and hence they have

extra stability. Because of their stability, they are chemically inactive.

e.g. : He, Ne, Ar, Kr, Xe and Rn

Type–II (Representative elements) : Except inert gases, the remaining elements of s and p – blocks are called representative elements. All the elements with an electronic configuration ns^1 to $ns^2\ np^5$ excluding inert gases comes under this type. These are atoms in which all except the outermost shells (n^{th}) are incomplete. Elements of this type enter into chemical combination by loosing, gaining or sharing electrons to get stable inert gas configuration. Many of the metals, all non – metals and metalloids come under this type. Chemically these elements are reactive.

Type–III (Transition elements): All the elements with an electronic configuration $(n-1)\ d^{1-9}\ ns^{1or2}$ belongs to this type. Atoms in which the two outermost shells are incomplete. These elements show variable oxidation states, form complex ions and coloured ions.

The electronic configuration of d – block elements is $(n-1)\ d^{1-10}\ ns^{1-2}$.

Small size, high nuclear charge and unpaired'(n-1)d orbitals impart characteristic properties to the transition elements.

Type- IV (Inner transition elements): All the elements with an electronic configuration $(n-2)\ f^{1-14}\ (n-1)\ d^{0,1}\ ns^2$ belongs to this type. Atoms in which three outermost shells are incomplete. Lanthanides and Actinides belong to this type.

4. **What is a periodic property? How the following properties vary in a group and in a period? Explain**

a) Atomic radius

b) Ionisation enthalpy

c) Electro negativity

Ans: Recurrence of similar properties of elements at definite regular intervals with increasing atomic number i.e., according to their electronic configurations is known as periodicity. Any property which is periodic in nature is called periodic property.

a) Atomic radius : The atomic radius decreases from left to right in a period. With an increase in the atomic number in a period the nuclear charge increases. As a result the effective nuclear charge over the outermost electrons increases, due to this the orbitals are pulled closer to the nucleus causing in a decrease in the atomic radius.

The atomic radius increases from top to the bottom in a group because – with an increase in the atomic number the electrons are added to new shells resulting an increase in the number of inner shells. Hence atomic radius increases from top to bottom in a group.

b) IE : In groups and periods of the periodic table the ionization enthalpy values are periodically change depend upon the electronic configuration and size of elements.

In a group of elements ionization energy decreases from top to bottom because atomic radius increases. In a period ionization energy increase from left to right as atomic radius decreases.

c) Electronegativity: Electronegativity increases from left to right in a period since the atomic: radii decreases and nuclear attraction increases.

In a group electronegativity decreases from top to bottom due to an increase in atomic radii and a decrease in nuclear attraction.

5. **What is a periodic property? How the following properties vary in a group and period?**
a) Electron gain enthalpy
b) Metallic and covalent radius
c) Nature of oxides

Recurrence of similar properties of elements at definite regular intervals with increasing atomic number i.e., according to their electronic configurations is known as periodicity. Any property which is periodic in nature is called periodic property.

Ans: **a) Electron gain enthalpy:** Electron gain enthalpy increases in a period from left to right because the size of the atom decreases and the nature of the element changes from metallic to non – metallic nature when we move from left to right in a period.

Electron gain enthalpy decreases from top to bottom in a group because there is an increase in the atomic size. But the second element has greater electron gain enthalpy than the first element.

e.g. : Chlorine has more electron affinity value (- 348 kJ mol^{-1}) than Fluorine (-333 kJ mol^{-1}). It is because fluorine atom is smaller in size than chlorine atom. There is repulsion between the incoming electron and electrons already present in fluorine atom i.e., due to stronger inter electronic repulsions

b) Metallic radius: The term is used for metal atoms. A metallic crystal contains metal atoms in close packing. These metal atoms are considered spherical. They are supposed to touch each other in the crystal. The crystal radius is half the internuclear distance between two adjacent atoms of a solid metallic crystal. The metallic radius increases down a group and decreases across a period.

e.g.: The internuclear distance between two adjacent sodium atoms in a crystal of sodium metal is 3.72 A. So crystal radius of sodium is 3.722 = 1.86 A

For potassium it is 2.31 A.

Covalent radius : It is used generally for non – metals. Covalent radius is half the equilibrium distance between the nuclei of two atoms held together by a covalent bond.

Covalent radii of two atoms can be added to give internuclear distance between them.

As the number of covalent bonds between the two atoms increases the inter atomic distance between carbon atoms decreases. The covalent radius increase on going down in a group & decreases as we move from left to right in a period.

e.g. : Covalent radius of H is 0.37A and for chlorine it is 0.99A. Hence internulear distance between H and Cl in HCl is 1.36A.

c) Nature of oxides of elements : All IA group elements are alkali metals. Their oxides are basic in nature. They dissolve in water to give basic solutions which changes red litmus blue.

e.g. : Na_2O, CaO , MgO etc.

$CaO + H_2O \rightarrow Ca(OH)_2$

$MgO + H_2O \rightarrow Mg(OH)_2$

The basic nature of these oxides increases from top to bottom in the group. In a period basic properties decreases and acidic properties increases.

6. **Define IE_1 and IE_2. Why is IE_2 is always greater then IE_1 for a given atom? Discuss the factors that effect IE of an element.**

Ans: 1) Ionization energy is the amount of energy required to remove the most loosely held electron from isolated a neutral gaseous atom to convert it into gaseous ion. It is also known as first ionization energy because it is the energy
required to remove the first electron from the atom.
It is denoted as I_1, and is expressed in electron volts per atom, kilo calories (or) kilo joules per mole.

$M_{(g)} + I_1 \rightarrow M_{(g)}^{+} + e^{-}$

I_1 is first ionization potential.

2) The energy required to remove an electron from the unipositive ion is called the second ionization energy. It is denoted as I_2.

$M^{+}_{(g)} + I_2 \rightarrow M_{(g)}^{2+} + e^{-}$

3) The second ionization potential is greater than the first ionization potential. On removing an electron from an atom, the unipositive ion formed will have more effective nuclear charge than the number of electrons. As a result the effective nuclear charge increases over the outermost electrons. Hence more energy is required to remove the second electron. This shows that the second ionization potential is greater than the first ionization potential.
For sodium, I_1 is 5.1 eV and I_2 is 47.3 eV.

$I_1 < I_2 < I_3 \ldots\ldots I_n$

Factors affecting ionization potential:

1. **Atomic radius:** As the size of the atom increases the distance between the nucleus and the outermost electrons increases. So the effective nuclear charge on the outermost electrons decreases. In such a case the energy required to remove the electrons also decreases. This shows that with an increase in atomic radius the ionization energy decreases.

$$I.E\alpha \frac{1}{atomicsize}$$

2. Nuclear charge: As the positive charge of the nucleus increases its attraction increases over the electrons. So it becomes more difficult to remove the electrons. This shows that the ionization energy increases as the nuclear charge increases.

$$I.E\alpha NuclearCharge$$

3. Screening effect: or shielding effect: In multielectron atoms, valence electrons are attracted by the nucleus as well as repelled by electrons of inner shells. The electrons present in the inner shells screen the electrons present in the outermost orbit from the nucleus. As the number of electrons in the inner orbits increases, the screening effect increases. This reduces the effective nuclear charge over the outermost electrons. It is called screening or shielding effect. With the increase of screening effect the ionization potential decreases.
Screening efficiency of the orbitals falls off in the order s > p > d > f.

$$\text{Magnitude of screening effect} \propto \frac{1}{\text{Ionization enthalpy}}$$

4.Penetrating power of orbitals:- As Penetrating power increase I.P values is also increases
The order of penetrating power of orbitals is s > p > d > f

$IE\alpha$ Penetrating power

5.Electronic Configuration:

Atoms of elements with half-filled or completely filled electronic configuration are more stable. So IE value also increases.

Example:

Nitrogen **Neon**

7. Explain the following

1) Noble gases

2) Representative elements

3) Transition elements

4) Inner Transition elements

1) Noble gases:

Noble gases, also known as inert or group 18 elements, are a group of chemically unreactive gases, including helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), radon (Rn). They are characterized by having full outer electron shells, leading to their low reactivity and monatomic nature. Generally have an electron configuration of ns^2 np^6 in their outermost shell, except for helium, which has $1s^{2.}$ This full outer shell contributes to their chemical inertness.

2) Representative elements :

Representative elements, also known as main group elements, are located in the s and p blocks of the periodic table, excluding the noble gases (group 18). These elements (groups 1, 2, and 13-17) are characterized by their incomplete outermost electron shells (valence shells) and tend to exhibit a wide range of chemical properties, including both metallic and non-metallic behavior. Their general electron configuration is characterized by $ns^2np^{(1-5)}$.

3.Transition elements : Transition elements, also known as d-block elements, have a general electron configuration of $(n-1)d^{1-10}$ ns^{1-2}, where 'n' represents the outermost electron shell. This means they have partially filled d-orbitals in their ground state or common oxidation states,

Transition elements exhibit a wide range of properties due to their unique electron configuration, particularly they have partially filled (n-1)d orbitals. These elements are known for their metallic character, high melting and boiling points, variable oxidation states, magnetic properties, and the ability to form colored compounds and complex ions

4. Inner transition elements : The general electronic configuration for inner transition elements is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$. This refers to the filling of the f-orbitals, which are located in the antepenultimate shell (n-2)

They include lanthanides (6th period) and actinides (7thperiod). They are also called

inner transition elements.

•Since lanthanum (57La) closely resembles lanthanides, it is also included along with them. Similarly, actinium (89Ac) is included along with actinoids because of its close resemblance with them.

UNIT-4
CHEMICAL BONDING AND MOLECULAR STRUCTURE

I. Multiple choice questions (1 mark)

1 The octet rule is valid for which of the following molecules

1) SF_6 2) PCl_5 3) $BeCl_2$ 4) NH_3

Ans: 4) NH_3

2 The valency shell of calcium contains

1) 2 electrons 2) 4 electrons 3) 6 electrons4) 8 electrons

Ans: 1) 2 electrons

3 Which of the following compound has an electrovalent bond

1) CH_4 2) $Mgcl_2$ 3) $SiCl_4$ 4) BI_3

Ans: 2) $Mgcl_2$

4 Which of the following is ionic?

1) KI 2) CH_4 3) Diamond 4) H_2

Ans: 1)KI

5 The low solubility of $BaSO_4$ in water can be attributed to

1) high lattice energy 2) dissociation energy 3) low lattice energy 4) ionic bond

Ans: 1) high lattice energy

6 The number of bonds and number of lone pair of electrons actually present in O_2 as per Valence bond theory are.

1) 2,2 2) 2,4 3) 2,1 4) 2,3

Ans: 2) 2,4

7 A covalent bond is formed

1) by the transfer of electrons 2) by sharing of electrons
3) by donating electrons 4) all of these

Ans: 2) by sharing of electrons

8 The shape of molecule of the type AX_5 where the central atom has no lone pairs as per VSEPR theory is

1) octahedral 2) square pyramidal.
3) tetrahedral 4) trigonal bipyramid.

Ans: 4) trigonal bipyramid.

9 Water shows abnormal properties due to

1) intra molecular hydrogen bonding 2) covalent bonds
3) inter molecular hydrogen bonding 4) polarity.

Ans: 3) inter molecular hydrogen bonding

10 A central atom in a molecule has two lone pairs of electrons and forms three single bonds. The shape of the molecule is

1) Trigonal pyramidal 2) Planar triangular 3) T-shaped 4) See- saw

Ans: 3) T-shaped

11 What is the shape of AB_4E type of molecule like SF_4

a) Distorted tetrahedron b) A folded square c) sea-saw d) All

Ans: d) All

12 Which of the following molecules has a triple bond?

1) CH_4 2) C_2H_4 3) C_2H_2 4) CO_2

Ans: 3) C_2H_2

13 If the bond enthalpy of O_2,N_2 & H_2 are 498 kJ/mol. 946 kJ/mol and 435.8kJ / mol respectively. Chose the correct order of decreasing bond strength

1) $H_2 > N_2 > O_2$ 2) $N_2 > O_2 > H_2$ 3) $H_2 > O_2 > N_2$ 4) $N_2 > H_2 > O_2$

Ans: 2) $N_2 > O_2 > H_2$

14 Which of the following have zero dipole moment

1) HF 2) H_2O 3) NH_3 4) BF_3

Ans: 4) BF_3

15 Which of the following is correct?

1) PCl_5 has 3 equitorial and 2 axial bonds

2) In PCl_5 bond angles are 120° and 90°

3) Axial bond are longer but weaker than equatorial bonds, which makes PCl_5 molecule more reactive.

4) All the above

Ans: 4) All the above

II. **Fill in the blanks (1 Mark)**

1 **A chemical bond in which the electron cloud is un evenly shared is known as ---------- bond.**

Ans: Polar Covalent bond

2 **Hybridisation produces a set of ____ orbitals.**

Ans: Hybrid

3 **Bond order in N_2 molecule is _____**

Ans: 3

4 **The shape of ammonia molecule is ----------**

Ans: Trigonal Pyramidal

5 **The total number of sigma and pi bonds in C_2H_4 molecule is**

Ans: 5 Sigma and 1 Pi bond

III. One Word answer questions: (1 Mark)

1 **What is the carbon Oxygen bond length in CO_2 molecule.**

Ans: 116 pm or 1.16 A°

2 **How many electrons are shared during the formation of a double bond?**

Ans 4 electrons

3 **Define formal charge?**

Ans Formal charge is a hypothetical charge assigned to an atom in a molecule,

assuming that all electrons in a bond are shared equally, regardless of electronegativity. It helps predict the most likely structure of a molecule when multiple structures are possible.

4 **What is the shape of NH_4^+ ion?**

Ans Tetrahedral

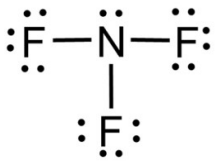
5 **What is the bond angle in SO_2 molecule.**

Ans 119.5^o

IV. VERY SHORT ANSWER (2 MARKS)

1. **Draw the Lewis structures for the NF_3molecule?**

Ans:



2. **BF_3 molecule is trigonal planar, but NF_3 is pyramidal. Why?**

Ans: BF3 is trigonal planar because the boron atom has three bonding pairs of electrons and no lone pairs, leading to trigonal planar shape.NH3 is pyramidal because the nitrogen atom has three bonding pairs and one lone pair, due to repulsion between lone pair and bond pair its shape become pyramidal.

3. **O_2 is paramagnetic while O_2^{2-} is diamagnetic .Why?**

Ans: According to molecular orbital theory two unpaired electrons are present in the antibonding π*2p orbitals. So O_2 molecule paramagnetic.But in O_2^{2-}, one extra electron enters into the $2p_x$ orbital and one more electron enters into the $2p_y$ orbital. Since, all the orbitals have paired electrons. Hence O_2^{2-} ion is diamagnetic.

4. **N-F bond is more polar than N-H bond, but NH_3 is more polar than NF_3 Why?**

Ans: The N-F bond is more polar than the N-H bond. This is primarily due to the higher electronegativity of fluorine compared to hydrogen. The greater electronegativity difference between N and F leads to a more unequal sharing of electrons in the N-F bond, resulting in a larger dipole moment.But, NF_3 is less polar than NH_3 because in NF_3 individual polarity is towards 'F' therefore the net dipole will cancel. But in NH_3, 'N' is more electronegative than 'H' therefore this all add up to get more dipole moment.

5. **Water is a liquid at room temperature, but Hydrogen sulphide is a gas Give**

Ans: **reason?**

In water due to strong inter molecular hydrogen bonding it is liquid at room temperature. While in H_2S there is no hydrogen bonding so it exits as a gas.

6. **Write the bond order and magnetic behaviour of H_2?**

Ans: Bond order of H_2 molecule can be calculated as $\frac{Nb - Na}{2} = \frac{2-0}{2} = \frac{2}{2} = 1$.

Since no unpaired electron is present in hydrogen molecule, it is diamagnetic.

7. **What is Hybridisation?**

Ans: The phenomenon of intermixing of suitable atomic orbitals of an atom resulting in the formation of new set of orbitals of equivalent energies and shape is known as Hybridisation.

8. **State Octet rule?**

Ans: Octet rule: Every atom must possess 8 electrons in its outermost energy level for its stability.

9. **What is meant by bond order?**

Ans: Bond order is defined as one half the difference between the number of electrons present in the bonding and the anti bonding orbitals.

$Bond\ order = \frac{Nb - Na}{2}$.

10. **Give two examples of odd electron molecule?**

Ans: NO, NO_2, ClO_2 etc

V. SHORT ANSWER(4 MARKS)

1. State Fajan's rules and give suitable examples?

Ans: Fajan's rules are useful to predict the nature of the chemical bond in a molecule.

1.As the size of cation increases, the ionic nature of the bond increases.

Ex: Among alkali metal ions the ionic nature of the bond is in the order

$Li^+ < Na^+ < K^+ < Rb^+$

2.Smaller the size of the anion, greater is its ionic nature.

Ex: Among CaF_2 & CaI_2, CaF_2 is more ionic, as the size of F^- ion is smaller than that of I^- ion.

3.Low charge on cation (or) anion (or) both the ions, favour the formation of ionic bond.

Ex: NaCl is more ionic than $AlCl_3$ as the charge on Na (Na^+) is less than that of Al (Al^{+3}).

4.Cations with inert gas configuration form ionic compounds, while cations with pseudo inert gas configuration favour covalent bond formation.

Ex: NaCl is ionic, since Na^+(2, 8) has inert gas configuration.

CuCl is more covalent, since Cu^+ (2, 8, 18) has pseudo inert gas configuration.

2. Define dipole moment. Write its applications?

Ans: Dipole moment (μ): The product of the magnitude of the charge (Q) on either of the poles and the distance(r) between the centres of positive and negative charges is called dipole moment.

Mathematically, $\mu = Q \times r$

Where μ = Dipole moment; Q= charge;

r = distance between the charges.

Units: Debye units

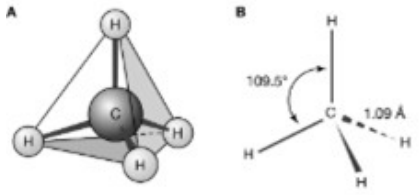
<u>Applications</u>:

1. Dipole moment predicts the polarity of molecules.
   a) Molecules with dipole moment greater than zero are polar.
   b) Molecules with dipole moment is equal to zero are non polar.
2. It predicts the shape of the molecules.
   It predicts the % ionic character of covalent bonds.
   % ionic character of a covalent bond = $\frac{\mu_{experimental}}{\mu_{calculated}} \times 100$.

3. Explain the structure of CH_4 molecule?

Ans. Structure of CH_4 (Methane) :

1. The central atom of CH_4 is Carbon.
2. Atomic number of C is 6.
   Its ground state E.C = $1s^2 2s^2 2p^2$
   Its Excited state E.C = $1s^2 2s^1 2p^1_x 2p^1_y 2p^1_z$
3. In its excited state, the central Carbon atom undergoes sp^3 hybridisation
4. One 2s orbital and three 2p orbitals of Carbon, form 4 sp^3 hybrid orbitals.
5. Now, these 4 hybrid orbitals overlap in a head-on position with s- orbital of four H atoms and they form 4 σ bonds.
6. The structure of CH_4 is Tetrahedral. The bond angle is 109°28′.



Since there are no lone pairs, there is no distortion in the shape of the molecule.

4. What are σ -and π bonds? Specify the differences between them.

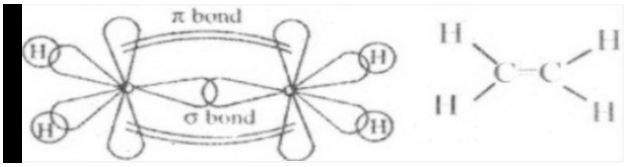
Ans:

σ – bond	π – bond
1) σ-bond is a covalent bond formed by the axial overlapping of orbitals.	1) π -bond is a covalent bond formed by the side wise overlapping of orbitals.
2) σ -bond is a strong bond.	2) π -bond is a weak bond.
3) It allows free rotation of atoms.	3) It restricts the free rotation of atoms.
4) σ - bonds determine the shape of the molecules.	4) The shape of the molecules is not influenced by π bonds.
5) It forms independently.	5) π bond always follows σ-bond.
6) There can be only one σ- bond between two atoms.	6) There can be one or two π – bonds between two atoms.

5. Explain the structure of Ethylene?

Ans. C_2H_4 (Ethylene):

1. In C_2H_4, the two carbon atom undergoes sp^2 hybridisation.
2. They both form six sp^2hybrid orbitals.
3. At first, one sp^2 hybrid orbital of one C atom overlaps axially with sp^2 orbital of other C atom and forms one C-C σ bond.
4. The remaining four sp^2 hybrid orbitals overlap axially with s- orbitals of four ‘H’ atoms and they form four σ bonds.
5. Now, each C atom is left with one pure p-orbital. They overlap each other laterally and form one π bond.
6. Thus,a double bond(one σ and one π bond) is formed in between the two C atoms.



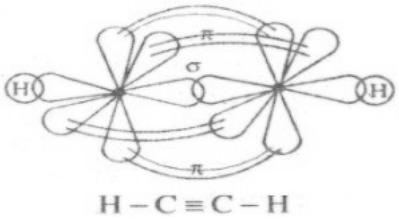
The shape of the molecule trigonal planer with bond angle 120°

6. **Explain the structure of Acetylene**?

Ans. C_2H_2 (Acetylene)

1. In C_2H_2, the two carbon atoms undergo sp hybridisation.
2. They both form 4 sp hybrid orbitals.
3. At first, one sp hybrid orbital of one C atom overlaps axially with sp orbital of other C atom and forms one C-C σ bond.
4. The remaining 2 sp hybrid orbitals overlap axially with s- orbitals of two 'H' atoms and they form two σ bonds.
5. Now, each C atom is left with two pure p-orbitals. They overlap each other laterally and form two π bonds.

5. Thus, a triple bond (one σ and two π bonds) is formed between the two C atoms.

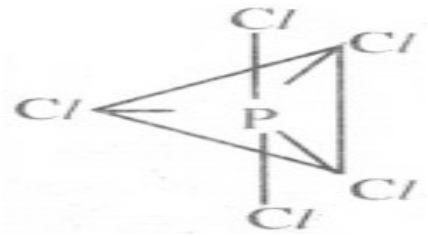


The shape of the molecule linear with bond angle 180°

7. Explain the hybridisation involved in PCl_5 molecule?

Ans.

1. The central atom of PCl_5 is Phosphorus
2. Atomic number of P is 15.
   Its ground state E.C= $[Ne]3s^2 3p^3$
   Its Excited state E.C= $[Ne]\ 3s^1 3p^1_x\ 3p^1_y\ 3p^1_z,\ 3d^1$
3. In its excited state the central P atom undergoes sp3d hybridisation.
4. It forms five sp^3d hybrid orbitals.
5. The five 'sp^3d' hybrid orbitals of P, overlap axially with $3p_z$ orbital of five Cl atoms and they form five strong sp^3d a bonds.
6. The shape of PCl_5 molecule is Trigonal bipyramid with bond angles 120°, 90°,180°.

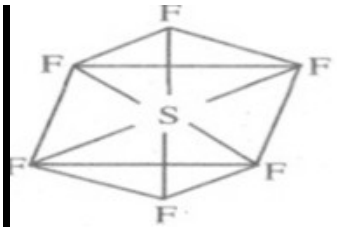


8. Explain the hybridisation involved in SF_6 molecule?

Ans.

1. The central atom of SF_6 is Sulphur.
2. Atomic number of S is 16.
   Its ground state E.C= $[Ne]3s^2 3p^4$
   Its Excited state E.C
   = $[Ne]\ 3s^1 3p^1_x\ 3p^1_y\ 3p^1_z\ 3d^1_{(x^2-y^2)}\ 3d^1_{z^2}$
3. In its excited state the central S atom undergoes sp^3d^2 hybridisation.
4. It forms six sp^3d^2 hybrid orbitals.
5. The 6 sp^3d^2 hybrid orbitals of S overlap axially with p orbital of six F atoms and they form six sp3d2 sigma (a) bonds.

The shape of SF_6 molecule is Octahedral with bond angles 90^o and 180°.



9. What is Hydrogen bond? Explain the different types of Hydrogen bonds with examples?

Ans. The weak electrostatic force of attraction between Hydrogen atom of one molecule and most electronegative atom of another molecule (or) same molecule is called Hydrogen bond.

Conditions for the formation of Hydrogen bond :

1. The size of electronegative atom should be small.
2. The electronegativity of the atom to which Hydrogen is attached should be high.

Strength of Hydrogen bond:

The strength of hydrogen bond is between 5-10 K Cal/mol. It is, thus, weaker than a covalent bond and stronger than Vander Waals forces of attraction.

Types of Hydrogen bonds :

1. Inter molecular Hydrogen bond
2. Intra molecular Hydrogen bond.

1) Inter molecular Hydrogen bond:

Hydrogen bond formed between two different molecules is called inter molecular hydrogen bond.

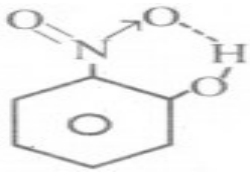
Ex : The bonds present in H_2O, HF, NH_3

H–F····H–F····H–F····H–F····H–F

2) Intra molecular hydrogen bond :

A hydrogen bond formed within the same molecule is called intra molecular Hydrogen bond.

Ex : The bonds present in Orthonitrophenol, Ortho hydroxy benzaldehyde.



10. Explain the formation of ionic bond with a suitable example?

Ans. An ionic bond is formed by the complete transfer of electrons from the outer most shell of one atom (with low I.P) to outer most shell of another atom (with high E.A). In this process, each atom attains the nearest noble gas configuration or octet configuration.

The atom which looses electrons becomes cation and the atom which gains electrons becomes anion.

The attractive force established between those oppositely charged ions is called ionic bond.

Explanation using the formation ionic bond in $NaCl$.

The electronic configuration of Na is $1s^2 2s^2 2p^6 3s^1$

The electronic configuration of Cl is $1s^2 2s^2 2p^6 3s^2 3p^5$

Atom is electropositive and has low I.P, and Cl is electronegative and has high E.A.

So, Na atom looses one electron and transfers it to Cl atom. Then Na atom becomes Na+ cation and Cl atom becomes Cl^- anion.

Now the electronic configuration of the cation Na* becomes $1s^2 2s^2 2p^6$. = Ne configuration.

The electronic configuration of the anion Cl^- becomes $1s^2 2s^2 2p^6 3s^2 3p^6$ = Ar configuration. Hence, both the ions get the octet configuration.

Thus $Na^+$and Cl^- are held together by strong electrostatic forces of attraction called ionic bond.

11. Explain Valency Bond Theory with suitable examples?

Ans. Valence Bond Theory (VBT):

This theory explains the shapes of covalent molecules as well as the directions of the bonds in them.

Postulates of VBT :

1. A covalent bond is formed by the overlapping of half filled atomic orbital of one atom with half filled atomic orbital of another atom.
2. The electrons involved in overlapping must have opposite spin.
3. Except the bond pair of electrons, the remaining electrons do not loose their identity.. Such electrons are called non-bonding electrons or lone-pair electrons.
4. Greater the extent of overlap, greater is the strength of covalent bond.
5. The direction of covalent bond lies in the direction of maximum overlapping side.
6. All atomic orbitals, except s-orbital, are directional. So the bonds formed due to their overlap are also directional. This determines the shape of the molecule.
7. A covalent bond formed by the axial overlap of atomic orbitals is called a sigma bond. Thus head-on overlappings of s-s, s-p , p – p orbitals leads to the formation of σ bonds.
8. A covalent bond formed by the lateral or sidewise overlap of atomic orbitals is called a π bond.

A sigma bond is always stronger than a π bond.

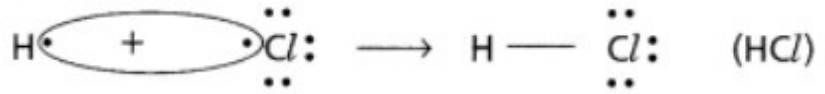
12. Explain the polar covalent bond with suitable examples?

Ans. The covalent bond which is formed by the mutual sharing of electron pairs between two dissimilar atoms is called polar covalent bond.

Dissimilar atoms means two atoms having different electronegativity values (or) atoms of different elements.

Eg : HF, HCl, H_2O, CO_2 etc.,

Formation of HCl :



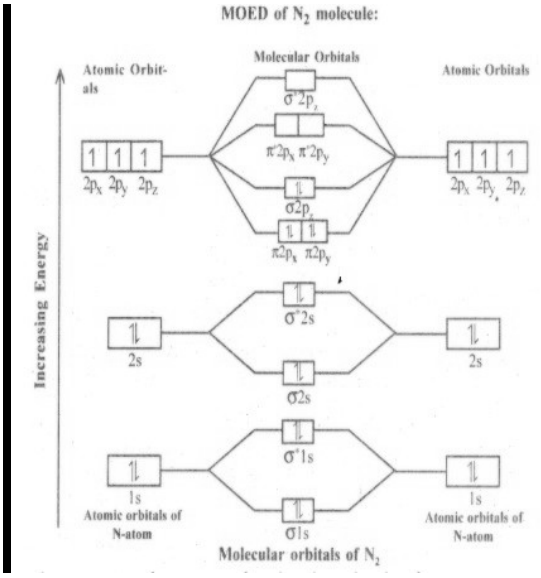
In the above example H and Cl are two atoms of different elements having different electro negativities. These two atoms (H, Cl) mutually share the electron pairs and form the polar covalent bond.

VI. LONG ANSWER QUESTIONS (8 MARKS)

1. Draw the MOED of N_2 molecule. Calculate the bond order and write its magnetic behaviour.

Ans : Electronic configuration of N (7) = $1s^2\ 2s^2\ 2\boldsymbol{P_x^1}\ 2p^1{}_y 2p^1{}_z$.

N atom has 7 electrons. So the molecular orbital of N_2 contains 14 electrons.



Electronic Configuration of molecular orbitals of N_2 :

$(\sigma\ 1s^2)\ (\sigma^*\ 1s^2)\ (\sigma\ 2s^2)\ (\sigma^*\ 2s^2)\ (\pi 2p^2{}_x = \pi 2p^2{}_y)\ (\sigma 2p^2{}_z)$

Here, the number of bonding electrons (N_b) = 10

the number of anti-bonding electrons (N_a) = 4

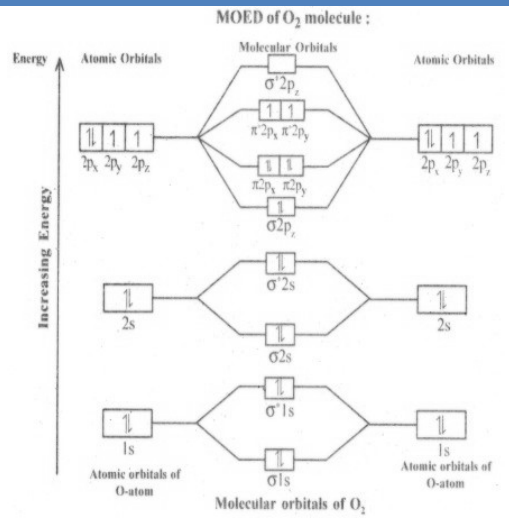
Bond order $= \frac{N_b - N_a}{2} = \frac{10-4}{2} = \frac{6}{2} = 3.$

N_2 is diamagnetic due to the absence of unpaired electrons.

2. **Draw the MOED of O_2 molecule. Calculate the bond order and write its magnetic behaviour.**

Ans. Electronic Configuration of O (8) = $1s^2\ 2s^2\ 2p^2{}_x 2p^1{}_y 2p^1{}_z$.

Since the O atom has 8 electrons, the molecular orbital of O_2 contains 16 electrons.



Electronic Configuration of molecular orbitals of O_2 :

$\sigma(1s^2)\ \sigma^*(1s^2)\ \sigma(2s^2)\ \sigma^*(2s^2)\ \sigma(2p^2_z)\ (\pi 2p^2_x = \pi 2p^2_y)\ (\pi^* 2p^1_x - \pi^* 2p^1_y)$

Here, the number of bonding electrons (N_b) = 10

the number of anti-bonding electrons (N_a) = 6

Bond order = $\frac{N_b - N_a}{2} = \frac{10-6}{2} = \frac{4}{2} = 2$

O_2 is Paramagnetic due to the presence of two unpaired electrons.

3. **Explain the structure of Ethane and BCl_3.**

Ans. The central atom of C_2H_6 is Carbon.

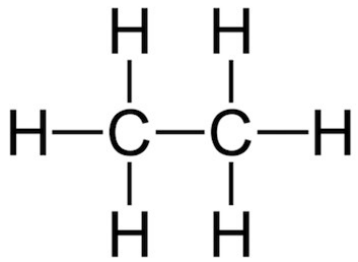
1. Atomic number of C is 6.

   Its ground state E.C = $1s^2 2s^2 2p^2$

   Its Excited state E.C = $1s^2 2s^1 2p^1_x 2p^1_y 2p^1_z$

2. In its excited state, the central Carbon atom undergoes sp^3 hybridisation at first one SP^3 hybrid orbital of one carbon atom overlaps with SP^3hybrid orbital of other carbon forms one σ (C – C) bond. The remaining six SP^3 hybrid orbitals overlaps with s- orbitals of six hydrogen atoms form six σ (C – H) bonds.

The structure of C_2H_6 is Tetrahedral. The bond angle is 109°28′.

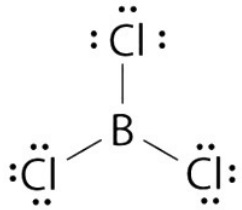


Structure of BCl_3 (Boron trichioride) molecule:

1. The electronic configuration of 'B' in the ground state is $1S^2 2S^2 2P^1_x 2P^0_y 2P^0_z$

2. On excitation the configuration is $1S^2 2S^1 2P_x^1 2P_y^1 2P_z^0$ now there are three half filled orbitals are available for hybridisation.
3. Now sp^2 hybridisation takes place at boron atom giving three sp^2 hybrid orbitals.

Each of them with one unpaired electron forms 'σ' bond with one chlorine atom. The overlapping is σsp^2–p (Cl atom has the unpaired electron in 2Pz orbital). In boron trichloride there are three 'σ' bonds.



The shape of the molecule is trigonal planar with bond angle 120^o

4. Write the postulates of VSEPR theory and how it is helpful in predicting the shapes of $NH_3$and H_2O molecules?

Ans. VSEPR theory was proposed by Sidgwick and Powell and later extended by Gillespie and Nyholm. It was developed by Ronald and Nyholm.

This theory explains the shapes of simple molecules having electron pairs bonded or non-bonded. The repulsions among the electron pairs present in the valence shell of the central atom decide the shape of the molecules.

<u>According to this theory :</u>

a) The shape of the molecule is determined by repulsions between all of the electron pairs present in the valency shell of central atom.

b) The electron pairs orient in space so as to have minimum repulsions among them.

c) The magnitude of repulsions between bonding pairs of electrons depends on the electronegativity difference between the central atom and the other atoms.

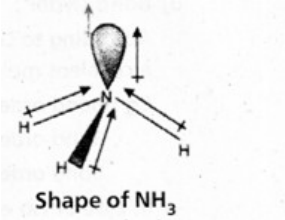
d) The order of repulsions between various electron pairs is lone pair – lone pair > lone pair – bond pair > bond pair – bond pair.

e) The repulsive forces between different bonds is of the order triple bond > double bond > single bond.

f) The shapes of molecules can be predicted as.

Total no.of valence shell electron pairs	No. of bond pairs	No. of lone pairs	Shape of the molecule	Examples
2	2	0	Linear	$BeCl_2$, $HgCl_2$, CO_2
3	3 2	0 1	Trigonal planar Angular	BCl_3 $SnCl_2$
4	4 3 2	0 1 2	Tetrahedral Pyramidal Angular	CH_4 NH_3 H_2O
5	5	0	Trigonal bipyramidal	PCl_5
6	6	0	Octahedral	SF_6

Shape of ammonia molecule: In NH_3 molecule the central nitrogen atom shares its '3' unpaired electrons with three hydrogen atoms to form 3σ bonds. Hence NH_3 molecule contains one lone pair, three bond pairs.

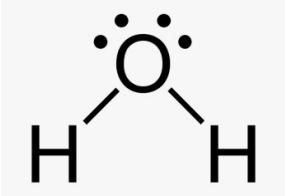


Shape of NH_3

a) Because of the repulsion between the lone pair and the bond pairs the angle reduces to 107°.

b) According to VSEPR theory the geometry of the molecule is pyramidal with bond angle 107°.

Shape of water molecule: In H_2O molecule the central oxygen atom shares its '2' unpaired electrons with two hydrogen atoms to form 2σ bonds. Hence H_2O molecule contains two lone pairs, two bond pairs.



a) Because of the repulsion between the lone pairs and the bond pairs the angle reduces to 104.5°.

b) According to VSEPR theory the geometry of the molecule is angular with bond angle 104.5°.

UNIT-5
THERMODYNAMICS

I MULTIPLE CHOICE QUESTIONS (1 mark)

1 **According to the third law of thermodynamics which one of the following quantities for a perfectly crystalline solid is zero at absolute zero (-273.15^{0}C)?**

1) Gibbs Energy 2) Entropy 3) Enthalpy 4) Internal energy

Ans: 2) Entropy

2 **The heat of combustion of carbon is -393.5kJ/mol. The enthalpy changes in the formation of 35.2g of CO_2 from carbon and oxygen gas is**

1) - 315 kJ 2) + 315 kJ 3) - 630 kJ 4) -3.15 kJ

Ans: 1) - 315 kJ

Solution:

Formation of CO_2 from carbon and dioxygen gas can be represented as

$C(s)+O_2(g) \rightarrow CO_2(g)$ $\Delta_f H=-393.5 kJmol^{-1}$

Heat released on formation of 44 g (1 mole of CO_2) of CO_2 = $-393.5 kJmol^{-1}$

Heat released on formation of 35.2 gm of $CO_2 = \frac{-393.5 \times 35.2}{44}$ = -315 kJ

3 **For the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, ΔH =?**

1)ΔU +2RT 2) ΔU - 2RT 3)Δ H=RT 4) ΔU – RT

Ans: 2) ΔU - 2RT

Solution: $\Delta H = \Delta U + \Delta n_g RT$

Δn =2-4= -2

$\Delta H = \Delta U$ - 2RT

4 **Which amongst the following options is the correct relation between change in enthalpy and change in internal energy?**

1) $\Delta H=\Delta U + \Delta n_g RT$ 2) $\Delta H- \Delta U = - \Delta nRT$ 3) $\Delta H+ \Delta U = \Delta nR$ 4) $\Delta H=\Delta U - \Delta n_g RT$

Ans:1) $\Delta H=\Delta U + \Delta n_g RT$

5 **A thermodynamic state function is a quantity**

1) used to determine heat changes
2) whose value is independent of path
3) used to determine pressure volume work
4) whose value depends on temperature only.

Ans: 2) Whose value is independent of path

6 **For the process to occur under adiabatic conditions, the correct condition is:**

1) $\Delta T = 0$ 2) $\Delta p = 0$ 3) q =0 4) w = 0

Ans: 3) q = 0

7 **The enthalpies of all elements in their standard states are**

1) Unity 2) Zero 3) < 0 4) Different for every element

Ans :2) Zero

8 **The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, –890.3 kJ/ mol, –393.5 kJ mol^{-1} and –285.8 kJ mol^{-1} respectively. Enthalpy of formation of CH_4 (g) will be**

1) –74.8kJmol^{-1} 2) 52.27kJ mol^{-1} 3)+74.8kJmol^{-1} 4) -52.26 kJ mol^{-1}

Ans: 1) -74.8 kJ mol^{-1}

Solution:

Given condition:

$(1)\,CH_4(s)+2O_2(g)\rightarrow CO_2(g)+2H_2O(g) \qquad \Delta H=-890.3\ kJ\ mol^{-1}$

$(2)\,C(s)+O_2(g)\rightarrow CO_2(g) \qquad \Delta H=-393.5\ kJ\ mol^{-1}$

$(3)\,2H_2(g)+O_2(g)\rightarrow 2H_2O(g) \qquad \Delta H=-285.8\ kJ\ mol^{-1}$

For the above reactions the enthalpy of formation of $CH_4(g)$ is as follows

$C(s)+2H_2(g)\rightarrow CH_{4(g)} \quad \Delta H=?$

$\Delta_f H_{CH_4}=\Delta_c H_C+2\Delta_C H_{H_2}-\Delta_C H_{CO_2}$

$=-393.5+2(-285.8)-(-890.3)$

$=-74.8kJ\ mol^{-1}$

9 **A reaction, A + B → C + D + q, is found to have a positive entropy change. The reaction will be**

1) possible at high temperature
2) possible only at low temperature
3) not possible at any temperature
4) possible at any temperature

Ans: 4) possible at any temperature

10 **Which of the following are not state functions?**

1) work and entropy 2) heat and work 3) entropy and internal energy 4) heat and entropy

Ans: 2) heat and work

11 **The Gibbs energy change (ΔG) at constant temperature is equal to**

1) ΔH –TS 2) ΔH +TS 3) ΔH +TΔS 4) ΔH -TΔS

Ans: 4) ΔG= ΔH -TΔS

12 **For the reaction, 2Cl(g) → Cl_2(g), the correct option is**

1) Δr H > 0 and Δr S< 0 2) Δr H < 0 and Δr S> 0
3) Δr H < 0 and Δr S< 0 4) Δr H > 0 and Δr S>0

Ans: 3) Δr H < 0 and Δr S< 0

13 **Which of the following is not an extensive property.?**

1)Mass 2) Volume 3) Temperature 4) Enthalpy

Ans:3) Temperature

14 **The correct thermodynamic conditions for the spontaneous reaction at all temperatures is**

1) $\Delta_rH>0$ and $\Delta_rS<0$ 2) $\Delta_rH<0$ and $\Delta_rS>0$
3) $\Delta_rH<0$ and $\Delta_rS<0$ 4) $\Delta_rH>0$ and $\Delta_rS>0$

Ans: 2) $\Delta_rH<0$ and $\Delta_rS>0$

15 **If a process is carried out at constant volume (ΔV = 0), the correct expression is**

1) $\Delta U = q - P_{ex}\Delta V$ 2) $\Delta U = q$ 3) $\Delta U = q + P_{ex}\Delta V$ 4) $\Delta U = w$

Ans: 2) $\Delta U = q$

II FILL IN THE BLANKS (1 mark)

1 **$q = w = -P_{ext}(v_f - v_i)$ is for irreversible _____change.**
Ans : Isothermal

2 **$q = -w = nRT \ln (v_f/v_i)$ is for isothermal _____change.**
Ans: Reversible

3 **For an isolated system, ΔU = 0, the value of ΔS will be _____**
Ans: ≥ 0

4 **In _____ system there is no exchange of matter and energy between the system and surroundings.**
Ans: Isolated

5 **For chemical reactions, _____is used to measure the value of heatat constant volume.**
Ans: Bomb calorimeter

III ONE WORD ANSWER QUESTIONS (1 mark)

1. **Work is done by the system and 'q' amount of heat is supplied to the system. What type of system would it be ?**
Ans : Closed system

2 **The system loses 'q' amount of heat though no work is done on the system. What type of wall does the system have ?**
Ans: Thermally conducting wall

3 **What is the workdone in the free expansion of an ideal gas in reversible and irreversible processes ?**
Ans: No work done

4 **In isothermal reversible change of an ideal gas, what is the value of q ?**
Ans:

$$q = 2.303nRT\ log(\frac{V_f}{V_i})$$

5 **For an adiabatic change in an ideal gas what is the relationship between its ΔU and W (adiabatic) ?**
Ans : ΔU = W

IV VERY SHORT ANSWER QUESTIONS (2 marks)

1 **Define a system.**
Ans: System: A small part of the universe chosen for thermodynamic study is called system.

2 **State the first law of the thermodynamics.**

Ans:

First law of thermo dynamics:

The law of conservation of energy is known as the first law of thermodynamics.

1. "Energy can neither be created nor destroyed, although it can be transformed from one form to another".
2. "The energy of an isolated system is constant".

3 **State the second law of thermodynamics.**

Ans:

1. "All spontaneous processes are thermodynamically irreversible and entropy of the system increases in all spontaneous processes."
2. "For any spontaneous process taking place in an isolated system, the change in entropy (ΔS) is positive."
3. "It is impossible for a self acting machine unaided by any external agency to convert heat from a body at low temperature to a body at higher temperature".

4 **State the third law of thermodynamics.**

Ans: "The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero . (-273° C)".

$$\lim_{T \to 0} \Delta S = 0$$

5 **What are intensive and extensive properties?**

Ans:

Intensive properties: The properties which do not depend on the quantity of matter present in the system are called intensive properties.

Eg: density, pressure, temperature, surface tension, viscosity, specific heat, boiling point, vapour pressure etc.

Extensive properties: The properties whose value depends on the quantity of matter present in the system are called extensive properties.

Eg: mass, volume, heat capacity, internal energy, entropy, Gibbs free energy, Enthalpy etc.

6 **Define the state function. Give two examples.**

Ans:

State Function: Properties of the systems which depends on the initial and the final states of the system but are independent of the path are called state functions.

Eg.: Energy, Volume, Enthalpy, Gibbs Energy.

7 **The equilibrium constant for a reaction is 10. What will be value of ΔG°?**

$R = 8.314 JK^{-1} mol^{-1}$, $T = 300K$.

Ans: Formula $\Delta G° = -2.303\ RT \log k$

$\Delta G° = -2.303 \times 8.314 \times 300 \times \log 10$

$= -5744$ J/mole

$\Delta G° = -5.744$ KJ/mole

ΔG = Change in Gibbs free energy

K = Equilibrium constant

8 **Two litres of an ideal gas at a pressure of 10 atm expands isothermally into a vacuum until its total volume is 20 litres. How much heat is absorbed and how much work is done in the expansion.**

Ans:

Heat absorbed = 0

'P' of gas = 10 atm

$P_{Exp} = 0$

$V_1 = 2$ lit

$V_2 = 20$ lit

Because the given process is isothermal

$\therefore \Delta U = 0$

$q + w = 0$

$q = -w$

$q = p_{ex} (V_2 - V_1)$

$= P_{ex}(20 - 2) = 0$

$= 0\ (18) = 0$

q = 0 and work done also zero

$\therefore w = 0$

9 **Calculate the entropy change in surroundings when 1.00 mole of $H_2O_{(l)}$ is formed under standard conditions $\Delta_f H° = -286k$ J mol^{-1}.**

Ans: $\Delta S = +286k$ J mol^{-1}, T=298K

Formula $\Delta S = \frac{-\Delta H_f^{\Theta}}{T}$

$= \frac{286}{298} = 0.95973$ k J mol^{-1}.

$\Delta S = 959.73$ Jk^{-1}

10 **Given N_2 (g) + $3H_2$ (g) → $2NH_3$ (g) ; $\Delta_r H^0 = -92.4$ kJ**

What is the standard enthalpy of the formation of NH_3 gas?

Ans: $\Delta_r H = -46.2$ kJ

Solution :

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

2 moles of $NH_3 \rightarrow -92.4$kJ

For 1 mole of $NH_3 \rightarrow -\frac{92.4}{2} = -46.2$

$\Delta H°_{(NH3)} = -46.2$ KJ .

V SHORT ANSWER QUESTIONS (4 marks)

1 What are open, closed and Isolated systems? Give one example for each.

Types of systems : The systems are classified into three types.

They are :

a) **Open system:** A system which can exchange matter as well as energy with the surroundings is called an open system.

Ex: Evaporation of water from a open beaker.

b) **Closed system**: A system which may exchange energy but not matter with surroundings is called a closed system.

Ex: boiling of water in a closed metallic vessel.

c) **Isolated system:** A system which can neither exchange matter nor energy with the surroundings is called an isolated system.

Ex: Hot coffee in a thermo flask.

2 State and explain the Hess's law of constant Heat summation.

Hess's law states that "The total enthalpy change for a reaction is same whether the reaction is carried out in one step (or) in several steps.

Ex: Consider the formation of CO_2. It can be prepared in two ways.

1) Direct method: By heating carbon in excess of O_2

$$C(s) + O_2(g) \rightarrow CO_2(g);\ \Delta H = -393.5\ kJ$$

2) Indirect method :

Carbon can be converted into CO_2 in the following two steps.

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g); \qquad \Delta H_1 = -110.5\ kJ$$

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g);\ \Delta H_2 = -283.0\ kJ$$

Total $\Delta H = -393.5$ kJ ($\Delta H_1 + \Delta H_2$)

The two ΔH values are same.

3 Define heat capacity. What are C_p and C_v ? Show that $C_p - C_v = R$.

Ans:

Heat Capacity: The amount of heat required to raise its temperature through one degree Celsius(or one kelvin).

$$C = \frac{q}{dt}$$

C = heat capacity; q = Heat absorbed, dT = rise in temperature

From First law of thermodynamics

$$q = dU + pdV$$

There are two different types of heat capacities.

i) Heat capacity at constant volume (C_v)

ii) Heat capacity at constant pressure (C_p).

C_p :- At constant pressure the heat capacity 'C' is denoted by C_p.

Cv :- At constant volume the heat capacity 'C' is denoted by C_v.

We can write equation for heat 'q'.

At constant pressure $q_p = C_p \Delta T = \Delta H$ ---- (1)

At constant volume $q_v = C_v \Delta T = \Delta U$ ---- (2)

The difference between C_p and C_v can be derived for a mole of an ideal gas ideal gas

$\Delta H = \Delta U + \Delta(PV)$

$\Delta H = \Delta U + \Delta(RT)$

$\Delta H = \Delta U + R\,\Delta T$

On putting the values of ΔH and ΔU we have

$C_p \Delta T = C_v \Delta T + R\Delta T$

$C_p = C_v + R$

$C_p - C_v = R$

4 What is entropy? Explain with examples.

Ans:

Entropy (S): Entropy is taken as a measure of disorder of molecules (or) randomness of the system. Greater the disorder of molecules in a system, the higher is the entropy. Entropy is a state function. It depends on the temperature, pressure of the state.

Entropy change, $\Delta S = \frac{q_{rev}}{T}$

[q_{rev} = heat absorbed by the system isothermally and reversibly at T]

For a spontaneous process in an isolated system the entropy change is positive.

(ΔS = positive)

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$

Ex : Solid (low entropy) $\xrightarrow{heat}$ liquid (moderate) $\xrightarrow{heat}$ vapour (high entropy)

5 Show that $\Delta H = \Delta U + \Delta n_{(g)} RT$

Ans:

The energy change taking place at constant pressure and at a constant temperature is called enthalpy change (ΔH).

Mathematically, $\Delta H = \Delta U + P.\,\Delta V$.

When ΔU = Internal energy change.

Enthalpy is state function. Thus, the magnitude of enthalpy change depends only upon the enthalpies in the initial and the final states.

$\Delta H = [H_{Products} - H_{reactants}]$

For gaseous reaction, $\Delta H = \Delta U + \Delta nRT$

Consider $PV_1 = n_1 RT$

$PV_2 = n_2 RT$

$PV_2 - PV_1 = n_2 RT - n_1 RT$

$P(V_2 - V_1) = (n_2 - n_1 1)RT$

$P \times \Delta V = \Delta n_g RT$

[We know that $\Delta H = \Delta U + P\Delta V$]

$\Delta H = \Delta U + \Delta n_g RT$

6 What is enthalpy of a reaction ? Explain the standard enthalpy of a reaction.

Ans:

Enthalpy (H) : "Enthalpy is the amount of heat exchanged by a system with its surroundings at constant pressure and temperature".

The energy change taking place at constant pressure and at a constant temperature is called enthalpy change (ΔH).

Mathematically, $\Delta H = \Delta U + P.\Delta V$.

When ΔU = Internal energy change.

For gaseous reactions,

$\Delta H = \Delta U + \Delta nRT$

Δn_g = the number of moles of gaseous products minus the number of moles of gaseous reactants.

standard enthalpy of a reaction.

The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.

The standard state of a substance at a specified temperature is its pure form at 1 bar.

Eg: The standard state of liquid ethanol at 298 k is pure liquid ethanol at 1 bar.

7 Define and explain the standard enthalpy of formation ($\Delta_f H^\theta$).

Ans:

The heat change involved in the reaction of formation of one mole of a compound is called enthalpy of formation.

If all the substances are in the standard states the enthalpy of formation is called standard enthalpy of formation.

Example:

$C(s) + O_2(g) \rightarrow CO_2(g)\ \Delta_f H^\theta = -393.5 kJ$

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l) \Delta_f H^\theta = -285.8 kJ mol^{-1}$

$C(graphite) + 2H_2(g) \rightarrow CH_4(g), \Delta_f H^\theta = -74.8 kJ\ mol^{-1}$

8 Define and explain the enthalpy of combustion ($\Delta_c H^\theta$).

Ans:

Standard enthalpy of combustion is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the reactants and products being in their standard states at the specified temperature.

Cooking gas in cylinders contains mostly butane ($C_4 H_{10}$). During complete combustion of one mole of butane, 2658 kJ of heat is released.

$C_4 H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(1)\ ;\ \Delta_c H^\theta = -2658.0\ kJ\ mol^{-1}$

$C_6H_{12}O_6(g) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l);\ \Delta_c H^\theta = -2802.0\ kJ\ mol^{-1}$

9 In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?

Ans:

q = 701 J

w = -394 J

$\Delta U = q + w$

$\Delta U = 701 - 394$

$= 307$ J

Ans:q =+701 J; w=-394J;

ΔU =307J

10 Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminum from 35°C to 55°C. Molar heat capacity of Al is 24 J mol^{-1} K^{-1}.

Ans:

Given molar heat capacity of Al = 24J mol^{-1} K^{-1}.

$= \frac{24}{27}$J/gm. k

The heat necessary to raise the temp, of 60 g. of Al from 35°C to 55°C

$= 60 \times \frac{24}{27} \times 55 - 35$

$= 60 \times \frac{24}{27} \times 20 = 1.067$kJ

Ans: 1.067kJ

VI LONG ANSWER QUESTIONS

1 **Explain the experiment to determine the internal energy change of a chemical reaction.**

Ans:

Internal energy (U): "The total energy stored in the substance at constant temperature and pressure is called its internal energy (U)".

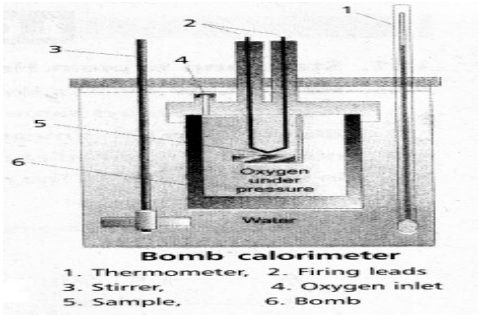
It is state function and is an extensive property.

Internal energy change (ΔU) is considered as the difference the internal energies of products and reactants.

$\Delta U = (U_p - U_R)$

In any path taken (Q – W) is equal to ΔU.

Where Q = heat and W = work.

- The technique of measuring heats of reactions is called calorimetres. The apparatus used is calorimeter.
- Calorimeter is a vessel properly insulated and contains water as the calorimetric liquids
- A combustible substance is burnt in oxygen.
- Heat evolved during the reaction is measured from the rise in temperature.
- Here there is no worke done as $\Delta V = 0$
- By the raise of temperature of water bath and calorimeter the amount of heat evolved can be determined.
- 

Bomb calorimeter
1. Thermometer, 2. Firing leads
3. Stirrer, 4. Oxygen inlet
5. Sample, 6. Bomb

Internal Energy $\Delta U = Q.\ \Delta t \times \frac{M}{m}$

Q = heat capacity
$\Delta t = t_2 - t_1$
M = molar mass of substance
m = mass of the substance

2 **Explain the experiment to determine the enthalpy change of chemical reaction.**

Ans:

Enthalpy (H) : "Enthalpy is the amount of heat exchanged by a system with its surroundings at constant pressure and temperature".

Mathematically, change in enthalpy $\Delta H = \Delta E. P\Delta V$

Enthalpy is state function. Thus, the magnitude of enthalpy change depends only upon the enthalpies in the initial and final states.

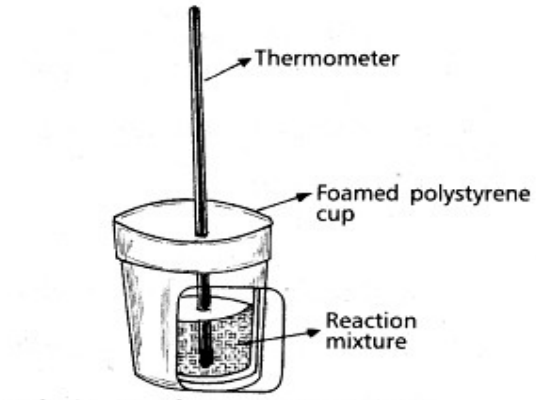
$\Delta H = [H_{products} - H_{reactants}]$

Heat change at constant pressure can be measured in a calorimeter at constant pressure

$\Delta H = q_p$

∴ For Exothermic reaction ΔH = -ve

For Endothermic reaction ΔH = +ve



Calorimeter for measuring heat changes at constant pressure

3 **Explain the spontaneity of a reaction interms of enthalpy change, entropy change and Gibb's energy change.**

Ans:

Spontaneous reaction :

A process is said to be spontaneous if it occurs on its own without intervention of any external agency of any kind.

All natural processes are spontaneous.

Entropy increases in all spontaneous processes.

Change in entropy "(ΔS) = positive" is a condition but is not necessary and sufficient condition for the spontaneous nature of a reaction.

Change in enthalpy "(ΔH) = negative" may be a condition but not a necessary and sufficient condition for the spontaneous nature of a reaction.

At this juncture, "Gibbs" introduced another thermodynamic function which involves both enthalpy (H) and entropy (S) functions. This is known as free energy function (G). This is given

by the equation, G = H – TS. 'G' is now referred as 'Gibbs energy (or) Gibbs function.

"ΔG_{sys} is negative" for spontaneous reactions (or) processes. Thus the spontaneity of a reaction and the algebraic signs of ΔH, ΔS, ΔG and the magnitude of 'T' can be related as follows :

Δ_rH^Θ	Δ_rS^Θ	Δ_rG^Θ	Nature of the reaction
-	+	-	Spontaneous at all temperatures
+	-	+	Non-spontaneous at all T values
-	-	-	Spontaneous at low temperatures
-	-	+	Non-spontaneous at high temperatures.
+	+	+	Non-spontaneous at low temperatures
+	+	-	Spontaneous at high temperatures

Change in entropy "(ΔS) = positive" is a condition but it is not necessary and sufficient condition for the spontaneous nature of a reaction.

For a spontaneous process change in entropy is- positive

ΔS = +ve (spontaneous)

ΔS = -ve (backward reaction is spontaneous)

ΔS = 0 (Equilibrium reaction)

∴ ΔH = -ve, ΔS = +ve, ΔG = -ve then the reaction

Spontaneous at all T values (Reaction is irreversible)

UNIT -6
EQUILIBRIUM

I **MULTIPLE CHOICE QUESTIONS (1 mark)**

1. **The pH of a solution of hydrochloric acid is 4. The molarity of the solution is**
   1) 4.0 M 2) 0.4 M 3) 0.0001 M 4) 0.04 M
   Ans: 3) 0.0001
   : pH = – log $[H^+]$
   Here $[H^+] = 10^{-4}$,
   Molarity=0.0001 M

2 **The strong conjugate base in the following is**
   1)NO_3^- 2) Cl^- 3) SO_4^{2-} 4) CH_3COO^-
   Ans: 4) CH_3COO^-
   Hint: CH_3COO^- is the strongest conjugate base because CH_3COOH is a weak acid.

3 **When NH_4Cl is added to NH_4OH solution the dissociation of ammonium hydroxide is reduced. It is due to:**
   1) common ion effect 2) hydrolysis 3) oxidation 4) reduction
   Ans: 1) Common ion effect
   Hint: dissociation of ammonium hydroxide is reduced due to presence of common ion i.e, NH_4^+

4 **The following reaction is at equilibrium**
   $Fe^{+3}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons [Fe(SCN)]^{2+}_{(aq)}$
   In the above reaction, colour intensity of red colour can be increased by
   1) addition of oxalic acid which reacts with Fe^{3+} ions
   2) addition of Hg^{2+} ions which reacts with SCN^- ions
   3) addition of KSCN
   4) red colour intensity cannot be changed
   Ans: 3) addition of KSCN

5 **K_{sp} of a sparingly soluble salt AB_2 is 4 x 10^{-12}.The solubility of the salt is**
   1) 2 x 10^{-6}M 2)4 x 10^{-4} M 3)1x 10^{-12} M 4)1x10^{-4}M
   Ans: 4) 1x10^{-4}M
   Solution:
   $AB_2 \rightleftharpoons A^{2+} + 2B$
   S 2S
   $Ksp = [A^{2+}][B]^2$

   $= (s)(2s)^2 = 4S^3$

   $S^3 = \frac{Ksp}{4} = \frac{4\times10^{-12}}{4} = 1\times10^{-12}$
   $S = 1\times10^{-4}$M

6 **An aqueous solution of ammonia consists of**

1) H^+only 2)OH^- *only* 3)NH_4^+only 4) NH_4^+ and OH^-

Ans: 4) NH_4^+ and OH^-

7 **The pH of a 0.05 M of H_2SO_4 solution is**

1) 0.05 2)1 3) -1 4)1.3010

Ans: 2) 1

Solution: $[H^+]$ of $H_2SO_4 = 2 \times 0.05 = 0.1$

$P^H = 1$

8 **If the molar Solubility of Zirconium phosphate $Zr_3(PO_4)_4$ is 'S'. Solubility product Ksp of Zirconium phosphate is**

1) 6912 $(S)^5$ 2) 6912$(S)^7$ 3) 108 $(S)^7$ 4) 27$(S)^5$

Ans: 2) 6912$(S)^7$

Solution:

$Zr_3(PO_4)_4(s) \rightleftharpoons 3Zr_4+(aq)+4PO_3^{-4}(aq)$

3s 4s

$Ksp=(Zr_4+)^3\times(PO_3-^4)^4$

$Ksp=(3s)^3\times(4s)^4$

$Ksp=(27s^3)\times(256s^4)$

$Ksp=6912\ (s)^7$

9 **For a reversible reaction, if the concentration of reactants is increased, the equilibrium constant of the reaction**

1) Increases 2)Remains constant 3)Decreases 4)Depends on amount of reactant

Ans: 2) Remains constant

10 **The P^{Ka} of acetic acid and P^{Kb} of ammonium hydroxide are 4.76 and 4.75 respectively. The pH of ammonium acetate solution is**

1) 6.098 2) 7.005 3)8 4) 5.0

Ans: 2) 7.005

Solution: $p^H = P_{Ka} + \log\frac{[salt]}{[acid]}$

$$p^H = 7 + \frac{1}{2}[p_{Ka} - p_{Kb}]$$

$$= 7 + \frac{1}{2}[4.76 - 4.75]$$

$$= 7 + \frac{1}{2}[0.01]$$

$$= 7.005$$

11 **Which among the following salt solutions is basic in nature?**

1) Ammonium chloride 2)Ammonium sulphate

3) Ammonium nitrate 4) Sodium acetate

Ans: 4) Sodium acetate

12 **Observe the following equilibrium at T (Kelvin)**

$H_2(g)+I_2(g) \rightleftharpoons 2HI(g)$

Which one of the following does not disturb the above equilibrium at constant volume?

1) Addition of $H_2(g)$ 2)Removal of HI (g)

3)Addition of $I_2(g)$ 4) Addition of He (g)

Ans: 4) Addition of He (g)

13 **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.**

1) 9.25 2) 4.75 3) 3.75 4) 8.25

Ans:2) 4.75

Solution:

pH+pOH=14

pOH=4.75.

$pOH = pKb + \log \frac{[salt]}{[base]}$

pOH=pKb+log (1)

pOH=pKb ($\because \log 1=0$)

$pK_b=4.75$.

14 **For the following process the expression for the K_c**

$Ni_{(S)} + 4CO_{(g)} \rightleftharpoons 2Ni(CO)_{4(g)}$

$1)K_c = \frac{[Ni(CO)_4]^2}{[Ni][CO]^4}$ $2)K_c = \frac{[Ni(CO)_4]}{[CO]^4}$ $K_c = \frac{[Ni][CO]^4}{[Ni(CO)_4]^{2-}}$ $4)K_c = \frac{[CO]^4}{[Ni(CO)_4]^2}$

Ans : $2)K_c = \frac{[Ni(CO)_4]}{[CO]^4}$

15 **K_1 and K_2 are equilibrium constants for reactions (i) & (ii) then the relation between K_1 and K_2**

(i) $H_{2(g)} + I_{2\,(g)} \rightleftharpoons 2HI_{\,(g)}$

(ii) $HI_{\,(g)} \rightleftharpoons \frac{1}{2} H_{2(g)} + \frac{1}{2} I_{2\,(g)}$

1) $K_1 = K_2^{\,2}$ 2) $K_1 = \frac{1}{K_2}$ 3) $K_1 = K_2^{\,0}$ 4) $K_1 = \frac{1}{K_2^{\,2}}$

Ans: 4) $K_1 = \frac{1}{K_2^2}$

II. FILL IN THE BLANKS (1 mark)

1 **Acidity of BF_3 can be explained on the basis of _____ theory of acids and bases.**

Ans: Lewis

2 **The Nature of aqueous solution of ammonium chloride (NH_4Cl) is _____**

Ans: Acidic

3 **Kp for the following equation _____**
$CaCO_{3\,(S)} \rightleftharpoons CaO(s) + CO_2\,(g)$
Ans: Kp = P_{CO_2}

4 **Molarity of pure water is _____**
Ans: 55.5M

5 **If K_c is in the range of _____ appreciable concentrations of both reactants and products are present.**
Ans: 10^{-3} to 10^{3}

III. ONE WORD ANSWER QUESTIONS (1 mark)

1 **What is a Bronsted base ?**
Ans: The substance which accepts a proton from the other substance is called Bronsted base
e.g.: NH_3, H_2O etc.

2 **What is Lewis acid?**
Ans: A substance which can accept an electron pair to from a co-ordinate covalent bond with donor is called Lewis acid.
e.g. : H^+, BF_3, $SnCl_2$ etc.

3 **What is the value of Kw at 25^0 C ?**
Ans : At 25°C Ionic product of water $K_w = 1.008 \times 10^{-14}$ $mole^2/lit^2$
Units : $mole^2/lit^2$

4 **What is conjugate acid-base pair?**
Ans: Conjugate acid – base pair:
A pair of a Bronsted acid and a base that differs by one proton (H^+) is known as conjugate acid – base pair.

5 **Write the relation between Gibbs free energy and Equilibrium constant.**
Ans: $\Delta G° = -RT\ln K$ $\Delta G° = -2.303RT \log K$

IV **VERY SHORT ANSWER QUESTIONS (1 mark)**

1 **State law of chemical equilibrium.**
Ans: The ratio of product of molar concentrations of the products to the product of molar concentrations of the reactants has a constant value. This is known as the equilibrium law (or) law of chemical equilibrium.

2 **What is homogenous equilibrium? Give two examples.**
Ans: In a homogeneous system all the reactants and products are in the same phase.
Ex:
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)})$
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

3 **What is heterogeneous equilibrium? Give two examples.**
Ans: Equilibrium in a system having more than one phase is called heterogeneous equilibrium.

$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

$Ni(s) + 4CO_{(g)} \rightleftharpoons Ni(CO)_4)_{(g)}$

$CaCO_{3\,(S)} \rightleftharpoons CaO\,(s) + CO_2(g)$

4 **What is meant by dynamic equilibrium?**

Ans: Dynamic equilibrium: The forward and reverse reactions of a reversible reaction continue to take place with equal rates simultaneously at the equilibrium stage also. Hence the equilibrium is called Dynamic equilibrium.

5 **Give two chemical equilibrium reactions for which $K_p > K_c$.**

Ans:

1) $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$
2) $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$

6 **Give two chemical equilibrium reactions for which $K_p < K_c$.**

Ans:

1) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
2) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

7 **Write the equations for the conversion of K_c to K_p for the following reaction**

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

Ans:

$$K_p = \frac{P_{CO_2} \times P_{H_2}}{P_{CO} \times P_{H_2O}}$$

$$K_C = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

K_c to K_p conversion

8 **What are the factors which influence the chemical equilibrium?**

Ans: The factors influencing chemical equilibrium are

1. Concentration of reactants and the products
2. Temperature of reaction
3. Pressure of reaction
4. Inert gas addition etc.

9 **What is meant by ionic product of water?**

Ans: At a given temp, the product of the concentrations of H^+ and OH^- ions in water is called ionic product

Ionic product $K_w = [H^+]\,[OH^-]$

10 **Give two examples of salts whose aqueous solutions are acidic.**

Ans: Ammonium chloride (NH_4Cl), Ammonium sulphate [$(NH_4)_2\,SO_4$] salts aqueous solutions are acidic in nature.

V **SHORT ANSWER QUESTIONS (4 marks)**

1 **Derive the relation between K_p and K_c for the equilibrium reaction**
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Ans: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$K_P = \frac{\left(P_{NH_3}\right)^2}{\left(P_{N_2}\right)\times\left(P_{H_2}\right)^3} \quad \ldots\ldots\ldots (1)$$

$$K_C = \frac{\left[NH_3\right]^2}{\left[N_2\right]\times\left[H_2\right]^3} \quad \ldots\ldots\ldots (2)$$

PV = nRT =

$$P = \frac{n}{v}RT = CRT$$

$$P_{NH_3} = \left[NH_{3(g)}\right]RT$$

$$P_{H_2} = \left[H_{2(g)}\right]RT$$

$$P_{N_2} = \left[N_{2(g)}\right]RT$$

$$K_P = \frac{\left[NH_3\right]^2\left[RT\right]^2}{\left[N_2\right]RT\left[H_2\right]^3\left(RT\right)^3}$$

$$K_p = \frac{\left[NH_3\right]^2}{\left[N_2\right]\left[H_2\right]^3}\frac{(RT)^2}{(RT)^4}$$

From equation eq. (2)

$$K_p = K_c(RT)^{-2}$$

So, $K_P < K_C$

Note: Relation between Kp and Kc

$$K_p = K_c(RT)^{\Delta n}$$

Δn = No. of moles of gases products – no. of moles of gaseous reactants

$\Delta n = 2 - 4 = -2$

$$K_p = K_c(RT)^{-2}$$

So, $K_p < K_c$

2 **State LeChateliers's Principle. Discuss the application of LeChatelier's principle for the industrial synthesis of Ammonia by Haber's process?**

Ans: Le Chatelier's Principle: "If a system at equilibrium is subjected to the change of pressure, temperature (or) concentration, the system is shifted in such a way as to nullify the effect of change".

Applications of Le Chatelier's principle to synthesis of Ammonia by Haber's process:

$$N_2g + 3H_2g \rightleftharpoons 2NH_3g;\ \Delta H = -92\ kJ$$

4 volumes 2 volumes

Nitrogen and Hydrogen combine to form ammonia. The formation of ammonia is reversible and exothermic reaction. It is accompanied by decrease in volume.

Effect of Pressure: 1 volume of N_2 combines with 3 volumes of H_2 to form 2 volumes of NH_3. There is decrease in volume in the forward reaction (4 volumes to 2 volumes). According to Le Chatelier's principle higher the pressure, greater the yield of ammonia. In practice 200 atmospheres are used in the manufacture of ammonia by Haber's process.

Effect of Temperature: The formation of ammonia (forward reaction) is exothermic reaction $N_2 + 3H_2 \rightarrow 2\ NH_3;\ \Delta H = -92$ kJ.

Low temperatures favour the forward reaction. But at low temperatures the reaction is too slow. Therfore an optimum temperature (725 K- 775 K) is chosen in Haber's process.

Effect of Catalyst : To speed up the reaction, a catalyst, finely divided iron is used. To increase the activity of the catalyst molybdenum or a mixture of oxides of K_2O and Al_2O_3 is used as promoter.

Pressure : 200-500 atm

Temperature : 725-775 K

Catalyst : Fe (Powered)

Promoter : Mo (olden days) $K_2O + Al_2O_3$ (Now a days)

3 State LeChateliers's Principle. Discuss the application of Lechatelier's principle for the manufacture of SO_3 by contact process.?

Ans: Le Chatelier's Principle : "If a system at equilibrium is subjected to the change of pressure, temperature (or) concentration, the system is shifted in such a way as to nullify the effect of change".

Application of Le Chatelier's principle to the synthesis of SO_3 :

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g);\ \Delta H = -189\ kJ$$

3 volumes (2 + 1) 2 volumes

The formation of SO_3 is reversible and exothermic reaction. It is accompanied by decrease in volume.

1. Effect of Pressure : 2 volumes of SO_2 and one volume of O_2 combine to give 2 volumes of SO_3. According to Le Chatelier's Principle increase of pressure favours the reaction where there is decrease in volume. The formation of SO_3 is accompanied by decrease in volume (3 volumes to 2 volumes). Higher the pressure greater is the yield of S03. But in contact process high pressures are not used because towers used in the manufacture are corroded by the acid at these high pressures. Therefore optimum pressures are used (1 to 2 atmosphere).

2. Effect of Temperature: The formation of SO_3 is exothermic. So Low temperatures are favourable for the formation of SO_3. At low temperature the reaction is too slow. Therefore an optimum temperature 673 K is used.

3. Effect of catalyst: To speed up the reaction V_2O_5 is used as catalyst.

Thus the optimum conditions are

Pressure : 1-2 atm

Temperature : 673 K.

Catalyst : V_2O_5 (or) Platinised asbestos.

4 **The species H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Bronsted acids and bases. Give the corresponding conjugate acid and base for each of them.**

Ans:

Species	Conjugate acid	Conjugate base
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{-2}
HSO_4^-	H_2SO_4	SO_4^{-2}
NH_3	NH_4^+	NH_2^-

5 **Write notes on**

(i) Common ion effect.

(ii) solubility product

Ans:Common ion effect : The decrease in the ionisation (dissociation) of a weak electrolyte, by the addition of a strong electrolyte having an ion common with the weak electrolyte, is known as common ion effect.

Example : The dissociation of NH_4OH is diminished by the addition of NH_4Cl due to the common ion, NH_4^+ ion.

$$NH_4OH \overset{NH_4^{\oplus}}{\rightleftharpoons} NH_4^{\oplus} + OH^- (addition\ of\ NH4Cl)$$

Solubility product (K_{SP}) : The product of the concentrations of the cation and the anion in a saturated solution of a salt at room temperature is called solubility product (K_{sp}).

Example:

$$BaSO_4(s) \underset{in\ water}{\overset{Saturated\ Solution}{\rightleftharpoons}} Ba^{+2}_{(aq)} + SO_4^{-2}(aq)$$

$$K_{sp} = \left[Ba^{+2}\right]\left[SO_4^{-2}\right]$$

$$K_{sp} = s \times s = s^2$$

6 **Explain the concept of Bronsted-Lowry acids and bases. Illustrate with suitable examples.**

Ans: According to Bronsted – Lowry theory.

Acid: Acidis a substance that is capable of donating a Hydrogen ion H^+.

Eg: CH_3COOH, HCl.

Base: Base is a substance capable of accepting a hydrogen ion, H^+.

Eg: NH_3, H_2O.

Eg: Dissolution of NH_3 in H_2O.

ads proton

$$NH_{3(aq)} + H_2O_{(l)} \rightleftarrows NH_{4\ (aq)}^{\oplus} + OH^-_{(aq)}$$

Base acid Conjugate acid Conjugate base

loses proton

∴ Acids are proton donors and bases are proton acceptors.

7 **Explain Lewis acids and bases with suitable example. Classify the following species into Lewis acids and Lewis bases.**

a) OH^- b) F^- c) H^+ d) BCl_3

Ans: Lewis theory of acids and bases: According to this theory.

Acid: A substance that can accept an electron pair to form a co-ordinate covalent bond is called an acid.

Types of Lewis acids:

Lewis acids are of 5 types.

1) All Cations : Simple cations $Ag^{\oplus}$, CO^{+3}, Cu^{+2}, Fe^{+3}, Al^{+3} can act as Lewis acids.

2) Compounds in which the central atom has an incomplete octet and possessing an empty orbital

Ex : BF_3, BCl_3, $AlCl_3$, $FeCl_3$.

3) Compounds in which the central atom has vacant d-orbitals and may expand its octet .

Ex : SiF_4, SF_4, TeF_4, $SnCl_4$, $FeCl_3$.

4) Molecules having multiple bonds between atoms of dissimilar electronegativities .

Ex : CO_2, SO_2, SO_3, NO_2, Cl_2O_7, P_4O_{10}

5) Elements with six electrons in the valence shell

Ex : O, S

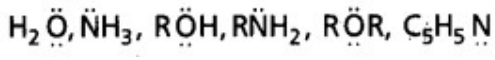
Base : According to Lewis theory a base is a substance which can donate an electron pair to form a co-ordinate covalent bond.

Types of Lewis bases: Lewis bases are divided into three types.

1) All anions

Ex: Cl^-, OH^-, CN^-, NH^-, F^-, SCN^-

2) Molecules with one or two lone pairs on the central atom can act as Lewis bases.

Ex : 

a) Hydrenyl ion is a lewis base as it can donate an electron lone pair (OH^-).

b) Flouride ion acts as a Lewis base as it can donate any one of its four electron lone pairs.

c) A Proton is a lewis acid as it can accept alone pair of electrons from bases like hydrenyl ion and flowride ion.

d) BCl_3 acts as a lewis acid as it can accept a lane pair electron from species like ammonia.

8 **Calculate the p^H of**

a)10^{-3} M HC1 b) 10^{-3} M H_2SO_4 [log 2=0.3010]

Ans: a) 3 b) 2.699

a) 10^{-3} M HCl

$p^H = -\log (H+)$

$= -\log 10^{-3}$

$= 3$

b) 10^{-3} M H_2SO_4

$p^H = -\log_{10}[H^+]$

$= 0.001 \times 2$

$= 0.002$

$p^H = -\log 0.002$

$= -\log 2 \times 10^{-3}$

$= -\log 2 - \log 10^{-3}$

$= 3 - \log 2$

$= 3 - 0.3010$

$= 2.699$

9 **Calculate the p^H for**

a. 0.001 M NaOH

b. 0.01M $Ca(OH)_2$

Ans: a) 11 b) 12.3010

a) $pH = -\log\left[H^+\right] = -\log_{10}\frac{1}{\left[H^+\right]}$

0.001 M NaOH

pOH = -log[OH^-]

pOH = – log (0.001)

$= -\log 10^{-3}$

= 3

pH = 14 – pOH

= 14 – 3 = 11

b) 0.01 M Ca $(OH)_2$

pOH = -log [OH^-]

[OH^-] = 0.01 × 2

= 0.02 N

pOH = – log 0.02

pOH = -log 2×10^{-2}

pOH = – log2 + 2 log 10

= 2 – 0.3010

= 1.699

∴ pH = 14 – pOH

= 14 – 1.699 = 12.3010

10 **The pH of 0.1M solution of weak mono protic acid is 4.0 calculate its [H^+] and Ka.**

Ans: 10^{-4} ,10^{-7}

Solution:

Given pH = 4.0

$\therefore [H^+] = ?$

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

$[H^+] = 10^{-pH}$

$= 10^{-4}$

$\therefore [H^+] = C \times \alpha$

$\alpha = 10{-}40.1$

$= 10^{-3}$

$K_a = C \times \alpha^2$

$= 0.1 \times (10^{-3})^2$

$= 0.1 \times 10^{-6}$

$= 10^{-7}$.

11 **One litre of buffer solution contains 0.1 mole of acetic acid and 1 mole of sodium acetate. Find its pH if pK_a of CH_3COOH is 4.8**

Ans: 5.8

Solution:

For an acid buffer $pH = PK_a + \log \frac{[Salt]}{[Acid]}$

$pH = 4.8 + \log \frac{1}{0.1}$

$= 4.8 + \log 10$

$pH = 4.8 + 1$

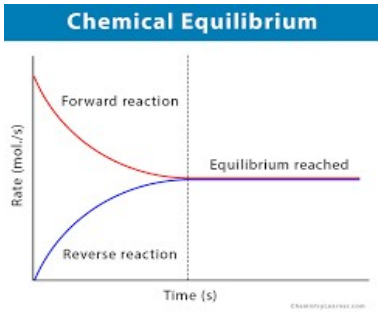
$pH = 5.8$

VI LONG ANSWER QUESTIONS (8 marks)

1 **What are equilibrium processes? Explain equilibrium in physical and chemical processes with examples.**

Ans:

Equilibrium State (or) Equilibrium Process : The state at which the velocity of forward reaction becomes equal to the velocity of backward reaction or reverse reaction is called 'equilibrium state'. Consider a reversible reaction.



$A + B \rightleftharpoons C + D$ taking place in a closed vessel. At the beginning we have only the reactants A and B. Their concentrations are maximum. As the reaction proceeds the reactants A and B change into the products C and D. The concentrations of the products increase gradually. The rate of forward reaction diminishes while the reverse reaction sets in and proceeds with increasing speed. A state is soon reached where the speeds of forward and backward reactions become equal. If the rate of forward reaction V_f = The rate of reverse reaction (V_b).

The system is said to have attained a state of equilibrium. Once equilibrium is reached there is

no further change in the composition of the system. The system appears to be stand still although it is dynamic. The products are formed by forward reaction just as fast as they change back into reactants by the reverse reaction.

The state at which the rate of forward reaction is equal to the rate of the reverse reaction in a reversible reaction is known as the equilibrium state or chemical equilibrium.

Examples :

i) Equilibrium physical processes :

a) Equilibrium between two phases (i.e.,) physical transformation processes.

Solid ⇌ Liquid (melting or fusion)

Solid ⇌ Vapour (sublimation)

b) Equilibrium between two different allotropic forms of same substance

α – Sulphur ⇌ β – Sulphur

ii) Equilibrium chemical processes :

a) N_2 (g) + $3H_2$ (g) ⇌ $2NH_3$ (g)

b) $2SO_2$ (g) + O_2 (g) ⇌ $2SO_3$ (g)

c) H_2(g) + I_2(g) ⇌ 2HI(g)

2 What is meant by dynamic equilibrium ? Explain with suitable examples.

Ans:

Dynamic equilibrium : The forward and reverse reactions of a reversible reaction continue to take place with equal rates simultaneously at the equilibrium stage also. Hence the equilibrium is called Dynamic equilibrium.

Explanation : In order to understand the dynamic nature of the reaction, synthesis of ammonia is carried with exactly the same starting conditions but using D_2 (deuterium) in place of H_2. The reaction mixtures starting either with H_2 or D_2 reach equilibrium with the same composition, except that D_2 and ND_3 are present instead of H_2 and NH_3. After equilibrium is attained, these two mixtures (H_2, N_2, NH_3 and D_2, N_2, ND_3) are mixed together and left for a while. Later when this mixture analysed, it is found that the concentration of ammonia is just the same as before.

However, when this mixture is analysed by a moss spectrometer, it is found that ammonia and all deuterium containing forms of ammonia (NH_3, NH_2D, NHD_2 and ND_3) and dihydrogen and its deutrated forms (H_2, HD and D_2) are present. Thus one can conclude that scrambling of H and D atoms in the molecules must result from a continuation of the forward and reverse reactions in the mixture. If the reaction had simply stopped when they reached equilibrium, then there would have been no mixing of isotopes in this way.

Use of isotope (deuterium) in the formation of ammonia clearly indicates that chemical reaction reaches a state of dynamic equilibrium in which the rates of forward and reverse reactions are equal and there is no net change in composition.

3 What are the important features of equilibrium constant ? Discuss any two applications of equilibrium constant.

Ans:

The ratio of product of molar concentrations of products to the product of molar concentrations of reactants is called equilibrium constant (K_c)

Ex : aA + bB⇌cC + dD

$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

K_C for reverse reaction is the inverse of the K_C for the reaction in the forward direction.

Concentration equilibrium constant (K_C) and pressure equilibrium constant (K_p) are related as follows

$K_p = K_C(RT)^{\Delta n}$

$\Delta n = n_p - n_R$

While writing K_C expression pure liquids, pure solids concentration are ignored Applications :

a) In predicting the extent of reaction :

The numerical value of the equilibrium constant for a reaction indicates the extent of the reaction. But it is important to note that an equilibrium constant does not give any information about the rate at which the equilibrium is reached the Magnitude of k_e or K_p is directly proportional to the concentrations of products (as these appear in the numerator of equilibrium constant expression) and inversely proportional to the concentrations of the reactants (these appear in the denominator). This implies that a high value of K is suggestive of a high concentration of products and vice- versa.

We can make the following generalisation concerning the composition of equilibrium mixtures : If $K_c > 10^3$ products predominate over reactants, i.e., if K_c is very large, the reaction proceeds nearly to completion. Consider the following examples :

a) The reaction of H_2 with O_2 at 500 K has a very large equilibrium constant $K_c = 2.4 \times 10^{47}$

b) $H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl(g)$ at 300 K has $K_c = 4.0 \times 10^{31}$

c) $H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)}$ at 300 K. $K_c = 5.4 \times 10^{18}$

If $K_c = < 10^{-3}$ reactants predominate over products i.e, if K_c is very small the reaction proceeds rarely. Consider the following examples : –

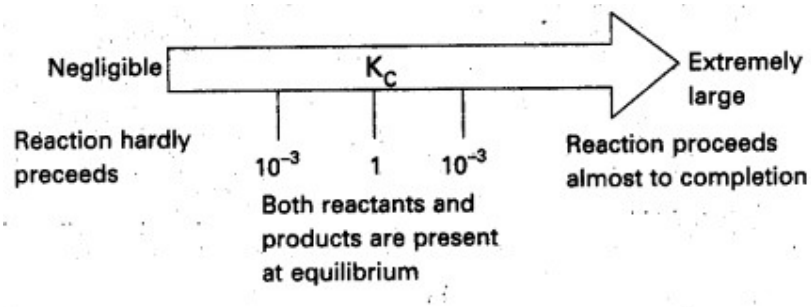
a) The decomposition of H_2O into H_2 and O_2 at 500 K has a very small equilibrium constant. $K_c = 4.1 \times 10^{-48}$

b) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

at 298 K has $K_c = 4.8 \times 10^{-31}$

If K_c is in the range of 10^{-3} to 10^3 appreciable concentrations of both reactants and products are present. Consider the following examples :

a) For reaction of H_2 with I_2 to give HI.



b) Also, gas phase decomposition of N_2O_4 to NO_2 is another reaction with a value of $K_c = 4.64 \times 10^{-3}$ at 25°C which is neither too small nor too large. Hence equilibrium mixtures contain appreciable concentrations of both N_2O_4 and NO_2.

These generarlisations are illustrated.

b) In predicting the direction of reaction: A and K are compared to predict the direction of

reaction

a) Q = K indicates that the reaction mixture is already at equilibrium

b) Q < K indicates that the reaction proceeds in the direction. c) Q > K indicates that the reaction proceeds in the direction of reactants (Reverse reaction)

4 **What is Lechatlier'sprinciple? Discuss briefly the factors which can influence the equilibrium.**

Ans:

Le *Chatelier's Principle* – Statement: "If a system at equilibrium is subjected to the change of pressure, temperature (or) concentration, the system is shifted in such a way as to nullify the effect of change".

Explanation :

1) Concentration: Increase of reactant concentrations pushes the equilibrium state to the products side and increase of the reactions concentrations pushes to the equilibrium to the reactants side. For example in the chemical equilibrium

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Increase of H_2 or I_2 concentrations pushes the equilibrium in favours of HI and similarly the increase of HI concentrations pushes the equilibrium in favour of H_2 and I_2.

2) Pressure : Pressure will have no effect on the equilibrium reactions in which there is no change in the number of moles of the reactants and the products.

For example pressure will have no effect on

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ equilibrium

(or) $N_2 (g) + O_2 (g) \rightleftharpoons 2NO (g)$ equilibrium

But in the case of reactions in which there is a change in the number of moles of the reactants and the products increase of pressure pushes the reaction equilibrium in the direction in which there is a decrease in the number of moles.

For example in the reaction $PCl_5 (g) \rightleftharpoons PCl_3 (g) + Cl_2 (g)$

Increase of pressure favours the backward reaction $PCl_3 (g) + Cl_2(g) \rightarrow PCl_5 (g)$ and the decrease of pressure favour the forward reaction $PCl_5 (g) \rightarrow PCl_3 (g) + Cl_2 (g)$

3) Temperature : Increase of temperature favour the endothermic reaction and decrease of temperature favours exothermic reactions.

For example .

$N_2 (g) + O_2 (g) \rightleftharpoons 2N0(g) – 180.8$ kJ

Increase of temperature favours the forward reaction

$N_2 (g) + O_2 (g) \rightarrow 2NO (g)$ (since endothermic)

decrease of temperature favour the dissociation of NO into N_2 and O_2 since it is exothermic. The backward reaction

$2NO (g) \rightarrow N_2 (g) + O_2 (g)$ (exothermic)

5 **Describe the effect of :**

a) addition of H_2

b) addition of CH_3OH

c) removal of CO

d) removal of CH_3OH on the equilibrium of the reaction

$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$

Ans:

a) Addition of H_2 (Reactant):

Increasing the concentration of reactants in the reaction mixture at equilibrium favours the forward reaction.

b) Addition of CH_3OH (Product):

Increasing the concentration of products in the reaction mixture at equilibrium favours the reverse reaction.

c) Removal of CO (Reactant):

Decreasing the concentration of reactants in the reaction mixture at equilibrium favours the reverse reaction.

d) Removal of CH_3OH (Product):

Decreasing the concentration of products in the reaction mixture at equilibrium favours the forward reaction.

6 **What is degree of ionization in respect of weak acids and weak bases ? Derive the relationship between degree of ionization (α) and ionization constant (K_a) for the weak acid HX.**

Ans:

Degree of ionization (α):

The extent of ionization (or) dissociation of a weak acid or weak base is termed as its Degree of ionization (α). Let the concentration of weak acid (HX) be 'C moles/lit and the degree of ionization be 'α'. Hence at equilibrium,

$$HX \rightleftharpoons H^+ + X^-$$

$$C(1-\alpha) \quad C\alpha \quad C\alpha$$

$$K_a = \frac{[H^+][X^-]}{[HX]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

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

If 'α' is neglected compared to 'one' in the denominator.

We have $K_a = C\alpha^2 \Rightarrow \alpha^2 = \frac{K_a}{C} \Rightarrow \alpha = \sqrt{Ka} / c$

Similar equation can be written for the ionization of weak base (BOH) in aq. solution.

$$BOH \xrightleftharpoons{H_2O} B^+ + OH^-$$

$$C(1-\alpha) \qquad C\alpha \quad C\alpha$$

$$K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

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

Neglecting 'α' in the denominator, we have

$$K_b = C\alpha^2 \Rightarrow \alpha^2 = \frac{K_b}{C}$$

$$\therefore \alpha = \sqrt{\frac{K_b}{C}}$$

Therefore strengths of two acids or two bases are compared generally by their K_a or K_b values. Higher K_a or K_b value, stronger is the acid or base.

7 **Define pH. What is buffer solution? Derive Henderson – Hasselbalch equation for calculating the pH of an acid buffer solution.**

Ans: pH : "The negative value of the logarithm to the base 10, of the hydrogen ion concentration, expressed in moles / lit, in a solution is known as the pH of the solution".

Mathematically, $pH = -\log_{10}[H^+]$

Buffer Solution:

"A buffer solution is that solution which resists any change in its pH value on dilution (or) on addition of a small amount of a strong acid or a strong base

Ex : Acidic buffer: ($CH_3COOH + CH_3COONa$)

Basic buffer: ($NH_4OH + NH_4Cl$)

Preparation of buffer solutions :

1) Acidbuffer solutions : An acid buffer consists of weak acid and its salt with strong base.

Ex : ($CH_3COOH + CH_3COONa$)

Acid buffer solutions are normally prepared by mixing either equal or different volumes of equimolar solutions of a weak acid and its salt.

2) Basebuffer solutions : A basic buffer solution consists of a mixture of a weak base and its salt with a strong acid.

Ex : ($NH_4OH + NH_4Cl$)

Base buffer solutions are prepared generally, by mixing either equal or different volumes of equimolar solutions of a weak base and its salt.

Derivation of Hendersen's equation for an acid buffer :

i) Consider the acid buffer HA + NaA

$HA \rightleftharpoons H^+ + A^-$

$NaA \rightleftharpoons Na^+ + A^-$

Acid dissociation constant $K_a = \frac{[H]^+[A]^-}{[HA]}$

Here due to common ion effect

$$\left[H^+\right] = K_a \frac{\left[HA\right]}{\left[A^-\right]} = K_a \frac{\left[Acid\right]}{\left[Salt\right]}$$

$$pH = -\log\left[H^+\right]$$

$$= -\log\left[K_a \frac{\left[Acid\right]}{\left[Salt\right]}\right]$$

$$= -\log K_a - \log\frac{\left[Acid\right]}{\left[Salt\right]}$$

$$= -\log K_a + \log\frac{\left[Salt\right]}{\left[Acid\right]}$$

$$\therefore pK_a = -\log K_a$$

$$\boxed{\therefore pH = pK_a + \log\frac{\left[Salt\right]}{\left[Acid\right]}}$$

8 **Write notes on**

(i) Common ion effect.

(ii) The relation between K_{sp} and solubility (S) of a sparingly soluble salt $BaSO_4$.

Ans:

i) Common ion effect : The decrease in the ionisation of a weak electrolyte, by the addition of a strong electrolyte having an ion common with the weak electrolyte, is known as common ion effect.

Example : The dissociation of NH_4OH is diminished by the addition of NH_4Cl due to the common ion, NH_4^+ ion

$NH_4OH \rightleftharpoons NH_4^{\oplus} + OH^{\ominus}$

$NH_4OH \overset{NH_4^{\oplus}}{\rightleftharpoons} NH_4^+ + OH^{\ominus}$ (addition of NH_4Cl)

Importance of this effect In qualitative analysis :

1. This principle is used in the systematic qualitative analysis of cations.
2. The concentration of S^{2-} in II group or OH^- ion in III group of chemical analysis is controlled by HCl and NH_4OH on the basis of common ion effect.
   H^+ ion is common to H_2S (II group)
   NH_4^+ ion is common to NH_4OH (IV group) .
3. The common ion effect principle is also used in controlling the H^+ ion concentration in buffer solutions.
4. It is also used in the purification of common salts by passing dry HCl gas into impure salt solution.

ii) Relation between K_{SP} and 'S' of salt at $BaSO_4$

$$BaSO_4 \rightleftharpoons Ba^{+2} + SO_4^{-2}$$
$$S \quad S$$

$$K_{SP} = S \times S$$
$$K_{SP} = S^2$$
$$S = \sqrt{K_{SP}}$$

UNIT-7
REDOX REACTIONS

I. Multiple choice questions (1 mark)

1) The oxidation number of an element in a compound is evaluated on the basis of certain rules.Which of the following rule is incorrect?

1) Oxidation number of hydrogen is always +1
2) The algebraic sum of all the oxidation numbers of all elements is equal to charge present on a compound.
3) An Element in the free state or uncombined state, it's oxidation number is zero
4) In all its compounds, the oxidation number of fluorine is -1

Ans: 1

2) When hydrogen sulphide gas is passed through a solution of Cu^{2+} solution, then

1) Black cupric sulphide is formed 2) White cupric sulphide is formed
3) Red cupric sulphide is formed 4) No reaction

Ans: 1

3) The Oxidation number of oxygen in O_2F_2 and OF_2 are respectively

1) +2 and +1 2) +1 and +1
3) +1 and +2 4) +2 and +2

Ans: 3

4) Which of the molecules can undergo disproportionation in the alkaline medium?

1) S_8 2) P_4 3) Cl_2 4) All of these

Ans: 4

5) The oxidation number of Sulphur in $Na_2S_4O_6$ is

1)2.5 2) 1.5 3)2 4) 3

Ans: 1

6) $PbO_2 + 4HCl \rightarrow PbCl_2 + Cl_2 + 2H_2O$. In this reaction PbO_2 act as an

1) Reducing agent 2) Both reducing agent and oxidising agent
3) Oxidising agent 4) Bleaching agent

Ans: 3

7) Oxidation state of middle carbon in C_3O_2 is

1) +2 2) +3 3)-2 4) 0

Ans: 4

8) $xMnO_4^- + Br^- + H_2O \rightarrow xMnO_2 + BrO_3^- + 2OH^-$. The value of x is

1)1 2)2 3)3 4) 4

Ans: 2

9) When a strip of metallic zine is placed in aqueous solution of copper sulphate, the blue colour of the solution disappears due to the formation of

1) Cu^{2+} 2) Zn^{2+} 3) ZnS 4) CuS

Ans: 2

10) In which of the compounds, does manganese exhibits highest oxidation number?

1) MnO_2 2) $KMnO_4$ 3) K_2Mno_4 4) $MnSO_4$

Ans: 2

11) What is change in oxidation number of Carbon in the following reaction?

$CH_{4(g)} + 4Cl_{2(g)} \rightarrow CCl_{4(g)} + 4HCl_{(g)}$

1)0 to +4 2)-4 to +4 3)0 to -4 4) +4 to -4

Ans: 2

12) Which of the following is the correct order for reducing activity?

1) $Zn < Cu > Ag$ 2) $Zn > Cu < Ag$ 3) $Zn < Cu < Ag$ 4) $Zn > Cu > Ag$

Ans: 4

13) The indicator to be used to detect end point in titration of $FeSO_4$ solution with $KMnO_4$ solution in the presence of acid is

1) Phenolphthalein 2) $KMnO_4$ Itself acts as self indicator

3) starch solution 4)methyl orange

Ans: 2

14) The salt which is commonly used in salt bridge is

1) Barium sulphate 2) Aluminium chloride

3) Silver chloride 4) Potassium chloride

Ans: 4

15) Which of the following have no reaction with hydrochloric acid?

1) Mg, Au 2) Ca, Ag 3) Ag, Au 4) Mg, Ca

Ans: 3

II. Fill in the blanks (1 mark)

1. Oxidation Number of sulphur in S_8 molecule is _____

Ans: Zero

2. The element that cannot undergo disproportionation is_____

Ans: Fluorine

3. In any compounds oxidation states of I A & II A group elements are ____ and _____

Ans: $+1 \; and \; +2$

4. Reluctant is the element which can reduce the other substances and itself undergoes _____

Ans: Oxidation

5. Oxidation state of oxygen in peroxides and super oxides are _____ and _____ respectively.

Ans: -1 and $-\frac{1}{2}$

III Very short answer questions (2 marks)

1) What is a redox reaction ? Give an example.

Ans:- In a chemical reactions both oxidation and reduction takes place.

Ex:- $\overset{(0)}{H_2}(g) + \overset{(0)}{Cl_2}(g) \rightarrow 2\overset{(+1)(-1)}{HCl}(g)$

2) What is disproportionation reaction? Give example.

Ans:-The chemical reactions in which same element udder goes both oxidation and reduction simultaneously are called disproportionation reaction.

$\overset{(0)}{Cl_2}(g) + 6\,NaOH(q) \rightarrow 5Na\overset{(-1)}{Cl} + Na\overset{(+5)}{ClO_3} + 3H_2O$

3) Assign oxidation number to the underlined elements in each of the following.

1) $K_2\underline{Mn}O_4$ 2) $\underline{C}_3O_2$

Ans: 1) $K_2\underline{Mn}O_4$

$2(+1)+x+4(-2)=0$

$x-6=0$

$x=+6$

2) $\underline{C}_3O_2$

$3x+2(-2)=0$

$3x-4=0$

$3x=+4$

$x=+4/3$

4) Write formulae for the following compounds:

1)Nickel(II)sulphate 2)Thallium(I) sulphate

Ans: 1)Nickel(II)sulphate 2)Thallium(I) sulphate

Ni^{+2} SO_4^{-2} → $NiSO_4$

Ti^{+1} SO_4^{-2} → Tl_2SO_4

5) What are the oxidation numbers of the underlined elements in the following compounds.

1) $Na\underline{B}H_4$ 2) $\underline{C}_6H_{12}O_6$

2) **Ans:** 1) $Na\underline{B}H_4$

$+1+x+4(-1)=0$

$+1+x-4=0$

$x-3=0$

$x=+3$

2) $\underline{C}_6H_{12}O_6$

$6x+12(+1)+6(-2)=0$

$6x+12-12=0$

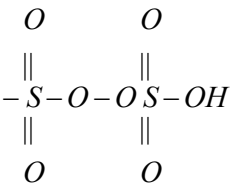
$6x=0$

$x=0$

6) What is the oxidation number of the underlined elements in the following compounds?

1) $H_2S_2O_8$

Ans: 1)



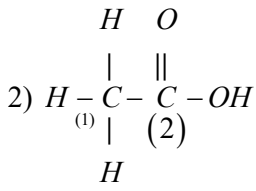
$2x+6(-2)+2(-1)+2(+1)=0$

$2x=+12$

$x=+6$

2) $\underline{C}H_3\underline{C}OOH$

2)



Oxidation state at 1st carbon : -3

Oxidation state at 2nd carbon : +3.

IV. Short answer questions (4 marks)

1) Balance the following redox reactions by ion-electron method (in acidic medium):

$Cr_2O_{7(aq)}^{2-} + Fe_{(aq)}^{2+} \rightarrow Cr_{(aq)}^{3+} \rightarrow Fe_{(aq)}^{3+}$

Ans:-

	Oxidation Half reaction	Reduction Half Reaction
	$Fe^{+2} \rightarrow Fe^{+3}$	$Cr_2O_7^{-2} \rightarrow Cr^{+3}$
Balance the Atoms other than O &H	-	$Cr_2O_7^{-2} \rightarrow 2Cr^{+3}$
Balance of "O" Atoms	-	$Cr_2O_7^{-2} \rightarrow 2Cr^{+3} + 7H_2O$
Balance of "H" Atoms	-	$Cr_2O_7^{-2} + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O$
Balance of charges	$Fe^{+2} \rightarrow Fe^{+3} + e^-$	$Cr_2O_7^{-2} + 14H^+ + 6\bar{e} \rightarrow 2Cr^{+3} + 7H_2O$
Equalizing of electrons	$\left(Fe^{+2} \rightarrow Fe^{+3} + e^-\right)_{\times 6}$	$(Cr_2O_7^{-2} + 14H^+ + 6\bar{e} \rightarrow 2Cr^{+3} + 7H_2O)_{\times 1}$

Adding two half reactions

$$6Fe^{+2} \rightarrow 6Fe^{+3} + 6e^-$$

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

$$\underline{Cr_2O_7^{-2} + 14H^+ + 6Fe^{+2} \rightarrow 2Cr^{+3} + 6Fe^{+3} + 7H_2O}$$

2) Balance the following reactions by ion-electron method (in acidic medium):

$$Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$$

Ans:-

	Oxidation half reaction	Reduction half reaction
	$SO_3^{-2} \rightarrow SO_4^{-2}$	$Cr_2O_7^{-2} \rightarrow Cr^{+3}$
Balance the Atoms other than O & H	-	$Cr_2O_7^{-2} \rightarrow 2Cr^{+3}$
Balance of "O" Atoms	$SO_3^{-2} + H_2O \rightarrow SO_4^{-2}$	$Cr_2O_7^{-2} \rightarrow 2Cr^{+3} + 7H_2O$
Balance of "H" Atoms	$SO_3^{-2} + H_2O \rightarrow SO_4^{-2} + 2H^+$	$Cr_2O_7^{-2} + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O$
Balance of charges & equalizing the electrons	$(SO_3^{-2} + H_2O \rightarrow SO_4^{-2} + 2H^+ + 2e^-)_{\times 3}$	$(Cr_2O_7^{-2} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O)_{\times 1}$

Adding to Half reactions

$$3SO_3^{-2} + 3H_2O \rightarrow 3SO_4^{-2} + 6H^+ + 6e^-$$

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

$$\underline{3SO_3^{-2} + Cr_2O_7^{-2} + 8H^+ \rightarrow 3SO_4^{-2} + 2Cr^{+3} + 4H_2O}$$

3) Balance the following redox reaction by ion- electron method (in basic medium):

$$Cr(OH)_3 + IO_3^- \rightarrow I^- + CrO_4^{2-}$$

Ans:

	Oxidation Half Reaction	Reduction Half Reaction
	$Cr(OH)_3 \rightarrow CrO_4^{-2}$	$IO_3^- \rightarrow I^-$
Balance the Atoms other than O & H	-	-
Balance of "O" Atoms	$Cr(OH)_3 + H_2O \rightarrow CrO_4^{-2}$	$IO_3^- \rightarrow I^- + 3H_2O$
Balance of "H" Atoms	$Cr(OH)_3 + H_2O + 5OH^- \rightarrow CrO_4^{-2} + 5H_2O$	$IO_3^- + 6H_2O \rightarrow I^- + 3H_2O + 6OH^-$
Balance of charge & Equalizing the electrons	$\left(Cr(OH)_3 + H_2O + 5OH^- \rightarrow CrO_4^{-2} + 5H_2O + 3e^-\right)_{\times 2}$	$(IO_3^- + 6H_2O + 6e^- \rightarrow I^- + 3H_2O + 6OH^-)_{\times 1}$

Adding two half reactions

$$2Cr(OH)_3 + 2H_2O + 10OH^- \rightarrow 2CrO_4^{-2} + 10H_2O + 6e^-$$

$$\underline{IO_3^- + 6H_2O + 6e^- \rightarrow I^- + 3H_2O + 6OH^-}$$

$$\underline{2Cr(OH)_3 + IO_3^- + 4OH^- \rightarrow 2CrO_4^{-2} + I^- + 5H_2O}$$

4) Balance the following redox reaction by ion- electron method (in basic medium):

$$MnO_4^-(aq) + Br^-(aq) \rightarrow MnO_2(s) + BrO_3^-(aq)$$

Ans:

	Oxidation Half Reaction	Reduction Half Reaction
	$B\bar{r} \rightarrow BrO_3^-$	$MnO_4^- \rightarrow MnO_2$
Balance the Atoms other then O & H	-	-
Balance of "O" Atoms	$B\bar{r} + 3H_2O \rightarrow BrO_3^-$	$MnO_4^- \rightarrow MnO_2 + 2H_2O$
Balance of "H" Atoms	$B\bar{r} + 3H_2O + 6OH^- \rightarrow BrO_3^- + 6H_2O$	$MnO_4^- + 4H_2O \rightarrow MnO_2 + 2H_2O + 40H^-$
Balance of charge & equalizing the electrons	$\left(B\bar{r} + 3H_2O + 60H^- \rightarrow BrO_3^- + 6H_2O + 6e^-\right)_{\times}$	$\left(MnO_4^- + 4H_2O + 3\bar{e} \rightarrow 2H_2O + 4OH^-\right)_{\times 2}$

Adding two half reactions

$$B\bar{r} + 3H_2O + 6OH^- \rightarrow BrO_3^- + 6H_2O + 6e^-$$

$$\underline{2MnO_4^- + 8H_2O + 6e^- \rightarrow 2MnO_2 + 4H_2O + 8OH^-}$$

$$2MnO_4^- + B\bar{r} + H_2O \rightarrow 2MnO_2 + BrO_3^- + 2OH^-$$

5) Write the net ionic equation for the reaction of potassium dichromate with sodium nitrite. In an acid solution to give chromium (III) ion and nitrate ion.

Ans:

	Oxidation Half reactions (OHR)	**Reduction Half reaction (RHR)**
	$NO_2^- \rightarrow NO_3^-$	$Cr_2O_7^{-2} \rightarrow Cr^{+3}$
Balance the Atoms other than O &H	-	$Cr_2O_7^{-2} \rightarrow 2Cr^{+3}$
Balance of "O" Atoms	$NO_2^- + H_2O \rightarrow NO_3^-$	$Cr_2O_7^{-2} \rightarrow 2Cr^{+3} + 7H_2O$
Balance of "H" Atoms	$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+$	$Cr_2O_7^{-2} + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O$
Balance of charge & equalizing the electrons	$\left(NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-\right)_{\times 3}$	$(Cr_2O_7^{-2} + 14H^+ + 6e^- \rightarrow 2Cr^{+2} + 7H_2O)_{\times 1}$

Adding two half reactions

$$3NO_2^- + 3H_2O \rightarrow 3NO_3^- + 6H^+ + 6e^-$$

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

$$\underline{3NO_2^- + Cr_2O_7^{-2} + 8H^+ \rightarrow 3NO_3^- + 2Cr^{+3} + 4H_2O}$$

6. Balance the following redox reactions by ion-electron method (in acidic medium):

$MnO_4^-{}_{(aq)} + SO_2(g) \longrightarrow Mn^{2+}{}_{(aq)} + HSO^-{}_{4\,(aq)}$

Ans:

	Oxidation Half reaction	**Reduction half Reaction**
	$SO_2 \rightarrow HSO_4^-$	$MnO_4^- \rightarrow Mn^{+2}$
Balance the atoms other then O & H	-	-
Balance of "O" Atoms	$SO_2 + 2H_2O \rightarrow HSO_4^-$	$MnO_4^- \rightarrow Mn^{+2} + 4H_2O$
Balance of "H" Atoms	$SO_2 + 2H_2O \rightarrow HSO_4^- + 3H^+$	$MnO_4^- + 8H^+ \rightarrow Mn^{+2} + 4H_2O$
Balance of charge & equalizing the electrons	$\left(SO_2 + 2H_2O \rightarrow HSO_4^- + 3H^+ + 2e^-\right)_{\times 5}$	$\left(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{+2} + 4H_2O\right)_{\times 2}$

Adding two half reactions

$$5SO_2 + 10H_2O \rightarrow 5HSO_4^- + 15H^+ + 10e^-$$

$$\underline{2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{+2} + 8H_2O}$$

$$\underline{2MnO_4^- + 5SO_2 + 2H_2O + H^+ \rightarrow 2Mn^{+2} + 5HSO_4^-}$$

7. Explain the following.

1) Oxidation 2) Reduction 3)Oxidizing agent 4) Reducing agent

Ans: 1) **Oxidation**: Loss of electrons

Or

Addition of oxygen atom.

Or

Removal of hydrogen atom.

2) **Reduction**: Gain of electrons

Or

Addition of hydrogen atom

Or

Removal of Oxygen atom.

3) **Oxidising Agent:** Chemical reactions in which a substance can oxidize the other substance and its self reduced is called oxidising Agent .

4) **Reducing Agent:** Chemical reactions in which a substance can reduce the other substance and its self oxidised is called reducing agent.

8. Justify that the following reactions are redox reactions:

1) $CuO(s)+H_2(g)\rightarrow Cu(s)+H_2O(g)$

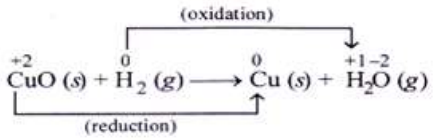
2) $Fe_2O_3(s)+3CO(g)\longrightarrow 2Fe(s)+3CO_2(g)$

3) $2K(s)+F_2(g)\rightarrow 2KF(s)$

4) $4NH_3(g)+5O_2(g)\rightarrow 4NO(g)+6H_2O(g)$

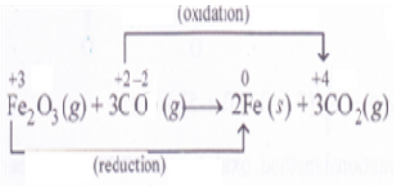
Ans:

1)



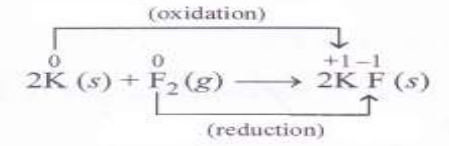
In the above reaction both oxidation & reduction takes Place. So it is redox reaction.

2)



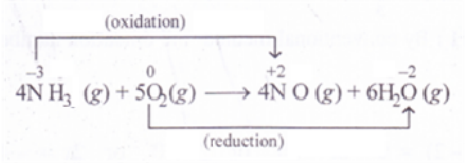
In the above reaction both oxidation and reduction takes place. So it is redox reaction.

3)



In the Above reaction both oxidation & Reduction takes place. So it is redox reaction.

4)



In the above reaction both oxidation & reduction takes place. So it is redox reaction.

9. Consider the elements : Cs, Ne, I and F

1) Identify the element that exhibits only negative oxidation state

2) Identify the element that exhibits only positive oxidation state

3) Identify the element that exhibits both positive and negative oxidation states

4) Identify the element that exhibits neither positive nor negative oxidation states

Ans: 1) "F" Exhibit only negative oxidation state because it is the highest Electro Negative element.

2)"Cs" Exhibit only positive oxidation state because it Is the highest electropositive element .

3)"I" Can exhibit both positive and negative oxidation states.

Ex: In IF_7, I exhibits "+7"

In KI, I exhibit "-1"

4)"Ne" is the inert gas element, does not participate in chemical reactions. So it exhibits neither negative nor positive oxidation states.

10. Write about different types of redox reactions.

Ans: A chemical reaction in which both oxidation and reduction takes place are called redox reactions

Type: 1.Combinaiton reactions:- The redox reactions, in which two

(Or) More elements combine to form a new compound

Ex:- $\overset{(o)}{C}(S)+\overset{(o)}{O_2}(g)\rightarrow \overset{(+4)(-2)}{CO_2}(g)$

2.Decompositon reactions : The redox reactions in which chemical compounds decomposed into two (or) more simple compounds (or) elements.

Ex:- $\overset{(+1)(+5)(-2)}{2KClO_3}\rightarrow \overset{(+1)(-1)}{2KCl}+3\overset{(o)}{O_2}$

3.Displacement reactions: The redox reactions in which an ion in a compound is replaced with an another ion (or)Element .

$\overset{(o)}{Zn}+\overset{(+2)}{Cu}SO_4(aq)\rightarrow \overset{(+2)}{Zn}SO_4(aq)+\overset{(O)}{C}u(s)$

4.Disproportionate reactions: The redox reactions, in which an element in one oxidation state is simultaneously oxidised and reduced.

Ex:- $3\overset{(O)}{Cl_2}+6NaOH\rightarrow 5Na\overset{(-1)}{Cl}+Na\overset{(+5)}{Cl}O_3+3H_2O$

5.Comproportionation reaction :- The redox reactions, in which two species with the same element in different oxidation states form a single product

Ex:- $\overset{+2}{A}g(aq)+Ag(s)\rightarrow 2\overset{+}{A}g(aq)$

11. Identify the substance oxidised, reduced, oxidising agent and reducing agent for the following reaction.

$$\underset{(+1)}{2AgBr(s)} + \underset{(-1/3)}{C_6H_6O_2} - (aq) \rightarrow \underset{(o)}{2Ag(s)} + 2HBr(aq) + \underset{(o)}{C_6H_4O_2(aq)}$$

Ans: $2AgBr(s) + C_6H_6O_2 - (aq) \rightarrow 2Ag(s) + 2HBr(aq) + C_6H_4O_2(aq)$

Oxidised substance: $C_6H_6O_2$

Reduced substance: $AgBr$

Oxidising agent: $Ag\ Br$

Reducing agent: $C_6H_6O_2$

V .LONG ANSWER QUESTIONS (8 marks)

1. Write the balanced equation for the oxidation of sulphite ions to sulphate ions in acid medium by permanganate ion.

Ans:

	Oxidation Half reaction(OHR)	**Reduction Half reaction(RHR)**
	$SO_3^{-2} \rightarrow SO_4^{-2}$	$MnO_4^- \rightarrow Mn^{+2}$
Balance the Atoms other then O & H	-	-
Balance of "O" atoms	$SO_3^{-2} + H_2O \rightarrow SO_4^{-2}$	$MnO_4^- \rightarrow Mn^{+2} + 4H_2O$
Balance of "H" atoms	$SO_3^{-2} + H_2O \rightarrow SO_4^{-2} + 2H^+$	$MnO_4^- + 8H^+ \rightarrow Mn^{+2} + 4H_2O$
Balance of charge & equalizing the electrons	$\left(SO_3^{-2} + H_2O \rightarrow SO_4^{-2} + 2H^+ + 2e^{-1}\right)_{\times 5}$	$\left(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{+2} + 4H_2O\right)_{\times 2}$

Adding two half reactions

$$5SO_3^{-2} + 5H_2O \rightarrow 5SO_4^{-2} + 10H^+ + 10e^-$$

$$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{+2} + 8H_2O$$

$$5SO_3^{-2} + 2MnO_4^- + 6H^+ \rightarrow 5SO_4^{-2} + 2Mn^{+2} + 3H_2O$$

2) Oxalic acid is oxidised by permanganate ion in acid medium of Mn^{+2} balance the reaction by ion-electron method.

Ans:

	Oxidation half reaction (OHR)	**Reduction Half reaction (RHR)**
	$C_2O_4^{-2} \rightarrow CO_2$	$MnO_4^- \rightarrow Mn^{+2}$
Balance the Atoms other than O& H	$C_2O_4^{-2} \rightarrow 2CO_2$	$MnO_4^- \rightarrow Mn^{+2}$
Balance of "O" Atoms	-	$MnO_4^- \rightarrow Mn^{+2} + 4H_2O$
Balance of H atoms	-	$MnO_4^- + 8H^+ \rightarrow Mn^{+2} + 4H_2O$
Balance of charge & equalizing the electrons	$\left(C_2O_4^{-2} \rightarrow 2cO_2 + 2e^-\right)_{\times 5}$	$\left(MnO_4^- + 8H^+ + 5e^- \rightarrow 4H_2O\right)_{\times 2}$

Adding two half reactions

$$5C_2O_4^{-2} \rightarrow 10\,CO_2 + 10e^{-1}$$

$$2MnO_4^- + 16H^+ 10e^- \rightarrow 2Mn^{+2} + 8H_2O$$

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

3. Assign oxidation number to the underlined elements in each of the following species:

1) $NaH_2\underline{P}O_4$ 2) $NaH\underline{S}O_4$ 3) $H_4\underline{P_2}O_7$ 4) $K_2\underline{Mn}O_4$ 5) $Ca\underline{O_2}$ 6) $H_2\underline{S}_4O_6$

7) $H_2\underline{S_2}O_7$ 8) $KAI(\underline{S}O_4)_2 12H_2O$

Answer:- 1) $NaH_2\underline{P}O_4$

$$+1+2(+1)+x+4(-2)=0$$
$$+3+x-8=0$$
$$x=+5$$

2) $NaH\underline{S}O_4$

$$(+1)+(+1)+x+4(-2)=0$$
$$+2+x-8=0$$
$$x=+6$$

3) $H_4\underline{P_2}O_7$

$$4(+1)+2x+7(-2)=0$$
$$+4+2x-14=0$$
$$2x=+10$$
$$x=+5$$

4) $K_2\underline{Mn}O_4$

$$2(+1)+x+4(-2)=0$$
$$+2+x-8=0$$
$$x-6=0$$
$$x=+6$$

5) CaO_2 (Calcium peroxide)

$$+2+2x=0$$
$$2x=-2$$
$$x=-1$$

6) $NaBH_4$

$$+1+x+4(-1)=0$$
$$x-3=0$$
$$x=+3$$

7) $H_2S_2O_7$

$$2(+1)+2x+7(-2)=0$$
$$+2+2x-14=0$$
$$2x-12=0$$
$$2x=+12$$
$$x=+6$$

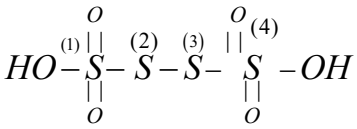
8) $KAl(\underline{S}O_4)_2$

$$+1+(+3)+2x+8(-2)=0$$
$$+4+2x-16=0$$
$$2x-12=0$$
$$2x=+12$$
$$x=+6$$

4) What are the oxidation numbers of the underlined elements in each of the following and how do you rationalise your results?

1) $H_2\underline{S_4}O_6$ 2) $\underline{Fe}_3O_4$ 3) $\underline{C}H_3\underline{C}H_2OH$ 4) $\underline{C}H_3\underline{C}OOH$

Ans: 1) $H_2\underline{S_4}O_6$



For 1^{st} and 4^{th} sulphur O.N is ‘’+5”

For 2^{nd} and 3^{rd} Sulphur’s having O.N is zero

Average O.N Of “S” is +2.5

2) Fe_3O_4

$$3x+4(-2)=0$$
$$3x=+8$$
$$x=+8/3$$

3) $\overset{(2)}{\underline{C}}H_3\overset{(1)}{\underline{C}}H_2OH$

For 1^{st} carbon having O.N is "-1"

For 2^{nd} carbon having O.N is "-3"

So, Average O.N of carbon in ethyl Alcohol is –"2"

4) $\overset{(2)}{C}H_3\overset{(1)}{C}OOH$

For 1^{st} Carbon O.N is "-3"

For 2^{nd} Carbon O.N is "+3"

So, Average O.N of Carbon in Acetic Acid is zero.

5) Phosphorus when heated with $NaOH$ solution gives phosphine (PH_3) and $H_2PO_2^-$.

Give the balanced equation.

Ans:

	Oxidation half reaction (OHR)	**Reduction Half reaction (RHR)**
	$P_4 \rightarrow H_2PO_2^-$	$P_4 \rightarrow PH_3$
Balance the atoms other than O & H	$P_4 \rightarrow 4H_2PO_2^-$	$P_4 \rightarrow 4PH_3$
Balance of "O" atoms	$P_4 + 8H_2O \rightarrow 4H_2PO_2^-$	-
Balance of "H" atoms	$P_4 + 8H_2O + 8OH^- \rightarrow 4H_2PO_2^- + 8H_2O$	$P_4 + 12H_2O \rightarrow 4PH_3 + 120H^-$
Balance of charge & Equalizing elections	$\left(P_4 + 8H_2O + 80\overline{H} \rightarrow 4H_2PO_2^- + 8H_2O + 4e^-\right)_{\times 3}$	$\left(P_4 + 12H_2O + 12e^- \rightarrow 4PH_3 + 12OH^-\right)_{\times 1}$

Adding two half reactions

$$3P_4 + 24H_2O + 24OH^- \rightarrow 12H_2PO_2^- + 24H_2O + 12e^-$$

$$\underline{P_4 + 12H_2O + 12e^- \rightarrow 4PH_3 + 12OH^-}$$

$$\underline{4P_4 + 12H_2O + 12\overline{OH} \rightarrow 4PH_3 + 12H_2PO_2^-}$$

UNIT 8
ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES AND TECHINQUES

I **Multiple choice questions (1 mark)**

1 **Alicyclic compounds are**

(1) Aromatic compounds (2) Aliphatic cyclic compounds

(3) Heterocyclic compounds (4) None of the above

Ans: 2) Aliphatic cyclic compounds

2 **What is the formula of Anisole?**

(1) $C_6H_5OCH_3$ (2) $C_6H_5NH_2$

(3) $C_6H_5COCH_3$ (4) C_6H_5OH

Ans: 1) $C_6H_5OCH_3$

3 **Which of the following is an example for heterocyclic and aromatic compound?**

(1) Aniline (2) Benzene (3) Furan (4) Naphthalene

Ans: 3) Furan

4 **In which of the following functional groups are arranged as per the priority order of the functional groups?**

(1) –COOH > –CHO > –CN > C = O (2) –COOH > –CHO > C=O > –CN

(3) > C = O > – CN > –COOH > –CHO (4) –COOH > –CN > –CHO > C=O

Ans: 2) –COOH > –CN > –CHO > C=O

5 **The IUPAC name of neopentane is**

(1) 2–methylpropane (2) 2, 2–dimethylbutane

(3) 2–methylbutane (4) 2, 2–dimethylpropane

Ans: 4) 2, 2–dimethylpropane

6 **Hybridisation of Carbon in $\overset{+}{C}H_3$**

1) SP^3 (2) SP^2 (3) SP (4) SP^3d

Ans: 2) SP^2

7 **Which of the following involves the displacement or shifting of sigma bonded electrons?**

(1) Mesomeric effect (2) Inductive effect

(3) Resonance (4) Electromeric effect

Ans: 2) Inductive effect

8 **Kjeldahl method is not applicable to compounds containing nitrogen in**

1) Nitro group (2) Azo group (3) Nitrogen present in the ring (4) All

Ans: 4) All

9 **Crude oil in petroleum industry is separated by**

(1) Distillation (2) Fractional distillation

(3) Crystallisation (4) solvent extraction

Ans: 2) Fractional Distillation

10 **Chloroform and aniline are easily separated by the technique**

1) Distillation 2) Fractional Distillation

3) Sublimation 4) Chromatography

Ans: 1) Distillation

II Fill in the blank type questions (1 mark)

1 **Ethy alcohol and methyl alcohol can be separated by_____**
Ans: Distillation

2 **Steam distillation is applied to separate substances which are ____**
Ans: Steam volatile

3 **Nitrogen, sulphur and halogens present in an organic compound are detected by ____**
Ans: Lassiagne's Test

4 **Methoxy propane and Ethoxy propane are ____ isomers**
Ans: Metamers or meta isomers

5 **Propanone and propanal are ____isomers**
Ans: Functional group isomers

III. **One Word Answer Questions (1Mark)**

1. **Define Catenation**

Ans The self linking ability of an element to form long chains and rings is called catenation.

2. What is the hybridization of Carbon in ethane?

Ans SP^3

3. What is the hybridization of Carbon in CH_3F

Ans SP^3

4. Define functional group.

Ans Functional Groups are a "particular grouping of components in which the distinctive chemical reactions of these molecules are accountable".

5. What is homologous series?

Ans Homologous series is a series of compounds with similar chemical properties and some functional groups differing from the successive member by CH_2. Carbon chains of varying lengths have been observed in organic compounds having the same general formula.

6. How many chain isomers possible for alkane having molecular formula C_5H_{12}

Ans 3. Those are n-pentane, isopentane and neopentane

7. What is an electrophile?

Ans The species which is electron deficient and can accept the electrons is called electrophile.
Ex: BF_3

8. **What is an electromeric effect?**

Ans The electromeric effect is a temporary effect in organic compounds that occurs when a reagent attacks a multiple bond. The effect is characterized by the transfer of a pair of electrons to one of the atoms in the bond. This transfer creates a dipole in the molecule.

9. What is Differential extraction?

Ans Differential extraction is a technique used to isolate specific components from a mixture. It's used in forensic DNA analysis, and in labs to test DNA samples.

10. What is distillation?

Ans This method is used to separateVolatile liquids from non volatile impurities and the liquids having enough difference in their boiling points.
Liquids having different boiling points vapourises at different temperatures.
These vapours are cooled and the liquids formed are collected separately.
Eg : $CHCl_3$ (b.pt. 334 K) and $C_6H_5NH_2$ (b.pt. 457 K) are easily separated by distillation

technique.

11. What is retardation factor?

Ans In chromatography, the retardation factor, often represented as R_f is a ratio that indicates how far a component (solute) has travelled in a chromatographic separation relative to the solvent front.

12. Write the principle involved in paper chromatography.

Ans The Principle behind paper chromatography is differential movement of substances through a stationary phase (paper containing water) and a mobile phase (solvent)

13. Give two examples for alicyclic compounds.

Ans Cyclopropone, cyclobutane, cyclopean, cyclohexane and this derivatives, as well as compounds with fased like decalin

14. Give examples for benzenoid aromatic compounds.

Ans Benzene, flune, Phenol and naphthalene.

1V. Very short answer questions (2 marks)

1. How many π and σ it bonds are present in each of the following molecules?

(a) $HC \equiv CCH = CHCH_3$

(b) $CH_2 = C = CHCH_3$

Ans a) $4\sigma C-C; 6\sigma C-H; 1\pi C=C; 2\pi C \equiv C$

(b) $3\sigma C-C; 6\sigma C-H; 2\pi C=C$

2. What is the type of hybridisation of each carbon in the following compounds?

$CH_3CH = CHCN$

Ans sp^3, sp^2, sp^2, sp

3. What is carbocation? Give example.

Ans The species having positively charged carbon is called carbonium ion.

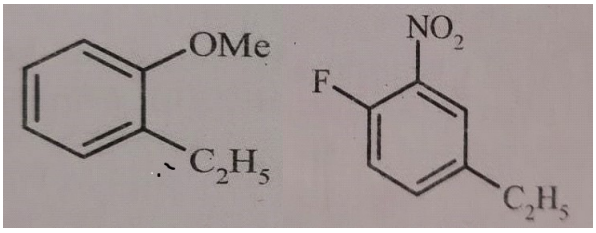
Ex : $\overset{+}{C}H_3$

4. What is metamerism? Give example

Ans Metamerism is a type of structural isomerism where compounds have the same molecular formula but differ in the arrangement of alkyl groups around a polyvalent functional group, such as ether or an amine. Consider ethers. Two ethers with the same molecular formula (C4H10O) but different alkyl groups attached to the oxygen atom are metamers. For example, methoxypropane (CH_3-O-CH_2-CH2-CH3) and ethoxyethane (CH_3-CH_2-O-CH_2-CH_3) are metamers.

5. Write the IUPAC names of

a) b)

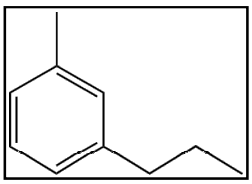


Ans a) 1-ethyl Anisole

b) 4-Ethyl – 1 – fluoro-2-nitrobenzene.

6. Write the IUPAC names of

a) $CH_3CH(OH)CH_3$ b)

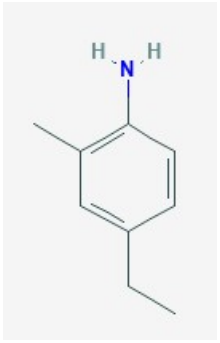


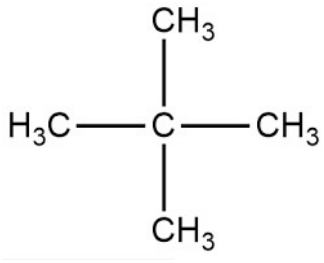
Ans a) 2-propanol

b) 1-Methyl 3-propyl cyclohexane

7. Write the structures of a) 4-ethyl 2-methyl aniline b)Neopentane.

Ans

a) 

b) 

8. Explain the principle of adsorption chromatography.

Ans Chromatography has been developed as a method of separation components of a mixture generally between the stationary phase and a mobile phase.

Chromatography involves the three steps given below:

a) Adsorption and retention of a mixture of substances on the stationary phase and separation of adsorbed substances by the mobile phase to different distances on the stationary phase.

b) Recovery of the substances separated by a continuous flow of the mobile phase (known as elution) and

c) Qualitative and quantitative analysis of the eluted substances.

9. Explain the following term "Crystallisation"

Ans

- This technique is used for the purification of solid organic compounds.
- This method is based on the difference in the solubilities of the compound and the impurities in a suitable solvent.
- The impure compound is dissolved in a solvent in which it is partially soluble at room temperature and appreciably soluble at higher temperature.
- The solution is concentrated to get a nearly saturated solution on cooling the solution pure compound crystallises.
- On repeating this process finally gets the very pure compound.

10. What are electrophiles and nucleophiles? Give examples.

Ans Electrophiles: The species which are electron deficient and can accept electrons are called electrophiles.

Ex: BF_3

Nucleophiles: The species which are electron rich and can accept electrons are called nucleophiles.

Ex: OH^-, CN^-

V .Short answer questions (4 marks)

1. What is position isomerism and functional isomerism? Give one example for each

Ans **Position isomerism:** This type of isomerism arises due to the difference in the position of substituent group or in the position of multiple bond.

e.g.:

1. $CH_3 - CH_2 - CH_2 - CH_2 - Cl$ — 1 – chloro butane

   $CH_3 - CH(Cl) - CH_2 - CH_3$ — 2 – chloro butane

e.g.: 2. $CH_3 - CH_2 - C = CH$ 1 – butyne

$CH_3 - C = C - CH_3$ 2 – butyne

Functional group isomerism: This type of isomerism arises in carbon compounds having the same molecular formula but with different functional groups.

e.g.: 1. $CH_3 - CH_2 - CH_2 - OH$ 1 – proparal (C_3H_3O)

$CH_3 - CH_2 - O - CH_3$ methoxy ethane (C_3H_8O)

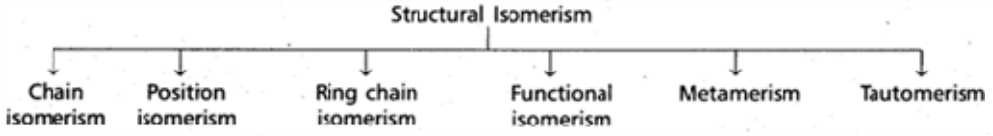
e.g.: 2. $CH_3 - CH_2 - OH$ Ethanol

$CH_3 - O - CH_3$ methoxy methane

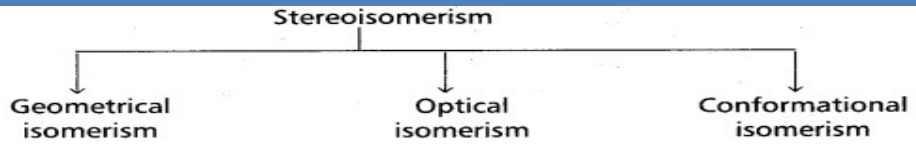
2. Explain the difference between structural isomers and stereo isomers.

Ans Structural isomerism: When the isomerism is due to difference in the arrangement of atoms within the molecule, without any reference to space, the phenomenon is known as Structural isomerism. In this type of isomerism, the isomers possess the same molecular formula, but different structural formula.

Structural isomerism is further classified into different types :



Stereoisomerism : The stereoisomers have the same molecular and structural formula, but differ in the arrangement of atoms or groups in space. Thus the phenomenon exhibited by two or more compounds with the same molecular and structural formulae, but different spatial arrangement of atoms or groups. The spatial arrangement of atoms or groups is also referred to as configuration of the molecule. It is further classified into three types.



3. Write about hyperconjugation?

Ans Hyperconjugation is a stabilizing effect where electrons in a sigma bond (σ-bond) interact with an adjacent empty or partially filled p-orbital or pi-orbital, leading to delocalization and increased stability, often seen in alkenes, carbocations, and free radicals.

Hyperconjugation, also known as "no-bond resonance," involves the delocalization of electrons from a sigma bond (typically a C-H or C-C bond) into an adjacent empty or partially filled p-orbital or pi-orbital.

The electrons in a sigma bond, which are usually localized between two atoms, can interact with an adjacent empty or partially filled p-orbital or pi-orbital.

This interaction leads to the delocalization of electrons, meaning they are no longer confined to a single bond but are spread out over a larger region of the molecule. The delocalization of electrons stabilizes the molecule by reducing electron density in specific regions and increasing it in others.

4. Write a note on :

a) Distillation

b) Distillation under reduced pressure

Ans **a) Distillation:** This process is useful for the purification of liquids contaminated with nonvolatile impurities. The impure liquid is boiled in a distillation flask and the vapours are condensed and collected in a receiver. This method can also be used to separate liquids if only their boiling points differ by above 40°C. However, in the case of liquids that have boiling point difference less than 40°C fractional distillation method is used.

b) Distillation under reduced pressure : This method is useful to purify liquids that have very high boiling points and those which decompose at or below their boiling points. If the external pressure is reduced the liquid boils at lower temperature than its normal boiling point without decomposition.

5. What are the different types of organic reactions?

Ans Organic reactions are mainly classified into four types known as

i) Addition rections.

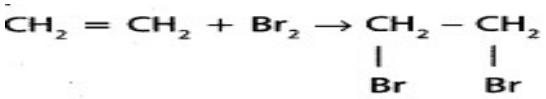
ii) Substitution reactions

iii) Elimination reactions

iv) Molecular rearrangements.

i) Addition reactions: In these reactions the reagent and the substract combine together to give a single product.

e.g.:



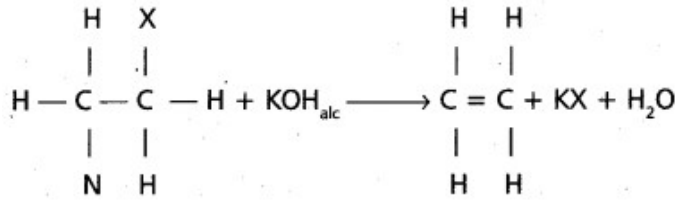
Depending on the reagent added in the slow rate determining step, addition reactions are again classified as

a) Electrophilic addition reactions,
b) Nucleophilic addition reactions
c) Free radical addition reactions.

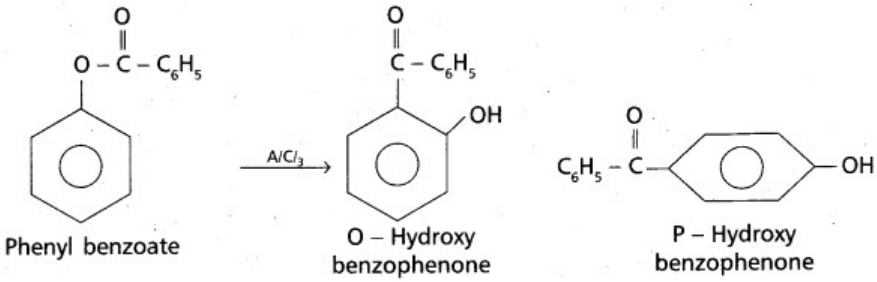
ii) Substitution reactions: In these reactions on atom or a group of the substrate species is replaced by another atom or group. These are again classified as a) Electrophilic substitution b) Nucleophilic substitution and c) Free radical substitution reactions on the basis of the reagent involved in the rate determining step.

e.g.-: $O H^{-}_{(aq)} + R - X \rightarrow HO - R + X^{-}_{(aq)}$

iii) Elimination reactions: In these reactions two or more atoms or groups of an organic substrate are removed to form multiple bonds.



iv) Molecular rearrangements: Here one organic species (generally less stable) rearranges to other species (generally more stable). For example. Fries rearrangement.



6. Write the equations involved in the detection of Nitrogen, Halogens and sulphur in organic compounds.

Ans Lassaigne's Test : –

- A small dry sodium piece is taken in a fusion tube and heated gently till the sodium melts.
- To this molten sodium a small amount of organic compound is added and heated until it changes red hot.
- This red hot tube is plunged in a china dish containing water and this content is boiled, cooled and filtered.
- The obtained filtrate is known as Lassaigne's extract.
- This test is used to detect the elements Nitrogen, Sulphur, halogens etc..

a) Detection of Nitrogen: –

The Lassaigne's extract is made alkaline by adding few drops of dol. NaOH. to this freshly prepared $FeSO_4$ solution is added and warmed then few drops of $FeCl_3$ are added followed by acidification with Cone. HCl (or) H_2SO_4. A bluish green colouration indicates the nitrogen.

$Na + C + N \rightarrow NaCN$

$2NaCN + FeSO_4 \rightarrow Na_2SO_4 + Fe(CN)_2$

$Fe(CN)_2 + 4NaCN \rightarrow Na_4[Fe(CN)_6]$

$3Na_4[Fe(CN)_6] + 4FeCl_3 \rightarrow Fe_4[Fe(CN)_6]_3 + 12\ NaCl$ (Prussian blue colouration)

b) Detection of Halogens: The sodium fusion extract is acidified with HNO_3 and is treated with $AgNO_3$ solution.

$Ag + X \rightarrow AgX$

- White PPt indicates $Cl^{\ominus}$ ion
- Pale yellow PPt indicates $Br^{\ominus}$ ion
- Yellow PPt indicates $I^{\ominus}$ ion

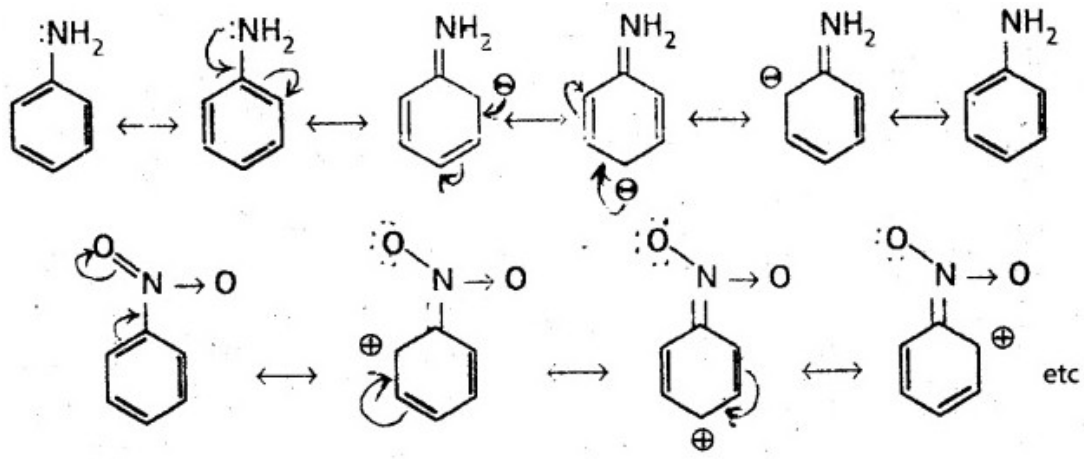
c) Detection of Sulphur: To the sodium extract freshly prepared sodium nitroprusside solution. A deep violet colouration takes place.

$S^{-2} + [Fe(CN)_5NO]^{2+} \rightarrow [Fe(CN)_5\ NOS]^{4-}$ Violet

7. Write a note on resonance effect.

Ans Resonance effect: It is the polarity produced in a molecule by the interactions of two n bonds or between a π bond and a lone pair of electrons present on adjacent atoms. This effect is transmitted through the chain.

If the transfer of electron is away from the atoms or substituent group attached to the conjugated system, then the molecule gets some of its positions high electron density as in aniline and it is given (+ R). If the shift of electrons are towards the atom or substituent group it is (- R) as in nitrobenzene.



Groups showing (+ R) are X, – OH, – OR, – COOR, – NH_2, – NHR, – NR_2, – NHCOR etc.

(- R) effect are – COOH, CHO, > C = O, – CN, – NO_2.

8. Explain inductive effect with a suitable example.

Ans Inductive effect: The electron donating or electron with drawing effect of a groups an atom that is transmitted by the polarisation of electrons in σ bonds is called inductive effect.

Illustration: Consider the molecule $CH_3 – CH_2 – CH_2 – Cl$. There is a 'σ' covalent bond between carbon atom and chlorine atom. The electron pair between them is not equally shared. The more electronegative chlorine atom tends to attract the shared pair more towards itself. Due to this, the electron density tends to be greater nearer chlorine atom than carbon atom. It is generally represented

as $\overset{\delta+}{C}-\overset{\delta-}{Cl}$ (or) $-C\longrightarrow Cl$ But, carbon atom bonded to chlorine atom is itself attached to other carbon atoms. Therefore, the effect can be transitted further $H_3\overset{3}{C}-\overset{2}{C}H_2\longrightarrow \overset{1}{C}H_2\longrightarrow Cl$

"Inductive effect is defined as the polarisation of a bond caused by the polarization of adjacent σ bond".

(-I) effect i.e., electron with drawing effect is in the order

$^{+}NH_3 > NO_2 > CN > SO_3H > CHO > CO > COOH > COCl > COOR > CONH_2 > F > G > Br > I > OH > OR > NH_2 > C_6H_5 > H.$

+ I effect is $-N^{-}R > -O^{--}$; – Se > S > -O ; $-C(CH_3)_3 > -CH(CH_3)_2 > -CH_2CH_3 > -CH_3$.

9. Write about homolytic fission and heterolytic fission

Ans Homolytic fission (or homolysis) is the symmetrical breaking of a covalent bond where each fragment receives one electron of the shared pair, forming free radicals,

In homolyric fission, two free radicals, which are neutral species with an unpaired electron.While heterolytic fission (or heterolysis) is the asymmetrical breaking where one fragment takes both electrons, resulting in ions.

10. Discuss the chemistry of Lassaigne's test.

Ans Lassaigne's Test: –

- A small dry sodium piece is taken in a fusion tube and heated gently till the sodium melts.
- To this molten sodium a small amount of organic compound is added and heated until it changes red hot.
- This red hot tube is plunged in a china dish containing water and this content is boiled, cooled and filtered.
- The obtained filtrate is known as Lassaigne's extract.
- This test is used to detect the elements Nitrogen, Sulphur, halogens etc.,

Detection of Nitrogen: –

The Lassaigne's extract is made alkaline by adding few drops of dil. NaOH. to this freshly prepared $FeSO_4$ solution is added and warmed then few drops of $FeCl_3$ are added followed by acidification with Cone. HQ (or) H_2SO_4. A bluish green colouration indicates the nitrogen.

$Na + C + N \rightarrow NaCN$

$2NaCN + FeSO_4 \rightarrow Na_2SO_4 + Fe(CN)_2$

$Fe(CN)_2 + 4NaCN \rightarrow Na_4[Fe(CN)_6]$

$3Na_4[Fe(CN)_6]$ 4- $4FeCl_3 \rightarrow Fe_4[Fe(CN)_6]_3 + 12\ NaCl$ (Prussian blue colouration)

VI .Long answer questions

1 Write a note on :

a) Distillation

b) Fractional distillation

c) Distillation under reduced pressure

d) Steam distillation

Ans **a) Distillation:** This process is useful for the purification of liquids contaminated with nonvolatile impurities. The impure liquid is boiled in a distillation flask and the vapours are condensed and collected in a receiver. This method can also be used to separate liquids if only their boiling points differ by above 40°C. However, in the case of liquids that have boiling point difference less than 40°C fractional distillation method is used.

b) Fractional distillation: Fractional distillation for liquids that have B.Pt difference less than 40°C. The technique here is that vapours of liquid mixture. When pass through long fractionating column vapours of the liquid with high B.Pt condense and those with low B.Pt pass over through the condenser get condensed and collected in the receiver.

Here, long tubes having different shapes and designs to fit for particular requirements are used.

These are called fractionating columns. The liquid mixture is taken in a distillation flask i.e., fitted with a fractionating column at its mouth. At the upper end of the column, there is a provision to connect it to the water condenser.

c) Distillation under reduced pressure: This method is useful to purify liquids that have very high boiling points and those which decompose at or below their boiling points. If the external pressure is reduced the liquid boils at lower temperature than its normal boiling point without decomposition.

d) Steam distillation: Here liquids which are immiscible in water passes high boiling point and steam volatile are purified. In this method steam is passed into the hot liquid that is to be purified. The mixture of steam and vapour of volatile organic compound come out. This is because of the sum of the vapour pressures of steam and the liquid to be purified become equal to the atmospheric pressure. They are passed through the condenser and condensed and finally collected in the receiver. The water layer and the organic liquid layer are separated using a separating funnel.

2 **Write a brief note on chromatography.**

Ans .Chromatography has been developed as a method of separation components of a mixture generally between the stationary phase and a mobile phase.

Chromatography involves the three steps given below :

a) Adsorption and retention of a mixture of substances on the stationary phase and separation of adsorbed substances by the mobile phase to different distances on the stationary phase.

b) Recovery of the substances separated by a continuous flow of the mobile phase (known as elution) and

c) Qualitative and quantitative analysis of the eluted substances.

Classification :

Two general chromatography techniques are discussed below. They are : adsorption chromatography

Partition chromatography.

Adsorption chromatography is based on the adsorption of different compounds on an adsorbent to different degrees. Generally used adsorbents are silica gel and alumina. A mobile phase is allowed to move over a stationary phase, the adsorbent. The components of the mixture move to different distances over the stationary phase.

Differential adsorption principle is used in

a) column chromatography and

b) thin layer chromatography.

Column chromatography: In the column chromatography the components of a mixture are separated by a column of adsorbent packed in a glass tube. The column is fitted with a stopcock at its lower end. The mixture to be adsorbed on the adsorbent is placed at the top of the stationary phase. A suitable eluant, either a single solvent or a mixture of solvents is allowed to flow down the column slowly. Depending on the degree to which the compounds are adsorbed the components are separated. The most readily absorbed substances are retained near the top and other come down accordingly to various distances.

Thin layer chromatography (TLC): This also involves adsorption differences. Here the adsorbent, say silica gel or alumina is coated over a glass plate of suitable size in thin layer. The plate is called TLC plate or chromoplate. The solution of the mixture to be separated is applied as a small spot at about 2 cm from the bottom of the plate. The plate is then kept in a closed jar containing the eluant. As the eluant rises up the plate, the components of the mixture move up along with the eluant to various distances depending on their degree of adsorption.

The relative adsorption of a component of the mixture is expressed in terms of its Retardation factor (R_f) value.

$$R_f = \frac{\text{Distance moved by the substance from base line(X)}}{\text{Distance moved by the solvent from base line (Y)}}$$

3 **Explain the following :**

a) Column chromatography

b) Thin layer chromatography

c) Partition chromatography

Ans **a) Column chromatography :** In the column chromatography the components of a mixture are separated by a column of adsorbent packed in a glass tube. The column is fitted with a stopcock at its lower end. The mixture to be adsorbed on the adsorbent is placed at the top of the stationary phase. A suitable eluant, either a single solvent or a mixture of solvents is allowed to flow down the column slowly. Depending on the degree to which the compounds are adsorbed the components are separated. The most readily absorbed substances are retained near the top and other come down

accordingly to various distances.

b) Thin layer chromatography (TLC): This also involves adsorption differences. Here the adsorbent, say silica gel or alumina is coated over a glass plate of suitable size in thin layer. The plate is called TLC plate or chromoplate. The solution of the mixture to be separated is applied as a small spot at about 2 cm from the bottom of the plate. The plate is then kept in a closed jar containing the eluant. As the eluant rises up the plate, the components of the mixture move up along with the eluant to various distances depending on their degree of adsorption.

The relative adsorption of a component of the mixture is expressed in terms of its Retardation factor (R_f) value.

$$R_f = \frac{\text{Distance moved by the substance from base line(X)}}{\text{Distance moved by the solvent from base line (Y)}}$$

c) Partition chromatography : This is based on continuous differential partitioning of components of a mixture between the Stationary phase and the mobile phase. In paper chromatography, for example, a special paper called chromatography paper contains water trapped in it which acts as the stationary phase. The chromatography paper spotted with the solution of the mixture at the base is suspended in a suitable solvent or a mixture of solvents.This solvent acts as the mobile phase. The solvent rises up the paper by capillary action and moves over the spot. The paper selectively retains different components as per their differing partition in mobile and stationary phase. The paper strip so developed is known as chromatogram. The spots of the separated coloured compounds are detected and for colourless compounds other methods like spraying suitable reagent, are used.

4 Explain the estimation of nitrogen of an organic compound by

a) Duma's method

b) Kjeldahl's method.

Ans **Estimation of nitrogen:** There are two methods to estimate nitrogen in the given organic compound known as

i) Duma's method and

ii) Kjeldahl's method.

i) Duma's method : In this method a known weight of organic compound is heated strongly with coarse cupric oxide. Carbon and hydrogen get oxidised to carbon dioxide and water vapour respectively. Nitrogen if present is converted to nitrogen gas. Even if some nitrogen is converted to its oxides. They are reduced by hot copper gauze to nitrogen. The product gases are collected over a solution of potassium hydroxide. CO_2 is absorbed by KOH solution. Nitrogen is collected over potassium hydroxide solution and its volume is found out.

$$C_xH_yN_z + \left[2x + \frac{y}{2}\right]CuO \longrightarrow xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2 + \left[2x + \frac{y}{2}\right]Cu$$

Suppose that 'a' g of organic compound gives V_1 ml of N_2 at room temperature TK. If atmosphere pressure is P and aqueous tension at TK is P, then the pressure of nitrogen gas at TK is (P – p). Let (P – p) = P_1 Reduce the volume of nitrogen to standard temperature 273 K and standard pressure 760 mm.

Volume of nitrogen at STP is v = P1 V1 T1×273760

28 g of nitrogen at STP occupies 22400 ml

? g. of nitrogen at STP occupies Vml. of nitrogen.

28 × V22400g

'a' g. of organic compound 28×V22400 g of nitrogen.

100 g organic compound has ? of nitrogen = 100a×28×V22400 g

ii) Kjeldah's method : This is another method to estimate nitrogen. In this method, the compound is heated with concentrated sulphuric acid in the presence of small amount of $CuSO_4$.

Nitrogen is quantitatively converted into ammonium sulphate. The contents of the flask are transferred to another flask and heated with excess of sodium hydroxide solution to liberate ammonia gas. Ammonia gas so liberated is passed and absorbed in a known volume of known concentrated sulphuric acid that is relatively more in amount than that is required to neutralise NH_3 gas. Now, the excess of acid remained after the neutralisation by NH_3 is titrated against a standard solution of alkali. From the above, the amount of H_2SO_4 used to neutralise NH_3 is calculated. From this, the mass of ammonia formed is calculated and from that percentage of nitrogen is calculated.

Organic compound + H_2SO_4 →$(NH_4)_2$ SO_4

$(NH_4)_2SO_4$ + 2 NaOH → Na_2SO_4 + 2 H_2O + 2 NH_3

2 NH_3 + H_2SO_4 → $(NH_4)_2SO_4$

Calculation :

Let the mass of organic compound taken be 'a' g.

Let the volume of H_2SO_4 initially taken be 'V_{ml}' and its molarity M.

After passing the NH_3 gas into the above acid, if the remaining acid is titrated with M molar NaOH and it consumes V_1 ml. of NaOH for complete neutralisation, then from the formula

MV_1n1 (NaOH) = MV_2n_2 (H_2SO_4)

From the stoichiometric equation

2 NaOH + H_2SO_4 → Na_2SO_4 + 2H_2O

n_1 = number of moles of NaOH = 2; n_2 = number of moles of H_2SO_4 = 1

$$\frac{M_1V_1}{2}(NaOH) = \frac{M_2V_2}{1}(H_2SO_4)$$

Therefore, the volume of H_2SO_4 neutralised by NH_3 is [V – V1/2] ml

(or) it is equal to 2 [V – V1/2] ml. of M molar NH_3 solution.

1000 ml. of 1M NH_3 solution contains 17g. of NH_3 or 14g. of N_2

2[V – V1/2] ml ml. of 'M' NH_3 solution contains

$14\times M\times 2[V-V_1/2]/1000$ g. of nitrogen.

Percentage of nitrogen = $\frac{14\times M\times 2\left(V-\frac{V_1}{2}\right)}{1000}\times\frac{100}{a}$

5 Explain inductive effect with a suitable example.

Ans Inductive effect: The electron donating or electron with drawing effect of a group an atom that is transmitted by the polarisation of electrons in σ bonds is called inductive effect.

Illustration: Consider the molecule $CH_3 - CH_2 - CH_2 - Cl$. There is a 'σ' covalent bond between carbon atom and chlorine atom. The electron pair between them is not equally shared. The more electronegative chlorine atom tends to attract the shared pair more towards itself. Due to this, the electron density tends to be greater nearer chlorine atom than carbon atom. It is generally represented

as $\overset{\delta+}{C}-\overset{\delta-}{Cl}$ (or) $-C\longrightarrow Cl$ But, carbon atom bonded to chlorine atom is itself attached to other carbon atoms. Therefore, the effect can be transitted further $H_3\overset{3}{C}-\overset{2}{C}H_2\longrightarrow\overset{1}{C}H_2\longrightarrow Cl$

"Inductive effect is defined as the polarisation of a bond caused by the polarization of adjacent σ bond".

(-I) effect i.e., electron with drawing effect is in the order

$^{+}NH_3 > NO_2 > CN > SO_3H > CHO > CO > COOH > COCl > COOR > CONH_2 > F > G > Br > I > OH > OR > NH_2 > C_6H_5 > H.$

+ I effect is $-N^{-}R > -O^{--}$; $-Se > S > -O$; $-C(CH_3)_3 > -CH(CH_3)_2 > -CH_2CH_3 > -CH_3$.

6 Write a note on mesomeric effect.

Ans **<u>Mesomeric effect:</u>**

"The electron pair displacement caused by an atom or group along a chain by a conjugative mechanism is called the mesomeric effect of that atom or group".

Salient features of the mesomeric effect:

i) Permanent effect operating in the ground state of the molecule.

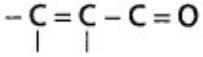
ii) Lone pairs and n electrons are involved and operate through conjugative mechanism of electron displacement.

iii) It influences the physical properties, reaction rates etc.

Groups which tend to increase the electron density of the rest of the molecule are said to have (+M) effect. Such groups tend to posses lone pairs of electrons.

e.g. : $H_2\ddot{N}-\underset{|}{C}=\underset{|}{C}$ – Hence $-NH_2$ group has + M effect

Groups that decrease the electron density of the rest of the molecule are said to have (-M) effect. Unsaturated groups having polar character have – M effect.



. Here C = O group decreases the electron density of the remaining molecule. It has – M effect.

+ M effect is – F > – Cl > – Br > – I;

$-NR_2$ > OR > F;

– NH_2 > – OH > – F;

– OR > – SR > SeR

– O > – OR

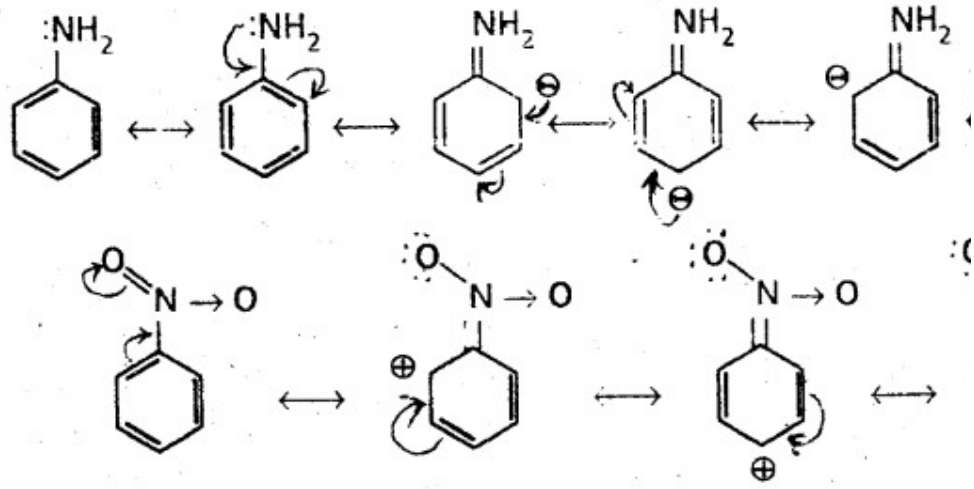
– M effect is = O > = NR > = CR_2

= NR_2< =NR ≡ N > ≡ CR

7 **Describe resonance effect with one example.**

Ans Resonance effect: It is the polarity produced in a molecule by the interactions of two n bonds or between a π bond and a lone pair of electrons present on adjacent atoms. This effect is transmitted through the chain.

If the transfer of electron is away from the atoms or substituent group attached to the conjugated system, then the molecule gets some of its positions high electron density as in aniline and it is given (+ R). If the shift of electrons are towards the atom or substituent group it is (- R) as in nitrobenzene.



Groups showing (+ R) are X, – OH, – OR, – COOR, – NH_2, – NHR, – NR_2, – NHCOR etc.

(- R) effect are – COOH, CHO, > C = O, – CN, – NO_2.

8 **Explain different types of organic reactions with suitable examples.**

Ans Organic reactions are mainly classified into four types known as

i) Addition rections.

ii) Substitution reactions

iii) Elimination reactions

iv) Molecular rearrangements.

i) Addition reactions: In these reactions the reagent and the substract combine together to give a single product.

e.g:

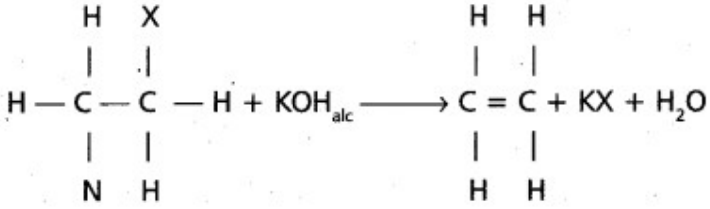
$$CH_2 = CH_2 + Br_2 \rightarrow \underset{\underset{Br}{|}}{CH_2} - \underset{\underset{Br}{|}}{CH_2}$$

Depending on the reagent added in the slow rate determining step, addition reactions are again classified as a) Electrophilic addition reactions, b) Nucleophilic addition reactions c) Free radical addition reactions.

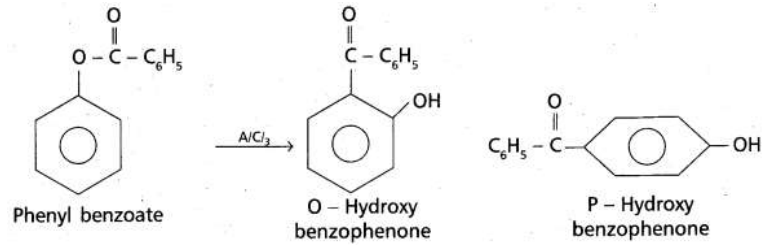
ii) Substitution reactions: In these reactions on atom or a group of the substrate species is replaced by another atom or group. These are again classified as a) Electrophilic substitution b) Nucleophilic substitution and c) Free radical substitution reactions on the basis of the reagent involved in the rate determining step.

e.g.-: $O\overline{\quad}H_{(aq)} + R - X \rightarrow HO - R + X_{(aq)}$

iii) Elimination reactions: In these reactions two or more atoms or groups of an organic substrate are removed to form multiple bonds.



iv) Molecular rearrangements: Here one organic species (generally less stable) rearranges to other species (generally more stable). For example. Fries rearrangement.



UNIT-9
HYDROCARBONS

I Multiple choice questions: (1 Mark)

1. **Alkyl halides reacts with sodium in the presence of dry ether give alkanes this reaction is named as**

   1. Wurtz reaction
   2. Kolbe's reaction
   3. Decarboxylation
   4. Dehydrohalogenation

   Ans: 1) Wurtz reaction.

   Bromo methane + 2 Sodium + Bromo methane $\xrightarrow{dry\ Ether}$ Ethane +2Sodium

   Bromo ethane + 2 Sodium + Bromoethane $\xrightarrow{dry\ Ether}$ n-butane + 2Sodium

   Imp: This reaction is used for the preparation of higher alkane having even number of carbon atoms.

2. **Complete combustion of methane gives**

   1) $CO_2 + H_2O$ 2) $CO_2 + H_2$ 3) $COCl_2$ 4) $CO + CO_2 + H_2O$

   Ans: 1) $CO_2 + H_2O$

   Methane +oxygen gas $\xrightarrow[oxidized\ \ to]{completely}$ $CO_{2(g)} + H_2O$ + large Amount of heat.

   $CH_{4(g)} + 2O_2 \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

3. **How many conformations are possible for ethane**

   1) 2 2) 3 3) Infinite 4) 5

   Ans: 3) Infinite

4. **By which reaction ethene is obtained from ethyne**

   1.Oxidation 2.Polymerisation
   3. Hydrogenation 4. Dehydrogenation

   Ans: 3) Hydrogenation.

   $HC \equiv CH + H_2 \xrightarrow{Pt|pd|Ni} H_2C = CH_2$

   Ethyne on the electrophilic addition of dihydrogen give, Ethene

5. **When one mole of an alkene produces one mole of methanal and one mole of ethanal on ozonolysis followed by hydrolysis. The alkene is**

   1. Ethylene 2. Propene 3. 2- butene 4. 2,3 dimethyl 1,2- butene

   Ans: 2) Propene.

   $H_3C-CH=CH_2 + O_3 \rightarrow H_3C-CH(O-O)CH_2 \xrightarrow{Zn-H_2O} CH_3CHO + HCHO$

   propene ozonide Ethanal Methanal

6. **The reaction of HBr with $CH_3 - CH = CH_2$ at 400^0C yields.**

   1. $CH_2Br\ CH = CH_2$ 2. $CH_3 - CH\ Br - CH_3$
   3. $CH_3 - CH_2 - CH_2\ Br$ 4. $CH_2Br - CH_2 - CH_2\ BR$

   Ans: 2) $\mathbf{CH_3 - CH\ Br - CH_3}$.

According to Markovnikov's rule where hydrogen atom adds to the carbon atom with more hydrogens. Bromine to carbon with less hydrogens .

$$H_3C-CH=CH_2+\overset{+}{H}Br^{-1}\xrightarrow{400^{o}c}H_3C-\underset{\underset{Br}{|}}{CH}-CH_3$$

2 - Bromo propane .

7. When acetylene is passed through dil H_2SO_4 in presence of the $\prod$ the compound formed is .

1.Ethanol 2.Ethanal 3.Ethanoic acid 4.Propanone

Ans: 2) Ethanal

$$HC\equiv CH\xrightarrow[Hg\ SO_4]{dil\ H_2SO_4}H\underset{\underset{OH}{|}}{C}=CH_2\leftrightarrow H\underset{\underset{O}{||}}{C}-CH_3\ \text{(Kolbe reaction)}$$

Isomerisation = Keto - enol tautomerism

8. Acetylene hydrogens are acidic because

1. Sigma electron density of C-H bond in acetylene is nearer to carbon which has 50% S- Character .
2. Acetylene has only one hydrogen on each carbon.
3. Acetylene contains least number of hydrogen among the possible hydrocarbons having two carbons .
4. Acetylene belongs to the class of alkynes with Molecular Formula C_nH_{2n-2}.

Ans: 1) Sigma e^- density of (Carbon – hydrogen) bond in acetylene is nearer to carbon which has 50% S- Character .

9. Aromatic compounds burn with sooty flame because

1.They have a ring structure of carbon atoms
2.They have a relatively high percentage of hydrogen
3.They have a relatively high percentage of carbon
4.They resist reaction with oxygen of air .

Ans: 3) They have a relatively high percentage of carbon.

Explanation: - In aromatic hydrocarbons 1) High carbon to $\mathbf{H_2}$ ratio, this means they have more carbon atoms relative to hydrogens .

2. In sufficient oxygen: These need more oxygen for fully combust. In many cases there is insufficient oxygen available lead into incomplete combustion.

3. Formation of polycyclic aromatic hydrocarbons (PAHS) are Known to be soot precursors .

II. Fill in the blanks : (1Mark)

1) Decreasing order of Acidic behaviour of Ethane, Ethene, Ethyne are _____

Ans: Ethyne > Ethene > Ethane

2) Carbon – carbon single bond length _____ &
Carbon- carbon double bond length_____

Ans: $1.54A^0, 1.34A^0$

3) When Benzene treated with 1- chloropropane in presence of anhydrous $Alcl_3$ _____ is formed.

Ans. Isopropyl benzene (also known as cumene)

$$\mathbf{C_6H_6 + CH_3CH_2CH_2Cl \rightarrow C_6H_5CH(CH_3)_2}$$

According to Friedel-crafts alkylation due to the formation of secondary carbocation (positive charge on the second carbon) which is more stable than primary cation. As a result the reaction favours the formation of Isopropyl benzene over n-propylbenzene.

4) The possible isomers for C_4H_{10} are _____

Ans:- 2 chain Isomers

5) Calcium carbide on hydrolysis gives_____

Ans: Acetylene

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

III. One word answer questions: (1Mark)

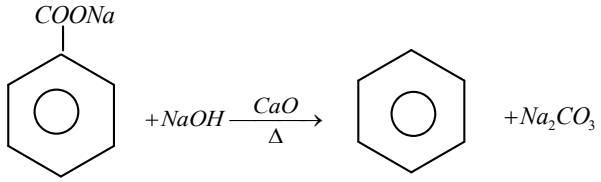
1) How do you prepare ethyl bromide from ethylene?

Ans: By the addition of **HBr** to ethylene

$$\mathbf{H_2C = CH_2 + H^+Br^- \rightarrow H_3C - CH_2Br}$$

2) What is decarboxylation?

Ans. Sodium salt of benzoic acid on heating with soda lime $(NaOH + CaO)$ on heating gives benzene



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

Removal of - COOH group is called decarboxylation this takes place in presence of soda lime $(\mathbf{NaOH + CaO})$

3) What is halogenation?

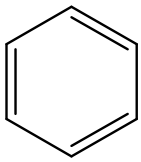
Ans: Halogenation is a chemical reaction where a halogen (Cl_2, Br_2, I_2) is added to molecule like alkane, Alkene, Alkyne, Benzene resulting in the substitution (Alkane, Benzene) addition (Alkene, Alkyne)

$$1.\ \mathbf{CH_4 \xrightarrow[U.V]{Cl_2} CH_3Cl + HCl} \quad 2)\ \mathbf{H_2C = CH_2 \xrightarrow{Br_2} H_2CBr - CH_2Br}$$

$$3)\ \mathbf{C_6H_6 + Cl_2 \xrightarrow[Anhyd]{Fecl_3} C_6H_5Cl + HCl}$$

4) What is meant by aromatization or reforming?

Ans: Aromatization is a chemical reaction where non aromatic compound is converted into an aromatic compound through the loss of hydrogen or other leaving group.

$$3HC \equiv CH \xrightarrow[873\,k]{Red\ hot\ iron\ tube} C_6H_6$$ *or* 

A planar, ring shaped molecule with alternate double bonds is formed.

5) What is meant by Isomerisation?

Ans. Conversion of one Isomer into another isomer is called Isomerisation in presence of $AlCl_3 + ConcHCl$

$$H_3C - CH_2 - CH_2 - CH_3 \xrightarrow[200^0 c - 35 Atm]{conc\ ALCL_3 + HCl} H_3C - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3$$

n-butane. iso butane

6) What is Pyrolysis or cracking?

Ans: Higher alkane when heated to higher temp in the absence of air, break down to form lower alkanes, alkenes & H_2. Breaking of C-C & C-H bonds takes place.

$$C_6H_{14} \xrightarrow{773K} \begin{matrix} C_6H_{12} + H_2 \\ C_4H_8 + C_2H_6 \\ C_3H_6 + C_2H_4 + CH_4 \end{matrix}$$

7) What is Lindlar's catalyst?

Ans: Palladised charcoal partially deactivated with poisons like sulphur compound or quinoline is known as Lindlar's catalyst or partially deactivated palladised charcoal (Pd/C)

8) What is Ozonolysis?

Ans: Unsaturated hydrocarbons like Alkenes, Alkynes reacts with O_3 gives unstable ozonide by the cleavage of double, triple bond and subsequent hydrolysis in presence of Zn/H_2O gives carbonyl compound.

9) What is polymerization?

Ans: It is a chemical reaction in which small molecules (monomers) combine to form a large molecule (polymer)

$$Ethene \xrightarrow[catalyst]{Hightemp\ \&\ press} Polythene$$

$$n(CH_2 = CH_2) \longrightarrow (-CH_2 - CH_2 -)_n\ (Homopolymer)$$

Polymers consisting of a single monomer are homopolymers

Polymers formed from two different monomers are co-polymers

If the reaction is an addition reaction the process is addition polymerization

Condensation reactions cause condensation polymerization. In which a small molecule is eliminated during reaction.

10) What is linear polymerization?

Ans: It is a type of polymerization reaction where monomer units are added to the growing Polymer chain in a linear, sequential manner forming in a long straight chain polymer,

Ethyne →Polyacetylene

Ethene→Polythene

11) What is cyclic polymerization?

Ans: (Three molecules of) ethyne passing through red hot Iron at 873 k undergoes cyclic polymerization to form Benzene.

$$3HC \equiv CH \xrightarrow[tube, 873k]{Red\ Hot\ Iron} \mathbf{C_6H_6} \quad \text{(Benzene)}$$

12) What are arenes?

Ans. Aromatic hydrocarbons are called arenes. (aroma meaning pleasant odour). Most of such compounds were found to contain benzene ring.

13) Give any two examples for o – and p- directing groups

Ans: The groups which direct the incoming group to ortho, para position are called ortho, para directive groups

$-OH$	$-NH_2$	$-NHR$	$-NHCOCH_3$	$-OCH_3$	$-CH_3$	$-C_2H_5$
Hydroxyl	Amino	2°Amino	Acetamido	Methoxy	Methyl	Ethyl

14) What is meant by carcinogenicity?

Ans: Cancer producing property (by causing damage DNA- Human body)

Ex: Benzene and polynuclear compounds

1,2 Benzanthracene, 3-Methyl cholanthrene, 1,2 Benzpyrene etc

15) Give any two examples for m-directing groups

Ans: The groups which direct the incoming group into meta position

$-NO_2$	$-CN$	$-CHO$	$-COR$	$-COOH$	$-COOR$	$-SO_3H$
Nitro	Cyano	Aldehydic	Acyl	Carboxylic	Ester	Sulphonic acid

IV Very Short Answer questions: (2Marks)

1) What is substitution reaction? Explain with one example

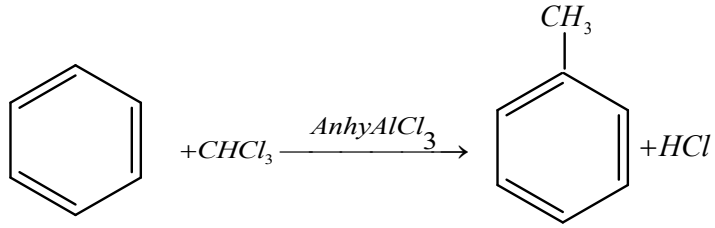
Ans: In organic chemistry, substitution refers to a type of chemical reaction where an atom or group of atoms in a molecule is replaced by another atom or group of atoms.

Ex:- One or more hydrogen atom of Alkanes can be replaced by halogens

$$\mathbf{CH_4 + Cl_2} \xrightarrow{hv} \mathbf{CH_3Cl} \xrightarrow[Cl_2]{hv} \mathbf{H_2CCl_2} \xrightarrow[Cl_2]{hv} \mathbf{HCCl_3} \xrightarrow[Cl_2]{hv} \mathbf{CCl_4 + 4HCl}$$

2) What is Friedel – Crafts alkylation?

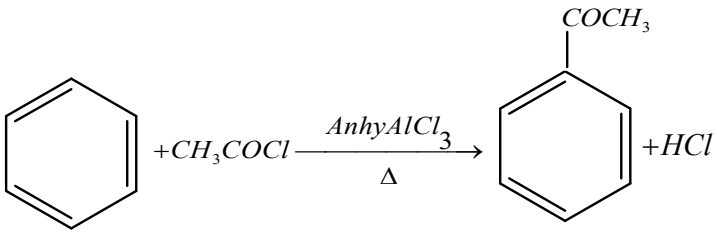
Ans: When benzene is treated with an alkyl halide in the presence of anhydrous, aluminum chloride alkyl benzene is formed



Benzene **Toluene**

3) What is Friedel-Crafts acylation?

Ans: The reaction of benzene with an acyl halide or acid anhydride in the presence of Lewis acids $(AlCl_3)$ yields acyl benzene.



Acetylchloride Acetophenone

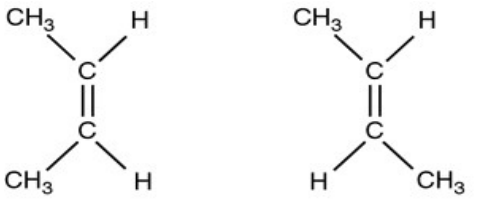
4) Explain the structural isomerism with one example?

Ans: As in alkanes, ethene (C_2H_4) and propene (C_3H_6) can have only one structure but alkenes higher than propene have different structures. " Molecules having same Molecular Formula but differ in their structures called structural Isomers"

$$C_4H_8 \begin{cases} CH_2 = CH - CH_2 - CH_3 & \text{But-1-ene} \\ CH_3 - CH = CH - CH_3 & \text{But-2-ene} \end{cases}$$

5) What is stereo isomerism? Give one example

Ans: Molecules have the same molecular formula and sequence of bonded atoms, but differ in the position of atoms or groups in space. These structures are known as stereo isomers.



cis-2-Butene *trans*-2-Butene

6) Kharash effect is not applicable to the addition of HI to Alkene. Why?

Ans. The **H-I** bond is weaker and Iodine free radicals combine to form Iodine molecules instead of adding to the double bond. Kharasch effect is not applicable to the addition of HI to alkene is not possible.

7) What is meant by Torsional strain?

Ans: Torsional strain also known as eclipsed interaction, when the staggered form changes into the eclipsed form the electron clouds of the carbon-hydrogen bonds come closer to each other resulting in increase in electron cloud repulsions. Which effects stability of a conformation is called torsional strain.

8) How ethane prepared from ethene?

Ans:- Hydrogen gas adds to alkene like ethene in the presence of finely divided catalysts like platinum, pd, Nickel to form ethane this process is called hydrogenation

$$H_2C = CH_2 + H_2 \xrightarrow{pt\ /\ pd\ /\ Ni} H_3C - CH_3$$

Ethane

9) What is Wurtz reaction? Give one example

Ans.: Alkyl halides on treatment with sodium metal in dry ethereal (free from moisture) solution give higher alkanes. This reaction is known as Wurtz reaction and is used for the preparation of higher alkanes containing even number of carbon atoms.

$$H_3C\ Br + 2Na + Br\ CH_3 \xrightarrow{dry\ ether} C_2\ H_6 + 2Na\ Br$$

10) Explain Kolbe's Electrolytic method with an example

Ans: An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms at the anode.

$$2CH_3COONa + 2H_2O \xrightarrow{Electrolysis} CH_3 - CH_3 + 2CO_2 + H_2 + 2NaOH$$

11) Write the halogenations of methane

Ans. All the 4 hydrogens of methane can be replaced by one after one in presence of UV light with $\mathbf{Cl_2}$ atoms called Halogenation and also called chlorination. It is an example for substitution reaction.

$$CH_4 + Cl_2 \xrightarrow[hv]{uv} H_3CCl + HCl$$

Chlo methane

$$H_3CCl + Cl_2 \xrightarrow[hv]{uv} H_2CCl_2 + HCl$$

Dichloromethane

$$H_2CCl_2 + Cl_2 \xrightarrow[hv]{uv} HCCl_3 + HCl$$

Trichloromethane

$$HCCl_3 + Cl_2 \xrightarrow[hv]{uv} CCl_4 + HCl$$

Tetrachloromethane

12) What is the product obtained when methane reacts with steam? Write the equation.

Ans: Methane reacts with steam at 1273 K in the presence of nickel catalyst to form carbon monoxide and dihydrogen

$$H_4C + H_2O \xrightarrow[\Delta]{Ni} CO + 3H_2$$

13) State Markovnikov rule

Ans: Markovnikov rule states that negative part of the addendum (adding molecule) gets attached to the carbon atom which containss lesser number of hydrogen atoms.

$$H_3C-CH=CH_2+H^+-Br^{-1}\begin{cases} H_3C-CH_2-\overset{+}{C}H_2+Br^- & less\ stable \\ H_3C-\overset{+}{C}H-CH_3+Br^- & more\ stable \end{cases}$$

14) Write the bond enthalpy of Carbon - Carbon single bond, Carbon – Carbon double bond and triple bond in kJ/mole

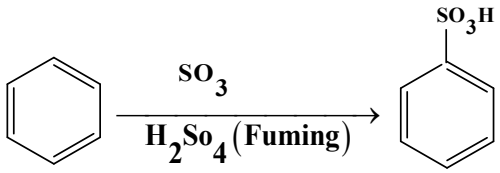
Ans: $C-C$ Single bond enthalpy = 348KJ/mol.

$C=C$ Double bond enthalpy = 681KJ/mol.

$C\equiv C$ Triple bond enthalpy = 823KJ/mol.

15) What is Sulphonation of benzene?

Ans: The replacement of a hydrogen atom by a sulphonic acid group in a ring is called Sulphonation. It is carried out by heating benzene with fuming sulphuric acid (oleum)



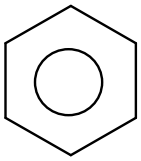
Benzene *Benzene sulphonic acid*

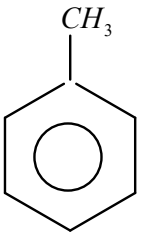
V. Short Answer Questions: (4 Marks)

1) Complete the following reaction and name the products A ,B and C

$$CaC_2 \xrightarrow{H_2O} \mathbf{A} \xrightarrow{hot\ metal\ tube} \mathbf{B} \xrightarrow{AlCl_3+CH_3Cl} \mathbf{C}$$

A is C_2H_2 *or* $(HC\equiv CH)$ *or Ethyne*

B is C_6H_6 *or*  *or Benzene*

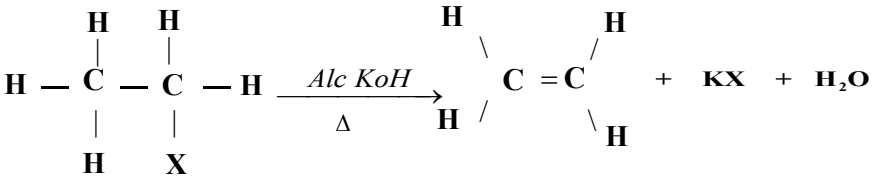
C is $C_6H_5CH_3$ *or*  *or Toluene*

2) What is dehydrohalogenation ? Write the equation for the formation of alkene from alkyl halide .

Ans: Alkyl halides $(R-X)$ on heating with alcoholic potash (Potassium hydroxide dissolved in alcohol say ethanol). Eliminate one molecule of halogen acid to from alkenes. This reaction is

known as dehydrohalogenation i.e removal of halogen acid.

This is example of β - elimination reaction. Since hydrogen atom is eliminated from the β carbon atom (carbon atom next to the carbon to which halogen is attached)

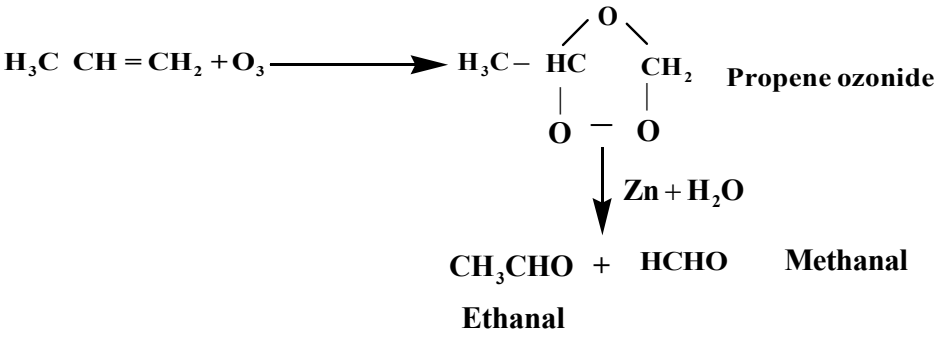


X is = Cl, Br, I . Nature of halogen atom and the alkyl group determine the rate of the reaction . For halogen the rate is $\mathbf{I}_2 > Br_2 > Cl_2$ for alkyl group $3^o > 2^o > 1^o$.

3) Which type of organic compounds reacts with ozone? Explain with one example.

Unsaturated organic compounds, including alkenes, alkynes and some aromatic Compounds reacts with ozone.

The reaction with O_3 : ozonolysis of alkenes invoives the addition of O_3 molecule to alkene to from ozonide, and then cleavage of the ozonide by $Zn + H_2O$ to smaller molecules.



This reaction is highly useful in detecting the position of the double bond in alkenes or other unsaturated compounds.

4) Explain the reactions of acetylene with

a) Na in liquid $\mathbf{NH}_3$ b) Water.

Ans: a) Na **in liquid**

$$\mathbf{HC \equiv CH + Na \rightarrow HC \equiv C^- \ Na^+ + \frac{1}{2} H_2}$$

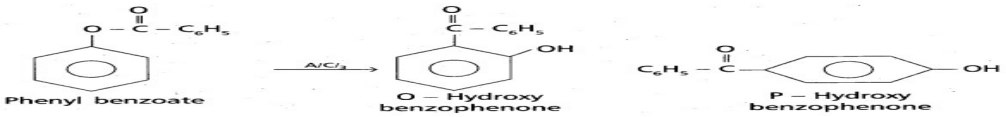
mono sodium ethyinde

$$HC = C^- Na^+ + Na \rightarrow Na^+ C^- \equiv C^- Na^+ \frac{1}{2} H_2$$

Disodium ethynide

Sodium metal & sodamide $\left(\mathbf{NaNH_2}\right)$ are strong bases. They react with ethyne to form sodium acetylide with the liberation of dihydrogen gas. These reactions have not been observed in case of ethene & ethane. Indicating that ethyne is acidic in nature in comparison to ethene and ethane.

b) With Water: Like Alkanes, alkenes and alkynes are also immiscible with water. However one molecule of water adds to alkynes on warming with mercuric sulphate and dilute sulphuric acid at 333k to form carbonyl compounds



5) Explain the addition of HBr to propene with ionic mechanism.

Ans: Addition of hydrogen halides: Hydrogen halides (HCl, HBr, HI) add up to alkenes to form alkyl halides. The order of reactivity is $HI > HBr > HCl$. Like addition of halogens to alkenes, addition of hydrogen halides is also an example of electrophilic addition reaction. Let us illustrate this by taking addition of HBr to symmetrical and unsymmetrical alkenes.

Addition reaction of HBr to unsymmetrical alkenes (Markovnikov Rule):- How will H- Br add to propene ? The two possible products are I and II.

$$CH_3-CH=CH_2+H-Br \rightarrow \begin{cases} \text{I} & CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 \\ & 2-Bromopropane \\ \text{II} & CH_3-CH_2-CH_2-Br \\ & 1-Bromopropane \end{cases}$$

Markovnikov rule- This rule states that negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms. Thus according to this rule, product I i.e…, 2- bromopropane is expected. In actual practice, this is the principal product of the reaction. This generalisation of Markovnikov rule can be better understood in terms of mechanism of the reaction.

Mechanism:- Hydrogen bromide provides an electrophile, H^+, which attacks the double bond to from carbocation as shown below:

$$\overset{3}{H_3C}-\overset{2}{C}H=\overset{1}{C}H_2+H-Br \xrightarrow{H^+}$$

$$H_3C-CH_2-\overset{+}{C}H_2+Br^- \qquad H_3C-\overset{+}{C}H-CH_3+Br^-$$

(*a*) *less stable* primary carbocation

(*b*) *more stable* secondary carbocation

(i)The secondary carbocation (b) is more stable than the primary carbocation (a), therefore, the former predominates because it is formed at a faster rate.

(ii)The carbocation (b)is attacked by Br^- ion to form the product as follows:

$$H_3C-\overset{+}{C}H-CH_3 \xrightarrow{Br^-} H_3C-\underset{\underset{Br}{|}}{CH}-CH_3$$

$2-Bromopropane$ $(major\ product)$

VI. Long Answer Questions: (8 Marks)

1. Describe two methods of preparation of Ethane. Give any three reactions of Ethane.

Ans: Petroleum and natural gas are the main sources of alkanes. Alkanes can be prepared by following methods.

1.From unsaturated hydrocarbons:- Dihydrogen gas to ethene in the presence of finely divided catalyst like platinum, palladium or nickel to from Ethane .

This process is called hydrogenation :

$$CH_2 = CH_2 + H_2 \xrightarrow{Pt/pd/Ni} H_3C - CH_3$$

Ethene Ethane

2.From alkyl halides : - Chloro ethane on reduction with zinc and dil HCl acid give Ethane.

$$C_2H_5Cl \xrightarrow{Zn, H^+} C_2H_6 + HCl$$

Chloro Ethane Ethane

3.Wurtz reaction :- Two molecules of Bromomethane on treatment with sodium metal in dry ether (free from moisture) give ethane

$$CH_3 - Br + 2Na + Br - CH_3 \xrightarrow{dry\ ether} H_3C - CH_3 + 2Na$$ Bromo methane .Ethane .

Bromo methane Ethane

4.Kolbe's Electrolytic method :- An aqueous solution of sodium or potassium salt of acetic acid on electrolysis gives Ethane at the anode.

$$2CH_3C\bar{O}\bar{O}Na^+ + 2H_2O \xrightarrow{Electrolysis} CH_3 - CH_3 + 2CO_2 + H_2 + 2NaOH$$

Sodium acetate Ethane

Reactions of Ethane

1) Halogenation :- It is a substitution reaction. Ethane in presence of diffused sunlight or ultraviolet light reacts with Cl_2 gives chloro ethane .

$$CH_3 - CH_3 + Cl_2 \xrightarrow{hv} H_3C - CH_2Cl + HCl$$

Chloroethane

2) Controlled oxidation :- Ethane on heating with a regulated supply of dioxygen or air at high pressure and in the presence of catalyst like $(CH_3COO)_2$ Mn gives. Ethanoic acid .

$$2CH_3 - CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2 Mn} 2CH_3COOH + 2H_2O$$

Ethanoic acid

2. Describe two methods of preparation of ethylene (Ethene). How does it reacts with the following.Give equations.

a)Ozone b)Cold and dil. alk $\mathbf{KMnO_4}$ c) $\mathbf{Br_2}$

1) From Ethyne :- Partial reduction with calculated amount of dihydrogen in presence of palladised charcoal partially deactivated with poisons like sulphur compound or quinoline give

ethene (Lindlar's catalyst)

$$HC \equiv CH + H_2 \xrightarrow[(Lindlar's\ catalyst)]{Pd/C} H_2C = CH_2$$

2)Dehydrohalogenation of alkyl halide :- $Ethyl\ halide(R-X)\ halide(X) - Cl.Br, I$ on heating with alcoholic potash (KOH dissolved in Alcohol) elimination of one molecule of hydrogen halide to from ethene . $H_3C - \underset{X}{C}H_2 \xrightarrow[\Delta]{alc\ KoH} H_2C = CH_2 + HX$.

This reaction is example for β - elimination reaction.

3)From vicinal dihalides :- Vicinal dihalide means in which two halogen atoms are attached to two adjacent carbon atoms are known as vicinal dihalides. 1,2 dibromo ethane on treatment with Zn metal lose a molecule of $ZnBr_2$ and to form ethane.

$CH_2Br - CH_2Br \xrightarrow{Zn} H_2C = CH_2 + ZnBr_2$. This reaction is known as dehalogenation.

4)From Alcohols by acidic dehydration :- Ethanol on heating with Conc H_2SO_4 form Ethene with elimination of one H_2O molecule .i.e this reaction is an example for acidic dehydration of alcohols , $(Conc\ H_2SO_4)$ and also for B- elimation (Hydrogen from B- Carbon taken by – OH group)

$$\overset{B}{H_3C} - \overset{\infty}{\underset{OH}{CH_2}} \xrightarrow[\Delta]{Conc\ H_2SO_4} CH_2 = CH_2 + H_2O$$

Ethanol Ethene

Reactions :-

1) With Ozone (O_3) :- Ethene with O_3 molecule gives ozonide which on hydrolysis in presence of zinc gives 2 molecules of formaldehyde .

$$CH_2 = CH_2 + O_3 \rightarrow H_2C \underset{O}{\overset{O}{\diagdown\diagup}} CH_2 \xrightarrow[H_2O]{Zn} 2\ \mathbf{HCHO}$$

"Addition of O_3 across the double bond and subsequent hydrolysis is called Ozonolysis ". This reaction is highly useful in detecting (or locating) The position of the double bond in alkenes & other unsaturated compounds.

2) Cold and dil. Alk $KMnO_4$:- Ethene on reaction with cold dil, aqueous solution of $KMnO_4$ (Baeyers' reagent) Produce vicinal glycol.

$$H_2C = CH_2 + H_2O + O \xrightarrow[273K]{dil\ KMnO_4} H_2\underset{OH}{C} - \underset{OH}{CH_2}$$

Glycol(Ethene –1,2 diol)

With this test unsaturation either = bond or ≡bond can be identified by the decolourisation of pink colour of $KMnO_4$

3) With Br_2 :- (Addition of halogens: Halogoens like bromine, chlorine add up to Ethene to from vicinal dihalide.

$$CH_2 = CH_2 + Br - Br \xrightarrow{CCl_4} \underset{Br}{CH_2} - \underset{Br}{CH_2}$$ 1,2 (Dibromoethane)

"Example for electrophilic addition .

"The reddish orange colour of bromine solution in carbon tetra chloride is discharged when bromine adds up to an unsaturation site. This reaction is used as a test for unsaturation"

3. Give two methods of preparation of acetylene. How does it react with water?

1) From calcium carbide: - On industrial scale ethyne is prepared by treating calcium carbide with water. 1) CaC_2 is prepared by heating quick lime with coke . 2) Quick lime can be obtained by heating limestone

$$CaCO_3 \xrightarrow{\Delta} Ca.O + O_2$$

$$CaO + 3C \rightarrow CaC_2 + CO$$

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

2)From vicinal dihalides :- Vicinal dihalides on treatment with alcoholic KOH undergo dehydrohalogenation one molecule of hydrogen halide is eliminated to from alkenyl halide which on treatment with sodamide gives alkynes

$$H_2\underset{Br}{C} - \underset{Br}{C}H_2 + KoH \xrightarrow[-KBr \\ -H_2O]{alochol} H_2C = CHBr \xrightarrow[-NaBr \\ -NH_2]{NaNH_2} HC \equiv CH$$

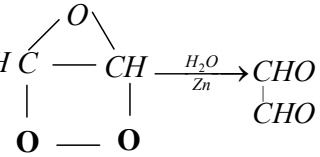
Reactions

1) With H_2O :- Ethyne reacts with one molecule of H_2O with mercuric sulphate & dilute sulphuric acid at 233 K to from carbonyl compounds .

$$HC \equiv CH + H - OH \xrightarrow[233K]{Hg^{2+}, H^+} H_2C = \underset{OH}{C} - H \xrightarrow{Isomerisation} H_3C - \underset{O}{\overset{\|}{C}} - H$$

Ethanal

2) With O_3 : - Ethyne adds Ozone to from unstable Ozonide. Which on hydrolysis in presence of zinc glyoxal is formed on reductive ozonolysis.

$$HC \equiv CH + O_3 \rightarrow$$ 

In Oxidative Ozonolysis, ethyne yield carboxylic acid

$$HC \equiv CH \xrightarrow[H_2O + H_3CCOOH]{O_3} 2HCOOH$$ Formic acid .

4. How does acetylene react with the following reagents? Give the corresponding equations and name the products formed in the reaction.

a)Water b) Hydrogen c)Halogens d) Hydrogen halide

a) With H_2O :- Ethyne reacts with one molecule of H_2O with mercuric sulphate & dilute sulphuric acid at 233 K to from carbonyl compounds .

$$HC \equiv CH + H-OH \xrightarrow[233K]{Hg^{2+},H^+} H_2C = \underset{OH}{C} - H \xrightarrow{Isomerisation} H_3C-\underset{O}{C}-H$$

Ethanal

b) Hydrogen:- $HC \equiv CH + H_2 \xrightarrow{Pt/Pd/Ni} \underset{Ethene}{[H_2C = CH_2]} \xrightarrow{H_2} \underset{Ethane}{H_3C - CH_3}$

This addition reaction is example for electrophilic addition.

c)Halogens: $HC \equiv CH + Br_2 \xrightarrow{CCl_4} HC = \underset{Br}{CH}$ 1,2 di bromo ethene

It is an example of an electrophilic addition.

$$\underset{Br}{HC} = \underset{Br}{CH}\ Br_2 \xrightarrow{CCl_4} HCBr_2 - HCBr_2$$ 1,1,2,2, - tetra bromo ethane

This step is very difficult takes place in high temperature, pressure and catalyst .

*Reddish orange colour of the solution of Br_2 in CCl_4 is decolourised. This is used as a test for unsaturation.

d)Hydrogen halide :-

$$HC \equiv CH + H-Br \rightarrow H_2C = CH-Br \xrightarrow{HBr} H\ \underset{CH_3}{C}\ Br_2$$

1,1 di bromoethane

Two molecules of hydrogen halides (HCl, HBr, HI) add to ethyne to from gem dihalides (in which two halogens are attached to the same carbon atom.

5. What is conformational Isomerism? Write the conformers of ethane?

Ans: Alkanes contain carbon-carbon sigma (σ) bonds. Electron distribution of the sigma molecular orbital is symmetrical around the inter nuclear axis of the C-C bond which is not disturbed due to rotatin about its axis. This permits free rotation about C-C single bond. This rotation results into different spatial arrangements of atoms in space which can change into one another.

Such spatial arrangements of atoms which can be converted into one another by rotation

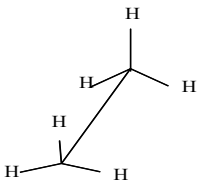
around a C-C single bond are called **conformations** or **conformers** or **rotamers**. Alkanes can thus have infinite number of conformations by rotation around C-C single bonds. However, it may be remembered that rotation around a C-C single bond is not completely free. It is hindered by a small energy barrier of 1-20 kJ mol^{-1} due to weak repulsive interaction between the adjacent bonds. Such a type of repulsive interaction is called torsional strain.

Conformations of ethane: Ethane molecule (C_2H_2) contains a carbon - carbon single bond with each carbon atom attached to three hydrogen atoms. Considering the ball and stick model of ethane, keep one carbon atom stationary and rotate the other carbon atom around the C-C axis. This rotation results into infinite number of spatial arrangements of hydrogen atoms attached to one carbon atom with respect to the hydrogen atoms attached to the other carbon atom. These are called **conformational isomers** (conformers).

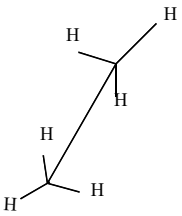
Thus there are infinite numbers of conformations of ethane. However, there are two extreme cases. One such conformation in which hydrogen atoms attached to two carbons are as close together as possible is called eclipsed conformation and the other in which hydrogens are as far apart as possible is known as the staggered conformation. Any other intermediate conformation is called a skew conformation. It may be remembered that in all the conformations, the bond angles and the bond lengths remain the same. Eclipsed and the staggered conformations can be represented by **Sawhorse** and **Newman** projections.

1. Sawhorse projections of ethane

In this projection, the molecule is viewed along the molecular axis. It is then projected on paper by drawing the central C-C bond as somewhat longer straight line. Upper end of the line is slightly tilted towards right or left hand side. The front carbon is shown at the lower end of the line, whereas the rear carbon is shown at the upper end. Each carbon has three lines attached to it corresponding to three hydrogen atoms. The lines are inclined at an angle of 120° to each other. Sawhorse projections of eclipsed and staggered conformations of ethane are depicted like below.



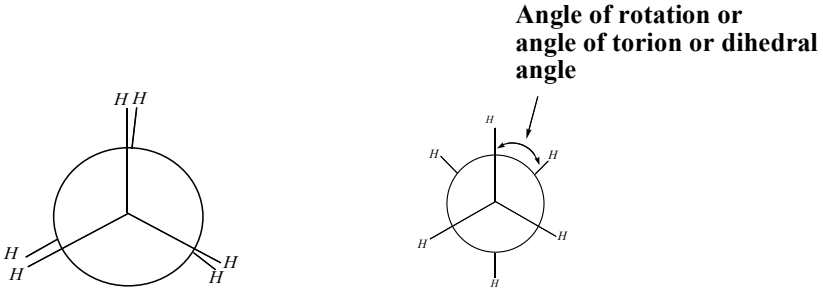
(i) Eclipsed



(ii) Straggered

2. Newman projections of ethane

In this projection, the molecule is viewed at the C-C bond head on. The carbon atom nearer to the eye is represented by a point. Three hydrogen atoms attached to the front carbon atom are shown by three lines drawn at an angle of 120° to each other. The rear carbon atom (the carbon atom away from the eye) is represented by a circle and the three hydrogen atoms are shown attached to it by the shorter lines drawn at an angle of 120° to each other. The Newman's projections are depicted like below



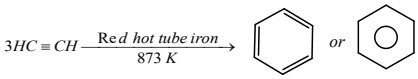
(i) Eclipsed (ii) Straggered

Relative stability of conformations:

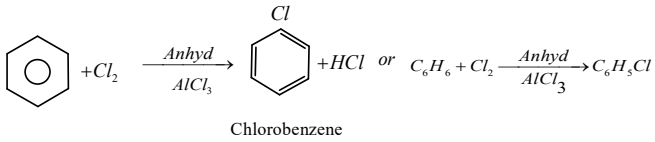
- As mentioned earlier, in staggered form of ethane, the electron clouds of carbon-hydrogen bonds are as far apart as possible. Thus, there are minimum repulsive forces, minimum energy and maximum stability of the molecule.
- On the other hand, when the staggered form changes into the eclipsed form, the electron clouds of the carbon- hydrogen bonds come closer to each other resulting in increase in electron cloud repulsions.
- To check the increased repulsive forces, molecule will have to possess more energy and thus has lesser stability. As already mentioned, the repulsive interaction between the electron clouds. Which affects stability of a conformation, is called torsional strain.
- Magnitude of torsional strain depends upon the angle of rotation about C-C bond. This angle is also called dihedral angle or torsional angle.
- Of all the conformations of ethane, the staggered form has the least torsional strain and the eclipsed form, the maximum torsional strain. Thus it may be inferred that rotation around C-C bond in ethane is not completely free. The energy difference between the two extreme forms is of the order of 12.5 kJ mol^{-1}, which is very small. Even at ordinary temperatures, the ethane molecule gains thermal or kinetic energy sufficient enough to overcome this energy barrier of 12.5 kJ mol^{-1} through intermolecular collisions. Thus, it can be said that rotation about carbon-carbon single bond in ethane is almost free for all practical purposes. It has not been possible to separate and isolate different conformational isomers of ethane.

6. How do we get benzene from acetylene? Give corresponding equations and name the products. Explain the halogenation, alkylation, acylation, nitration and sulphonation of Benzene

Answer: - Benzene from acetylene: - Ethyne on passing through red hot iron tube at 873 K undergoes cyclic polymerization: Three molecules polymerise to from benzene. This is the best route for entering from aliphatic to aromatic compounds.

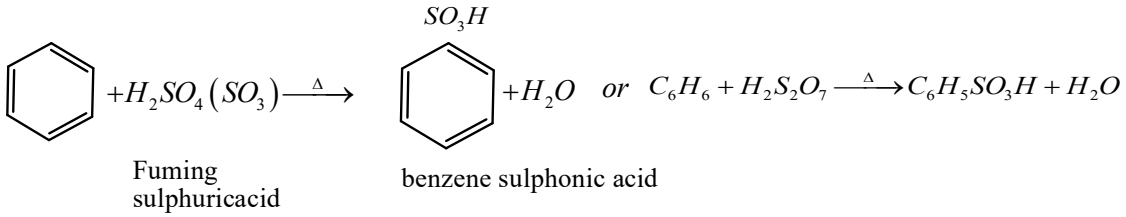


Halogenation: Arenes react with halogens in the presence of a lewis acid like anhydrous $FeCl_3, AlCl_3, FeBr_3$ to yield haloarenes



Chlorobenzene

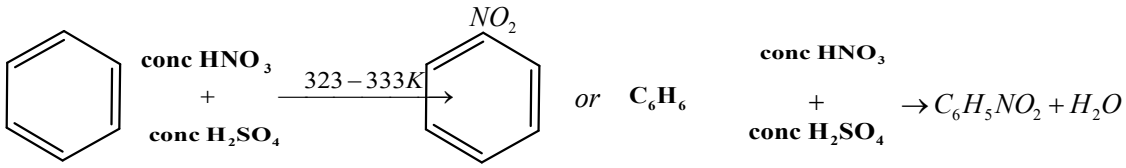
Sulphonation:- The replacement of hydrogen atom by sulphonic acid group in a ring is called sulphonation . It is carried out by heating benzene with fuming sulphuric acid (oleum)



Fuming sulphuricacid

benzene sulphonic acid

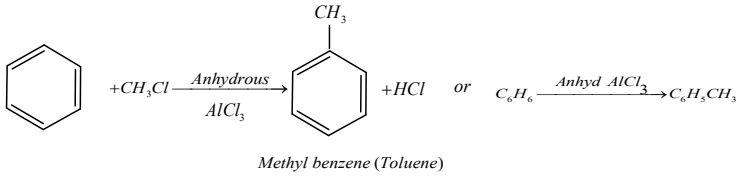
Nitration :- A nitro group is introduced into benzene ring when benzene is heated with a mixture of conc HNO_3 + conc H_2SO_4 (Nitration mixture)



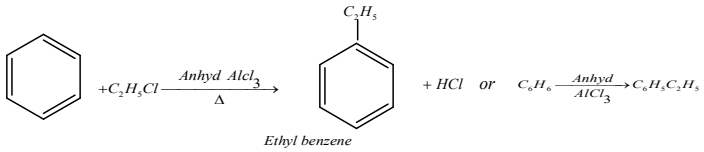
Nitration Mixture

Nitrobenzene

Alkylation : When benzene is treated with an alkyl halide in the presence of anhydrous aluminium chloride alkyl benzene is formed this reaction is called Friedel Crafts alkylation reaction.

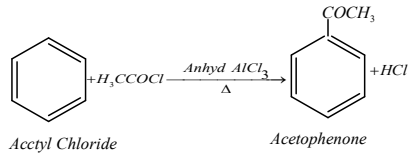


Methyl benzene (Toluene)



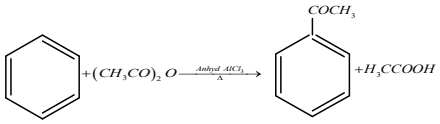
Ethyl benzene

Acylation :- The reaction of Benzene with an acyl halide or acid anhydride in the presence of Lewis acids $(AlCl_3)$ yields acyl benzene .

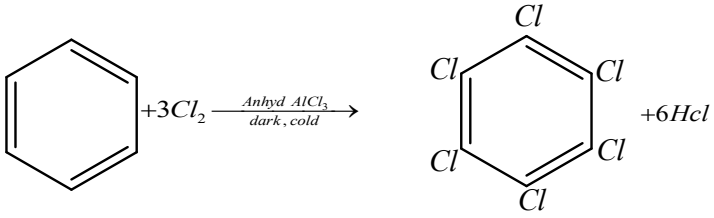


Acctyl Chloride

Acetophenone



Note:- In halogenation of benzene , like with excess Cl_2 in presence of Anhyd $AlCl_3$ all the 6H of Benzene molecule replaced by 6 Chlorine atoms takes place and gives hexachlorobenzene .



Hexachloro benzene (C_6Cl_6)

7. Explain aromatic electrophilic substitution reactions of Benzene

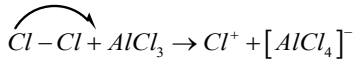
Ans: According to experimental evidences, *SE means S = Substitution, E = Electrophilic* reactions are supposed to proceed via the following 3 steps .

1) Generation of the electrophile

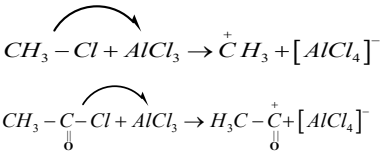
2) Formation of carbocation intermediate.

3) Removal of proton from the carbocation intermediate.

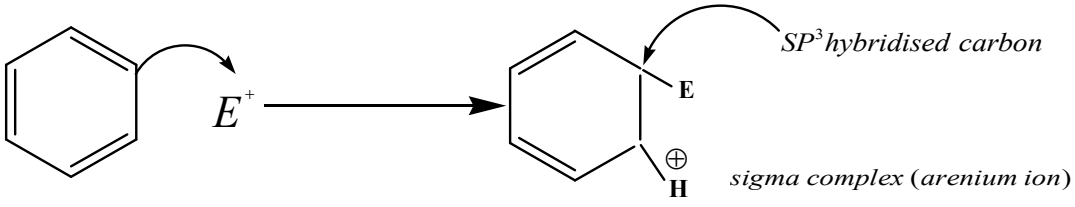
1) Generation of electrophile: - $\mathbf{E}^{\oplus}$ During chlorination, alkylation, and acylation of benzene , anhydrous $AlCl_3$ being a Lewis acid help in generation of the electrophile $Cl^+, R^+, R\overset{+}{C}O$ (acylium ion) respectively by combining with the attacking reagent .



$Cl^+ = Chloronium\ ion$



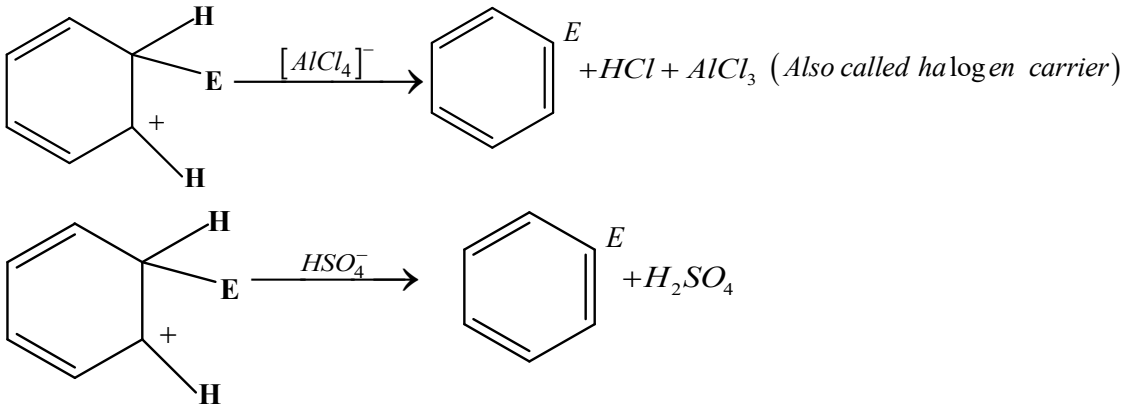
2) Formation of carbocation: σ complex (arenium ion):- Attack of electrophile results in the formation of σ - complex or arenium ion in which one of the carbon is SP^3 hybridised σ complex is resonance- stabilised cation is hybridised. With positive charge delocalized across the ring



Sigma Complex or arinium ion loses its Aromatic character because delocalisation of electrons stops at SP^3 hybridised 'C' atom. This step is rate determining step.

3) Removal of proton :- This is called deprotonation . A base (typically the conjugate base of the acid catalyst) abstracts a proton from the σ complex, forming the substituted benzene product .

In case of halogenation, alkylation & acylation σ complex releases proton from SP^3 carbon on attack by $[AlCl_4]^-$ & HSO_4^- in case of Nitration.



To Restore the aromatic character: The substituted benzene product regains its aromaticity, with the electrons rearranging to from a stable planar ring

Ex:- Nitration of Benzene :- $C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$

1) $HNO_3 + H_2SO_4 \rightarrow HSO_4^+ + HNO_3^+$ (Nitration equilibrium)

2) $HNO_3^+ \rightarrow NO_2^+ + H_2O$ (After series of proton transfers & Elimination) H_2SO_4 acts as catalyst facilitating the protonation and subsequent decomposition of the Nitricacid to from Nitronium ion NO_2^+

8. Explain electrophilic addition reactions of ethylene with mechanism?

Ans: Alkenes are the rich source of loosely held $\prod$ (pi) electrons, due to which they show addition reactions .In which the electrophiles add on to the carbon -carbon double bond to from the addition product.

There are 4 steps in electrophilic addition reactions

1)Formation of the electrophile

2)Attack of the electrophile

3) Nucleophilic attack

4)Product formation

1) Formation of the electrophile

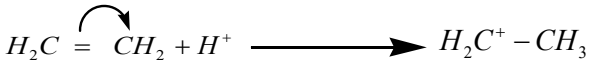
$H - Br \rightarrow H^+ + Br^-$ $\quad Br^- is$ $\quad nucleophile (Electron\ rich\ species)$

$\mathbf{H^+}$ is Electrophile (electron seeking or less e^- species)

$H-H \rightarrow H^+ + H^-$, $Cl-Cl \rightarrow Cl^+ + Cl^-$

$Br-Br \rightarrow Br^- + B^+$, $H_2O \rightarrow H^+ + OH^-$

$H_2SO_4 \rightarrow H^+ + HSO_4^-$



Proton **Carbocation intermediate**

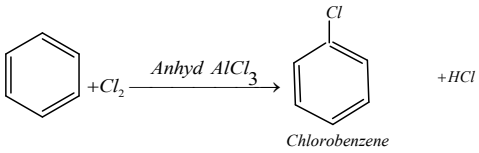
3) Nucleophilic attack & final product formation :-

$H_2C^+ - CH_3 + Br^- \rightarrow BrH_2C - CH_3$ Bromo ethane (saturated compound)

9. How do you convert the following compounds from benzene

a) Chloro benzene b) Toluene c) Acetopheneone

a) Benzene: Benzene reacts with Cl_2 in the presence of a Lewis acid like $Fecl_3$ or $AlCl_3$ gives chlorobenzene .

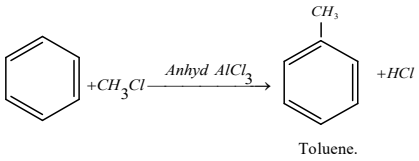


Chlorobenzene

$C_6H_6 + Cl_2 \xrightarrow{Anhyd\ AlCl_3} C_6H_5Cl + HCl$.

This reaction is called " halogenation" an electrophilic substitution reaction.

b)Toluene:- Benzene when treated with Methyl Chloride in the presence of anhydrous aluminium chloride Methyl benzene or Toluene is formed .

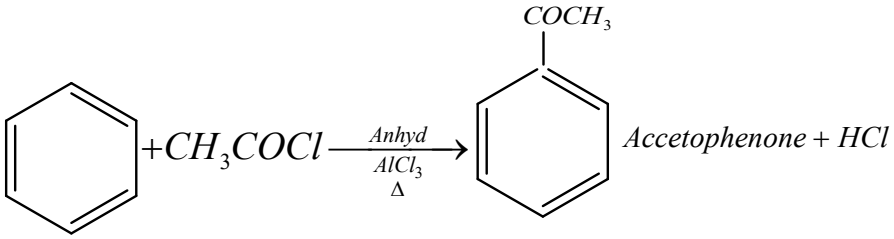


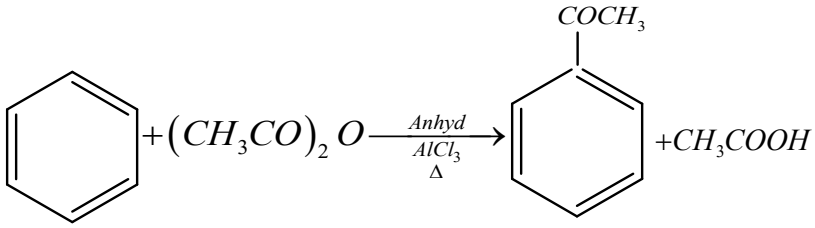
Toluene.

$C_6H_6 + CH_3Cl \xrightarrow[ACl_3]{Anhyd} C_6H_5CH_3$ Toluene.

This reaction is called Friedel crafts alkylation an electrophilic substitution reaction.

c) Acetophenone: The reaction of Benzene with an acyl halide or acetic anhydride in the presence of Anhyd $AlCl_3$ (Lewis acid) Acetophenone is formed.





$$C_6H_6 + CH_3COCl \xrightarrow[AlCl_3]{An\ hyd} C_6H_5COCH_3 + HCl$$

Acetophenone

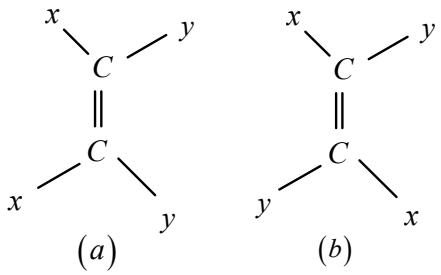
$$C_6H_6 + (CH_3CO)_2\,O \xrightarrow[AlCl_3\Delta]{An\ hyd} C_6H_5COCH_3 + CH_3COOH$$

This reaction is named as Friedel - Craft acylation reaction. (Electrophilic substitution) reaction.

10. What do you understand about geometrical isomerism? Explain the geometrical Isomers of 2-butene.

Ans: Doubly bonded caron atoms have to satisfy the remaining two valences by joining with two atoms or groups.

If two atoms or groups attached to each carbon atom are different they can be represented by **YXC = CXY** like structure. The spatial arrangement of the structure.



In (a) Structure the two identical atoms i.e.both The 'X' or both 'Y' lie on the same side. Of the double bond.

In structure (b) two 'X' or two 'Y lie across the double bond or on the opposite sides of the double bond . This results in different geometry of two structures of (a) & (b).

Disposition of atoms or groups in space in the two arrangements is different therefore they are called stereoisomers

The stereoisomers are formed due to restricted rotation of double bond, it is not free rotation around a double bond or a ring gives rise to different geometries of such compounds. The isomers of this type are called geometrical isomers or cis, trans isomers, This is called Geometrical Isomerism or cis- trans isomerism .

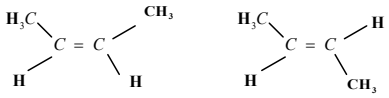
Due to restricted rotation of atoms or groups around the doubly bonded carbon atoms gives rise to different geometries of such compounds . The stereoisomers of this type are called Geometrical isomers .'

The structure is which the two identical atoms or groups lie on the same side of the double bond is called cis isomer .

The structure in which identical atoms or groups lie on the opposite sides of the double bond is called trans isomer .

Due to different arrangements of atoms or groups in space these isomers differ in their properties like M.P, B.P dipolemoments , solubility etc.

Geometrical or cis- trans Isomers of but -2- ene



Cis- But- 2 – ene

b.p – 277 K

Trans -But – 2 -ene

b.p - 274K

a) Dipole moment of cis- but -2 ene is 0.33 Debye

Dipole moment of trans – but -2 ene is zero

b) cis form of alkene is found to be more polar than the trans form, trans but – 2- ene is non polar.

c)In case of solids, it is observed that the trans isomer has higher melting point than the cis form.

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