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Unit 1 Basic Concepts of Chemistry and Chemical Calculations

Matter is defined as anything that has mass and occupies space. All matter is composed of atoms.

Physical Classification of Matter:

Matter can be classified as solids, liquids and gases based on their physical state.

Chemical Classification:

Matter can be classified into mixtures and pure substances based on chemical compositions. Mixtures classified as homogeneous or heterogeneous mixtures based on their physical appearance.

An **element** consists of only one type of atom.

Monatomic unit – Gold (Au), Copper (Cu) & Inert gases

Polyatomic unit - Hydrogen (H_2), Phosphorous (P_4) and Sulphur (S_8)

Compounds are made up of molecules which contain two or more atoms of different elements.

Example : Carbon dioxide (CO_2), Glucose ($C_6H_{12}O_6$), Hydrogen Sulphide (H_2S), Sodium Chloride (NaCl)

Average atomic mass is defined as the average of the atomic masses of all atoms in their naturally occurring isotopes.

Example:

${}_{17}Cl^{35}$ and ${}_{17}Cl^{37}$ in the ratio 77 : 23, the average relative atomic mass of chlorine is

$$= \frac{(35 \times 77) + (37 \times 23)}{100}$$

= 35.46 u

Empirical formula

Empirical formula of a compound is the formula written with the **simplest ratio** of the number of different atoms present in one molecule of the compound as subscript to the atomic symbol.

Molecular formula

Molecular formula of a compound is the formula written with the **actual number** of different atoms present in one molecule as a subscript to the atomic symbol.

Example:

The molecular formula of acetic acid (CH_3COOH) is $C_2H_4O_2$

The ratio of C : H : O is 1 : 2 : 1 and hence the empirical formula is CH_2O.

Oxidation Number: (oxidation state)

It is defined as the imaginary charge left on the atom when all other atoms of the compound have been removed in their usual oxidation states that are assigned according to set of rules.

General rules of oxidation Number:

1) The oxidation state of a free element (i.e. in its uncombined state) is zero.

Example : each atom in H_2, Cl_2, Na, S_8 have the oxidation number of zero.

2) For a monatomic ion, the oxidation state is equal to the net charge on the ion.

Example : The oxidation number of sodium in Na^+ is +1.

The oxidation number of chlorine in Cl^- is –1.

3) The algebraic sum of oxidation states of all atoms in a molecule is equal to zero, while in ions, it is equal to the net charge on the ion.

Example:

In H_2SO_4, = 0 . In SO_4^{2-} =+ 4

4) Hydrogen has an oxidation number of +1 in all its compounds except in metal hydrides where it has – 1 value.

Example:

Oxidation number of hydrogen in hydrogen chloride (**H**Cl) is + 1.

Oxidation number of hydrogen in sodium hydride (Na**H**) is –1.

5) **Fluorine** has an oxidation state of – 1 in all its compounds.

6) The oxidation state of **oxygen** in most compounds is **–2**. Exceptions are peroxides, super oxides and compounds with fluorine.

Example : Oxidation number of oxygen, i) in **water** (H_2O) is **–2**.

ii) in **hydrogen peroxide** (H_2O_2) is **–1**.

iii) **in super oxides** such as KO_2 is **–1/2**

iv) in **oxygen difluoride** (OF_2) is **+ 2**.

7) Alkali metals have an oxidation state of + 1 and alkaline earth metals have an oxidation state of + 2 in all their compounds.

Limiting reagent

when a reaction is carried out using non-stoichiometric quantities of the reactants, the product yield will be determined by the reactant that is completely consumed. It limits the further reaction from taking place and is called as the limiting reagent.

(**Limiting Reagent-** The reactant which gets consumed first or limits the amount of product formed is known as **limiting reagent**)

The other reagents which are in excess are called the **excess reagents**.

Example: $S + 3F_2 \rightarrow SF_6$

Sulphur is the limiting reagent and **fluorine** is the excess reagent.

A reaction in which oxidation number of the element **increases** is called oxidation.

A reaction in which oxidation number of the element **decreases** is called reduction.

Redox reactions in which

- two substances combine to form compound(s) are called combination reaction.
- a compound breaks down into two (or) more components is called decomposition reaction
- a compound is replaced by an ion (or atom) of another element are called displacement reactions
- the same compound can undergo both oxidation and reduction and the oxidation state of one and the same element is both increased and decreased called disproportionate reactions.
- competition for electrons occurs between various metals is called competitive electron transfer reaction.

The equation of redox reaction is balanced either by oxidation number method or by ion-electron method.

I. Choose the best answer.

1. 40 ml of methane is completely burnt using 80 ml of oxygen at room temperature. The volume of gas left after cooling to room temperature is

(a) 40 ml CO_2 gas (b) 40 ml CO_2 gas and 80 ml H_2O gas
(c) 60 ml CO_2 gas and 60 ml H_2O gas (d) 120 ml CO_2 gas

2. An element X has the following isotopic composition $^{200}X = 90$ %, $^{199}X = 8$ % and $^{202}X = 2$ %. The weighted average atomic mass of the element X is closest to

(a) 201 u (b) 202 u (c) 199 u **(d) 200 u**

3. Assertion : Two mole of glucose contains 12.044×10^{23} molecules of glucose
Reason : Total number of entities present in one mole of any substance is equal to 6.02×10^{22}

(a) both assertion and reason are true and the reason is the correct explanation of assertion
(b) both assertion and reason are true but reason is not the correct explanation of assertion
(c) Assertion is true but reason is false (d) both assertion and reason are false

4. Carbon forms two oxides, namely carbon monoxide and carbon dioxide. The equivalent mass of which element remains constant?

(a) Carbon **(b) oxygen** (c) both carbon and oxygen (d) neither carbon nor oxygen

5. The equivalent mass of a trivalent metal element is 9 g eq^{-1} the molar mass of its anhydrous oxide is **(a) 102 g** (b) 27 g (c) 270 g (d) 78 g

6. The number of water molecules in a drop of water weighing 0.018 g is

(a) 6.022×10^{26} (b) 6.022×10^{23} **(c) 6.022×10^{20}** (d) 9.9×10^{22}

7. 1 g of an impure sample of magnesium carbonate (containing no thermally decomposable impurities) on complete thermal decomposition gave 0.44 g of carbon dioxide gas. The percentage of impurity in the sample is

(a) 0 % (b) 4.4 % **(c) 16 %** (d) 8.4 %

8. When 6.3 g of sodium bicarbonate is added to 30 g of acetic acid solution, the residual solution is found to weigh 33 g.The number of moles of carbon dioxide released in the reaction is (a) 3 (b) 0.75 **(c) 0.075** (d) 0.3

9. When 22.4 litres of H_2 (g) is mixed with 11.2 litres of Cl_2 (g), each at 273 K at 1 atm the moles of HCl (g), formed is equal to

(a) 2 moles of HCl(g) (b) 0.5 moles of HCl(g) (c) 1.5 moles of HCl(g) **(d) 1 moles of HCl(g)**

10. How concentrated sulphuric acid is a moderately strong oxidising agent. Which of the following reactions does not show oxidising behaviour?

(a) $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$ (b) $C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$
(c) $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$ (d) none of the above

11. Choose the disproportionation reaction among the following redox reactions.

(a) $3Mg_{(s)} + N_{2(g)} \rightarrow Mg_3N_{2(s)}$ **(b) $P_4 (s) + 3NaOH + 3H_2O \rightarrow PH_{3(g)} + 3NaH_2PO_{2(aq)}$**
(c) $Cl_{2(g)} + 2KI_{(aq)} \rightarrow 2KCl_{(aq)} + I_2$ (d) $Cr_2O_{3(s)} + 2Al_{(s)} \rightarrow Al_2O_{3(s)} + 2Cr_{(s)}$

12.The equivalent mass of potassium permanganate in alkaline medium is

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

(a) 31.6 **(b) 52.7** (c) 79 (d) None of these

13.Which one of the following represents 180g of water?

(a) 5 Moles of water (b) 90 moles of water

(c) $\frac{6.022 \times 10^{23}}{180}$moleculesof water **(d) $6.022x10^{24}$ molecules of water**

14.7.5 g of a gas occupies a volume of 5.6 litres at 0^o C and 1 atm pressure. The gas is

(a) NO (b) N_2O (c) CO (d) CO_2

15.Total number of electrons present in 1.7 g of ammonia is

(a) 6.022×10^{23} (b) $\frac{6.022 \times 10^{22}}{1.7}$ (c) $\frac{6.022 \times 10^{24}}{1.7}$ (d) $\frac{6.022 \times 10^{23}}{1.7}$

16.The correct increasing order of the oxidation state of sulphur in the anions

SO_4^{2-}, SO_3^{2-} , $S_2O_4^{2-}$, $S_2O_6^{2-}$ is

(a) $SO_3^{2-} < SO_4^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$ (b) $SO_4^{2-} < S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$

(c) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-} < SO_4^{2-}$ (d) $S_2O_6^{2-} < S_2O_4^{2-} < SO_4^{2} SO_3^{2-}$

17.The equivalent mass of ferrous oxalate is

(a) $\frac{Molar\ mass\ of\ ferrous\ oxalate}{1}$ b) $\frac{Molar\ mass\ of\ ferrous\ oxalate}{2}$ **c) $\frac{Molar\ mass\ of\ ferrous\ oxalate}{3}$**

(d) none of these

18.If Avogadro number were changed from 6.022×10^{23} to 6.022×10^{20}, this would change

(a) the ratio of chemical species to each other in a balanced equation

(b) the ratio of elements to each other in a compound

(c) the definition of mass in units of grams **(d) the mass of one mole of carbon**

19.Two 22.4 litre containers A and B contains 8 g of O_2 and 8 g of SO_2 respectively at 273 K and 1 atm pressure, then

(a) Number of molecules in A and B are same

(b) Number of molecules in B is more than that in A.

(c) The ratio between the number of molecules in A to number of molecules in B is 2:1

(d) Number of molecules in B is three times greater than the number of molecules in A.

20.What is the mass of precipitate formed when 50 ml of 8.5 % solution of $AgNO_3$ is mixed with 100 ml of 1.865 % potassium chloride solution?

(a) 3.59 g (b) 7 g (c) 14 g (d) 28 g

21.The mass of a gas that occupies a volume of 612.5 ml at room temperature and pressure (250 °C and 1 atm pressure) is 1.1g. The molar mass of the gas is

(a) 66.25 g mol^{-1} **(b) 44 g mol^{-1}** (c) 24.5 g mol^{-1} d) 662.5 g mol^{-1}

22.Which of the following contain same number of carbon atoms as in 6 g of carbon-12.

(a) 7.5 g ethane (b)8 g methane (c) both (a) and (b) (d) none of these

23. Which of the following compound(s) has /have percentage of carbon same as that in ethylene (C_2H_4) **(a) propene** (b) ethyne (c) benzene (d) ethane

24.Which of the following is/are true with respect to carbon -12.

(a) relative atomic mass is 12 u (b) oxidation number of carbon is +4 in all its compounds.
(c) 1 mole of carbon-12 contain 6.022×10^{22} carbon atoms. (d) all of these

25. Which one of the following is used as a standard for atomic mass.
(a) $_6C^{12}$ (b) $_7C^{12}$ (c) $_6C^{13}$ (d) $_6C^{14}$

Answer the following

26. Define relative atomic mass

The relative atomic mass is defined as the ratio of the average atomic mass factor to the unified atomic mass unit.

$$\text{Relative atomic mass } (A_r) = \frac{\textit{Average mass of the atom}}{\textit{Unified atomic mass}}$$

27. What do you understand by the term mole.

One mole is the amount of substance of a system, which contains as many elementary particles as there are atoms in 12 g of carbon -12 isotope. The elementary particles can be molecules , atoms, ions, electrons or any other specified particles.

28. Define equivalent Mass

Equivalent mass of an element, compound or ion is the number of parts of mass of an element combines or displaces 1.008 g hydrogen or 8 g oxygen or 35.5g chlorine.

29. What do you understand by the term oxidation number.

When all other atoms of the compound have been removed in their usual oxidation states that are assigned according to set of rules.

30. Distinguish between oxidation and reduction

	Oxidation	**Reduction**
(i)	Addition of oxygen and removal of hydrogen	Additional of hydrogen and removal of oxygen
(ii)	This process involves loss of electrons $Fe^{2+} \rightarrow Fe^{3+} + e^-$	This process involves gain electrons. $Cu^{2+} + 2e^- \rightarrow Cu$
(iii)	Oxidation number increases	Oxidation number decreases
(iv)	Addition of non-metal	Removal of non-metal $2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$
(v)	Removal of metal $2KI + H_2O_2 \rightarrow 2KOH + I_2$	Addition of metal $HgCl_2 + Hg \rightarrow Hg_2Cl_2$

31. Calculate the molar mass of the following compounds (i) urea [$CO(NH_2)_2$] (ii) acetone [CH_3COCH_3] (iii) boric acid [H_3BO_3] (iv) sulphuric acid [H_2SO_4]

(i) urea [$CO(NH_2)_2$]

C : 1 × 12.01 = 12.01
O : 1 × 16 = 16.00
N : 2 × 14.01 = 28.02
H : 4 × 1.01 = 4.04
60.07 g mol^{-1}

(ii) acetane [CH_3COCH_3]

C : 3 × 12.01 = 36.03
H : 6 × 1.01 = 6.06
O : 1 × 16 = 16.00
58.09 g mol^{-1}

(iii) boric acid [H_3BO_3]

H : 3 × 1.01 = 3.03
B : 1 × 11 = 11.00
O : 3 × 16 = 48.00
62.03 g mol^{-1}

(iv) sulphuric acid [H_2SO_4]

H : 2 × 1.01 = 2.02
S : 1 × 32.06 = 32.06
O : 4 × 16 = 64.00
98.08 g mol^{-1}

32. The density of carbon dioxide is equal to 1.965 kgm^{-3} at 273 K and 1atm pressure. Calculate the molar mass of CO_2.

Given : The density of CO_2 at 273K and 1 atm pressure = 1.965 kgm^{-3} At 273 K and 1 atm pressure, 1 mole of CO_2 occupies a volume of 22.4L

$$\text{Mass of 1 mole of } CO_2 = \frac{1.965Kg}{1m^3} \times 22.4L = \frac{1.965 \times 10^3\ g \times 22.4 \times 10^{-3} m^3}{1m^3}$$

Molar mass of CO_2 = **44 $gmol^{-1}$**

ANOTHER METHOD:

Molecular mass = Density x Molar mass

Molar volume of CO_2 = 2.24 x 10^{-2} m^3

Density of CO_2 = 1.965kgm^{-3}

Molecular mass of CO_2 = 1.965 x $10^3 gm^{-3}$ x 2.24 x $10^{-2}m^3$
=1.965 x 10^1 x 2.24
= 44g

33. Which contains the greatest number of moles of oxygen atoms (i) 1 mol of ethanol (ii) 1 mol of formic acid (iii) 1 mol of H_2O

Compound	**Given no. of moles**	**No. of oxygen atoms**
Ethanol (C_2H_5OH)	1	$1 \times 6.022 \times 10^{23}$
Formic acid (HCOOH)	1	$2 \times 6.022 \times 10^{23}$
Water (H_2O)	1	$1 \times 6.022 \times 10^{23}$

34. Calculate the average atomic mass of naturally occurring magnesium using the following data

Isotope	**Isotopic atomic mass**	**Abundance (%)**
Mg^{24}	**23.99**	**78.99**

Mg^{26}	**24.99**	**10.00**
Mg^{25}	**25.98**	**11.01**

Average atomic mass $= \frac{(78.99 \times 23.99)+(10 \times 24.99)+(11.01 \times 25.98)}{100}$

$= \frac{2430.9}{100} = 24.31u.$

35. In a reaction $x + y + z_2 \rightarrow xyz_2$ identify the Limiting reagent if any, in the following reaction mixtures

Q	Number of moles of reactants allowed to react			Number of moles of reactants consumed during reaction			Limiting reagent
	X	Y	z_2	X	y	z_2	
(a	200 atoms	200atoms	50 molecules	50 atoms	50atoms	50 molecules	**z_2**
b	1 mol	1mol	3 mol	1 mol	1 mol	1mol	**x and y**
(c	50atom	25atom	50 molecules	25atom	25atom	25 molecules	**y**
d	2.5 mol	5 mol	5 mol	2.5mol	2.5 mol	2.5 mol	**x**

(a) 200 atoms of x + 200 atoms of y + 50 molecules of z_2

(b) 1 mol of x + 1 mol of y + 3 mol of z_2

(c) 50 atoms of x + 25 atoms of y + 50 molecules of z_2

(d) 2.5 mol of x + 5 mol of y + 5 mol of z_2

Reaction : $x + y + z_2 \rightarrow xyz_2$

36. Mass of one atom of an element is 6.645×10^{-23}g. How many moles of element are there in 0. 320 kg.

Given: Mass of one atom $= 6.645 \times 10^{-23}$ g

∴ mass of 1 mole of atom $= 6.645 \times 10^{-23}$ g $\times 6.022 \times 10^{23}$

$= 40g$

∴ number of moles of element in 0.320 kg **(number of moles = mass/atomic mass)**

$= \frac{1 mole}{40g} \times 0.320kg$

$= \frac{1\ mol \times 320g}{40g} = 8$ mol.

37. What is the difference between molecular mass and molar mass ? Calculate the molecular mass and molar mass for carbon monoxide

	Molecular mass	**Molar mass**
1	Molecular mass is defined as the ratio of the mass of a molecule to the unified this is relative molecular mass atomic mass unit	Molar mass is defined as the mass of one mole of a substance.
2	The relative molecular mass of any compound is calculated by adding the relative atomic masses of its constituent atoms	The molar mass of a compound is equal to the sum of the relative atomic masses of its constituents

3	Its unit is u or amu	Its unit is g mol^{-1}
4	Molecular mass of CO: (1 × at.mass of C) + (1 × at. Mass of O) 1× 12.01 amu + 1 × 16 amu = 28. 01 am	Molar mass of CO: 1×12.01+ 1× 16 = 28.01g mol^{-1}

38. What is the empirical formula of the following ?

(i) Fructose ($C_6H_{12}O_6$) found in honey

(ii) Caffeine ($C_8H_{10}N_4O_2$) a substance found in tea and coffee.

Compound	**Molecular Formula**	**Empirical Formula**
Fructose	$C_6H_{12}O_6$	CH_2O
Caffeine	$C_8H_{10}N_4O_2$	$C_4H_5N_2O$

39. The reaction between aluminium and ferric oxide can generate temperatures up to 3273 K and is used in welding metals. (Atomic mass of Al = 27u Atomic mass of O = 16u) $2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$; If, in this process , 324 g of aluminium is allowed to react with 1.12 kg of ferric oxide. (i) Calculate the mass of Al_2O_3 formed. (ii) How much of the excess reagent is left at the end of the reaction?

Given: $2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$

	Reactants		**Products**	
	Al	**Fe_2O_3**	**Al_2O_3**	**Fe**
Amount of reactant allowed to react	324 g	1.12 kg	-	-
Number of moles allowed to react	$\frac{324}{27} = 12\ mol$	$\frac{1.12 \times 10^3}{160} =$ 7mol	-	-
Stoichiometric Co-efficient	2	1	1	2
Number of moles consumed during reaction	12 mol	6 mol	-	-
Number of moles of reactant unreacted and number of moles of product formed	-	1mol	6mol	12mol

Molar mass of Al_2O_3 formed

$$= 6\ \text{mol} \times 102\ \text{g mol}^{-1} \quad \left[\begin{array}{c} Al_2O_3 \\ (2 \times 27) + (3\ \times 16) \\ 54 + 48 = 102 \end{array}\right] = 612\text{g}$$

Excess reagent = Fe_2O_3

Amount of excess reagent left at the end of the reaction = 1mol × 160 g mol^{-1}

$$= 160\ \text{g} \left[\begin{array}{c} Fe_2O_3 \\ (2 \times 56) + (3\ \times 16) \\ 112 + 48 = 160 \end{array}\right] = 160\ \text{g}$$

40. **How many moles of ethane is required to produce 44 g of $CO_2(g)$ after combustion.**

Balanced equation for the combustion of ethane

$$C_2H_6 + 3\frac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2O$$

⇨ $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

To produce 4 moles of CO_2, 2 moles of ethane is required

To produce 1 mole (44 g) of CO_2 required number of moles of ethane

$= \frac{2\ mol\ ethane}{4\ mol\ CO_2} \times 1\ mol\ CO_2$ = ½ mole of ethane = 0.5 mole of ethane

41. Hydrogen peroxide is an oxidising agent. It oxidises ferrous ion to ferric ion and reduced itself to water. Write a balanced equation.

H_2O_2 → Oxidising agent

-1 -2

$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + H_2O$ (Acidic medium)

$(1e^{-} \times 2)$ $1e^{-}$

Ferrous ion is oxidized by H_2O_2 to Ferric ion.

The balanced equation is $Fe^{2+} \rightarrow Fe^{3+}$ +e- X 2

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

$2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$

$H_2O_2 + 2Fe^{2+} + 2H^+ \rightarrow Fe^{3+} + 2H_2O$

42. Calculate the empirical and molecular formula of a compound containing 76.6% carbon, 6.38 % hydrogen and rest oxygen its vapour density is 47.

Element	Percentage	Atomic mass	Relative number of atoms	Simple ratio	Whole no
C	76.6	12	$\frac{76.6}{12} = 6.38$	$\frac{6.38}{1.06} = 6$	6
H	6.38	1	$\frac{6.38}{1} = 6.38$	$\frac{6.38}{1.06}$	6
O	17.02	16	$\frac{17.02}{16} = 1.06$	$\frac{1.06}{1.06} = 1$	1

Empirical Formula = C_6H_6O

$$n = \frac{Molar\ mass}{Calculated\ empirical\ formula\ mass}$$

$$= \frac{2 \times vapour\ density}{94} = \frac{2 \times 47}{94} = 1,$$

since Molar mass = 2 × Vapour density

Molecular formula n × n empirical formula

Molecular formula $(C_6H_6O) \times 1 = C_6H_6O$

43.A Compound o analysis gave Na = 14.31 % S = 9.97% H = 6.22% and O = 69.5% calculate the molecular formula of the compound if all the hydrogen in the compound is present in combination with oxygen as water of crystallization. (molecular mass of the compound is 322).

Element	%	Relative number of atoms	Simple ratio

Na	14.31	$\frac{14.31}{23} = 0.62$	$\frac{0.62}{0.31} = 2$
S	9.97	$\frac{9.97}{32} = 0.31$	$\frac{0.31}{0.31} = 1$
H	6.22	$\frac{6.22}{1} = 6.22$	$\frac{6.22}{0.31} = 20$
O	69.5	$\frac{69.5}{16} = 4.34$	$\frac{4.34}{0.31} = 14$

Empirical formula = $Na_2SH_{20}O_{14}$

$$n = \frac{molar\ mass}{Calculated\ empirical\ formula\ mass}$$

$$= \frac{322}{322} = 1$$

$$\left[\begin{array}{c} Na_2SH_{20}O_{14} \\ = (2 \times 23) + (1 \times 32) + (20 \times 1) + 14(16) \\ = 46 + 32 + 20 + 224 \\ = 322 \end{array}\right]$$

Molecular formula = $Na_2\,S\,H_{20}\,O_{14}$

Since all the hydrogen in the compound present as water

Molecular formula is $Na_2\,SO_4.10H_2O$.

44. Balance the following equations by oxidation number method

i) $K_2Cr_2O_7 + KI + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + I_2 + H_2O$

ii) $KMnO_4 + Na_2SO_3 \rightarrow MnO_2 + Na_2SO_4 + KOH$

iii) $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$

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

+6 -1 +3 0

i) $K_2Cr_2O_7 + KI + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + I_2 + H_2O$

$2 \times 3e^-$ $1e^-$

$K_2Cr_2O_7 + 6KI + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + I_2 + H_2O$

$K_2Cr_2O_7 + 6KI + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + H_2O$

$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \rightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$

+7 +4 +4 +6

ii) $KMnO_4 + Na_2SO_3 \rightarrow MnO_2 + Na_2SO_4 + KOH$

$3e^-$ $2e^-$

⇨ $2KMnO_4 + 3Na_2SO_3 \rightarrow MnO_2 + Na_2SO_4 + KOH$

⇨ $2KMnO_4 + 3Na_2SO_3 \rightarrow 2MnO_2 + 3Na_2SO_4 + KOH$

⇨ $2KMnO_4 + 3Na_2SO_3 \rightarrow 2MnO_2 + 3Na_2SO_4 + 2KOH$

0 +5 +2 +4

iii) $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$

$2e^-$ $1e^-$

$Cu + 2HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$

$Cu + 2HNO_3 + 2HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

iv) $\overset{+7}{KMnO_4} + \overset{+3}{H_2C_2O_4} + H_2SO_4 \rightarrow K_2SO_4 + \overset{+2}{MnSO_4} + \overset{+4}{CO_2} + H_2O$

$\downarrow$ $\uparrow$

$5e^-$ $1e^- \times 2$

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

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

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

45. Balance the following equations by ion electron method.

i) $KMnO_4 + SnCl_2 + HCl \rightarrow MnCl_2 + SnCl_4 + H_2O + KCl$

ii) $C_2O_4^{2-} + Cr_2O_7^{2-} \rightarrow Cr^{3+} + CO_2$ (in acid medium)

iii) $Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + NaI$ (in acid medium)

iv) $Zn + NO_3^- \rightarrow Zn^{2+} + NO$

(i) Half reaction are:

$\overset{+7}{MnO_4^-} \rightarrow Mn^{2+}$ ---- (1)

And $Sn^{2+} \rightarrow Sn^{4+}$ ---- (2)

(1) ➔ $MnO_4^- + 8H^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$

(2) ➔ $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

(1)× 2 ➔ $2MnO_4^- + 16H^- + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$

(2) × 5➔ $5Sn^{2+} \rightarrow 5Sn^{4+} + 10e^-$

➔ $2MnO_4^- + 5Sn^{2+} + 16H^+ \rightarrow 2Mn^{2+} + 5Sn^{4+} + 8H_2O$

(ii) $\overset{+3}{C_2O_4^{2-}} \rightarrow \overset{+4}{CO_2}$ ---- (1)

$Cr_2O_7^{2-} \rightarrow Cr^{3+}$ ---- (2)

(1) ➔ $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$ ---- (3)

$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$ ---- (4)

(2) × 3 ➔ $3C_2O_4^{2-} \rightarrow 6CO_2 + 6e-$ ---- (5)

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ ---- (4)

➔ $Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 6CO_2 + 7H_2O$

(iii) $S_2O_3^{2-} \rightarrow S_4O_6^{2-}$ ---- (1)

Half reaction ➔ $I_2 \rightarrow I$ ---- (2)

(1) ➔ $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$ ---- (3)

(2) ➔ $I_2 + 2e^- \rightarrow 2I^-$ ---- (4)

(3) + (4) ➔ $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

(iv) $Zn \rightarrow Zn^{2+}$ ---- (1)

$NO_3^- \rightarrow NO$ ---- (2)

(1) ➔ $Zn \rightarrow Zn^{2+} + 2e^-$ ---- (3)

(2) ➔ $NO_3^- + 3e^- + 4H^+ \rightarrow NO + 2H_2O$ ---- (4)

(3) × 3 ➔ $3Zn \rightarrow Zn^{2+} + 6e-$ ---- (5)

(4) × 2 ➔ $2NO_3^- + 6e^- + 8H^+ \rightarrow 2NO + 4H_2O$ ---- (6)

$3Zn + 2NO_3^- + 8H^+ \rightarrow 3Zn^{2+} + 2NO + 4H_2O$

2. QUANTUM MECHANICAL MODEL OF ATOM

Important Formulae

1. $\Delta E = h\upsilon$ or $\upsilon = \frac{E_2 - E_1}{h}$
2. $r_n = \frac{(0.529)n^2}{Z}$ Å
3. $E_n = \frac{(-13.6)Z^2}{n^2}$ eV atom^{-1} (or) $\frac{(-1312.8)Z^2}{n^2}$ KJ mol^{-1}
4. $E = h\upsilon$, $E = mc^2$
5. $\lambda = \frac{h}{mv}$ or $\frac{h}{p}$
6. $2\pi = nh/mv$ (or) $mvr = nh/2\pi$
7. $\Delta x.\Delta p \geq \frac{h}{4\pi}$, (or) $\Delta x.\ m.\Delta v \geq \frac{h}{4\pi}$,
8. $\hat{H}\Psi = E\Psi$
9. $\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\Psi = 0$
10. Angular momentum = $\sqrt{l(1+1)}\frac{h}{2\pi}$

Important Points to Remember

- **Atom** – The basic unit that makes up all matter
- **Planck's constant (h)** – 6.626 x 10^{-34} Js.
- **Angular momentum** – mvr ; mvr = nh/2π
- **Bohr's atomic model** – The electron is revolving around the nucleus in a certain fixed circular path called stationary orbit. The energies of electrons are quantized. Electron can revolve only in orbits in which the angular momentum (mvr) of the electron must be equal to an integral multiple of h/2π
- **Radius of the nth orbit** – $r_n = \frac{(0.529)n^2}{Z}$ A
- **Energy of the nth orbit -** $E_n = \frac{(-13.6)Z^2}{n^2}$ eV atom^{-1} (or) $\frac{(-1312.8)Z^2}{n^2}$ KJ mol^{-1}
- **Louis de Broglie** – All forms of matter showed dual character such as particle and wave.
- **de Broglie** – All forms of matter showed dual character such as particle and wave.
- **de Broglie equation -** λ = h/mv
- **Mass of an electron** – 9.11 x 10^{-31} kg.
- **λ -** de Broglie wavelength

Quantization of de Broglie concept - $2\pi r = nh/mv$ (or) $mvr = nh/2\pi$

- **Heisenberg's uncertainty principle -** $\Delta x.\Delta p \geq \frac{h}{4\pi}$, where Δx = uncertainty in position.
  Δp = uncertainty in momentum.
- **Bohr's radius of 1st orbital** – 0.529 Å
- **Schrödinger equation** – $\hat{H}\ \Psi - E\ \Psi$
  $\hat{H}$ = Hamiltonian operator.
  E = wave function
  Ψ = Energy of the system
- **Schrödinger wave equation -** $\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\Psi = 0$
- **Quantum numbers** – The set of four quantum number which can characterize an electron in an atom. They represent the energy level, sub, shell, number of electron in an orbit, orientation of orbitals in space and the spin of the electron.
- **Atomic orbitals** – Permitted energy values called eigen values which are known as atomic orbitals.
- $[\Psi]^2$ – **I**t is the probability of finding the electrons.
- **Node** – The region where the probability density function reduces to zero is called nodal surface (or) a radial node.
- **Shapes of orbital** -s-orbital - spherical shape, p-orbital - dumb bell shape
  d-orbital – clover leaf
- **Effective nuclear charge** – The net charge experienced by the electron.
- **Order of E.N.C** – s > p > d > f in an orbital.
- **Energy order in orbital** – s < p < d < f.
- **Aufbau's principle** – "In the ground state of the atoms, the orbitals are filled in the order of their increasing energies".
- **Pauli's exclusion principle** – "No two electrons in an atom can have the same set of values for all four quantum numbers".
- **Types of quantum numbers** – Principal quantum (n), azimuthal quantum number (*l*), magnetic quantum number (m) and spin quantum number (s).

	Principal quantum number (n):	**Azimuthal quantum number (*l*)**	**Magnetic quantum number (m):**	**Spin quantum number (s):**
1	It represents the energy level in which electron is present	It represents the subshell in which electron is present	It represents different orientation of orbitals in space	It represents that spin of the electron
2	Maximum number of electrons that can be accommodated in the shell is $2n^2$.	Maximum number of electrons that can be accommodated in subshell is 2(21+1)	The magnitude of angular momentum is determined.	Electron revolves in clockwise and anti-clockwise directions.

3	$E_n = \frac{-(1312.8)Z^2}{n^2}$ kJ mol^{-1}.	It is used to calculate the orbital angular momentum by the formula $\sqrt{l(1+1)}\frac{h}{2\pi}$	If l = 1, m = -1, 0, +1	S values are $+{}^1/_2$ (or) $-{}^1/_2$.
4	It represents the distance of the electron from the nucleus.	1 = 0, 1, 2, 3 Subshell = s, p, d, f No. of electrons = 2, 6, 10, 14		
	n = 1, 2, 3, 4 K L M N			

- **Hund's rule of maximum multiplicity** – It states that electron pairing in the degenerate orbitals does not take place until all the available orbitals contains one electron each.
- **Electronic configuration** – The distribution of electrons into various orbitals of an atom is called its electronic configuration.
- **Exchange energy** – During the exchanging process of two or more electrons with the same spin present in degenerate orbitals, the amount of energy released in called exchange energy.

Unit 2 Quantum Mechanical Model of Atom

Choose the best answer

1. Electronic configuration of species M^{2+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$ and its atomic weight is 56. The number of neutrons in the nucleus of species M is

a) 26 b) 22 **c) 30** d) 24

2. The energy of light of wavelength 45 nm is

a) 6.67×10^{15}J b) 6.67×10^{11}J **c) 4.42×10^{-18}J** d) 4.42×10^{-15}J

3. The energies E_1 and E_2 of two radiations are 25 eV and 50 eV respectively. The relation between their wavelengths ie λ_1 and λ_2 will be

a) $\frac{\lambda_1}{\lambda_2} = 1$ **b) $\lambda_1 = 2\lambda_2$** c) $\lambda_1 = \sqrt{25 \times 50}\lambda$ d) $2\lambda_1 = \lambda_2$

4. Splitting of spectral lines in an electric field is called

a) Zeeman effect b) Shielding effect c) Compton effect **d) Stark effect**

5. Based on equation $E = -2.178 \times 10^{-18}\ J\ \frac{z^2}{n^2}$, certain conclusions are written. Which of them is not correct ? (NEET)

a) Equation can be used to calculate the change in energy when the electron changes orbit **b) For n = 1, the electron has a more negative energy than it does for n = 6 which means that the electron is more loosely bound in the smallest allowed orbit**

c) The negative sign in equation simply means that the energy of electron bound to the nucleus is lower than it would be if the electrons were at the infinite distance from the nucleus.

d) Larger the value of n, the larger is the orbit radius.

6. According to the Bohr Theory, which of the following transitions in the hydrogen atom will give rise to the least energetic photon ?

a) n = 6 to n = 1 b) n = 5 to n = 4 c) n = 5 to n = 3 **d) n = 6 to n = 5**

7. Assertion : The spectrum of He^+ is expected to be similar to that of hydrogen Reason : He^+ is also one electron system.

(a) If both assertion and reason are true and reason is the correct explanation of assertion

(b) If both assertion and reason are true but reason is not the correct explanation of assertion. (c) If assertion is true but reason is false (d) If both assertion and reason are false

8. Which of the following pairs of d-orbitals will have electron density along the axes ? (NEET Phase - II)

a) $d_{z}2$, d_{xz} b) d_{xz}, d_{yz} **c) $d_{z}2$, $d_{x}2{-}_{y}2$** d) d_{xy}, $d_{x}2{-}_{y}2$

9. Two electrons occupying the same orbital are distinguished by

a) azimuthal quantum number **b) spin quantum number**

c) magnetic quantum number d) orbital quantum number

10. The electronic configuration of Eu (Atomic no. 63) Gd (Atomic no. 64) and Tb (Atomic no. 65) are (NEET - Phase II)

a) [Xe] $4f^6$ $5d^1$ $6s^2$, [Xe] $4f^7$ $5d^1$ $6s^2$ and [Xe] $4f^8$ $5d^1$ $6s^2$

b) [Xe] $4f^7$, $6s^2$, [Xe] $4f^7$ $5d^1$ $6s^2$ and [Xe] $4f^9$ $6s^2$

c) [Xe] $4f^7$, $6s^2$, [Xe] $4f^8$ $6s^2$ and [Xe] $4f^8$ $5d^1$ $6s^2$

d) [Xe] $4f^6$ $5d^1$ $6s^2$, [Xe] $4f^7$ $5d^1$ $6s^2$ and [Xe] $4f^9$ $6s^2$

11. The maximum number of electrons in a sub shell is given by the expression

a) $2n_2$ b) 2l + 1 **c) 4l + 2** d) none of these

12. For d-electron, the orbital angular momentum is

a) $\frac{\sqrt{2}h}{2\pi}$ b) $\frac{\sqrt{2}h}{2\pi}$ c) $\frac{\sqrt{2\times4}\,h}{2\pi}$ **d) $\frac{\sqrt{6}h}{2\pi}$**

13. What is the maximum numbers of electrons that can be associated with the following set of quantum numbers ? n = 3, l = 1 and m = –1

a) 4 b) 6 **c) 2** d) = 10

14. Assertion : Number of radial and angular nodes for 3p orbital are 1, 1 respectively. Reason : Number of radial and angular nodes depends only on principal quantum number.

(a) both assertion and reason are true and reason is the correct explanation of assertion. (b) both assertion and reason are true but reason is not the correct explanation ofassertion. **(c) assertion is true but reason is false** (d) both assertion and reason are false

15. The total number of orbitals associated with the principal quantum number n = 3 is

a) 9 b) 8 c) 5 d) 7

16. If n = 6, the correct sequence for filling of electrons will be,

a) ns→(n – 2)f → (n – 1)d→ np b) ns →(n – 1)d →(n – 2)f → np

c) ns → (n – 2) f → np → (n – 1)d d) none of these are correct

17. Consider the following sets of quantum numbers :

n l m s

(i) 3 0 0 + ½
(ii) 2 2 1 – ½
(iii)4 3 –2 + ½
(iv)1 0 –1 + ½
(v) 3 4 3 – ½

Which of the following sets of quantum number is not possible ?

a) (i), (ii), (iii) and (iv) **b) (ii), (iv) and (v)** c) (i) and (iii) d) (ii), (iii) and (iv)

18. How many electrons in an atom with atomic number 105 can have (n + l) = 8 ?

a) 30 **b) 17** c) 15 d) unpredictable

19. Electron density in the yz plane of $3d_{x^2-y^2}$ orbital is

a) zero b) 0.50 c) 0.75 d) 0.90

20. If uncertainty in position and momentum are equal, then minimum uncertainty in velocity is

a) $\frac{1}{m}\sqrt{\frac{h}{\pi}}$ b) $\sqrt{\frac{h}{\pi}}$ **c)** $\boldsymbol{\frac{1}{2m}\sqrt{\frac{h}{\pi}}}$ d) $\frac{h}{4\pi}$

21. A macroscopic particle of mass 100 g and moving at a velocity of 100 cm s^{-1} will have a de Broglie wavelength of

a) 6.6×10^{-29}cm b) 6.6×10^{-30}cm **c)** $\boldsymbol{6.6 \times 10^{-31}}$ **cm** d)6.6×10^{-32} cm

22. The ratio of de Broglie wavelengths of a deuterium atom to that of an α - particle, when the velocity of the former is five times greater than that of later, is

a) 4 b) 0.2 c) 2.5 **d) 0.4**

23. The energy of an electron in the 3rd orbit of hydrogen atom is –E. The energy of an electron in the first orbit will be

a) –3E b) –E / 3 c) –E / 9 **d) –9E**

24. Time independent Schnodinger wave equation is

a) $\boldsymbol{\hat{H}\psi = E\psi}$ b) $\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E + V)\psi = 0$

c) $\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{h^2}(E - V)\psi = 0$ d) all of these

25. Which of the following does not represent the mathematical expression for the Heisenberg uncertainty principle ?

a) $\Delta x \,.\, \Delta p \geq \frac{h}{4\pi}$ b) $\Delta x.\, \Delta v \geq \frac{h}{4\pi m}$ c) $\Delta E \,.\, \Delta t \geq \frac{h}{4\pi}$ **d)** $\boldsymbol{\Delta E.\, \Delta x \geq \frac{h}{4\pi}}$

Answer the following

26. Which quantum number reveal information about the shape, energy, orientation and size of orbitals?

Magnetic quantum number

	Quantum Number	**Information Obtained**
(i)	Principal Quantum no.	Size and energy
(ii)	Azimuthal Quantum no.	Shape
(iii)	Magnetic Quantum no.	Orientation

27. How many orbitals are possible for n = 4?

n = 4, l = 0, 1, 2, 3 four sub-shells => s, p, d, f

l = 0 m_l = 0; one 4s orbital

l = 1 m_l = -1, 0, +1; three 4p orbitals.

l = 2 m_l = -2, -1, 0, +1, +2; five 4d orbitals.

l = 3 m_l = -3, -2, -1, 0, +1, +2, +3; seven 4f orbitals Over all sixteen orbitals.

(Or) $\mathbf{n^2=4^2=16}$

28. How many radial nodes for 2s, 4p, 5d and 4f orbitals exhibit? How many angular nodes?

Orbital	**N**	**l**	**Radial node n-l-1**	**Angular node l**
2s	2	0	1	0
4p	4	1	2	1
5d	5	2	2	2
4f	4	3	0	3

29. The stabilization of a half filled d- orbital is more pronounced than that of the p-orbital why?

(i) The half filled d- orbital is much stabilized than the p-orbital.

(ii) This is due to its high exchange energy and symmetry than that of p-orbital.

30. Consider the following electronic arrangements for the d^5 configuration.

⥮	⥮	↿		

(a)

↿	↿	↿	⥮	

(b)

↿	↿	↿	↿	↿

(c)

(i) which of these represents the ground state

(ii) which configuration has the maximum exchange energy.

(i) C) Ground state

(ii) c) Maximum exchange energy :

↿	↿	↿	↿	↿

31. **State and explain pauli's exclusion principle**

" No two electrons in an atom can have the same set of values of all four quantum number".

For the lone electron present in hydrogen atom, the four quantum numbers are: n = 1; l = 0; m =0 and s = +1/2. For the two electrons present in **Helium**,1s^2

	N	l	m	S
First electron	1	0	0	+1/2
Second electron	1	0	0	-1/2

Spin quantum number can have only two values +1/2 and -1/2, only two electrons can be accommodated in a given orbital in accordance with pauli exclusion principle.

32. Define orbital? What are the n and l values for $3p_x$ and $4d_{x2-y2}$ electron?

An orbital is the region of space around the nucleus within the probability of finding an electron of given energy is maximum.

Orbital	n	l
$3p_x$	3	1
$4d_{x2-y2}$	4	2

33. Explain briefly the time independent Schrödinger wave equation?

Erwin Schrodinger expressed the wave nature of electron in terms of a differential equation. This equation determines the change of wave function in space depending on the field of force in which the electron moves. The time independent Schrodinger equation can be expressed as, $\hat{H}\psi = E\psi$

Where $\hat{H}$ is called Hamiltonian operator, ψ is the wave function and is a function of position co-ordinates of the particle and is denoted as ψ (x, y, z) E is the energy of the system

$$\hat{H} = \left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V\right]$$

Can be written as, $\left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V\psi\right] = E\psi$

Multiply by - $\frac{8\pi^2 m}{h^2}$ and rearranging

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

The above Schrödinger wave equation does not contain time as a variable and is referred to as time independent Schrödinger wave equation. This equation can be solved only for certain values of E, the total energy. i.e. the energy of the system quantised . The permitted total energy values are called Eigen values and corresponding wave functions represent the atomic orbitals.

34. Calculate the uncertainty in position of an electron, if $\Delta v = 0.1\%$ and $\upsilon = 2.2 \times 10^6\ ms^{-1}$

$$\Delta x.\ \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x.\ \Delta v.m = \frac{h}{4\pi}$$

$$\Delta x = \frac{h}{4\pi\Delta v.m}$$

$$\Delta x = \frac{6.626 \times 10^{-34}\ Kgm^2s^{-1}}{4x3.14x\ 9.1 \times 10^{-31}\ Kg \times 2.2 \times 10^3 ms^{-1}}$$

$$\Delta x = \frac{6.626 \times 10^{-34}\ x\ 10^{-3} \times 10^{31}}{4x3.14x\ 9.1 \times 2.2}$$

$$\Delta x = \frac{6.626 \times 10^{-6}}{251.45}$$

$\Delta x = 0.02635\ x\ 10^{-6}$

$\Delta x = 2.635x10^{-8}$ m

Another method:

$$\Delta x.\ \Delta p \geq \frac{h}{4\pi}$$

$\Delta x.\ \Delta p \geq 5.28 \times 10^{-35}\ Kgm^2s^{-1}$

$\Delta x.\ (m\Delta v) \geq 5.28 \times 10^{-35}\ Kgm^2s^{-1}$

Given $\Delta v = 0.1\%$

$\upsilon = 2.2 \times 10^6\ ms^{-1}$; $m = 9.1 \times 10^{-31}$ Kg

$$\Delta v = \frac{0.1}{100} \times 2.2 \times 10^6\ ms^{-1} = 2.2 \times 10^3\ ms^{-1}$$

$$\Delta x \geq \frac{5.28 \times 10^{-35}\ Kgm^2s^{-1}}{9.1 \times 10^{-31}\ Kg \times 2.2 \times 10^3 ms^{-1}}$$

$$\mathbf{\Delta x \geq 2.64 \times 10^{-8}\ m}$$

35. Determine the values of all the four quantum numbers of the 8th electron in O- atom a 15th electron in the Cl atom and the last electron in chromium.

Electronic configuration of oxygen (Z=8)= $1s^2\ 2s^2\ 2p_x{}^2 2p_y{}^1 2p_z{}^1$

⥮	⥮	⥮	1	1

8th electron present in **$2p_x$ orbital** and an the quantum numbers are

n = principal quantum number =2

l= azimuthal quantum number= 1

m_l =magnetic quantum number = either +1or -1

m_s=+1/2

Electronic configuration of chlorine (Z=17) = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x{}^2 3p_y{}^2\ 3p_z{}^1$

$1s^2$	$2s^2$	$2p^6$			$3s^2$	$3p^5$		
⥮	⥮	⥮	⥮	⥮	⥮	⥮	⥮	1
						$3p_x$	$3p_y$	$3p_z$

15th electron present in **$3p_z$ orbital** and

the quantum numbers are n = 3, l =1 m_l = either +1 or -1 and m_s = +1/2

Electronic configuration of chromium (Z=24) = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^5\ 4s^1$

n=3 l=2, m=+2 s =+1/2

36. The quantum mechanical treatment of the hydrogen atom gives the energy value: $E_n = \frac{-13.6}{n^2}$ ev atom^{-1}

(i) use this expression to find ΔE between n=3 and m=4

(ii) Calculate the wavelength corresponding to the above transition

$$E_n = \frac{-13.6}{n^2} \text{ eV atom}^{-1}$$

n = 3 $\quad E_3 = \frac{-13.6}{3^2} = \frac{-13.6}{9} = -1.51 \text{ eV atom}^{-1}$

n = 4 $\quad E_4 = \frac{-13.6}{4^2} = \frac{-13.6}{16} = -0.85 \text{ eV atom}^{-1}$

$\Delta E = (E_4 - E_3)$

$= (-0.85) - (-1.51) \text{ eV atom}^{-1}$

$= (-0.85 + 1.51)$

$= 0.66 \text{ eV atom}^{-1} \quad (1\text{eV} = 1.6 \times 10^{-19} \text{ J})$

$\Delta E = 0.66 \times 1.6 \times 10^{-19}$ J

$\Delta E = 1.06 \times 10^{-19}$ J

$h\nu = 1.06 \times 10^{-19} \text{ J} \quad \frac{hc}{\lambda} = 1.06 \times 10^{-19} \text{ J}$

$$\lambda = \frac{hc}{1.06 \times 10^{-19} \text{J}} = \frac{6.626 \times 10^{-34}\ JS \times 3 \times 10^8\ ms^{-1}}{1.06 \times 10^{-19} J}$$

$\lambda = 1.875 \times 10^{-6}$ m

37. how fast must a54g tennis ball in order to have a de Broglie wavelength that is equal to that a photon of green light 5400Å ?

De Broglie wavelength of the tennis ball equal to 5400 Å

$m = 54\text{ g} ; v = ? \quad \lambda = \frac{h}{mV} \qquad V = \frac{h}{m\lambda}$

$V = \frac{6.626 \times 10^{-34}\ JS}{54 \times 10^{-3}\ Kg \times 5400 \times 10^{-10} m}$ **$V = 2.27 \times 10^{-26}\ ms^{-1}$**

38. For each of the following, give the sub level designation , the allowable m values and the number of orbitals (i) n=4, l=2 (ii) n=5, l=3 (iii) n=7, l=0

N	l	Sub Energy levels	m_1 values	Number of orbitals
4	2	4d	-2, -1, 0,+1,+2	Five 4d orbitals
5	3	5f	-3,-2, -1, 0, +1,+2, +3	Seven 5f orbitals
7	0	7s	0	One 7s orbitals

39. **Give the electronic configuration of Mn^{2+} an Cr^{3+}**

Ions	No. of electrons	Electronic configuration
Mn^{2+}	23	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5$
Cr^{3+}	21	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^3$

40. Describe the Aufbau principle

The word Aufbau in German means 'building up'.

- In the ground state of the atoms, the orbitals are filled in the order of their increasing energies.
- That is the electrons first occupy the lowest energy orbitals available to them.
- Once the lower energy orbitals are completely filled, then the electrons enter the next higher energy orbitals.
- The order of filling of various orbitals as per Aufbau principle is 1s<2s <2p<3s<3p<4s<3d<4p<5s<4d<……

For example: Electronic configuration of chromium (Z=24) = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^5\ 4s^1$

41. An atom of an element contains 35 electrons and 45 neutrons. Deduce

(i) the number of protons

(ii) the electronic configuration for the element

(iii) All the four quantum numbers for the last electron

Ans. (i) No of protons= 35

(ii) Electronic configuration $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^5$

(iii)

⇅	⇅	↿
$4p_x$	$4p_y$	$4p_z$

Last electron present in $4P_y$ orbital

$n = 4, l = 1\ m_l =$ either +1 or -1 and s = -1/2

42. Show that the circumference of the bohr's orbit for the hydrogen atom is an integral multiple of the de Broglie wave length associated with the electron revolving around the nucleus.

Ans: Quantization of angular momentum and de Broglie concept.

- According to the de Broglie concept, the electron that revolves around the nucleus exhibits both particle and wave character.
- In order for the electron wave to exist in phase , the circumference of the orbit should be an integral multiple of the wavelength of the electron wave. Otherwise, the electron wave is out of phase .

Circumference of the orbit = nλ

$2\pi r = n\lambda$ $2\pi r = nh / mv$

Rearranging, $mvr = nh/2\pi$ Angular momentum = $nh/2\pi$

The above equation was already predicted by Bohr. Hence , De Broglie and Bohr's concepts are in agreement with each other.

43. Calculate the energy required for the process. $He^{+}_{(g)} \rightarrow He^{2+} + e^{-}$ The ionisation energy required for the H atom in its ground state is -13.6 ev atom^{-1}.

$He^{+} \rightarrow He^{2+} + e^{-}$

$E_n = \frac{-13.6z^2}{n^2}$ $E_1 = \frac{-13.6(2)^2}{(1)^2} = -54.4$

$E_\infty = \frac{-13.6(2)^2}{(\infty)^2} = 0$

∴ Required Energy for the given process

$= E_\infty - E_1 = 0 - (-54.4) = 54.4$ev.

44. An ion with the mass number 37 possesses unit negative charge . If the ion contains 11.1 % more neutrons than electrons. Find the symbol of the ion.

	Atom	**Uni-negative ion**
Number of electron	X – 1	X
Number of protons	X – 1	X - 1
Number of neutrons	Y	Y

Given that y, = x + 11.1% of x

$= \left(x + \frac{11.1}{100}\ x\right) = x + 0.111x$

$y = 1.111\ x$

Mass number = 37

Number of protons number of neutrons = 37

$(x-1) + 1.111\ x = 37$

$X + 1.111x = 38$

$2.111\ x = 38$ $x = \frac{38}{2.11}$; $x = 18.009$

$x = 18$ (whole number)

∴ Atomic number = x – 1 = 18 – 1 = 17

Mass number = 37

Symbol of the ion $^{37}_{17}Cl^{-}$

45. The Li ion is a hydrogen like ion that can be described by the Bohr's model. Calculated the Bohr radius of the third orbit and calculate the energy of the electron in 4th orbit

$r_n = \frac{(0.529)n^2}{z}$ Å $\qquad E_n = \frac{-13.6\,(z^2)}{n^2}$ ev atom^{-1}

for Li^{2+} Z = 3

Bohr radius for the third orbit (r_3)

$$= \frac{(0.529)(3)^2}{3} = 0.529 \times 3 = \mathbf{1.587\ Å}$$

Energy of an electron in the fourth orbit

$$(E_4) = \frac{-13.6(3)^2}{(4^2)} = \mathbf{-7.65\ eV\ atom^{-1}}$$

46. Protons can be accelerated in particle accelerators. Calculate the wavelength (in Å) of such accelerated proton moving at 2.85 × 10⁸ms⁻¹ (the mass of proton is 1.673 × 10⁻²⁷ Kg)

$V = 2.85 \times 10^8\ ms^{-1}$; $m_p = 1.673 \times 10^{-27}$ Kg

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ kgm^2ms^{-1}}{1.673 \times 10^{-27} kg \times 2.85 \times 10^8\ ms^{-1}} = 1.389 \times 10^{-15} m \quad [\text{Å} = 10^{-10} m]$$

➔ $\lambda = \mathbf{1.389 \times 10^{-5}\ Å}$

47. What is the de Broglie wave length(in cm) of a 160g cricket ball travelling at 140 Km hr⁻¹.

$m = 160g = 160 \times 10^{-3}$ kg

$v = 140\ Km\ hr^{-1} = \frac{140 \times 10^3}{60 \times 60}\ ms^{-1}$

$v = 38.88 ms^{-1}$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ kgm^2ms^{-1}}{160 \times 10^{-3} kg \times 38.88\ ms^{-1}}$$

$\lambda = \mathbf{1.065 \times 10^{-34} m}$

wave length in cm =1.065 x 10⁻³⁴ x 100 =1.065 x 10⁻³²cm

48. Suppose that the uncertainty in determining the position of an electron in an orbit is 0.6Å. what is the uncertainty in its momentum?

$\Delta x = 0.6Å = 0.6 \times 10^{-10}m$

$\Delta p = ?$; $\mathbf{\Delta x\ .\ \Delta p \geq \frac{h}{4\pi}}$

$\Delta x\ .\ \Delta p \geq 5.28 \times 10^{-35}\ kgm^2s^{-1}$

$(0.6 \times 10^{-10})\ .\ \Delta p \geq 5.28 \times 10^{-35}$

$\Delta p \geq \frac{5.28 \times 10^{-35}\ kgm^2s^{-1}}{0.6510^{-10}m}$ $\qquad \mathbf{\Delta p \geq 8.8 \times 10^{-25}\ kgm\ s^{-1}}$

49. Show that if the measurement of the uncertainty in the location of the particle is is equal to its de Broglie wavelength, the minimum uncertainty in its velocity/4π.

$$\mathbf{\Delta x = \Delta v = ?} \qquad \mathbf{\Delta x \,.\, \Delta p \geq \frac{h}{4\pi}} \qquad \lambda(\mathrm{m}\ \Delta\mathrm{v}) \geq \frac{h}{4\pi}$$

$$\Delta v \geq \frac{h}{4\pi\ (m\lambda)} \quad \Delta v \geq \frac{h}{4\pi \times m \times \frac{h}{mv}} \quad [\lambda = \frac{h}{mv}]\ \mathbf{\Delta v \geq \frac{v}{4\pi}}\ ;$$

Therefore, minimum uncertainty in velocity $= \frac{v}{4\pi}$

50. What is the de Broglie wavelength of an electron, which is accelerated from the rest, through a potential difference of 100V?

Potential difference = 100V

$= 100 \times 1.6 \times 10^{-19}$J

$$\lambda = \frac{h}{\sqrt{2mev}} \quad = \frac{6.626 \times 10^{-34}\ \mathrm{kgm^2ms^{-1}}}{\sqrt{2 \times 9.1 \times 10^{-31}\ Kg \times 100 \times 1.6 \times 10^{-19} J}}$$

$$\mathbf{\lambda = 1.22 \times 10^{-10} m}$$

51. Identify the missing quantum numbers and the sub energy level

n	l	m	Sub energy level
?	?	0	4d
3	1	0	?
?	?	?	5p
?	?	-2	3d

Answer:

n	l	M	Sub energy level
4	2	0	4d
3	1	0	3p
5	1	Any one value -1, 0, +1	5p
3	2	-2	3d

LESSON 3.PERIODIC CLASSIFICATION

1. Frequency of X-ray = $\sqrt{v} = a(Z-b)$ where υ is frequency, Z is atomic number and a, b are constants.
2. Atomic radius of homonuclear diatomic molecule = r_A

   $r_A = \frac{d_{A-A}}{2}$ where d_{A-A} =Inter nuclear distance
3. Atomic radius of heteronuclear diatomic molecule.

   $r_A + r_B = d_{A-B}$

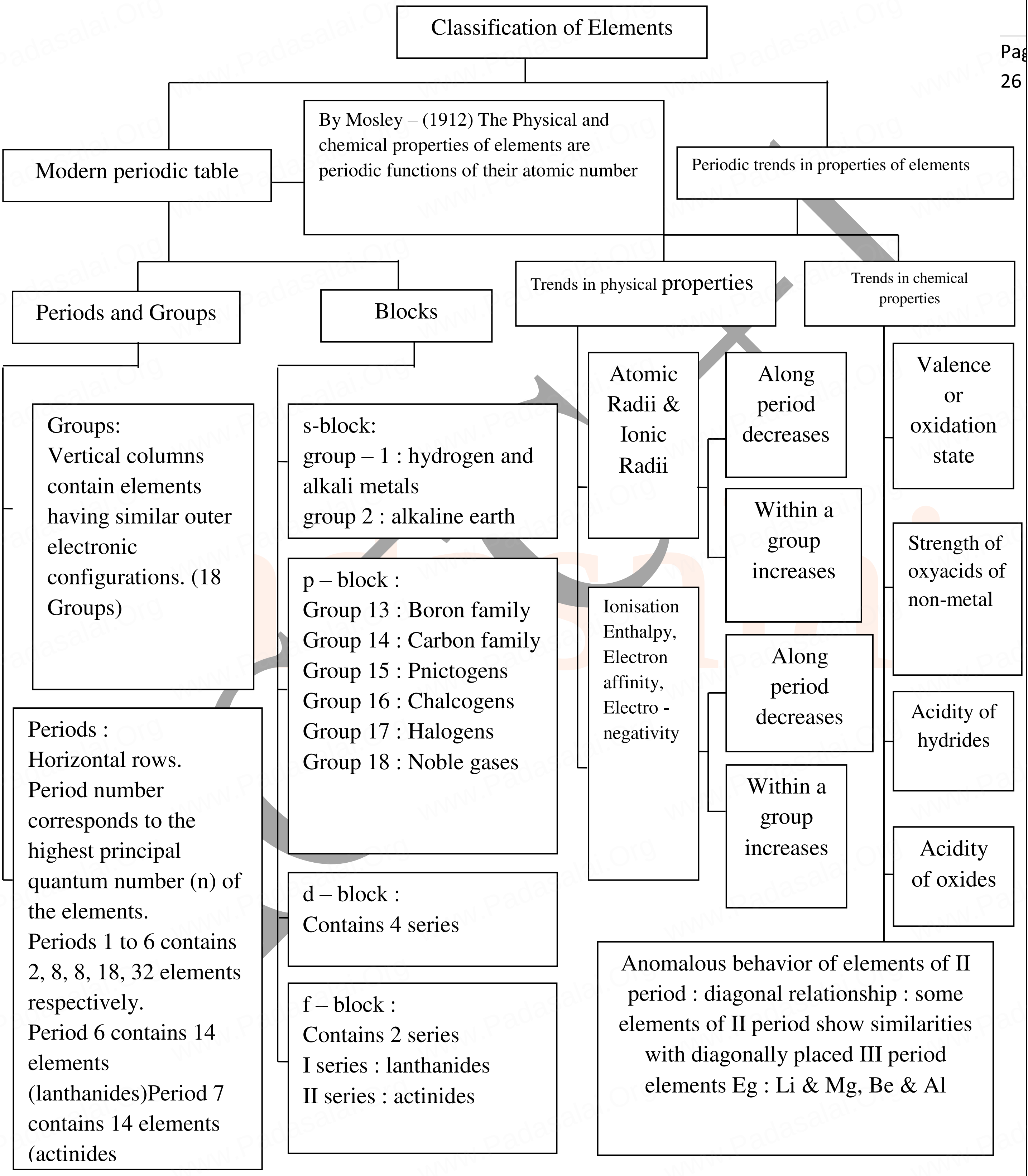
   $\therefore r_A = d_{A-B} - r_B,\quad r_B = d_{A-B} - r_A$
4. $Metallic\ radius = \frac{Dis\tan ce\ between\ two\ adjacent\ atom}{2}$
5. Effective nuclear charge = $Z_{eff} = Z - S$
6. Electronegativity $= X_A - X_B = 0.182\sqrt{E_{A-B}} - (E_{AA}\ x\ E_{BB})^{1/2}$

Important points in periodic variation

	Periodic property	Unit	Across the period	Down the group
1.	Atomic radii	Å	decreases	Increases
2.	Ionic radii	Å	decreases	Increases
3.	Ionisation energy	kJ mol^{-1}	increases	decreases
4.	Electron affinity	kJ mol^{-1}	increases	decreases
5.	Electronegativity	No unit	increases	decreases
6.	Valency	No unit	increases	remains the same
7.	Chemical reactivity	No unit	increases	decreases
8.	Electropositive character	No unit	increases	decreases
9.	Metallic character	No unit	increases	decreases

10	Basic character	No unit	increases	Decreases

CHAPTER MAP



Classification of Elements

Modern periodic table

By Mosley – (1912) The Physical and chemical properties of elements are periodic functions of their atomic number

Periodic trends in properties of elements

Periods and Groups

Blocks

Trends in physical properties

Trends in chemical properties

Groups: Vertical columns contain elements having similar outer electronic configurations. (18 Groups)

Periods : Horizontal rows. Period number corresponds to the highest principal quantum number (n) of the elements. Periods 1 to 6 contains 2, 8, 8, 18, 32 elements respectively. Period 6 contains 14 elements (lanthanides)Period 7 contains 14 elements (actinides

s-block:
group – 1 : hydrogen and alkali metals
group 2 : alkaline earth

p – block :
Group 13 : Boron family
Group 14 : Carbon family
Group 15 : Pnictogens
Group 16 : Chalcogens
Group 17 : Halogens
Group 18 : Noble gases

d – block :
Contains 4 series

f – block :
Contains 2 series
I series : lanthanides
II series : actinides

Atomic Radii & Ionic Radii

Along period decreases

Within a group increases

Ionisation Enthalpy, Electron affinity, Electro - negativity

Along period decreases

Within a group increases

Valence or oxidation state

Strength of oxyacids of non-metal

Acidity of hydrides

Acidity of oxides

Anomalous behavior of elements of II period : diagonal relationship : some elements of II period show similarities with diagonally placed III period elements Eg : Li & Mg, Be & Al

Important Points to Remember

- **Elements known during 19th Century** – 118 Elements. Out of 118 known 92 elements are found in nature.
- **Johann Dobereiner's classification** – Law of triads – It was seen that invariable, the atomic weight of the other two members of the triad. He noted that elements with similar properties occur in groups of three which he called triads.
- **Chancourtois classification** – In this system, elements that differed from each other in atomic weight by 16 or multiples of 16 fell very nearly on the same vertical line. Elements lying directly under each other showed a definite similarity. This was the First periodic law.
- **Newland's classification** – **Law of octaves** – This law states that, when elements are arranges in the order of increasing atomic weights, the properties of the eighth element are a repetition of the properties of the first element. This law was seemed to be applicable only for elements upto atomic number 20 (Calcium).
- **Mendeleev's classification** – **Mendeleev's periodic law** – This law states that the properties of the elements can be represented as periodic function of their atomic weights.
- **Modern periodic law** – It was given by Henry Moseley in 1913. This law states that "The physical and chemical properties of the elements are periodic functions of their atomic numbers".
- Moseley's correlation – between atomic number and the frequency of X-rays. $\sqrt{\upsilon} = a(Z-b)$, where υ = frequency of the X-rays emitted by the elements concerned. Z = atomic number; a and b = constants and have same values for all the elements.
- **Periodicity** – The repetition of physical and chemical properties at regular intervals is called periodicity.
- Groups – The vertical columns in the periodic table are called groups. There are 18 vertical columns which constitute 18 groups or families.
- Periods – There are 7 horizontal rows in the periodic table known as periods.

First period	2 elements	very short	$_1$H and $_2$He
Second period	8 elements	short	$_3$Li to $_{10}$Ne
Third period	8 elements	short	$_{11}$Na to $_{18}$Ar
Fourth period	18 elements	long	$_{19}$K to $_{36}$Kr
Fifth period	18 elements	long	$_{37}$Rb to $_{54}$Xe

Sixth period 32 elements very long $_{55}$Cs to $_{86}$Rn

Seventh period 32 elements very long $_{87}$Fr to $_{118}$Ogcontinued.

- **Electronic configuration –** The distribution of electrons into orbitals, s, p, d and f, of an atom is called its electronic configuration.
- **Lanthanides –** The first f-transition series consisting of 14 elements placed separately as panel at the bottom of the periodic table.
- **Actinoids –** The second f – transition series consisting of 14 elements placed separately as panel at the bottom of the periodic table.
- **Group 17 –** Halogen family.
- **Group 16 –** Chalcogen family (or) oxygen family.
- **Division of elements based on electronic configuration –** The entire periodic table can be divided into s, p, d and f blocks.
- **Group 18 –** Noble gases.
- **Group 1 –** Alkali metals.
- **Group 2 –** Alkaline earth metals.
- **d-block elements –** The elements of the groups 3 to 12 are called p-block elements or transition elements with general valence shell electronic configuration ns$^{1-2}$, (n-1)d$^{1-10}$.
- p-block elements – The elements of groups 13 to 18 are called p-block elements or representative elements and have a general electronic configuration ns^{2}, np$^{1-6}$.
- **s-block elements –** The elements of group 1 and group 2 are called s-block elements, since the last valence electron enters the ns orbital. general electronic configuration ns$^{1-2}$.
- f-block elements – The lanthanides (4f$^{1-14}$, 5d$^{0-1}$, 6s^{2}) and the actinides (5f$^{0-14}$, 6d$^{0-2}$, 7s^{2}) are called f-block elements.
- **Types of elements –**

Basis of chemical behavior	**Basis of physical properties**
Main group elements	Metals
Noble gases	Non-metals
Transition elements	Metalloids
Inner transition elements	Metals

- **Example for periodic properties –** (i) Atomic radius (ii) Ionic radius (iii) Ionization enthalpy (iv) Electron gain enthalpy (v) Electrongativity.
- **Atomic radius –** It is the distance between the centre of the nucleus of an atom and the outermost shell containing the valence electron.

- **Covalent radius** – It is one half of the internuclear distance between two identical atoms linked together by a single covalent bond.

- **Metallic radius** – It is defined as one half of the distance between two adjacent metal atoms in the closely packed metallic crystal lattice.

- **Ionic radius** – It is defined as the distance from the centre of the nucleus of the ion up to which it exerts its influence on the electron cloud of the ion.

- **Isoelectronic ions** – The ions of different elements having the same number of electrons are called isoelectronic ions. e.g. Na^+, Mg^{2+}, Al^{3+}, F^-, O^{2-}, N^{3-}

- **Ionization enthalpy** – The energy required to remove the most loosely bound electron from the valence shell of an isolated neutral gaseous atom is called as Ionization energy.

  The unit of Iionization energy = KJ $mole^{-1}$.

- **Electron gain enthalpy (or) Electron affinity** – The electron gain enthalpy of an element is the amount of energy released when an electron is added to a neutral gaseous atom. The unit of electron affinity = KJ $mole^{-1}$.

- **Electronegativity** – The relative tendency of an element present in a covalently bonded molecule, to attract the shared pair of electrons towards itself.

- **Valency** – It is defined as the combining capacity of an element.

- Valence electrons – The total number of electrons in the valence shell or equal to eight minus the number of valence electrons.

- **Diagonal relationship** – In a periodic table, a diagonal relationship exists among certain pairs of elements. Thus Li is similar to Mg, Be is similar to Al and B is similar to Si.

I. Choose the best Answer:

1. **What would be the IUPAC name for an element with atomic number 222?**

a) bibibiium b) bididium c) didibium **d)bibibium**

2. **The electronic configuration of the elements A and B are $1s^2$, $2s^2$, $2p^6$,$3s^2$ and $1s^2$, $2s^2$, $2p^5$ respectively. The formula of the ionic compound that can be formed between these elements is**

a) AB **b) AB_2** c) A_2B d) none of the above.

3. **The group of elements in which the differentiating electron enters the anti penultimate shell of atoms are called**

a) p-block elements b) d-block elements c)s-block elements **d) f-block elements**

4. **In which of the following options the order of arrangement does not agree with the variation of property indicated against it? (NEET 2016 Phase 1)**

a) I < Br < Cl < F (increasing electron gain enthalpy)

b) Li < Na < K < Rb (increasing metallic radius)

c) $Al^{3+} < Mg^{2+} < Na^{+} < F^{-}$ (increasing ionic size)

d) B < C < O < N (increasing first ionisation enthalpy)

5. **Which of the following elements will have the highest electronegativity?**

a) Chlorine b) Nitrogen c) Cesium **d) Fluorine**

6. Various successive ionisation enthalpies (in kJ mol^{-1}) of an element are given below.

IE_1	**IE_2**	**IE_3**	**IE_4**	**IE_5**
577.5	**1,810**	**2,750**	**11,580**	**14,820**

The element is

a) phosphorus b) Sodium **c) Aluminium** d) Silicon

7. In the third period the first ionization potential is of the order.

a) Na > Al > Mg > Si > P **b) Na < Al < Mg < Si < P**

c) Mg > Na > Si > P > Al d) Na< Al < Mg < Si < P

8. Identify the wrong statement.

- **a) Amongst the isoelectronic species, smaller the positive charge on cation, smaller is the ionic radius**
- b) Amongst isoelectric species greater the negative charge on the anion, larger is the ionic radius
- c) Atomic radius of the elements increases as one moves down the first group of the periodic table
- d) Atomic radius of the elements decreases as one moves across from left to right in the 2nd period of the periodic table.

9. Which one of the following arrangements represent the correct order of least negative to most negative electron gain enthalpy

a) Al < O < C < Ca < F b) Al < Ca < O < C < F

c) C < F < O < Al < Ca **d) Ca < Al < C < O < F**

10. The correct order of electron gain enthalpy with negative sign of F, Cl, Br and I having atomic number 9, 17, 35 and 53 respectively is

a) I > Br > Cl > F b) F > Cl > Br > I **c) Cl > F > Br > I** d) Br > I > Cl > F

11. Which one of the following is the least electronegative element?

a) Bromine b) Chlorine c) Iodine **d) Hydrogen**

12. The element with positive electron gain enthalpy is

a) Hydrogen b) Sodium **c) Argon** d) Fluorine

13. The correct order of decreasing electronegativity values among the elements X, Y, Z and A with atomic numbers 4, 8 , 7 and 12 respectively

a) Y > Z > X > A b) Z > A > Y > X c) X > Y > Z > A d) X > Y > A > Z

14. Assertion: Helium has the highest value of ionisation energy among all the elements known

Reason: Helium has the highest value of electron affinity among all the elements known

a) Both assertion and reason are true and reason is correct explanation for the assertion

b) Both assertion and reason are true but the reason is not the correct explanation for the assertion

c) **Assertion is true and the reason is false**

d) Both assertion and the reason are false

15. The electronic configuration of the atom having maximum difference in first and second ionisation energies is

a) $1s^2, 2s^2, 2p^6, 3s^1$ b) $1s^2, 2s^2, 2p^6, 3s^2$

c) $1s^2, 2s^2, 2p^6, 3s^2, 3s^2, 3p^6, 4s^1$ d) $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$

16. Which of the following is second most electronegative element?

a) Chlorine b) Fluorine **c) Oxygen** d) Sulphur

17. IE_1 and IE_2 of Mg are 179 and 348 kcal mol^{-1} respectively. The energy required for the reaction $Mg \rightarrow Mg^{2+} + 2e^-$ is

a) +169 kcal mol^{-1} b) - 169 kcal mol^{-1} **c) + 527 kcal mol^{-1}** d) - 527 kcal mol^{-1}

18. In a given shell the order of screening effect is

a) s > p > d > f b) s > p > f > d c) f > d > p > s d) f > p > s > d

19. Which of the following orders of ionic radii is correct?

a) $H^- > H^+ > H$ b) $Na^+ > F^- > O^{2-}$ c) $F > O^{2-} > Na^+$ **d) None of these**

20. The First ionisation potential of Na, Mg and Si are 496, 737 and 786 kJ mol^{-1} respectively. The ionisation potential of Al will be closer to

a) 760 kJ mol^{-1} **b) 575 kJ mol^{-1}** c) 801 kJ mol^{-1} d) 419 kJ mol^{-1}

21. Which one of the following is true about metallic character when we move from left to right in a period and top to bottom in a group?

a) Decreases in a period and increases along the group

b) Increases in a period and decreases in a group

c) Increases both in the period and the group

d) Decreases both in the period and in the group

22. How does electron affinity change when we move from left to right in a period in the periodic table?

a) Generally increases b) Generally decreases
c) Remains unchanged d)First increases and then decreases

23. Which of the following pairs of elements exhibit diagonal relationship?

a) Be and Mg b) Li and Mg c) Be and B **d) Be and Al**

Write Brief Question with Answer

24. Define modern periodic law.

The modern periodic law states that, “the physical and chemical properties of the elements are periodic functions of their atomic numbers.”

25. What are isoelectronic ions? Give examples.

Ions of different elements having the same number of electrons are called iso electronic ions.

Ions of different elements	Na^+	Mg^{+2}	Al^{+3}	F^-	O^{2-}	N^{3-}
No. of electrons	10	10	10	10	10	10

26.What is effective nuclear charge?

The net nuclear charge experienced by valence electrons in the outermost shell is called the effective nuclear charge. $\mathbf{Z_{eff} = Z - S}$

Where Z -atomic number ‘S’ - screening constant

27. Is the definition given below for ionisation enthalpy correct? “Ionisation enthalpy is defined as the energy required to remove the most loosely bound electron from the valence shell of an atom”

No the above definition is incorrect .

The correct definition is, Ionisation energy is defined as the *minimum amount of* energy required to remove the most loosely bound electron from the valence shell of the *isolated neutral gaseous atom in its ground state.*

28. Magnesium loses electrons successively to form Mg^+, Mg^{2+} and Mg^{3+} ions. Which step will have the highest ionisation energy and why?

$Mg + I.E_1 \rightarrow Mg^+ + 1e^-$ ------ (i)
$Mg + I.E_2 \rightarrow Mg^{2+} + 1e^-$ ------- (ii)
$Mg^{2+}\ I.E_3 \rightarrow Mg^{3+} + 1e^-$ ------- (iii)

As Mg^{2+} ion having the stable [Ne] inert gas configuration, it requires more energy to loose one electrons and forming Mg^{3+} ions. So **third step** will have the highest ionisation energy.

$I.E_1 > I.E_2 > I.E_3$

(Or)

- Mg^{2+} consist of 10 electrons (2, 8) attaining the stable noble gas configuration of Neon (Z = 10)

- Since the valence orbital is completely filled, more energy will be required to remove electrons.

29. Define electronegativity

It is defined as the relative tendency of an element present in a covalently bonded molecule, to attract the shared pair of electrons towards itself.

30. How would you explain the fact that the second ionisation potential is always higher than the ionisation potential?

The total number of electrons are less in the cation than the neutral atom while the nuclear charge remains the same. Therefore the effective nuclear charge of the cation is higher than the corresponding neutral atom. Thus the successive ionisation energies, always increase in the following order**$IE_1 < IE_2 < IE_3 <$ ……..**

31. Energy of an electron in the ground state of the hydrogen atom is -2.18×10^{-18} J. Calculate the ionisation enthalpy of atomic hydrogen in terms of $kJ\ mol^{-1}$

Ionisation energy is the amount of energy required to remove the electron from the ground state (E_1) to excited state (E_∞). $E_1 = -2.18 \times 10^{-18}$ J; $E_\infty = 0$

$\Delta E = E_\infty - E_1$ $= 0 - (-2.18 \times 10^{-18}\ J) = 2.18 \times 10^{-18}$ J

I.E per hydrogen atom = 2.18×10^{-18} J

I.E per mole of H-atom = $2.18 \times 10^{-18}\ J \times 6.023 \times 10^{23}$

$= 13.13 \times 10^5\ J\ mol^{-1}$ $= +1313 KJmol^{-1}$

32. Give the general electronic configuration of atom is one of the important factor which affects the value of ionisation potential and electron gain enthalpy. Explain

i. Electronic configuration of an atom affects the value of ionization potential and electron gain enthalpy.

ii. **Half-filled** valence shell electronic configuration and **completely filled** valence shell electronic configuration are **more stable** than partially filled electronic configuration.

iii. **For example: Be (Z=4) $1s^2 2s^2$ (Completely filled electronic configuration)**
N (Z=7) $1s^2 2s^2 2p^3$ (half filled electronic configuration)

iv. Beryllium, Nitrogen the addition of extra electron will disturb their stable electronic configuration and they have almost zero electron affinity.

v. Ionisation energy and electron affinity is the amount of energy released or required in pulling out or adding an electron to a neutral atom. So both depend electronic configuration of the element

33. In what period and group will an element with Z = 118 will be present?

Ans: 7th period, 18th group .

Explanation:

(Z = 118; $[_{86}Rn]\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^6$

In the periodic table the element with Z = 118 is located in p – block. Period no. = 7 (as n = 7 for valence shell)

Group no. = 18 (group no = 10 + ns electrons + np electrons) (n – outer most shell))

34. Justify that the fifth period of the periodic table should have 18 elements on the basis of quantum numbers.

i. According to Aufbau's principle 5th period has nine orbital (one 5s, five 4d and three 6p) to be filled.

ii. Nine orbitals can accommodate a maximum of 18 electrons. Hence fifth period of the periodic table should has 18 elements from rubidium (2 = 37) to Xenon (Z = 54).

35. Elements a, b, c and d have the following electronic configuration:

a : $1s^2, 2s^2, 2p^6$ **b : $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$**

c : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$ **d:$1s^2,2s^2,2p^1$**

Which group of element among will belongs to the same group of the periodic table

Elements of **a** and **c** belongs to **group18**; Elements of **b** and **d** belongs to **group 13**

36. Give the general electronic configuration of lanthanides and actinides

Lanthanides : $[_{54}Xe]\ 4f^{1-14}\ 5d^{0-1}\ 6s^2$

Actinides : $[_{86}Rn]\ 5f^{0-14}\ 6d^{0-2}7s^2$

37. Why halogens acts as a oxidizing agents

i. (i) Due to low bond dissociation enthalpy, high electronegativity and large negative electron gain enthalpy halogens have a strong tendency to accept electron and thus get reduced $\mathbf{X_2 + 2e^- \rightarrow 2X^-}$

ii. (ii) The ready acceptance of the electron is due to the strong oxidising nature of the the halogens.

iii. F_2 is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase. In general, a halogen oxidises halide ions of higher atomic number

iv. Hence, the oxidising ability of halogens decreases from fluorine to iodine as:

$\mathbf{F_2 > Cl_2 > Br_2 > I_2}$

38. Mention any two anomalous properties of second period elements.

i. Lithium and Beryllium form more covalent compounds, unlike the alkali and alkali earth metals which predominantly form ionic compounds.

ii. The elements of the second period have only four orbitals (2s & 2p) in the valence shell and have a maximum co-valence of 4, whereas the other members of the subsequent periods have more orbitals in their valence shell and shows higher valences.

For example, boron forms BF^-_4 and aluminium forms AlF_6^{3-}

39. Explain the pauling method for the determination of ionic radius.

Ionic radius:

Definition : The distance from the centre of the nucleus of the ion upto which it exerts its influence on the electron cloud of the ion.

Ionic radius of uni-univalent crystal can be calculated using Pauling's method from the inter ionic distance between the nuclei of the cation and anion. Ex: NaF, KCl, RbBr, CsI

i. Pauling assumed that ions present in a crystal lattice are perfect spheres, and they are in contact with each other therefore,

$$d = r_{C^+} + r_{A^-} \quad ------ (1)$$

Where d - the distance between the centre of the nucleus of cation C^+ and anion A^- .

r_{C+}, r_{A^-} - the radius of the cation and anion respectively .

Pauling also assumed that the radius of the ion having noble gas electronic configuration is inversely proportional to the effective nuclear charge.

$$r_C{}^+ \alpha \frac{1}{(Z_{eff})_{C^+}} \quad \text{------- (2)} \quad \text{and}$$

$$r_A{}^- \alpha \frac{1}{(Z_{eff})_{A^-}} \quad \text{------- (3)}$$

Where Z_{eff} is the effective nuclear charge and $Z_{eff} = Z - S$

Dividing the equation 2 by 3

$$\frac{r_{C^+}}{r_{A^-}} = \frac{(Z_{eff})_{A^-}}{(Z_{eff})_{C^+}} \quad \text{------- (4)}$$

On solving equation and (1) and (4) the values of $r_C{}^+$ and r_{A^-} can be obtained.

40. Explain the periodic trend of ionisation potential.

The energy required to remove the most loosely held electron from an isolated gaseous atom is called as ionisation potential.

Variation along a period :

- Ionisation energy usually ***increases along a period***.
- This is due to ***increase of nuclear charge*** and ***decrease in size*** as we move from left to right in a period.

Periodic variation in group:

- Ionisation energy ***decreases down a group***.
- A gradual ***increase in atomic size***.
- As we move down a group, the valence electron occupies new shells, the distance between the nucleus and the valence electron increases .
- So, nuclear forces of attraction on valence electron decreases and hence ionisation energy also decreases down a group.

41. Explain the diagonal relationship.

- On moving diagonally across the periodic table the second and third period elements show certain similarities.
- Even though the similarity is not same as we see in a group, it is quite pronounced in the following pair of elements.

Li Be B C
↘ ↘ ↘
Na Mg Al Si

- The similarity in properties existing between the diagonally placed elements is called diagonal relationship.

42. Why the first ionisation enthalpy of sodium is lower than that of magnesium while its second ionisation enthalpy is higher than that of magnesium?

The electronic configuration of sodium (Z = 11) $1s^2\ 2s^2\ 2p^6\ 3s^1$

Magnesium (Z = 12) $1s^2\ 2s^2\ 2p^6\ 3s^2$

Magnesium atom has a ***smaller radius*** and ***higher nuclear charge*** than a sodium atom, thus more energy will be required to remove the electron from the same orbital (3s), making. The first ionisation energy of magnesium higher than that of sodium.

However, the second ionization enthalpy of sodium is higher than that of magnesium. This is because after losing 1 electron, sodium attains the stable noble gas configuration of neon ($1s^2\ 2s^2\ 2p^6$). On the other hand, magnesium, after losing 1 electron still has one electron in the 3s- orbital($1s^2\ 2s^2\ 2p^6\ 3s^1$). In order to attain the stable noble gas configuration, Thus, the energy required to remove the second electron in case of sodium is much higher than that required in case of magnesium. Hence, the second ionization enthalpy of sodium is higher than that of magnesium.

43. By using paulings method calculate the ionic radii of K^+ and Cl^- ions in the potassium chloride crystal. Given that d_{K+-Cl-} = 3.14 Å

$r(K^+) + r(Cl^-) = d(K^+ - Cl^-) = 3.14$ Å -------- (1)

The effective nuclear charge for K+ and Cl- can be calculated as follows.

K^+ =	$(1s^2)$	$(2s^2\ 2p^6)$	$(3s^2\ 3p^6)$
	Innershell	$(n-1)^{th}$ shell	n^{th} shell

$Z^*(K\text{-}) = Z - S$

$= 19 - [(0.35 \times 7) + (0.85 \times 8) + (1 \times 2)]$

$= 19 - 11.25 = 7.75$

$Z^*(Cl^-) = 17 - [(0.35 \times 7) + (0.85 \times 8) + (1 \times 2)]$

$= 17 - 11.25 = 5.75$

$$\frac{r(K^+)}{r(Cl^-)} = \frac{Z^*(Cl^-)}{Z^*(K^+)} = \frac{5.75}{7.75} = 0.74$$

$r(K^+) = 0.74\ r(Cl^-)$ ------ (2)

Substitute (2) in (1)

$0.74\ r(Cl^-) + r(Cl^-) = 3.14$ Å

$0.74\ r(Cl^-) = 3.14$ Å;

$r(Cl^-) = \frac{3.14 Å}{1.74} =$ **1.81Å**

44. Explain the following, give appropriate reasons.

(i) Ionisation potential of N is greater than that of O.

(ii) First ionisation potential of C-atom is greater than that of B atom, where as the reverse is true is for second ionisation potential.

(iii) The electron affinity values of Be, Mg and noble gases are zero and those of N (0.02 eV) and P (0.80 eV) are very low

(iv) The formation of $F^-_{(g)}$ from $F_{(g)}$ is exothermic while that of $O^{2-}_{(g)}$ from $O_{(g)}$ is endothermic.

i. Electron configuration of nitrogen (Z = 7) $1s^2\ 2s^2\ 2p^3$

Electron configuration of oxygen (Z = 8) $1s^2\ 2s^2\ 2p^4$

Nitrogen has a ***half filled electronic configuration*** and its ***more stable***. Due to stability , ionisation energy of nitrogen is high.

Hence nitrogen would require more ionization energy to remove an electron from it's outer shell than oxygen.

ii. Electron configuration of Carbon (Z = 6) $1s^2\ 2s^2\ 2p^2$
Electron configuration of Boron (Z = 5) $1s^2\ 2s^2\ 2p^1$

- The size of a carbon atom is smaller than boron. So the valence electron of carbon has ***greater nuclear charge*** than that of boron.
- Hence the first I.E of carbon is greater than that of boron.
- However, the second ionization enthalpy of boron is higher than that of carbon.
- This is because after losing 1 electron, Boron has a fully filled orbital ($2s^2$) than carbon ($2p^1$). ***Fully filled orbitals have more stability*** than partially filled orbitals so greater amount of energy will be needed to remove an electron from boron. So in this case, the second I.E of boron is higher than that of carbon.

iii. The electron affinities of Be, Mg and noble gases are almost zero.
Be (Z= 4; $1s^2\ 2s^2$) and
Mg (Z = 12 ; $1s^2\ 2s^2\ 2p^6\ 3s^2$) are having s ***fully filled in their valence shell***.

- Fully filled orbitals are ***most stable due to symmetry***.
- Therefore, these elements would be having least tendency to accept electron.

Hence, Be and Mg would be having zero electron affinity.

- N (Z = 7 ; $1s^2\ 2s^2\ 2px^1\ 2py^1\ 2pz^1$) and

P (Z = 15) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$ is having ***half-filled 2p- subshell***.

- Half-filled sub shells are ***most stable due to symmetry*** (Hund's rule).
- Thus, nitrogen and phosphorous are having least tendency to accept electron.

Hence, have low electron affinity.

iv. F (Z = 9) $1s^2\ 2s^2\ 2p^5$
Fluorine is ***highly electro negative*** in nature therefore as it gains the one electron to attain the nearest inert gas configuration, become stable and releases the energy so exothermic.
O (Z = 8) $1s^2\ 2s^2\ 2p^4$
While in oxygen the addition of first electron is exothermic in nature but addition of second electron experiences high repulsive force. So needs extra external energy to enter outer shell, hence endothermic in nature.

45. What is screening effect?

Screening effect: The repulsive force between the inner shell electrons and the valence electrons leads to a decrease in the electrostatic attractive forces acting on the valence electrons by the nucleus. Thus, the inner shell electrons act as a shield between the nucleus and the valence electrons. This effect is called shielding effect (or) Screening effect.

46. Briefly give the basis for pauling's scale of electronegativity.

Pauling's scale: Pauling, he assigned arbitrary value of electro negatives for hydrogen and fluorine as 2.2 and 4.0 respectively. Based on this the electronegativity values for other elements can be calculated using the following expression.

$$(X_A - X_B) = 0.182\sqrt{E_{AB}} - (E_{AA} * E_{BB})^{\frac{1}{2}}$$

Where E_{AB} , E_{AA} and E_{BB} are the bond dissociation energies of AB, A_2 and B_2 molecules respectively.

The electronegativity of any given element is not a constant and its value depends on the element to which it is covalently bound.

The electronegativity values play an important role in predicting the nature of the bond.

Pauling assigned arbitrary value of electro negativities for hydrogen and fluorine as 2.1 and 4.0 respectively.

47. State the trends in the variation of electronegativity in group and periods.

(i) Variation of Electronegativity in a period:

- The electronegativity generally ***increases across a period from left to righ***t.
- The atomic radius decreases in a period, as the attraction between the valence electron and the nucleus increases.
- Hence the tendency to attract shared pair of electrons increases.
- Therefore, electronegativity also increases in a period.

(ii) Variation of Electronegativity in a group :

- The electronegativity generally ***decreases down a group***.
- As we move down a group the atomic radius increases and the nuclear attractive force on the valence electron decreases.
- Hence, the electronegativity decreases.

LESSON 4 HYDROGEN

IMPORTANT REACTIONS

1. $CO + H_2O \rightarrow CO_2 + H_2$
2. $^{6}_{3}Li + ^{1}_{0}n \rightarrow He + ^{3}_{1}T$
3. $2D_2O \xrightarrow{\text{Electrolysis}} 2D_2 + O_2$
4. $4LiH + AlCl_3 \rightarrow LiAlH_4 + 3LiCl$
5. $4NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3CH_3ONa$
6. $^{3}_{1}T \rightarrow ^{3}_{2}He\ ^{0}_{-1}e$
7. $CH_4 + 2D_2 \rightarrow CD_4 + 2H_2$
8. $2NH_3 + 3D_2 \rightarrow 2ND_3 + 3H_2$
9. $2Na + 2H_2O \rightarrow 2NaOH + H_2$
10. $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$
11. $Cl_2 + H_2O \rightarrow HCl + HOCl$
12. $2F_2 + 2H_2O \rightarrow 4HF + O_2$

13. $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$
14. $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$
15. $2NaOH + D_2O \rightarrow 2NaOH + HOD$
16. $HCl + D_2O \rightarrow DCl + HOD$
17. $NH_4Cl + 4\ D_2O \rightarrow ND_4Cl + 4HOD$
18. $H_3PO_2 + D_2O \rightarrow H_{FVFCCCGZ}DPO_2 + HOD$
19. $2NaOH + D_2O \rightarrow 2NaOH + HOD$
20. $CaC_2 + 2D_2O \rightarrow Ca(OD)_2 + C_2D_2$
21. $Mg_3H_2 + 6\ D_2O \rightarrow 3Mg(OD)_2 + 2ND_3$
22. $Ca_3P_2 + 6\ D_2O \rightarrow 3Ca(OD)_2 + 2PD_3$
23. $2FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + 2H_2O$

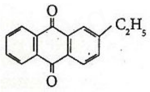
224. $2KMnO_4 + 3H_2O_2 \rightarrow 2MnO_2 + 2KOH + 2H_2O + 3O_2$

24.25. $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$

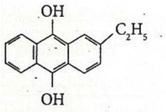
IMPORTANT FORMULA

- Water Gas – $CO + H_2$ (Synthetic or syn gas)
- Heavy water – (D_2O)
- Protium or Ordinary hydrogen – $_1H^1$
- Deuterium or Heavy hydrogen – $_1D^2$
- Tritium or Radioactive hydrogen – $_1T^3$
- Lithium Aluminium Hydride – $LiAlH_4$
- Sodium borohydride – $NaBH_4$
- Deutero Methane – CD_4
- Deutero Ammonia – ND_3
- Copper sulphate pentahydrate – $CuSO_{4}.{}_5H2O$
- Hypochlorous acid – ND_3
- Zeolite or Hydrated sodium alumino silicate – $NaO.Al_2O_3.\ xSiO_2.\ yH_2O$, where $x = 2$ to 10 and $y = 2$ to 6.
- Sodium deuteroxide – NaOD

- Deuterium chloride – DCl
- Deuterium ammonium chloride – ND_4Cl
- Deutero acetylene – C_2D_2
- Deutero phosphine – PD_2
- Deutero hypophosphorous acid – H_2DPO_2
- 2 – ethyl anthro quinine -



- 2 – ethyl anthro quinol-



- Hydrogen peroxide – H_2O_2

Important Points to Remember

❖ **Occurrence of Hydrogen –** The sun and stars are composed of 85-95% Hydrogen. It is present in the form of water, organic compounds and in all living matter.

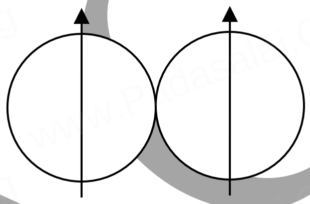
H → electrically neutral

H^+ → Proton

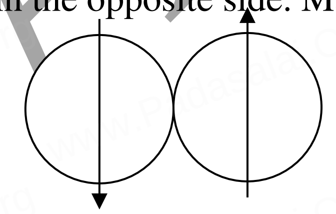
H^- → Hydride

H_2 → diatomic gaseous molecule.

❖ **Ortho hydrogen –** The hrdrogen molecule in which the nuclear spins of the two hydrogen atoms are in the same side. Magnetic moment of it is twice.

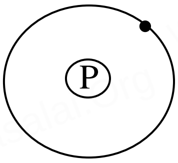
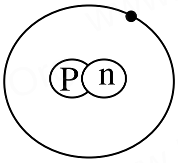
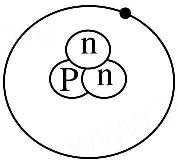


❖ **Para hydrogen –** The hydrogen molecule in which the nuclear spins of the two hydrogen atoms are in the opposite side. Magnetic moment of it is zero.



❖ **Isotopes of hydrogen –** Protium ^1_1H, Deuterium ^2_1H, and Tritium ^3_1H.

Protium	Deuterium	Tritium
^1_1H (or)	^2_1H (or)	^3_1H (or)

H	D	T
No. of electrons 1	1	1
No. of Protons 1	1	1
No. of neutrons 0	1	2
Ordinary Hydrogen occurrence 99.984% 	Heavy Hydrogen 0.0156% 	Radioactive Hydrogen very little amount. 1 atom per 10^{18}H atoms. 

- **Half life period of Tritium** – 12.33 years.
- **Isotopic effect** – In a chemical reaction, when one of the atoms in the reactants is replaced by one of its isotoes.
- **Uses of Deuterium** – It is used to study the movement of ground water and the hydrogen atom transfer mechanism in chemical reactions.
- **Uses of Tritium** – It is used as a tracer element and it find applications such as emergency exit signs, illumination of wrist watches.
- **Preparation of Tritium** – It occurs naturally as a result of nuclear reactions induced by cosmic rays in the upper atmosphere.

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{12}_{6}C + ^{3}_{1}H$$

$$^{2}_{1}H + ^{2}_{1}H \rightarrow ^{3}_{1}H + ^{1}_{1}H$$

$${}_{3}Li^{6} + ^{1}_{0}n \rightarrow {}_{2}He^{4} + {}_{1}H^{3}$$

- **Preparation of Hydrogen**
  - Electrolysis of water.
  - Action of dilute acids with metals like zinc, iron, tin.
  - Steam reforming of hydrocarbons.
  - Reaction of steam with red hot coke.
  - Reaction of carbon monoxide with water.
  - Cracking of long chain hydrocarbons.
- **Properties of hydrogen** – It is a colourless, odourless, tasteless, lightest and inflammable ges.

- **Uses of hydrogen**

  (i) In the manufacture of Ammonia and Nitric acid.

  (ii) In the synthesis of methanol.

  (iii) As hydrogenating agent.

  (iv) As reducing agent in metallurgy.

  (v) Calcium hydride is used as desiccant (drying agent).

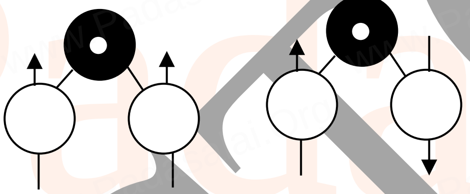
  (vi) $NaBH_4$, $LiAlH_4$ used as reducing agent in organic chemistry.

  (vii) Atomic hydrogen and oxyhydrogen torches for cutting and welding.

  (viii) Liquid hydrogen is used as rocket fuel.

  (ix) H_2 is used in fuel cells for generating electricity.

- **Water** – H_2O. It is the universal solvent. It occurs in the form of rivers and oceans (97.33%).
- **Ortho H_2O and Pare H_2O** – At the temperature conditions of the earth (300K), the OPR of H_2O is 3. It is known that the OPR of water in interstellar clouds and comets has more para-H2O (OPR = 2.5) than on Earth.



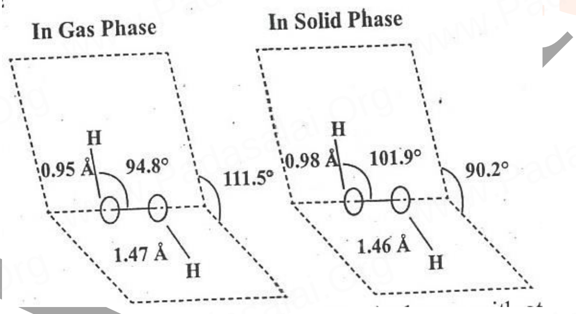
- **Physical properties** – Water is a colourless and volatile liquid. Hydrogen bonding responsible for high melting and boiling points of water.
- **Chemical properties** – Water reacts with metals, non-metals and compounds.
- **Hard water** – Water containing high amounts of bicarbonate, chloride and sulphate of magnesium and calcium is called hard water.
- **Soft water** – Water containing soluble salts of calcium and magnesium is called soft water.
- **Soap** – Sodium or Potassium salts of long chain fatty acids.
- **Temporary hardness** – It is due to the presence of soluble bicarbonates of magnesium and calcium. It is removed by heating or by treating with lime.
- **Permanent hardness** – It is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in water. It can be removed by washing soda or by ion exchange.
- **Ion exchange** – Hardness of water can be removed by passing through as ion exchange bed like zeolites or polymer (resin) containing column.

- **Zeolites** – Hydrated sodium alumino-silicates

  $NaO.Al_2O_3.xSiO_2.yH_2O$ (x = 2-10, y=2-6).

- **Premutit (or) zeolite process** – The softening of water process by using complex structure represented as $Na_2 – Z$ with sodium as exchangeable cations.

- **Methods used to soften hard water** – Chelating method and reverse osmosis.
- **Chelating method** – EDTA is used in this.
- **Reverse osmosis** – High pressure to force water through a semipermeable membrane.
- **Heavy water** – D_2O. It is present as one part in 5000 parts of ordinary water.
- **Proparation of D_2O** – It is prepared by continuous electrolysis of ordinary water. It undergoes exchange reactions.
- **Uses of D_2O – D_2O** is used in isotopic effect, used as moderator in nuclear reactors, used to prepare deuterium compounds.
- **Hydrogen peroxide (H_2O_2)** – It is a pale blue (almost colourless) liquid. It is prepared by the action of dilute acid with metal peroxide.
- **Uses of H_2O_2** – Oxidising agent, mild antiseptic, as a bleaching agent in textile, paper and hair-care industry and used as reducing agent.
- **Structure of H_2O_2** –



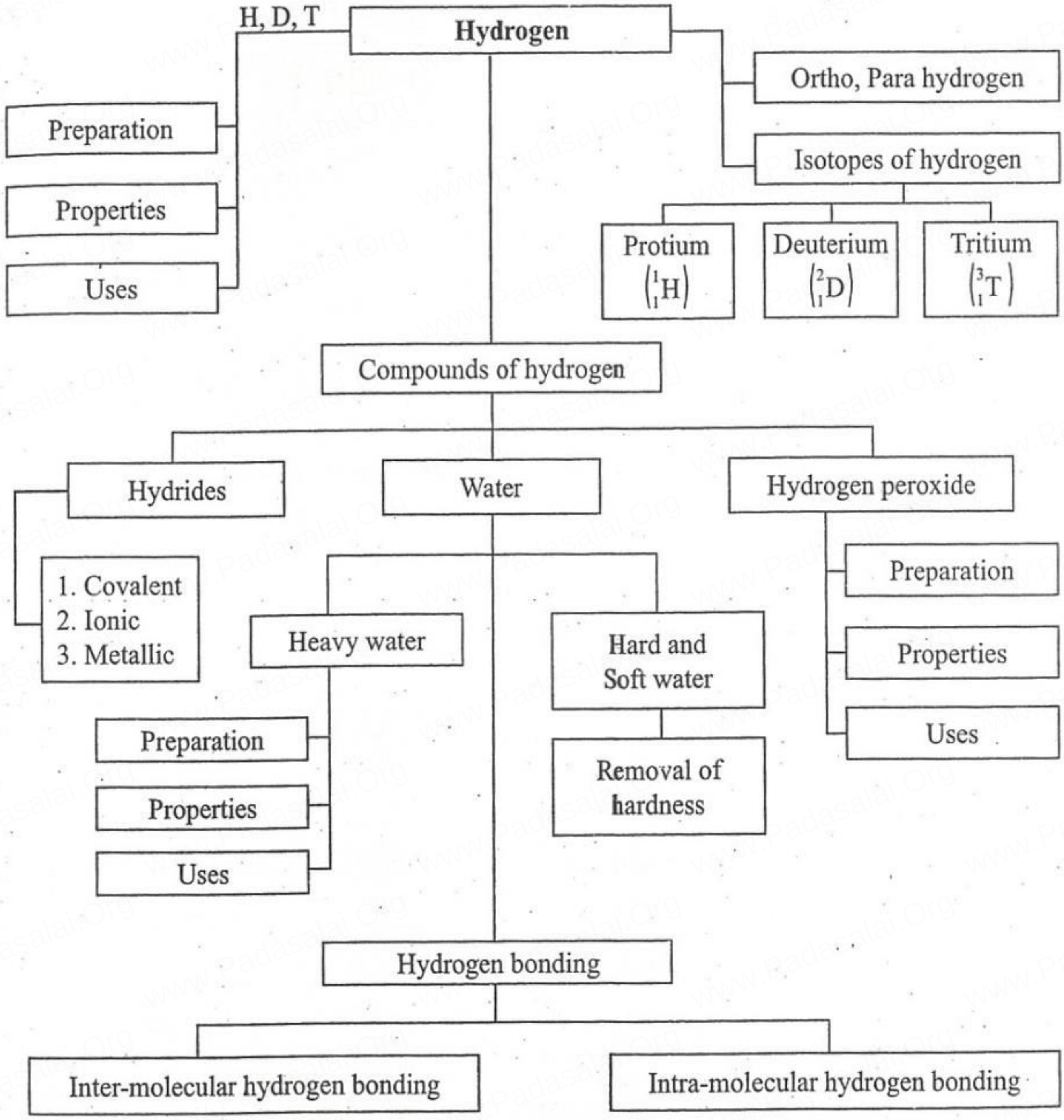
- **Hydrides** – A binary hydride is a compound formed by hydrogen with other electropositive elements. e.g. LiH, MgH_2.
- **Ternary hydrides** – Compounds in which molecule is constituted by hydrogen and two types of elements. e.g. $LiBH_4$, $LiAlH_4$.
- **Types of hydrides-**

Ionic hydrides	Covalent hydrides	Metallic hydrides
Electropositive metal + hydrogen	Non-metals + Hydrogen	Metals + Hydrogen
Formation of hydrogen by transfer of electrons.	Formation of hydride by equal sharing of electrons.	Hydrogen occupies voids in metals.

e.g. LiH, CaH_2	e.g. CH_4, SiH_4	e.g. ZnH_2, TiH.

- **Hydrogen sponge** – Metal hydride as (PdH) Palladium hydride. It is formed by a chemical reaction but it behaves like a physical storage method. i.e., it is absorbed and released like a water sponge.
- **Hydrogen bonding** – When a hydrogen atom is covalenty bonded to a highly electronegative atom [N (or) D (or) F], the bond is polarised in such a way that the hydrogen atom is able to form a weak bond between the hydrogen atom and the electronegative atom of a second molecule. This is called a hydrogen bond and denoted as dotted lines (……..).
- **Type of hydrogen bonding** – Intra molecular hydrogen bonding and inter molecular hydrogen bonding.
- **Intra molecular hydrogen bonding** – These bonds are those which occur within one single molecule. e.g., ortho-nitrophenol and salicylaldehyde.
- **Inter molecular hydrogen bonding** – These bonds are formed between two separate molecules. e.g., Ammonia, water, hydrogen fluoride, acetic acid.
- **Gas hydrates** – They are a kind of inclusion compounds, where gas molecules are trapped in a crystal lattice having voids of right size, with being chemically bonded. e.g., H_3O^+ in gas phase similar to methane hydrate.
- **Clatharate hydrate** – Gas hydrates in which guest molecules are not bonded chemically but retained by the structure of host is called Clatharate hydrates. e.g., Methane hydrate CH_420H_2O.
- **Crystalline hydrates** – In this type, hydrogen bonding is present. Water molecules serve to fill in the interstices and bind together structure. e.g., $CuSo_4.5H_2O$, $Na_2CO_3.10H_2O$, $FeSO_4.7H_2O$.
- **The atomic bomb** – The hydrogen bomb uses both nuclear fission and fusion is called atom bomb or Thermonuclear bombs.
- **The future fuel** – Hydrogen is considered as a potential fuel as it is a clean burning fuel. This fuel is free from pollutants.

CHAPTER MAP


H, D, T
Hydrogen
Preparation
Properties
Uses
Ortho, Para hydrogen
Isotopes of hydrogen
Protium (^1_1H)
Deuterium (^2_1D)
Tritium (^3_1T)
Compounds of hydrogen
Hydrides
Water
Hydrogen peroxide
1. Covalent
2. Ionic
3. Metallic
Heavy water
Hard and Soft water
Preparation
Properties
Uses
Preparation
Properties
Uses
Removal of hardness
Hydrogen bonding
Inter-molecular hydrogen bonding
Intra-molecular hydrogen bonding

Choose the correct answer:

1. **Which of the following statements about hydrogen is incorrect ? (NEET - 2016)**

a) Hydrogen ion, H_3O^+ exists freely in solution. b) Dihydrogen acts as a reducing agent.

c) Hydrogen has three isotopes of which tritium is the most common.

d) Hydrogen never acts as cation in ionic salts.

2. Water gas is

a) $H_2O_{(g)}$ b) $CO + H_2O$ **c) $CO + H_2$** d) $CO + N_2$

3. Which one of the following statements is incorrect with regard to ortho and para dihydrogen?

a) They are nuclear spin isomers

b) Ortho isomer has zero nuclear spin whereas the para isomer has one nuclear spin

c) The para isomer is favoured at low temperatures

d) The thermal conductivity of the para isomer is 50% greater than that of the ortho isomer.

4. Ionic hydrides are formed by

a) halogens b) chalogens c) inert gases **d) group one elements**

5. Tritium nucleus contains

a) 1p + 0 n b) 2 p + 1n **c) 1p + 2n** d) none of these

6. Non-stoichiometric hydrides are formed by

a) palladium, vanadium b) carbon, nickel c) manganese, lithium d) nitrogen, chlorine

7. Assertion : Permanent hardness of water is removed by treatment with washing soda.

Reason : Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates

a) Both assertion and reason are true and reason is the correct explanation of assertion.

b) Both assertion and reason are true but reason is not the correct explanation of assertion.

c) Assertion is true but reason is false d) Both assertion and reason are false

8. If a body of a fish contains 1.2 g hydrogen in its total body mass, if all the hydrogen is replaced with deuterium then the increase in body weight of the fish will be

a) 1.2 g b) 2.4 g c) 3.6 g d) $\sqrt{4.8}$ g

9. **The hardness of water can be determined by volumetrically using the reagent**

a) sodium thio sulphate b) potassium permanganate c) hydrogen peroxide **d) EDTA**

10. **The cause of permanent hardness of water is due to**

a) $Ca(HCO_3)_2$ b) $Mg(HCO_3)_2$ **c) $CaCl_2$** d) $MgCO_3$

11. **Zeolite used to soften hardness of water is, hydrated**

a) Sodium aluminium silicate b) Calcium aluminium silicate

c) Zinc aluminium borate d) Lithium aluminium hydride

12. **A commercial sample of hydrogen peroxide marked as 100 volume H_2O_2, it means that**

a) 1 ml of H_2O_2 will give 100 ml O_2 at STP b) 1 L of H_2O_2 will give 100 ml O_2 at STP

c) 1 L of H_2O_2 will give 22.4 L O_2 d) 1 ml of H_2O_2 will give 1 mole of O_2 at STP

13. **When hydrogen peroxide is shaken with an acidified solution of potassium dichromate in presence of ether, the ethereal layer turns blue due to the formation of**

a) Cr_2O_3 b) CrO_4^{2-} **c) $CrO(O_2)_2$** d) none of these

14. **For decolourisation of 1 mole of acidified $KMnO_4$, the moles of H_2O_2 required is**

a) 1/2 b) 3/2 **c) 5/2** d) 7/2

15. **Volume strength of 1.5 N H_2O_2 is**

a) 1.5 b) 4.5 c) 16.8 **d) 8.4**

16. **The hybridisation of oxygen atom is H_2O and H_2O_2 are, respectively**

a) sp and sp^3 b) sp and sp c) sp and sp^2 **d) sp^3 and sp^3**

17. **The reaction $H_3PO^2 + D_2O \rightarrow H_2DPO_2 + HDO$ indicates that hypo-phosphorus acid is**

a) tribasic acid b) dibasic acid **c) mono basic acid** d) none of these

18. **In solid ice, oxygen atom is surrounded**

a) tetrahedrally by 4 hydrogen atoms

b) octahedrally by 2 oxygen and 4 hydrogen atoms

c) tetrahedrally by 2 hydrogen and 2 oxygen atoms d) octahedrally by 6 hydrogen atoms

19. **The type of H-bonding present in ortho nitro phenol and p-nitro phenol are respectively**

a) inter molecular H-bonding and intra molecular H-bonding

b) intra molecular H-bonding and inter molecular H-bonding

c) intra molecular H - bonding and no H - bonding

d) intra molecular H - bonding and intra molecular H - bonding

20. **Heavy water is used as**

a) modulator in nuclear reactions b) coolant in nuclear reactions

c) both (a) and (b) d) none of these

21. Water is a

a) basic oxide b) acidic oxide **c) amphoteric oxide** d) none of these

Answer the following:

22**. Explain why hydrogen is not placed with the halogen in the periodic table.**

(i) Hydrogen has a tendency to gain one electron to from hydride ion whose electronic configuration is similar to the noble gas (He).

(ii) However the electron affinity of hydrogen is much less than that of halogen atoms.

(iii) Hence hydrogen is less reactive as compared to halogens.

(iv) Due to this unique behavior hydrogen is not placed with halogens in the periodic table.

23. Discuss the three types of Covalent hydrides.

Covalent hydrides are compounds in which hydrogen is attached to another element by sharing of electrons.

Covalent hydrides are further divided into three categories, viz.,

- electron precise (CH_4, C_2H_6, SiH_4, GeH_4),
- electron-deficient (B_2H_6), and

- electron-rich hydrides (NH_3,H_2O)

24. Predict which of the following hydrides is a gas on a solid (a) HCl (b) NaH. Give your reason.

- HCl is a gas because of absence of intermolecular hydrogen bonding
- NaH is a solid because of electron transfer.

(OR)

(a) Gas- due to the absence of their molecular hydrogen bonding.

(b) Solid- Reason : NaH is a ionic hydride formed by transfer of electrons from metal to hydrogen. They have high lattice enthalpy and high density since hydride ions occupy holes in the lattice of metal without distorting the metal lattice.

25. Write the expected formulas for the hydrides of 4th period elements. What is the trend in the formulas? In what way the first two numbers of the series different from the others ?

(i) The first two elements of period 4, K and Ca form hydrides with the formula MH and MH_2 ie,(MHn). They are ionic hydrides and have high melting and boiling points.

(ii) Elements from Sc to Zn form metallic or interstitial hydrides are non stoichiometric hydrides which do not follow the law of constant composition.

(iii) Elements from Ga to Br, the general formula is XH_{8-n}, where n is the number of valence electrons.

26. Write chemical equation for the following reactions.

i) reaction of hydrogen with tungsten (VI) oxide NO_3 on heating.

ii) hydrogen gas and chlorine gas.

(i) $WO_3 + 3H_2 \rightarrow W + 3H_2O$

(ii) $H_2 + Cl_2 \rightarrow 2HCl$.

27. Complete the following chemical reactions and classify them in to (a) hydrolysis (b) redox (c) hydration reactions.

1) $KMnO_4 + H_2O_2 \rightarrow 2MnO_2 + 2KOH + 2H_2O + 3O_2$

2) $CrCl_3 + H_2O \rightarrow CrCl_3.6H_2O$ (hydration)

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

28. Hydrogen peroxide can function as an oxidising agent as well as reducing agent. substantiate this statement with suitable examples.

Hydrogen peroxide can act both as an usually performed in acidic medium while the reduction reactions are performed in basic medium.

In acidic conditions:

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ ($E^\circ = +1.77$ V)

For example

$2FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + 2H_2O$

In basic conditions:

$HO^{2-} + OH^- \rightarrow O_2 + H_2O + 2e-$ ($E^\circ = + 0.08$ V)

For example

$2KMnO_{4(aq)} + 3H_2O_{2(aq)} \rightarrow MnO_2 + 2KOH + 2H_2O + 3O_{2(g)}$

29. Do you think that heavy water can be used for drinking purposes ?

(i) The chemical reactions shown by water and heavy water are nearly identical.

(ii) However, due to differences in masses of hydrogen and deuterium, such reactions occur at different rates.

(iii) The rates of reactions involving D_2O are slower than those involving H_2O

(iv) If D_2O is consumed, the enzyme catalyzed biochemical reactions will occur slower than their optimum rate.

(v) The enzymes may than lose their ability to catalyze a biochemical reaction

(vi) Thus heavy water will interfere and disturb the biological process and hence it is not suitable for drinking purposes.

30. What is water-gas shift reaction ?

The carbon monoxide of the water gas can be converted to carbon dioxide by mixing the gas mixture with more steam at 400° C and passed over a shift converter containing iron/copper catalyst. This reaction is called as water-gas shift reaction.

$$CO + H_2O \rightarrow CO_2 + H_2$$

The CO_2 formed in the above process is absorbed in a solution of potassium carbonate.

$$CO_2 + K_2CO_3 + H_2O \rightarrow 2KHCO_3$$

31. Justify the position of hydrogen in the periodic table ?

(i) Hydrogen has the electronic configuration of $1s^1$ which resembles with ns^1 general valence shell configuration Of alkali metals and shows similarity with them as follows:

1. It forms unipositive ion (H^+) like alkali metals (Na^+, K^+, Cs^+)

2. It forms halides (HX), oxides (H_2O), peroxides (H_2O_2) and sulphides (H_2S) like alkali metals(NaX, Na_2O, Na_2O_2, Na_2S)

3. It also acts as reducing agent.

(ii) Since, hydrogen has similarities with alkali metals as well as the halogens ; it is difficult to find the right right position in the periodic table. However, in most of its compounds hydrogen exists in +1 oxidation state. Therefore, it is reasonable to place the hydrogen in group 1 along with alkali metals as shown in the latest periodic table published by IUPAC.

(iii) Unlike alkali metals hydrogen has higher ionization energy.

(iv) Hydrogen also has a tendency to gain one electron to form hydride ion (H^-) whose electronic configuration is similar to the noble gas, helium. However, the electron affinity of hydrogen is much less than that of halogen atoms.

32. What are isotopes? Write the names of isotopes of hydrogen.

Isotopes: Atoms of the same element having same atomic number but different mass number are called isotopes.

	Isotopes of Hydrogen	Symbol	Atomic No	Mass No
(i)	Protium or hydrogen	${}_1H^1$	1	1
(ii)	Deuterium	${}_1H^2$	1	2

(iii)	Tritium	$_1H^3$	1	3

33. Give the uses of heavy water.

i. Heavy water is widely used as moderator in nuclear reactors.
ii. It is commonly used as a tracer to study element reaction mechanisms.
iii. It is used as a coolant in nuclear reactors.
iv.

34. Explain the exchange reactions of deuterium.

Deuterium can replace reversibly hydrogen in compounds either partially or completely depending upon the reaction conditions.

$$CH_4 + 2D_2 \rightarrow \underset{\text{Deutero methane}}{CD_4} + 2H_2$$

$$2NH_3 + 3D_2 \rightarrow \underset{\text{Deutero ammonia}}{2ND_3} + 3H_2$$

35. How do you convert parahydrogen into ortho hydrogen ?

i. By treatment with catalyst like Pt **or** Fe
ii. By passing an electric discharge
iii. By heating to 800°C or more
iv. By mixing with paramagnetic molecules like O_2, NO, NO_2.
v. By mixing with nascent hydrogen or atomic hydrogen.

36. Mention the uses of deuterium.

i. It is used as tracers in the study of mechanism of chemical reactions
ii. High speed deuterons are used in artificial radioactivity
iii. Deuterium is mainly used in the preparation of heavy water (D_2O). Which is employed as moderator in nuclear reactor to slow down the speed of fast moving neutrons.

37. Explain preparation of hydrogen using electrolysis.

Obtained by electrolysis of water

i. **Electrolyte:** Water containing traces of acids or alkali or the electrolysis of aqueous solution of sodium hydroxide or potassium hydroxide
ii. **Anode:** Nickel
iii. **Cathode:** Iron
iv. **At anode:** $2OH^- \rightarrow H_2O + ½\, O_2 + 2e-$
v. **At Cathode :** $2H_2O + 2e^- \rightarrow 2OH^- + H_2$
vi. **Overall reaction:** $H_2O \rightarrow H_2 + ½\, O_2$

38. A groups metal (A) which is present in common salt reacts with (B) to give compound (C) in which hydrogen is present in –1 oxidation state. (B) on reaction with a gas (D) to give universal solvent (E). The compound (E) on reacts with (A) to give (B), a strong base. Identify A, B, C, D , E and F. Explain the reactions.

(i) Metallic **sodium (A)** reacts with **hydrogen (B)** to give **sodium hydride (C).**

$$\underset{(A)}{2\,Na} + \underset{(B)}{H_2} \rightarrow \underset{(C)}{2NaH}$$

(ii) Hydrogen reacts with a gas (oxygen) to give **water (D)**

$$\underset{(B)}{2H_2} + \underset{(D)}{O_2} \rightarrow \underset{(E)}{2H_2O}$$

(iii) Water reacts with sodium to give **sodium hydroxide (E)** and hydrogen (B)

$$\underset{(E)}{2H_2O} + \underset{(A)}{2Na} \rightarrow \underset{(F)}{2NaOH} + \underset{(B)}{H_2}$$

A	Na	Sodium
B	H_2	Hydrogen
C	NaH	Sodium Hydride
D	O_2	Oxygen
E	H_2O	Water
F	NaOH	Sodium hydroxide

39. An isotope of hydrogen (A) reacts with diatomic molecule of element which occupies group number 16 and period number 2 to give compound (B) is used as a modulator in nuclear reaction. (A) adds on to a compound (C), which has the molecular formula C_3H_6 to give (D). Identify A, B, C and D.

(i) Isotope of hydrogen reacts with which is oxygen to give **heavy water (B)**

$$\underset{(A)}{2D_2} + O_2 \rightarrow \underset{(B)}{2D_2O}$$

(ii) Deuterium (A) undergoes addition reaction with **propane (C)** to give **propane deuteride (D)**

$$CH_3CH = CH_2 + D_2 \rightarrow CH_3 - CHD - CH_2D$$

A	D_2	Deuterium
B	D_2O	Heavy water or deuterium oxide
C	$CH_3 - CH = CH_2$	Propene
D	$CH_3 - CHD - CH_2D$	Propane deuteride

40. NH_3 has exceptionally high melting point and boiling point as compared to those of the hydrides of the remaining element of group 15 - Explain.

- **NH_3** has higher boiling and melting point **compared to** all other hydrides of **group 15** elements due to intermolecular hydrogen bonding**.**
- Each molecule can from a maximum of 4 hydrogen bonds but on average 1 hydrogen bond per molecule as there is only one lone pair on NH_3 available for hydrogen bonding.
- Hydrogen bonding is strong intermolecular attraction as H on NH_3 acts like a proton due to partial positive on it whole N atom in another NH_3 molecule, a very strong hydrogen bond is formed.
- Due to much strong intermolecular interactions compared to weaker permanent dipole-dipole interactions between other XH_3 molecules in group 15, large amount of energy are required to overcome the forces, giving it the highest point and highest melting point.

41. Why interstitial hydrides have a lower density than the parent metal.

Metallic hydrides or interstitial hydrides are less dense than the parent metal. This is due to slight expansion of the lattice during the formation of their hydrides.

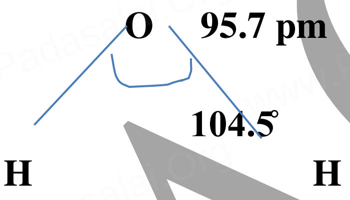
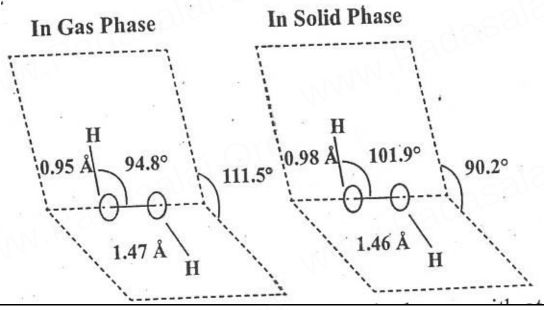
22. How do you expect the metallic hydrides to be useful for hydrogen storage ?

In some of the transition metal hydrides, hydrogen is absorbed as H-atoms. Due to the inclusion of H-atoms , the metal lattice expands and thus becomes less stable . Therefore, when such metallic hydride is heated, it decomposes to release hydrogen gas and very finely divided metal. The hydrogen evolved in this manner can be used as a fuel. Thus, transition metals or their alloys can act as sponge and can be used to store and transport hydrogen to be used as a fuel.

43. Arrange NH_3, H_2O and HF in the order of increasing magnitude of hydrogen banding and explain the basis for your arrangement.

- **i.** The order of increasing magnitude of H-bonding is, **$NH_3 < H_2O < HF$**
- **ii.** Strength of H bond depends upon the atomic size and electronegativity of the other atom to which H atom is covalently bonded. Smaller size and higher electronegativity favour H bonding
- **iii.** Among N, F and O the order of electronegativity is **F > O > N.**
- **iv.** Hence HF will have highest magnitude of H bonding.

44. Compare the structures of H_2O and H_2O_2.

STRUCTURE OF H_2O	STRUCTURE OF H_2O_2
H_2O has a bent structure	**H_2O_2** has a open book like structure
The **HOH** bond angle is 104.5°	The **H-O-O** bond angle is 94.8° and the dihedral angle 111.5° in gas phase.
It is a polar molecule 	H_2O_2 has a non polar structure 

5. Alkali and Alkaline Earth metals

1. $4Li + O_2 \rightarrow 2Li_2O$
2. $2Na + O_2 \rightarrow Na_2O_2$
3. $Rb + O_2 \rightarrow RbO_2$
4. $2Na + 2C_2H_5OH \rightarrow 2C_2H_5ONa + H_2\uparrow$
5. $\mathrm{H{-}C{=}C{-}H \xrightarrow{Na} H{-}C{=}C{-}Na \xrightarrow{Na} Na{-}\,C{=}C\text{-}Na}$
6. $Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2\uparrow$
7. **Solvay process:**
   (i) $2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3$
   (ii) $(NH_4)_2CO_3 + H_2O + CO_2 \rightarrow 2NH_4HCO_3$
   (iii) $NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$
   (iv) $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2\uparrow + H_2O$
8. $Na_2CO_3.\ 10H_2O \xrightarrow{-9H_2O} Na_2CO_3.H_2O \overset{-H_2O}{\xrightarrow{\Delta}} Na_2CO_3$
9. $BeO + C + Cl_2 \xrightarrow{600\text{–}800K} BeCl_2 + CO$
10. $BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$
11. $2BaO + O_2 \rightarrow 2BaO_2$
12. $Be(OH)_2 + 2NaOH \rightarrow Na_2BeO_2 + 2H_2O$
13. $Be(OH)_2 + 2HCl \rightarrow BeCl_2 + 2H_2O$
14. $CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow$
15. $CaO + H_2O \rightarrow Ca(OH)_2$
16. $2Ca(OH)_2 + 2Cl_2 \rightarrow CaCl_2 + Ca(OCl)_2 + 2H_2O$
17. $CaSO_4.2H_2O \xrightarrow[-^1/_2H_2O]{393K} CaSO_4.^1/_2H_2O$
18. $CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$

Important formula:

1. Lithium oxide : Li_2O (Simple oxide)
2. Sodium peroxide : Na_2O_2 (Peroxide)
3. Potassium superoxide : KO_2 (Superoxide)
4. Lithium hydride : LiH
5. Sodium acetylide : Na – C = C – Na
6. Lithium hydroxide : LiOH
7. Lithium carbide : Li_2C_2
8. Lithium fluoride : LiF
9. Lithium carbonate : Li_2CO_3
10. Sodium carbonate deca hydrate (or) washing soda:$Na_2CO_3.10H_2O$
11. Sodium bicarbonate (or) baking soda : $NaHCO_3$
12. Sodium chloride : NaCl (Cooking or table salt)
13. Beryllium chloride : $BeCl_2$
14. Beryllium hydride : BeH_2
15. Beryllium oxide : BeO
16. Barium oxide : BaO
17. Barium Peroxide : BaO_2
18. Beryllium hydroxide : $Be(OH)_2$
19. Quick lime : CaO
20. Lime stone : $CaCO_3$
21. Slaked lime (or) lime water : $Ca(OH)_2$
22. Bleaching powder : $CaOCl_2$
23. Gypsum : $CaSO_4.2H_2O$
24. Plaster of Paris : $CaSO4.\ ^1/_2H_2O$

Important Points to Remember

- **s – block elements –** Group 1 and 2 elements are those in which the last electron enters the outermost s – orbital.
- **Group 1 elements –** Alkali metals Li, Na, K, Rb, Cs, and Fr with electronic configuration as noble gas [ns^1].
- **Half-life of francium –** 21 minutes.

- **Oxidation state of alkali metals** + 1
- **Atomic radii and ionic radii of alkali metals** – On moving down the group increases and across the period decreases.
- **Periodic trends in alkali group** – Reactivity, atomic radius, formation of electropositive ion and density increases down the group. Melting point and boiling point decreases down the group.

- **Occurrence of Alkali metals**

	Element	Occurrence
1.	Lithium	Spodume and lepidolite (Silicate minerals
2.	Sodium	Rock salt (NaCl)
3.	Potassium	Nitre and carnallite
4.	Rubidium and cesium	Minerals with other alkali metals
5.	Francium	Radioactive. It does not occur in nature

- **Distinctive behavior of lithium** – Extremely small size, greater polarizing power of ion, least electropositive character and non-availability of d-orbitals.
- **Chemical properties** – Alkali metals are highly reactive and reacts with oxygen, hydrogen, halogen and liquid ammonia.
- **Uses of alkali metals** – Oxidizing agents (oxide of alkali metals), strong bases (hydroxides of alkali metals), sodium and potassium ions perform important biological functions such as ion balance and nerve impulse conduction.
- **Fruits rich in potassium** – Avocadoes, potatoes and bananas.
- **Group 2 elements** – Alkaline earth elements with general electronic configuration as [noble gases] ns^2. They are Be, Mg, Ca, Sr, Ba and Ra.
- **Alkaline earth metals** – Except Be, all other oxides and hydroxides are alkaline in nature.
- **Occurrence of alkaline earth metals** –

	Element	Occurrence
1.	Beryllium	Rare
2.	Radium	The rarest
3.	Magnesium and calcium	Rocks and minerals
4.	Magnesium	8th most abundant element and occur as carnallite, magnesite and dolomite
5.	Calcium	5th most abundant element and occur as chalk, limestone and gypsum
6.	Strontium	Celestite and strontianite
7.	Barium	Less common and occur as barite

- **Pyrotechnics –** Alkaline earth metals are used to produce colours in firework shows.
- **Oxidation state of alkaline earth metals -** +2.
- **Trends in periodic properties -**
  (i) Atomic and ionic radii increases down the group.
  (ii) Ionization enthalpy and hydration enthalpy decreases down the group.
- **Anomalous behavior of beryllium –** (i) Small size (ii) high polarizing power (iii) high electro negativity (iv) absence of vacant d-orbital (v) high ionization enthalpy.
- **Chemical properties –** Alkali metals react with H_2 and halogens.
- **Uses of beryllium –**
  (i) Used as radiation windows for X-ray tube and X-ray detectors.
  (ii) As sample holder in X-ray emission studies.
  (iii) Used to build the beam pipe in accelerators.
  (iv) Used in detectors.
- **Uses of magnesium –**
  (i) For the removal of sulfur from iron and steel.
  (ii) For the refining of titanium.
  (iii) Used as photoengrave plates in printing industry.
  (iv) Magnesium alloys are used in airplanes and missile construction.
  (v) Mg ribbon is used in Grignard reagent synthesis. (vi) As desiccant.
  (vii) As sacrificial anode in controlling galvanic corrosion.
  (viii) As a reducing agent.
  (ix) Mg + Al alloy used in fabrication and welding.
- **Uses of calcium –**
  (i) Used as a reducing agent in the metallurgy of uranium, zirconium and thorium.
  (ii) As a deoxidizer, desulfurizer or decarbonizer for ferrous and non-ferrous alloys.
  (iii) As a getter in vacuum tubes.
  (iv) In making of cements and mortars.
  (v) In dehydrating oils.
  (vi) In fertilizers, concrete and making Plaster of Paris.
- **Uses of strontium –**
  (i) ^{90}Sr is used in cancer therapy.
  (ii) $^{87}Sr/^{86}Sr$ ratio is used in marine investigations as well as in teeth, tracking animal migrations or in criminal forensics.

(iii) Used in dating of rocks.

(iv) Used as a radioactive tracer.

- **Uses of barium –**

  (i) Used in metallurgy, pyrotechnics, petroleum mining and radiology.

  (ii) Deoxidizer in copper refining.

  (iii) Ba + Ni alloy is used in electron tubes and in spark plug electrodes.

  (iv) As a scavenger to remove oxygen and other gases in television and electronic tybes.

  (v) ^{133}Ba is used as a source in the calibration of gamma ray detector.

- **Uses of radium** – Used in self – luminous paints for watches, nuclear panels, aircraft switches, clocks and instrument dials.

- **Chemical properties of alkaline earth metals –**

  (i) They form monoxides and peroxide with oxygen.

  (ii) The oxides of alkaline earth metals react with water to give hydroxides.

  (iii) They form halides when react with halogens.

  (iv) Alkaline earth metals form salts of oxo-acids such as carbonates, sulphates and nitrates.

- **Important compounds of calcium –**

- **Quick lime** – CaO

- **Slaking of lime** – The process of addition of limited amount of water breaks the lump of lime is called slaking of lime.

- **Uses of quick lime –**

  (i) To manufacture cement, mortar and glass.

  (ii) To manufacture sodium carbonate and slaked lime.

  (iii) In the purification of sugar.

  (iv) As drying agent.

- **Slaked lime** – $Ca(OH)_2$

- **Bleaching powder** – $Ca(OCl)_2$

- **Uses of slaked lime –**

  (i) In the preparation of mortar, a building material.

  (ii) In white wash.

  (iii) In glass making and in tanning industry.

  (iv) For the preparation of bleaching powder and in purification of sugar.

- **Gypsum** – $CaSO_4.2H_2O$

- **Desert Rose** – Gypsum crystals are found to occur in a form that resembles the petals of a flower and this occur in desert terrains.

- **Alabaster** – A variety of gypsum and valued as an ornamental stone.
- **Plaster of Paris** – $CaSO_4.{}^1/_2H_2O$
- **Uses of gypsum -**
  - (i) It has been used by the sculptors.
  - (ii) To prepare Plaster of Paris.
  - (iii) Used in making dry walls or plaster boards.
  - (iv) It is used in making surgical and orthopedic casts, casting molds and surgical splints.
  - (v) It is used in agriculture as a soil additive, conditioner and fertilizer.
  - (vi) It is used in toothpaste, shampoo and hair products.
- **Calcium sulphate** – Acts as a coagulator in making tofu. It is used in baking, as a dough conditioner. It is used to treat upset stomach and eczema.
- **Gypsum** – It is used as a hardening retarder to control the speed at which concrete sets.
- **Satin spar** – It is a variety of gypsum, used as an ornamental stone, while alabaster is used for sculpting.
- **Gypsum** – It is used to give colour to cosmetics and drugs. It can be found in canned vegetables, flour, ice cream, blue cheese and white bread. It is mainly used in wine making.
- **Uses of Plaster of Paris -**

(i) It is used in building industry as well as plasters.

(ii) It is used for immobilizing the affected part of organ, where there is a bone fracture or sprain.

(iii) It is also used in dentistry, making casts of statues and busts.

- **Biological importance of magnesium and calcium –**

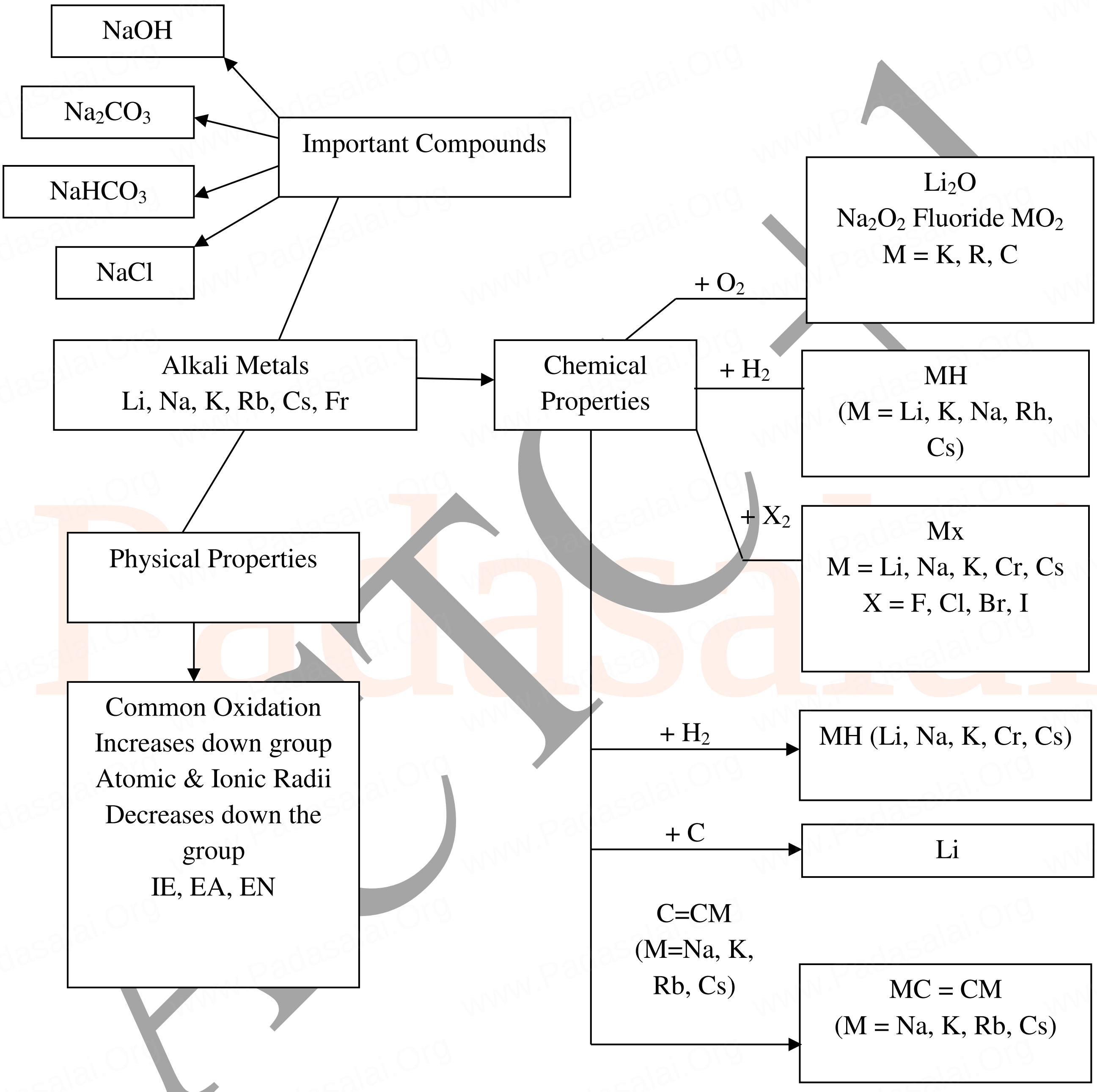
(i) An adult body contains about 25g of Mg and 1200g of Ca. The daily requirement in the human body has been estimated to be 200 – 300mg.

(ii) All enzymes transfer requires magnesium as the co-factor. The main pigment of chlorophyll is magnesium.

(iii) 99% of body calcium is present in bones and teeth. It also play important roles in neuromuscular function, inter neuronal transmission, cell membrane integrity and blood coagulation.

(iv) The calcium concentration is maintained by two hormones – calcitonin and parathyroid hormones.

CHAPTER MAP


$NaOH$
Na_2CO_3
$NaHCO_3$
$NaCl$
Important Compounds
Li_2O
Na_2O_2 Fluoride MO_2
M = K, R, C
+ O_2
Alkali Metals
Li, Na, K, Rb, Cs, Fr
Chemical Properties
+ H_2
MH
(M = Li, K, Na, Rh, Cs)
+ X_2
Mx
M = Li, Na, K, Cr, Cs
X = F, Cl, Br, I
Physical Properties
Common Oxidation
Increases down group
Atomic & Ionic Radii
Decreases down the group
IE, EA, EN
+ H_2
MH (Li, Na, K, Cr, Cs)
+ C
Li
C=CM
(M=Na, K, Rb, Cs)
MC = CM
(M = Na, K, Rb, Cs)

Choose the correct answer

1. For alkali metals, which one of the following trends is incorrect ?
a) Hydration energy : Li > Na > K > Rb b) Ionisation energy : Li > Na > K > Rb
c) Density : Li < Na < K < Rb d) Atomic size : Li < Na < K < Rb

2. Which of the following statements is incorrect ?
a) Li^+ has minimum degree of hydration among alkali metal cations.
b) The oxidation state of K in KO_2 is +1
c) Sodium is used to make Na / Pb alloy d) $MgSO_4$ is readily soluble in water

3. Which of the following compounds will not evolve H_2 gas on reaction with alkali metals?
a) ethanoic acid b) ethanol c) phenol **d) none of these**

4. Which of the following has the highest tendency to give the reaction
$M^+_{(g)} \xrightarrow[\text{Medium}]{\text{Aqueous}} M^+_{(aq)}$
a) Na **b) Li** c) Rb d) K

5. sodium is stored in
a) alcohol b) water **c) kerosene** d) none of these

6. RbO_2 is
a) superoxide and paramagnetic b) peroxide and diamagnetic
c) superoxide and diamagnetic d) peroxide and paramagnetic

7. Find the wrong statement
a) sodium metal is used in organic qualitative analysis
b) sodium carbonate is soluble in water and it is used in inorganic qualitative analysis
c) potassium carbonate can be prepared by solvay process
d) potassium bicarbonate is acidic salt

8. Lithium shows diagonal relationship with
a) sodium **b) magnesium** c) calcium d) aluminium

9. In case of alkali metal halides, the ionic character increases in the order
a) MF < MCl < MBr < MI **b) MI < MBr < MCl < MF**
c) MI < MBr < MF < MCl d) none of these

10. In which process, fused sodium hydroxide is electrolysed for extraction of sodium ?
a) Castner's process b) Cyanide processc) Down process d) All of these

11. The product obtained as a result of a reaction of nitrogen with CaC_2 is (NEET)
a) $Ca(CN)_3$ b) CaN_2 **c) $Ca(CN)_2$** d) Ca_3N_2

12. Which of the following has highest hydration energy
a) $MgCl_2$ b) $CaCl_2$ c) $BaCl_2$ d) $SrCl_2$

13. Match the flame colours of the alkali and alkaline earth metal salts in the Bunsen burner

(p) Sodium	(1) Brick red
(q) Calcium	(2) Yellow
(r) Barium	(3) Violet
(s) Strontium	(4) Apple green
(t) Cesium	(5) Crimson red
(u) Potassium	(6) Blue

a) p - 2, q - 1, r - 4, s - 5, t - 6, u - 3
b) p - 1, q - 2, r - 4, s - 5, t - 6, u - 3
c) p - 4, q - 1, r - 2, s - 3, t - 5, u - 6
d) p - 6, q - 5, r - 4, s - 3, t - 1, u - 2

14. Assertion : Generally alkali and alkaline earth metals form superoxides
Reason : There is a single bond between O and O in superoxides.
a) both assertion and reason are true and reason is the correct explanation of assertion
b) both assertion and reason are true but reason is not the correct explanation of assertion
c) assertion is true but reason is false **d) both assertion and reason are false**

15. Assertion : $BeSO_4$ is soluble in water while $BaSO_4$ is not
Reason : Hydration energy decreases down the group from Be to Ba and lattice energy remains almost constant.
a) both assertion and reason are true and reason is the correct explanation of assertion
b) both assertion and reason are true but reason is not the correct explanation of assertion
c) assertion is true but reason is false d) both assertion and reason are false

16. Which is the correct sequence of solubility of carbonates of alkaline earth metals?
a) $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$ **b) $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$**
c) $CaCO_3 > BaCO_3 > SrCO_3 > MgCO_3$ d) $BaCO_3 > CaCO_3 > SrCO_3 > MgCO_3$

17. In context with beryllium, which one of the following statements is incorrect ? (NEET Phase - 2)
a) It is rendered passive by nitric acid b) It forms Be_2C
c) Its salts are rarely hydrolysed d) Its hydride is electron deficient and polymeric

18. The suspension of slaked lime in water is known as (NEET Phase - II)
a) lime water b) quick lime **c) milk of lime** d) aqueous solution of slaked lime

19. A colourless solid substance (A) on heating evolved CO_2 and also gave a white residue, soluble in water. Residue also gave CO_2 when treated with dilute HCl.
a) Na_2CO_3 **b) $NaHCO_3$** c) $CaCO_3$ d) $Ca(HCO_3)_2$

20. The compound (X) on heating gives a colourless gas and a residue that is dissolved in water to obtain (B). Excess of CO_2 is bubbled through aqueous solution of B, C is formed. Solid (C) on heating gives back X. (B) is
a) $CaCO_3$ **b) $Ca(OH)_2$** c) Na_2CO_3 d) $NaHCO_3$

21. Which of the following statement is false ? (NEET - Phase - I)

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

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

c) Mg^{2+} ions form a complex with ATP d) Ca^{2+} ions are important in blood clotting

22. The name 'Blue John' is given to which of the following compounds?

a) CaH_2 **b) CaF_2** c) $Ca_3(PO_4)_2$ d) CaO

23. Formula of Gypsum is

a) $CaSO_4 . 2H_2O$ b) $CaSO_4 . ½ H_2O$ c) $3CaSO_4 . H_2O$ d) $2CaSO_4 . 2H_2O$

24. When CaC_2 is heated in atmospheric nitrogen in an electric furnace the compound formed is

a) $Ca(CN)_2$ **b) CaNCN** c) CaC_2N_2 d) $CaNC_2$

25. Among the following the least thermally stable is

(a) K_2CO_3 b) Na_2CO_3 (c) $BaCO_3$ **d) Li_2CO_3**

Part II

26.Why sodium hydroxide is much more water soluble than chloride?

NaOH , NaCl

- In both case Na^+ is common. In NaOH, OH^- is the conjugate base of weak acid H_2O, **OH^- is strong base**.
- In NaCl, Cl^- is the conjugate base of strong acid HCl. Hence **Cl^- is weak base.**
- So, sodium hydroxide is much more water soluble than chloride.

(NaOH is much more soluble than NaCl. Enthalpy of a solution can be expressed as the sum of lattice enthalpy and enthalpy of hydration of a compound. Dissolution of NaCl is accompanied by very small heat change so solubility of NaCl is less than NaOH.)

27. Write the chemical equations for the reactions involved in solvay process of preparation of sodium carbonate.

The equations involved in solvay process are,

$2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3$ Ammonium carbonate

$(NH_4)_2CO_3 + H_2O + CO_2 \rightarrow 2NH_4HCO_3$ ammonium bicarbonate

$2NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$ sodium bicarbonate

$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

Sodium carbonate

The ammonia used in this process can be recovered by treating the resultant ammonium chloride solution with calcium hydroxide. Calcium chloride is formed as a by-product.

28. An alkali metal (x) forms a hydrated sulphate, X_2SO_4. $10H_2O$. Is the metal more likely to be sodium (or) potassium.

The metal more likely to form a hydrated sulphate is **sodium** of formula $Na_2SO_4.10H_2O$. it is otherwise called as Glauber's salt.

Reason:

Smaller the size of the ion greater is the degree of hydration. Hydration energy is in the order of $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ so sodium is hydrated more easily than potassium.

29. Write balanced chemical equation for each of the following chemical reactions.

(i) Lithium metal with nitrogen gas **(ii) heating solid sodium bicarbonate**

(iii) Rubidum with oxgen gas **(iv) solid potassium hydroxide with CO_2**

(v) heating calcium carbonate **(vi) heating calcium with oxygen**

(i) $6Li_{(s)} + N_{2(g)} \rightarrow 2Li_3N_{(s)}$

(ii) $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

(iii) $Rb + O_2 \rightarrow RbO_2$

(iv) $KOH + CO_2 \rightarrow KHCO_3$

(v) $CaCO_3 \leftrightarrow CaO + CO_2$

(vi) $2Ca + O_2 \rightarrow 2CaO$

30. Discuss briefly the similarities between beryllium and aluminium.

Beryllium shows a diagonal relationship with aluminium. In this case the size of these ions is not as close. However, their charge per unit area and electro-negativity values are almost similar. Similarities between Beryllium and Aluminium.

	Properties
1	Beryllium chloride forms a **dimeric structure** like aluminium chloride with chloride bridges. Both are soluble in organic solvents and are strong Lewis acids.
2	Beryllium hydroxide dissolves in excess of alkali and gives beryllate ion $[Be(OH)_4]^{2-}$ as aluminium hydroxide which gives aluminate ion, $[Al(OH)_4]^-$.
3	Beryllium and Aluminium ions have strong tendency to form complexes, BeF_4^{2-}, AlF_6^{3-}
4	Both beryllium and aluminium hydroxides are **amphoteric** in nature.
5	Carbides of beryllium (Be_2C) like aluminium carbide (Al_4C_3) give methane on hydrolysis
6	Both beryllium and aluminium are rendered passive by nitric Acid.

31. Give the systematic names for the following (i) milk of magnesia (ii) lye (iii) lime (iv) Caustic potash (v) washing soda (vi) soda ash (v) trona

(i)	Magnesium hydroxide	$Mg(OH)_2$
(ii)	Sodium hydroxide	NaOH
(iii)	Calcium oxide	CaO
(iv)	Potassium hydroxide	KOH
(v)	Sodium carbonate decahydrate	$Na_2CO_3.10H_2O$
(vi)	Sodium carbonate	Na_2CO_3
(vii)	Sodium sesquicarbonate	$Na_2CO_3.NaHCO_3.2H_2O$ (mineral)

32. Substantiate Lithium fluoride has the lowest solubility among group one metal fluorides.

(i) The solubility of alkali metal fluorides is in the order LiF < NaF < KF < RbF < CsF.

(ii) The solubility of LiF is due to its Very **high lattice energy** because of small sizes of both Li^+ and F^-

33. Mention the uses of plaster of Paris.

(i) In the building industry as well as plasters.

(ii) It is used for immobilizing the affected part of organ where there is abone fracture.

(iii) In dentistry, in ornamental work.

(v) For making casts of statues and busts.

34. Beryllium halides are Covalent whereas magnesium halides are ionic why?

Due to small size of Be^{2+}, the charge density is very high. According to Fajan's Rule, cation with small size has high polarizing power and prefers to form covalent bonds. So beryllium halides are Covalent in nature.

Whereas magnesium ion(Mg^{2+}) is bigger and it is involved in transfer of electrons to form ionic bond.

35. Alkaline earth metal (A), belongs to 3rd period reacts with oxygen and nitrogen to form compound (B) and (C) respectively. It undergo metal displacement reaction with $AgNO_3$ solution to form compound (D).

(i) Alkaline earth metal (A) belonging to 3rd period is magnesium

(ii) Magnesium reacts with oxygen and nitrogen to form magnesium oxide (B) and magnesium nitride (C).

$$2Mg + O_2 \rightarrow 2MgO$$

$$3Mg + N_2 \rightarrow Mg_3N_2$$

(iii) Magnesium undergoes metal displacement reaction with $AgNO_3$ to form magnesium nitrate (D). $Mg + 2AgNO_3 \rightarrow Mg(NO_3)_2 + 2Ag$

Compound / Element	**Formula**	**Name**
A	Mg	Magnesium
B	MgO	Magnesium oxide
C	Mg_3N_2	Magnesium nitride
D	$Mg(NO_3)_2$	Magnesium nitrate

36. Write balanced chemical equation for the following processes
(a) heating calcium in oxygen (b) heating calcium carbonate
(c) evaporating a solution of calcium hydrogen carbonate
(d) heating calcium oxide with carbon

(a) $2Ca_{(s)} + O_{2(g)} \rightarrow 2CaO_{(s)}$

(b) $CaCO_3 \leftrightarrow CaO + CO_2$

(c) $Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$

(d) $2CaO_{(s)} + 5C_{(s)} \rightarrow 2CaC_{2(s)} + CO_{2(g)}$

37. Explain the important common features of Group 2 elements.

Group 2 elements are known as alkaline earth metals. It includes beryllium , magnesium, calcium, strontium, barium, and radium. They exist in +2 oxidation states.

The general outer electronic configuration of alkaline earth metal is ns^2

Physical Characteristics:

- They are silvery, white, and hard metals. They are softer but harder than alkali metals.
- Their melting and boiling points are higher compared to alkali metals
- They are strongly electropositive in nature Alkaline earth metals give different color with flame test.

Chemical Properties:

- All alkaline earth metals forms monoxide.
- All alkaline earth metals forms peroxide except beryllium.
- They have high electrical and thermal conductivities as they have metallic bonding .
- The oxides of alkaline earth metals are basic but less basic than alkali metals.
- Hydroxides of alkaline earth metals are basic in nature except beryllium hydroxide.
- Group 2 metals forms solid carbonates
- Alkaline earth metals also form sulphates such as $BeSO_4$,and $MgSO_4$.
- Group 2 elements form hydrated, crystallized nitrates.
- Alkaline earth metals forms halides after reacting with halogens.

38. Why alkaline earth metals are harder than alkali metals.

- due to the presence of 2 electrons in its outermost shell as compared to alkali metals, which have only 1 electron in valence shell.

(Or)

(i) Atomic radius of alkaline earth metals are small and their densities are larger than those of alkali metals

(ii) Alkaline earth metals have close packed crystal structure

(iii) Generally alkaline earth metals are soft yet less than that of alkali metals.

(iv) This is because the metallic bonding in alkaline earth metals are stronger than alkali metals.

39. How is plaster of Paris prepared?

Plaster of pairs is obtained when gypsum, $CaSO_4.2H_2O$, is heated to 393K

($CaSO_4.2H_2O \rightarrow CaSO_4.1/2H_2O + 1\ 1/2H_2O$)

Calcium sulphate
hemihydrate

$2(CaSO_4.2H_2O) \rightarrow 2CaSO_4.H_2O + 3H_2O$

40. Give the uses of gypsum.

(i) Gypsum is used in making drywalls or plaster boards.

(ii) It is used in the production of plaster of Paris, which is used as a sculpting material.

(iii) It is used in making surgical and orthopedic cats.

(iv) It plays an important role in agriculture as a soil additive, conditioner, and fertilizer.

(vi) It is used in toothpastes, shampoos, and hair products.

(vii) It is used in baking as a dough conditioner.

(viii) It is used to give colour to cosmetics and drugs.

(ix) It plays a very important role in wine making.

41. Describe briefly the biological importance of Calcium and magnesium.

(i) Magnesium plays an important role in many biochemical reactions catalyzed by enzymes.

(ii) Magnesium is the co-factor of all enzymes that utilize ATP in phosphate transfer and energy release.

(iii) Magnesium also essential for DNA synthesis and is responsible for the stability and proper functioning of DNA.

(iv) Magnesium is also used for balancing electrolytes in our body.

(v) Deficiency of magnesium results into convulsion and neuromuscular irritation.

(vi) Calcium is a major component of bones and teeth.

(vii) Calcium is also present in blood and its concentration is maintained by hormones (calcitonin and parathyroid hormone).

(viii) Deficiency of calcium in blood causes it to take longer time to clot.

(ix) Calcium is also important for muscle contraction.

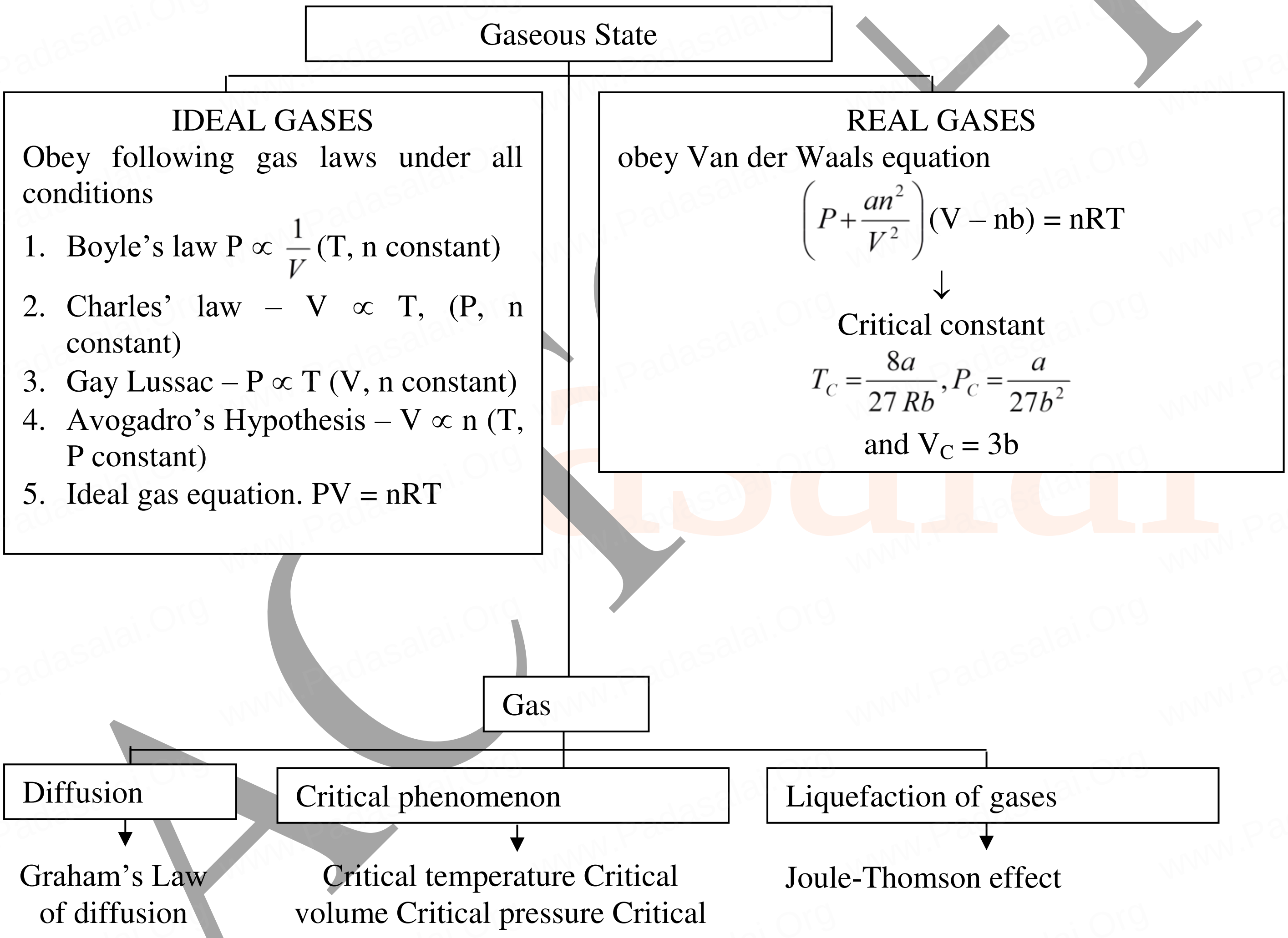
(x) Chlorophyll, contains magnesium which plays an important role in photosynthesis.

42. Which would you expect to have a higher melting point, magnesium oxide or magnesium fluoride? Explain your reasoning

- Magnesium oxide has very strong ionic bonds as compared to magnesium fluoride.
- Mg^{2+} and O^{2-} have charges of +2 and -2 respectively.
- Oxygen ion is smaller than fluoride ion.
- The smaller the ionic radii, the smaller the bond length in MgO and the bond is stronger than MgF_2.
- Due to more strong bond nature in MgO, it has high melting point than MgF_2.

Unit 6 GASEOUS STATE

CHAPTER MAP



Gaseous State

IDEAL GASES

Obey following gas laws under all conditions

1. Boyle's law P $\propto \frac{1}{V}$ (T, n constant)
2. Charles' law – V $\propto$ T, (P, n constant)
3. Gay Lussac – P $\propto$ T (V, n constant)
4. Avogadro's Hypothesis – V $\propto$ n (T, P constant)
5. Ideal gas equation. PV = nRT

REAL GASES

obey Van der Waals equation

$$\left(P+\frac{an^2}{V^2}\right)(V - nb) = nRT$$

$\downarrow$

Critical constant

$$T_C = \frac{8a}{27\,Rb}, P_C = \frac{a}{27b^2}$$

and $V_C = 3b$

Gas

Diffusion → Graham's Law of diffusion

Critical phenomenon → Critical temperature Critical volume Critical pressure Critical

Liquefaction of gases → Joule-Thomson effect

Important formula

1. Pressure = $\frac{Force\,(N)}{Area\,(m^2)}$
2. Boyle's law = PV = K (or) $P_1V_1 = P_2V_2 = K$
3. Charles' law = $\frac{V}{T}$ = Constant (or) V = KT (or) $\frac{V_1}{T_1}=\frac{V_2}{T_2}=K$
4. Gay-Lussac's law = P ∝ T (or) $\frac{P}{T}$ = K (or) $\frac{V_1}{T_1}=\frac{V_2}{T_2}=K$
5. Avogadro's hypothesis = V ∝ n (or) $\frac{V_1}{n_1}=\frac{V_2}{n_2}$ = Constant
6. Ideal gas equation = PV = nRT
7. Dalton's law of Partial pressure : $P_{total} = p_1 + p_2 + p_3$ …….
8. $P_{dry\ gas} = P_{total} - P_{water\ vapour}$
9. Graham's law of Diffusion : $\frac{r_A}{r_B}=\sqrt{\frac{M_B}{M_A}}$
10. Compressibility factor = Z = $\frac{PV}{nRT}(or)\frac{V_{real}}{V_{ideal}}$
11. Van der Waals equation of state: $\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$
12. Critical volume $V_C = 3b$
13. Critical pressure $P_C = \frac{a}{27b^2}$
14. Critical temperature $T_C = \frac{8a}{27\,Rb}$
15. Inversion temperature $T_i = \frac{2a}{Rb}$

- **Gases at STP** – H_2, N_2, O_2, F_2, Cl_2, O_3, He, Ne, Ar, Kr, Xe and Rn (Only 11 elements).
- **The Earth** – The Earth is surrounded by a atmosphere of air whose composition is 78% Nitrogen, 21% Oxygen and 1% other gases.
- **Oxygen** – It is highly essential for our survival.
- **Hydrogen cyanide (HCN)** – Deadly poison
- **Carbon monoxide (CO)** – Highly toxic
- **NO_2 and SO_2** – less toxic
- **Chemically inert gases** – He, Ne, Ar, Kr, Xe and Rn.
- **Gas** – A substance is normally in a gaseous state at ordinary temperature and pressure.
- **Vapour** – The gaseous form of any substance that is a liquid or solid at NTP.
- **Pressure** – It is defined as the force exerted by a gas on unit area of the wall. Pressure = $\frac{Force}{area} = \frac{F}{a}$
- **Unit of pressure (Pascal)** – 1 Pascal = 1 Nm^{-2},where 1 N = 1 Kg ms^{-2}. Other units of pressure are Bar, atmosphere, Torr, mm of Hg.
- **Atmospheric pressure** – The force exerted on a unit area of earth by the column of air above it is called atmospheric pressure.
- **1 atm** – 760 mm Hg
- **Boyle's law** – At a given temperature, the volume occupied by a fixed mass of a gas is inversely proportional to its pressure.

  $V \propto \frac{1}{P}$ at constant T (or)

  $PV = K_1$ at constant T (or)

  $P_1V_1 = P_2V_2 = K_1$
- **Charles' law** – For a fixed mass of a gas at constant pressure, the volume is directly proportional to temperature (K).

  $V \propto T$ and constant P and n ; $\frac{V}{T}$ = Constant
- **Absolute zero :** -273.15°C.
- **Gay-Lussac's law** – At constant volume, the pressure of a fixed mass of gas is directly proportional to temperature. $P \propto T$ at constant V ; $\frac{P}{T}$ = Constant.
- **Avogadro's hypothesis** – Equal volumes of all gases under the same condition of temperature and pressure contain equal number of molecules.

  $V \propto n$ (or) $\frac{V_1}{n_1} = \frac{V_2}{n_2}$ = Constant

- **Ideal gas equation** – PV = nRT where R is universal gas constant.
- **Values of R** –

  $R = 0.082057\ dm^3\ atm\ mol^{-1}\ K^{-1}$

  $R = 8.314\ x\ Pa\ m^3\ K^{-1}\ mol^{-1}$

  $R = 8.314\ x\ 10^{-2}\ bar\ dm^3\ K^{-1}\ mol^{-1}$

  $R = 8.314\ J\ K^{-1}\ mol^{-1}$

- **Dalton's law of partial pressures** – It states that the total pressure of a mixture of gases is the sum of partial pressures of the gases present.

  $P_{total} = p_1 + p_2 + p_3 \ldots\ldots$

- **Graham's law of Diffusion** – The rate of effusion or diffusion is inversely proportional to the square of molecular mass of a gas through an orifice.

  $$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}$$

- **Ideal gases** – Gases that obey ideal gas equation PV = nRT are ideal gases.
- **Real gases** – Gases that do not obey the ideal gas equation PV = nRT are real gases. For them either PV > nRT or PV < nRT
- **Van der Waals equation of state** –

  $\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$. Where a and b are Van der Waals constant.

- **Compression factor (Z)** –

  It is the ratio of PV to nRT. $Z = \frac{PV}{nRT}$.

  For ideal gases Z = 1 and for real gases Z > 1 or Z < 1. $Z = \frac{V_{real}}{V_{ideal}}$

- **Critical constants** –

  Critical Volume $V_C = 3b$

  Critical Pressure $P_C = \frac{a}{27b^2}$

  Critical Temperature $T_C = \frac{8a}{27\,Rb}$

- **Critical temperature of CO_2** – 303.98 K
- **Critical Temperature -** T_C is defined as the temperature below which a gas can be liquefied by the application of pressure.
- **Critical Pressure -** P_C is the pressure required to liquefy a gas at its critical temperature.

- **Critical Volume –** V_C is the volume occupied by one mole of a gas at its critical temperature and critical pressure.
- **Joule Thomson effect –** The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure.
- **Inversion temperature (T_i) –** The temperature below which a gas obey Joule Thomson effect is called inversion temperature. $T_i = \frac{2a}{Rb}$

Choose the correct Answer:

1. Gases deviate from ideal behavior at high pressure. Which of the following statement(s) is correct for non-ideality?

a) at high pressure the collision between the gas molecule become enormous

b) at high pressure the gas molecules move only in one direction

c) at high pressure, the volume of gas become insignificant

d) at high pressure the intermolecular interactions become significant

2. Rate of diffusion of a gas is

a) directly proportional to its density

b) directly proportional to its molecular weight

c) directly proportional to its square root of its molecular weight

d) inversely proportional to the square root of its molecular weight

3. Which of the following is the correct expression for the equation of state of van der Waals gas?

a) $\left[P + \frac{a}{n^2v^2}\right](V - nb) = nRT$ b) $\left[P + \frac{na}{n^2v^2}\right](V - nb) = nRT$

c) $\boldsymbol{\left[P + \frac{an^2}{v^2}\right](V - nb) = nRT}$ (d) $\left[P + \frac{n^2a^2}{v^2}\right](V - nb) = nRT$

4. When an ideal gas undergoes unrestrained expansion, no cooling occurs because the molecules

a) are above inversion temperature **b) exert no attractive forces on each other** c) do work equal to the loss in kinetic energy d) collide without loss of energy

5. Equal weights of methane and oxygen are mixed in an empty container at 298 K. The fraction of total pressure exerted by oxygen is

(a) 1/3 (b) ½ (c) 2/3 (d) 1/3 × 273 × 298

6. The temperatures at which real gases obey the ideal gas laws over a wide range of pressure is called

a) Critical temperature **b) Boyle temperature**

c) Inversion temperature d) Reduced temperature

7. In a closed room of 1000 m^3 a perfume bottle is opened up. The room develops a smell. This is due to which property of gases?

a) Viscosity b) Density **c) Diffusion** d) None

8. A bottle of ammonia and a bottle of HCl connected through a long tube are opened simultaneously at both ends. The white ammonium chloride ring first formed will be

a) At the center of the tube **b) Near the hydrogen chloride bottle**

c) Near the ammonia bottle d) Throughout the length of the tube

9. The value of universal gas constant depends upon

a) Temperature of the gas b) Volume of the gas

c) Number of moles of the gas **d) units of Pressure and volume.**

10. The value of the gas constant R is

a) 0.082 dm^3*atm.* b) 0.987 cal mol^{-1} K^{-1} **c) 8.3 J $mol^{-1}K^{-1}$** d) 8 erg $mol^{-1}K^{-1}$

11. Use of hot air balloon in sports at meteorological observation is an application of

a) Boyle's law b) Newton's law c) Kelvin's law d) Brown's law

12. The table indicates the value of van der Waals constant 'a' in $(dm^3)^2$*atm*. mol^{-2}

Gas	O_2	N_2	NH_3	CH_4
A	1.360	1.390	4.170	2.253

The gas which can be most easily liquefied is

a) O_2 b) N_2 **c) NH_3** d) CH_4

13. Consider the following statements

i) Atmospheric pressure is less at the top of a mountain than at sea level

ii) Gases are much more compressible than solids or liquids

iii) When the atmospheric pressure increases the height of the mercury column rises

Select the correct statement

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

14. Compressibility factor for CO_2 at 400 K and 71.0 bar is 0.8697. The molar volume of CO_2 under these conditions is

a) 22.04 dm^3 b) 2.24 dm^3 **c) 0.41 dm^3** d) 19.5dm^3

15. If temperature and volume of an ideal gas is increased to twice its values, the initial pressure P becomes

a) 4P b) 2P **c) P** d) 3P

16. At identical temperature and pressure, the rate of diffusion of hydrogen gas is 3 3 times that of a hydrocarbon having molecular formula C_nH_{2n-2}. What is the value of n ?

a) 8 **b) 4** c) 3 d) 1

17. Equal moles of hydrogen and oxygen gases are placed in a container, with a pin-hole through which both can escape what fraction of oxygen escapes in the time required for one-half of the hydrogen to escape.

a) 3/8 b) 1/2 **c) 1/8** d) 1/4

18. The variation of volume V, with temperature T, keeping pressure constant is called the coefficient of thermal expansion ie $\alpha = \frac{1}{v}\left(\frac{\partial V}{\partial T}\right)_P$. For an ideal gas α is equal to

a) T **b) 1/T** c) P d) none of these

19. Four gases P, Q, R and S have almost same values of 'b' but their 'a' values (a, b are Vander Waals Constants) are in the order Q < R < S < P. At a particular temperature, among the four gases the most easily liquefiable one is

a) P b) Q c) R d) S

20. Maximum deviation from ideal gas is expected from

a) $CH_{4\,(g)}$ **b) $NH_{3\,(g)}$** c) $H_{2\,(g)}$ d) $N_{2\,(g)}$

21. The units of Vander Waals constants 'b' and 'a' respectively

a) mol L^{-1} and L atm^2 mol^{-1} b) mol L and L atm mol^2

c) $mol^{-1}L$ and L^2 atm mol^{-2} d) none of these

22. Assertion : Critical temperature of CO_2 is 304K, it can be liquefied above 304K.

Reason : For a given mass of gas, volume is to directly proportional to pressure at constant temperature

a) both assertion and reason are true and reason is the correct explanation of assertion

b) both assertion and reason are true but reason is not the correct explanation of assertion

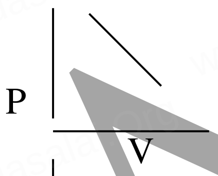
c) assertion is true but reason is false **d)both assertion and reason are false**

23. What is the density of N_2 gas at 227°C and 5.00 atm pressure? (R = 0.082 L atm K^{-1} mol^{-1})

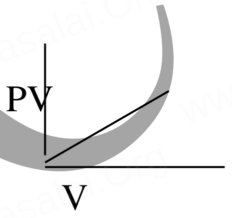
a) 1.40 g/L b) 2.81 g/L **c) 3.41 g/L** d) 0.29 g/L

24. Which of the following diagrams correctly describes the behaviour of a fixed mass of an ideal gas? (T is measured in K)

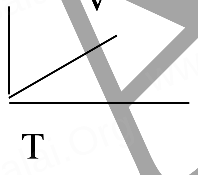
a)



b) PV



c) V



d) all the above

25. 25g of each of the following gases are taken at 27°C and 600 mm Hg pressure. Which of these will have the least volume ?

a) HBr b) HCl c) HF **d) HI**

Answer these questions briefly

26. State Boyle's law.

At a given temperature the volume occupied by a fixed mass of a gas is inversely proportional to its pressure. Mathematically, the Boyle's law can be written as

$V \alpha \frac{1}{P}$ ------ (1)

(T and n are fixed, T-temperature, n- number of moles)

$V = k \times \frac{1}{P}$ ------ (2)

k – proportionality constant When we rearrange equation (2)

PV = k at constant temperature and mass

27. Name two items that can serve as a model for Gay Lusaac' law and explain.

P α T at constant volume.

(i) Pressure in well inflated tyre is almost constant but when temperature increases in summer days it increases the pressure and sometimes tyres may burst.

(ii) **Guns and other firing equipment's** are thrilling examples of Gay Lussac's law. When gun pin strikes, it ignites the gun powder and this increases the temperature which in turn increases the pressure and bullet is fired from the gun.

iii) **Heating a closed aerosol cane.** The increased pressure may cause the container to explode. You don't toss an "empty" can of hair spray into a fire.

iv) **The egg in the bottle experiment.**

A glass bottle is taken, inside the bottle put some pieces of cotton with fire. Then place a boiled egg (shell removed) at the top of the bottle. The temperature inside the bottle increases from the fire, rising the pressure. By sealing the bottle with egg, the fire goes on, dropping the temperature and pressure. This causes the egg to be sucked into the bottle.

28. Give the mathematical expression that relates gas volume and moles. Describe in words what the mathematical expression means.

- The Mathematical expression between the volume of gas and number of moles is **V α n**
  $V_1/n_1 = V_2/n_2 =$ constant
- **where** V_1 & n_1 are the volume and number of moles of a gas,
  V_2 & n_2 are a different set of values of volume and number of moles of the same gas at same temperature and pressure.
- The above relation is expressed as " **Equal volumes of all gases under the same condition of temperature and pressure contain equal number of molecules".**

29. What are ideal gases? In what way real gases differ from ideal gases.

An ideal gas a gas which obeys the gas laws and ideal gas equation

PV=nRT.

An ideal gas is defined as **"one in which all collisions between atoms or molecules are perfectly elastic forces".**

The difference between ideal gas and real gas is

Ideal gas	Real gas
1. It obeys gas laws under all conditions of temperature and pressure	It obeys gas laws only under low pressure and high temperature
2. No gas is ideal	All gases are real

3. Volume occupied by the molecules is negligible as compared to the total volume occupied by the gas.	Volume occupied by the molecules is not negligible as compared to the total volume occupied by the gas.
4. The forces of attraction among the molecules of the gas are negligible.	The forces of attraction among the molecules cannot be neglected at high pressure and low temperature
5. It obeys ideal gas equation PV = nRT	It obeys Van der Waals equation $(P + an^2/V^2)$ (V-nb) = nRT

30. Can a Van der Waals gas with a=0 be liquefied? explain.

- The van der Waals constant ‘a’ is a measure of the attractive forces among the molecules of the gas
- Greater the value of ‘a’ larger the intermolecular force of attraction and the gas can be liquefied.
- Here a=0 means there is intermolecular attraction and the gas **cannot be liquefied.**

31. Suppose there is a tiny sticky area on the wall of a container of gas. Molecules hitting this area stick there permanently. Is the pressure greater or less than on the ordinary area of walls?

- Molecule hitting the tiny sticky area on the wall of the container of gas moves faster as they get closer to adhesive surface, but this effect is not permanent.
- The pressure on the sticky wall is greater than on the ordinary area of walls.

32. Explain the following observations

a) Aerated water bottles are kept under water during summer

- In aerated water bottles the CO_2 is passed through the aqueous solution under pressure.
- The solubility of gas is decreases with increase of temperature. In summer season the temperature is raise the solubility is decreases.
- Due to this will increase very high pressure above the surface of the liquid inside the bottle and bottle will not able to withstand the pressure and bottle may explode.
- To avoid this Aerated water bottles are kept under water during summer.
- As a result, the temperature decrease and solubility of CO_2 is increases in aqueous solution resulting the pressure inside the bottle decreases.

b) Liquid ammonia bottle is cooled before opening the seal

- Liquid ammonia bottle contains the gas under very high pressure. If the bottle is opened, the sudden decrease in pressure will increase the volume of gas.
- As result, the gas is come out the bottle with greater force will cause breakage of bottle and accident.
- The pressure of the gas over liquid ammonia is decreased by dipping H_2O.
- Once it attains the temperature of water, it can be opened so that no gas will come out of the mouth of the tube with force.

c) The tyre of an automobile is inflated to slightly lesser pressure in summer than in winter.

- In summer due to high temperature the air expands and hence to avoid tyre burst, the pressure is kept less.
- As a result, when the vehicle runs and the tyre air gets heated and expands, resulting increased pressure is still kept below the bursting limit.

d) The size of a weather balloon becomes larger and larger as it ascends up into larger altitude.

- According Boyle's law the volume of gas is inversely proportional to the pressure at a given temperature.
- As the weather balloon ascends, the atmospheric pressure is less, pressure of the gas tends to decrease and so volume as well as the size of the balloon increases.

33. Give suitable explanation for the following facts about gases.

a) Gases don't settle at the bottom of a container

- Gases are less denser than solids and liquids. They have negligible intermolecular force of attraction between free particles, so are free to move.
- Hence gases don't settle at bottom of the container.

b) Gases diffuse through all the space available to them

- Gases have the tendency to mix with one another spontaneously and form a homogeneous mixture.
- This is due to the fact that gas particles are mainly in random at very high velocities and there in so much of inter molecular empty space in the volume of any gas.
- This permit them to mix spontaneous and this phenomenon is known as diffusion.

34. Suggest why there is no hydrogen (H_2) in our atmosphere. Why does the moon have no atmosphere?

- Under ordinary conditions on earth, hydrogen exist as diatomic (H_2). Because of its light weight, which enable into escape from earth gravity more easily than heavier gases. So, no hydrogen is there in atmosphere.
- Moon has no atmosphere because the value of acceleration due to gravity (g) on the surface of moon is small. The molecules of atmospheric gases on the surface of the moon have thermal velocities greater than escape velocity.

35. Explain whether a gas approaches ideal behavior or deviates from ideal behaviour if

a) it is compressed to a smaller volume at constant temperature.

When the gas is compressed, there is a decrease in volume and molecules are close to each other and hence inter molecular attraction becomes more and hence it deviates from ideal behavior.

b) the temperature is raised at while keeping the volume constant

- When volume constant, the pressure is directly proportional to the temperature.

- The temperature is raised the pressure is always increases which leads the intermolecular force of attraction between the gas molecules.
- So it deviates from the ideal behavior

c) more gas is introduced into the same volume and at the same temperature.

- If more gas is introduced in the same volume and temperature is constant, more will be the pressure.
- The increase in pressure is always increases which leads the intermolecular force of attraction between the gas molecules.
- So it deviates from the ideal behavior

36. Which of the following gases would you expect to deviate from ideal behaviour under conditions of low temperature F_2, Cl_2, or Br_2? Explain.

- These molecules are held together by a weak van der Waals forces.
- The forces of attraction between the molecules with increase in the size of the molecule.
- Br_2 deviate from ideal behavior, since the Br_2 has the biggest size provides maximum attraction between bromine molecules.

37. Distinguish between diffusion and effusion.

Diffusion	Effusion
1. The spreading of the molecules of a gas throughout the available space or second substance is called diffusion.	Effusion is the escape of gas molecules through a very small hole.
2. Diffusion refers to the ability of the gases to mix with each other	Effusion is a ability of a gas to travel through a small pin-hole.
3. **Example:** spreading of something such as brown tea liquid spreading through the water in a tea cup.	**Example:** pouring out something like the soap studs bubbling out from a bucket of water.

38. Aerosol cans carry clear warning of heating of the can. Why?

- Aerosols are colloids in which air (gas) is dispensed in liquid. On heating the can, the pressure of the gas increases and it can burst out.
  - Hence they carry clear warning that they should not be heated or kept in near fire.

39. Would it be easier to drink water with a straw on the top of Mount Everest?

- Drinking through a straw is slightly more difficult on the top a mountain.
- This is because the atmospheric pressure and the temperature is low at top mountain.
- When you drink through a straw you are decreasing the pressure in your mouth, so the atmospheric pressure pushes the liquid up the straw.
- On mountain there is less pressure so there is less pressure to push the water into the straw.

40. Write the Van der Waals equation for a real gas. Explain the correction term for pressure and volume.

The Vander Waals equation for a real gas is

$$\left(P + \frac{an^2}{V^2}\right)(V - \text{nb}) = \text{nRT}$$

Pressure Correction:

The pressure of a gas is directly proportional to the force created by the bombardment of molecules on the walls of the container. The speed of a molecule moving towards the wall of the container is reduced by the attractive forces exerted by its neighbours . Hence, the measured gas pressure is lower than the ideal pressure of the gas. Hence, Vander Waals introduced a correction term to this effect.

Inter-molecular forces of attraction

Van der Waals found out the forces of attraction experienced by a molecule near the wall are directly proportional to the square of the density of the gas.

$$p` \propto \rho^2 \qquad \rho = \frac{n}{V}$$

Where n is the number of moles of gas and V is the volume of the container

$$\Rightarrow \quad P' \propto \frac{n^2}{V^2}$$

$$\Rightarrow \quad P' = \frac{an^2}{V^2}$$

Where a is proportionality constant and depends on the nature of gas

Therefore, $\mathbf{P_{ideal} = P +} \frac{an^2}{V^2}$

Volume Correction:

As every individual molecule of a gas occupies a certain volume, the actual volume is less than the volume of the container, V. Van der Waals introduced a correction factor V' to this effect. Let us calculate the correction term by considering gas molecules as spheres.

V = excluded volume

Excluded volume for two molecules $= \frac{4}{3}\pi(2r)^3$

$$= 8\left(\frac{4}{3}\pi r^3\right) = 8\text{ V}_m$$

Where V is a volume of a single molecule $= \frac{8V_m}{2} = 4\text{V}_m$

Excluded volume for n molecule = $n(4V_m)$ = nb

Where b is van der waals constant

Which is equal to $4V_m$ $\Rightarrow$ V = nb

$$V_{ideal} = V - nb$$

Replacing the corrected pressure and volume in the ideal gas equation PV = nRT we get the van der Waals equation of state for real gases as below,

$$\left(P + \frac{an^2}{V^2}\right)(V - \text{nb}) = \text{nRT}$$

The constants a and b are van der Waals constants and their values vary with the nature of the gas. It is an approximate formula for the non-ideal gas.

41. Derive the values of van der Waals equation constants in terms of critical constants.

The van der waals equation for n moles is

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT \qquad \text{-------- (1)}$$

For 1 mole

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \qquad \text{-------- (2)}$$

From the equation we can derive the values of critical constants Pc, Vc and Tc in terms of a and b, the van der waals constant, on expanding the above equation

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} - RT = 0 \qquad \text{--------- (3)}$$

Multiply equation (3) by $\frac{V^2}{P}$

$$\frac{V^2}{P}\left(PV + \frac{a}{V} - Pb - \frac{ab}{V^2} - RT\right) = 0$$

$$V^3 + \frac{aV}{P} + - bV^2 - \frac{ab}{V^2} - \frac{RTV^2}{P} \qquad \text{-------- (4)}$$

When the above equation is rearranged in powers of V.

$$V^3 + \left[\frac{RT}{P} + b\right]V^2 + \left[\frac{a}{P}\right]V - \left[\frac{ab}{P}\right] = 0 \qquad \text{-------- (5)}$$

When equation (5) is a cubic equation in V. On solving this equation,

We will get three solutions. At the critical point all these three solutions of V are equal to the critical volume Vc. The pressure and temperatures becomes Pc and Tc respectively

i.e., V = Vc;

V – Vc=0

$(V - Vc)^3$=0 [$(a-b)^3$ =a3-3a^2b+3ab^2-b^3]

$$V^3 - 3VcV^2 + 3Vc^2V - Vc^3 = 0 \qquad \text{-------- (6)}$$

As equation (5) is identical with equation (6), we can equate the coefficients of V2, V and constant terms in (5) and (6)

$$-3VcV^2 = -\left[\frac{RT_c}{P_c} + b\right]V^2$$

$$3Vc = \frac{RT_c}{P_c} + b \qquad \text{---------- (7)}$$

$$3Vc^2 = \frac{a}{P_c} \qquad \text{--------- (8)}$$

$$3Vc^2 = \frac{ab}{P_c} \qquad \text{-------(9)}$$

Divide equation (9) by equation (8)

$$\frac{{V_c}^3}{3{V_c}^2} = \frac{ab/P_c}{a\,/P_c}$$

$$\frac{V_c}{3} = b$$

i.e., $V_c = 3b$ -------- (10)

when equation (10) is substituted in (8)

$$3V_c^2 = \frac{a}{P_c}$$

$$P_c = \frac{a}{3V_c^2} = \frac{a}{3(3b^2)} = \frac{a}{3 \times 9b^2} = \frac{a}{27b^2}$$

$$P_c = \frac{a}{27b^2} \quad \text{------- (11)}$$

Substituting the values of Vc and Pc in equation (7),

$$3V_c = b + \frac{RT_c}{P}$$

$$3(3b) = b + \frac{RT_c}{\left(\frac{a}{27b^2}\right)}$$

$$9b - b = \left(\frac{RT_c}{a}\right) 27b^2$$

$$8b = \frac{T_c R 27b^2}{a}$$

$$T_c = \frac{8ab}{27Rb^2} = \frac{8a}{27Rb} \quad \text{------- (12)}$$

The critical constants can be calculated using the values of van der waals constant of a gas and vice versa.

$$a = 3V_c^2P_c \text{ and } b = \frac{V_c}{3}$$

42. Why do astronauts have to wear protective suits when they are on the surface of moon?

- Astronauts must wear space suits since the surface of moon, there is no air to breath and no air pressure.
- Space is extremely cold and filled with dangerous radiation.
- Space suits are specially designed to protect astronauts from the cold, radiation and low pressure in space. It also provide air to breathe.

43. When ammonia combines with HCl, NH_4Cl is formed as white dense fumes. Why do more fumes appear near HCl?

$NH_3 + HCl \rightarrow NH_4Cl$

- The rate of diffusion is inversely proportional to the molecular weight of the gas.
- Lower the molecular weight faster is the diffusion.
- The molar mass of HCl is 36.5 $g.mol^{-1}$ while the molar mass of NH_3 is 17 $g.mol^{-1}$.
- Hence NH_3 diffuses faster than HCl. Hence white fumes appear near HCl.

(Or)

i) When ammonia combines with HCl, NH_4Cl is formed as white dense fumes. The reaction takes place in neutralization between a weak base and a strong acid.

ii) The property of the gas is diffusion.

iii) Diffusion of gases- Ammonia and hydrogen chloride. Concentrated ammonia solution is placed on a pad in one end of a tube and concentrated HCl on the pad at the other. After about a minute, the gases diffuse far enough to meet and a ring of solid ammonium chloride is formed near the HCl end.

7.THERMODYNAMICS

IMPORTANT FORMULA

1. For an adiabatic process q = 0
2. For an isothermal process dT = 0
3. For an isobaric process dP = 0
4. For an isochoric process dV = 0
5. For an cyclic process dU = 0, dH = 0, dP = 0, dV = 0, and dT = 0.
6. Internal energy $U = U_t + U_v + U_r + U_b + U_e + U_i$
7. Change in internal energy $\Delta U = U_f - U_i$
8. Work = -w = Fx (or) $w = P_{ext}\Delta V$
9. $w_{rev} = -2.303\ nRT \log \frac{V_f}{V_i}$
10. First law of thermodynamics = $\Delta U = q + w$
11. For a cyclic process, first law of thermodynamics $q = -w$
12. For an isochoric process, first law of thermodynamics $\Delta U = q_V$
13. For an adiabatic process, first law of thermodynamics $\Delta U = w$

14.For an isobaric process, first law of thermodynamics $\Delta U = q - P\Delta V$

15.Relationship between ΔH and ΔU

$\Delta H = \Delta U + P\Delta V$ (or) $\Delta H = \Delta U + \Delta n_{(g)}RT$

16.Standard enthalpy of reaction ΔH_r^0

$$\Delta H_r^0 = \sum \Delta H_{r\,(Products)}^0 - \sum \Delta H_{r\,(reactants)}^0$$

17.Heat capacity (C) $C = \left[\frac{q}{m(T_2 - T_1)}\right]$

18.Heat capacity at constant volume $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

19.Heat capacity at constant pressure $C_P = \left(\frac{\partial U}{\partial T}\right)_P$

20.Relation between C_P and C_V for an ideal gas: $C_P - C_V = nR$

21.$\Delta U = n.C_V [T_2 - T_1]$

$\Delta H = n.C_P [T_2 - T_1]$

22.Hessis law = $\Delta H_r = \Delta H_1 + \Delta H_2 + \Delta H_3$ …………

23.Efficiency in percentage = $\left[1 - \frac{T_2}{T_1}\right] \times 100$

24.Standard entropy change = ΔS_f^0

$$\Delta S_r^0 = \sum S^0_{(Products)} - \sum \Delta S^0_{(reactants)}$$

25.Change in entropy $\Delta S = \frac{q_{rev}}{T} = \frac{\Delta H_{rev}}{T}$

26.Entropy of fusion = $\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_f}$

27.Entropy of vapourisation = $\Delta S_V = \frac{\Delta H_V}{T_b}$

28.Entropy of transition = $\Delta S_t = \frac{\Delta H_t}{T_t}$

29.Gibb's free energy = G = H – TS (or) $\Delta G = \Delta H - T\Delta S$

$\Delta G^0 = -RT \ln k_{eq}$

30.Relation between Gibb's free energy and net work done by the system = $-\Delta G = -w - P\Delta V$

31.Relationship between standard free energy change ΔG^0 and equilibrium constant K_{eq}:

$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln k_{eq}$

32.Third law of thermodynamics $\lim\limits_{T \to 0} S = 0$ for a perfectly ordered crystalline state.

IMPORTANT POINT

- **Thermodynamics** – It means flow of heat. It is a branch of science which deals the relation between energy, heat, work and accompanying changes in the nature and behaviour of various substances around us.
- **Macroscopic properties** – Heat and work.
- **First law of Thermodynamics** – It states that "The total energy of an isolated system remains constant though it may change from one form to another".

  $\Delta U = q + w$

  ΔU – Change in the internal energy

  q – Amount of heat supplied to the system

  w – Amount of work done on the system
- **System** – It is defined as any portion of matter under thermodynamic consideration, which is separated from the rest of the universe by real or imaginary boundaries.
- **Homogeneous system** – If the physical states of all its matter are uniform, it is called homogeneous system.
- **Heterogeneous system** – If the physical states of all its matter are not uniform, it is called heterogeneous system.
- **Surroundings** – Everything in the universe that is not the part of system is called surroundings.
- **Boundary** – Anything which separates the system from its surrounding is called boundary.
- **Isolated system** – A system which can exchange neither matter nor energy with its surrounding is called an isolated system. e.g., Hot water contained in a thermos flask.
- **Closed system** – A system which can exchange only energy but not matter with its surroundings is called a closed system. e.g., Hot water contained in a closed beaker.
- **Open system** – A system which can exchange both matter and energy with its surroundings is called an open system. e.g., Hot water contained in an open beaker.
- **Intensive properties** – The properties that are independent of the mass or size of the system is called as intensive property. e.g., Refractive index, surface tension, density, temperature, boiling point and freezing point etc.
- **Extensive properties** – The properties that are depended on the mass or size of the system is called as extensive property. e.g., Volume, number of moles, mass and internal energy etc.
- **Thermodynamic process** – The method of operation which can bring about the change in the system is called thermodynamics process. e.g., Heating, cooling and fusion.
- **Reversible processs** – The process in which the system and surroundings can be restored to the initial state from the final state without producing any changes in the thermodynamic properties of the universe is called a reversible process.

- **Irreversible process** – The process in which the system and surroundings cannot be restored to the initial state from the final state is called an irreversible process.
- **Adiabatic process** – It is defined as one in which there is no exchange of heat (q) between the system and surrounding during process. [$q = 0$]
- **Isothermal process** – It is defined as one in which the temperature of the system remains constant, during the change from its initial to final state. [$dT = 0$]
- **Isobaric process** – It is defined as one in which the pressure of the system remains constant during its change from the initial to final state. [$dP = 0$]
- **Isochoric process** – It is defined as one in which the volume of system remains constant during its change from initial to final state. [$dV = 0$]
- **Cyclic process** – When a system returns to its original state after completing a series of changes the process is known as a cyclic process. For a cyclic process. $dU = 0$, $dH = 0$, $dP = 0$, $dV = 0$ and $dT = 0$.
- **State functions** – The properties of P, V, T and 'n' that are used to describe the state of a system are called as state functions.
- **Path functions** – A path function is a thermodynamic property of the system whose value depends on the path by which the system goes from its initial to final states. e.g., Work and heat.
- **Internal energy** – Internal energy of a system is equal to the energy possessed by all its constituents namely atoms, ions and molecules.

  U = Internal energy = $U_t + U_v + U_r + U_b + U_e + U_i$
- ΔU – Change in internal energy = $U_f - U_i$
- **Heat (q)** – It is regarded as an energy in transit across the boundary separating a system from its surrounding. It is a path function.
- **Unit of heat** – SI unit of heat is joule (J). The other unit is calories (cal).
- **Calories (cal)** – It is defined as the quantity of heat required to raise the temperature of 1 gram of water by $1^{\circ}C$ in the vicinity of $15^{\circ}C$.
- **Work (w)** – It is defined as the force (F) multiplied by the displacement (x). [$- w = F. x$]
- **Unit of work** – SI unit of work is joule (J) or kilojoule (kJ).
- **Joule** – It is defined as the work done by a force of one Newton through a displacement of one meter (J = Nm).
- **Gravitational work** – When an object is raised to a certain height against the gravitational field, gravitational work is done on the object. [$w = m.g.h$]
- **Electrical work** – When a charged body moves from one potential region to another, electrical work is done. [$w = QV$]

- **Mechanical work** – It is defined as force multiplied by the displacement through which the force acts. [w = F. x]
- **Pressure – Volume work** – The work done in expansion or compression of a gas. PV work (or) expansion work.
- **Work in volved in expansion and compression process** – [$w = -P\Delta V$]
- **Expansion** – During expansion, work is done by the system. Since $V_f > V_i$, the sign obtained for work will be negative.
- **Compression** – During compression, work is done on the system. Since $V_f < V_i$, the sign obtained for work will be positive.
- **For reversible process – w_{rev}** = $- 2.303\, nRT \log \frac{V_f}{V_i}$
- **Zeroth law of thermodynamics** – This law states that 'If two systems are separately in thermal equilibrium with a third one, then they tend to be in thermal equilibrium with themselves'.
- **First law of thermodynamics** – "Energy can neither be created nor destroyed, but may be converted from one form to another".

(or)

The total energy of a system and surroundings remains constant (or conserved).

$$\Delta U = q + w$$

- **Mathematical statement of first law** –

	$\Delta U = q + w$	
Cyclic process	$\Delta U = 0$	$\therefore q = - w$
Isochoric process	$\Delta V = 0$ $w = 0$	$\therefore \Delta U = q_V$
Adiabatic process	$q = 0$	$\therefore \Delta U = w$
Isobaric process	$\Delta U = q + w$	$\Delta U = q - P\Delta V$

- **Enthalpy (H)** – It is defined as the sum of the internal energy (U) of a system and the product of pressure and volume of the system.

$$H = U + PV$$

$$\Delta H = \Delta U + P\Delta V$$

- **Relation between enthalpy 'H' and internal energy 'U'** –

$$\Delta H = \Delta U + \Delta n_{(g)} RT$$

- **Standard heat of formation** – It is defined as "the change in enthalpy that takes place when one mole of a compound is formed from its elements, present in their standard states (298K and 1 bar pressure).
- **Thermochemical equations** – It is a balanced stoichiometric chemical equation that includes the enthalpy change (ΔH).

- **Standard enthalpy or reaction** $\left(\Delta H_r^0\right)$ **-** It is the enthalpy change for a reaction when all the reactants and products are present in their standard states.

$$\Delta H_r^0 = \sum \Delta H^0_{r\,(\text{Products})} - \sum \Delta H^0_{r\,(reactants)}$$

- **Heat of combustion (ΔH_C)** – It is defined as the change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen.
- **Specific heat capacity (C)** – It is defined as the heat absorbed by one kilogram of a substance in raising its temperature by one Kelvin at a specified temperature.

$$C = \left[\frac{q}{m(T_2 - T_1)}\right]$$

- **Molar heat capacity** – It is defined as the amount of heat absorbed by one mole of the substance to raise its temperature by 1 Kelvin.

$$C_m = \frac{q}{\Delta T}$$

- **Unit of heat capacity** – JK^{-1} mol^{-1}.
- **C_V : (Molar heat capacity at constant volume)** – It is defined as the rate of change of internal energy with respect to temperature at constant volume.

$$C_V = \left(\frac{dU}{dT}\right)_V$$

- **C_P : (Molar heat capacity at constant pressure)** – It is defined as the rate of change of enthalpy with respect to temperature at constant pressure.

$$C_P = \left(\frac{dU}{dT}\right)_P$$

- **Relation between C_P and C_V for an ideal gas** –

$$C_P - C_V = nR$$

- **Calorimetry** – It is the science associated with determining the changes in energy of a system by measuring the heat exchanged with the surroundings.
- **Exothermic reaction** – The reaction in which heat is evolved and system loses heat to the surroundings. $[\Delta H_r = -ve]$
- **Endothermic reaction** – The reaction in which heat is absorbed and system gains heat from the surroundings. $[\Delta H_r = +ve]$

- **Calorific value** – It is defined as the amount of heat produced in calories (or joules) when one gram of a substance is completely burnt. The SI unit is J kg_{-1}.
- **Heat of solution** – It is defined as the change in enthalpy of the system when one mole of a substance is dissolved in a specified quantity of a solvent at a given temperature.
- **Heat of neutralization** – It is defined as the change in enthalpy of the system when one gram equivalent of an acid is completely neutralized by one gram equivalent of a base in dilute solution.

- **Molar heat of fusion** – It is defined as the change in enthalpy when one mole of a solid substance is converted into the liquid state at its melting point.
- **Molar heat of vapourisation** – It is defined as the change in enthalpy when one mole of a liquid is converted into vapour or gaseous state at its boiling point.
- **Molar heat of sublimation** – It is defined as the change in enthalpy when one mole of a solid is directly converted into the gaseous state at its sublimation temperature..
- **Heat of transition** – It is defined as the change in enthalpy when one mole of an element change from one allotropic form to another.
- **Hess's law of constant heat summation** – It states that "the enthalpy change of a reaction either at constant volume or constant pressure is the same whether it takes place in a single step or multiple steps provided the initial and final states are same".
- **Lattice energy** – It is defined as the amount of energy required to completely remove the constituent ions from its crystal lattice to an infinite distance.
- **Born Haber's cycle** – It applies Hess's law to calculate lattice enthalpy.
- **Second law of thermodynamics** –
  - (i) **Entropy statement :** "Whenever a spontaneous process takes place, it is accompanied by an increase in the total entropy of the Universe".

    $\Delta S_{\text{universe}} > \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$
  - (ii) **Kelvin-Planck statement** – It is impossible to take heat from a hotter reservoir and convert it completely into work by a cyclic process without transferring a part of heat to a cooler reservoir.
- **% Efficiency** - $\left[\frac{T_1 - T_2}{T_1}\right] \times 100$
- **Clausius statement** – It states that heat flows spontaneously from hot objects to cold objects and to get it flow in the opposite direction, we have to expend some work.
- **Spontaneous process** – A reaction that does occur under the given set of conditions without any external driving force is called a spontaneous reaction.
- **Non-spontaneous process** – A reaction that does not occur under given set of conditions without any external driving force is called a non-spontaneous reaction.

- **Entropy (S)** – It is defined as "for a reversible change taking place at a constant temperature (T), the change in entropy (ΔS) of the system is equal to heat energy absorbed or evolved (q) by the system divided by the constant temperature (T)". $\Delta S_{sys} = \frac{q_{rev}}{T}$
- **Unit of entropy** – JK^{-1} (SI unit).
- **Standard entropy of formation** – It is defined as the entropy of formation of 1 mole of a compound from the elements under standard conditions. It is denoted as ΔS_f^0 .
- **Standard entropy change ΔS^0** –

  $\Delta S_r^0 = \sum S^0_{(Products)} - \sum \Delta S^0_{(reactants)}$
- **Entropy of fusion** – When one mole of the solid melts at its melting point reversibly, the heat absorbed is called molar heat of fusion.

  $$\Delta S_f = \frac{\Delta H_f}{T_f}$$

  ΔH_f = Molar heat of fusion

  T_f = Melting point
- **Entropy of vapourisation** – When one mole of liquid is boiled at its boiling point reversibly, the heat absorbed is called molar heat of vapourisation.

  $$\Delta S_V = \frac{\Delta H_V}{T_b}$$

  ΔH_V = Molar heat of vapourisation

  T_b = Boiling point
- **Entropy of transition** – The heat change, when one mole of a solid changes reversibly from one allotropic form to another at its transition temperature.

  $$\Delta S_t = \frac{\Delta H_t}{T_t}$$

  ΔH_t = Molar heat of transition

  T_t = Transition temperature
- **Gibbs free energy** – It is the available energy to do the work. It is defined as the part of total energy of a system that can be converted (or) available for conversion into work.

  $G = H - TS$

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

  $-\Delta G = -w - P\Delta V$

Spontaneous (irreversible)	**Equilibrium (reversible)**	**Non-spontaneous (non-feasible)**
$\Delta H < 0$	$\Delta H = T\Delta S$	$\Delta H > 0$

$\Delta S < 0$	$\Delta S = \frac{\Delta H}{T}$	$\Delta S > 0$
$\Delta G < 0$	$\Delta G = 0$	$\Delta G > 0$

- **Reaction quotient (Q)** – It is defined as the ratio of concentration of the products to the concentrations of the reactants under non equilibrium conditions.

- **ΔG^0 = Standard free energy change of the reaction.**

  $\Delta G^0 = \Delta G^0 + RT \ln Q$

  $\Delta G^0 = -RT \ln K_{eq}$

  $\Delta G^0 = -2.303\ RT \log K_{eq}$

  $\Delta G^0 = \Delta H^0 - T\Delta S^0 = -\ RT \ln k_{eq}$

- **Third law of thermodynamics** – It states that the entropy of pure crystalline substance at absolute zero is zero (or) it is impossible to lower the temperature of an object to absolute zero in a finite number of steps. $\lim_{T \to 0} S = 0$.

I. Choose the best answer

1. The amount of heat exchanged with the surrounding at constant temperature and pressure is given by the quantity

a) ΔE **b) ΔH** c) ΔS d) ΔG

2. All the naturally occurring processes proceed spontaneously in a direction which leads to

a) decrease in entropy b) increase in enthalpy

c) increase in free energy **d) decrease in free energy**

3. In an adiabatic process, which of the following is true ?

a) $q = w$ **b) $q = 0$** c) $\Delta E = q$ d) $P \Delta V = 0$

4. In a reversible process, the change in entropy of the universe is

a) > 0 b) > 0 c) < 0 **d) $= 0$**

5. In an adiabatic expansion of an ideal gas

a) $w = -\Delta u$ b) $w = \Delta u + \Delta H$ c) $\Delta u = 0$ d) $w = 0$

6. The intensive property among the quantities below is

a) mass b) volume c) enthalpy **d) $\frac{mass}{volume}$**

7. An ideal gas expands from the volume of 1×10^{-3} m^3 to 1×10^{-2} m^3 at 300 K against a constant pressure at 1×10^5 Nm^{-2}. The work done is

a) – 900 J b) 900 kJ c) 270 kJ d) – 900 kJ

8. Heat of combustion is always

a) positive **b) negative** c) zero d) either positive or negative

9. The heat of formation of CO and CO_2 are – 26.4 kCal and – 94 kCal, respectively. Heat of combustion of carbon monoxide will be

a) + 26.4 kcal **b) – 67.6 kcal** c) – 120.6 kcal d) + 52.8 kcal

10. C(diamond) → C(graphite), ΔH = –ve, this indicates that

a) graphite is more stable than diamond b) graphite has more energy than diamond

c) both are equally stable d) stability cannot be predicted

11. The enthalpies of formation of Al_2O_3 and Cr_2O_3 are – 1596 kJ and – 1134 kJ, respectively. ΔH for the reaction $2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$ is

a) – 1365 kJ b) 2730 kJ c) – 2730 kJ **d) – 462 kJ**

12. Which of the following is not a thermodynamic function ?

a) internal energy b) enthalpy c) entropy **d) frictional energy**

13. If one mole of ammonia and one mole of hydrogen chloride are mixed in a closed container to form ammonium chloride gas, then

a) ΔH > ΔU b) ΔH - ΔU = 0 c) ΔH + ΔU= 0 **d) ΔH < ΔU**

14. Change in internal energy, when 4 kJ of work is done on the system and 1 kJ of heat is given out by the system is

a) +1 kJ b) – 5 kJ **c) +3 kJ** d) – 3 kJ

15. The work done by the liberated gas when 55.85 g of iron (molar mass 55.85 g mol^{-1}) reacts with hydrochloric acid in an open beaker at 25^0C

a) – 2.48 kJ b) – 2.22 kJ c) + 2.22 kJ d) + 2.48 kJ

16. The value of ΔH for cooling 2 moles of an ideal gas monatomic gas from 125^0 C to 25^0 C at constant pressure will be $\left[given\ Cp = \frac{5}{2}R\right]$

a) – 250 R **b) – 500 R** c) 500 R d) + 250 R

17. Given that $C_{(g)} + O_{2\ (g)} \rightarrow CO_{2\ (g)}$ $\Delta H^0 = -$ a kJ; $2\ CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$ $\Delta H^0 = -$b kJ; Calculate the ΔH^0 for the reaction $C_{(g)} + ½\ O_{2(g)} \rightarrow CO_{(g)}$

a) $\frac{b+2a}{2}$ b) 2a-b c) $\frac{2a-b}{2}$ **d)** $\frac{b-2a}{2}$

18. When 15.68 litres of a gas mixture of methane and propane are fully combusted at 00 C and 1 atmosphere, 32 litres of oxygen at the same temperature and pressure are consumed. The amount of heat of released from this combustion in kJ is (ΔH C (CH_4) = – 890 kJ mol^{-1} and ΔHC (C_3H_8) = – 2220 kJ mol^{-1})

a) – 889 kJ b) – 1390 kJ c) – 3180 kJ **d) – 653.66 kJ**

19. The bond dissociation energy of methane and ethane are 360 kJ mol^{-1} and 620 kJ mol^{-1} respectively. Then, the bond dissociation energy of C-C bond is

a) 170 kJ mol^{-1} b) 50 kJ mol^{-1} **c) 80 kJ mol^{-1}** d) 220 kJ mol^{-1}

20. The correct thermodynamic conditions for the spontaneous reaction at all temperature is (NEET Phase - I)

a) $\Delta H < 0$ and $\Delta S > 0$ b) $\Delta H < 0$ and $\Delta S < 0$ c) $\Delta H > 0$ and $\Delta S = 0$ d) $\Delta H > 0$ and $\Delta S > 0$

21. The temperature of the system, decreases in an ____________________

a) Isothermal expansion b) Isothermal Compression

c) adiabatic expansion d) adiabatic compression

22. In an isothermal reversible compression of an ideal gas the sign of q, ΔS and w are respectively

a) +, –, – b) –, +, – c) +, –, + **d) –, –, +**

23. Molar heat of vapourisation of a liquid is 4.8 kJ mol–1. If the entropy change is 16 J mol–1 K–1, the boiling point of the liquid is

a) 323 K **b) 27^0 C** c) 164 K d) 0.3 K

24. ΔS is expected to be maximum for the reaction

a) $Ca(S) + ½ O_2(g) \rightarrow CaO(S)$ b) $C(S) + O_2(g) \rightarrow CO_2(g)$

c) $N_2(g) + O_2(g) \rightarrow 2NO(g)$ **d) $CaCO_3(S) \rightarrow CaO(S) + CO_2(g)$**

25. The values of ΔH and ΔS for a reaction are respectively 30 kJ mol^{-1} and 100 JK^{-1} mol^{-1}. Then the temperature above which the reaction will become spontaneous is

a) 300 K b) 30 K c) 100 K d) 20^0 C

Question and Answer

25.State the first law of thermodynamics.

The first law of thermodynamics, also known as the law of conservation of energy, states that "The total energy of an isolated system remains constant though it may change from one form to another."

The mathematical statement of the Frist Law is: **$\Delta U = q + w$**

Where q- the amount of heat supplied to the system; w – work done on the system

27.Define Hess's law of constant heat summation.

The enthalpy change of a reaction either at constant volume or constant pressure is the same whether it takes place in a single or multiple steps provided the initial and final states are same.

$$\begin{tikzcd}
A \arrow[r, "\Delta H_r"] \arrow[d, "\Delta H_1"'] & B \arrow[d, "\Delta H_3"] \\
X \arrow[r, "\Delta H_2"] & Y
\end{tikzcd}$$

$$\Delta H_r = \Delta H_1 + \Delta H_2 + \Delta H_3$$

28. Explain intensive properties with two examples

The property that is independent of the mass or the size of the system is called an intensive property. Examples: Refractive index, Surface tension, density, temperature, Boiling point, Freezing point, molar volume, etc.,

29. Define the following terms:

(a) isothermal process (b) adiabatic process (c) isobaric process (d) isochoric process

(a) Isothermal process: An isothermal process is defined as one in which the temperature of the system remains constant, during the change from its initial to final state. The system exchange heat with its surrounding and the temperature of the system remains constant.

For an isothermal process dT = 0

(b) Adiabatic process

An adiabatic process is defined as one in which there is no exchange of heat (q) between the system and surrounding during the process.

For an adiabatic process q = 0

(c) Isobaric process

An isobaric process is defined as one in which the pressure of the system remains constant during its change from the initial to final state.

For an Isochoric process dP = 0

(d) Isochoric process

An isochoric process is defined as the one in which the volume of system remains constant during its change from initial to final state.

For an isochoric process, dV = 0

30. What is the usual definition of entropy? What is the unit of entropy?

(i) Entropy is a measure of the molecular disorderliness (randomness) of a system.

$\Delta S = dq_{rev} / T$

ii)The entropy (S) is equal to heat energy exchanged (q) divided by the temperature (T) at which the exchange takes place. Therefore, The SI unit of entropy is JK^{-1}

31. Predict the feasibility of a reaction when

i) both ΔH and ΔS positive ii) both ΔH and ΔS negative

iii) ΔH decreases but ΔS increases

(i) the reaction is not feasible. (Non-spontaneous)

(ii) the reaction is not feasible. (Non-spontaneous)

(iii) the reaction is feasible. (Spontaneous)

32. Define is Gibb's free energy.

Gibbs free energy is defined as the part of total energy of a system that can be converted (or) available for conversion into work.

Gibb's free energy is defined as **G = H – TS**

Where, H = enthalpy or heat content of the system, T = Temperature in Kelvin and

S = Entropy

33.Define enthalpy of combustion.

The heat of combustion of a substance is defined as "The change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen". It is denoted by ΔH_c.

34.Define molar heat capacity. Give its unit.

Molar heat capacity is define as "The amount of heat absorbed by one mole of the substance to raise its temperature by 1 kelvin". It is denoted as C_m.

The SI unit of molar heat capacity is $JK^{-1}\ mol^{-1}$

35.Define the calorific value of food. What is the unit of calorific value?

The calorific value is defined as "The amount of heat produced in calories (or joules) when one gram of the substance is completely burnt."

The SI unit of calorific value is $J\ Kg^{-1}$.

It is usually expressed in cal g^{-1}

36.Define enthalpy of neutralization.

The heat of neutralization is defined as "The change in enthalpy when one gram equivalent of an acid is completely neutralized by one gram equivalent of a base or vice versa in dilute solution".

$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$ $\Delta H = -57.32kJ$

37.What is lattice energy?

Lattice energy is defined as " The amount of energy required to completely remove the constituent ions from its crystal lattice to an infinite distance".

It is also referred as lattice enthalpy.

38. What are state and path functions? Give two examples.

(i) State Function: A state function is a thermodynamic property of a system, which has a specific value for a given state and does not depend on the path (or manner) by which the particular state is reached.

Example: Pressure (P), Volume (V), Temperature (T)

(ii) Path Functions: A path function is a thermodynamic property of the system whose value depends on the path by which the system changes from its initial to final states.

Examples: Work (w), Heat (q).

39.Give Kelvin statement of second law of thermodynamics.

It is impossible to construct a machine that absorbs heat from a hot source and converts it completely into work by a cyclic process without transferring a part of heat to a cold sink.

40.The equilibrium constant of a reaction is 10, what will be the sign of ΔG? Will this reaction be spontaneous?

Given $K_{eq} = 10$ Gas constant $R = 8.314\ JK^{-1}\ mol^{-1}$ $T = 300K$

The relationship between Free energy change ΔG and equilibrium constant K is

$$\Delta G^\circ = -RT \ln K$$

Since K, T and Rare positive values, **ΔG° will be negative**.

When ΔG is –ve, the process is **spontaneous and feasible.**

41.Enthalpy of neutralization is always a constant when a strong acid is neutralized by a strong base: account for the statement.

Strong acids and strong bases exist in the fully ionized from in aqueous solutions as below:

$$H_3O^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+Cl^- + 2H_2O$$

(or)

$$H_3O^+_{(aq)} + OH^-_{(aq)} \rightarrow 2H_2O_{(l)} \qquad \Delta H^\circ = -57.32\ KJ$$

The H^+ ions produced in water by the acid molecules exist as H_3O^+. Thus, enthalpy change per mole of water formed from H_3O^+ and OH^- ions. Therefore, irrespective of the chemical nature, the enthalpy of neutralization of strong acid by strong base is a constant value which is equal to -57.32 KJ.

42.State the third law of thermodynamics.

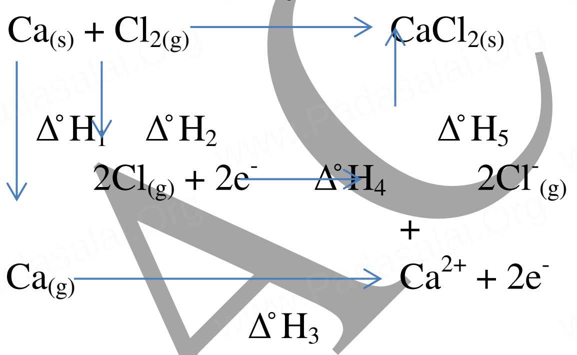
(i) The third law of thermodynamics states that the entropy of pure crystalline substance at absolute zero is zero.

(ii) It can also be stated as it is impossible to lower the temperature of an object to absolute zero in a finite number of steps.

(iii) Mathematically, $\lim_{T\to 0} S = 0$ for a perfectly ordered crystalline state.

43.Write down the Born-Haber cycle for the formation of $CaCl_2$.

- Born – Haber cycle for the formation of $CaCl_2$
- Born – Haber cycle is used to calculate the lattice enthalpy of $CaCl_2$.



44.Identify the state and path functions out of the following: a)Enthalpy b)Entropy c) Heat d)Temperature e) Work f)Free energy.

State Function: Enthalpy, entropy, temperature, free energy

Path Function: Heat, Work.

45.State the various statements of second law of thermodynamics.

(i) Kelvin-Planck statement: It is impossible to construct a machine that absorbs heat from a hot source and converts it completely into work by a cyclic process without transferring a part of heat to a cold sink.

(ii) **Clausius statement:** It is impossible to transfer heat from a cold reservoir to a hot reservoir without doing some work.

iii)Entropy statement: The entropy of an isolated system increases during a spontaneous process.

(iv) **Efficiency statement:** Even an ideal, frictionless engine cannot convert 100% of its input heat into work.

46. What are spontaneous reactions? What are the conditions for the spontaneity of a process?

(i) Spontaneous reaction: A reaction that occurs under the given set of conditions without any external driving force is called a spontaneous reaction.

(ii) **Criteria for spontaneity of a process:** The spontaneity of any process depends on three different factors.

ΔH = -ve,
ΔS = +ve,
ΔG = -ve.

47. List the characteristics of internal energy.

- The internal energy of a system is an extensive property
- The internal energy of a system is a state function
- The change in internal energy of a system is expressed as $\Delta U = U_f - U_i$
- In a cyclic process, there is no internal energy change. $\Delta U_{(cyclic)} = 0$
- If the internal energy of the system in the final state (U_f) is less than the internal energy of the system in its initial state (U_i), then ΔU would be negative. $\mathbf{\Delta U = U_f - U_i = -ve\ (U_f < U_i)}$
- If the internal energy of the system in the final state (U_f) is greater than the internal energy of the system in its initial state (U_i), then ΔU would be positive. $\mathbf{\Delta U = U_f - U_i = +ve\ (U_f > U_i)}$

48. Explain how heat absorbed at constant volume is measured using bomb calorimeter with a neat diagram.

(i) Heat evolved at constant volume, is measured in a bomb calorimeter.

(ii) Apparatus setup: The inner vessel (the bomb) and its cover are made of strong steel. The cover is fitted tightly to the vessel by means of metal lid and screws.

(iii) Experiment: A weighed amount of the substance is taken in a platinum cup connected with electrical wires for striking an arc instantly to kindle combustion. The bomb is then tightly closed and pressurized with excess oxygen. The bomb is immersed in water, in the inner volume of the calorimeter. A stirrer is placed in the space between the wall of the calorimeter and the bomb, so that water can be stirred the substance through electrical heating.

(iv) Calculation: A known amount of combustible substance is burnt oxygen in the bomb. Heat evolved during the reaction is absorbed by the calorimeter as well as the water in which the bomb is immersed. The change in temperature is measured using a Backman thermometer. Since the bomb is sealed its volume does not change and hence the heat measurement is equal to the heat of combustion at a constant volume $(\Delta U)_c$.

The amount of heat produced in the reaction (ΔU)c is equal to the sum of the heat absorbed by the calorimeter and water.

Heat absorbed by the calorimeter $q_1 = k.\Delta T$

Where m_w is molar mass of water C_w is molar heat capacity of water ($4,184\ kJ\ K^{-1}\ mol^{-1}$)

Therefore $\Delta Uc = q_1 + q_2$

$= k.\Delta T + m_w\ C_w\ \Delta T$

$= (k + m_w\ C_w)\ \Delta T$

Calorimeter constant can be determined by burning a known mass of standard sample (benzoic acid) for which the heat of combustion is known (-3227 kJmol-1) The enthalpy of combustion at constant pressure of the substance is calculated from the equation

$$\Delta H^0_{C(pressure)} = \Delta U^0_{C(vol)} + \Delta n_g RT$$

49.Calculate the work involved in expansion and compression process.

i. For understanding pressurevolume work, let us consider a cylinder which contains 'n' moles of an ideal gas fitted with a frictionless piston of cross sectional area A. The total volume of the gas inside is V*i* and pressure of the gas inside is P_{int}.

ii. If the external pressure P_{ext} is greater than P_{int}, the piston moves inward till the pressure inside becomes equal to P_{ext}. Let this change be achieved in a single step and the final volume be V_f.

iii. In this case, the work is done on the system (+w). It can be calculated as follows

$$w = -F\ .\Delta x \quad \text{------------}\ (1)$$

iv. where dx is the distance moved by the piston during the compression and F is the force acting on the gas.

$$F = P_{ext}\ A \quad \text{----}\ (2)$$

Substituting 2 in 1

$w = -P_{ext}\ .\ A.\ \Delta x$

$A\ \ .\Delta x$ = change in volume $= V_f - V_i$

$w = -P_{ext}\ .\ (V_f - V_i)$ ——— (3)

$w = -P_{ext}\ .\ (-\Delta V)$ ——— (4)

$= P_{ext}\ .\ \Delta V$

v. Since work is done on the system, it is a positive quantity.

vi. If the pressure is not constant, but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV. In such a case we can calculate the work done on the gas by the relation

$$w_{rev} = \int_{v_i}^{v_f} P_{int}\ dV$$

vii. In a compression process, P_{ext} the external pressure is always greater than the pressure of the system. **i.e** $P_{ext} = (P_{int} + dP)$.

viii. In an expansion process, the external pressure is always less than the pressure of the system i.e. $P_{ext} = (P_{int} - dP)$.

ix. When pressure is not constant and changes in infinitesimally small steps (reversible conditions) during compression from V_i to V_f , the P-V plot looks like in fig Work done on the gas is represented by the shaded area. In general case we can write,

x. $P_{ext} = (P_{int} + dP)$. Such processes are called reversible processes. For a compression process work can be related to internal pressure of the system under reversible conditions by writing equation

$$w_{rev} = \int_{v_i}^{v_f} P_{int}\, dV$$

For a given system with an ideal gas

$$P_{int} V = nRT$$

$$P_{int} = \frac{nRT}{V}$$

$$W_{rev} = \int_{v_i}^{v_f} \frac{nRT}{V} dV$$

$$W_{rev} = -\, nRT \int_{v_i}^{v_f} \left(\frac{dV}{V}\right)$$

$$W_{rev} = -\, nRT \ln\left(\frac{V_f}{V_i}\right)$$

$$W_{rev} = -\, 2.303\ nRT \log\left(\frac{V_f}{V_i}\right)$$

xi. If $V_f > V_i$ (expansion), the sign of work done by the process is negative.

xii. If $V_f < V_i$ (compression) the sign of work done on the process is positive.

50. Derive the relation between ΔH and ΔU for an ideal gas. Explain each term involved in the equation.

When the system at constant pressure undergoes changes from an initial state with H_1, U_1 and V_1 to a final state with H_2, U_2 and V_2 the change in enthalpy ΔH, can be calculated as follows:

$$H = U + PV$$

In the initial state

$$H_1 = U_1 + PV_1 \quad \text{------ (1)}$$

In the final state

$$H_2 = U_2 + PV_2 \quad \text{---- (2)}$$

change in enthalpy is (2) - (1)

$$(H_2 - H_1) = (U_2 - U_1) + P(V_2 - V_1)$$

$$\Delta H = \Delta U + P\Delta V \quad \text{--------- (3)}$$

As per first law of thermodynamics,

$$\Delta U = q + w$$

Equation (3) becomes

$$\Delta H = q + w + P\Delta V$$

$$W = -\, P\Delta V$$

$$\Delta H = q_p - P\Delta V + P\Delta V$$

$$\Delta H = q_p \qquad \text{———— (4)}$$

q_p– is the heat absorbed at constant pressure and is considered as heat content.

Consider a closed system of gases which are chemically reacting to form gaseous products at constant temperature and pressure with V_i and V_f as the total volumes of the reactant and product gases respectively, and n_i and n_f as the number of moles of gaseous reactants and products, then,

For reactants (initial state) :

$$PV_i = n_i RT \qquad \text{--------- (5)}$$

For products (final state) :

$$PV_f = n_f RT \qquad \text{--------- (6)}$$

(6) - (5)

$$P (V_f - V_i) = (n_f - n_i) RT$$

$$P \Delta V = \Delta n_{(g)} RT \qquad \text{——— (7)}$$

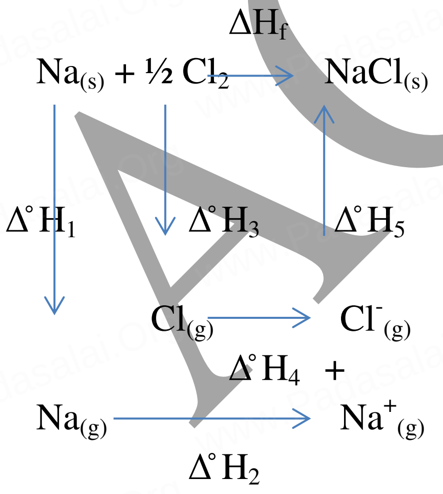
Substituting in (7) in (3)

$$\Delta H = \Delta U + \Delta n_{(g)} RT \qquad \text{——— (8)}$$

51.Suggest and explain an indirect method to calculate lattice enthalpy of sodium chloride crystal.

Let us use the Born - Haber cycle for determining the lattice enthalpy of NaCl as follows: Since the reaction is carried out with reactants in elemental forms and products in their standard states, at 1 bar, the overall enthalpy change of the reaction is also the enthalpy of formation for NaCl. Also, the formation of NaCl can be considered in 5 steps. The sum of the enthalpy changes of these steps is equal to the enthalpy change for the overall reaction from which the lattice enthalpy of NaCl is calculated.

Let us calculate the lattice energy of sodium chloride using Born-Haber cycle



$\Delta^\circ H_f$ = heat of formation of sodium chloride = – 411.3 kJ mol^{-1}

$\Delta^\circ H_1$ = heat of sublimation of $Na_{(S)}$ = 108.7 kJ mol^{-1}

$\Delta^\circ H_2$ = ionisation energy of $Na_{(S)}$ = 495.0 kJ mol^{-1}

$\Delta^\circ H_3$ = dissociation energy of $Cl_{2(S)}$ = 244 kJ mol^{-1}

$\Delta^\circ H_4$ = Electron affinity of $Cl_{(S)}$ $= -349.0 \text{ kJ mol}^{-1}$

$\Delta^\circ H_f = \Delta^\circ H_1 + \Delta^\circ H_2 + ½\, \Delta^\circ H_3 + \Delta^\circ H_4 + \Delta^\circ H_5$

$\therefore \Delta^\circ H_5 = (\Delta^\circ H_f) - (\Delta^\circ H_1 + \Delta^\circ H_2 + \Delta^\circ H_3 + \Delta^\circ H_4)$

$\Rightarrow \Delta^\circ H_5 = (-411.3) - (108.7 + 495.0 + 122 - 349)$

$\Delta^\circ H_5 = (-411.3) - (376.7)$

$\therefore \Delta^\circ H_5 = -788$ kJ mol–1

This negative sign in lattice energy indicates that the energy is released when sodium is formed from its constituent gaseous ions Na^+ and Cl^-

52.List the characteristics of Gibbs free energy.

(i) Free energy is defined as G = H – TS. 'G' is a state function

(ii) G- Extensive property; ΔG – intensive property. When mass remains constant between initial and final states of system

(iii) 'G' has a single value for the thermodynamic state of the system

(iv) Gibbs free energy is defined as the part of total energy of a system that can be converted (or) available for conversion into work.

(v) G and ΔG values correspond to the system only.

Process	Spontaneous	Equilibrium	Non-spontaneous
ΔG	-Ve	Zero	+Ve

(vi) Gibbs free energy and the network done by the system:

For any system at constant pressure and temperature

$\Delta G = \Delta H - T\Delta S$ ——— (1)

We know that,

$\Delta H = \Delta U + P\Delta V$

$\therefore \Delta G = \Delta U + P\Delta V - T\Delta S$

from first law of thermodynamics

$\Delta U = q + w$

from second law of thermodynamics

$\Delta S = \frac{q}{T}$ $\Delta G = q + w + P\Delta V - T\left(\frac{q}{T}\right)$

$\Delta G = w + P\,\Delta V$

$-\Delta G = -w - P\Delta V$ ------- (2)

But –PΔV represents the work done due to expression against a constant external pressure.

53.Calculate the work done when 2 moles of an ideal gas expands reversibly and isothermally from a volume of 500 ml to a volume of 2 L at 25°C and normal pressure.

Given :

n = 2 moles; V_i = 500 ml = 0.5 lit ; V_f = 2 lit

T = 25°C = 298 K

$$w = -2.303\ nRT\log\left(\frac{V_f}{V_i}\right)$$

$$w = -2.303 \times 2 \times 8.314 \times 298 \times \log\left(\frac{2}{0.5}\right)$$

$$w = -2.303 \times 2 \times 8.314 \times 298 \times \log(4)$$

$$w = -2.303 \times 2 \times 8.314 \times 298 \times 0.6021$$

$$w = -\ 6871\ J$$

$$w = -6.871\ kJ$$

54. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298 K. The temperature of the calorimeter was found to increase from 298 K to 298.45 K due to the combustion process. Given that the calorimeter constant is 2.5 kJ K^{-1}. Calculate the enthalpy of combustion of the gas in kJ mol^{-1}.

Given :

$T_i = 298$ K; $T_f = 298.45$ K; $k = 2.5$ kJ K^{-1}; $m = 3.5$g; $M_m = 28$

heat evolved = k ΔT

$= k\ (T_f - T_i)$

$= 2.5$ kJ K^{-1} (298.45–298) K

= 1.125kJ

$$\Delta H_c = \frac{1.125}{3.5} \times 28\ kJ\ mol^{-1}$$

$$\mathbf{\Delta H_c = 9\ kJ\ mol^{-1}}$$

55. Calculate the entropy change in the system, and surroundings, and the total entropy change in the universe during a process in which 245 J of heat flow out of the system at 77°C to the surrounding at 33°C.

Given :

$T_{sys} = 77\,^\circ C = (77 + 273) = 350\ K$

$T_{surr} = 33\,^\circ C = (33 + 273) = 306\ K$

$q = 245\ J$

$\Delta S_{sys} = q$

$$T_{sys} = \frac{q}{T_{sys}} = \frac{-245}{350} = -\ 0.7\ JK^{-1}$$

$$\Delta S_{surr} = \frac{q}{T_{sys}} = \frac{+245}{306} = +\ 0.8\ JK^{-1}$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{univ} = -\ 0.7\ JK^{-1} + 0.8\ JK^{-1}$$

$$\mathbf{\Delta S_{univ} = 0.1\ JK^{-1}}$$

56. 1 mole of an ideal gas, maintained at 4.1 atm and at a certain temperature, absorbs heat 3710J and expands to 2 litres. Calculate the entropy change in expansion process.

Given :

n = 1mole; P = 4.1 atm; V= 2 Lit; T = ?; q=3710 J

$$\Delta S = \frac{q}{T}; \qquad \Delta S = \frac{q}{\left(\frac{PV}{nR}\right)}; \qquad \Delta S = \frac{nRq}{PV}$$

$$\Delta S = \frac{1 \times 0.082\ lit\ atm\ K^{-1} \times 3710 J}{4.1\ atm \times 2\ lit}$$

$$\mathbf{\Delta S = 37.10\ JK^{-1}}$$

57. 30.4 kJ is required to melt one mole of sodium chloride. The entropy change during melting is 28.4 JK^{-1} mol^{-1}. Calculate the melting point of sodium chloride.

ΔH_f (NaCl) = 30.4 kJ = 30400 J mol^{-1}

ΔS_f(NaCl) = 28.4 JK^{-1} mol^{-1}; T_f = ?

$$\Delta S_f = \frac{\Delta H_f}{T_f}\ ;\ T_f = \frac{\Delta H_f}{\Delta S_f}$$

$$T_f = \frac{30400\ J\ mol^{-1}}{28.4\ J\ K^{-1}\ mol^{-1}}$$

$$\mathbf{T_f = 1070.4\ K}$$

58. Calculate the standard heat of formation of propane, if its heat of combustion is −2220.2 kJ mol^{-1}. the heats of formation of $CO_{2(g)}$ and $H_2O(l)$ are −393.5 and −285.8 kJ mol^{-1} respectively.

SOLUTION :

Given

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

$\Delta H^\circ_c = -2220.2\ kJmol^{-1}$ ------(1)

$C + O_2 \rightarrow CO_2$

$\Delta H^\circ_f = -393.5\ kJ\ mol^{-1}$ ------(2)

$H_2 + ½\ O_2 \rightarrow H_2O$

$\Delta H^\circ_f = -285.8\ kJ\ mol^{-1}$ ------ (3)

$3C + 4H_2 \rightarrow C_3H_8$

$\Delta H^\circ_C = ?$

(2) × 3 ⇒ $3C + 3O_2 \rightarrow 3CO_2$

$\Delta H^\circ_f = -1180.5\ kJ$ ------(4)

(3)× 4 ⇒ $4\ H_2 + 2O_2 \rightarrow 4H_2O$

$\Delta H^\circ_f = -1143.2\ kJ$ ------(5)

(4) + (5) − (1) ⇒ $3C + 3O_2 + 4H_2 +$

$2O_2 + 3CO_2 + 4H_2O \rightarrow 3CO_2 + 4H_2O + C_3H_8 + 5O_2$

$\Delta H^\circ_f = -1180.5 - 1143.2 - (-2220.2)\ kJ$

$3C + 4\ H_2 \rightarrow C3H8$

$\Delta H^\circ_f = -103.5\ kJ$

Standard heat of formation of propane is $\mathbf{\Delta H^\circ_f\ (C_3H_8) = -103.5\ kJ}$

59. You are given normal boiling points and standard enthalpies of vapourisation. Calculate the entropy of vapourisation of liquids listed below.

S.No	Liquid	Boiling points (°C)	ΔH (KJ mol^{-1})
1.	Ethanol	78.4	+ 42.4
2.	Toluene	110.6	+ 35.2

For ethanol :

Given :

$T_b = 78.4^{\circ}C = (78.4 + 273)$

$= 351.4\ K$

ΔH_V (ethanol) $= +\ 42.4\ kJ\ mol^{-1}$

$\Delta S_v = \frac{\Delta H_V}{T_b}$; $\Delta S_v = \frac{+\ 42.4\ KJ\ mol^{-1}}{351.4\ K}$

$\Delta S_v = \frac{+42400\ J\ mol^{-1}}{351.4\ K}$;

$\mathbf{\Delta S_v = +\ 120.66\ JK^{-1}\ mol^{-1}}$

For Toluene :

Given :

$T_b = 110.6^{\circ}C = (110.6+273)$

$= 383.6\ K$

ΔH_V (toluene) $= +\ 35.2\ kJ\ mol^{-1}$

$\Delta S_v = \frac{\Delta H_V}{T_b}$

$\Delta S_v = \frac{+35.2\ KJ\ mol^{-1}}{383.6K}$; $\Delta S_v = \frac{+\ 35200\ J\ mol^{-1}}{383.6\ K}$

$\mathbf{\Delta S_v = +\ 91.76\ JK^{-1}}$

60. For the reaction $Ag_2O(s) \rightarrow 2Ag(s) + 1/2\ O_2(g)$: $\Delta H = 30.56\ kJ\ mol^{-1}$ and $\Delta S = 6.66 JK^{-1} mol^{-1}$(at1 atm). Calculate the temperature at which ΔG is equal to zero. Also predict the direction of the reaction (i) at this temperature and (ii) below this temperature.

Solution :

Given : $\Delta H = 30.56\ kJ\ mol^{-1}$ $= 30560\ J\ mol^{-1}$

$\Delta S = 6.66 \times 10^{-3}\ kJK^{-1}mol^{-1}$

T = ? at which $\Delta G = 0$

$\mathbf{\Delta G = \Delta H - T\Delta S}$

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

$T = \frac{\Delta H}{\Delta S}$; $T = \frac{30.56\ kJ\ mol^{-1}}{6.66 \times 10^{-3} kJ\ K^{-1} mol^{-1}}$

T = 4589K

(i) At 4589K ; ΔG = 0 the reaction is in equilibrium.

(ii) at temperature below 4598 K , $\Delta H > T\Delta S$ $\Delta G = \Delta H - T\Delta S > 0$, the reaction in the forward direction, is nonspontaneous. In other words the reaction occurs in the backward direction.

61.What is the equilibrium constant Keq for the following reaction at 400K.

$2NOCl\ (g) \rightleftharpoons 2NO(g) + Cl_2(g)$, given that $\Delta H^0 = 77.2 kJ\ mol^{-1}$;and $\Delta S^0 = 122 JK^{-1}mol^{-1}$.

Solution :

Given

$T = 400K$; $\Delta H^\circ = 77.2$ kJ $mol^{-1} = 77200$ J mol^{-1} ;

$\Delta S^\circ = 122$ JK^{-1} mol^{-1}

$\Delta G^\circ = -2.303$ RT log K_{eq}

$$\log K_{eq} = \frac{\Delta G^\circ}{2.303\ RT}$$

$$\log K_{eq} = \frac{(\Delta H^\circ - T\,\Delta\,S^\circ)}{2.303\ RT}$$

$$\log K_{eq} = -\left(\frac{77200 - 400 \times 122}{2.303 \times 8.314 \times 400}\right)$$

$$\log K_{eq} = \frac{(28400)}{7659}$$

$\log K_{eq} = -\ 3.7080$

$K_{eq} = \text{antilog}\ (-3.7080)$

$K_{eq} = 1.95 \times 10^{-4}$

62. Cyanamide (NH_2CN) is completely burnt in excess oxygen in a bomb calorimeter, ΔU was found to be −742.4 kJ mol^{-1}, calculate the enthalpy change of the reaction at 298K. $NH_2CN(s) + 3/2\ O_2(g) \rightarrow N_2\ (g) + CO_2\ (g) + H_2O(l)$ ΔH= ?

Solution :

Given: $T = 298K$; $\Delta U = -\ 742.4$ kJ mol^{-1} $\Delta H = ?$

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

$\Delta H = \Delta U + (n_p - n_r)\ RT$

$$\Delta H = -\ 742.4 + \left(2 - \frac{3}{2}\right) \times 8.314 \times 10^{-3} \times 298$$

$= -\ 742.4 + (0.5 \times 8.314 \times 10^{-3} \times 298)$

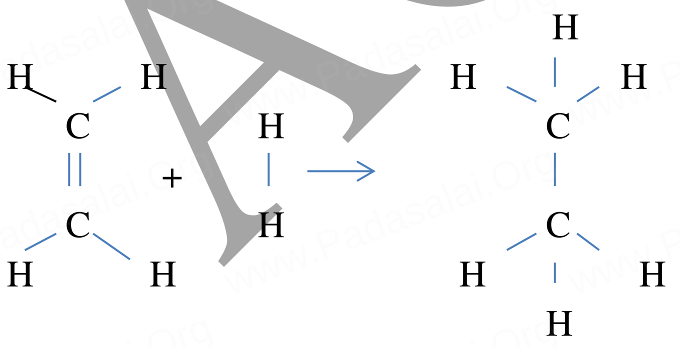
$= -\ 742.4 + 1.24$

$\Delta H = -\ 741.16$ kJ mol^{-1x}

63. Calculate the enthalpy of hydrogenation of ethylene from the following data. Bond energies of C− H, C − C , C = C and H − H are 414, 347, 618 and 435 kJ mol^{-1}.

Given : $E_{C-H} = 414$ kJ mol^{-1} $E_{C-C} = 347$ kJ mol^{-1} $E_{C=C} = 618$ kJ mol^{-1}

$E_{H-H} = 435$ kJ mol^{-1}



Ethylene Ethane

$\Delta H_r = \Sigma\ (\text{Bond energy})_r - \Sigma\ (\text{Bond energy})p$

$\Delta H_r = (E_{C=C} + 4E_{C-H} + E_{H-H}) - (E_{C-C} + 6E_{C-H})$

$\Delta H_r = (618 + (4 \times 414) + 435) - (347 + (6 \times 414)\ )$

$\Delta H_r = 2709 - 2831$; $\Delta H_r = -122$ kJ mol^{-1}

64. Calculate the lattice energy of $CaCl_2$ from the given data $Ca(s)+Cl_2(g) \rightarrow CaCl_2(s)$; $\Delta H_f^0 = -795\ kJ\ mol^{-1}$

Atomization : $Ca(s) \rightarrow Ca(g)$; $\Delta H_1^0 = +121\ kJ\ mol^{-1}$

Ionisation : $Ca(g) \rightarrow Ca_2+(g) + 2e^-$; $\Delta H_2^0 = +2422\ kJ\ mol^{-1}$

Dissociation : $Cl_2(g) \rightarrow 2Cl(g)$; $\Delta H_3^0 = +242.8\ kJ\ mol^{-1}$

Electron affinity : $Cl(g) + e^- \rightarrow Cl^-(g)$; $\Delta H_4^0 = -355\ kJ\ mol^{-1}$

$$\begin{tikzcd}
Ca_{(s)} \arrow[ddd, "\Delta H_1^\circ"'] & + & Cl_{2(g)} \arrow[r, "\Delta H_f"] \arrow[d, "\Delta H_3^\circ"'] & CaCl_{2(s)} \\
 & & 2Cl(g) \arrow[r, "\Delta H_4^\circ"] & 2Cl^- \arrow[u, "U"'] \\
 & & & + \\
Ca_{(g)} \arrow[rrr, "\Delta H_2^\circ"] & & & Ca^{2+}_{(g)}
\end{tikzcd}$$

$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + U$

$-795 = 2422 + 242.8 + (2 \times -255) + U$

$-795 = 2785.8 - 710 + U$

$-795 = 2075.8 + U$

$U = -795 - 2075.8$

$U = -2870.8\ KJmol^{-1}$

65. Calculate the enthalpy change for the reaction $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ from the following data.

$2Fe + 3/2\ O_2 \rightarrow Fe_2O_3$; $\Delta H = -741\ kJ$

$C + 1/2\ O_2 \rightarrow CO$; $\Delta H = -137\ kJ$

$C + O_2 \rightarrow CO_2$; $\Delta H = -394.5\ kJ$

Given:

$\Delta H_f\ (Fe_2O_3) = -741\ kJmol^{-1}$

$\Delta H_f\ (CO) = -137\ kJmol^{-1}$

$\Delta H_f\ (CO_2) = -394.5\ kJmol^{-1}$

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

$\Delta H_f = ?$

$\Delta H_r = \Sigma\ (\Delta H_f)products - \Sigma\ (\Delta H_f)reactants$

$\Delta H_r = [2\Delta H_f(Fe) + 3\Delta H_f\ (CO_2)] - [\Delta H_f\ (Fe_2O_3) + 3\ \Delta H_f\ (CO)]$

$\Delta H_r = [0 + 3\ (-394.5)] - [-741 + 3\ (-137)]$

$\Delta H_r = [-1183.5] - [-1152]$

$\Delta H_r = -1183.5 + 1152$ **$\Delta H_r = -31.5 kJmol^{-1}$**

66. When 1-pentyne (A) is treated with 4N alcoholic KOH at 175°C, it is converted slowly into anequilibrium mixture of 1.3% 1-pentyne(A) , 95.2% 2-pentyne(B) and 3.5% of 1,2 pentadiene (C)the equilibrium was maintained at 175°C, calculate ΔG^0 for the following equilibria.

$B \rightleftharpoons A$ $\Delta G_1^0 = ?$

$B \rightleftharpoons C$ $\Delta G_2^0 = ?$

Solution:

Given: T = 175°C = 175 + 273 = 448 K

Concentration of 1-pentyne [A] = 1.3%

Concentration of 2-pentyne [B] = 95.2%

Concentration of 1,2 -pentyne [C] = 3.5%

At equilibrium

$B \rightleftharpoons A$

95.2% 1.3%

$K_1 = \frac{1.3}{95.2} = 0.0136$

$B \rightleftharpoons C$

95.2% 3.5%

$K_2 = \frac{3.5}{95.2} = 0.0367$

$\Delta G_1^\circ = -2.303RT\log K_1$

$\Delta G_1^\circ = -2.303 \times 8.314 \times 448 \times \log 0.0136$

$\Delta G_1^\circ = +16010J$

$\Delta G_1^\circ = +16\ KJ$

$\Delta G_2^\circ = -2.303\ RT\ \log K_2$

$\Delta G_2^\circ = -2.303 \times 8.314 \times 448 \times \log 0.00367$

$\Delta G_2^\circ = +12312\ J = +12.312\ kJ$

67. At 33K, N_2O_4 is fifty percent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

Solution:

Given: T = 33K

	$N_2O_4 \rightleftharpoons$	$2NO_2$
Initial Concentration	1	0
Dissociated	0.5	1
At equilibrium	0.5	1

$Keq = \frac{1}{0.5} = 2$

$\Delta G^\circ = -2.303\ RT\ K_{eq}$

$\Delta G^\circ = -2.303 \times 8.314 \times 33 \times \log 2$

$\Delta G^\circ = -190.18\ Jmol^{-1}$.

68. The standard enthalpies of formation of SO_2 and SO_3 are −297 kJ mol^{-1} and −396 kJ mol^{-1} respectively. Calculate the standard enthalpy of reaction for the reaction:

$SO_2 + 1/2\ O_2 \rightarrow SO_3$

Solution:

Given: $\Delta G_f^\circ(SO_2)$ = -297 kJ mol^{-1} ΔG_f° (SO_3) = -396 kJ mol^{-1} $SO_2 + \frac{1}{2} O_2 \rightarrow SO_3$ ΔH_f^0 = ?

$\Delta H_r^0 = (\Delta H_f^0)$ Compound $-\sum \Delta H_f$ reactants

$\Delta H_r^0 = \Delta H_f^0(SO_3) - (\Delta H_f^0(SO_2) + \frac{1}{2} \Delta H_f^0\ (O_2))$

ΔH_r^0 = -396 kJ mol^{-1} – (-297 kJmol^{-1} + 0)

ΔH_r^0 = -396 kJmol^{-1} + 297

ΔH_r^0 = -99 kJmol^{-1}

69. For the reaction at 298 K: 2A +B → C ΔH=400 J mol^{-1} ; ΔS = 0.2 JK^{-1} mol^{-1} Determine the temperature at which the reaction would be spontaneous.

Solution:

Given: T = 298 K ΔH = 400 J mol^{-1} ΔS = 0.2 JK^{-1}mol^{-1}

$\Delta G = \Delta H$ - TΔS

If T = 2000K

ΔG = 400 – (0.2 × 2000) = 0

If T > 2000 K

ΔG will be negative

The reaction would be spontaneous only beyond 2000 K.

70.Find out the value of equilibrium constant for the following reaction at 298K, 2 $NH_3(g) + CO_2(g) \rightleftharpoons NH_2CONH_2\ (aq) + H_2O\ (l)$ Standard Gibbs energy change, ΔG_r^0 at the given temperature is–13.6 kJ mol^{-1}.

Solution:

Given:

T = 298 K

ΔG_r° = -13.6 kJ mol^{-1}

= - 13600 J mol^{-1}

ΔG_r° = -2.303 RT log K_{eq}

$\log K_{eq} = \frac{-\Delta G^\circ}{2.303RT}$

$\log K_{eq} = \frac{13.6\ KJmol^{-1}}{2.303\times 8.314\times 10^{-3} JK^{-1}mol^{-1}\times 298K}$

log K_{eq} = 2.38

K_{eq} = antilog (2.38)

K_{eq} = 239.88

71.A gas mixture of 3.67 lit of ethylene and methane on complete combustion at 25°C and at 1 atm pressure produce 6.11 lit of carbon dioxide. Find out the amount of

heat evolved in kJ, during this combustion. ($\Delta HC(CH_4)= -890$ kJ mol^{-1} and ($\Delta HC(C_2H_4)= -1423$ kJ mol^{-1}

Solution:

Given:

ΔH_c (CH_4)= -890 $KJmol^{-1}$

ΔH_c (C_2H_4) = -1423 $KJmol^{-1}$

Let the mixture contain x lit of CH_4 and (3.67 – x) lit of ethylene.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
x lit x lit

$C_2H_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O$
(3.67 – x) lit 2 (3.67 – x)

Volume of carbon dioxide formed = x + 2(3.67 – x) = 6.11 lit
= x + 7.34 – 2x = 6.11
= 7.34 – x = 6.11
X = 1.23 lit

Given mixture contains 1.23 lit of Methane and 2.44 lit of ethylene, hence

$$\Delta H_c = \left[\frac{\Delta H_c\,(CH_4)}{22.4\ lit} \times (x) lit\right] + \left[\frac{\Delta H_c\,(C_2H_4)}{22.4\ lit} \times (3.67 - x) lit\right]$$

$$\Delta H_c = \left[\frac{-890\ KJmol^{-1}}{22.4\ lit} \times 1.23\ lit\right] + \left[\frac{-1423}{22.4\ lit} \times (3.67 - 1.23) lit\right]$$

ΔH_c=[-48.87$kJmol^{-1}$]+[-155$kJmol^{-1}$]

ΔH_c= -203.87 $kJmol^{-1}$

Unit 8: Physical and Chemical Equilibrium

26. If there is no change in concentration, why is the equilibrium state considered dynamic ?

Rate of forward reaction=Rate of backward reaction

(Chemical reactions which are reversible do not cease, when equilibrium is attained. At equilibrium the forward and the backward reactions are proceeding at the same rate and no macroscopic change is observed. So chemical equilibrium is in a state of dynamic equilibrium.)

27. For a given reaction at a particular temperature, the equilibrium constant has constant value. Is the value of Q also constant ? Explain.

K_c and Q are constant at equilibrium both are temperature dependent. When K_c is constant at given temperature, Q also constant. (No. The value of Q is determined by the concentration of product and reactants that are not necessarily equilibrium concentration. Thus its value is not a constant. At equilibrium $K_C = Q$)

28. What the relation between K_P and K_C. Give one example for which K_P is equal to K_C.

Relation between K_P and K_C **$K_P = K_C (RT)^{(\Delta ng)}$**

When $\Delta ng = 0$; $K_P = K_C (RT)^0 = K_C$

Example : $H_2(g) + I_2 \rightleftharpoons 2HI\ (g)$

29. For a gaseous homogeneous reaction at equilibrium, number of moles of products are greater than the number of moles of reactants. Is K_C is larger or smaller than K_P.

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Δn_g = No. of moles of product – No. of moles of reactant

$\Delta n_g = 2 - 1 = 1$

When $\Delta n_g = +ve$

$K_P = K_C (RT)^{+ve}$; $K_P > K_C$

30. When the numerical value of the reaction quotient (Q) is greater than the equilibrium constant (K), in which direction does the reaction proceed to reach equilibrium ?

If $Q > K_c$, the reaction will proceed in the **reverse direction** i.e., formation of reactants.

31. For the reaction, $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$; ΔH is –ve. the following molecular scenes represent different reaction mixture (A – green, B – blue)

- **i) Calculate the equilibrium constant K_P and (K_C).**
- **ii) For the reaction mixture represented by scene (x), (y) the reaction proceed in which directions ?**
- **iii) What is the effect of increase in pressure for the mixture at equilibrium.**

$K_C = \frac{[AB]^2}{[A_2][B_2]}$ A – green ; B – blue

Given that 'V' is constant (closed system) At equilibrium,

$$K_C = \frac{\left[\frac{4}{V}\right]^2}{\left(\frac{2}{V}\right)\left(\frac{2}{V}\right)} = \frac{16}{4} = 4$$

$K_P = K_C (RT)^{\Delta n}$; $K_P = 4(RT)^0 = 4$

At stage 'x'

$Q = \frac{\left(\frac{6}{V}\right)^2}{\left(\frac{2}{V}\right)\left(\frac{1}{V}\right)} = \frac{36}{2} = 18$; $Q > K_C$ (ie.), reverse reaction is favoured At Stage 'y'

$Q = \frac{\left(\frac{3}{V}\right)^2}{\left(\frac{3}{V}\right)\left(\frac{3}{V}\right)} = \frac{9}{3 \times 3} = 1$; $K_C > Q$ (ie.), forward reaction is favoured

32. State Le-Chatelier principle.

It states that " if a system at equilibrium is disturbed, then the system shifts itself in a direction that nullifies the effect of that disturbance."

33. Consider the following reactions,

a) $H_2(g) + I_2(g) \rightleftharpoons 2HI$ b) $CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2(g)$

c) $S(s) + 3F_2 (g) \rightleftharpoons SF_6 (g)$ In each of the above reaction find out whether you have to increase (or) decrease the volume to increase the yield of the product.

a) $H_2(g) + I_2(g) \rightleftharpoons 2HI$

According to Le Chateliers principle increase in pressure will shift the equilibrium a direction that has lesser number of moles.

In the above equilibrium, pressure and volume has no effect, since no. of product is equal to no. of moles of reactant.

b) $CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2(g)$

In this equilibrium no. of moles of product is greater than no. of moles of reactant. So increase of pressure will shift the equilibrium towards the backward reaction. To increase the yield of product, pressure should be decrease and hence volume increases.

c) $S(s) + 3F_2 (g) \rightleftharpoons SF_6 (g)$

In the above equilibrium increase in pressure favours formation of product hence volume should be decreased.

34. State law of mass action.

The law states that, " At any instant, the rate of a chemical reaction at a given temperature is directly proportional to the product of the active masses of the reactants at that instant".

Rate α [Reactant]^x

Where, x is the stoichiometric coefficient of the reactant.

35. Explain how will you predict the direction of a equilibrium reaction.

From the knowledge of equilibrium constant, it is possible to predict the direction in which the net reaction is taking place for a given concentration or partial pressure of reactants and products.

Consider a general homogeneous reversible reaction,

$xA + yB \rightleftharpoons lC + mD$

For the above reaction under nonequilibrium conditions, reaction quotient 'Q' is defined as the ratio of the product of active masses of reaction products raised to the respective stoichiometric coefficients in the balanced chemical equation to that of the reactants.

Under non-equilibrium conditions, the reaction quotient Q can be calculated using the following expression. As the reaction proceeds, there is a continuous change in the concentration of reactants and products and also the Q value until the reaction reaches the equilibrium. At equilibrium Q is equal to Kc at a particular temperature. Once the equilibrium is attained, there is no change in the Q value. By knowing the Q value, we can predict the direction of the reaction by comparing it with Kc.

- If Q = Kc, the reaction is in equilibrium state.
- If Q > Kc, the reaction will proceed in the reverse direction i.e., formation of reactants.
- If Q < Kc, the reaction will proceed in the forward direction i.e., formation of products.

36. Derive a general expression for the equilibrium constant K_P and K_C for the reaction

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

Let us consider the formation of ammonia in which, 'a' moles nitrogen and 'b' moles hydrogen gas are allowed to react in a container of volume V. Let 'x' moles of nitrogen react with 3x moles of hydrogen to give 2x moles of ammonia.

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

	N_2	**H_2**	**NH_3**
Initial number of moles	**a**	**b**	**0**

number of moles reacted	x	3x	0
Number of moles at equilibrium	a-x	b-3x	2x
Active mass or molar concentration at equilibrium	$\frac{a-x}{V}$	$\frac{b-3x}{V}$	$\frac{2x}{V}$

Applying law of mass action,

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K_C = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3} = \frac{\left(\frac{4x^2}{V}\right)}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3} = \frac{4x^2V^2}{(a-x)(b-3x)^2}$$

The equilibrium constant K_P can also be calculated as follows:

$$\mathbf{K_P = K_C\,(RT)^{(\Delta ng)}}$$

$$\Delta n_g = n_p - n_r = 2 - 4 = -2$$

$$K_P = \frac{4x^2V^2}{(a-x)(b-3x)^2}\,(RT)^{-2}$$

Total number of moles at equilibrium,

$$n = a-x + b-3x + 2x = a+b-2x$$

$$K_P = \frac{4x^2V^2}{(a-x)(b-3x)^3}\left(\frac{PV}{n}\right)^{-2}$$

$$K_P = \frac{4x^2V^2}{(a-x)(b-3x)^3}\left(\frac{n}{PV}\right)^{2}$$

$$K_P = \frac{4x^2V^2}{(a-x)(b-3x)^3}\left(\frac{a+b-2x}{PV}\right)^{2}$$

$$K_P = \frac{4x^2V(a+b-2x)^2}{P^2(a-x)(b-3x)^3}$$

37. Write a balanced chemical equation for a equilibrium reaction for which the equilibrium constant is given by expression $K_C = \frac{[NH_3]^4[O_2]^5}{[NO]^4[H_2O]^6}$

$$\mathbf{K_C} = \frac{[NH_3]^4[O_2]^5}{[NO]^4[H_2O]^6}$$

Chemical equation is,

$4NO + 6H_3O \rightleftharpoons 4NH_3 + 5O_2$

38. What is the effect of added inert gas on the reaction at equilibrium.

When an inert gas (i.e, a gas which does not react with any other species involved in equilibrium) is added to an equilibrium system at constant volume, the total number of moles of gases present in the container increases, that is, the total pressure of gases increases. The partial pressure of the reactants and the products or the molar concentration of the substance involved in the reaction remains unchanged. Hence at constant volume, addition of inert gas has no effect on equilibrium.

39. Derive the relation between K_P and K_C.

Let us consider the general reaction in which all reactants and products are ideal gases.

$$xA + yB \rightleftharpoons lC + mD$$

The equilibrium constant, K_C is, $\mathbf{K_C} = \frac{[C]^l[D]^m}{[A]^x[B]^y}$ **---- (1)**

And K_P is, $K_P = \frac{P_C^l P_D^m}{P_A^x P_B^y}$ ---- (2)

The ideal gas equation is

$$PV = nRT \quad \text{or} \quad P = \frac{n}{V}RT$$

Since Active mass = molar concentration = n/V

P = active mass × RT

Based on the above expression the partial pressure of the reactants and products can be expressed as,

$P_A^x = [A]^x\,[RT]^x$

$P_B^y = [B]^y\,[RT]^y$

$P_C^l = [C]^l\,[RT]^l$

$P_D^m = [D]^m\,[RT]^m$

On substitution in Eqn. 2,

$$k_P = \frac{[C]^l[RT]^l[D]^m[RT]^m}{[A]^x[RT]^x[B]^y[RT]^y} \quad \text{---- (3)}$$

$$k_P = \frac{[C]^l[D]^m[RT]^{l+m}}{[A]^x[B]^y[RT]^{x+y}}$$

$$k_P = \frac{[C]^l[D]^m}{[A]^x[B]^y}\,RT^{(l+m)-(x+y)} \quad \text{---- (4)}$$

By comparing equation (1) and (4), we get

$$k_P = K_C\,(RT)^{(\Delta ng)} \quad \text{---- (5)}$$

where, Δn_g is the difference between the sum of number of moles of products and the sum of number of moles of reactants in the gas phase.

40. One mole of PCl_5 is heated in one litre closed container. If 0.6 mole of chlorine is found at equilibrium, calculate the value of equilibrium constant.

Given that $[PCl_5]_{initial} = \frac{1\ mole}{1\ dm^3}$

$[Cl_2]_{eq} = 0.6$ mole dm^{-3}

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$[PCl_3]_{eq} = 0.6$ mole dm^{-3}

$[PCl_5]_{eq} = 0.4$ mole dm^{-3}

$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{0.6 \times 0.6}{0.4} = \mathbf{0.9}$

41. For the reaction $SrCO_3$ (s) ⇌ SrO (s) + CO_2(g), the value of equilibrium constant $K_P = 2.2 \times 10^{-4}$ at 1002 K. Calculate K_C for the reaction.

For the reaction, $SrCO_3$ (s) ⇌ SrO (s) + CO_2(g)

$\Delta n_g = 1 - 0 = 1$

$\therefore K_P = K_C (RT)$

$2.2 \times 10^{-4} = K_C (0.0821)(1002)$

$K_C = 2.674 \times 10^{-6}$

42. To study the decomposition of hydrogen iodide, a student fills an evacuated 3 litre flask with 0.3 mol of HI gas and allows the reaction to proceed at 500 0C. At equilibrium he found the concentration of HI which is equal to 0.05 M. Calculate K_C and K_P.

V = 3L ; $[HI]_{initial} = \frac{0.3\ mol}{3L} =$ 0.1M

$[HI]_{eq}$ = 0.05M

$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

	HI(g)	H_2(g)	I_2(g)
Initial Concentration	0.1	-	-
Reacted	0.05	-	-
Equilibrium Concentration	0.05	0.025	0.025

$K_C = \frac{[H_2][I_2]}{[HI]^2} = K_C = \frac{0.025 \times 0.025}{0.05 \times 0.05} =$ 0.25

$K_P = K_C (RT)^{\Delta ng}$

$\Delta n_g = 2 - 2 = 0$

$K_P = 0.25 (RT)^0 = \mathbf{0.25}$

43. Oxidation of nitrogen monoxide was studied at 200 ^{0}C with initial pressures of 1 atm NO and 1 atm of O_2. At equilibrium partial pressure of oxygen is found to be 0.52 atm calculate K_P value.

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

	NO	O_2	NO_2
Initial Pressure	1	1	-
Reacted	0.96	0.48	-
Equilibrium partial pressure	0.04	0.52	0.96

$K_P = \frac{(P_{NO_2})^2}{(P_{NO})^2 (Po)} = \frac{0.96 \times 0.96}{0.04 \times 0.04 \times 0.52} = \mathbf{1.017 \times 10^3}$

44. 1 mol of CH_4, 1 mole of CS_2 and 2 mol of H_2S are 2 mol of H_2 are mixed in a 500 ml flask. The equilibrium constant for the reaction $K_C = 4 \times 10^{-2}$ mol^2 lit^{-2}. In which direction will the reaction proceed to reach equilibrium ?

$CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$

$K_C = 4 \times 10^{-2}$ mol lit^{-2}

Volume = 500ml = ½ L

$[CH_4]_{in} = \frac{1mol}{\frac{1}{2}L}$ = 2 mol L^{-1} $[CS_2]_{in} = \frac{1mol}{\frac{1}{2}L}$ = 2 mol L^{-1}

$[H_2S]_{in} = \frac{2mol}{\frac{1}{2}L}$ = 4 mol L^{-1} $[H_2] = \frac{2mol}{\frac{1}{2}L}$ = 4 mol L^{-1}

$Q = \frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2} = \frac{2 \times (4)^4}{(2)(2)^2} = 64$; **Q > K_C**

45. At particular temperature $K_C = 4 \times 10^{-2}$ for the reaction

$H_2S(g) \rightleftharpoons H_2(g) + ½ S_2(g)$ Calculate KC for each of the following reaction i) $2H_2S$ (g) ⇌ $2H_2$ (g) + S_2 (g)

ii) $3H_2S$ (g) ⇌ $3H_2$ (g) + 3/2 S_2(g)

$K_C = 4 \times 10^{-2}$ for the reaction,

$H_2S(g) \rightleftharpoons H_2(g) + ½ S_2(g)$

$$K_C = \frac{[H_2][S_2]^{\frac{1}{2}}}{[H_2S]}$$

$$4 \times 10^{-2} = \frac{[H_2][S_2]^{\frac{1}{2}}}{[H_2S]}$$

For the reaction, **i) $2H_2S$ (g) ⇌ $2H_2$ (g) + S_2 (g)**

$$K_C = \frac{[H_2]^2[S_2]}{[H_2S]^2} = (4 \times 10^{-2})^2 = 16 \times 10^{-4}$$

For the reaction, **ii) $3H_2S$ (g) ⇌ $3H_2$ (g) + 3/2 S_2(g)**

$$K_C = \frac{[H_2]^3[S_2]^{\frac{3}{2}}}{[H_2S]^3} = (4 \times 10^{-2})^2 = 64 \times 10^{-6}$$

46. 28 g of Nitrogen and 6 g of hydrogen were mixed in a 1 litre closed container. At equilibrium 17 g NH_3 was produced. Calculate the weight of nitrogen, hydrogen at equilibrium.

Given $m_{N_2} = 28g$; $m_{H_2} = 6g$; V = 1L

$$\left(n_{N_2}\right)_{initial} = \frac{28}{28} = 1 \text{ mol}$$

$$\left(n_{N_2}\right)_{initial} = \frac{6}{2} = 3 \text{ mol}$$

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

	N_2(g)	H_2(g)	NH_3(g)
Initial Concentration	1	3	-
Reacted	0.5	1.5	-
Equilibrium Concentration	0.5	1.5	1

$$[NH_3] = \left(\frac{17}{17}\right) = 1 \text{ mol}$$

Weight of N_2 = (no.of moles of N_2) × molar mass of N_2

= 0.5 × 28 = **14g**

Weight of H_2 = (no.of moles of H_2) × molar mass of H_2

= 1.5 × 2 = **3g**

47. The equilibrium for the dissociation of XY_2 is given as, $2XY_2$ (g) ⇌ $2XY$ (g) + Y_2(g) if the degree of dissociation x is so small compared to one. Show that 2 KP = PX^3 where P is the total pressure and K_P is the dissociation equilibrium constant of XY_2.

$2XY_2(g) \rightleftharpoons 2XY(g) + Y_2(g)$

	XY_2	XY	Y_2
Initial no.of moles	1	-	-
No. of moles dissociated	X	-	-
No. of moles at equilibrium	(1 – X) ≅1	X	X/2

Total no. of moles = 1-X + X + X/2 = 1 + X/2 ≅1

[therefore Given that x<< 1; 1 – x ≅1 and 1 + X/2 ≅ 1]

$$K_p = \frac{(P_{XY})^2(P_{Y_2})}{\left(P_{XY_2}\right)^2} = \frac{\left(\frac{x}{1}\times P\right)^2\left(\frac{\frac{X}{2}}{1}\times P\right)}{\left(\frac{1}{1}\times P\right)^2}$$

$$K_P = \frac{X^2P^2\times P}{2P^2} = \mathbf{2K_P = X^3P}$$

48. A sealed container was filled with 1 mol of A_2 (g), 1 mol B_2 (g) at 800 K and total pressure 1.00 bar. Calculate the amounts of the components in the mixture at equilibrium given that K = 1 for the reaction A_2 (g) + B_2 (g) ⇌ 2AB (g)

$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$

	A2	B2	AB
Initial Concentration	1	1	-
No.Of moles dissociated	X	X	-
No. of moles at equilibrium	1 - x	1- x	2x

Total no. of moles = 1- x + 1 – x + 2x = 2

$$K_p = \frac{(P_{AB})^2}{\left(P_{A_2}\right)\left(P_{B_2}\right)} = \frac{\left(\frac{2x}{2}\times P\right)^2}{\left(\frac{(1-x)}{2}\times P\right)\left(\frac{1-x}{2}\times P\right)}$$

$$K_P = \frac{4x^2}{(1-x)^2}$$

Given that $K_P = 1$; $\frac{4x^2}{(1-x)^2} = 1$

⇨ $4x^2 = (1 - x)^2$

⇨ $4x^2 = 1 + x^2 - 2x$

3x2 + 2x -1 = 0

$$x = \frac{-b\pm\sqrt{b^2-4ac}}{2a} = \frac{-2\pm\sqrt{4-4\times3\times-1}}{2(3)} = \frac{-2\pm\sqrt{4+12}}{6} = \frac{-2\pm\sqrt{16}}{6} = \frac{-2+4}{6};\frac{-2-4}{6}$$

$$= \frac{2}{6};\frac{-6}{6}$$

x = 0.33; -1 (not possible)

$[A_2]_{eq} = 1 - x = 1 – 0.33 = 0.67$

$[B_2]_{eq} = 1 – x = 1 – 0.33 = 0.67$

$[AB]_{eq} = 2x = 2 \times 0.33 = 0.66$

49. Deduce the Vant Hoff equation.

This equation gives the quantitative temperature dependence of equilibrium constant (K). The relation between standard free energy change (ΔG°) and equilibrium constant is

$$\Delta G^\circ = –RT\ln K \quad \text{-------- (1)}$$

We know that

$$\Delta G^\circ = \Delta H^\circ – T\Delta S^\circ \quad \text{-------- (2)}$$

Substituting (1) in equation (2)

$$–RT\ln K = \Delta H^\circ – T\Delta S^\circ$$

Rearranging

$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad \text{------- (3)}$$

Differentiating equation (3) with respect to temperature,

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2} \quad \text{------- (4)}$$

Equation 4 is known as differential form of van’t Hoff equation. On integrating the equation 4, between T_1 and T_2 with their respective equilibrium constants K_1 and K_2.

$$\int_{K_1}^{K_2} d(\ln K) = \frac{\Delta H^\circ}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

$$[\ln K]_{K_1}^{K_2} = \frac{\Delta H^\circ}{R}\left[-\frac{1}{T}\right]_{T_1}^{T_2}$$

$$\ln K_2 – \ln K_1 = \frac{\Delta H^\circ}{R} – \left[\frac{1}{T_2} + \frac{1}{T_1}\right]$$

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left[\frac{T_2-T_1}{T_2T_1}\right]$$

$$\log\frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R}\left[\frac{T_2-T_1}{T_2T_1}\right] \quad \text{------- (5)}$$

Equation 5 is known as integrated form of van’t Hoff equation.

50. The equilibrium constant K_P for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 8.19×10^2 at 298 K and 4.6×10^{-1} at 498 K. Calculate ΔH^0 for the reaction.

K_{P_1} = 8.19 × 102 T1= 298K

K_{P_2} = 4.6 × 10-2 T2 = 498K

$$\log\left(\frac{K_{P_2}}{K_{P_1}}\right) = \frac{\Delta H^\circ}{2.303R}\left[\frac{T_2-T_1}{T_2T_1}\right]$$

$$\log\left(\frac{4.6\times10^{-1}}{8.19\times10^2}\right) = \frac{\Delta H^\circ}{2.303\times8.314}\left(\frac{498-298}{498\times298}\right)$$

$$\frac{-3.2505\times2.303\times8.314\times498\times298}{200} = \Delta H^\circ$$

$\Delta H^\circ = - 46181 \text{ J mol}^{-1}$

$\Delta H^\circ = - 46.18 \text{ kJ mol}^{-1}$

51. The partial pressure of carbon dioxide in the reaction $CaCO_3$ (s) ⇌ CaO (s) + CO_2(g) is 1.017×10^{-3} atm at 500^0 C. Calculate K_P at 600^0C C for the reaction. ΔH for the reaction is 181 KJ mol^{-1} and does not change in the given range of temperature.

$P_{CO_2} = 1.017 \times 10^{-3}$ atm ; T = 500^0 C

$K_P = P_{CO_2}$

$K_{P_1} = 1.017 \times 10^{-3}$; T = 500 + 273 = 773K

K_{P_1} = ? T = 600 + 273 = 873K

$\Delta H^\circ = 181 \text{ kJ mol}^{-1}$

$$\log\left(\frac{K_{P_2}}{K_{P_1}}\right) = \frac{\Delta H^\circ}{2.303R}\left[\frac{T_2-T_1}{T_2T_1}\right]$$

$$\log\left(\frac{K_{P_2}}{1.017\times10^{-3}}\right) = \frac{181\times10^3}{2.303\times8.314}\left(\frac{873-773}{873\times773}\right)$$

$$\log\left(\frac{K_{P_2}}{1.017\times10^{-3}}\right) = \frac{181\times10^3\times100}{2.303\times8.314\times873\times773}$$

$$\frac{K_{P_2}}{1.017\times10^{-3}} = \text{anti log of } (1.40)$$

$$\frac{K_{P_2}}{1.017\times10^{-3}} = 25.12$$

$K_{P_2} = 25.12 \times 1.017 \times 10^{-3}$

$\boldsymbol{K_{P_2} = 25.54 \times 10^{-3}}$

Unit 9:Solutions

31. Define (i) molality (ii) Normality

(i) molality: Molarity is defined as the number of moles of the solute per kilogram of the solvent

Molality $= \frac{No.of\ moles\ of\ solute}{Mass\ of\ the\ solvent\ (in\ kg)}$

(ii) Normality: Normality is defined as number of gram equivanlents of solute present in one litre of solution.

Normality $= \frac{No.of\ gram\ equivalent\ of\ solute}{Volume\ of\ solution\ (in\ L)}$

32. What is a vapour pressure of liquid? What is relative lowering of vapour pressure?

Vapour pressure of liquid :

The pressure of the vapour in equilibrium with its liquid is called vapour pressure of the liquid at the given temperature.

Relative lowering of vapour pressure:

The ratio of lowering of vapour pressure to vapour pressure of pure solvent.

Relative lowering of vapour pressure= $\frac{P^{\circ}_{solvent} - P_{solution}}{P^{\circ}_{solvent}}$

33. State and explain Henry's law

Henry's law states that, "the partial pressure of the gas in vapour phase is directly proportional to the mole fraction(x) of the gaseous solute in the solution at low concentrations".

Henry's law can be expressed as, $P_{solute} \alpha\ x_{solute\ in\ solution}$

$P_{solute} = K_H\ x_{solute\ in\ solution}$

34. State Raoult law and obtain expression for lowering of vapour pressure when nonvolatile solute is dissolved in solvent.

Raoult law states that "in the case of a solution of volatile liquids, the partial vapour pressure of each component (A & B) of the solution is directly proportional to its mole fraction".

According to Raoult's law

$P_A\ \alpha\ x_A\ ;\ P_A = k\ x_A$

when $x_A = 1$, $k = P^{\circ}_A$

where P°_A is the vapour pressure of pure component 'A' at the same temperature.

Therefore, $P_A = P^{\circ}_A\ x_A$

When a nonvolatile solute is dissolved in a pure solvent, the vapour pressure of the pure solvent will decrease.

Volatile solvent Particles

Nonvolatile solute particles

$P_{solution} \propto x_A$; Where x_A is the mole fraction of the solvent

$P_{solution} = k\ x_A$ When $x_A = 1$, $K = P^{o}_{solvent}$

($P^{o}_{solvent}$ is the partial pressure of pure solvent)

$P_{solution} = P^{\circ}_{solvent}\ x_A$

$\frac{P_{solution}}{P^{\circ}_{solvent}} = x_A$

$1 - \frac{P_{solution}}{P^{\circ}_{solvent}} = 1 - x_A$

$\frac{P^{\circ}_{solvent} - P_{solution}}{P^{\circ}_{solvent}} = x_B$

Where x_B is the fraction of the solute

($\therefore x_A + x_B = 1$, $x_B = 1 - x_A$)

The above expression gives the relative lowering of vapour pressure. Based on this expression, Raoult's Law can also be stated as "the relative lowering of vapour pressure of an ideal solution containing the nonvolatile solute is equal to the mole fraction of the solute at a given temperature"

35. What is molal depression constant? Does it depend on nature of the solute ?

$$\Delta T_f = K_f \; . \; m$$

If m=1 then $\Delta T_f = K_f$

The molal depression constant K_f is equal to the depression is freezing point for 1 molal solution.

Depression constant **does not depend on the nature of the solute**. (but depends on the number of solution particles in the solution solvent).

36. What is osmosis?

Osmosis is a spontaneous process by which the solvent molecules pass through a semi permeable membrane from a solution of lower concentration to a solution of higher concentration.

37. Define the term 'isotonic solution'.

Two solutions having same osmotic pressure at a given temperature are called isotonic solutions.

38. You are provided with a solid 'A' and three solutions of A dissolved in water – one saturated, one unsaturated, and one super saturated. How would you determine which solution is which ?

Saturated Solution: It can dissolve salt an additional to it.

(A Solution in which no more solute can be dissolved in a definite amount of solvent at a given temperature is called a saturated solution.)

Unsaturated solution: Further solubility of salt do not takes place but solubility can takes place on heating.

(A solution which has more of solute than the saturated at a given temperature is called super saturated solution.)

Super saturated solution: Solubility of salt do not takes place on even an further heating.

(A Solution which has more of solute than the saturated solution at a given temperature is called super saturated solution.)

39. Explain the effect of pressure on the solubility.

The change in pressure does not have any significant effect in the solubility of solids and liquids as they are not compressible. However, **the solubility of gases generally increases with increase of pressure.**

Consider a saturated solution of a gaseous solute dissolved in a liquid solvent in a closed container. In such a system, the following equilibrium exists.

Gas (in gaseous state) ⇆ Gas (in solution)

According to Le-Chatelier principle, **the increase in pressure will shift the equilibrium in the direction which will reduce the pressure.** Therefore, more number of gaseous molecules dissolves in the solvent and the solubility increases.

40. A sample of 12 M Concentrated hydrochloric acid has a density 1.2 gL^{-1} Calculate the molality

Molarity = 12 M HCl

Density of the solution = 1.2 gL^{-1}

In 12 M HCl solution, there are 12 moles of HCl in 1 litre of the solution

$$\text{Molarity} = \frac{No.of\ moles\ of\ solute}{Mass\ of\ the\ solvent\ (in\ kg)}$$

Calculate mass of water (solvent)

Mass of 1 litre HCl solution = density × volume

= 1.2 gmL^{-1} × 1000mL

= 1200 g

Mass of HCl = No. of moles of HCl × molar mass of HCl

= 12 mol × 36.5g mol^{-1}

= 438 g

Mass of water = mass of HCl solution – mass of HCl

Mass of water = 1200 – 438 = 762 g

$$\text{Molarity} = \frac{12}{0.762} = \mathbf{15.75\ m}$$

41. A 0.25 M glucose solution at 370.28 K has approximately the pressure as blood does what is the osmotic pressure of blood ?

C = 0.25 M; T = 370.28 K

$(\pi)_{glucose}$ = CRT

(π) = 0.25 mol L^{-1} × 0.082L atm K^{-1} mol^{-1} × 370.28 K

(π) = **7.59 atm**

42. Calculate the molality of a solution containing 7.5 g of glycine (NH_2-CH_2 - COOH) dissolved in 500 g of water.

$$\text{Molarity} = \frac{No.of\ moles\ of\ solute}{Mass\ of\ the\ solvent\ (in\ kg)}$$

$$\text{No. of moles of glycine} = \frac{mass\ of\ glycine}{molar\ mass\ of\ glycine}$$

$$= \frac{7.5}{75} = 0.1$$

$$\text{Molarity} = \frac{0.1}{0.5\ Kg} = 0.2m$$

43. Which solution has the lower freening point?10 g of methanol (CH_3OH) in 100g of water (or) 20 g of ethanol (C_2H_5OH) in 200 g of water. $\Delta T_f = K_f\ m$

i.e., $\Delta T_f\ \alpha\ m$

$$m_{CH3-OH} = \frac{\left(\frac{10}{32}\right)}{0.1} = 3.125\ m$$

$$m_{C2H5-OH} = \frac{\left(\frac{20}{46}\right)}{0.2} = 2.174\ m$$

∴

Depression in freezing point is more in me thanol solution and it will have lower freezing point.

44. How many moles of solute particles are present in one litre of 10^{-4} M potassium sulphate?

In 10^{-4} M K_2SO_4 solution, there are 10^{-4} moles of potassium sulphate.

K_2SO_4 molecule contains 3 ions ($2K^+$ and $1SO_4^{2-}$)

1moleof K_2SO_4 contains 3 × 6.023 ×10^{23} ions

10^{-4} mole of K_2SO_4 contains 3 × 6.023 × 10^{23} × 10^{-4} ions

= 18.069 × 10^{19} [therefore $n_1 >> n_2$; $n_1 + n_2 \approx n_1$]

45. Henry's law constant for solubility of methane in benzene is 4.2×10^{-5} mm Hg at a particular constant temperature At this temperature. Calculate the solubility of methane at

i) 750 mm Hg ii) 840 mm Hg

$(K_H)_{\text{benzene}} = 4.2 \times 10^{-5}$ mm Hg

Solubility of methane = ? ; P = 750 mm Hg ; P = 840 mm Hg

According to Henrys Law,

$P = K_H \, . \, X_{\text{in solution}}$

750 mm Hg = $4.2 \times 10_{-5}$ mm Hg . $X_{\text{in solution}}$

➔ $X_{\text{in solution}} = \frac{750}{4.2 \times 10^{-5}}$

i.e, solubility = 178.5×10^5

similarly at P = 840 mm Hg

solubility = $\frac{840}{4.2 \times 10^{-5}} = 200 \times 10^{-5}$

46. The observed depression in freezing point of water for a particular solution is 0.093^0C. Calculate the concentration of the solution in molality. Given that molal depression constant for water is 1.86 KKg mol^{-1}

$\Delta T_f = 0.093\,^\circ C = 0.093 K; m = ?$

$K_f = 1.86\,^\circ C \text{ kg mol}^{-1}$

$\Delta T_f = K_f \, . \, m$

$m = \frac{0.093\,K}{1.86 K \, kg \, mol^{-1}} = 0.05 \text{ mol kg}^{-1} = 0.05m$

47. The vapour pressure of pure benzene (C_6H_6) at a given temperature is 640 mm Hg. 2.2 g of non-volatile solute is added to 40 g of benzene. The vapour pressure of the solution is 600 mm Hg. Calculate the molar mass of the solute?

$P^\circ_{C6H6} = 640$mm Hg

$W_2 = 2.2$ g (non volabile solute); $W_1 = 40$ g (benzene)

$P_{\text{solution}} = 600$mm Hg; M_2 = ?

$\frac{P^\circ - P}{P^\circ} = x_2$; $\frac{640-600}{640} = \frac{n_2}{n_1 + n_2}$; $\frac{40}{640} = \frac{n_2}{n_1}$

$0.0625 = \frac{W_2 \times W_1}{M_2 \times M_1}$

$M_2 = \frac{2.2 \times 78}{0.0625 \times 40}$ = **68.64 g mol^{-1}**

Unit : 10 Chemical Bonding

31. Define the following i) Bond order ii) Hybridisation iii) σ- bond

i) Bond order: The number of bonds formed between the two bonded atoms in a molecule is called the bond order

ii) Hybridisation: Hybridisation is the process of mixing of atomic orbitals of the same atom with comparable energy to form equal number of new equivalent orbitals with same energy.

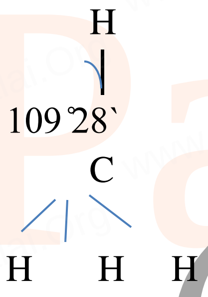
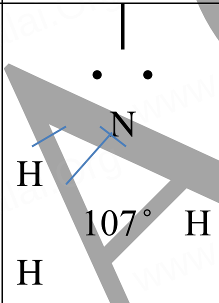
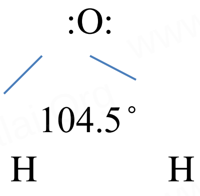
iii) σ- bond: When two atomic orbitals overlap linearly along the axis, the resultant bond is called a sigma (**σ**) bond

32. What is a pi bond?

When two atomic orbitals overlaps sideways, the resultant covalent bond is called a pi (π) bond

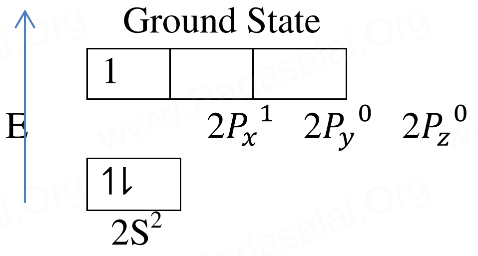
33. In CH_4, NH_3 and H_2O, the central atom undergoes sp^3 hybridisation - yet their bond angles are different. why?

Bond angles are different due to the presence of lone pair of electrons.

Molecule	Structure	Atomic arrangement	Bond angle	Reason for reduction in bond angle
CH_4		The central carbon atom has four valence electrons and each hydrogen atom gives and electrons Minimum repulsions between the bond pairs	109˚28`	The minimum repulsion between the bond pairs leads to a regular tetrahedron with an angle of 109˚28`
NH_3		The central N – atom is surrounded by three bone pairs and one bone pair Lp – lp repulsions > lp – lp repulsion	107˚	The Repulsion between these electron pairs will be minimum if the shape of NH_3 is pyramidal. Hence the bond angle gets reduced from 109˚28` to 107˚
H_2O		The central O – atom has 2 lone pairs & 2 bond pairs. The lp – lp repulsions > lp – lp repulsion.	104˚ 5’	Due to greater lp – lp repulsion the bond angle gets reduced to 104˚5’

34. Explain Sp^2 hybridisation in BF_3

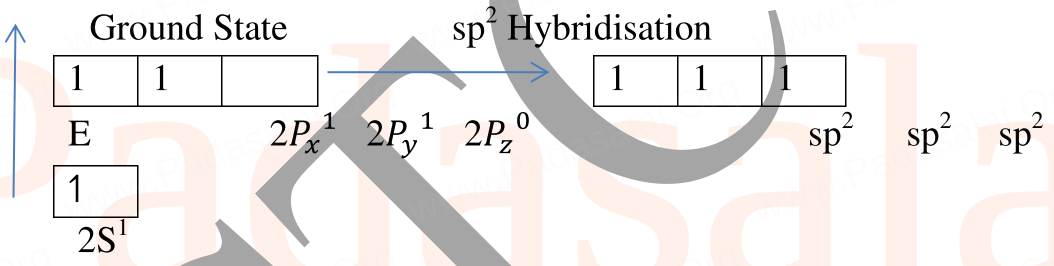
Sp^2 Hybridisation :Consider boron trifluoride molecule. The valence shell electronic configuration of boron atom is [He] $2s^2\ 2p^1$



In the ground state boron has only one unpaired electron in the valence shell. In order to form three covalent bonds with fluorine atoms, three unpaired electrons are required. To achieve this, one of the paired electrons in the 2s orbital is promoted to the

$2p_y$ orbital in the excite state.

In boron, the s orbital and two p orbitals (p_x and p_y) in the valence shell hybridises, to generate three equivalent sp^2 orbitals as shown in the Figure. These three orbitals lie in the same xy plane and the angle between any two orbitals is equal to 120^0



Overlap with 2pz orbitals of fluorine:

The three sp^2 hybridised orbitals of boron now overlap with the 2pz orbitals of fluorine (3 atoms). This overlap takes place along the axis as shown below.

35. Draw the M.O diagram for oxygen molecule calculate its bond order and show that O_2 is paramagnetic.

Molecular orbital diagram of oxygen molecule (O_2)

Electronic configuration of O atom $1s^2\,2s^2\ 2p^4$

Electronic configuration of O2 molecule

$\sigma 1s^2, \sigma^{*2}{}_{1s}, \sigma^2{}_{2s}, \sigma^{*2} 2s\ , \sigma^2{}_{2px}, \pi^2{}_{2py}\ , \pi^2{}_{2pz}, \pi^{*1}{}_{2py}\ , \pi^{*1}{}_{2pz},$

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

Molecule has two unpaired electrons hence it is paramagnetic.

36. Draw MO diagram of CO and calculate its bond order.

Bonding in some heteronuclear di-atomic molecules

Molecular orbital diagram of Carbon monoxide molecule (CO)

Electronic configuration of C atom $1s^2\ 2s^2\ 2p^2$

Electronic configuration of O atom $1s^2\ 2s^2\ 2p^4$

Electronic configuration of CO molecule

$\sigma^2 1s, \sigma^{*2} 1s\ , \sigma^2 2s, \sigma^{*2} 2s\ , \pi^2 2py\ , \pi^2 2pz, \sigma^2 2px$

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

Molecule has no unpaired electrons hence it is diamagnetic.

37. What do you understand by Linear combination of atomic orbitals in MO theory.

i) The wave functions for the molecular orbitals can be obtained by solving Schrodinger wave equation for the molecule. Since solving the Schrodinger equation is too complex, approximation methods are used to obtain the wave function for molecular orbitals. The most common method is the linear combination of atomic orbitals (LCAO).

ii) Atomic orbitals are represented by the wave function Ψ. Let us consider two atomic orbitals represented by the wave function ψ_A and ψ_B with comparable energy, combines to form two molecular orbitals.

iii) One is bonding molecular orbital($\psi_{bonding}$) and the other is antibonding molecular orbital($\psi_{antibonding}$).

iv) The wave functions for these two molecular orbitals can be obtained by the linear combination of the atomic orbitals ψ_A and ψ_B as below.

$$\psi_{bonding} = \psi_A + \psi_B$$

$$\psi_{antibonding} = \psi_A - \psi_B$$

v) The formation of bonding molecular orbital can be considered as the result of constructive interference of the atomic orbitals and the formation of anti-bonding molecular orbital can be the result of the destructive interference of the atomic orbitals.

vi) The formation of the two molecular orbitals from two 1s orbitals is shown below.

38. Discuss the formation of N_2 molecule using MO Theory

Molecular orbital diagram of nitrogen molecule (N_2)

Electronic configuration of N atom $1s^2\ 2s^2\ 2p^3$

Electronic configuration of N_2 molecule

$\sigma^2 1s, \sigma^{*2} 1s\ , \sigma^2 2s, \sigma^{*2} 2s\ , \pi^2 2py\ , \pi^2 2pz\ ,\sigma^2 2px$

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

Molecule has no unpaired electrons hence it is diamagnetic.

39. What is dipole moment?

i)The polarity of a covalent bond can be measured in terms of dipole moment which is defined as **$\mu = q \times 2d$**

Where, μ - dipole moment,

q - the charge and

2d - distance between the two charges.

ii) The dipole moment is a vector quantity and the direction of the dipole moment points from the negative charge to positive charge.

iii) The unit of dipole moment is coulomb metre(C m) (Debye= 3.336×10^{-30} C m).

40. Linear form of carbondioxide molecule has two polar bonds. yet the molecule has Zero dipolement why?

In CO_2, the dipole moments of two polar bonds (C=O) are equal in magnitude but have opposite direction. Hence, the net dipole moment of the CO_2 is, $\mu = \mu_1 + \mu_2 = \mu_1 + (-\mu_1) = 0$

O = C = O
$\rightarrow$ $\leftarrow$
μ_1 μ_2

$\rightarrow$ $\rightarrow$ $\rightarrow$ $\rightarrow$
In this case $\mu = \mu_1 + \mu_2 = \mu_1 + (-\mu_1) = 0$

41. Draw the Lewis structures for the following species.

i) NO_3^- ii) SO_4^{2-} iii) HNO_3 iv) O_3

42. Explain the bond formation in $BeCl_2$ and $MgCl_2$.

Bond formation in $MgCl_2$:

Mg is a metal with 2 valence electrons. Cl is a non-metal with 7 valence electrons and hence it needs one electron to complete the octet. Thus Mg donates one electron to each Cl and becomes positively charged. Each Cl accepts one electron and becomes negatively charged.

Bond formation in $BeCl_2$:

In AB_2 type the central atom A has two bond pairs only the two bond pairs orient themselves at 180° to have minimum repulsion among themselves.

$BeCl_2$ is linear and forms a pair of covalent bonds instead for forming ionic bonds. Be uses its two hybrid orbitals to form two Be – Cl bonds. The bond angle is 180°

43. Which bond is stronger σ or π? Why?

- Sigma(σ) bonds are strong than pi (π) bonds.
- Sigma bonds are formed by head on overlap of atomic orbitals so extent of overlapping is maximum.(axial overlapping)
- Pi bonds are weaker, since according to quantum mechanics, the orbital path are parallel to there is much less overlap between the p orbitals. (lateral overlapping)

44. Define bond energy.

The bond enthalpy (bond energy) is defined as **the minimum amount of energy required to break one mole of a particular bond in molecules in their gaseous state.**

The unit of bond energy is **$kJmol^{-1}$.**

45. Hydrogen gas is diatomic where as inert gases are monoatomic – explain on the basis of MO theory.

- Hydrogen gas is diatomic where as inert gases are monoatomic because noble gases are having its valence shell filled with octet electrons.
- So there is no necessity for the noble gases to involve in the formation of covalent bonds.
- This could be further explained by MO diagram of H_2 and He_2
- **Molecular orbital diagram of hydrogen molecule (H_2):**

  Electronic configuration of H atom $1s^1$

  Electronic configuration of H_2 molecule $\sigma^2{}_{1s}$

  Bond order $= \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$

Molecule has no unpaired electrons hence it is diamagnetic.

- The electronic configuration of He (Z = 2) in the ground state is $1s^1$
- As each helium atom contains two electrons, there will be four electrons in He_2 molecule. Keeping in view the Aufbau principle and pauli's exclusion principle its electronic configuration would be as follows.
- $He_2 : (\sigma_{1s})^2 (\sigma^*{}_{1s})^2$

  $N_b = 2$ and $N_a = 2$ Bond order $= \frac{N_b - N_a}{2} = \frac{2-2}{2} = 0$
- As the bond order of He_2 come out to be zero, this molecule does not exist.

46. What is Polar Covalent bond? Explain with example.

Polar covalent bond is formed between atoms having different electronegativities, the atom with higher electronegativity will have greater tendency to attract the shared pair of electrons towards itself than other atom.

Example: HF

consider the covalent bond between hydrogen and fluorine in hydrogen fluoride. The electronegativities of hydrogen and fluorine on Pauling's scale are 2.1 and 4 respectively. It mean that fluorine attracts the shared pair of electrons approximately twice as much as the hydrogen which leads to partial negative charge on fluorine and partial positive charge on hydrogen. Hence , the H-F bond is said to be polar covalent bond.

47. Considering x- axis as molecular axis, which out of the following will form a sigma bond.

i) 1s and $2p_y$ ii) $2P_x$ and $2P_x$ iii) $2P_x$ and $2P_z$ iv) 1s and $2P_z$

i) 1s and $2p_y$ – No sigma bond

ii) $2P_x$ and $2P_x$ – sigma bond

iii) $2P_x$ and $2P_z$– No sigma bond

iv) 1s and $2P_z$– No sigma bond

When we consider x- axis as molecular axis , the $p_x - p_x$ overlap will result in σ- bond

48. Explain resonance with reference to carbonate ion?

The skeletal structure of carbonate ion (The oxygen atoms are denoted as O_A, O_B & O_C)

Total number of valence electrons = [1 x 4(carbon)] + [3 x 6 (oxygen)] + [2 (charge)] = 24 electrons.

Distribution of these valence electrons gives us the following structure.
Complete the octet for carbon by moving a lone pair from one of the oxygens (OA) and write the charge of the ion (2-) on the upper right side as shown in the figure.

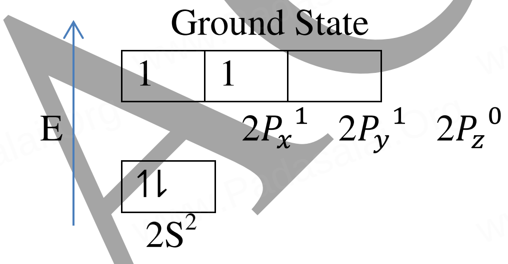
In this case, we can draw two additional Lewis structures by moving the lone pairs from the other two oxygens (OB and OC) thus creating three similar structures as shown below in which the relative position of the atoms are same. They only differ in the position of bonding and lone pair of electrons. Such structures are called resonance structures (canonical structures) and this phenomenon is called resonance.

It is evident from the experimental results that all carbon-oxygen bonds in carbonate ion are equivalent. The actual structure of the molecules is said to be the resonance hybrid, an average of these three resonance forms. It is important to note that carbonate ion does not change from one structure to another and vice versa. It is not possible to picturise the resonance hybrid by drawing a single Lewis structure. However, the following structure gives a qualitative idea about the correct structure.

It is found that the energy of the resonance hybrid (structure 4) is lower than that of all possible canonical structures (Structure 1, 2 & 3). The difference in energy between structure 1 or 2 or 3, (most stable canonical structure) and structure 4 (resonance hybrid) is called resonance energy

49. Explain the bond formation in ethylene and acetylene.

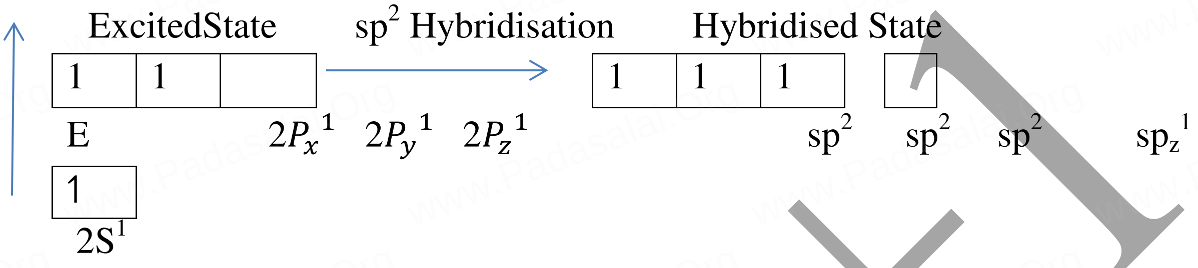
The bonding in ethylene can be explained using hybridisation concept. The molecular formula of ethylene is C2H4. The valency of carbon is 4. The electronic configuration of valence shell of carbon in ground state is $[He]2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$. To satisfy the valency of carbon promote an electron from 2s orbital to 2pz orbital in the excited state.



In ethylene both the carbon atoms undergoes sp2 hybridisation involving 2s, 2px and 2py orbitals, resulting in three equivalent sp^2 hybridised orbitals lying in the xy plane at an angle of 120^0 to each other. The unhybridised $2p_z$ orbital lies perpendicular to the xy plane.

Formation of sigma bond:

One of the sp_2 hybridised orbitals of each carbon lying on the molecular axis (x-axis) linearly overlaps with each other resulting in the formation a C-C sigma bond. Other two sp^2 hybridised orbitals of both carbons linearly overlap with the four 1s orbitals of four hydrogen atoms leading to the formation of two C-H sigma bonds on each carbon.



Formation of pi bond:

The unhybridised 2pz orbital of both carbon atoms can overlap only sideways as they are not in the molecular axis. This lateral overlap results in the formation a pi bond between the two carbon atoms as shown in the figure.

Bonding in acetylene:

Similar to ethylene, the bonding in acetylene can also be explained using hybridization concept. The molecular formula of acetylene is C_2H_2. The electronic configuration of valence shell of carbon in ground state is $[He]2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$. To satisfy the valency of carbon promote an electron from 2s orbital to $2p_z$ orbital in the excited state.

In acetylene molecule, both the carbon atoms are in sp hybridised state. The 2s and $2p_x$ orbitals, resulting in two equivalent sp hybridised orbitals lying in a straight line along the molecular axis (x-axis). The unhybridised $2p_y$ and 2pz orbitals lie perpendicular to the molecular axis.

Formation of sigma bond:

One of the two sp hybridised orbitals of each carbon linearly overlaps with each other resulting in the formation a C-C sigma bond. The other sp hybridised orbital of both carbons linearly overlap with the two 1s orbitals of two hydrogen atoms leading to the formation of one C-H sigma bonds on each carbon.

Formation of pi bond:

The unhybridised $2p_y$ and 2pz orbitals of each carbon overlap sideways. This lateral overlap results in the formation of two pi bonds (py-py and pz-pz) between the two carbon atoms as shown in the figure.

50. What type of hybridisations are possible in the following geometeries? a) octahedral b) tetrahedral c) square planer.

Molecular Geometry	Hybridisation	Example

Octahedral	Sp^3d^2	SF_6
Tetrahedral	Sp^3	CH_4
Square planner	dsp^2	$[Ni(CN)_4$

51. Explain VSEPR theory. Applying this theory to predict the shapes of IF_7, and SF_6

1. The shape of the molecules depends on the number of valence shell electron pair around the central atom.
2. There are two types of electron pairs namely bond pairs and lone pairs.
3. The bond pair of electrons are those shared between two atoms, while the lone pairs are the valence electron pairs that are not involved in bonding.
4. Each pair of valence electrons around the central atom repels each other and hence, they are located as far away as possible in three dimensional space to minimize the repulsion between them.
5. The repulsive interaction between the different types of electron pairs is in the following order.

lp - lp > lp - bp> bp-bp lp- lone pair ; bp- bond pair

52. CO_2 and H_2O both are triatomic molecule but their dipole moment values are different. Why?

$\mu = \mu_1 + \mu_2 = \mu_1 + (-\mu_1) = 0$

O== C == O

→ ←

μ_1 μ_2

→ →

In this case $\mu = \mu_1 + \mu_2$

$= \mu_1 + (-\mu_1) = 0$

In case of water net dipole moment is the vector sum of $\mu_1 + \mu_2$ as shown.

53. Which one of the following has highest bond order? N_2, N_2^+ or N_2^-

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

Where N_b = Number of electrons in bonding molecular orbitals

N_a = Number of electrons in anti bonding molecular orbitals.

Bond Order of N_2:

Total no. of electrons = 14

Electronic configuration = $\sigma^2_{1s}, \sigma^{*2}_{1s}, \sigma^2_{2s}, \sigma^{*2}_{2s}, \pi^2_{2py}, \pi^2_{2pz}, \sigma^2_{2px}$

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

Bond Order of N_2^+ :

Total no. of electrons = 13

Electronic configuration = $\sigma^2_{1s}, \sigma^{*2}_{1s}$, $\sigma^2_{2s}, \sigma^{*2}_{2s}$, π^2_{2py} = π^2_{2pz} ,$\sigma^2{}_{px}{}^1$

Bond order = $\frac{N_b - N_a}{2} = \frac{9-4}{2} = 2.5$

Bond Order of N_2^- :

Total no. of electrons = 15

Electronic configuration = $\sigma^2_{1s}, \sigma^{*2}_{1s}$, $\sigma^2_{2s}, \sigma^{*2}_{2s}$, π^2_{2py} = π^2_{2pz} ,$\sigma^2_{2px}\,\sigma^2{}_{py}{}^1$

Bond order = $\frac{N_b - N_a}{2} = \frac{10-5}{2} = 2.5$

Stability of the molecule is directly proportional to bond order.

Hence, $N_2 > N_2^+ = N_2^-$

54. Explain the covalent character in ionic bond.

The partial covalent character in ionic compounds can be explained on the basis of a phenomenon called polarisation. We know that in an ionic compound, there is an electrostatic attractive force between the cation and anion. The positively charged cation attracts the valence electrons of anion while repelling the nucleus. This causes a distortion in the electron cloud of the anion and its electron density drift s towards the cation, which results in some sharing of the valence electrons between these ions. Thus, a partial covalent character is developed between them. This phenomenon is called polarisation.

55. Describe fajan's rule.

The ability of a cation to polarize an anion is called its polarising ability and the tendency of an anion to get polarized is called its polarisability. The extent of polarisation in an ionic compound is given by the Fajans rules

Fajans Rules:

i. To show greater covalent character, both the cation and anion should have high charge on them. Higher the positive charge on the cation, greater will be the attraction on the electron cloud of the anion. Similarly higher the magnitude of negative charge on the anion, greater is its polarisability. (Hence, the increase in charge on cation or in anion increases the covalent character Let us consider three ionic compounds aluminum chloride, magnesium chloride and sodium chloride.) Since the charge of the cation increase in the order $Na^+ < Mg^{2+} < Al^{3+}$, the covalent character also follows the same order $NaCl < MgCl_2 < AlCl_3$.

ii. The smaller cation and larger anion show greater covalent character due to the greater extent of polarisation. Lithium chloride is more covalent than sodium chloride. (The size of Li^+ is smaller than Na^+ and hence the polarising power of Li+ is more. Lithium iodide is more covalent than lithium chloride as the size of I^- is larger than the Cl^-). Hence I^- will be more polarized than Cl^- by the cation, Li^+ .

iii. Cations having $ns^2\ np^6\ nd^{10}$ configuration show greater polarizing power than the cations with $ns^2\ np^6$configuration. Hence, they show greater covalent character. CuCl is more covalent than NaCl. Compared to Na^+ (1.13 Å) . Cu^+ (0.6 Å) is small and have $3s^2\ 3p^6\ 3d^{10}$ configuration.

Electronic configuration of Cu^+
[Ar] $3s^2, 3p^6, 3d^{10}$
Electronic Configuration of Na^+
[He] $2s^2, 2p^6$

Unit: 12 Basic Concepts of Organic reactions

16. Write short notes on (a) Resonance (b) Hyperconjucation

(a) Resonance : Certain organic compounds can be represented by more than one structure and they differ only in the position of bonding and lone pair of electrons. Such structures are called resonance structures (canonical structures) and this phenomenon is called resonance.

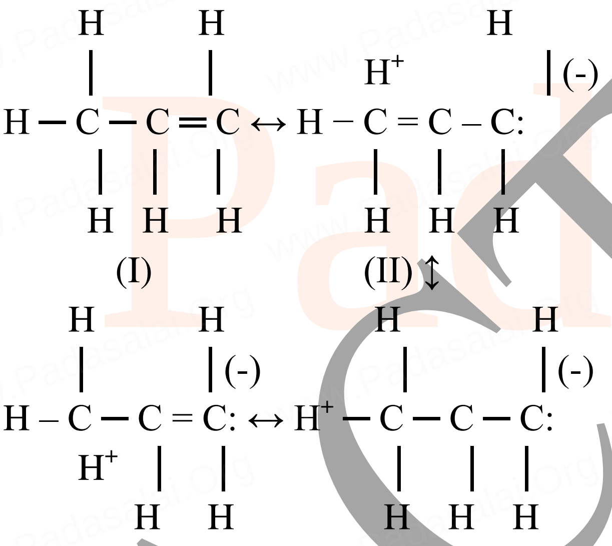
$$H_2C = CH - CH = CH_2 \leftrightarrow H_2C_+ - CH = CH - {}_-CH_2 \leftrightarrow H_2C_- - CH = CH - {}_+CH_2$$

1,3-BUTADIENE

b) Hyper conjugation :

- The delocalisation of electrons of **σ** bond is called as hyper conjugation.

It is a special stabilising effect that results due to the interaction of electrons of a **σ**-bond (usually **C-H** or **C-C**) with the adjacent, empty non-bonding p-orbital or an antibonding **σ*** or **π*-**orbitals resulting in an extended molecular orbital. Unlike electromeric effect, hyper conjugation is a permanent effect. In propene, the σ-electrons of C-H bond of methyl group can be delocalized into the π-orbital of doubly bonded carbon as represented below.



$$H-C-C=C \leftrightarrow H-C=C-C: \quad H^+ \quad (-)$$

(I) (II) ↕

$$H-C-C=C: \leftrightarrow H^+-C-C-C: \quad H^+ \quad (-)$$

17. What are electrophiles and nucleophiles? Give suitable examples for each.

Nucleophiles:

Phile means affinity: Nucleophile means nucleus loving species ie species which that are attracted towards positive charge. Nucleophiles are electron rich species. They may be neutral, or negatively charged. Neutral nucleophiles possess one or more lone pair of electrons. All lewis bases are nucleophiles.

Neutral Nucleophiles: NH_3, RNH_2, R_2NH and R_3N

Negatively Charged Nucleophiles: Cl^-, Br^-, CN^-

Electrophiles: Electron

Electrophiles means : electron loving species ie species which that are attracted towards negative charge. Electrophiles are electron deficient species. They may be neutral, or positively charged. Neutral electrophiles possess electron deficient centre. All Lewis acids are Electrophiles.

Neutral Electrophiles : $AlCl_3$, BF_3 and $FeCl_3$

Positively charged electrophiles: R^+, H^+, RX, H_3O^+, NO^+, etc.,

18. Show the heterolysis of covalent bond by using curved arrow notation and complete the following equations. Identify the nucleophile is each case.

(i) $CH_3 - Br + KOH \rightarrow$

(ii) $CH_3 - OCH_3 + HI \rightarrow$

(i) $CH_3 - Br + KOH \rightarrow CH_3 - OH + KBr$

Methyl bromide Methanol

OH^- from KOH is the nuclephile.

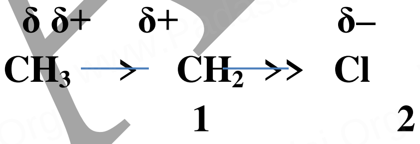
(ii) $CH_3 - O - CH_3 + HI \rightarrow CH_3I + CH_3OH$

Dimethyl ether Methyl iodide Methanol

I from HI acts as a nucleophile

19. Explain inductive effect with suitable example.

- Inductive effect is defined as the change in the polarisation of a covalent bond due to the presence of adjacent bonds, atoms or groups in the molecule. This is a permanent phenomenon.
- Let us explain the inductive effect by considering ethane and ethyl chloride as examples. The C-C bond in ethane is non polar while the C-C bond in ethyl chloride is polar. We know that chlorine is more electronegative than carbon, and hence it attracts the shared pair of electron between C-Cl in ethyl chloride towards itself. This develops a slight negative charge on chlorine and a slight positive charge on carbon to which chlorine is attached. To compensate it, the C1 draws the shared pair of electron between itself and C2. This polarisation effect is called inductive effect.
- This effect is greatest for the adjacent bonds, but they also be felt farther away. However, the magnitude of the charge separation decreases rapidly, as we move away from C1 and is observed maximum for 2 carbons and almost insignificant after 4 bonds from the active group.



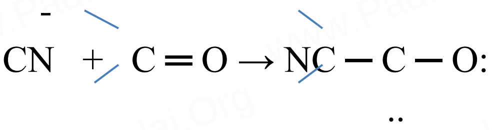
$$\overset{\delta\,\delta+}{CH_3} \rightarrow \underset{1}{\overset{\delta+}{CH_2}} \gg \underset{2}{\overset{\delta-}{Cl}}$$

- It is important to note that the inductive effect does not transfer electrons from one atom to another but the displacement effect is permanent. The inductive effect represents the ability of a particular atom or a group to either withdraw or donate electron density to the attached carbon. Based on this ability the substituents are classified as +I groups and –I groups. Their ability to release or withdraw the electron through sigma covalent bond is called +I effect and -I effect respectively.

20. Explain electromeric effect.

Electromeric effect (E) : Electromeric is a temporary effect which operates in unsaturated compounds (containing >C=C<, >C=O, etc...) in the presence of an attacking reagent. Let us consider two different compounds

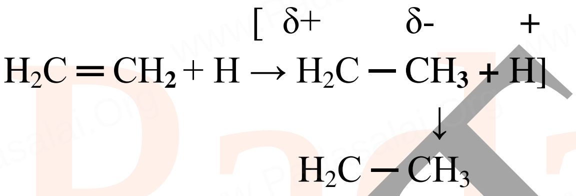
(i) compounds containing carbonyl group (>C=O) : When a nucleophile approaches the carbonyl compound, the **π** electrons between C and O is instantaneously shifted to the more electronegative oxygen. This makes the carbon electron deficient and thus facilitating the formation of a new bond between the incoming nucleophile and the carbonyl carbon atom.



$$\overset{-}{CN} + C=O \rightarrow NC-\underset{..}{C}-O:$$

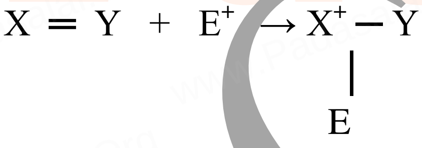
(ii) unsaturated compounds such as alkenes (>C=C<) :

when an electrophile such as H+ approaches an alkene molecule, the **π electrons** are instantaneously shifted to the electrophile and a new bond is formed between carbon and hydrogen. This makes the other carbon electron deficient and hence it acquires a positive charge.



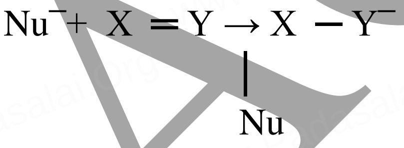
$$H_2C=CH_2 + H \rightarrow [\overset{\delta+}{H_2C}-\overset{\delta-}{CH_3}+\overset{+}{H}] \downarrow H_2C-CH_3$$

When the **π** electron is transferred towards the attacking reagent, it is called + E (positive electromeric) effect.



$$X = Y + E^+ \rightarrow \underset{\underset{E}{|}}{X^+}-Y$$

When the **π** electron is transferred away from the attacking reagent, it is called, -E (negative electromeric) effect

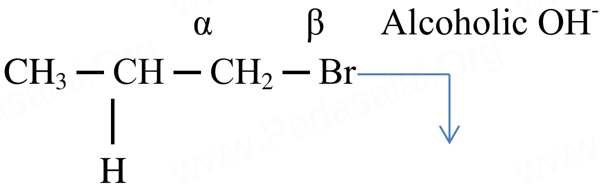


$$Nu^- + X=Y \rightarrow \underset{\underset{Nu}{|}}{X}-Y^-$$

21. Give examples for the following types of organic reactions

(i) β – elimination **(ii) electrophilic**

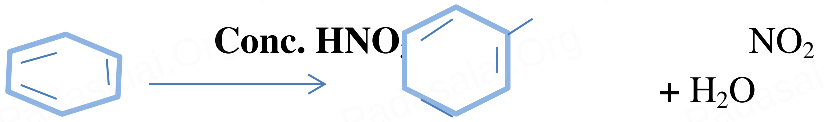
(i) β – elimination:



$$CH_3-\underset{\underset{H}{|}}{CH}-\overset{\alpha}{CH_2}-\overset{\beta}{Br}\xrightarrow{\text{Alcoholic } OH^-}$$

$$CH_3 - CH = CH_2 + H_2O + Br^-$$

(ii) electrophilic:



Unit 13: Hydrocarbons

BOOK BACK

31. Give IUPAC names for the following compounds

1) $CH_3–CH=CH–CH=CH–C≡C–CH_3$ Octa-4,6-diene-3-yne

C_2H_5 CH_3

| |

2) $CH_3– C – C – C ≡ C – CH_3$

|

CH_3 4,5,5- trimethylhepta-2-yne

3) $(CH_3)_3\ C – C ≡ C – CH\ (CH_3)_2$ 2,2,5 – trimethyl hex-3-yne

|

CH_3

4) ethyl isopropyl acetylene

$CH_3\ CH_2 – C ≡ C – CH\ (CH_3)_2$ 2 – methyl hex-3-yne

5) $CH ≡ C – C ≡ C – C ≡ CH$ 1,3,5- Hexa triyne

32. Identify the compound A, B, C and D in the following series of reactions

i) $CH_3 – CH_2–Br$

↓ **alc. KOH**

Cl_2 / CCl_4

A ⟶ **B**

i) O_3

↓ ii) Zn/H_2O ↓

$NaNH_2$

C **D**

A – $CH_2 = CH_2$ – Ethene

B – $CH_2 – CH_2$ - 1, 2 – dichloro ethane

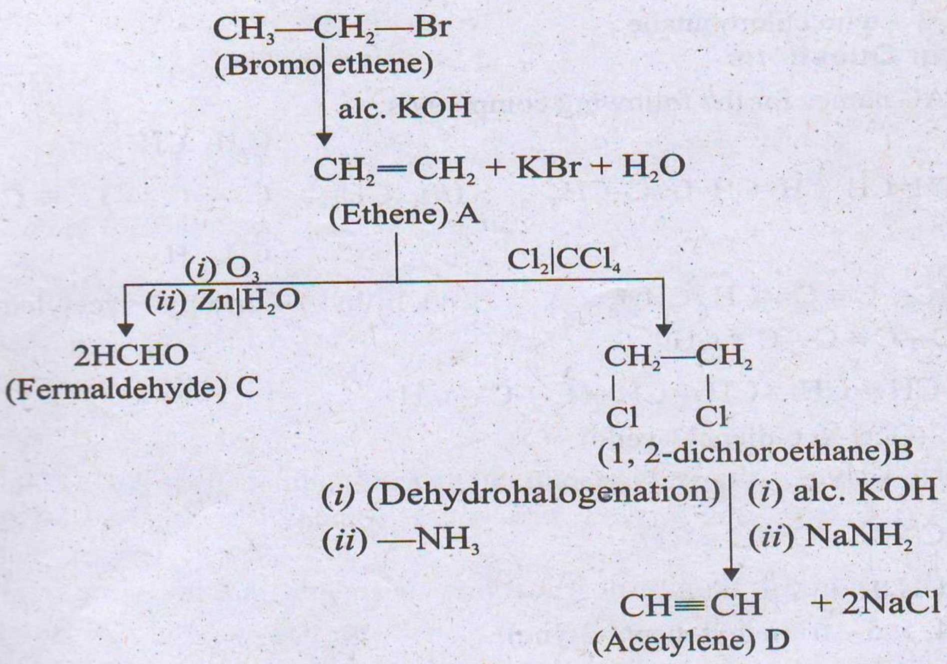
| |

Cl Cl

C – HCHO - Formaldehyde

D – $CH ≡ CH$ - Acetylane

Ans.



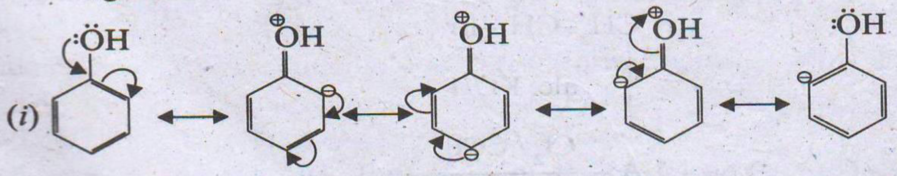
A	Ethene	$CH_2=CH_2$
B	1, 2-dichloroethane	CH_2CH_2 | | Cl Cl
C	Formaldehyde	HCHO
D	Acetylene	$CH\equiv CH$

33. Write a short note on ortho-para directors in aromatic electrophilic substitution reactions?

Ans. The group which increases the electron density at *ortho* and *para* positions of the ring are known as ortho-para directors.

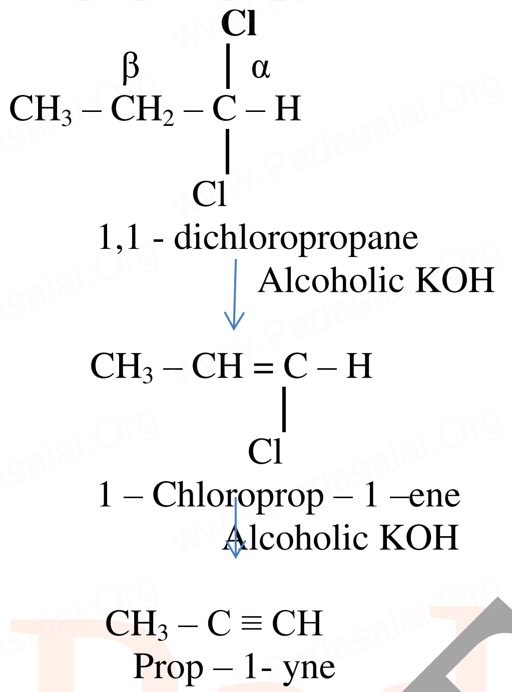
Example, —OH, $—NH_2$, —NHR, $—CH_3$, $—OCH_3$ etc.

Let us consider the directive influences of phenolic (–OH) group. Phenol is the resonance hybrid of following structure.



In these resonance structures the negative charge residue is present on *ortho* and *para* positions of the ring structure. Therefore the electron density at *ortho* and *para* positions increases as compared to the *meta* position, thus phenolic group activities the benzene ring for electrophilic attack at *ortho* and *para* positions and hence –OH group is an ortho-para director and an activator.

33. How is propyne prepared from an alkyenedihalide ?



$$CH_3-\overset{\beta}{CH_2}-\underset{Cl}{\overset{Cl\ \alpha}{C}}-H$$

1,1 - dichloropropane

$$\downarrow \text{Alcoholic KOH}$$

$$CH_3-CH=\underset{Cl}{C}-H$$

1 – Chloroprop – 1 –ene

$$\downarrow \text{Alcoholic KOH}$$

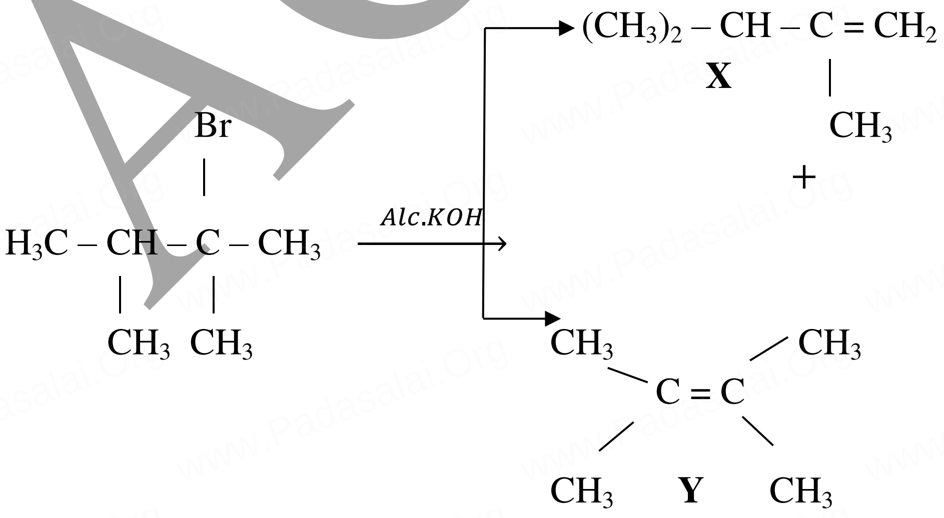
$$CH_3-C\equiv CH$$

Prop – 1- yne

34. An alkylhalide with molecular formula $C_6H_{13}Br$ on dehydro halogenation gave two isomeric alkenes X and Y with molecular formula C_6H_{12}. On reductive ozonolysis, X and Y gave fourcompounds CH_3COCH_3, CH_3CHO, CH_3CH_2CHO and $(CH_3)_2$ CHCHO. Find the alkylhalide.

(i) The alkyl halide with molecular formula $C_6H_{13}Br$ is bromohexane (2 – Bromo – 2, 3-dimethyl butane)

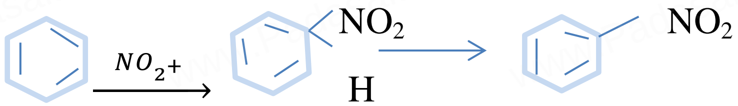
(ii) $C_6H_{13}Be$ on dehydro halogenation gives two isomeric alkenes 2,3 – dimethyl – 1-butane (X) and 2,3 – dimethyl – 2 – butene (y)



$$H_3C-\underset{CH_3}{CH}-\underset{CH_3}{\overset{Br}{C}}-CH_3 \xrightarrow{Alc.KOH} \underset{X}{(CH_3)_2-CH-\underset{CH_3}{C}=CH_2} + \underset{Y}{\begin{matrix}CH_3 & & CH_3\\ & C=C & \\ CH_3 & & CH_3\end{matrix}}$$

(iii) X and Y on reductive ozonolysis gave four compounds CH_3COCH_3, CH_3CHO, CH_3CH_2CHO and $(CH_3)_2$ CHCHO

35. Describe the mechanism of Nitration of benzene.

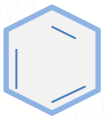


36. How does Huckel rule help to decide the aromatic character of a compound.

A compound may be aromatic, if it obeys Huckel rules

(i) The molecule must be co-planner
(ii) Complete delocalization of π electron in the ring.
(iii) Presence of (4n +2) π electrons in the ring where n is an integer(n = 0,1,2…..)

Eg:



Benzene

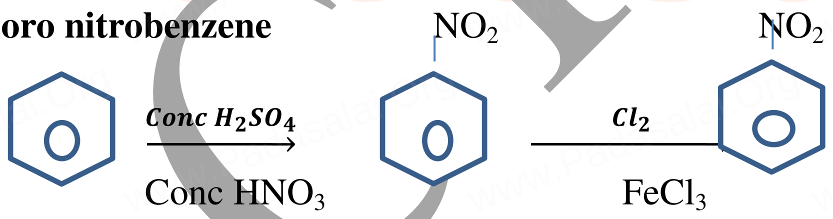
(i) The benzene is a planner molecule
(ii) It has six delocalised π electrons
(iii) 4n + 2 = 6; 4n = 6 -2; 4n= 4; n = 1

It obeys Huckel's (4n + 2) π electron rule with n = 1 hence , benzene is aromatic

37. Suggest the route for the preparation of the following from benzene.

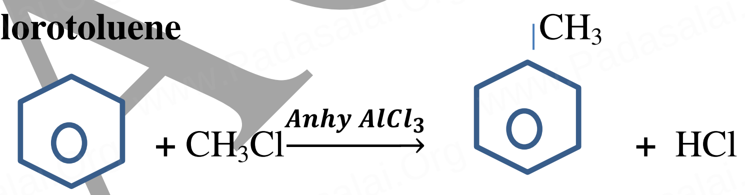
1) 3 – chloro nitrobenzene 2) 4 – chlorotoluene 3) Bromobenzene 4) m - dinitro benzene

1) 3 – chloro nitrobenzene

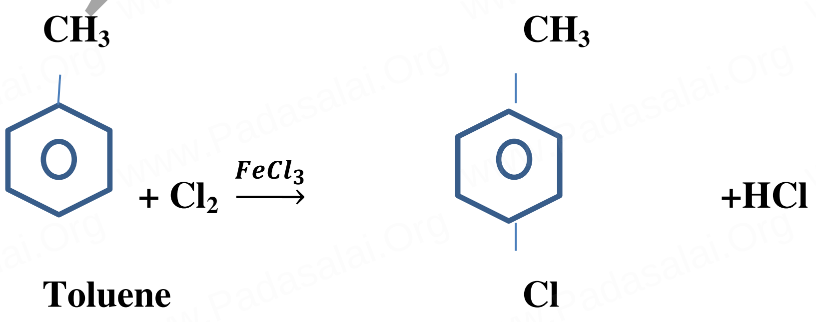


Benzene nitrobenzene 3- Chloronitro benzene

2) 4 – chlorotoluene



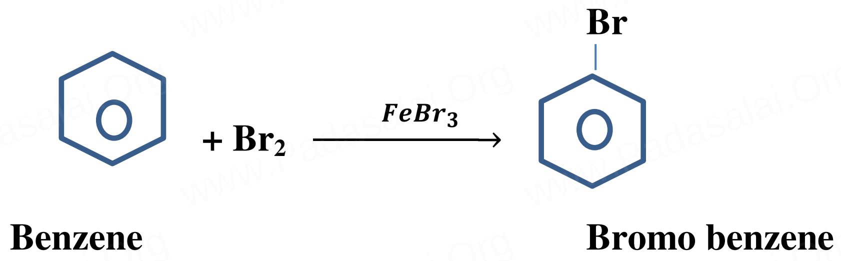
Benzene **Toluene**



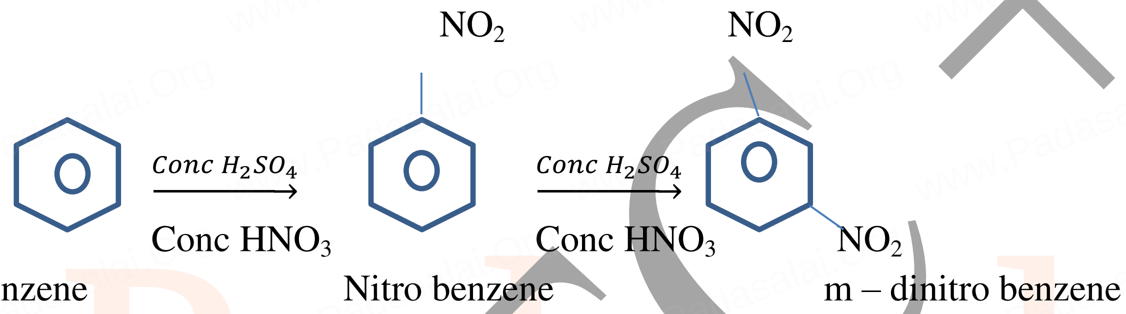
Toluene

4 – Chloro toluene

3) Bromo benzene



4) m - dinitro benzene



38. Suggest a simple chemical test to distinguish propane and propene.

Test to distinguish propane and propene

(i) Alkenes (propene) decolorize Br_2/H_2O where as alkanes (propane) does not unergo this reaction.

(ii) De – colorization of acidified $KMnO_4$, propene de-colorises acidified $KMnO_4$ whereas propane does not.

Both test for unsalunation.

39. What happens when isobutylene is treated with acidified potassium permanganate ?

(i) Ethyl chloride to ethane

$$CH_3CH_2Cl \xrightarrow[Zn/\ HCl]{[H]} CH_3-CH_3 + HCl$$

Ethyl chloride

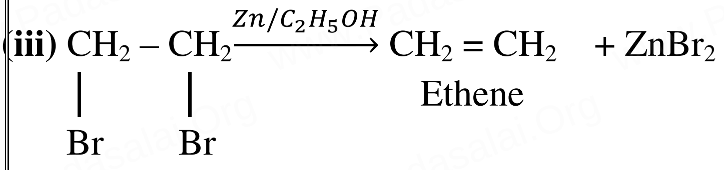
Alkyl halides when reduced gives the corresponding alkanes.

(ii) $CH_3CH_2Cl + CH_3CH_2Cl + \xrightarrow[\text{Dry ether}]{2Na} CH_3CH_2-CH_2CH_3 + 2NaCl$

Ethyl chloride Butane

This reaction is called wurtz reaction. Haloalkanes react with sodium metal in dry ether to give higher alkenes.

(iii)



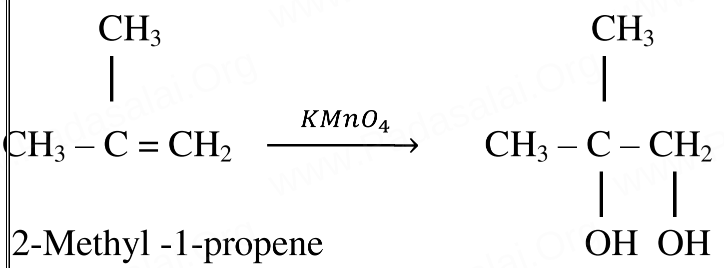
$$\underset{Br}{CH_2}-\underset{Br}{CH_2} \xrightarrow{Zn/C_2H_5OH} CH_2=CH_2 + ZnBr_2$$

Ethene

1,2 – di bromo ethane

(iv) $CaC_2 + \xrightarrow{H_2O} CH \equiv CH + Ca(OH)_2$

Calcium carbide Ethyne



$$\underset{\text{2-Methyl-1-propene}}{CH_3 - \overset{\overset{CH_3}{|}}{C} = CH_2} \xrightarrow{KMnO_4} CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}} - \underset{\underset{OH}{|}}{CH_2}$$

40. How will you convert ethyl chloride in to i) ethane ii) n – butane

(i) Ethyl Chloride → Ethane:

$$\underset{\text{Ethyl Chloride}}{CH_3 - CH_2 - Cl} \xrightarrow[\text{Zn/ HCl}]{[H]} \underset{\text{Ethane}}{CH_3 - CH_3} + HCl$$

(ii) Ethyl Chloride → n – Butane (Wurtz reaction):

$$\underset{\text{Ethyl chloride}}{CH_3 - CH_2 - Cl} + 2Na + Cl - CH_2 - CH_3 \xrightarrow{Dry\ Ether} \underset{\text{n – Butane}}{CH_3 - CH_2 - CH_2 - CH_3} + 2NaBr$$

41. Describe the conformers of n - butane.

Conformations Of n – Butane: n – butane may be considered as a derivative of ethane, as one hydrogen on each carbon is replaced by a methyl group

Eclipsed Conformation: In this conformation, the distance between the two methyl group is minimum. So there is maximum repulsion between them and it is the least stable conformer.

Anti or Staggered form: In this conformation, the distance between the two methyl groups is maximum. So there is minimum repulsion between them and it is the most stable conformer

42. Write the chemical equations for combustion of propane.

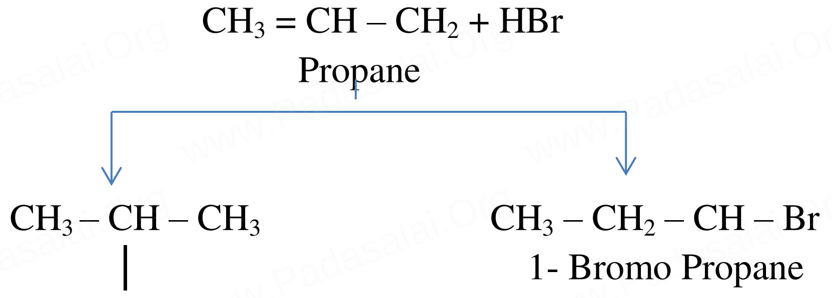
Propane burns in excess of oxygen to form water and carbon di oxide.

$$\underset{\text{Propane}}{CH_3CH_2CH_3} + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

43. Explain Markownikoff's rule with suitable example.

Markovikoff's rule: " When an unsymmetrical alkene reacts with hydrogen halide, the hydrogen adds to the carbon that has more number of hydrogen and halogen add to the carbon having fewer hydrogen".

Eg: Addition HBr to unsymmetrical alkene: In the addition of hydrogen halide to an unsymmetrical alkene, two products are obtained.



$$\underset{\text{Propane}}{CH_3 = CH - CH_2} + HBr$$

$$CH_3 - \underset{|}{CH} - CH_3 \qquad \underset{\text{1- Bromo Propane}}{CH_3 - CH_2 - CH - Br}$$

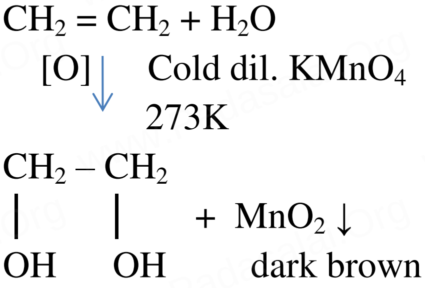
Br (minor product)

2 – Bromo propane

(major product)

44. What happens when ethylene is passed through cold dilute alkaline potassium permanganate.

Ethene reacts with cold alk KMnO4 (Balyer's regent to give ethane 1,2 – diol

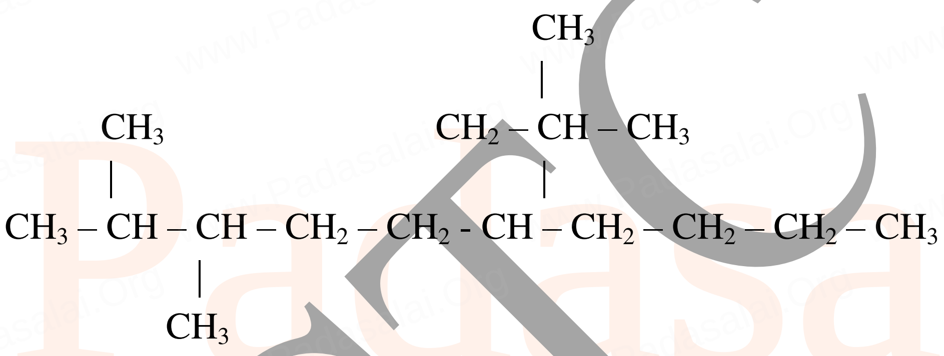


$$CH_2 = CH_2 + H_2O \xrightarrow[273K]{[O]\ \text{Cold dil. } KMnO_4} \underset{OH}{CH_2} - \underset{OH}{CH_2} + \underset{\text{dark brown}}{MnO_2\downarrow}$$

Ethane – 1, 2 - diol

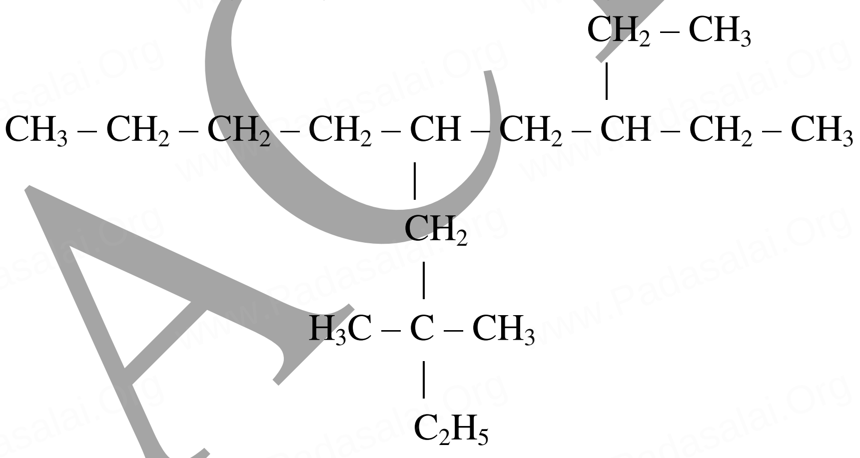
45. Write the structures of folowing alkanes.

1) 2, 3 – Dimethyl – 6 – (2 – methyl propyl) decane



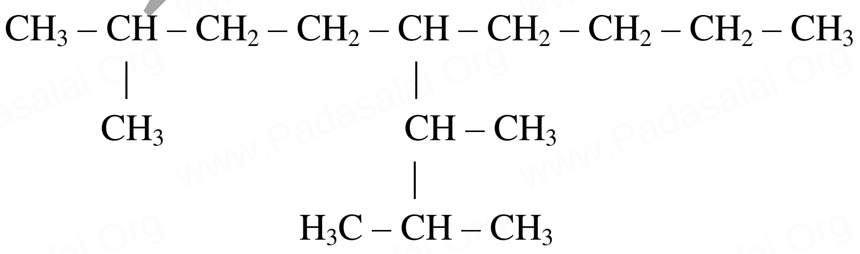
$$CH_3 - \overset{CH_3}{CH} - \underset{CH_3}{CH} - CH_2 - CH_2 - \overset{\overset{CH_3}{CH_2 - CH - CH_3}}{CH} - CH_2 - CH_2 - CH_2 - CH_3$$

2) 5 – (2 – Ethyl butyl) – 3, 3 – dimethyldecane



$$CH_3 - CH_2 - CH_2 - CH_2 - \underset{\underset{\underset{C_2H_5}{H_3C - C - CH_3}}{CH_2}}{CH} - CH_2 - \overset{CH_2 - CH_3}{CH} - CH_2 - CH_3$$

3) 5 – (1, 2 – Dimethyl propyl) – 2 – methylnonane



$$CH_3 - \underset{CH_3}{CH} - CH_2 - CH_2 - \underset{\underset{H_3C - CH - CH_3}{CH - CH_3}}{CH} - CH_2 - CH_2 - CH_2 - CH_3$$

46. How will you prepare propane from a sodium salt of fatty acid ?

$$CH_3CH_2CH_2COONa + NaOH \xrightarrow[\Delta]{CaO} CH_3CH_2\,CH_3 + Na_2CO_3$$

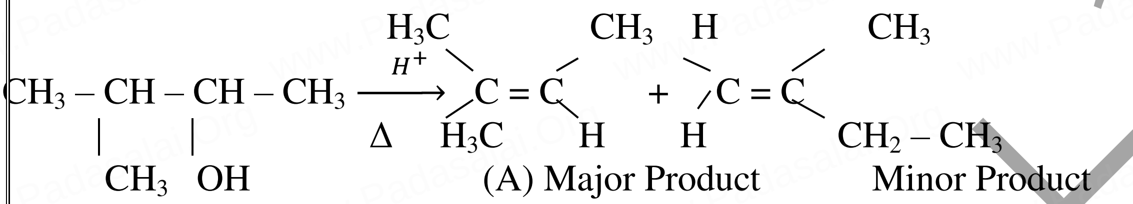
Sodium salt of butanaic acid   Propane

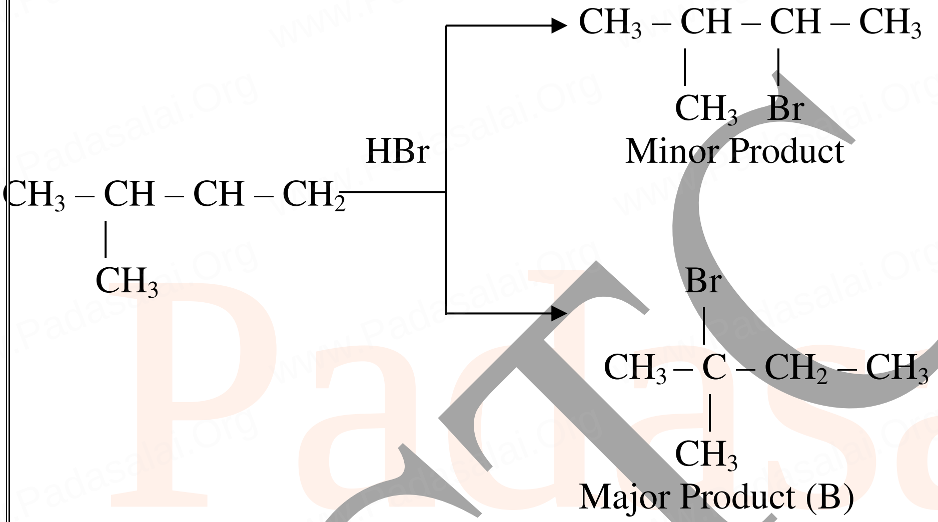
Heating sodium salt of butanoic acid (Sodium butanoate) with soda lime gives propane.

47. $CH_3 – CH\ (CH_3) – CH\ (OH) – CH_3$

↓ H^+/heat

(A) major product $\xrightarrow{HBr}$ (B) major product   Identify A and B





48. Complete the following :

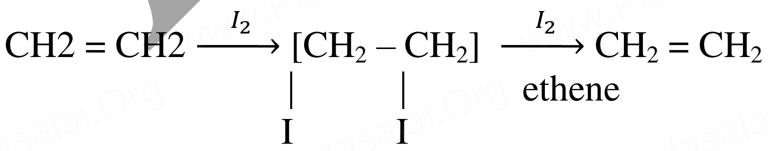
i) 2 – butyne $\xrightarrow{\textbf{Lindlar Catalyst}}$

$$CH_3 – C \equiv C – CH_3 + H_2 \xrightarrow[\text{Catalyst}]{Lindlar} CH_3 – CH = CH – CH_3$$

2 – Butyne   2 – Butene

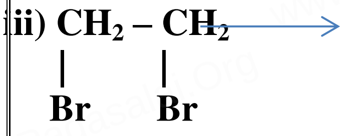
Lindlar catalyst consist of pd deposited on $CaCO_3$ and then poisoned by lead on sulphur.

ii) $CH_2 = CH_2 \xrightarrow[Zn/C_2H_5OH]{I_2}$

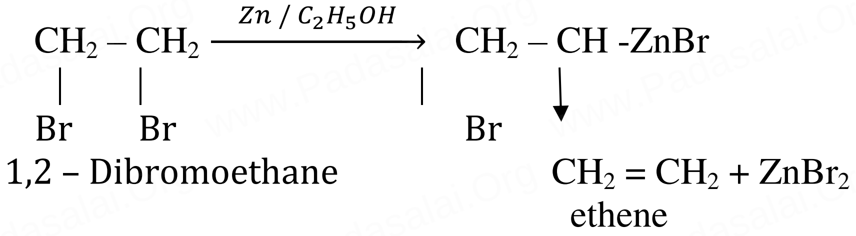


$$CH2 = CH2 \xrightarrow{I_2} [\underset{I}{CH_2} – \underset{I}{CH_2}] \xrightarrow{I_2} CH_2 = CH_2$$

ethene

iii)


$$\underset{Br}{CH_2} – \underset{Br}{CH_2} \longrightarrow$$



$$CH_2(Br)-CH_2(Br) \xrightarrow{Zn\,/\,C_2H_5OH} CH_2(Br)-CH\text{-}ZnBr \rightarrow CH_2=CH_2+ZnBr_2$$

iv) $CaC_2 \xrightarrow{H_2O} CH\equiv CH + Ca(OH)_2$

$CaC_2 \xrightarrow{H_2O} CH\equiv CH + Ca(OH)_2$

Calcium Carbride ethyne

49. How will you distinguish 1 – butyne and 2 – butyne?

An alkyne shows acidic nature only if it contains terminal hydrogen.

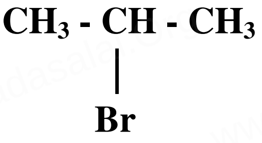
$CH_3-CH_2-C\equiv CH + 2AgNO_3 + 2NH_4OH \rightarrow CH_3-CH_2-C\equiv C-Ag + 2NH_4NO_3 + 2H_2O$

1 – butyne Silver butynide

$CH_3-C\equiv C-CH_3 + 2AgNO_3 + 2NH_4OH \rightarrow$ No Reaction due to absence of acidic hydrogen

Unit 14: Haloalkanes and Haloarenes

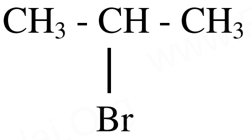
26. Classify the following compounds in the form of alkyl, allylic, vinyl, benzylic halides. (i) $CH_3 - CH = CH - Cl$ (ii) $C_6H_5CH_2I$

(iii)

$CH_3 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3$

(iv) $CH_2 = CH - Cl$

(i) $CH_3 - CH = CH - Cl$- allyl chloride → allylic

(ii) $C_6H_5CH_2I$ - Benzyl iodide → Benzylic Halides

(iii)

$CH_3 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3$ - 2-bromo propane → alkyl

(iv) $CH_2 = CH - Cl$ – Vinyl chloride → Vinyl

27. Why chlorination of methane is not possible in dark?

Methane does not react with chlorine in dark. Reaction of methane with chlorine proceeds by free radical mechanism. The initiation step in the free radical chain reaction is $Cl_2 \rightarrow 2Cl$. This step requires chain more energy. The excess energy is provided by heat or light.

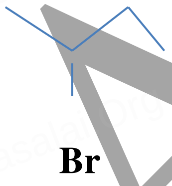
28. How will you prepare n propyl iodide from n-propyl bromide?

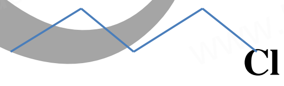
n-propyl iodide from n-propyl bromide. n-propyl bromise on heating with concentrated solution of sodium iodide in acetone gives n-propyl Iodide. This reaction is called **Finkelstein reaction.**

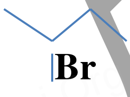
$$CH_3CH_2CH_2Br + NaI \overset{\Delta}{\xrightarrow{acetone}} CH_3CH_2CH_2I + NaBr$$

n-propyl bromide n-propyl iodide

29. Which alkyl halide from the following pair is i) chiral ii) undergoes faster SN_2 reaction?





(i)


is chiral

(ii)


30. How does chlorobenzene react with sodium in the presence of ether? What is the name of the reaction?

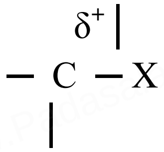
Haloarenes react with sodium metal in dry ether, two aryl groups combine to give biaryl products is reaction is called **fittig reaction.**

$C_6H_5Cl + 2Na + Cl - C_6H_5 \xrightarrow[\Delta]{Ether} C_6H_5 - C_6H_5 + 2NaCl$

Chlorobenzene Biphenyl

31. Give reasons for polarity of C-X bond in halo alkane.

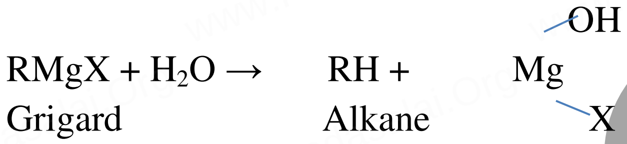
Carbon halogen bond is a polar bond as halogens are more electro negative than carbon. The carbon. The carbon atom exhibits a partial positive charge (δ+) and halogen atom a partial negative charges (δ-)



$$-\overset{\delta^+}{\underset{|}{\overset{|}{C}}}-\overset{\delta^-}{X}$$

32. Why is it necessary to avoid even traces of moisture during the use of Grignard reagent?

The Grignard carbon is highly basic and reacts with acidic protons of polar solvents like water to form an alkane so all reagents should be pure and dry.

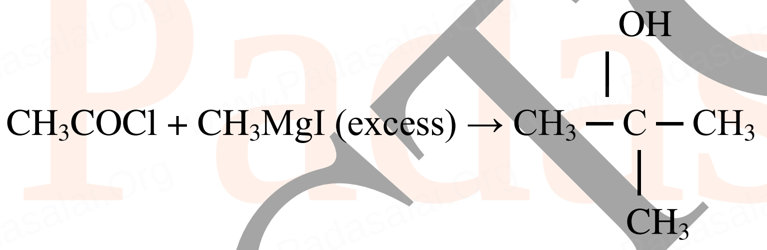


$$RMgX + H_2O \rightarrow RH + Mg\genfrac{}{}{0pt}{}{OH}{X}$$

Grigard Alkane

33. What happens when acetyl chloride is treated with excess of CH_3MgI?

When acetyl chloride is treated with excess of CH_3 MgI , tertiary alcohols are formed.



$$CH_3COCl + CH_3MgI\ (excess) \rightarrow CH_3 - \overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_3$$

t- Butyl alcohol

34. Arrange the following alkyl halide in increasing order of bond enthalpy of RX CH_3Br, CH_3F, CH_3Cl, CH_3I.

The bond strength of C-X bond decreases form C-F to C-I in CH_3X.

Increasing order of bond enthalpy.

$CH_3I < CH_3Br < CH_3Cl < CH_3F$

35. What happens when chloroform reacts with oxygen in the presence of sunlight?

Chloroform undergoes oxidation in the presence of light and air to form phosgene (carbonyl chloride).

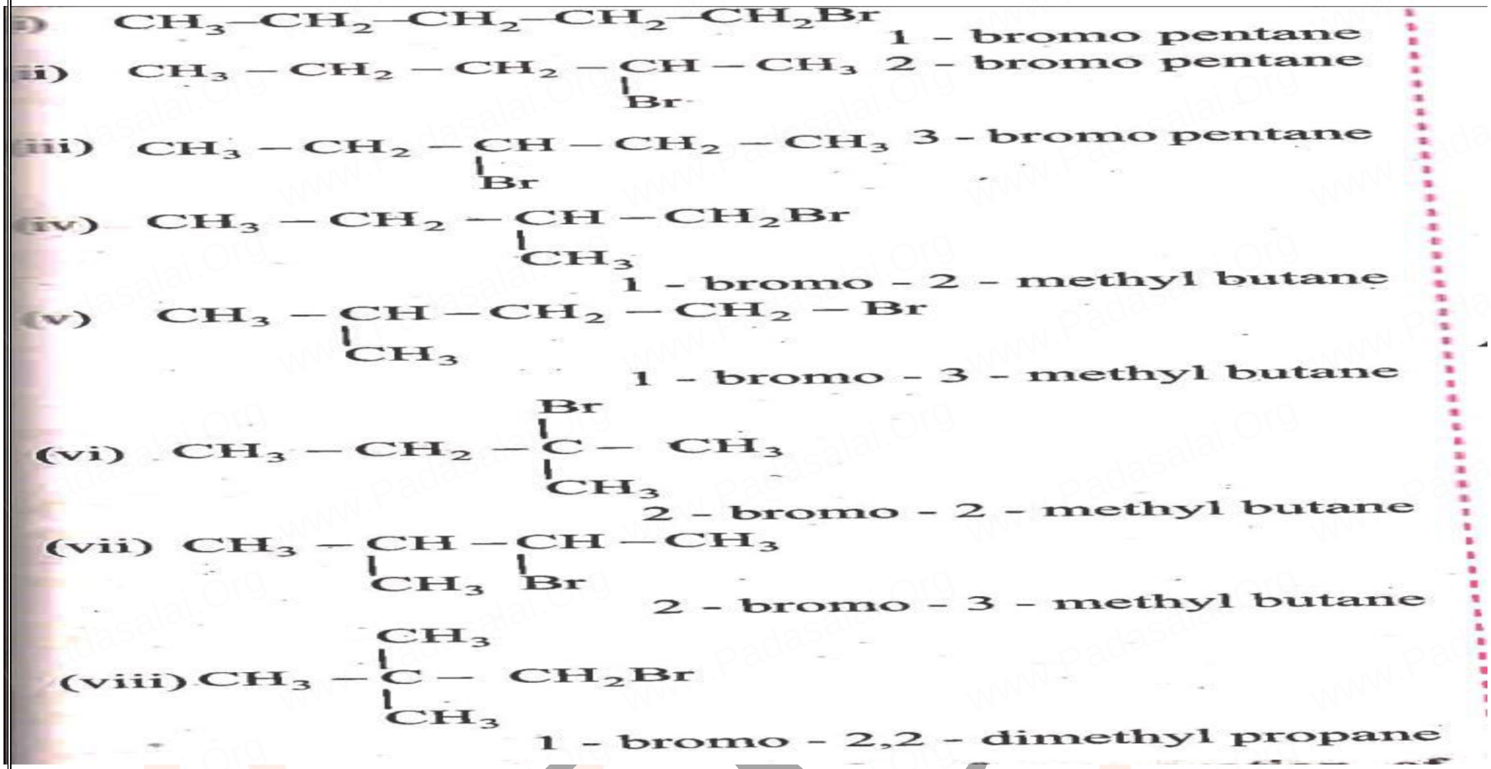
$CHCl_3 + \frac{1}{2} O_2 \xrightarrow{Air/light} COCl_2 + HCl$

Chloroform Phosgene

Since phosgene is very poisonous, its presence makes chloroform unfit for use as **anaesthetic.**

36. Write down the possible isomers of $C_5H_{11}Br$ and give their IUPAC and common names.

All possible isomers of $C_5H_{11}Br$. There are 8 isomers that have the molecule formula $C_5H_{11}Br$.



i) $CH_3-CH_2-CH_2-CH_2-CH_2Br$ 1 - bromo pentane

ii) $CH_3-CH_2-CH_2-\underset{Br}{CH}-CH_3$ 2 - bromo pentane

iii) $CH_3-CH_2-\underset{Br}{CH}-CH_2-CH_3$ 3 - bromo pentane

iv) $CH_3-CH_2-\underset{CH_3}{CH}-CH_2Br$ 1 - bromo - 2 - methyl butane

v) $CH_3-\underset{CH_3}{CH}-CH_2-CH_2-Br$ 1 - bromo - 3 - methyl butane

vi) $CH_3-CH_2-\overset{Br}{\underset{CH_3}{C}}-CH_3$ 2 - bromo - 2 - methyl butane

vii) $CH_3-\underset{CH_3}{CH}-\underset{Br}{CH}-CH_3$ 2 - bromo - 3 - methyl butane

viii) $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2Br$ 1 - bromo - 2,2 - dimethyl propane

37. Mention any three methods of preparation of haloalkanes from alcohols.

- **Reaction with HCl(lucas reagent)**

$$CH_3CH_2OH + HCl \xrightarrow[\Delta]{AnhydrousZnCl2} CH_3CH_2Cl + H_2O$$

Ethanol chloro ethane

- **Reaction with PCl_5**

$$CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + POCl_3 + HCl$$

Ethanol chloro ethane

- **Reaction with $SOCl_2$**

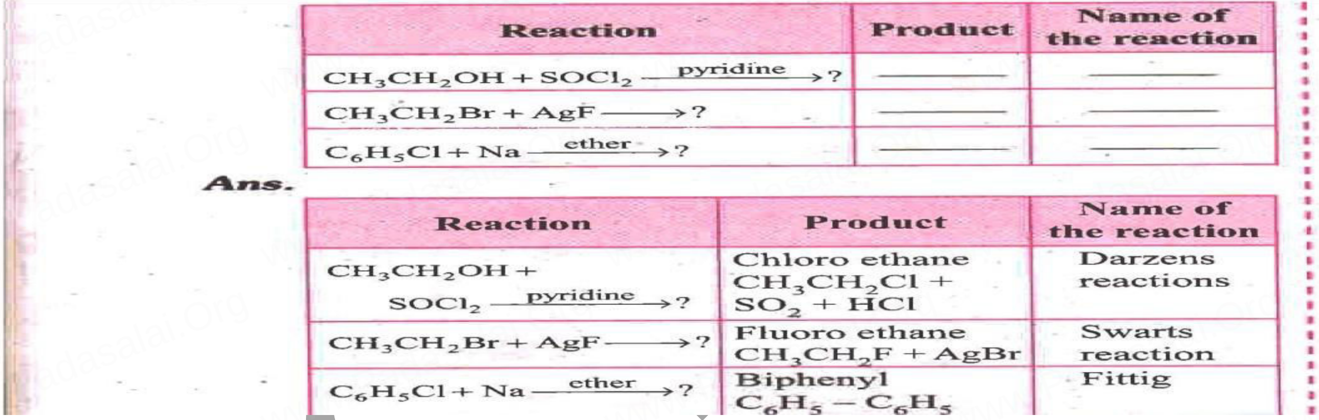
$$CH_3CH_2OH + SOCl_2 \xrightarrow{pyridine} CH_3CH_2Cl + SO_2 + HCl$$

Ethanol chloro ethane

38. Compare SN_1 and SN_2 reaction mechanisms.

SN^1	SN^2
It is **Unimolecular Nucleophilic substitution** reaction.	It is a **bimolecular Nucleophilic substitution** reaction.
Its mechanism occurs in **two steps**.	It is a **one step** process.
It follows **second order** kinetics.	It follows **first order** kinetics.
It involves the **formation of an intermediate.**	It involves the **formation of transition state.**
Rate =k[Alkyl halide]	**Rate =k[Alkyl halide][nuclophile]**
Products have both retained and inverted configuration.	**Products have inverted configuration.**
Carbocation rearrangement occurs.	No carbocation rearrangement occurs
Reactivity: methyl <1°< 2°<3°	**Reactivity:** methyl >1°>2°>3°

39. Reagents and the conditions used in the reactions are given below. Complete the table by writing down the product and the name of the reaction.



Reaction	Product	Name of the reaction
$CH_3CH_2OH + SOCl_2 \xrightarrow{pyridine} ?$	________	________
$CH_3CH_2Br + AgF \longrightarrow ?$	________	________
$C_6H_5Cl + Na \xrightarrow{ether} ?$	________	________

Ans.

Reaction	Product	Name of the reaction
$CH_3CH_2OH + SOCl_2 \xrightarrow{pyridine} ?$	Chloro ethane $CH_3CH_2Cl + SO_2 + HCl$	Darzens reactions
$CH_3CH_2Br + AgF \longrightarrow ?$	Fluoro ethane $CH_3CH_2F + AgBr$	Swarts reaction
$C_6H_5Cl + Na \xrightarrow{ether} ?$	Biphenyl $C_6H_5 - C_6H_5$	Fittig

40. Discuss the aromatic Nucleophilic substitutions reaction of chlorobenzene.

Halo arenes do not undergo nucleophilic substitution reaction readily. This is due to C–X bond in aryl halide is short and strong and also the aromatic ring is a centre of high electron density.

The halogen of haloarenes can be substituted by OH^- , NH_2^-, or CN^- with appropriate nucleophilic reagents at high temperature and pressure.

For Example

$$C_6H_5Cl + NaOH \xrightarrow[300\ atm]{350°C} C_6H_5OH + NaCl$$

Chlorobenzene Pheno1

This reaction is known as **Dow's Process.**

41. Account for the follo following (i) t-butyl chloride reacts with aqueous KOH by SN_1 mechanism while n-butyl chloride reacts with SN_2 mechanism. (ii) p-dichloro benzene has higher melting point than those of o-and m-dichloro benzene.

i) This is because rate of SN_2 reaction is directly proportional to delta inversely proportional to steric crowding. Tert-butyl chloride has vast steric crowding and thus it is more stable for SN_1 reaction rather then SN_2 reaction.

ii)The higher melting point of p-isomer is due to its symmetry which leads to more close packing of its molecules in the crystal lattice and consequently strong intermolecular attractive force which requires more energy for melting.

p –Dihalo benzene > o- Dichloro benzene > m-Dichloro benzene

42. In an experiment ethyl iodide in ether is allowed to stand over magnesium pieces. Magnesium dissolves and product is formed a) Name the product and write the equation for the reaction.

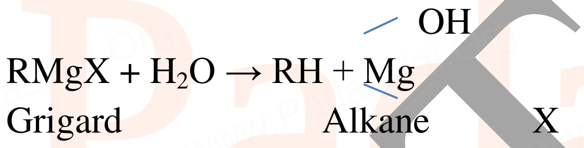
b) Why all the reagents used in the reaction should be dry? Explain

c) How is acetone prepared from the product obtained in the experiment.

a) The product formed is ethyl magnesium iodide.(Grignard reagent)

$$C_2H_5I + Mg \xrightarrow{dry\ ether} C_2H_5MgI$$

b) The Grignard carbon is highly basic and reacts with acidic protons of polar solvents like water to form an alkane so all reagents should be pure and dry.



$$RMgX + H_2O \rightarrow RH + Mg\begin{matrix}OH\\X\end{matrix}$$

Grigard Alkane

43. **Write a chemical reaction useful to prepare the following: i) Freon-12 from Carbon tetrachloride ii) Carbon tetrachloride from carbon disulphide.**

i) Freon – 12 is prepared by the action of hydrogen fluoride on carbon tetrachloride in the presence of catalylic amount of antimony patachloride. This is called **Swartz reaction.**

$$\underset{\text{Carbon Tetrachloride}}{CCl_4} + 2HF \xrightarrow{SbCl5} 2HCl + \underset{\text{Freon - 12}}{CCl_2F_2}$$

ii) Carbon disulphide reacts with chlorine gas in the presence of anhydrous $AlCl_3$ as catalyst giving carbon tetrachloride.

$$\underset{\text{carbon disulphide}}{CS_2} + 3Cl_2 \xrightarrow{anhydrous\ AlCl3} \underset{\text{carbon tetrachloride}}{CCl_4} + S_2Cl_2$$

44. **What are Freons? Discuss their uses and environmental effects**

i) Freons are a used as refrigerants in refrigerators and air conditioners.

(ii) It is used as a propellant for aerosols and foams.

(iii) It is used as propellant for foams to spray out deodorants, shaving creams, and insecticides.

45. Predict the products when bromo ethane is treated with the following i) KNO_2 ii) $AgNO_2$

i) Haloalkanes react with alcoholic solution of $NaNO_2$ or KNO_2 to form alkyl nitrites.

$CH_3CH_2Br + KNO_2 \rightarrow CH_3CH_2–O–N=O+KBr$

Bromoethane Ethyl nitrite

ii) Haloalkanes react with alcoholic solution of $AgNO_2$ to form nitro alkanes.

$CH_3CH_2Br+AgNO_2 \rightarrow CH_3CH_2NO_2+ AgBr$

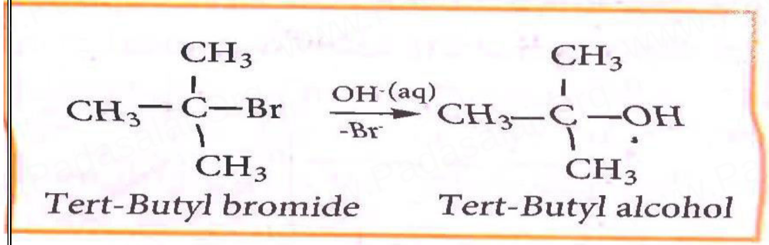
Bromo ethane Nitro ethane

46. **Explain the mechanism of SN_1 reaction by highlighting the stereochemistry behind it.**

S_N1 stands for Unimolecular Nucleophilic Substitution. The rate of the following S_N1 reaction depends upon the concentration of alkyl halide (RX) and is independent of the concentration of the nucleophile (OH^-)

Hence Rate of the reaction = k[alkyl halide]

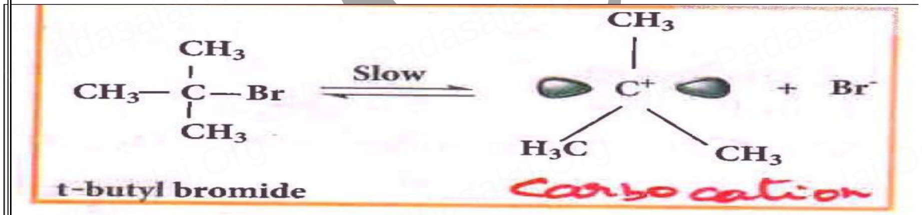
SN1 reaction mechanism by taking a reaction between tertiary butyl bromide with aqueous KOH.



This reaction takes place in two steps as shown below

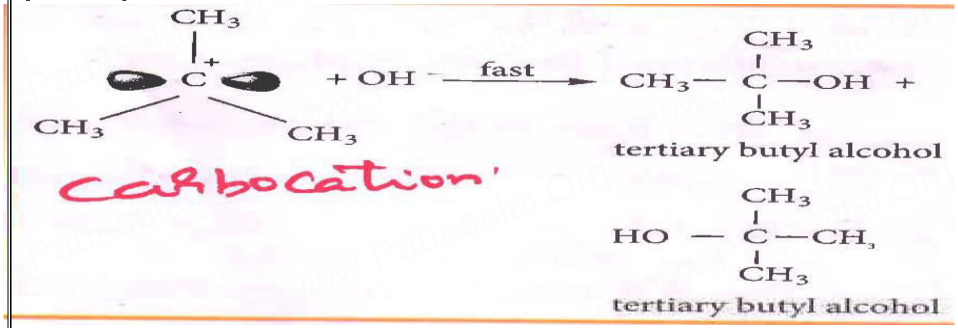
Step - 1 Formation of carbocation

The polar C - Br bond breaks forming a carbocation and bromide ion. This step is slow and hence it is the rate determining step.



The carbocation has 2 equivalent lobes of the vacant 2p orbital, so it can react equally rapidly from either face.

Step – 2 The nucleophile immediately reacts with the carbocation. This step is fast and hence does not affect the rate of the reactions.

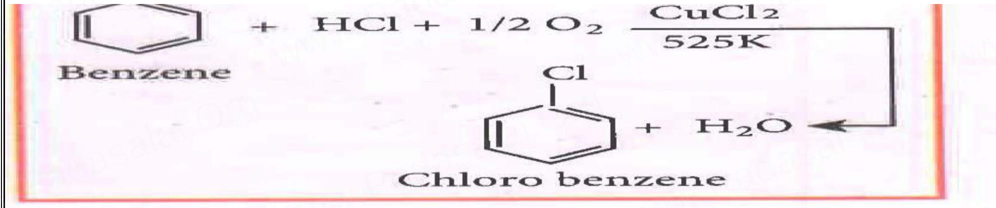


As shown above, the Nucleophilic reagent OH- can attack carbocation from both the sides.

47. Write short notes on the the following

i) Raschig process ii) Dows Process iii) Darzens process

i) **Raschig process**: Chloro benzene is commercially prepared by passing a mixture of benzene vapour, air and HCl over heated cupric chloride .This reaction is called Raschig process.



ii) Dows process:

$$C_6H_5Cl \quad + \quad NaOH \xrightarrow[300\ atm]{350°C} C_6H_5OH + NaCl$$

Chlorobenzene Phenol

This reaction is known as **Dow's Process.**

iii) Darzens process

$$CH_3CH_2OH + SOCl_2 \xrightarrow{pyridine} CH_3CH_2Cl + SO_2 + HCl$$

Ethanol chloro ethane

48. Starting from CH3MgI, How will you prepare the following?

i) Acetic acid ii) Acetone iii) Ethyl acetate iv) Iso propyl alcohol

v) Methyl cyanide

i) **Acetic acid :**Solid carbon dioxide reacts with Grignard reagent to form addition product which on hydrolysis yields carboxylic acids.

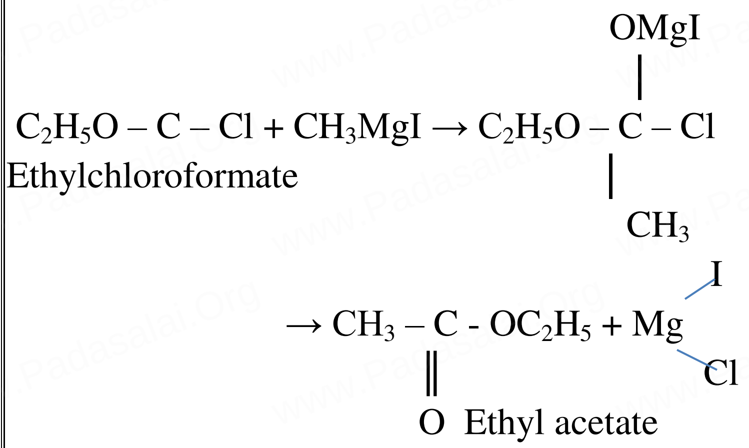
$$O = C = O + CH_3MgI \rightarrow CH_3 - \overset{O}{\overset{\|}{C}}\text{- }OMgI \xrightarrow{H2O\ H+} CH_3 - COOH \quad + Mg(OH)I$$

Acetic acid

ii) Acetone: $CH_3 - I + Mg \xrightarrow{dry\ ether} CH_3MgI$

Iodomethane Methyl magnesium iodide

ii) Ethyl acetate: Ethyl chloro formate reacts with Grignard reagent to form esters.

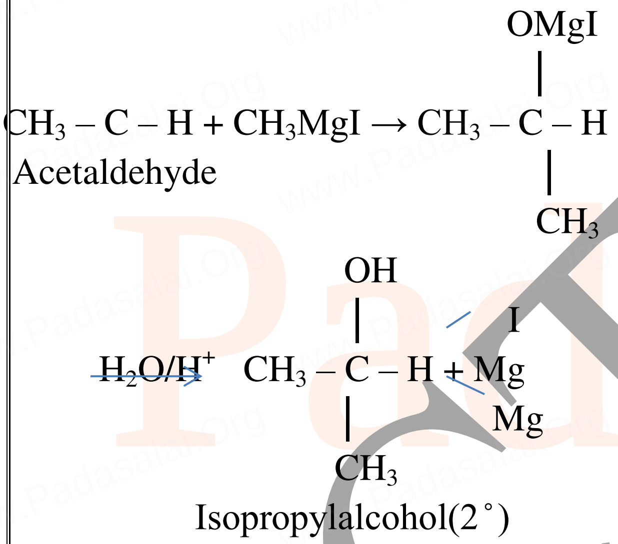


$$C_2H_5O-C-Cl + CH_3MgI \rightarrow C_2H_5O-\overset{OMgI}{\underset{CH_3}{C}}-Cl \rightarrow CH_3-\underset{O}{\overset{}{\underset{\parallel}{C}}}-OC_2H_5 + Mg\begin{smallmatrix}I\\Cl\end{smallmatrix}$$

Ethylchloroformate

Ethyl acetate

iv) Iso propyl alcohol : Aldehydes other than formaldehyde, react with Grignard reagent to give addition product which on hydrolysis yields secondary alcohol.

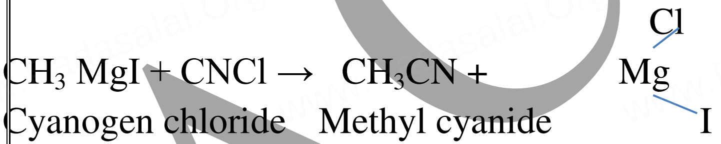


$$CH_3-C-H + CH_3MgI \rightarrow CH_3-\overset{OMgI}{\underset{CH_3}{C}}-H \xrightarrow{H_2O/H^+} CH_3-\overset{OH}{\underset{CH_3}{C}}-H + Mg\begin{smallmatrix}I\\Mg\end{smallmatrix}$$

Acetaldehyde

Isopropylalcohol(2°)

v) Methyl cyanide : Grignard reagent reacts with cyanogen chloride to form alkyl cynide



$$CH_3\,MgI + CNCl \rightarrow CH_3CN + Mg\begin{smallmatrix}Cl\\I\end{smallmatrix}$$

Cyanogen chloride Methyl cyanide

49. Complete the following reactions

) $CH_3 - CH = CH_2 + HBr \xrightarrow{Peroxide}$

i) $CH_3 - CH_2 - Br + NaSH \xrightarrow{alcohol}$

H_2O

ii) $C_6H_5Cl + Mg \xrightarrow{} THF$ iv) $CHCl_3 + HNO_3\ \Delta$ v) $CCl_4 + H_2O\ \Delta$

) The addition of HBr to an alkene in the presence of organic peroxide, gives the anti Markovniko's product. Is effect is called peroxide effect.

$$CH_3 - CH = CH_2 + HBr \xrightarrow[(C_6H_5CO)_2O_2]{Peroxide} CH_3 - CH_2 - CH_2 - Br$$

Propene **1- bromopropane**

i) Haloalkanes react with sodium or potassium hydrogen sulphide to form thio alcohols.

$CH_3 - CH_2 - Br + NaSH \xrightarrow{alcohol} CH_3CH_2SH + NaBr$

Bromo ethane H_2O Δ Ethane thiol

ii) Chloroform reacts with nitric acid to form chloropicrin. (Trichloro nitro methane) Δ

$CHCl_3 + HNO_3 \rightarrow CCl_3NO_2 + H_2O$

Chloroform Chloropicrin

v) Carbon tetrachloride reacts with hot water or with hot water vapour producing the poisonous gas, phosgene.

$CCl_4 + H_2O(g) \xrightarrow{\Delta} COCl_2 + 2H_2O$

Carbon tetrachloride Phosgene

50. Explain the preparation of the following compounds

) DDT ii) Chloroform iii) Biphenyl iv) Chloropicrin v) Freon-12

) DDT: DDT can be prepared by heating a mixture of chlorobenzene with chloral (Trichloro acetaldehyde) in the presence of con.H2SO4.

i)Chloroform : The reaction of methane with excess of chlorine in the presence of sunlight will give carbon tetrachloride as the major product.

$CH_4 + 4Cl_2 \xrightarrow{h\gamma}$ **CCl4 +** 4HCl

Methane carbon tetrachloride

ii) Biphenyl:

$C_6H_5Cl + 2Na + Cl - C_6H_5 \xrightarrow[\Delta]{Ether} C_6H_5 - C_6H_5 + 2NaCl$

Chlorobenzene Bipheyl

v) Chloropicrin: Chloroform reacts with nitric acid to form chloropicrin.(Trichloro nitro methane)

$CHCl_3 + HNO_3 \xrightarrow{\Delta} CCl_3NO_2 + H_2O$

Chloroform Chloropicrin

) Freon-12: Freon-12 is prepared by the action of hydrogen fluoride on carbon tetrachloride in the presence of catalylic amount of antimony pentachloride. It is called Swartz reaction.

$CCl_4 + 2HF \xrightarrow{SbCl_5} 2HCl + CCl_2F_2$

Carbon tetrachloride Freon - 12

51. An organic compound (A) with molecular formula C_2H_5Cl reacts with KOH gives compounds (B) and with alcoholic KOH gives compound (C). Identify (A), (B), and (C)

$CH_3CH_2Cl + KOH_{(Aq)} \rightarrow CH_3CH_2OH$

(A) (B)

Chloroethane Ethanol

\+

Alc KOH A CH_3CH_2Cl Chloroethane

↓ B CH_3CH_2OH Ethanol

$CH_2 = CH_2$ C $CH_2 = CH_2$ Ethene

(C)

Ethene

52. Simplest alkene (A) reacts with HCl to form compound (B).Compound (B) reacts with ammonia to form compound (C) of molecular formula C_2H_7N.Compound (C) undergoes carbylamine test. Identify (A), (B), and (C).

$CH_2 = CH_2 + HCl \rightarrow CH_3 - CH_2Cl$

(A) (B)

Ethene Chloroethane

$CH_3CH_2Cl + NH_3 \rightarrow CH_3CH_2NH_2$

(B) (C)

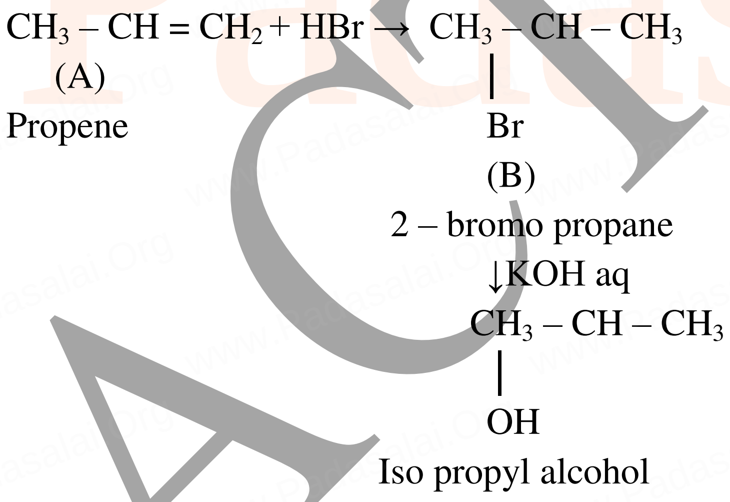
Chloroethane Ethyl amine

A $CH_2 = CH_2$ Ethene

B CH_3CH_2Cl Chloroethane

C $CH_3CH_2NH_2$ Ethylamine

53. A hydrocarbon C_3H_6 (A) reacts with HBr to form compound (B). Compound (B) reacts with aqueous potassium hydroxide to give (C) of molecular formula C_3H_6O.what are (A) (B) and (C). Explain the reactions.



$CH_3 - CH = CH_2 + HBr \rightarrow CH_3 - CH(Br) - CH_3$

(A) Propene

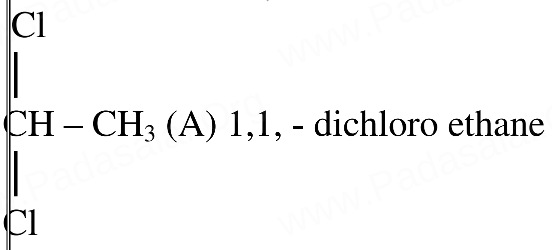
(B) 2 – bromo propane

↓KOH aq

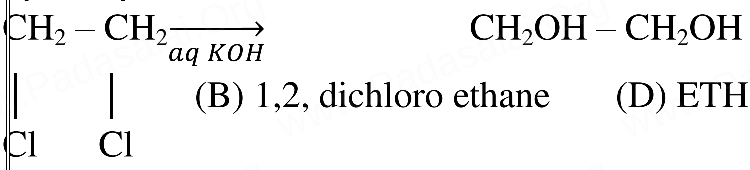
$CH_3 - CH(OH) - CH_3$

Iso propyl alcohol

54. Two isomers (A) and (B) have the same molecular formula $C_2H_4C_{l2}$.Compound (A) reacts with aqueous KOH gives compound (C) of molecular formula C_2H_4O.Compound (B) reacts with aqueous KOH gives compound (D) of molecular formula $C_2H_6O_2$

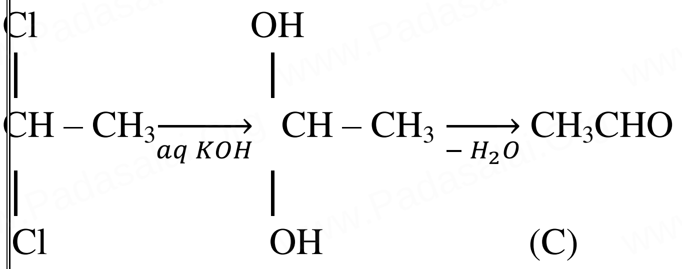


$CHCl_2 - CH_3$ (A) 1,1, - dichloro ethane



$$\underset{Cl}{\underset{|}{CH_2}} - \underset{Cl}{\underset{|}{CH_2}} \xrightarrow[aq\ KOH]{} CH_2OH - CH_2OH$$

(B) 1,2, dichloro ethane (D) ETHYLENE GLYCOL

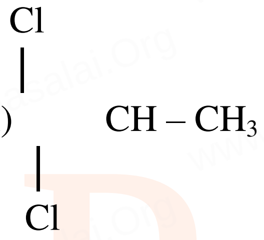


$$\overset{Cl}{\overset{|}{\underset{Cl}{\underset{|}{CH}}}} - CH_3 \xrightarrow[aq\ KOH]{} \overset{OH}{\overset{|}{\underset{OH}{\underset{|}{CH}}}} - CH_3 \xrightarrow[-H_2O]{} CH_3CHO$$

(C)

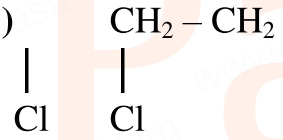
(A) Acetaldhyde

1,1, - dichloro ethane



$$\overset{Cl}{\overset{|}{\underset{Cl}{\underset{|}{CH}}}} - CH_3$$

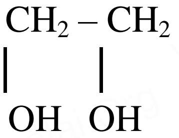
(A) - 1,1, - dichloro ethane



$$\underset{Cl}{\underset{|}{CH_2}} - \underset{Cl}{\underset{|}{CH_2}}$$

(B) - 1,2, dichloro ethane

(C) CH_3CHO - Acetaldhyde



$$\underset{OH}{\underset{|}{CH_2}} - \underset{OH}{\underset{|}{CH_2}}$$

(D) - Ethyleneglycol

18. Dissolved oxygen in water is responsible for aquatic life. What processes are responsible for the reduction in dissolved oxygen in water?

- The oxygen is dissolved in water either from atmosphere or by photosynthesis, however at night, there is no photosynthesis, so amount of oxygen dissolved in water reduces.

- Thus, water contains only a limited amount of dissolved oxygen.
- Thus, the decomposition of a moderate amount of organic matter by aerobic bacteria can make water deficient in dissolved oxygen.

19. What would happen, if the greenhouse gases were totally missing in the earth's atmosphere?

In the absence of greenhouse gases, the average temperature of earth will decrease drastically earth average temperature would be bear of on earth would be impossible .

20. Define smog.

Smog is a combination of smoke and fog which forms droplets that remain suspended in the air.

21. Which is considered to be earth's protective umbrella? Why?

- **Ozone layer** in the upper atmosphere is considered to be earth's protective umbrella.
- It protects us from harmful effect such as skin cancer.
- UV radiation can convert molecular oxygen into ozone as shown in the following reaction.

$$O_{2(g)} \xrightarrow{UV} O_{(g)} + O_{(g)}$$

$$O(g) + O_{2(g)} \xrightarrow{UV} O_{3(g)}$$

The ozone layer acts as a fitter for the shorten wavelength and highly hazardous ultraviolet radiation from the sun, protecting life on earth.

22. What are degradable and non-degradable pollutants?

Bio-degradable pollutants: The pollutants which can be easily decomposed by the natural biological processes are called bio-degradable pollutants. ***Examples:*** plant wastes, animal wastes….

Non- degradable pollutants:

The pollutants which cannot be decomposed by the natural biological processes are called Non bio-degradable pollutants.

Examples: metal wastes (mainly Hg and Pb), D.D.T, plastic, nuclear wastes etc.

23. From where does ozone come in the photo chemical smog?

In the **earth's lower atmosphere** ozone is formed when pollutants emitted by cars, power plants, industrial boilers, refineries etc chemically react in the presence of sunlight. It is formed by reaction between oxides of nitrogen and volatile organic compounds. (Or)

$$NO_2 \xrightarrow{Sun\ light} NO + (O)$$

O_3 are strong oxidizing agent and can react with unburnt hydrocarbons in polluted air to form formaldehyde, acrolein and peroxy acetyl nitrate(PAN).

24. A person was using water supplied by corporation. Due to shortage of water he started using underground water. He felt laxative effect. What could be the cause?

Excessive concentration (> 500ppm) of sulphates in drinking water causes laxative effect.

25. What is green chemistry?

Green chemistry means science of environmentally favorable chemical synthesis. Green chemistry is a chemical philosophy encouraging the design of products and processes that reduce or eliminate the use and generation of hazardous substances.

26. Explain how does green house effect cause global warming

Greenhouse effect may be defined as "the heating up of the earth surface due to trapping of infrared radiations reflected by earth's surface by CO_2 layer in the in the atmosphere". The heating up of earth through the greenhouse effect is called global warming.

27. Mention the standards prescribed by BIS for quality of drinking water

Standard characteristics prescribed for deciding the quality of drinking water by BIS

S.No	Characteristics	Desirable limit
I	**Physico-chemical Characteristics**	
i)	P^H	6.5 to 8.5
ii)	Total Dissolved Solids(TDS)	500 ppm
iii)	Total Hardness (as $CaCO_3$)	300 ppm
iv)	Nitrate	45ppm
v)	Chloride	250 ppm
vi)	Sulphate	200 ppm
vii)	Fluoride	1 ppm
II	**Biological Characteristics**	
i)	Escherichia Coli (E.Coli)	Not at all
ii)	Coliforms	Not to exceed 10 (In 100 ml water sample)

28. How does classical smog differ from photochemical smog?

No	Classical smog (London smog)	Photochemical smog (Los Angel smog)
1.	It occurs in cool humid climate.	It occurs in warm and dry climate.
2.	It consists of **coal smoke and fog.** The Chemical composition in the mixture of SO_2, SO_3 and humidity.	It is formed by the combination of **smoke, fog, dust and air pollutants** like oxides of nitrogen and hydrocarbons in the presence of sunlight.
3.	It is reducing in nature due to high concentration SO_2 and called **reducing smog.**	It is oxidizing in nature due to high concentration of oxidizing agents like NO_2 and O_3 and is called **oxidizing smog** .
4.	Classical smog is responsible for acid rain and causes bronchial irritation.	Photo chemical smog causes irritation of eyes skin and lungs, increase in chances of asthma.

29. What are particulate pollutants? Explain any three.

Particulate pollutants are small solid particles and liquid droplets suspended in air.

(i) Smoke:

Smoke particulate consists of solid particles (or) mixture of solid and liquid particles formed by combustion of organic matter. **For example**, cigarette smoke, oil smoke, smokes from burning of fossil fuel, garbage and dry leaves.

(ii) Dust :

Dustcomposed of fine solid particles produced during crushing and grinding of solid materials. **For example**, sand from sand blasting, saw dust from wood works, cement dust from cement factories and fly ash from power generating units.

(iii) Mists:

They are formed by particles of spray liquids and condensation of vapours in air. **For example**, sulphuric acid mist, herbicides and insecticides sprays can form mists.

30. Even though the use of pesticides increases the crop production, they adversely affect the living organisms. Explain the function and the adverse effects of the pesticides.

Pesticides are the chemicals that are used to kill or stop the growth of unwanted organisms. But these pesticides can affect the health of human beings.

These are further classified as

- **Insecticides:**

It like DDT, BHC, aldrin etc., can stay in soil for long period of time and are absorbed by soil. They contaminate root crops like carrot, raddish etc.,

- **Fungicide:** Organo mercury compounds are used as most common fungicide. They dissociate in soil to produce mercury which is highly toxic.
- **Herbicides:** Herbicides are the chemical compounds used to control unwanted plants. They are otherwise known as weed killers.

31. Ethane burns completely in air to give CO_2, while in a limited supply of air gives CO. The same gases are found in automobile exhaust. Both CO and CO_2 are atmospheric pollutants i) What is the danger associated with these gases

ii) How do the pollutants affect the human body?

(i)What is the danger associated with these gases

(a) Carbon monoxide:

Carbon monoxide is a poisonous gas produced as a result of incomplete combustion of coal are firewood. It is released into the air mainly by automobile exhaust. It binds with haemoglobin and form carboxy haemoglobin which impairs normal oxygen transport by blood and hence the oxygen carrying capacity of blood is reduced. This oxygen deficiency results in headache, dizziness, tension, Loss of consciousness, blurring of eye sight and cardiac arrest.

(b) Carbon dioxide:

Carbon dioxide is released into the atmosphere mainly by the process of respiration, burning of fossil fuels, forest fire, decomposition of limestone in cement industry etc.

Green plants can convert CO_2 gas in the atmosphere into carbohydrate and oxygen through a process called photosynthesis. The increased CO_2 level in the atmosphere is responsible for global warming. It causes headache and nausea.

i) a) How do the pollutants affect the human body?

i) Particulate pollutants bigger than 5 microns are likely to settle in the nasal passage whereas particles of about 10 micron enters the lungs easily and causes scaring or fibrosis of lung lining. They irritate the lungs and causes cancer and asthma

ii) Lead particulates affect children's brain, interferes maturation of RBCs and even cause cancer

iii) Acid rain causes respiratory ailment in humans and animals.

iv) Hydrocarbons are potential cancer causing (carcinogenic) agents

v) The increased CO_2 level in the atmosphere causes headache and nausea

vi) Carbon monoxide reduces the oxygen carrying capacity of blood. This oxygen deficiency results in headache, dizziness, tension, Loss of consciousness, blurring of eye sight and cardiac arrest.

b) Harmful effects of water pollutants:

i) Cadmium and mercury can cause kidney damage .

i) Lead poisoning can leads to the severe damage of kidneys, liver, brain etc.It also effects central nervous system

iii) Polychlorinated biphenyls (PCBs) causes skin diseases and are carcinogenic in nature.

Harmful effects of soil pollutants:

Pesticides used in soil for food cultivation can affect the health of human beings.

32. On the basis of chemical reactions involved, explain how do CFC's cause depletion of ozone layer in stratosphere?

In the presence of uv radiation, CFC's break up into chlorine free radical

$CF_2\,Cl_2 \xrightarrow{h\upsilon} CF_2\,Cl + Cl$

$CF\,Cl_3 \xrightarrow{h\upsilon} CFCl_2 + Cl$

$Cl^{\circ} + O_3 \rightarrow ClO + O_2$

$ClO^{\circ} + O \rightarrow Cl + O_2$

Chlorine radical is regenerated in the course of reaction. Due to this continuous attack of Cl° thinning of ozone layer takes place which leads to formation of ozone hole.

33. How is acid rain formed? Explain its effect.

Burning of fossil fuels (coal and oil) in power stations, furnaces and petrol, diesel in motor engines produce sulphur dioxide and nitrogen oxides. The main contributors of acid rain are SO_2 and NO_2. They are converted into sulphuric acid and nitric acid respectively by the reaction with oxygen and water.

$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$

$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$

The pH of rain water drops to 5:6 and hence its is called acid rain

Harmful effects of acid rain:

i. Acid rain causes extensive damage to buildings and structural materials of marbles. This attack on marble is termed as Stone leprosy. $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2\uparrow$

ii. Acid rain affects plants and animal life in aquatic ecosystem.

iii. It is harmful for agriculture, trees and plants as it dissolves and removes the nutrients needed for their growth.
iv. It corrodes water pipes resulting in the leaching of heavy metals such as iron, lead and copper into the drinking water which have toxic effects.
v. It causes respiratory ailment in humans and animals.

34. Differentiate the following (i) BOD and COD (ii) Viable and non-viable particulate pollutants

(i) BOD and COD: BOD: The total amount of oxygen in milligrams consumed by microorganisms in decomposing the waste in one litre of water at 20° C for a period of 5 days is called biochemical oxygen demand (BOD) and its value is expressed in ppm.

Chemical oxygen demand (COD) is defined as the amount of oxygen required by the organic matter in a sample of water for its oxidation by a strong oxidizing agent like $K_2Cr_2O_7$ in acid medium for a period of 2 hrs.

(ii) Viable and non-viable particulate pollutants

The viable particulates are the small size living organisms such as bacteria, fungi, moulds, algae, etc. Which are dispersed in air.

The non-viable particulates are small solid particles and liquid droplets suspended in air.

Example: Smoke, dust, mists, fumes etc

35. Explain how oxygen deficiency is caused by carbon monoxide in our blood? Give its effect

Carbon monoxide is a poisonous gas produced as a result of incomplete combustion of coal are firewood. It is released into the air mainly by automobile exhaust. It binds with hemoglobin and form carboxy hemoglobin which impairs normal oxygen transport by blood and hence the oxygen carrying capacity of blood is reduced. This oxygen deficiency results in headache, dizziness, tension, loss of consciousness, blurring of eye sight and cardiac arrest.

36. What are the various methods you suggest to protect our environment from pollution?

Strategies to control environment pollution.

1. Waste Management : Environmental pollution can be controlled by proper disposal of wastes.
2. Recycling reused by recycling the waste material can be reused by recycling the waste, thus it reduces the land fill and converts waste into useful forms.
3. Substitution of less toxic solvents for highly toxic ones used in certain industrial processes.
4. Use of fuels with lower sulphur content (e.g., washed coal)
5. Growing more trees.
6. Control measures in vehicle emissions are adequate.

ALL THE BEST

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