COURSE STRUCTURE

Class XI (Theory)

One Paper	Time : 3 Hours	70 Marks
Unit No.	**Title**	**Marks**
Unit I	Some Basic Concepts of Chemistry	5
Unit II	Structure of Atom	6
Unit III	Classification of Elements and Periodicity in Properties	4
Unit IV	Chemical Bonding and Molecular Structure	5
Unit V	States of Matter : Gases and Liquids	4
Unit VI	Thermodynamics	6
Unit VII	Equilibrium	6
Unit VIII	Redox Reactions	3
Unit IX	Hydrogen	3
Unit X	s-Block Elements	5
Unit XI	Some p-Block Elements	5
Unit XII	Organic Chemisty : Some Basic Principles and Techniques	7
Unit XIII	Hydrocarbons	8
Unit XIV	Environmental Chemistry	3
Total		**70**

The question paper will include value based question(s) of 4 marks.

SOME BASIC CONCEPTS OF CHEMISTRY

Law of conservation of mass : 'Mass can neither be created nor destroyed.' In all physical and chemical changes, the total mass of reactants is equal to that of products.

Law of constant composition : A chemical compound is always found to be made of same elements combined together in the same fixed ratio by mass.

Law of multiple proportion : Two elements combined together to form two or more chemical compounds then the masses of the elements which combine with a fixed mass of another bear a simple ratio to one another.

Gram atomic mass or molar mass of an element is mass of 1 mol of atoms or atomic mass expressed in grams. For example, atomic mass of $Ag = 108$ u, therefore, molar mass of Ag is 108 grams per mol. Molar mass of an element is also called one gram atom.

Gram molecular mass or the molar mass of molecular substances is the mass of 1 mol of molecules or molecular mass expressed is grams. For example, molecular mass of CO_2 in 44 u, therefore, molar mass of CO_2 is 44 grams/mol.

Molar mass of ionic substance is the mass of 1 mol of formula units of ionic substance.

Molar mass and standard molar volume of gaseous substances :

1 mole of any gas occupies a volume of 22.4 L at STP, *i.e.,* at 298 K and 1 atm. If standard pressure is taken as 1 bar, then the standard molar volume is taken as 22.7 L.

$$\text{Molarity (M)} = \frac{W_B \times 1000}{M_B \times V_{mL}}$$

$$\text{Molality } (m) = \frac{W_B \times 1000}{M_B \times W_A}$$

For binary solutions : Mole fraction (X_B) of solute $= \dfrac{n_B}{n_A + n_B}$

$$X_A = 1 - X_B$$

where X_A = mole fraction of solvent,
X_B = mol fraction of solute
W_A = mass of solvent
W_B = Mass of solute
M_B = Molar mass of solute
V_{mL} = Volume of solution in mL

Dilution Formula : $M_1V_1 = M_2V_2$

Where : M_1 = Molarity of concentrated solution

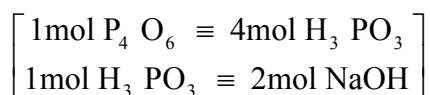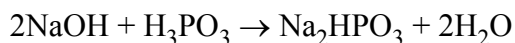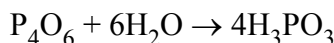V_1 = Volume of concentrated solution

M_2 = Molarity of dilute solution

V_2 = Volume of dilute solution

For a general chemical equation : $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$

Molarity relationship is : $\text{mol of B} = \text{mol of A} \times \dfrac{b \text{ mol of B}}{a \text{ mol of A}}$

Example : Calculate the volume of 0.1 M NaOH solution required to neutralise the solution produced by dissolving 1.1 g of P_4O_6 in water.

Solution :
$$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$$
$$2NaOH + H_3PO_3 \rightarrow Na_2HPO_3 + 2H_2O$$

$$\begin{bmatrix} 1\text{mol } P_4 O_6 \equiv 4\text{mol } H_3 PO_3 \\ 1\text{mol } H_3 PO_3 \equiv 2\text{mol NaOH} \end{bmatrix}$$

$$\text{mol of } P_4O_6 = 1.1g \; P_4O_6 \times \dfrac{1 \text{ mol } P_4O_6}{220g \; P_4O_6} = 0.5 \times 10^{-2} \text{mol } P_4O_6$$

$$\text{mol of NaOH} = 0.5 \times 10^{-2} \text{mol } P_4O_6 \times \dfrac{4 \text{ mol } H_3PO_3}{1 \text{ mol } P_4O_6} \times \dfrac{2 \text{ mol NaOH}}{1 \text{ mol } H_3PO_3}$$

$$= 4 \times 10^{-2} \text{ mol NaOH}$$

$$\because \text{Volume of NaOH solution in litres} = 4 \times 10^{-2} \text{mol NaOH} \times \dfrac{1 \text{ L NaOH solution}}{0.1 \text{ mol NaOH}}$$

$$= 4 \times 10^{-1} \text{ L} = 0.4 \text{ L}$$

1- MARK QUESTIONS

1. Why can't solids be compressed ?
2. Liquids take the shape of the container in which they are placed. Why ?
3. Give two examples of a homogeneous mixture.
4. Calculate the number of molecules present in 100.0 g of water.
5. Calculate the number of moles of oxygen atoms present in 22.0 g CO_2.
6. Write the SI unit of temperature.
7. Define law of multiple proportions.

8. N_2 and H_2 combine according to the following equation :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
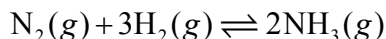
If 100 mL of N_2 gas combines with 300 mL of N_2 gas, calculate the volume of NH_3 produced at same temperature and pressure.

9. Out of 1 M NaCl solution and 1 m NaCl solution, which one is more concentrated ?

10. Write the S.I. unit of Avogadro constant.

11. How much CO_2 is produced when 6.0 g C is burnt in excess oxygen ?

12. Molarity is temperature dependent but molality is not. Why?

13. How many moles of HCl are present in 100 ml of 12 M HCl solution ?
Ans : 1.2 mol

14. Calculate the mole fraction of N_2 when 28 g N_2 is mixed with 64 g O_2 gas.
Ans. : 0.50

15. A water sample has 20.0 ppm (by mass) Cl_2 present in it. Calculate the quantity of Cl_2 present in 100 ml water. (Density of water = 1.0 g ml$^{-1.}$)

16. Calculate the number of electrons in 17.0 g NH_3.

17. Calculate the number of atoms present in 64.0 u helium.

18 If the density of 68% nitric acid solution is 1.41 g mL, calculate the mass of HNO_3 present in 1.0 L solution.

19. Express the strength of 0.5 M Na_2CO_3 solution in grams per litre.

20. Balance the following equation :

$$Mg + N_2 \rightarrow Mg_3N_2$$

21. Calculate the number of g-atoms of sulphur (S_8) in 8.0 g sample.

22. Calculate the mass of NaOH required to make 250 mL of $\dfrac{M}{20}$ solution.

23. Which of the following has highest mass ?
(a) 32 g O_2 gas   (b) 2 g atom of Cl_2
(c) 0.5 mol Fe   (d) 9.03×10^{23} atoms of C

24. How many moles of methane are required to produce 22.0 g CO_2 in combustion reaction ?

2 - MARK QUESTIONS

1. Calculate the mass percentage of Na and Cl atoms in common salt. (Given molar mass NaCl = 58.5 g/mol)

2. How many significant figures are present in ?
(a) 126000   (b) 126.0

3. How much CO_2 is produced when 1.0 mol of carbon is burnt in 16.0 g oxygen ?

4. 0.5 mol each of H_2S and SO_2 are mixed together in a reaction flask in which the following reaction takes place :

$$2H_2S (g) + SO_2 (g) \rightarrow 2H_2O (l) + 3S (s)$$

Calculate the number of moles of sulphur formed.

5. Pure oxygen is prepared by thermal decomposition of $KClO_3$ according to the equation :

$$KClO_3(s) \xrightarrow{\Delta} KCl(s) + \frac{3}{2}O_2(g)$$
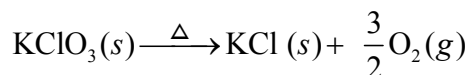
Calculate the volume of oxygen gas liberated at STP by heating 12.25 g $KClO_3(s)$.

6. Classify the following as pure substance or mixture ?
(a) Ethyl alcohol   (b) Blood
(c) 22 carat gold   (d) Air

7. How many significant figures are present in the answer of following calculations :

(a) $0.0125 + 0.7864 - 0.023$ (b) $\dfrac{0.025 \times 298.15 \times 0.1155}{0.5785}$

8. Which of the following samples has the largest number of atoms :
(a) 1.0 g $H_2(g)$ (b) 1.0 g $Na(s)$
(c) 1.0 g $CH_3OH(l)$ (d) 1.0 g $Br_2(l)$

9. Determine the molecular formula of an oxide of iron in which the mass percent of iron and oxygen are 69.9 and 30.1 respectively. Molar mass of this oxide is 170.0 g mol^{-1}.   **[Ans. : Fe_2O_3]**

10. The density of 3 M solution of NaCl is 1.25 g mL^{-1}. Calculate molality of solution. (Molar mass of NaCl is 58.5 g mol^{-1}).

11. Calculate the molarity of an aqueous solution of methanol in which the mole fraction of ethanol is 0.040. Assume the density of water to be 1.0 g mL^{-1}.   **[Ans. : 2.31 M]**

12. How many grams of HCl react with 5.0 g MnO_2 according to the equation :

$$4HCl(aq) + MnO_2(s) \rightarrow 2H_2O(l) + MnCl_2(aq) + Cl_2(g)$$

[Ans. : 8.40 g]

13. How are 0.5 mol Na_2CO_3 and 0.5 M Na_2CO_3 are different from each other?

14. If mass of air at sea level is 1034 g cm^{-2}, calculate the pressure in pascal. (Given $g = 9.8$ ms^{-2}, 1 Pa = 1 Nm^{-2})   **[Ans. : 1.01332×10^5 Pa]**

15. A polluted water sample has been found ($CHCl_3$) to have 15 ppm $CHCl_3$ in it.
(a) Express this value in percent by mass.
(b) Determine the molality of chloroform ($CHCl_3$) in the water sample.
Ans. :   (a) $= \sim 15 \times 10^{-4}$ g   (b) $= 1.25 \times 10^{-4}$ g

16. Use the following data to calculate the molar mass of naturally occurring argon :

Isotope	Isotopic molar mass	Abundance
^{36}Ar	35.96755 g mol^{-1}	0.337%
^{38}Ar	37.96272 g mol^{-1}	0.063%
^{40}Ar	35.9624 g mol^{-1}	99.600%

[Ans.: 39.948 g/mol]

17. If the speed of light is 3.0×10 ms^{-1}, calculate the distance covered by light in 2.00 ns. [**Ans.:** 0.600 m]

18. State the law of definite proportions. Explain it with the help of an example.

19. Burning a sample of a hydrocarbon gas gives 3.38 g CO_2 and 0.690 g H_2O. A volume of 10L (measured at STP) of this hydrocarbon weighs 11.6 g. Calculate the molecular formula of this hydrocarbon. [**Ans.:** $C_2 H_2$]

20. In three moles of ethane (C_2H_6), Calculate the following :
(i) Number of moles of carbon atoms
(ii) Number of moles of Hydrogen atoms
(iii) Number of Molecules of ethane

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3 - MARK QUESTIONS

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1. (a) State and explain Avogadro's law. Illustrate it with an example.
(b) 10.0 L of a welding gas weighs 11.6 g at STP. Calculate the molar mass of this gas. [**Ans.:** 26.0 g/mol]

2. (a) Calculate the mass of $CaCO_3$ required to react completely with 25mL of 0.75 M HCl. [**Ans.:** 0.938 g]
(b) Calculate volume of CO_2 released at STP in this reaction. [**Ans.:** 0.21 L]

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

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

(a) Calculate the mass of ammonia gas formed if 2.0 kg of nitrogen gas reacts with 1.0 kg of hydrogen gas.
(b) Which of the two reactants is the limiting reagent and why ?
(c) Which of the two reactants will remain unreacted and what will be the amount left unreacted ? [Ans.: m (NH_3) = 2.571 kg, H_2 will remain unreacted its mass is 571.5 g]

4. (a) Calculate the molarity of solution prepared by dissolving 175.5 g NaCl in enough water to form 1.0 L of brine solution.
(b) Calculate molality of solution if its density is 1.25 g ml^{-1}.
(c) Calculate the mole fraction of NaCl.

5. Calculate the number of atoms in :
(a) 5.0 L oxygen gas at STP   (b) 4.4 g of CO_2
(c) 52 u of He

6. Calculate the number of moles :
   (a) 05. L of 0.75 M Na_2CO_3 (b) 7.85 g iron
   (c) 34.2 g sucrose ($C_{12}H_{22}O_{11}$)
7. A compound contains 4.07% hydrogen, 24.27% carbon and 71.65% chlorine. Its molar mass is 98.96 g. Determine its empirical and molecular formulas.
8. In a reaction $A + B_2 \longrightarrow AB_2$
   Identify the limiting reagent, if any in the following reaction mixtures
   (i) 300 atom of A + 200 molecules of B_2
   (ii) 2 mole of A + 3 mol of B_2
   (iii) 100 atom of A + 100 molecules of B_2
9. Calculate the mass of Na which contain the same number of atom as are present in 4 gram of calcium

$$\boxed{\text{5 - MARK QUESTIONS}}$$

1. (a) Write the difference between a homogenous and a heterogeneous mixture.
   (b) State Gay Lussac's Law of gaseous volumes.
   (c) Calculate the volume of 0.1 M NaOH solution is required to neutralise 100 mL of concentrated aqueous sulphuric acid which contains 98% H_2SO_4 by mass. The density of conc. H_2SO_4 is 1.84 g/mL.
   NaOH reacts with H_2SO_4 according to the following equation :
   $$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$
   (At. mass/g mol^{-1} H = 1, S = 32, O = 16)
2. (a) How much Cu can be obtained from 100 g $CuSO_4$?
   (b) Boron occurs in nature in the form of two isotopes $^{11}_{5}B$ and $^{10}_{5}B$ in ratio 81% and 19% respectively. Calculate its average atomic mass.
   (c) If the density of methanol is 0.793 kg L^{-1}, what is its volume needed for making 2.5 L of its 0.25 L of 0.25 M solution ?
3. (a) Define molality of a solution. How is it different from molarity ?
   (b) Calculate the Molality of a solution of ethanol in water in which the mole fraction of ethanol is 0.040 (assume the density of water to be one).

<center>┌─────────┐
│ UNIT-2 │
└─────────┘</center>

STRUCTURE OF ATOM

- Atom is the smallest indivisible particle of the matter. Atom is made of electron, proton and neutrons.

	ELECTRON	PROTON	NEUTRON
Discovery	Sir. J. J. Thomson (1869)	Goldstein (1886)	Chadwick (1932)
Nature of charge	Negative	Positive	Neutral
Amount of charge	1.6×10^{-19} Coloumb	1.6×10^{-19} Coloumb	–
Mass	9.11×10^{-31} kg	1.672614×10^{-27} kg	1.67492×10^{-27} kg

- Nucleus was discovered by Rutherford in 1911.
- Atomic number (Z) : the number of protons present in the nucleus (Moseley 1913).
- **Mass Number (A) :** Sum of the number of protons and neutrons present in the nucleus.
- Wavelength, frequency and wave velocity are related to each other by

$$c = v\lambda$$

where c = velocity in light = 3.0×10^{-8} m/s

v = frequency of s^{-1} or Hz

λ = wavelength in metres

- Wave number $(\bar{v})$ is the reciprocal of wavelength $\left(\bar{v} = \dfrac{1}{\lambda}\right)$.

- According to Planck's quantum theory, the energy is emitted or absorbed not continuously but discontinuously in the form of energy packets called quanta. A quantum of light is called photon. The energy of a quantum is E = hv, where h = Planck's constant, v = frequency of radiation.
- The line spectrum of hydrogen consists of Lyman Series (in UV region), Balmer series (visible region), Paschen, Brackett and Pfund series (IR region).

  The wave number of lines can be calculated by the following relation :

$$\bar{v} = R_H \left(\frac{1}{n_1^{\ 2}} - \frac{1}{n_2^{\ 2}} \right)$$

R = Rydberg's constant = 109677 cm^{-1}

For, Lyman series : $n_1 = 1, n_2 = 2, 3, 4, \ldots\ldots$

Balmer series : $n_1 = 2, n_2 = 3, 4, 5, \ldots\ldots$

Paschen series : $n_1 = 3$ and $n_2 = 4, 5, 6 \ldots\ldots$

Brackett series : $n_1 = 4$ and $n_2 = 5, 6, 7, ...$
Pfund series : $n_1 = 5$ and $n_2 = 6, 7, 8, ...$

- The energy of electron in hydrogen atom is given by :

$$E_n = -\frac{2\pi^2 m Z^2 e^4}{n^2 h^2}$$

M = mass of electron, e = charge on electron, Z = atomic number of element

- For hydrogen atom, energy of electron in n^{th} orbit is :

$$E_n = \frac{-1.312 \times 10^6 Z^2}{n^2} \text{Jmol}^{-1} = \frac{-2.178 \times 10^{-18} Z^2}{n^2} \text{Jatom}^{-1} = \frac{-13.60 Z^2 eV}{n^2} \text{atom}^{-1}$$

where Z = atomic number of H or hydrogen like ions.

- The lowest energy state of an electron in atom is called ground state ($n = 1$), when an electron absorb energy, it jumps to higher energy level called excited state, (first excited state $n = 2$ for H).

- The energy absorbed or emitted during electronic transition is given by the difference of the energies of two levels, *i.e.,*

$$E_2 - E_1 = -2.18 \times 10^{-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ J/atom such that } n_2 > n_1.$$

- The radius of the nth orbit is given by $r_n = \frac{(0.529\text{Å}) n^2}{z}$.

- **Photoelectric effect :** When radiation with certain minimum frequency (v_0), called threshold frequency, strike the surface of a metal, electrons (called photoelectrons) are ejected from the surface. With this frequency, the kinetic energy of the photoelectrons ejected is zero. However, if the incident radiation having frequency $v > v_0$, the difference of energy ($hv - hv_0$) is

  converted into kinetic energy of the photoelectrons *i.e.,* $\frac{1}{2} mv^2 = hv - hv_0$.

  The minimum energy hv_0 required for emission of photoelectrons is called **threshold energy** or **work function.** No photoelectric effect is shown if incident frequency is less than v_0 even if intensity of a radiation is increased. However, number of photoelectrons ejected is proportional to the intensity of incident radiation.

- According to **de Broglie concept,** all material particles (microscopic as well as macroscopic) possess wave character as well as particle character. The wave associated with a material particle is called de Broglie wave or matter wave.
  The relationship between the wavelength (λ) of the wave and the mass (m)

of the material particle moving with a velocity ν is called **de Broglie equation**. It is given by

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

where h is Planck's constant and p is momentum of the particle.

The wave nature of electron has been confirmed by **Davisson and Germer's experiment** whereas the particle nature is confirmed by **scintillation method** as well as by the **photoelectric effect**.

- **Heisenberg's uncertainty Principle** states that "It is impossible to measure simultaneously the position and momentum of a microscopic particle with absolute accuracy. If one of them is measured with greater accuracy, the other becomes less accurate. The product of their uncertainties is always equal to or greater than $\frac{h}{4\pi}$."

Mathematically $\quad \Delta x \times \Delta p \geq \frac{h}{4\pi}$

where $\qquad\qquad \Delta x$ = uncertainty in position,

$\qquad\qquad\qquad \Delta p$ = uncertainty in momentum

de Broglie concept as well as uncertainty principle have no significance in everyday life because they have significance only for microscopic particles but we come across macroscopic bodies in everyday life.

- **Quantum numbers**

The four quantum numbers provide the following informations :

(1) **Principal quantum number (n)**

$\qquad\qquad n = 1, 2, 3, 4, ...\infty$

It identifies shell, determines sizes and energy of orbitals and number of orbitals in the nth shell which is equal to n^2.

(2) **Azimuthal quantum number (l)**

For a given value of n, it can have n values ranging from 0 to $n - 1$. It identifies subshell, determines the shape of orbitals, energy of orbitals in multi-electron atoms along with principal quantum number and orbital angular momentum, *i.e.,* $\sqrt{l(l+1)}\,\frac{h}{2\pi}$. The number of orbitals in a subshell $= 2l + 1$.

Subshell notation	s	p	d	f	g
Value of 'l'	0	1	2	3	4
Number of orbitals	1	3	5	7	9

(3) **Magnetic orbital quantum number (m_l)**
For a given value of 'l', m_l has a total of ($2l + 1$) values ranging from $-l$ to $+l$ including '0'. It determines the orientation of orbital.

(4) **Magnetic spin quantum number (m_s)**
It can take the values of $+\frac{1}{2}$ or $-\frac{1}{2}$ and determines the orientation of spin.

- **Pauli's Exclusion Principle :** "No two electrons in an atom can have the same set of four quantum numbers." Two electrons can have same values for n, l and m_l provided their spins are opposite (m_s is different). Therefore an orbital can have at the most two electrons if they have opposite spins.

- **Hund's Rule of maximum Multiplicity :** "The electrons start pairing only when all the degenerate orbitals of a subshell are singly occupied with parallel spins." *e.g.,* N : $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$.

- **Aufbau Principle :** "Orbitals are filled up in increasing order of their energy with the help of pauli principle and Hund's rule."
1. Orbitals are filled up in the increasing order of their ($n + 1$) values.
2. If two orbitals have same ($n + 1$) values, then the one which has lower n value, will be filled up first.

Increasing order of energy :
$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s$

Exception of Aufbau principle : Extra stability is associated with the exactly half-filled and fully-filled orbitals. Thus the $p^3, p^6, d^5, d^{10}, f^7, f^{14}$ etc. have extra stability, *i.e.,* lower energy and therefore, more stable.

1 - MARK QUESTIONS

1. Indicate the number of electrons, protons and neutrons in the element $^{238}_{92}$U.
   [**Ans.** $e = 92, p = 92, n = 146$]

2. Name the experiment used in determination of the charge of an electron.

3. Arrange the electron (e), protons (p) and alpha particle (α) in the increasing order for the values of e/m (charge/mass). [**Ans.** $\alpha < p < e$]

4. Calculate the mass of one mole of electron. [Given : $m_e = 9.11 \times 10^{-31}$ kg]
   [**Ans.** 0.55 mg]

5. Write the dimensions of Planck's constant. Mention some other physical quantity, which has the same dimension.

6. Name the element which was discovered in the sun by spectroscopic method.
   [**Ans.** Helium (He)]

7. Which of the following will not show deflection from the path on passing through an electric field,

Proton, Cathode rays, Anode rays, Electron, Neutron.

[**Hint :** Neutron (n) will not show deflection since it is electrically neutral]

8. Out of electron and proton, which one will have a higher velocity to produce matter waves of the same wavelength ?

   [**Hint :** $\lambda = \dfrac{h}{mv}$, For same wavelength, m_e is very small as compared to m_p.

   Therefore v_e will be higher as compared to v_p.]

9. An anion A^{3-} has 18 electrons. Write the atomic number of A.   [**Ans.** 15]

10. What is the value of orbital angular momentum of $6s$ orbital ?

11. What physical meaning is attributed to the square of the absolute value of wave function $|\Psi^2|$?

12. Name two physical quantities which can be estimated by principal quantum number (n).

13. Which shell would be the first to have g-subshell ?

14. How many electrons in an atom can have $n + l = 6$?   [**Ans.** 18]

15. Name three quantum numbers which arise as a result of the solution of Schrodinger wave equation.

16. Write electronic configuration of the Cr^{3+} ion. [Atomic number of Cr = 24]

17. The ion of an element has configuration $[Ar]3d^4$ in +3 oxidation state. Write the electronic configuration of its atom.

18. State Pauli's exclusion principle.

19. How many nodes are there in $3s$ orbital ?   [**Ans.** 2 nodes]

20. Why $1p$, $2d$ and $3f$ subshells are not possible ?

21. How many unpaired electrons are present in Fe^{3+} ion ?

22. State Hunds rule of maximum multiplicity.

23. Using s, p, d notations, describe the orbital with the following quantum numbers :

    (a) $n = 4, l = 2$ (b) $n = 1, l = 0$ [**Ans.** (a) $4d$ (b) $1s$]

24. Which quantum number determines the orientation of atomic orbital ?

25. Which orbital is non-directional ?

26. Write the correct set of four quantum numbers for the valence electron (outermost electron) of potassium (Z = 19).

27. Which principle is not obeyed in writing of electronic configuration :

↑		↑↓	↑	↑

　　2s　　　　　2p
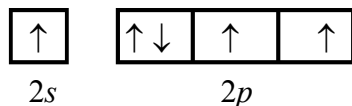
2- MARK QUESTIONS

1. Give examples of each of the following :

(a) Isotope of $^{35}_{17}Cl$ (b) Isobar of $^{40}_{18}Ar$

(c) Isotone of $^{15}_{7}N$ (d) Isoelectronic species of S^{2-}

[Ans. (a) $^{37}_{17}Cl$ (b) $^{40}_{20}Ca$ (c) $^{16}_{8}O$ (d) K^+, Ca^{2+}, Ar, Cl^-, S^{2-} **]**

2. Describe the cathode ray experiment. How will you detect the spot where the rays strike ?

3. Outline Rutherford's contribution to understand the nucleus of an atom.

4. Calculate the percentage of higher isotope of neon which has average atomic mass 20.2 and the isotopes have the mass numbers 20 and 22.

[Ans. 10% $^{22}_{10}Ne$ **]**

5. Account for the following :

(a) Cathode rays are produced only when the pressure of the gas inside the discharge tube is very very low.

(b) Can a thin foil of aluminium be used in place of gold (Au) in Ruther ford experiment ? Give suitable explanation.

[Hint : Lighter nuclei cannot exhibit proper deflection of α-particles.]

6. Distinguish between an atomic emission spectrum and an atomic absorption spectrum.

7. The energies of electrons are said to be quantized. Explain.

8.   A laser used to read compact disc (CD) emits red light of wavelength 700 nm. How many photons does it emit each second if its power is 1 W ?

[Ans. 3.5×10^{18} s^{-1}**]**

9. Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-1}.

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

11. Explain, giving reasons, which of the following sets of quantum numbers are not possible :

(a) $n = 0$ $l = 0$ $m_l = 0$ $m_s = +\frac{1}{2}$

(b) $n = 1$ $l = 0$ $m_l = 0$ $m_s = -\frac{1}{2}$

(c) $n = 1$ $l = 1$ $m_l = 0$ $m_s = +\frac{1}{2}$

(d) $n = 3$ $l = 1$ $m_l = 0$ $m_s = 0$

12. Calculate the energy required for the process $He^+ (g) \rightarrow He^{2+} (g) + e^-$

The ionisation energy for the H atom in the ground state is 2.18×10^{-18} J atom^{-1}.

[**Ans.** 8.72×10^{-18} J]

13. (a) An atomic orbital has $n = 3$. Write the possible values of l and m_l ?

(b) List the quantum numbers (m_l and l) of electrons for $3d$ orbital.

14. Draw the boundary surface diagrams of d_{xy} and $d_{x^2-y^2}$ orbitals.

15. What is meant by degenerate orbitals ? Illustrate with the help of one example.

16. How does a $1s$ orbital differ from a $2s$ orbital ? Mention two points in support of your answer.

17. Calculate the wave number for the shortest wavelength transition in the Balmer series of atomic hydrogen. [**Ans.** 27419.25 cm^{-1}]

18. Calculate (a) wave number and (b) frequency of yellow radiation having wavelength 5800Å.

$$\begin{pmatrix} \bar{v} = 1.724 \times 10^4 \text{ cm}^{-1} \\ v = 5.172 \times 10^{14}5 \text{ s}^{-1} \end{pmatrix}$$

19. Calculate the energy associated with the first orbit of He^+. What is the radius of this orbit. [**Ans. :** $E_1 - 8.72 \times 10^{-18}$ J, r = 0.2645 nm]

20. Nitrogen laser produces a radiation at a wavelength of 337.1 nm. If the number of photons emitted is 5.6×10^{24}, calculated the power of this laser.

[**Ans.** (3.3×10^6)]

21. 2×10^8 atoms of carbon at arranged side by side. Calculate the radius of carbon atom if the length of this arrangements is 2.4 cm. [**Ans.** 0.06 nm]

22. In milikan's experiment, static electric charge on the oil drops has been obtained by shining X-rays. If the statis electric charge on the oil drop is -1.282×10^{-18} C, calculate the number of electrons present on it [**Ans.** 8]

23. An ion with mass number 56 contains 3 units of positive charge and 30.4% more neutions than electron. Assign the symbol of this ion

24. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum.

$$\boxed{\text{3 - MARK QUESTIONS}}$$

1. Differentiate between :
(a) Photon and quantum
(b) Orbit and orbital
(c) de Broglie waves and electromagnetic waves

2. (a) State Heisenberg uncertainty principle.
(b) ''Electron cannot exist within the atomic nucleus.'' Justify the statement on the basis of Heisenberg uncertainty principle.
[**Hint :** Radius of nucleus = 10^{-15}m]

3. Calculate the wavelength of an electron that has been accelerated in aparticle accelerator through a potential difference of 1keV. [1 eV = 1.6×10^{-19} J]
[**Ans.** 3.87×10^{-7} m]

4. The kinetic energy of a subatomic particle is 5.86×10^{-25} J. Calculate the frequency of the particle wave. [**Ans.** 1.76×109 s^{-1}]

5. Calculate the energy required to excite the electron in the atom from $n = 1$ to $n = 2$. The ionization enthalpy of hydrogen atom is 1.312×10^6 J mol^{-1}.

6. Calculate and compare the products of uncertainty in position and uncertainty in velocity for a milligram-sized object and that of an electron ($m_e = 9.11 \times 10^{-31}$ kg). What conclusion would you draw from result ?

7. The electron energy in hydrogen atom is given by $E_n = (-2.18 \times 10^{-18})/n^2$ J. Calculate the energy required to remove an electron completely from the $n = 2$ orbit. Calculate the longest wavelength of light in cm that can be used to cause this transition.

8. How many series are found in the spectrum of atomic hydrogen ? Mention their names and the regions in which they appear.

9. (a) Write the electronic configurations of the followings :
(i) H$^-$ (ii) Na+ (iii) O^{2-}

(b) Symbols $_{35}^{79}Br$ and ^{79}Br can be written, whereas symbols $_{35}^{79}Br$ and ^{35}Br are not acceptable. Explain why ?

(c) An ion with mass number 37 possesses one unit of negative charge. If the ion contains 11.1% more neutrons than the electrons. Assign the symbol of this ion.

5 - MARK QUESTIONS

1. (a) Define photoelectric effect ? Mention its one practical application in daily life.

    (b) Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800 Å. Calculate threshold frequency (v_0) and work function (W_0) of the metal.

    [**Ans.** 4.41×10^{14} s^{-1}, 2.91×10^{-19} J]

2. (a) State de Broglie relation. Why it is not meaningful for a moving cricket ball ?

    (b) Which out of (i) electron (e), (ii) proton (p) (iii) α particle, has maximum de Broglie's wavelength ? [Assume that all are moving with the same velocity.]

    (c) The wavelength associated with particle 'A' is 5×10^{-8} m. Calculate the wavelength associated with particle B, if its momentum is half of A.

    [**Ans.** 1×10^{-7} m]

3. (a) What is the significance of the statement "Product of uncertainty in position and momentum is always constant." ?

    (b) Why is uncertainty principle not applicable to macroscopic and semimicro particles ?

    (c) An electron has a speed of 40 ms^{-1} accurate upto 99.99%. What is the uncertainty in locating its position ? $(m_e = 9.11 \times 10^{-31}$ kg)

    [**Ans.** 1.45×10^{-2} m]

4. (a) State Aufbau principle.

    (b) What is the physical significance of lines in the following depiction of atomic orbital ?
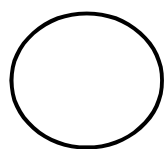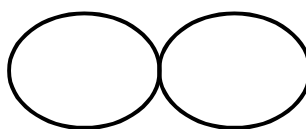
s-orbital   p-orbital

    (c) Explain the following with suitable reason :

(i) In potassium, the 19th electron enters in $4s$ subshell instead of $3d$ subshell.

(ii) Chromium has configuration $3d^5\,4s^1$ and not $3d^4\,4s^2$.

(iii) The three electrons present in $2p$ subshell of nitrogen (N) remain unpaired and have the parallel spins.

5. (a) The work function for caesium atom is 1.9 ev. Calculate (i) the threshold wave length and (ii) the threshold frequency of the radiation. If the caesium element is irradiated with a radiation of wave length 500 nm, calculatethe kinetic energy and the velocity of the ejected photo electron

    (i)   652 nm

    (ii) 4.598×10^{14} S^{-1}

    (iii) 3.97×10^{-13} J, 9.33×10^8 m S^{-1}

(b) Among the following pairs of orbitals, which orbital will experience the larger effective nuclear charge

    (i)   2s and 3s

    (ii)   3d and 3p

<div align="center">

UNIT-3

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

</div>

Moseley, the English physicist showed that atomic number is more fundamental property of an element than its atomic mass. Therefore, the position of an element in the periodic table depends on its atomic number.

Modern periodic laws : The physical and chemical properties of elements are the periodic functions of their atomic numbers.

Types of Elements : *s-, p-, d-* **and** *f-* **blocks :**

*s-***block elements :** Group 1 (alkali metals) and group 2 elements (alkaline earth metals) which respectively have ns^1 and ns^2 outermost electronic configurations.

*p-***block elements** belong to groups 13 to 18. The outermost electronic configuration is $ns^2\,np^{1-6}$. He ($1s^2$) is a *s*-block element but is positioned with the group 18 elements ($ns^2\,np^6$) because it has completely filled valence shell and as a result, exhibits properties characteristic of other noble gases.

*d-***block elements** (Transition elements) are the elements of group 3 to 12 having outer electronic configuration $(n-1)d^{1-10}\,ns^{1-2}$. Four transition series are $3d, 4d, 5d$ and $6d$. $6d$-series is incomplete. Atomic radius generally decreases across a period and increases as we descend the group.

A cation is smaller but the anion is larger than the parent atom. In case of isoelectronic species, the cation with greater positive charge has smaller radius but anion with greater negative charge has the larger radius.

Ionization enthalpy $(\Delta_i H)$ is the enthalpy change for the reaction : $X_{(g)} \rightarrow X^+{}_{(g)} + e^-$

Second ionization enthalpy $(\Delta_i H_2)$ is more than the first ionization enthalpy $(\Delta_i H_1)$.

$$\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3 < \text{...........}$$

For the elements of second period, the correct order of increasing ionization enthalpy $(\Delta_i H)$ is :

$\Delta_i H_1$: Li < B < Be < C < O < N < F < Ne ; $X(g) \rightarrow X(g)^+ + e^-$

For the elements of third period, the correct increasing order of ionization enthalpy is :
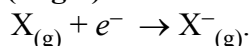
$$\Delta_i H_1 : \text{Na} < \text{Al} < \text{Mg} < \text{Si} < \text{S} < \text{P} < \text{Cl} < \text{Ar}$$

For the group 1 elements, the ionization enthalpy decreases in the order :

$$Li > Na > K > Rb > Cs$$

Ionization enthalpy and atomic radius are closely related properties depending upon the attraction of electrons towards the nucleus and repulsion of electrons from each other.

Electron gain enthalpy (ΔegH) is the enthalpy change for the reaction :
$$X_{(g)} + e^- \rightarrow X^-_{(g)}.$$

Δeg H for N atom is zero. All the elements except noble gases, have negative values of Δeg H whereas noble gases have positive values of Δeg H.

f-block Elements (Inner-transition Series)

Lanthanoides characterised by the filling of 4*f* orbitals, are the elements following lanthanum from $_{58}$Ce to $_{71}$Lu. Actinoides characterised by the filling of 5*f* orbitals, are the elements following actinium from $_{70}$Th to $_{103}$Lr. Characteristic outer electronic configuration is $(n - 2)f^{1-14} (n - 1)d^{0-1} ns^2$.

Cause of periodicity in the properties of elements is the periodic repetition of similar electronic configuration of elements as the atomic number increases. Regular variation in physical and chemical properties are observed as we descend the group and move across a period from left to right in the periodic table.

Trend in Δ egH : Electron gain enthalpy generally becomes more negative across a period as we move right to left and within a group becomes less negative down the group.

Exceptions : P, S, Cl have more negative ΔegH than N, O, F respectively.

Second electron gain enthalpy of an atom is always positive.

Electronegativity (EN) : It is the qualitative measure of an atom in a chemical compound to attract the shared electrons to itself.

The most widely used scale is Pauling scale which is based on bond energy data. By giving a reference value of 2.1 to H, the maximum electronegativity value of 4 is assigned to F.

Screening effect – Decrease in the force of attraction exerted by the nucleus on the valency electrons due to the presence of electrons in the inner shells, is called screening effect or shielding effect.

Effective nuclear charge denoted by Z^* is given as

$$= \text{Nuclear Charge} - \text{Shielding effect}$$

The magnitude of effective nuclear charge increases in a period when we move from left wright but decreases down the group.

Anomalous Properties of Second Period Elements

Each element of second period, *i.e.,* first element of each of group 1 and 2 and groups 13-17 shows many properties which are not shown by its cogeners. Their anomalous behaviour is attributed to their small size, large charge/radius ratio, high electronegativity, non-availability of *d*-orbitals in their valence shell. Thus the first member of each group has only four valence orbitals (one 2*s* and three 2*p* orbitals) for bonding, whereas the second member of the group has nine valence orbitals (one 3*s*, three 3*p* and five 3*d* orbitals). As a consequence of this, maximum covalency of first member of each group is limited to '4', whereas the other members of the group can expand their valence shell to accommodate more than four pairs of electrons. For example, B from $[BF_4]^-$ and Al, $[AlF_6]^{3-}$. In addition to this, the first member of each group of *p*-block elements displays greater ability to form *p*π-*p*π multiple bonds to itself (e.g. $C = C$, $C \equiv C$, $N = N$, $N \equiv N$, $O = O$) and to other second period elements (*e.g.,* $C = O$, $C = N$, $C \equiv N$, $N = O$) compared to subsequent members of the group.

1 - MARK QUESTIONS

1. Name the scientist who gave birth to the periodic table.
2. Name the property used by Mendeleev to classify the elements in his periodic table ?
3. State the Modern Periodic Law.
4. How many groups and periods are there in the long form of the periodic table ?
5. Write the IUPAC name and symbol for the element with atomic number 119.
6. How does ionization enthalpy vary in a group and in a period?
7. Arrange B, C, N, O elements in increasing order of electron gain enthalpy.
8. Write the electronic configuration of the element having atomic number 21.
9. Explain the term electron gain enthalpy.
10. Out of K and K^+, which one would have larger size ?
11. Arrange the following elements in the increasing order of metallic character:

    B, Al, Mg, K

12. Predict the position of the elements in the periodic table having the electronic configuration :

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

13. Among the elements of the second period Li to Ne, pick out the element :

(a) having the highest first ionization enthalpy.

(b) having the highest electronegativity.

14. The first ($\Delta_i H_1$) and the second ($\Delta_i H_2$) ionization enthalpies (kJ mol^{-1}) of the three elements are given below :

	I	II	III
$\Delta_i H_1$	403	549	1142
$\Delta_i H_2$	2640	1060	2080

Identify the element which is likely to be :

(a) a non-metal.

(b) an alkaline earth metal.

<div align="right">[Ans. II − alkaline earth metal, III − non-metal]</div>

15. Predict the formulae of the stable binary compounds that would be formed by the following pairs of elements :

(a) Aluminium and Bromine   (b) Element (Z = 120) and Oxygen

16. The following species are isoelectronic with noble gas Argon :

<div align="center">Ar, K$^+$, S^{2-}, Cl$^-$, Ca^{2+}</div>
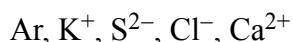
Arrange them in order of increasing size.

[**Hint :** Greater the nuclear charge, smaller is the size.)

17. The ionic radius of F - is 136pm whereas the atomic radius of F is only 64 pm. Explain why ?

[**Hint :** Size of an anion is larger than the parent atom]

18. Write the general electronic configuration of *f*-block elements.

19. Consider the elements N, P, O and S and arrange them in the order of increasing negative electron gain enthalpy.

20. Show by chemical reaction with water that K_2O is a basic oxide.

21. Elements A, B, C and D have the following electronic configurations :

A : $1s^2, 2s^2 2p^1$ B : $1s^2, 2s^2 2p^6, 3s^2 3p^1$

C : $1s^2, 2s^2 2p^6, 3s^2 3p^3$ D : $1s^2, 2s^2 2p^6, 3s^2 3p^5$

Which among these will belong to the same group in the periodic table ?

22. Predict the position of element in the periodic table having the electronic configuration $(n-1) d^1 ns^2$ for n = 4.

2 - MARK QUESTIONS

1. (a) State Newland's law of octaves.
   (b) Write two anomalies of Mendeleev's periodic table.

2. Name the groups of elements classified as *s-, p-, d-* and *f-*blocks in the modern periodic table.

3. How are Li and Mg related to each other in the periodic table ? Write the name of another pair having such a relationship.

4. (a) Name the first and last member of the *3d* series.

   (b) To which block (*s-, p-, d-* or *f-*) does the element with atomic number 50 belong ?

5. The ionization enthalpy per mole of atomic hydrogen is 1.313×10^6 J. Calculate the energy of the electron in the ground state of the hydrogen atom.

   [**Hint :** I.E./atom $= \dfrac{1.313 \times 10^6 \text{ J mol}^{-1}}{6.023 \times 10^{23} \text{ mol}^{-1}} = 2.18 \times 10^{-18}$ J

   I. E. $= E_{\infty} - E_1$]   [**Ans.** $E_1 = -2.18 \times 10^{-18}$ J]

6. An element belong to third period of *p*-block elements. It has four electrons in the outermost shell. Predict its group. How many unpaired electrons are present in an atom of that element ?

7. Write the atomic number and electronic configuration of the elements of fourth period which has maximum number of unpaired electrons ?

8. Why do the periodic properties such as ionization enthalpy, electron gain enthalpy and electronegativity shows a decreasing trend down the group but an increasing trend along a period ? Explain your answer.

9. Identify the elements having the following description and write their electronic configuration also :

   (a) Group 14, period 3

   (b) Group 18, period 2

   (c) Group 1, period 6   [**Ans.** (a) Si, (b) Ne, (c) Cs]

10. On the basis of quantum numbers, justify that fifth period of the periodic table should have eighteen elements.

11. Lanthanoids and actinoids are placed in separate rows at the bottom of the periodic table. Explain the reason for this arrangement.

12. The electronic configuration of three elements are given below :

$P = 1s^2, 2s^2 . 2p_x^1 . 2p_y^1$

$Q = 1s^2, 2s^2 . 2p_x^2 2p_y^1 2p_z^1$

$Q = 1s^2, 2s^2 . 2p_x^1 2p_y^1 2p_z^1$
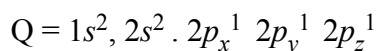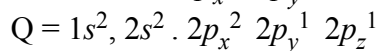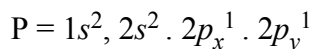
(a) Which element has the highest electron gain enthalpy ?

(b) Which element has the lowest electron gain enthalpy ?

13. The element with atomic number 120 has not yet been discovered. In which group would you place this element ? Write its electronic configuration also.

14. Write the formulae of the oxides formed by sodium and chlorine and by means of their chemical reaction with water. Classify them as acidic or basic oxide.

15. Arrange the following species as stated, giving reasons :

(a) Increasing order of electronegativity (H, F, Cl)

(b) Increasing order of ionic size : N^{3-}, Na^+, F^-, O^{2-}, Mg^{2+}

16. Write the oxidation state and covalency of Al in $[AlCl(H_2O)_5]^{2+}$.

17. Explain why cations are smaller than corresponding anions.

18. Why noble gases have largest atomic radii in their respective periods.

19. Which of the following will have the most negative electron gain enthalpy and which the least negative ?

P, S, Cl, F

Explain your answer.

20. Why is ionisation enthalpy of Boron

(B) less than that of Beryllium (Be) and of oxygen.

(O) is less than that of Nitrogen (N)?

<div align="center">

3 - MARK QUESTIONS

</div>

1. (a) Name the scientist who discovered that atomic number is the more fundamental periodic property of an element than its atomic mass.

(b) Mention three main features of the modern periodic table.

2. The diagram given below is a part of the periodic table. Study the table and answer the questions that follow :

1																	
3	4 Be											5	6	7	8 O	9	10
11	12											13	14 Si	15	16 S	17	18
19	20 Ca	21	22	23	24 Cr	25	26	27	28	29	30	31	32	33	34	35	36 kr

(a) (i) Name a transition metal.

(ii) Name an element whose oxide has very low melting point.

(b) How many atoms of element 35 can combine with an element having atomic number 20 ? Write the formula of the compound.

(c) Name the element which is gaseous at room temperature.

3. Among the elements X, Y and Z with atomic numbers 9, 12 and 36 respectively, identify an element which is :

(a) highly electropositive

(b) highly electronegative

(c) a noble gas

Give reason (s) for your choice.

4. (a) Define electronegativity.

(b) Explain the following :

(i) LiF is less ionic than CsF.

(ii) Li salts are predominantly covalent while Na salts are predominantly ionic.

5. Justify the following statements :

(a) There are only fourteen lanthanoids and only fourteen actinoids.

(b) There are 2, 8 and 8 elements in I, II and III period of the periodic table respectively.

(c) $3d$, $4d$ and $5d$ series consists of ten elements each.

6. Two elements P and Q have atomic numbers 16 and 19 respectively.

(a) Write the group numbers to which the elements belong to.

(b) Name the element which is a powerful reducing agent.

(c) Write the formula of the compound formed between P and Q.

7. Account for the following :

(a) Transition metals are less electropositive than group 1 and 2 metals.

(b) In group 13, Boron forms $[BF_4]^-$ whereas Aluminium forms $[AlF_6]^{3-}$.

(c) The increasing order of reactivity among group 1 elements is Li < Na < K < Rb < Cs whereas that among group 17 elements is F > Cl > Br > I.

8. Given below are the plots of first ionization enthalpy ($\Delta_i H$) of elements of the second period as a function of atomic number (Z) (Fig. 1) and $\Delta_i H$ of alkali metals as a function of Z (Fig. 2). Answer the questions that follows :
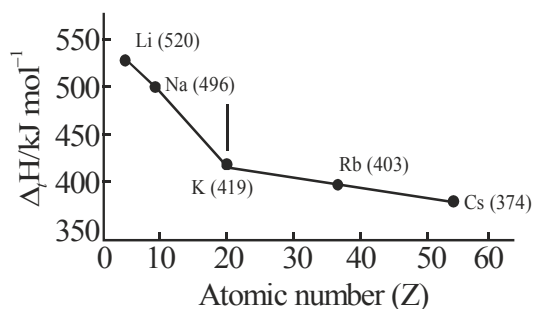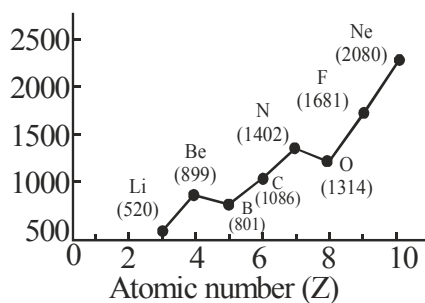
(a) First ionization enthalpy generally increases as we go across a period and decreases as we descend a group.

(b) Ionization enthalpy of boron is slightly less than that of beryllium.

(c) Ionization enthalpy of nitrogen is more than that of oxygen.

9. A, B, C are three elements with atomic number Z – 1, Z and Z + 1 respectively. B is an inert gas. Answer the following questions :

(a) Predict the groups of A and C.

(b) Which out of the three elements has positive electron gain enthalpy ?

(c) Which out of the three elements has the least value of ionization energy ?

10. The first ($\Delta_i H_1$) and the second ($\Delta_i H_2$) ionization enthalpies (in kJ/mol) and the ($\Delta_{eg} H$) electron gain enthalpy (in kJ/mol) of a few elements are given below :

Elements	$\Delta_I H_1$	$\Delta_I H_2$	$\Delta_{eg} H$
I	520	7300	–60
II	419	3051	–48
III	1681	3374	–328
IV	1008	1846	–295
V	2372	5251	+48
VI	738	1451	–40

Which of the above elements is likely to be :

(a) the least reactive element.

(b) the most reactive metal.

(c) the most reactive non-metal.

(d) the least reactive non-metal.

(e) the metal which can form a stable binary halide of the formula MX_2 (X = halogen).

(f) the metal which can form a predominately stable covalent halide of the formula MX (X = halogen).

UNIT-4

CHEMICAL BONDING AND MOLECULAR STRUCTURE

Atoms do form chemical bonds since their formation lead to the decrease in the energy of the system. Chemical bonds are :

(a) Covalent bonds involving the sharing of electrons.

(b) Ionic bonds formed by the transference of electrons from the metallic atom having low $\Delta_i H$ to the more electronegative and non-metallic atom having more -ve $\Delta_{eg} H$ resulting in the formation of a crystal having high lattice enthalpy ($\Delta_L H$).

(c) Hydrogen bonds and van der waals forces.

The strength of hydrogen bond depends on the electronegativity difference between H atom and the highly electronegative atoms like F, O and N having at least one lone pair of electron .

The strength of hydrogen bond decreases in the order :

F – H .... F > O – H .... O > N – H .... N

Effects of hydrogen bonding : Intermolecular hydrogen bonding increases m.p., b.p., solubility, viscosity and surface tension while intramolecular hydrogen bonding has reverse effects.

For example, 2-hydroxy benzoic acid is stronger than 2-methoxy benzoic acid because 2-hydroxybenzoate ion is stabilized by intramolecular hydrogen bonding (chelation).

(Chelation occurs)   (No Chelation)
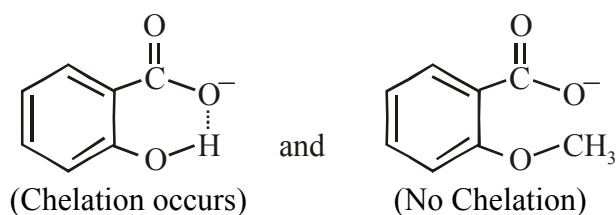
All single bonds are sigma bond. Double bond consists of one sigma and one π while a triple bond convert of one sigma and two π-bonds.

(a) Bond energy increases from a single bond to trople bond.

(b) Bond strength increase from a single bond to triple bond.

(c) Reactivity of a multiple bond is always more than a single band, due to mobile nature of π electrons.

Factors affecting bond length :

(1) Bond length increases with the increase in the size of bonded atoms.

(2) **Multiplicity of bonds :** It decreases with the increase in the multiplicity of bonds, for example bond length decreases in the order $C - C > C = C > C \equiv C$.

(3) **Type of hybridisation :** As an s-orbital is smaller in size, greater the s-character, the shorter (smaller) is the size of hybrid orbital and, therefore, shorter is the bond length. For example,

sp^3 C–H $> sp^2$ C – H $> sp$ C – H

Bond energy or bond dissociation enthalpy : Smaller the bond length, the stronger will be the bond formed and larger will be bond dissociation enthalpy.

Dipole moment : It is the product of the distance separating charges of equal magnitude and opposite signs, with the magnitude of charge $\mu = q \times d$. The dipole moment help to predict whether the molecule is polar or non-polar. A molecule may contain polar bonds but its dipole moment may be zero if it has symmetrical structure, that is, if it has no lone pair(s) of electrons in the valence shell of the central atom and all the terminal atoms are identical. For example, dipole moment $\mu = 0$ in case of CCl_4 but $\mu \neq 0$ in case of $CHCl_3$. Dipole moment of NH_3 is more than that of NF_3 although N–F bond is more polar than N–H bond.

Just as all covalent bonds have some partial ionic character, the ionic bond also have partial covalent character. The partial covalent character of ionic bonds can be discussed with the help of Fajan's rules.

Geometrical shapes can be predicated with the help of Valence shell-Electron pair Repulsion (VSEPR) Theory. The geometry of molecules or ions depends upon the no. of electron pairs around the central atom in its Lewis structure. While counting the electron pairs, lone pair(s) as well as bond pair(s), the multiple bond is treated as if it is a single bond or single electron pair. The repulsive interaction between electron pairs decreases in the order Ip–Ip > Ip–bp > bp–bp.

Presence of lone pair(s) on the central atom of a species results in deviation from idealized shapes and changes in bond angles.

Type of molecule	bp	lp	Total no. of electron pairs around the central atom	Geometry
CH_4	4	0	4	Tetrahedral, H–C–H angle 109.5°
NH_3	3	1	4	Pyramidal, H–N–H angle 107°
H_2O	2	2	4	Bent, H–O–H angle 104.5°

Hybridisation may be defined as the phenomenon of intermixing of atomic orbitals of nearly the same energy belonging to different subshells so as to redistribute their energies and to give rise to new orbitals of equivalent energies and shapes. The new orbitals that are formed are called hybridised or hybrid orbitals.

No. of hybrid orbitals = No. of combining atomic orbitals of similar energy.

Table 1
Arrangement of the electron pairs about a cental atom A

Type of molecule	Total no. of electron pairs		Shape of molecule/Ions	Hybridisation type	Example
	Bond pairs	Lone pairs			
AB_2	2	–	Linear	sp	BeF_2
AB_3	3	–	Trigonal planar	sp^2	$BF_3, AlCl_3$
AB_2E	2	1	Bent	sp^3	SO_2, O_3
AB_4	4	–	Tetrahedral	sp^3	CH_4, NH_4^+
AB_3E	3	1	Pyramidal	sp^3	NH_3, PX_3 (X = F, Cl, B, I)
AB_2E_2	2	2	Bent (angular)	sp^3	H_2O, OF_2, NH_2^-
AB_5	5	–	Trigonal bipyramidal	sp^3d	PF_5, PCl_5
AB_4E	4	1	See Saw/Irregular Tetrahedral	sp^3d	SF_4
AB_3E_2	3	2	Bent T-shaped	sp^3d	$Cl F_3$
AB_2E_3	5	–	Linear	sp^3d	XeF_2, ICl_2^-, I_3^-
AB_6	5	–	Octahedral	sp^3d^2	SF_6, PF_6
AB_5E	5	1	Square pyramidal	sp^3d^2	$BrF_5, XeOF_4, ClF_5$
AB_4E_2	4	2	Square planar	sp^3d^2	XeF_4, ICl_4^-
AB_7	7	–	Pentagonal bipyramidal	sp^3d^3	IF_7

Hybridization scheme in complex ions (co-ordination entities) can be discussed with the help of valence bond theory.

Shape of coordination entity	Hybridisation type	Example
Linear	sp	$[Ag(NH_3)_2]^+$
Tetrahedral	sp^3	$[Ni(CO)_4], [NiCl_4]^{2-}$
Square planar	dsp^2	$[Ni(CN)_4]^{2-}, [PtCl_4]^{2-}$
Trigonal bipyramidal	dsp^3	$[Fe(CO)_5]$
Octahedral	sp^3d^2	$[CrF_6]^{3-}, [CoF_6]^{3-}, [FeF_6]^{3-}$
	d^2sp^3	$[Fe(CN)_6]^{3-}, [Co(C_2O_4)_3]^{3-}$

Molecular orbital theory was developed by F. Hund & R. S. Mulliken in 1932. This theory was able to explain the stability of the molecule, to calculate bond order, to find out the nature of the bond formed (*e.g.,* single, double or triple bonds), to calculate the bond length and predict the magnetic nature of the species some of which was not explained by the **valence bond theory.**

The molecular orbitals, like atomic orbitals, are filled in accordance with Aufbau principle obeying the Pauli's exclusion principle and the Hund's rule. The increasing order of energies of various molecular orbitals (determined experimentally from spectroscopic data).

For O_2 & F_2 molecule

$\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^*2p_x = \pi^*2p_y) < \sigma^*2p_z$

For B_2, C_2, N_2 molecules

$\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^*2p_x = \pi^*2p_y) < \sigma^*2p_z$

<div align="center">

1- MARK QUESTIONS

</div>
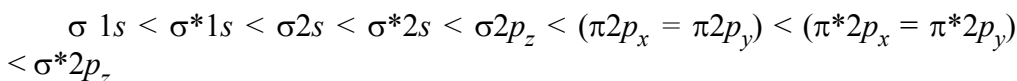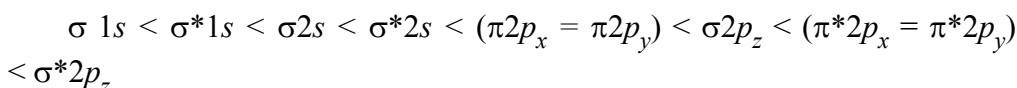
1. Write Lewis dot symbols for the atoms of the following elements :
<div align="center">Be, F, Ne, C</div>
   (Given atomic number of Be = 4, F = 9, Ne = 10, C = 6)
2. Define electrovalence of an element.
3. Arrange the following molecules according to the increasing order of their bond angles :
<div align="center">NH_3, H_2O, CH_4 [**Ans.** $H_2O < NH_3 < CH_4$]</div>
4. He_2 molecule does not exist. Give reason.
5. Define the term bond length.
6. $BeCl_2$ is a linear molecule while SCl_2 is an angular molecule. Give reason.
7. Write the state of hybridisation of C in CO_3^{2-} ion.
8. Which of the following species are paramagnetic ?
<div align="center">H_2, H_2^+ and H_2^-</div>
9. Predict the shape of ClF_3 molecule.
10. Density of ice is less than water. Why ?
11. The Lewis dot structures for N_2O are as follows :
<div align="center">$:N \equiv \overset{+}{N} - \overset{..}{\underset{..}{O}} \overset{-}{:} \longleftrightarrow \overset{-}{\underset{..}{N}} = \overset{+}{N} = \overset{..}{\underset{.}{O}}$</div>
   Which of the two structures has greater contribution to the resonance hybrid.
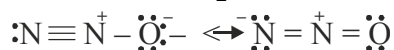
12. Arrange the repulsive interaction of electron pairs in the decreasing order as per the VSEPR theory :

[**Hint :**lone pair-lone pair, lone pair-bond pair, bond pair-bond pair.]

13. Considering x-axis as the internuclear axis which out of the following will form a sigma bond :

(a) $1s$ and $1s$ (b) $1s$ and $2p_x$

(c) $2p_y$ and $2p_y$ (d) $1s$ and $2s$

14. How is bond strength related to bond order ?

15. The H–P–H angle in PH_3 is smaller than the H–N–H angle in NH_3. Why ?

16. What is percentage of s-character in sp and sp^3 hybrid orbitals ?

17. Why do noble gases exist in monoatomic form.

18. The enthalpy needed to break the two O–H bonds in water are as folllows –

(a) H_2O (g) $\rightarrow$ H(g) + OH(g) $\Delta_aH_1° = 502$ kH/mol

(b) OH (g) $\rightarrow$ H(g) + O(g) $\Delta_aH_2° = 427$ kJ/mol.

what is the average bond enthalpy of H_2O.

19. Write the full form of (a) VSEPR, (b) LCAO.

20. Which of the two bonds ionic or covalent is directional.

21. Out of Mgo and NaCl, which has higher lattice energy?

2 - MARK QUESTIONS

1. Write the Lewis symbols for the following elements and predict their group valence :

Chlorine and Calcium (Given : Atomic number of Cl = 17, Ca = 20)

2. State octet rule. Give one example of a compound of sulphur in which it obeys octet rule.

3. Use Lewis symbols to show electron transfer between the following atoms to form cations and anions :

(a) Na and Cl (b) Ca and F

4. Why is the shape of NH_3 molecule pyramidal ?

5. Define electronegativity. How does it differ from electron gain enthalpy ?

6. Why are axial bonds longer than equatorial bonds is PCl_5?

7. Calculate the formal charges of the three atoms in O_3 molecule.

8. Write Lewis dot symbols for the following ions :

$$Li^+, O^{2-}, Mg^{2+}, N^{3-}$$

(Given Atomic no. of Li = 3, O = 8, Mg = 12, N = 7)

9. Give molecular orbital electronic configuration of O_2 molecule.

10. Why does L_{i2} molecule not exist in nature (z = 3).

11. Why BF_3 has azero dipole although B–F bond is Polar in nature !

12. You are given the electronic configurations of five neutral atoms A, B, C, D and E :

$$A = 1s^2\ 2s^2\ 2p^6\ 3s^2$$
$$B = 1s^2\ 2s^2\ 2p^6\ 3s^1$$
$$C = 1s^2\ 2s^2\ 2p^1$$
$$D = 1s^2\ 2s^2\ 2p^5$$
$$E = 1s^2\ 2s^2\ 2p^6$$
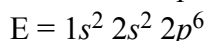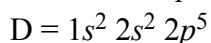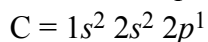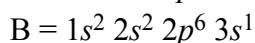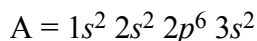
Write the empirical formula for the molecules containing (i) A and D, (ii) B and D, (iii) Only D, (iv) Only E.

13. Define bond enthalpy. Explain why bond enthalpy of fluorine is less than that of chlorine.

14. Write two points of difference between σ and π-bond.

15. Although F is more electronegative than N, the resultant dipole moment of NH_3 (4.90×10^{-30} c.m) is greater than that of NF_3 (0.80×10^{-30} c.m). Explain with their structures.

16. What is meant by the term bond order in Lewis concept ? Calculate the bond order of CO and Be_2.

17. Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in C_2H_4 and C_2H_2 molecules.

18. Using molecular orbital theory explain why the Be_2 molecule does not exist ?

19. What is formal charge? Calculate the formal charge on each atom in the Lewis structure of SO_2 given as $\left[:\overset{..}{\underset{..}{O}} - \overset{..}{\underset{..}{S}} = \overset{..}{\underset{..}{O}} \right]$.
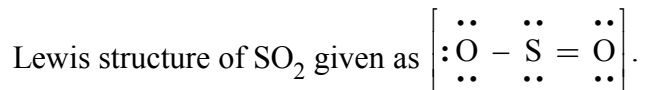
20. Explain the concept of reasonance, write the two structures of ozone which satisfy the octet rule ?

3 - MARK QUESTIONS

1. Draw Lewis structures for the following molecules :

$$C_2H_4, HNO_3, NF_3$$

2. Define an electrovalent bond. Write the factors that favour the formation of an electrovalent bond. Give two characteristics of an electrovalent compound.

3. Three elements have the following Lewis symbols :

$$A. \quad \cdot \dot{B} \cdot \quad : \dot{\ddot{C}} \cdot$$
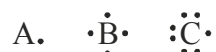
(a) Place the elements in the appropriate groups of the periodic table.

(b) Show the charges on the ions formed by the elements.

(c) Write the formulae and the Lewis structures of the covalent compounds formed between :

(i) A and B   (ii) A and C

4. Draw the Lewis structure of the species as mentioned below :

(a) in which the central atom has an incomplete octet.

(b) in which the central atom has an expanded octet.

(c) an odd electron molecule is formed.

5. How is the molecular orbital different from an atomic orbital ? Write the number of electrons which occupy the bonding molecular orbitals of H_2^- and H_2.

6. Which hybrid orbitals are used by carbon atoms in the following molecules :

(a) $CH_2=CH–C\equiv CH$ (b) CH_3COOH

7. The internuclear separation in a KCl molecule in the vapour is 2.60×10^{-8} c.m. Assuming the complete transfer of electron (charge $= 1.602 \times 10^{-19}$ Coulombs) from K to Cl atom.

(a) Calculate the dipole moment of KCl molecule.

(b) Show the direction of the dipole moment.

(c) Calculate the percentage ionic character of KCl.

(Given : dipole moment of KCl is 3.36×10^{-29} coulomb-metre)

Ans. (i) -4.1652×10^{-29} c.m.

     (ii)   80.1

$$[\textbf{Hint :} \text{ \% ionic character} = \left(\frac{\mu_{obs}}{\mu_{ionic}} \times 100 \right) = \frac{3.36 \times 10^{-29} \text{ cm}}{4.1652 \times 10^{-29} \text{ cm}} \times 100 = 80.1\%]$$

[**Ans.** (i) 4.1652×10^{-29} c.m. (ii) 80.1%]

9. Which of the following species is diamagnetic or paramagnetic?

$He_2^+, H_2, H_2^+.$

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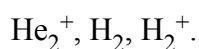
10. Define hydrogen bonds is it weaker or stronger than the covalent bond?

11. Calculate the formal charge on each atom of NO_2^- ion.

12. All the C–O bonds in carbonate ion (CO_3^{2-}) are identical. Explain why ?

5 - MARKS QUESTIONS

1. (a) Write the electron dot structure of :
$$H_3PO_4, COCl_2, H_2SO_4$$
   (b) Using VSEPR theory, identify the type of hybridisation of oxygen in OF_2 molecule. Draw the structure of OF_2 and mention the oxidation states each of O and F.

2. Write the molecular orbital configuration of the following species :
$$N_2, N_2^+, N_2^-, N_2^{2-}$$
   (a) Calculate their bond orders.
   (b) Predict their magnetic behaviour.
   (c) Which of these shows the highest paramagnetism.

3. (a) Mention important conditions required for the linear combination of atomic orbitals to form molecular orbitals.
   (b) Define hydrogen bond. Write the necessary conditions for the formation of hydrogen bond. Describe by giving one suitable example each of intermolecular and intramolecular hydrogen bonding.

4. Draw the molecular orbital diagram of O_2 molecule.
   For the species O_2, O_2^+, O_2^- (superoxide) and O_2^{2-} (peroxide)
   (a) Calculate their bond orders.
   (b) Compare their relative stabilities.
   (c) Indicate their magnetic properties.

5. (a) Define the term hybridisation.
   (b) State four salient features of hybridisation.
   (c) Describe the hybridisation in case of PCl_5. Why are the axial bonds longer as compared to equatorial bonds ?
   (d) Show the formation of triple bond its C_2H_2.

6. Give reason for the following :
   (i) H_2S is a gas at ordinary temperature but H_2O is liquid
   (ii) Pure HCl liquid is a bad conductor of electricity while aqueous HCl is a good conductor of electricity.

[**Hint.** Liquid HCl is a covalent compound. HCL when dissolved in H_2O furnishes ions due to its palarnalure and high hychation energy]

(iii) NCl_5 does not exist while PCl_5 does.

(iv) H_2O is more polar than H_2S.

(v) BF_3 is non polar while NF_3 is polar.

[**Hint :** BF_3 has symmetrical triangular planar structure in which net dipole moment is zero, where NF_3 has pyramidal strcuture, where dipole moment is considerable.]

STATES OF MATTER

- On the basis of nature of intermolecular forces/molecular interactions, matter exists in three physical states : solid, liquid and gas.

- Intermolecular forces are the forces of attraction or repulsion between interacting particles (atoms and molecules). Attractive/repulsive intermolecular forces are known as van der Waals forces.

  Different types of van der Waals forces are :

  (a) Dispersion forces or London forces

  (b) Dipole-dipole forces

  (c) Dipole-induce dipole forces

- **Boyle's Law :**

$$p \propto \frac{1}{V} \qquad \text{[constant pressure]}$$

$$P_1V_1 = P_2V_2 \qquad \text{[constant pressure]}$$

- **Charles's law :**

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad \text{[constant pressure and n]}$$

- **Gay Lussac's Law :**

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \qquad \text{[constant volume and } n\text{]}$$

- **STP (Standard Temperature and Pressure)**

  STP means 273.15 K (0° C) temperature and 1 bar (*i.e.,* exactly 10^5 pascal). Volume occupied by 1 mole gas at STP = 22.7 L.

  If pressure is taken as one atmosphere, then the standard molar volume is 22.4 L.

- **Ideal gas equation**

$$pV = nRT$$

R is universal gas constant.

$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1} = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}$

- **Combined gas law :**

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

- Relationship between different types of Molecular speeds :

  Most probable speed : average speed : Root mean square speed.

$$\sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$1.414 : 1.596 : 1.732$$

$$1 : 1.128 : 1.224$$

  Averge speed = $0.921 \times$ Root mean square speed.

  Most Probable speed = $0.817 \times$ Root mean square speed.

- **Density and molar mass of a gaseous substance :**

$$M = \frac{dRT}{P}$$

- **Dalton's Law of partial pressure :**

$$p_{total} = p_1 + p_2 + p_3 + \ldots\ldots\ldots\ldots \qquad [\text{ constant T, V}]$$
$$P_{dry\ gas} = P_{total} - \text{Aqueous tension}$$

  Here aqueous tension is the pressure exerted by the water vapours.

- **Compressibility factor :** The extent of deviation of a real gas from an ideal behaviour is expressed in terms of compressibility factor, Z, defined as $= \dfrac{PV}{nRT}$.

  For ideal gas, Z = 1 at all temperatures and pressures. For real gases, greater is the departure in the value of Z from 1, greater is the deviation from ideal behaviour. When Z < 1, the gas is said to show *negative* deviation. This implies that gas is more compressible then expected from ideal behaviour when Z > 1, the gas is said to show positive deviation and the gas is less compressible than expected from ideal behaviour.

  At ordinary temperatures $(T \geq 273K)$, only H_2 and He show positive deviations. However at low temperatures, even these gases show negative deviation *i.e.,* Z < 1. For example, in case of these gases, if T << 273 K, Z < 1.

  Boyle temperature : The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is called Boyle temperature or Boyle point.

  Causes of deviation from ideal behaviour : The following two assumptions of the kinetic theory of gases are faulty :

(a) The volume occupied by the gas molecules is negligible as compared to the total volume of the gas.

(b) The forces of attraction or repulsion between the gas molecules are negligible.

The above assumptions are correct only if the temperature is high or pressure is low.

van der Waals equation :

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad \text{for 1 mol of the gas}$$

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \qquad \text{for } n \text{ moles of the gas}$$

a and *b* are constants called van der Waals constants.

Significance and units of van der Waals constants : *a* gives the idea of the magnitude of attractive forces among the gas molecules. As correction in pressure is $p = \frac{an^2}{V^2}$, therefore $a = (p \times V^2)/n^2 = \text{atm L}^2 \text{ mol}^{-2}$. As correction in volume $v = nb$, therefore *b* has the unit of L mol^{-1}. The near constancy in the value of *b* shows that the gas molecules are incompressible.

Surface Tension is defined as force acting per unit length perpendicular to the line drawn on the surface. Its unit is Nm^{-1}.

Effect of temperature on surface tension : Surface tension decreases with increase in temperature because with the increase in temperature, Kinetic energy of molecules increases. As a result, intermolecular forces decreases and hence force acting per unit length decreases.

Viscosity : It is defined as resistance offered to the flow of liquid due to internal fiction between layers of fluids as they pass over each other.

$$f = \eta A . \frac{du}{dx}$$

η is called coefficient of viscosity.

Effect of temperature on viscosity : viscosity decreases with increase in temperature because with the increase in temperature the average kinetic energy increases and the intermolecular forces can be easily overcome.

$$\boxed{\text{1- MARK QUESTIONS}}$$

1. What type of intermolecular forces operate in :
   (a) noble gases   (b) Water

2. Name two measurable properties of the gases.

3. Name the instrument used to measure atmospheric pressure.

4. Why is mercury used in the barometer ?

5. How is pressure in atm related to the pressure in pascals ?

6. Name the device used to measure the pressure of a gas.

7. Define absolute zero of temperature.

8. Why is kelvin scale of temperature regarded better than celsius scale ?

9. Mention the SI unit of universal gas constant (R).

10. Define aqueous tension.

11. Why is it not possible to cool a gas to a temperature of absolute zero (0° K) ?

12. Name intermolecular forces that exist between HF molecule in liquid state.

> [**Ans.** Dispersion forces and intermolecular hydrogen bonding]

13. Write the units of van der Waals constant *a* and *b*.

14. Name the temperature at which real gases behave as ideal gases over appreciable range of pressure.   [**Ans.** Boyle temperature]

15. Out of NH_3 and N_2, which will have larger value of *a*.   [**Ans.** NH_3]

16. Dalton's law of partial pressures is not applicable to a gaseous mixture of CO (*g*) and O_2 (*g*). Why ?

17. Atmospheric pressure recorded in different cities are as follows :

Cities	Shimla	Bangalore	Delhi	Mumbai
p/N/m^2	1.01×10^5	1.2×10^5	1.02×10^5	1.21×10^5

Consider the above data and identify the place at which liquid will boil first.   [**Ans.** Shimla]

18. Mention the SI unit of viscosity coefficient (η).

19. Under what conditions do real gases tend to show ideal gas behaviour.

20. The magnitude of surface tension of liquid depends on the attractive forces between the molecules. Arrange the following in the increasing order of surface tension :

Water, alcohol and *n*-hexane.

21. Differentiate between normal boiling point and standard boiling point.

22. What property of moelcules of real gases in indicated by the van der Walls constant a?

2 - MARK QUESTIONS

1. Identify the states of matter in each case with following properties :
   (a) Highly compressible
   (b) Definite volume but indefinite shape
   (c) Molecules move randomly within restricted space
   (d) Intermolecular forces are strong

2. State Dalton's law of partial pressures. How is the law helpful in calculating the pressure of the gases which are collected over water ?

3. Define Boyle's law. How is it represented mathematically ?

4. List four important postulates of kinetic theory of gases.

5. Why do real gases show deviation from ideal behaviour ? Write van der Waals equation for n moles of a gas.

6. State Charles' law. How is this law used in the metorological observations ?

7. Write short notes on the following :
   (a) Surface tension   (b) Viscosity

8. Using the equation of state, $pV = nRT$, show that at a given temperature, density of a gas is proportional to gas pressure (p).

9. Give correct reason for the following :
   (a) Hot tea or coffee is sipped from a saucer.
   (b) Drop of liquid assumes spherical shape.

10. (i) Define critical temperature
    (ii) Critical temperature for CO_2 and CH_4 are 31.1° and –81.9°C respectively. Which of these has stronger intermolecular forces and why?

11. Explain the physical significance of van der Waals parameters.

12. Compressibility factor (Z) of a gas is given as $Z = \dfrac{pV}{nRT}$.
    (a) What is the value of Z for an ideal gas ?
    (b) For real gas, what will be effect of value of Z above Boyle temperature ?

    [**Ans.** (a) Z = 1, (b) Z > 1]

13. Write the flaws in the following statements.
    (a) The volume of gas is directly proportional to its absolute temperature.
    (b) The total pressure of a mixture of non-reacting gases is equal to the sum of pressures of individual gases.

14. Calculate the density of NH_3 (g) at 30°C and 5 bar pressure (R = 0.0831 bar $dm^3 mol^{-1} k^{-1}$).

15. Calculate the temperature at which the average speed of oxygen equals that of Hydrogen at 20K.

3 - MARK QUESTIONS

1. Account for the following :

    (a) Cooling is always caused during evaporation.

    (b) Carbon dioxide is heavier than oxygen and nitrogen but it does not form the lower layer of the atmosphere.

    (c) Gases like CO_2 and CH_4 show more deviation from the ideal gas behaviour as compared to gases like H_2 and He.

2. With the help of gas laws, deduce an expression for the ideal gas equation. What is the utility of the gas equation ?

3. List the three main points of difference between a solid, a liquid and a gas.

4. What will be the pressure of the gas mixture when 0.5 L of H_2 at 0.8 bar and 2.0 L of oxygen at 0.7 bar are introduced in a 1 L vessel at 27° C ?

5. Pressure of 10 g of an ideal gas 'A' at 27° C is found to be 2 bar. When 20 g of another ideal gas 'B' is introduced in the same flask at same temperature, the pressure becomes 3 bar. Find the relationship between their molecular masses.   [**Ans.** $M_B = 4M_A$]

6. Calculate the total pressure in a mixture of 8.0 g of oxygen and 4.0 g of hydrogen confined in a vessel of 1 dm^3 at 27° C. R = 0.083 bar $dm^3 K^{-1} mol^{-1}$.

    [**Ans.** 56.025 bar]

7. A neon-dioxygen mixture contains 70.6 dioxygen and 167.5g neon. If pressure of the mixture of gases in cylinder is 25 bar, what is the partial pressure of dioxygen and neon in the mixture.   [**Ans.** 5.25 bar, 17.75 bar]

8. Calculate the temperature at which the root mean square speed, average speed and the most probable speed of oxygen gas are all equal to 1500 $m\bar{s}^1$.

THERMODYNAMICS

A system is a part of universe in which observations are made. The remaining universe which can interact with the system constitutes the surroundings. A boundry, real or imaginary separate the system from the surroundings.

A process that occurs infinitesimally slowly such that system always remains in equilibrium with its surroundings is called reversible process.

Internal energy change (ΔU) : Heat absorbed or released by the system at constant volume *i.e.* $\Delta U = q_v = C_v \Delta T$.

The heat change at constant volume during the course of a reaction is measured by bomb calorimeter.

Enthalpy change (ΔH) : Heat absorbed or released by the system at constant pressure, i.e., $\Delta H = q_p$; $\Delta H < 0$ (Exothermic process), $\Delta H > 0$ (Endothermic process).

$$\Delta H = q_p = C_p \Delta T$$

Heat change at constant pressure is measured in ordinary calorimeter.

First law of thermodynamics : $\Delta U = q + w$. For a given change in state, q and w vary depending how the change is carried out. However, $q + w = \Delta U$ will depend upon the initial and final state of the system. Hence ΔU is also a state function.

The q is positive when heat is transferred from sounding to the system and is negative when it is transferred from the system.

Work done during the expansion of gas against external pressure

Mechanical work or pressure – volume work is given by $W = -P_{ex} (\Delta V) = -P_{ex} (V_f - V_i)$ where P_{ex} is external pressure acting on the system. During expansion $V_f > V_i$ and W is negative.

If external pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of gas (p_{in}). In an expansion process, the external pressure is always less than pressure of gas (p_{in} or simply p). The work done in a reversible process is given by

$$W_{rev} = -\int_{V_i}^{V_f} p_{in} dv = -\int_{V_i}^{V_f} p dv = -2.303 \; nRT \; \log \frac{V_f}{V_i}$$

where V_i = Initial volume; V_f = Final volume

$$= -2.303\,n\text{RT}\,\log\frac{P_i}{P_f}$$

where P_i = Initial pressure; P_f = Final pressure

In free expansion of an ideal gas in vaccum, no work is done by the gas because no force is opposing expansion ($p_{ex} = 0$) in a reversible or irreversible process. If the gas neither lose nor gain heat from the surroundings, then $q = 0$ and therefore, there will be no change in the internal energy of the system ($\Delta U = 0$).

For isothermal irreversible change : $\Delta U = 0$

$$\therefore \qquad q = -\,W = -\,[-p_{ex}\,(V_f - V_i)]$$

For isothermal reversible change : $\Delta U = 0$

$$q = -\,W = -\,2.303\,n\text{RT}\,\log\frac{V_f}{V_i}$$

Relationship between ΔU and ΔH for the reactions involving gaseous reactants and gaseous products occurring at constant T and P

$$\Delta H = \Delta U + \Delta n_g\,RT$$

where Δn_g = sum of stoichiometric coefficients of gaseous products minus sum of stoichiometric coefficients of gaseous reactants.

$$\Delta n_g = n_P - n_R \text{ (gaseous phase)}$$

Standard enthalpy of reaction ($\Delta r\,H^\theta$) is the enthalpy change for the reaction when the reactants and products are in their standard states. The standard state of a substance at a specified temperature (not necessarily 298 K) is its pure and most stable form at 1 bar pressure.

Second law of thermodynamics : For a spontaneous change in a system, the total entropy change ΔS_{total} is positive, *i.e.,* $\Delta S_{sys} + \Delta S_{surr.} > 0$

When a system is in equilibrium, the entropy is maximum. Hence, $\Delta S_{total} = 0$ (at equilibrium).

Third law of thermodynamics : The entropy of a perfectly crystalline substance approaches zero as the absolute zero of temperature is approached.

Residual entropy : There are certain substance which possess certain entropy even at absolute zero. This entropy is known as residual entropy.

Gibbs energy change ($\Delta_r\,G$) and spontaneity : The following criteria can be derived from second law of thermodynamics :

$\Delta_r\,G < 0$ Spontaneous process

$\Delta_r\,G > 0$ Non-spontaneous process

$\Delta_r G = 0$ At equilibrium

The reaction is called exoergonic if $\Delta G < 0$ and endoergonic if $\Delta G > 0$. The sign of $\Delta G = \Delta H - T\Delta S$ also depends upon temperature. The temperature at which equilibrium is attained, is given by $T = \dfrac{\Delta H}{\Delta S}$.

Important formulas used in thermodynamics calculations

$$\Delta_r S = \dfrac{q_{rev}}{T}$$

$$\Delta_{fus} S = \dfrac{\Delta_{fus} H}{T} \text{ and } \Delta_{vap} S = \dfrac{\Delta_{vap} H}{T}$$

$$\Delta_r S^{\varnothing} = \sum v_p \Delta S^{\varnothing} \text{ (products)} - \sum v_r \Delta S^{\varnothing} \text{ (reactants)}$$

$$\Delta_r H^{\varnothing} = \sum v_p \Delta_r H^{\varnothing} \text{ (products)} - \sum v_r \Delta_r H^{\varnothing} \text{ (reactants)}$$

$$\Delta_r G^{\varnothing} = \sum v_p \Delta_r G^{\varnothing} \text{ (products)} - \sum v_r \Delta_r G^{\varnothing} \text{ (reactants)}$$

Gibbs energy and useful work : $T\Delta S$ is the energy of the system which is not available to do useful work. ΔH is the enthalpy change of the reaction. Therefore, $\Delta H - T\Delta S$ is the energy which is available to do useful work. The decrease in the Gibbs energy is equal to the maximum possible useful work that can be derived from a process.

$$-\Delta_r G = W_{useful}$$

In case of galvanic cells, useful work done by the cell is given by $-\Delta_r G^{\theta} = -n E^{\varnothing}$ cell F and in standard states $\Delta_r G^{\theta} = -n E^{\varnothing}$ cell F

Hess's law of constant heat summation is based on the law of conservation of energy. If a reaction is the sum of two or more constituent reactions, then enthalpy of overall reaction is the sum of enthalpy changes of the constituent reactions.

$$\Delta_r H^{\theta} = \Delta_r H_a{}^{\theta} + \Delta_r H_b{}^{\theta} + \Delta_r H_c{}^{\theta} + \text{.......}$$

(For definition of $\Delta_c H^{\theta}$, $\Delta_a H^{\theta}$, mean bond dissociation enthalpy ($\Delta H^{\theta}{}_{A-B}$), lattice enthalpy ($\Delta_L H^{\theta}$), $\Delta_{fus} H^{\theta}$, $\Delta_{vap} H^{\theta}$, $\Delta_{sub} H^{\theta}$, please refer NCERT text book Class XI, Part I, page 171 to 173.

Gibbs energy and equilibrium : A reversible reaction occur in either direction simultaneously so that a dynamic equilibrium is set up. This means that forward and reverse reaction should proceed with the decrease in Gibbs energy which is possible if the free energy of the system in minimum at equilibrium, *i.e.,* $\Delta_r G = 0$.

$$0 = \Delta_r G^\theta + 2.303 \; RT \log K$$
and $$\Delta_r G^\theta = \Delta_r H^\theta - T\Delta_r S^\theta$$

1- MARK QUESTIONS

1. Give an example of an open system.
2. Differentiate between a closed system and an isolated system.
3. Specify the properties needed to describe the state of a thermodynamic system.
4. Define internal energy of the system.
5. Which of the following is not a state function :
   (a) P   (b) T   (c) W   (d) ΔU
6. Why ΔU is a state function ?
7. Assign positive or negative sign to W_{ad} when :
   (a) work is done on the system.
   (b) work is done by the system.
8. How does the state of thermodynamic system changes when electrical or mechanical work is done on an adiabatic system ?
9. Heat is transferred from the surroundings to the close system, then what is the change in internal energy ?
10. State first law of thermodynamics and write its mathematical equation.
11. What is the relationship between ΔH and ΔU for a reaction involving gases?
12. Give an example of a reaction for which $\Delta H = \Delta U$.
13. Define standard enthalpy of formation of a compound.
14. Write the equation for calculating enthalpy of formation of H_2O (l).
15. Define a state function.
16. Given : N_2 (g) + $3H_2$ (g) $\rightarrow$ $2NH_3$ (g) $\Delta_r H^\theta = -92.4$ kJ mol^{-1}
    What is the standard enthalpy of formation of ammonia gas ?
    [**Ans.** $- 46.2$ kJ/mol]
17. For an isolated system $\Delta U = 0$, what will be ΔS ?
18. For the reaction : H_2 (g) $\rightarrow$ $2H$ (g)
    What will be the sign of ΔH and ΔS ?   [**Ans.** $\Delta H > 0$, $\Delta S > 0$]
19. What is the relationship between standard Gibbs energy change and equilibrium constant of a reaction ?
20. Comment on thermodynamic stability of NO(g), given :

$$\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \rightarrow NO(g) \qquad \Delta_f H^0 = 90.0 \text{ kJmol}^{-1}$$
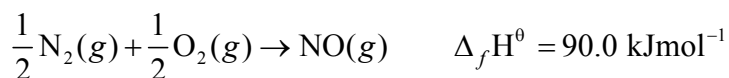
[**Hint :** Since enthalpy of formation of NO is positive, it is thermodynamically unstable.]

21. The enthalpy of combustion of methane is - 890 kJ mol^{-1}. Calculate its calorific value.

22. If the standard Gibbs energy change for a reaction is found to be less than zero, what is the value of equilibrium constant for the reaction ?

23. Predict the sign of $\Delta_r G$ for a reaction at equilibrium.

24. Predict the sign of ΔS_{surr} for an exothermic reaction.

25. Which of the following is not a state function and why ?
    (a) Internal energy (b) Enthalpy
    (c) Heat (d) Entropy

26. Explain the term residial entropy.

2 - MARK QUESTIONS

1. Write the mathematical expression for :
   (a) Irreversible work done on an ideal gas in a cylinder when it is compressed by a constant external pressure (P_{ex}) and the volume of the gas changes from V_i to V_f.
   (b) Reversible work done on the gas in a cylinder which is compressed in infinite number of steps and the volume changes from V_i to V_f. In this case P is not constant.

2. Differentiate between the following :
   (a) Extensive and intensive properties
   (b) Sublimation energy and enthalpy of atomisation

3. The following equations do not depict the enthalpy of formation. Explain why ?
   (a) H$_2$ (g) + Cl$_2$ (g) $\rightarrow$ 2HCl (g) $\qquad \Delta H_r = -184.62$ kJ mol^{-1}
   (b) CaO (s) + CO$_2$ (g) $\rightarrow$ CaCO$_3$ (s) $\Delta H_r = -178.3$ kJ/mol

4. Classify the following as extensive or intensive property :
   (a) Specific heat (b) Temperature
   (c) Volume (d) Molar heat capacity

5. Derive the relationship between the following :
   (a) C$_p$ and C$_v$ (b) ΔH and ΔU

6. Standard enthalpy of formation of hydrazine [N_2H_4 (*l*)], hydrogen peroxide [H_2O_2 (*l*)] and water [H_2O (*l*)] are −50.4, −193.2 and −242.7 kJ/mol respectively. Calculate the standard enthalpy of formation for the following reaction :

$$N_2H_4 (l) + 2H_2O (l) \rightarrow N_2 (g) + 4H_2O (l)$$
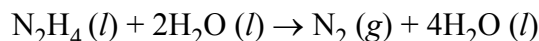
7. In a process 701.0 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process ?

[**Ans.** q = + 701 J, W = − 394 J, ΔU = 307 J]

8. Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g Al from 35° C to 55° C. Molar heat capacity of Al is 24 J mol^{-1} K^{-1}.

[**Ans.** 1.09 kJ]

9. Under what conditions the following reactions occur spontaneously :

    (a) Both ΔH and ΔS are negative for the reaction.

    (b) Both ΔH and ΔS are positive for the reaction.

10. Calculate $\Delta_r H^\theta$ for the reaction :

$$H_2 (g) + Br_2 (g) \rightarrow 2HBr (g)$$
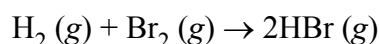
Bond enthalpy of various bonds are H–H = 436.0 kJ mol^{-1}, Br–Br = 192.0 kJ mol^{-1} and H–Br = 368.0 kJ mol^{-1}.

11. Hess's law is a corollary of the first law of thermodynamics. Explain.

12. Explain the following observations :

    (a) When an ideal gas expands in vacuum there is neither absorption or evolution of heat but when a real gas expands cooling is observed.

    (b) Although dissolution of NaCl in water is endothermic, but it readily dissolves.

13. (a) Decrease in enthalpy cannot be the sole criteria for spontaneity of a reaction. Justify with the help of an example.

    (b) How can a chemical reaction with positive enthalpy and entropy changes be made entropy driven spontaneous reaction ?

14. All spontaneous reactions follow the criteria $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} > 0$. Starting from this relation, how can we derive a relationship between ΔG and spontaniety ?

15. The equilibrium constant for a reaction is 10. What will be the value of ΔG^θ ?

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

16. Calculate the entropy change in surroundings when 1.0 mol of H_2O (*l*) is formed under standard conditions. Given : $\Delta_f H^\theta$ [H_2O (*l*)] = −286.0 KJ mol^{-1}, T = 298 K.

[**Hint :** $\Delta S_{surr} = \dfrac{q_{rev}}{T} = \dfrac{-\Delta_r H^\theta}{T}$]

17. Predict the spontaneity of the following reaction on the basis of ΔS_{total}.

$$4Fe\ (s) + 3O_2\ (g) \rightarrow 2Fe_2O_3\ (s)$$
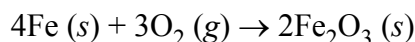
$\Delta_r H^\theta = -1648 \times 10^3$ J mol^{-1} $\qquad \Delta S^\theta = -549.4$ JK^{-1} mol^{-1}

[**Ans.** $\Delta_r S_{tolal} = 4980.6$ JK^{-1} mol^{-1}. Hence the reaction is spontaneous]

18. Give reason for the following :

(a) The enthalpy of neutralisation is always constant *i.e.,* 57.1 kJ/mol when a strong acid neutralises a strong base.

(b) The enthalpy of neutralisation is less than 57.1 kJ/mol when a weak acid reacts with a weak or strong base.

19. Compare the thermodynamic stability of NO and NO_2 from the following data :

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g) \qquad \Delta_f H^\theta = 90.0 \text{ kJ mol}^{-1}$$

$$NO\ (g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g) \qquad \Delta_f H^\theta = -74 \text{ kJ mol}^{-1}$$
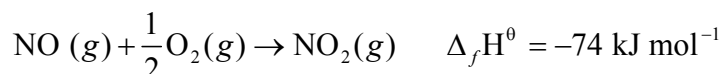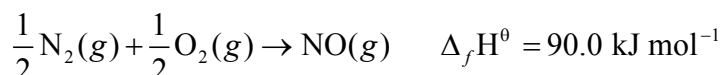
[**Hint :** Heat of formation of NO (*g*) is 90.0 kJ mol^{-1} and the heat of formation of NO_2 (*g*) is [90.0 + (−74.0) = +16.0 kJ mol^{-1}]. Since enthalpy of formation of NO_2 is less positive than that of NO, therefore NO_2 is more stable than NO.]

20. At 298k, k_p for the reaction N_2O_4 (g) $\rightleftharpoons$ 2NO_2 (g) is 0.98. Predict whether the reaction is spontaneous or not.

<div align="center">

3 - MARK QUESTIONS

</div>

1. Define the following :
   (a) Enthalpy of atomisation
   (b) Enthalpy of neutralisation
   (c) Enthalpy of solution

2. (a) Why internal energy is called a state function ?

   (b) Express the change in internal energy of a system when : no heat is absorbed by the system from the surroundings but work is done on the system. What type of wall does the system have ?

3. Calculate the lattice enthalpy of $MgBr_2$, given that :
   Enthalpy of formation of $MgBr_2 = 524$ kJ mol^{-1}

Sublimation enthalpy of Mg = 148 kJ mol^{-1}

Ionization enthalpy of Mg = 2187 kJ mol^{-1}

Vapourisation enthalpy of Br$_2$ (l) = 31 kJ mol^{-1}

Dissociation enthalpy of Br$_2$ (g) = 193 kJ mol^{-1}

Electron gain enthalpy of Br (g) = 331 kJ mol^{-1}

4. (a) Define enthalpy of vapourisation.

    (b) If enthalpy of vapourisation of water at 373 K = 40.66 kJ mol^{-1}, calculate the internal energy of vapourisation at 373 K.

    [**Ans.** ΔU = 37.904 kJ/mol]

    (c) A swimmer coming out from a pool is covered with a film of water weighing about 18.0 g. How much heat must be supplied to evaporate water at 298 k. Calculate internal energy of vaporisation at 373 K. The enthalpy of vaporisation at 373 K is 44.66 kJ/mol^{-1} ?

    [**Ans.** $\Delta_{vap} U$ = 37.56 kJ/mol^{-1}]

5. (a) Define bond enthalpy.

    (b) Calculate bond enthalpy of HCl if bond enthalpy of H–H bond is 436 kJ mol^{-1}, Cl–Cl B. E. is 242 kJ mol^{-1} and heat of formation of HCl is – 92.5 kJ mol^{-1}.

6. Calculate the standard enthalpy of formation of CH$_3$OH (l) from the following data :

    $$CH_3OH\ (l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O\ (l) \qquad \Delta_r H^{\varnothing} = -726 \text{ kJ mol}^{-1}$$

    $$C\ (graphite) + O_2(g) \rightarrow CO_2(g) \qquad \Delta_c H^{\varnothing} = -393 \text{ kJ mol}^{-1}$$

    $$H_2\ (g) + \frac{1}{2}O_2(g) \rightarrow H_2O\ (l) \qquad \Delta_f H^{0} = -286 \text{ kJ mol}^{-1}$$
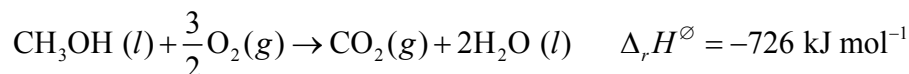
7. Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0° C to ice at –10.0° C. [**Ans.** –5.65 kJ/mol]

    Given : C_p [H$_2$O (l)] = 75.3 J mol^{-1} K^{-1}

    C_p [H$_2$O (s)] = 36.8 J mol^{-1} K^{-1}

    Δ_{fus} H = 6.03 kJ mol^{-1} at 0° C

8. Define the terms :

    (a) Open system

    (b) Average bond dissociation enthalpy

    (c) Entropy

9. During the combustion of 1 g graphite in bomb calorimeter, the temperature rised from 298 K to 299 K. The heat capacity of bomb calorimeter is 20.7 kJ/K.

(a) What is the amount of heat released ?

(b) What are the values of ΔU and ΔH for the combustion of carbon ?

[**Ans.** $q_v = -20.7$ kJ, $\Delta H = \Delta U = -2.48 \times 10^2$ kJ/mol]

10. (a) Define lattice enthalpy.

(b) Give the relationship between the lattice enthalpy and heat of solution of an inorganic salt.

11. Write the Born-Haber cycle to determine the lattice enthalpy of NaCl (*s*).

12. State Hess's law of constant heat summation. What are its applications ?

13. (a) Why enthalpy of fusion is always positive?

(b) Why diamond does not have $\Delta_f H^\theta = 0$ although it is an element ?

14. For the reaction :

$2A_{(g)} + B_{(g)} \rightarrow 2C_{(g)}$
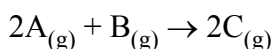
$\Delta U^\theta = -10.5$ kJ; $\Delta S^\theta = -44.1$ Jk^{-1}

Calculate $\Delta_r G^\theta$ for the reaction and predict wheather the reaction may occur spontaneously or not. [**Ans.** 0.164kJ. Not spontaneous]

15. Calculate $\Delta rH°$ for the reaction

$$H-\underset{\underset{Cl}{\overset{\overset{H}{|}}{|}}{C}}-Cl \rightarrow C_{(g)} + 2H_{(g)} + 2Cl_{(g)}$$
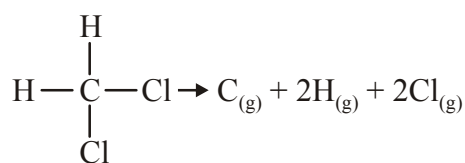
Average bond enthalpy of C–H and C–Cl hands are 414 kj.mol^{-1} and 330 kj mol^{-1} respectively.

16. ΔH and ΔS for the reaction

$$Ag_2O\,(s) \rightarrow 2Ag\,(s) + \frac{1}{2}O_2\,(g)$$
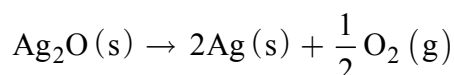
are 30.56 kJ mol^{-1} and 66Jk^{-1} mol^{-1} respectively. Calculate the temperature at which the Gibb's energy charge for the reaction will be zero. What be the

direction of the reaction at this temperature and at temperature below this temperature & why ?

5 - MARK QUESTIONS

1. (a) State Hess's law of constant heat summation. How does it follow from first law of thermodynamics ?

   (b) Determine the enthalpy of combustion of CH_4 (g) at 298° K. You are given following data :

   (i) C (graphite) $+ O_2(g) \rightarrow CO_2(g)$ $\Delta H_r^0 = -393.51$ kJ mol^{-1}

   (ii) H_2 $(g) + \dfrac{1}{2} O_2(g) \rightarrow H_2O$ (l) $\Delta H_r = -285.8$ kJ mol^{-1}

   (iii) CO_2 $(g) + 2H_2O$ $(l) \rightarrow CH_4$ $(g) + 2O_2$ $\Delta H_r^0 = +890.3$ kJ mol^{-1}

   [**Ans.** −891 kJ/mol]

2. (a) Use the following data to determine ΔG^θ value for the following reaction :

   $$N_2 \ (g) + 3H_2 \ (g) \rightarrow 2NH_3 \ (g)$$
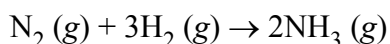
   Given data : ΔH_f^θ [NH_3 (g)] $= -46.2$ kJ mol^{-1}

   S^θ [N_2 (g)] $= 191.5$ JK^{-1} mol^{-1}

   S^θ [H_2 (g)] $= 130.6$ JK^{-1} mol^{-1}

   S^θ [NH_3 (g)] $= 192.5$ JK^{-1} mol^{-1}

   $R = 8.314$ JK^{-1} mol^{-1}

   (b) Calculate the value of K_p for the above reaction at 300 K ?

3. (a) Define entropy. What is the effect of temperature on entropy change ?

   (b) Calculate the entropy change in surroundings when 1.0 mol of H_2O (l) is formed under standard conditions. Melting point of ice is 273 K.

4. (a) A reaction is found to be endothermic and ΔS is +ve. What is the minimum temperature at which the reaction becomes spontaneous ?

   (b) What is the value of $\Delta_r H^\varnothing$ for the following reaction ?

   $$H^+ \ (aq) + OH^- \ (aq) \rightarrow H_2O \ (l)$$
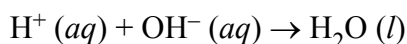
   (c) Calculate the enthalpy of formation of acetic acid (CH_3COOH) if its enthalpy of combustion is −867.0 kJ mol^{-1}. The enthalpy of formation of CO_2 (g) and H_2O (l) are −393.5 kJ mol^{-1} and −285.9 kJ mol^{-1} respectively.

5. (a) State first law of thermodynamics. Heat (q) and work done (W) are not state functions but their sum is a state function. Explain why ?

(b) Use the bond enthalpies listed in the table given below to determine the enthalpy of reaction :

$$\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{H-C-H}} (g) + 2O=O \;\rightarrow\; O=C=O \,(g) + 2H-O-H \,(g)$$

Given Bond	Bond Enthalpy (kJ mol^{-1})
C = O	741
C–H	414
O–H	464
O = O	489
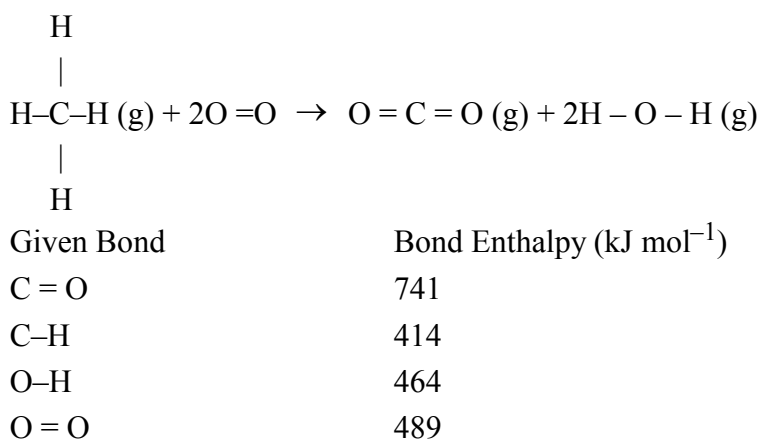
6. Predict the sign of ΔS for the following changes :

(a) $2Cl \,(g) \rightarrow Cl_2 \,(g)$

(b) $2A \,(g) + B \,(g) \rightarrow 2C \,(g)$

(c) $2CaCO_3 \,(s) \rightarrow 2CaO \,(s) + 2CO_2 \,(g)$

(d) Freezing of water

(e) Temperature of alum crystal is changed from 273 K to 298 K.

7. (a) Differentiate between reversible and irreversible changes.

(b) Two litres of an ideal gas expands isothermally against an external pressure of 1 atm until its final volume becomes 10 L at STP.

(i) Calculate the work done by the gas if it expands irreversibly.

(ii) Calculate the work done by the gas if it expands reversibly.

8. (a) Define Gibbs energy.

(b) Predict the direction in which a reversible reaction will move when

$$\Delta G < o.$$

(c) Using the data given below, calculate the value of $\Delta_r G^o$ and K_p for the following reaction at 298 K :
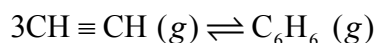
$$3CH \equiv CH \,(g) \rightleftharpoons C_6H_6 \,(g)$$

Assuming ideal gas behaviour, $\Delta_f G^\theta$ [CH≡CH (g)] = 2.09 × 10^5 J mol^{-1}, $\Delta_f G^\theta$ [$C_6H_6 \,(g)$] = 1.24 × 10^5 J mol^{-1}, R = 8.314 JK^{-1} mol^{-1}.

EQUILIBRIUM

A state of equilibrium is attained when two opposing process (forward and reverse) occur simultaneously at the same rate. The criterion for equilibrium for the reaction $aA + bB \rightleftharpoons cC + dD$ is $\Delta_r G = 0$. This is possible only if at equilibrium, Gibbs energy of system is minimum, *i.e.*, $\Delta_r G$ is zero. $\Delta_r G^{\varnothing}$ can never be zero because it is calculated from the $\Delta_r G^{\varnothing}$ of the reactants and products. The $\Delta_r G^{\varnothing}$ is related to equilibrium constant K_c or K_p as follows :

$$0 = \Delta_r G^{\varnothing} - 2.303 \, RT \log K$$

and $\quad \Delta_r G^{\varnothing} = \Delta_r H^{\varnothing} - T\Delta_r S^{\varnothing} = -2.303 \, RT \log K$

Law of equilibrium :

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \text{ and } K_p = \frac{p_C^c \, p_D^d}{p_A^a \, p_B^b}$$

(where K_c and K_p are equilibrium constants in terms of molar concentration and pressure respectively.)

where $\quad K_p = K_c \, (RT)^{\Delta ng}$

Δng = [sum of stoichiometric coefficients of gaseous products

$\quad\quad\quad\quad$ – sum of stoichiometric coefficients of gaseous reactants]

Predicting the direction of reaction : The direction of reaction can be predicted by the value of reaction quotient Q_c which is defined the same way as equilibrium constant K_c except that the concentrations in Q_c are not necessary equilibrium values. If $Q_c > K_c$, the reaction proceeds in the reverse direction and if $Q_c < K_c$, the reaction will proceed in the forward direction. If $Q_c = K_c$, no net reaction occurs.

Magnitude of equilibrium constant depends upon the way in which a reaction is written.

Chemical equation	Equilibrium constant
$aA + bB \rightleftharpoons cC + dD$	K
$cC + dD \rightleftharpoons aA + bB$	$K_1 = \dfrac{1}{K}$
$naA + nbB \rightleftharpoons ncC + ndD$	$K_2 = K^n$
$\dfrac{a}{n}A + \dfrac{b}{n}B \rightleftharpoons \dfrac{c}{m}C + \dfrac{d}{n}D$	$K_3 = K^{1/n}$
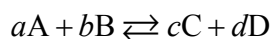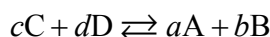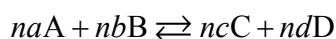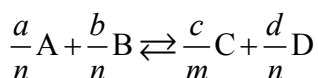
When individual balanced equations are combined, multiply their equilibrium constants to obtain the equilibrium constant for the net reaction. For example,

$$N_2 + O_2 \rightleftharpoons 2NO \; ; K_1$$

$$\underline{2NO + O_2 \rightleftharpoons 2NO_2 \; ; K_2}$$

$$N_2 + 2O_2 \rightleftharpoons 2NO_2 \; ; K = K_1 \times K_2$$
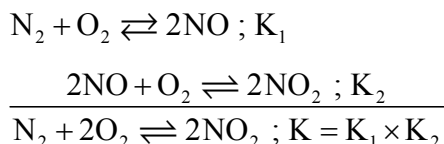
Le Chatelier's principle : When a system at equilibrium is subjected to a change in temperature, pressure or concentration of a reacting species, the system changes in a way that it reduces or concentrates the effect of the change while reaching a new state of equilibrium. Le Chatelier's principle can be used to study the effect of various factors such as temperature, concentration, pressure, catalyst and inert gases on the direction of equilibrium and to control the yield of products by controlling these factors.

Use of a catalyst does not effect the equilibrium composition of a reaction mixture but increases the rate of chemical reaction by making available a new lower energy pathway for conversion of reactants to products and vice-versa.

The pH scale :

Activity of hydrogen $(a_H+) = [H^+]/mol\ L^{-1}$

$$pH = -\log a_H+ = -\log \{[H^+]/mol\ L^{-1}\}$$

$$pOH = -\log \{[OH^-]/mol\ L^{-1}\}$$

and $pH + pOH = 14$

$\because \left[H^+ \right]\left[OH^- \right] = 1.0 \times 10^{-14}$ at 298 K

Ionisation constant of water and its ionic product

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
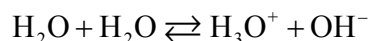
At 298k, $[H^+] = [OH^-] = 1 \times 10^{-7}$ M

$k_w = \left[H^+ \right] = \left[OH^- \right] = 10^{-14}$ at 298 K

Ionisation constants of Acids and Bases (Acid-Base Equilibrium)
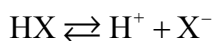
$$HX \rightleftharpoons H^+ + X^-$$

$$K_a = \frac{\left[H^+ \right]\left[X^- \right]}{[HX]} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

Similarly for base $MOH \rightleftharpoons M^+ + OH^-$

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

Product of ionisation constants of an acid (K_a) and its conjugate base (K_b) is equal to ionic product of water *i.e.,* $K_a \times K_b = K_w$

Ionisation of di and polybasic acids and di and polyacidic bases :

For example for diabasic acid (H_2X) :

$$H_2 \rightleftharpoons H^+ + HX^-$$

$$K_{a_1} = \frac{\left[H^+\right]\left[HX^-\right]}{[H_2X]}$$

and $\qquad HX^- \rightleftharpoons H^+ + X^{2-}$

$$K_{a_2} = \frac{\left[H^+\right]\left[X^{2-}\right]}{\left[HX^-\right]}$$

Higher order ionisation constants are smaller than lower order ionisation constants. Poly protic acid solution contain a mixture of acids like H_2X, HX^- and X^{2-} in case, of diprotic acids like H_2S, H_2CO_3 and oxalic acid.

Common ion effect : The depression of ionisation of weak electrolyte by the presence of common ion from a strong electrolyte is called common ion effect.

Hydrolysis of salts and pH of their solutions : Hydrolysis of salt is defined as the reaction of cation or anion with water as a result of which the pH of water changes.

1. Salts of strong acids and strong bases (e.g., NaCl) do not hydrolyse. The solution pH = 7.

2. Salts of weak acids and strong bases (e.g., CH_3COONa) hydrolyse, pH > 7. (The anion acts as a base).

$$X^- + H_2O \rightleftharpoons \underset{(Weak\ acid)}{HX} + \underset{(Strong\ base)}{OH^-}$$

pH = 7 + ½(pK_a + log c)

3. Salt of strong acids and weak bases (e.g., NH_4Cl) hydrolyse, pH < 7. (The cation acts as an acid).

$$M^+ + H_2O \rightleftharpoons MOH + H^+$$
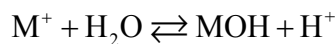
$$pH = 7 - \frac{1}{2}\left(pK_b + \log c\right)$$

4. Salt of weak acids and weak base (e.g., CH_3COONH_4) hydrolyse. The cation acts as an acid and anion as a base but whether the solution is acidic or basic depends upon the relative values of K_a and K_b for these ions.

$$M^+ + X^- + H_2O \rightleftharpoons MOH + HX$$
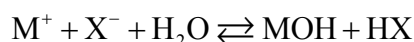
$$pH = 7 + \frac{1}{2}\left(pK_a - pK_b\right)$$

Buffer solutions : The solutions, which resist the change in pH on dilution or addition of small amounts of acid or base, are called buffer solutions.

Basic buffer : Solution of weak base and its salt with strong acid e.g., $NH_4OH + NH_4Cl$

Acidic buffer : Solution of weak acid and its salt with strong base, e.g., $CH_3COOH + NaOH$.

pH of buffer Solution : (Henderson-Hasselbach equation)

pH of an acidic buffer :

$$pH = pK_a + \log \frac{(Salt)}{(Acid)}$$

pH of a basic buffer :

$$pH = pK_a + \log \frac{(Base)}{(Salt)}$$

Solubility product constant (K_{sp}) : The equilibrium constant that represent the equilibrium between undissolved salt (solute) and its ions in a saturated solution is called solubility product constant (K_{sp}). In the absence of equilibrium, *i.e.,* if the concentration of one or more species is not the equilibrium concentration, the product of concentration of ions raised to powers equal to respective stoichiometric coefficients appearing in balanced chemical equation is called Q_{sp}, the ionic product of salt.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$
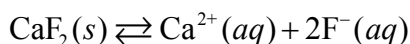
$$K_{sp} = \left[Ca^{2+}\right]\left[F^-\right]^2$$

If the concentration of any one of the ions is increase, it will combine with the ion of opposite charge and some of the salt will be precipitated till once

again $K_{sp} = Q_{sp}$ and if the concentration of any one of their ions decreased more salt will dissolve to increase the concentration of both the ions till once again $K_{sp} = Q_{sp}$.

1- MARK QUESTIONS

1. Define physical equilibrium. Give an example also.
2. Justify the statement : 'Both physical and chemical equilibria are dynamic in nature.'
3. At what temperature the solid and liquid phase of the same substance are in equilibrium with each other ?
4. State the law of chemical equilibrium.
5. Name the indicator used for titration of strong acid versus strong base.
6. Mention the effect of temperature on solubility of a gas in liquid.
7. State Henry's law.
8. Write the expression of K_c for the following reaction :

    $$CH_3COOC_2H_5 \ (aq) + H_2O \ (l) \rightleftharpoons CH_3COOH \ (aq) + C_2H_5OH \ (aq)$$
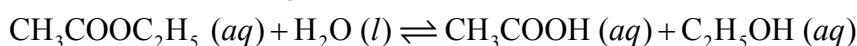
9. Write the expression of K_p for the following reaction :

    $$Cu(NO_3)_2 \ (s) \rightleftharpoons 2CuO \ (s) + 4NO_2 \ (g) + O_2 \ (g)$$
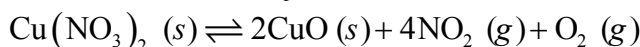
10. For the following equilibrium $K_c = 6.3 \times 10$ at 1000 K :

    $$NO \ (g) + O_3 \ (g) \rightleftharpoons NO_2 \ (g) + O_2 \ (g)$$
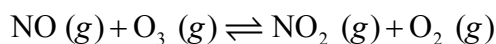
    Find the value of K_c for the following :

    $$\frac{1}{2} NO \ (g) + \frac{1}{2} O_3 \ (g) \rightleftharpoons \frac{1}{2} NO_2 \ (g) + \frac{1}{2} O_2 \ (g)$$
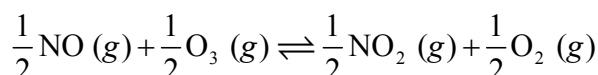
11. Equilibrium constant (K_c) for the reaction $N_2 \ (g) + 3H_2 \ (g) \rightleftharpoons 3NH_3 \ (g)$ at 500 K is 0.061. Calculate the value of K'_c for the reversible reaction.
12. Give an example of a heterogeneous equilibrium.
13. $N_2 \ (g) + 3H_2 \ (g) \rightleftharpoons 3NH_3 \ (g) +$ Heat

    What is the effect of increasing temperature on the value of K.
14. $H_2 \ (g) + I_2 \ (g) \rightleftharpoons 2HI \ (g)$

    Write the relationship between K_p and K_c for the given reaction.
15. Why does a catalyst not affect the magnitude of equilibrium constant ?
16. Define solubility product.
17. What is meant by ionic product of water ?

18. Calculate the pH of 0.01 M NaOH solution.

19. Why does BF_3 act as a Lewis acid ?

20. Write the conjugate acid of NH_3.

21. Write the expression of K_{sp} for Ag_2CrO_4.

22. Define common ion effect.

23. How does common ion effect affect the solubility of salts ?

24. Define dissociation constant of a base.

25. Predict the direction of reaction when $Q_c > K_c$.

26. NH_3 acts as Arrhenius base as well as Bronsted base. Explain.

27. Give the relationship between K_a, C and α where K_a is the dissociation constant of acid, C is the initial concentration of acid and α is its degree of dissociation. Write the condition when α is neglected in comparison to C.

28. Arrange the following acids in increasing order of their pK_a values :

    HCl, HBr, HF and HI.

29. Write the unit of K_p for the following equilibrium :

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

30. Define Le Chatlier's principle.

31. If K_a value for hydrofluoric acid (HF) is 6.8×10^{-4}, what is the K_b value of its conjugate base at 298 K. Given $K_w = 1.0 \times 10^{-14}$ at 298 K.

    [**Ans.** $K_b \ (F^-) = 1.5 \times 10^{-11}$]

32. Explain why pure NaCl precipitates out when HCl gas is passed in brine solution.

2 - MARK QUESTIONS

1. (a) Write an expression of K_p for the following reaction :
       $CaCO_3 \ (s) \rightleftharpoons CaO \ (s) + \ CO_2 \ (g)$
   (b) Mention the effect of decreasing the concentration of CO_2 on direction of reaction.

2. For an endothermic reaction, how does the value of K_c changes when :
   (a) temperature is increased ?
   (b) pressure is increased ?

3. (a) Define buffer solution.
   (b) Give one example each of an acidic buffer and a basic buffer.

4. Write the conjugate bases for the following acids :
   (a) HF   (b) NH_4^+ (c) HCO_3^- (d) H_2SO_4
5. With the help of examples explain the factors affecting the strength of an acid.
6. (a) Vapour pressure of water, acetone and ethanol at 293 K are 2.34, 12.36 and 5.85 kPa respectively. Which of these have the lowest and highest boiling point ?
   (b) At 293 K, which of these will evaporate least in a sealed container before equilibrium is reached ?
7. The concentration of hydrogen ion in soft drink is 3.8×10^{-3} mol L^{-1}. Calculate its pH.
8. For the general reaction :
$$aA \ (g) + bB \ (g) \rightarrow cC \ (g) + dD \ (g)$$
   Derive the relationship between K_c and K_p.
9. Assign reasons for the following :
   (a) A solution of NH_4Cl in water shows pH less than 7.
   (b) In qualitative analysis NH_4Cl is added before adding NH_4OH for testing Fe^{3+} or Al^{3+} ions.
10. (a) Mention the difference between a weak electrolyte and a strong electrolyte.
    (b) Which of the following species is a strong electrolyte :
$$CH_3COOH \text{ and } CH_3COONa$$
11. Calculate the pH of 1.0×10^{-8} M solution of HCl.   [**Ans.** pH = 6.98]
12. (a) Write the hydrolysis reaction of ammonium acetate.
    (b) The pK_a of acetic acid and pK_b of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution.
    [**Ans.** pH = 7.005]
13. (a) Write the conjugate acid and conjugate base of H_2O.
    (b) Write the relationship between equilibrium constant and standard Gibbs energy.
14. If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K, calculate the pH of this solution. (Molar mass of KOH = 56 g mol^{-1})
    [**Ans.** pH = 12.70]
15. The value of K_c for the reaction :
$$3O_2(g) \rightleftharpoons 2O_3(g)$$

is 2.0×10^{-5} at 25° C. If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2} M, calculate the concentration of O_3.

16. Calculate the minimum volume of water required to dissolve 1 g $CaSO_4$ at 298 K ? (For $CaSO_4$ $K_{sp} = 9.1 \times 10^{-6}$) **[Ans. 2.46 L of water]**

17. The pH of 0.1 M monobasic acid is 4.50. Calculate the concentration of species H_3O^+, A^- and HA at equilibrium.

18. The cations of strong bases like Na^+, K^+, Ca^{2+}, Ba^{2+} etc. and anions of strong acids like Cl^-, Br^-, NO_3^-, ClO_4^- etc. get hydrated in water but do not hydrolyse. Explain why ?

19. Calculate the pH of a buffer solution containing 0.2 mole of NH_4Cl and 0.1 mole of NH_4OH per letre. K_b for $NH_4OH = 1.85 \times 10^{-5}$.

20. How much CH_3COONa should be added to 1 litre of 0.1 M CH_3COOH to make a buffer of pH = 4.0 ? $K_a = 1.8 \times 10^{-5}$.

3 - MARK QUESTIONS

1. (a) Which of the following will act as Lewis acid :

    H_2O, BF_3 and H^+

    (b) Equal volumes of 0.02M $CaCl_2$ and 0.0004M Na_2SO_4 are mixed. Will a precipitate form ? Given : K_{sp} for $CaSO_4 = 2.4 \times 10^{-5}$.

2. (a) Assign reasons to the following :

    (i) Pure liquids and solids can be ignored while writing the equilibrium constant expression.

    (ii) H_2S is passed in acidic medium to precipitate group 2 cations.

    (b) Write the effect of temperature on ionic product of water.

3. (a) Explain the hydrolysis of salts.

    (b) For the reaction :

    $$2NOCl \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$$

    The value of $K_c = 3.75 \times 10^{-6}$ at 1069 K. Calculate K_p at this temperature.

    [Ans. $kp = 3.33 \times 10^{-2}$]

4. (a) Define reaction quotient.

    (b) A mixture of H_2, N_2 and NH_3 with molar concentrations of 3.0×10^{-3} mol L^{-1} and 2.0×10^{-3} mol L^{-1} respectively was prepared at 500 K. Predict whether at this stage the concentration of NH_3 will increase or

decrease. Given the value of K= 61 for the reaction :

$$N_2 (g) + 3H_2 (g) \rightleftharpoons 3NH_3 (g) \text{ at } 500 \text{ K.}$$

5. Consider the reaction :

$$2SO_2 (g) + O_2 (g) \rightleftharpoons 3SO_3 (g) \qquad \Delta_r H° = -190 \text{ KJ/mol}$$
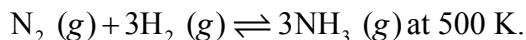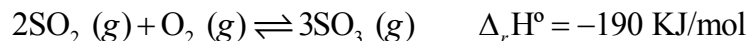
Indicate the direction in which the equilibrium will shift when :

(a) temperature is increased.

(b) pressure is decreased.

(c) an inert gas is added at constant volume and

(d) inert gas is added at constant pressure?

6. (a) Classify the following as homogeneous or heterogeneous equilibria :

(i) $2NO (g) + O_2 (g) \rightleftharpoons 2NO_2 (g)$

(ii) $Mg (s) + O_2 (g) \rightleftharpoons 2MgO (s)$

(b) Consider the following transformations :

$$A \rightleftharpoons B \qquad K_1 = 1$$
$$B \rightleftharpoons C \qquad K_2 = 2$$
$$C \rightleftharpoons D \qquad K_3 = 3$$

Calculate the value of K for $A \rightleftharpoons D$.

7. (a) Give one example each of a Lewis and a Lewis base.

(b) All Lewis bases are also Bronsted bases. Explain.

(c) K_b for NH_4OH and CH_3NH_2 are 1.8×10^{-5}, 4.4×10^{-4}. respectively. Which of them is stronger base and why?

8. Ammonia is prepared by Haber's process in which the following reaction occurs :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 93.6 \text{ KJ}$$

Mention the effect of following on the equilibrium conc. of ammonia :

(a) Increasing pressure

(b) Increasing temperature

(c) Use of a catalyst at an optimum temperature

9. Calculate the pH of following solution :

(i) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution.

(ii) 1.0 mL of 13.6M HCl is diluted with water to give 1.0L solution.

(iii) 10 mL of 0.1M H_2SO_4 + 10 mL of 0.1M KOH.

[**Ans.** (i)12.21; (ii) 1.87; (iii) 3.00]

10. At 700 K, equilibrium constant for the reaction :

$$H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$$
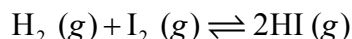
is 54.8. If 0.5 mol L^{-1} of HI (g) is present at equilibrium at 700 K, calculate the concentrations of H_2 (g) and I_2 (g) assuming that we initially started with HI (g) and allowed it to reach an equilibrium at 700 K.

[**Ans.** $[H_2] = [I_2] = 0.068M$]

11. One mole of H_2O and one mole of CO are taken in a vessel and heated to 725 K. At equilibrium 40% (by mass) of water reacts with CO according to the equation :

$$H_2O\ (g) + CO\ (g) \rightleftharpoons H_2\ (g) + CO_2\ (g)$$
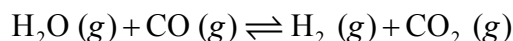
Calculate the equilibrium constant for the reaction. [**Ans.** 0.44]

12. The following reaction takes place in the blast furnace during the extraction of iron from haemetite ore :

$$FeO\ (s) + CO\ (g) \rightleftharpoons Fe\ (s) + CO_2\ (g)$$
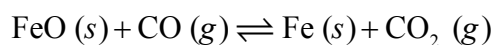
K_p = 0.265 atm at 1050 K

(a) If the initial partial pressure are p_{CO} = 1.4 atm and P_{CO2} = 0.80 atm, predict the direction of rector. [**Ans.** The reaction moves backwards]

(b) Calculate the equilibrium partial pressure of CO and CO_2 at 1050 K.

[**Ans.** $[P_{CO}]$ = 1.139 atm. $[P_{CO2}]$ = 0.461 atm.]

13. Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate Cu $(IO_3)_2$? For cupric iodate K_{sp} = 7.4 × 10^{-8}.

[**Ans.** Ionic product = 1 × 10^{-9}, No precipitation]

14. The pH of 0.1M solution of an acid (HA) is 2.34. Calculate the ionisation constant of the acid and its degree of ionization in solution.

[**Ans.** Ka = 2.09 × 10^{-4}, α = 4.57%]

15. The solubility of Sr(OH)$_2$ at 298 K is 19.23 g/L of solution. Calculate the molar concentrations of strontium and hydroxyl ions and the pH of the solution. [Molar mass of Sr(OH)$_2$ = 121.67 g/mol].

[**Ans.** $[Sr^{2+}]$ = 0.1581 M ; pH = 3.09, $[OH^-]$ = 0.3162 M]

1. (a) K_{a_2} of oxalic acid has much lower value than K_{a_1}. Explain.

    (b) The following species act as both Bronsted acids and bases. Write the conjugate acid and conjugate base formed by them :

    H_2O and HSO_4^-

    (c) At 450 K, $K_p = 2.0 \times 10^{10}$ /bar^{-1} for the following reaction :

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

    Calculate the value of K_c at this temperature.

    [**Ans.** $K_c = 7.47 \times 10^{11}\ M^{-1}$]

2. (a) Predict whether the following inorganic salts will give acidic, basic or neutral solutions. Give appropriate reasons.

    NH_4Cl, NaCN, NaCl

    (b) Calculate the pH of a 0.10M ammonia solution. Calculate the pH after 50.0 ml of this solution is treated with 25.0 ml of 0.10M HCl. The dissociation constant of ammonia (K_b) is 1.77×10^{-5}.

    [**Ans.** 11.12, 9.24]

3. Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as :

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

    (i) Write the reaction quotient, Q_c for this reaction .

    (ii) At 293 K, if one starts with 1.0 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.   [**Ans.** $K_c = 22.9$]

    (iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293K, 0.214 mol of ethylacetate is found after sometime. Has the equilibrium been attained ?

    [**Ans.** $Q_c < K_c$, therefore equilibrium is not reached]

4. For the reaction, $\Delta_r H$ is positive :

    $$CH_4\ (g) + H_2O\ (g) \rightleftharpoons CO\ (g) + 3H_2\ (g)$$

    How will the value of K_p and composition of equilibrium mixture be affected by :

    (a) Increasing the pressure

    (b) Increasing the temperature

(c) Using a catalyst ?

5. (a) Arrange the following in the increasing order of K_a :

HF, H_2O, NH_3, CH_4

(b) The K_b value for dimethylamine, $(CH_3)NH$, is 5.4×10^{-4}. Calculate its degree of ionization in its 0.02 M solution. **[Ans.** $\alpha = 0.162$]

(c) Calculate the percentage of dimethylamine ionized if the solution is also 0.1M in NaOH. **[Ans.** $\alpha = 0.0054$]

REDOX REACTIONS

Oxidation and Reduction :

Oxidation is a process which involves either of the following :

(a) addition of oxygen and removal of hydrogen.

(b) addition of electronegative element and removal of electropositive element.

(c) increase in the oxidation state of an electropositive element.

(d) loss of one or more electron by an atom or an ion or molecule.

reduction is the reverse process of oxidation.

Oxidation number (Oxidation state) is the charge that an atom appears to have in a given species when the bonding electrons are counted using following rules :

(a) The oxidation number (O. N.) of an atom in its elemental state is zero, no matter how complicated the molecule is, *e.g.,* H in H_2, S in S_8, P in P_8, O in O_2 or O_3.

(b) F has oxidation number -1.

(c) Oxidation number of oxygen is -2 in all compounds except in peroxides, superoxides and oxygen fluoride. In O_2^{2-} ox. no. is -1, in O_2^{-} is $-\frac{1}{2}$, in OF_2 is $+2$, O_2F_2 is $+1$.

(d) The oxidation number of hydrogen is $+1$ in all its compounds except metallic hydrides where it is -1.

(e) The oxidation number of group I elements is $+1$ and group 2 is $+2$.

(f) For complex ion, the algebric sum of oxidation numbers of all the atoms in equal to the net charge on the ion.

Note : In an organic compound containing C, H, O. The oxidation number of C can be calculated as given below

$$C = \frac{n_o \times 2 - n_H}{n_C}$$

When n_O = number of oxygen atoms

n_H = number of hydrogen atoms

n_C = number of carbon atoms.

Stock notations : Cu_2O (Cuprous oxide)

Oxidation state of Copper $= +1$

Stock notation of Cu_2O will be $Cu_2(I)O$.

Types of Redox reactions :
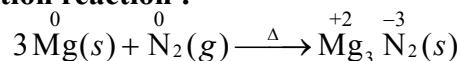
(a) Combination reaction :

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

(b) Decomposition :

$$3\overset{+1}{K}\overset{+5}{Cl}\overset{-2}{O_3} \rightarrow 2\overset{+1}{K}\overset{-1}{Cl} + 3\overset{0}{O_2}(g)$$

(c) Metal displacement :

$$3\overset{+2}{Cu}\overset{+6}{S}\overset{-2}{O_4} + \overset{0}{Zn}(s) \rightarrow \overset{+2}{Zn}\overset{+6}{S}\overset{-2}{O_4} + \overset{0}{Cu}$$

(d) Non-metal displacement :

$$3\overset{0}{Ca}(s) + 2\overset{+1}{H_2}\overset{-2}{O}(l) \rightarrow \overset{+2}{Ca}(\overset{-2}{O}\overset{+1}{H})_2(aq) + \overset{0}{H_2}(g)$$

(e) Disproportionation :

$$\overset{0}{Cl_2} + 2OH(aq) \rightarrow Cl^{-1}(aq) + \overset{+1}{Cl}O^- + H_2O$$
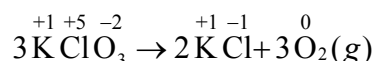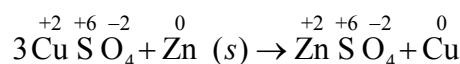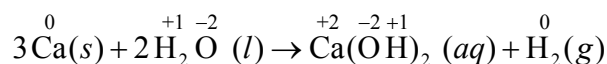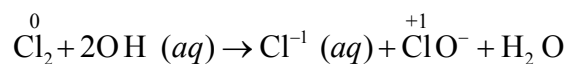
Salt bridge and its significance :

An inverted U-tube filled with concentrated solution of inert electrolyte like NH_4NO_3, KCl in agar agar or Gelatin.

(a) It connects the solution of two half-cells.

(b) It prevents the accumulation of charges in anodic as well as cathodic half-cells.

1 - MARK QUESTIONS

1. Identify the oxidants and reductants in the following reaction :

$$Zn(s) + \frac{1}{2}O_2(g) \rightarrow ZnO(s)$$
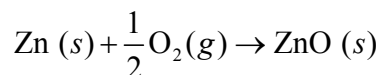
2. Define oxidation number or oxidation state of a chemically combined element.

3. Define the term oxidation and reduction in terms of oxidation number.

4. Identify the strongest and weakest reducing agent from the following metals :

Zn, Cu, Ag, Na, Sn.

5. Which one of the following is a case of reduction :

(a) $Sn^{4+} \rightarrow Sn^{2+}$ (b) $Sn^{2+} \rightarrow Sn^{4+}$

(c) $Fe^{2+} \rightarrow Fe^{3+}$ (d) $Cl^- \rightarrow Cl^0$

6. The oxidation number of iron in reaction :
$$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-}$$
changes from :
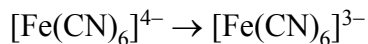
(a) –4 to –3   (b) –3 to –2

(c) +2 to +3   (d) +3 to +2

7. The reaction :
$$3ClO^- \, (aq) \rightarrow ClO_3^- \, (aq) + 2Cl^- \, (aq)$$
is an example of :

(a) Oxidation   (b) Reduction

(c) Disproportionation   (d) Decomposition

8. Calculate the oxidation number of chromium and nitrogen in $Cr_2O_7^{2-}$ and NO_3^-.

9. Arrange the following metals in the order in which they displace each other from the solution of their salts :

Al, Cu, Fe, Mg and Zn.

10. Sodium reacts with hydrogen to form an ionic compound Na^+H^-. Suggest half reactions in this process.

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2 - MARK QUESTIONS

</div>

1. Justify that the reaction :
$$2Cu_2O \, (s) + Cu_2S \, (s) \rightarrow 6Cu \, (s) + SO_2 \, (g)$$
is a redox reaction, identify the species oxidised/reduced.
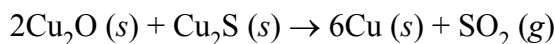
2. Construct the cell in which the given reactions are taking place, which electrode shall act as anode (negative electrode) and which one as cathode (positive electrode) :

(a) $ZnSO_4 + CuSO_4 = ZnSO_4 + Cu$

(b) $Cu + 2AgNO_3 = Cu(NO_3)_2 + 2Ag$

3. Four metals A, B, C, D have their standard reduction potential values equal to +.80, –0.76, –0.12 and 0.34 V respectively. Arrange them in decreasing order of their electropositive character.

[**Hint :** The metal which has high negative value of standard reduction potential possess great tendency to lose electron(s), that is, it is highly electropositive and reducing in nature.]

4. Given the standard electrode potential :

$K^+/K = -293$ V : $Ag^+/Ag = 0.80$ V

$Hg^{2+}/Hg = +0.79$ V : $Mg^{2+}/Mg = -2.37$ V

$Cr^{3+}/Cr = -0.74$ V
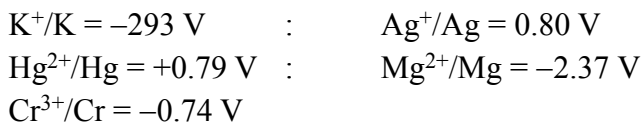
Arrange these in increasing reducing power.

5. Define the term redox couple. Write a practical application of redox couple.

6. (a) What are the functions of salt bridge in an electrochemical cell ?

(b) What is standard hydrogen electrode ?

7. Standard reduction potential of Flourine, chlorine, bromine and iodine is given below :

$E^\theta F_2/F^- = +2.87V; E^\theta Cl_2/Cl^- = +1.36V; E^\theta Br_2/Br^- = 1.09V; E^\theta I_2/I^- = 0.54V$

Identify (i) Which one of the halogen is best oxident and why

(ii) Among hydrohalic acids such as HF, HBr, HCl and HF which is best reductant.

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3 - MARK QUESTIONS

1. Explain why :

(a) The reaction $FeSO_4 + Cu \rightarrow CuSO_4 + Fe$ does not occur.

(b) Copper metal displace silver from silver nitrate solution but silver fails to displace zinc from zinc nitrate solution.

(c) Solution of $AgNO_3$ turns blue when copper rod is immersed in it.

2. Account for the following :

(a) HNO_3 acts only as an oxidising agent while HNO_2 can act both as reducing and oxidising agent.

(b) ClO_4^- does not show disproportionation reaction.

(c) Ozone acts as an oxidising agent.

[Hint :

(a) The oxidation number of nitrogen in HNO_3 is +5 thus increase in oxidation number +5 does not occur hence HNO_3 cannot act as reducing agent but acts as a oxidising agent. In HNO_2 oxidation number of nitrogen is +3, it can decrease or increase with range of –3 to +5, hence it can act as both oxidising and reducing agent.

(b) Chlorine is in maximum oxidation state +7 ClO_4^-, it does not show the disproportion reaction

(c) because it decompose to give nascent oxygen.]

3. Write the balanced ionic equation for the reaction of potassium dichromate (VI) $K_2Cr_2O_7$ with sodium sulphite in acid medium to give Cr (III) and sulphate ions.

4. Balance the following equation by oxidation number method :

$$P(s) + OH^- (aq) \rightarrow PH_3 + H_2PO_2^- (aq)$$

5. Write one example of each type of redox reactions :

(a) Combination reaction

(b) Decomposition reaction

(c) Metal displacement reaction

6. (a) Calculate the oxidation number of :

    (i) Cr in $Cr_2O_4^{2-}$ (ii) O in KO_2

(b) Balance the following equation in basic medium by half reaction method :

$$AsO_3^{3-} + MnO_4^- \rightarrow AsO_4^{3-} + Mn_2O_3$$

7. Identify the species undergoing oxidation and reduction :

(a) $H_2S (g) + Cl_2 (g) \rightarrow 2HCl (g) + S (s)$

(b) $3Fe_3O_4 (s) + 8Al (s) \rightarrow 9Fe (s) + 4Al_2O_3 (s)$

(c) $2Na (s) + H_2 (g) \rightarrow 2NaH (s)$

8. Account for the following :

(a) While H_2O_2 can act as oxidising as well as reducing agent in their reactions, O_3 and HNO_3 acts as oxidants only.

(b) When conc. H_2SO_4 is added to a inorganic mixture containing chloride, HCl is produced but if a mixture contains bromide, then we get red vapours of bromine.

(c) AgF_2 is unstable compound and a strong oxidising agent.

[Hint :

(a) In H_2O_2 oxidation number of O = −1 and can vary from 0 to −2 (+2 is possible in OF_2). The oxidation number can decrease or increase, because of this H_2O_2 can act both oxidising and reducing agent.

(b) HCl is a weak reducing agent and can reduce H_2SO_4 to SO_2 and hence HCl is not oxidised to Cl_2. When NaBr is heated HBr is produced, which is a strong reducing agent and itself oxidised to red vapour of Br_2.

$2NaBr + 2H_2SO_4 \rightarrow NaHSO_4 + 2HBr$
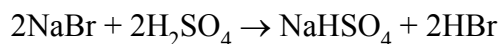
(c) $Ag^+ \rightarrow 4d^{10}. 5s^0$

$Ag^{2+} \rightarrow 4d^9. 5s^0$
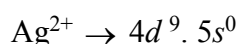
Configuration shows that Ag^+ is more stable than Ag^{2+}, thus Ag^{2+} changes to Ag^+ and it acts as a oxidising agent.

9. depict the galvanic cell in which following reaction :

$Zn(s) + 2Ag^+ ® Zn^{2+}_{(aq)} + 2Ag(s)$ takes place
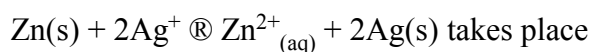
Further show–

(i) Which electrode is negatively charged?

(ii) Name the carried of current in the cell?

(iii) Reaction takes place at each electrode

10. Balance the following redox reaction by ion electron method (in basic medion) :

(i) $MnO_4^- + I^- \rightarrow MnO_2 + IO_3^-$

(ii) $Cl_2 + OH^- \rightarrow Cl^- + ClO_3^-$.

HYDROGEN

Unique position of Hydrogen in the periodic table.

Hydrogen ($1s^1$) can gain one electron to form H^- ion like halogens. It can also lose its electron to form H^+ ion like alkali metals. It resembles both alkali metals and halogens but also it differs from both as well, therefore it is placed separately.

Isotopes of Hydrogen :

(a) Protium, $_1^1H$

(b) Deuterium, $_1^2H$ or D

(c) Tritium, $_1^3H$ or **T**

Tritium is radioactive and shows β-activity ($t_{1/2}$ = 12.33 years)

Hydrides :

(1) Ionic hydrides are formed with most of *s*-block elements. Significant covalent character is found in LiH, BeH_2 and MgH_2. Infact BeH_2 and MgH_2 are polymeric in nature.

(2) Covalent or molecular hydrides are formed with most of *p*-block elements. They are further classified as :

(a) Electron deficient hydrides are formed by group 13 elements *e.g.*, B_2H_6. The act as Lewis acid.

(b) Electron precise hydrides are formed by group 14 elements, *e.g.,* CH_4.

(c) Electron rich hydrides have lone pair(s) of electrons on the central atoms of the molecules. Elements of group 15-17 form this type of hydrides.

Examples are NH_3, HF etc. Presence of lone pair(s) on highly electronegative atoms like N, O and F in hydrides results in intermolecular hydrogen bond formation leading to the association of molecules resulting in exceptionally high m.p. and b.p.

(3) Metallic or non-stoichiometric or interstitial hydrides are formed by *d*- and *f*-block elements. For example, $LaH_{2.87}$, $TiH_{1.5-1.8}$, $ZrH_{1.3-1.75}$ etc.

Properties :

The chemical behaviour of H_2 to a large extent is determined by high bond dissociation enthalpy. ($435.88 k/mol^{-1}$)

As its orbital is incomplete with $1s^1$ electronic configuration. It shows reactions by :

(a) loss of the only electron to give H^+.

(b) Gain of electron to form H^-.

(c) Sharing electrons to form a single covalent bond.

Hydrogen Peroxide (H_2O_2)

Oxidising action of H_2O_2 :

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad \text{(acidic medium)}$$
$$H_2O_2 + 2e^- \rightarrow 2OH^- \qquad \text{(basic medium)}$$

Reduction action of H_2O_2 :

$$H_2O_2 \rightarrow 2H^+ + O_2 + 2e^- \qquad \text{(acidic medium)}$$
$$H_2O_2 + 2OH^- \rightarrow 2H_2O + O_2 + 2e^- \qquad \text{(basic medium)}$$
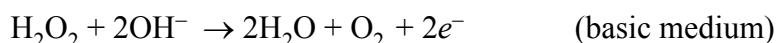
H_2O_2 oxidises :

(a) Fe^{2+} to Fe^{3+} (acidic as well as basic medium)

(b) S^{2-} to SO_4^{2-} (acidic medium)

H_2O_2 reduces :

(a) MnO_4^- to Mn^{2+} (acidic medium)

(b) MnO_4^- to MnO_2 (basic medium)

(c) I_2 to I^- (basic medium)

Bleaching action :

It acts as a bleaching agent and its bleaching action is due to the oxidation of colouring matter.

The strength of H_2O_2 solution is expressed as volume strength as given below :

$$\text{Molarity} \times 11.2 = \text{Volume strength of } H_2O_2$$
$$\text{Normality} \times 5.6 = \text{Volume strength of } H_2O_2$$

1 - MARK QUESTION

1. Justify the position of hydrogen in the periodic table.

2. Define 'autoprotolysis' of water.

3. Name the radioactive isotope of hydrogen.

4. Explain why covalent compounds like alcohol and carbohydrates are soluble in water ?

5. How many hydrogen-bonded water molecule(s) are present in $CuSO_4.5H_2O$?

6. Give an example of 'non-stoichiometeric hydrides'.

7. Why is hydrogen regarded as fuel for future ?

8. Write chemical formula for 'Colgon'.

9. Why hydrogen peroxide is kept in wax lined glass or plastic vessels in dark ?

10. Name the compound which is manufactured by repeated electrolytic enrichment of water.

11. Hydrogen gas is relatively inert at room temperature. Why?

12. Which property of water makes it a unique subvstance on earth?

13 Which groups in d-block elements do not form metallic hydrides.

2 - MARK QUESTIONS

1. Write two chemical reactions to show the atmospheric nature of water.

2. Complete the following reactions :

   (a) $NaH (s) + H_2O \longrightarrow$

   (b) $LiH + Al_2Cl_3 \longrightarrow$

3. Calculate the strength of 20 volume solution of hydrogen peroxide.

4. How can H_2O_2 be prepared by hydrated barium peroxide ($BaO_2 .8H_2O$) ?

5. Write the consequences of high enthalpy of H–H bond in terms of chemical reactivity of dihydrogen ?

6. Explain why hard water does not produce lather with soap ?

7. Assign the reason for the following :

   (a) Enthalpy of fusion of water is higher as compared to the hydrides of cogeners.

   (b) Water is quite stable and does not dissociate in to its elements even at high temperature.

   [Hint :

   (a) Due to the presence of intermolecular hydrogen bonding.

   (b) Due to its high negative enthalpy of formation ($\Delta_f H = -285.9$ KJmol^{-1})]

8. Write ionic equations for each of the following reactions :

   (a) H_2O_2 reduces acidified potassium permanganate solution to colourless manganese sulphate.

   (b) H_2O_2 oxidises ferrous sulphate to ferric sulphate in acidic medium.

9. Explain why hydrogen peroxide acts as a bleaching agent ? Name the type of reaction involved in its bleaching action.

10. Write any four uses of dihydrogen.

3 - MARK QUESTIONS

1. Define the following with one example of each :

   (a) electron-deficient hydride

   (b) electron-precise hydride

   (c) electron-rich hydride

2. Account for the following :

   (a) PCl_5 exists but PH_5 does not

   (b) Water is responsible for moderation of the climate and the body temperature of living beings

   (c) Hard water is not suitable for boilers as well as for laundary.

   [Hint :

   (a) High Δ_aH value of dihydrogen and less negative value of $\Delta_{eg}H$ of hydrogen do not favour to exhibit highest oxidation state of P and consequently the formation of PH_5, although P exhibit +3, +5 oxidation state.

   (b) High heat of vapourisation and high heat capacity.

   (c) Hard water form precipitate with soap and deposition of salts in the form of scales.]

3. Complete the following reactions :

   (a) $Ca_3H_2 + H_2O \rightarrow$

   (b) $AlCl_3\ (g) + H_2O \rightarrow$

   (c) $CaO\ (s) + H_2O \rightarrow$

4. Write chemical emulation involved in the preparation of hydrogen peroxide from

   (a) Barium peroxide

   (b) Peroxide sulphate

   (c) 2-Ethyl anthraquinol

5. Explain the following terms :
   (a) Hydrogenation

   (b) Syn gas

   (c) Water-shift reaction

6. What is permutit method for the removal of permanent hardness of water ? Give the name and chemical formula of the inorganic salt and the reaction involved in this method.

7. Assign the reason for the following observations :
   (a) The temporary hardness of water is removed by boiling.

   (b) In the Clark's method, only calculated amount of lime is added to hard water for removal of hardness.

   (c) Regeneration of sodium zeolite is essential by brine.

8. Complete the following reactions :

   (a) $CO\ (g) + H_2\ (g) \xrightarrow[\text{catalyst}]{\Delta}$

   (b) $Zn + NaOH \xrightarrow{\text{heat}}$

   (c) $P_4O_{10}\ (s) + 6H_2O \rightarrow$

9. Comment on the reaction of dihydrogen with :

   (a) Chlorine

   (b) Sodium

   (c) Copper(II) oxide

   [Hint :

   (a) H_2 reduces chlorine into chloride $[Cl^-]$ ion and itself get oxidised to H^+ ion by chlorine to form HCl.

   (b) Dihydrogen is reduced by Na to form NaH, *i.e.*, Na^+H^-.

   (c) H_2 reduces Cu(II) oxide to copper Cu(0) and itself get oxidised to H_2O.]

10. Explain the following

    (a) The density of ice is less than that of liquid water?

    (b) The boiling point of water is less than that of H_2S.

    (c) NaH has higher reducing character than H_2O.

11. Classify the following reactions as hydrolysis, redix and hydration reaction.

(a) $PbS + 4 H_2O_2 \rightarrow PbSO_4 + 4H_2O$

(b) $AlCl_3 + H_2O_{(l)} \rightarrow Al(OH)_3 + 3HCl$
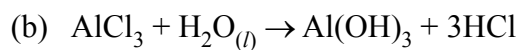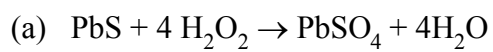
12. What are the main limitations of dihydrogen to be used as a fuel?

13. Complete the following equation—

(a) $Co(g) + 2H_2(g) \xrightarrow[\text{(Catalyst)}]{\text{CO}}$

(b) $LiH + B_2H_6 \longrightarrow$
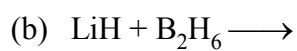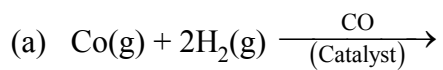
THE *s*-BLOCK ELEMENTS

Trends in atomic and physical properties

Flame colouration : All alkali metals impart characteristic colours to the flame. Due to the low ionization enthalpy, the electrons of alkali metals can be easily excited to the higher energy levels by the small energy provided by the Bunsen flame. When these excited electrons return to the ground state, the absorbed energy is emitted in the visible region of the electromagnetic spectrum and hence the flame appears coloured.

Photoelectric effect : Due to low ionization enthalpies, alkali metals especially K and Cs show photoelectric effect.

Reducing character : All the alkali metals are good reducing agents due to their low ionization enthalpies. Their reducing character in aq. medium, however, follows the order :

$$Na < K < Rb < Cs < Li$$

Mobility of ions in aqueous solution : The alkali metal ions exist as hydrated ions $M^+(H_2O)_x$ in the aqueous solution. The degree of hydration, however, decreases with the increase in ionic size as we move from Li^+ to Cs^+. In other words, Li^+ ion is most highly hydrated *e.g.,* $[Li(H_2O)_6]^+$. Since the mobility of ions is inversely proportional to the size of their hydrated ions, therefore, amongst the alkali metal ions, lithium has the lowest ionic mobility aqueous medium.

Chemical properties of alkali metals

Reaction with water : All the alkali metals readily react with water evolving hydrogen.

$$2M + 2H_2O \rightarrow 2MOH + H_2$$
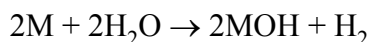
Reaction with oxygen : All the alkali metals when heated with oxygen form different types of oxides. For example, lithium forms mainly lithium oxide (Li_2O) sodium forms sodium peroxide (Na_2O_2) and some NaO_2, while K, Rb and Cs form their respective superoxides (MO_2 where M = K, Rb or Cs. In all these oxides, the oxidation state of the alkali metals is +1:) Superoxides are coloured and paramagnetic as these possess three electron bond (:O$\cdots$O:)where one unpaired electron is present. All oxides, peroxides and superoxides are basic in nature.

$$M_2O + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2$$

$$2M_2O_2 + H_2O \rightarrow 2M^+ + 2OH^-$$

$$2MO_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2 + O_2$$
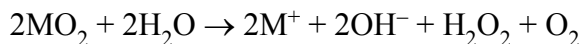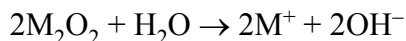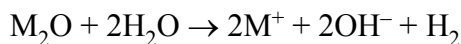
Reaction with hydrogen : All the alkali metals when heated with hydrogen form ionic crystalline hydrides of the general formula M^+H^-.

$$2M + H_2 \rightarrow 2M^+H^- \qquad \text{(where M = Li, Na, K, Rb or Cs)}$$
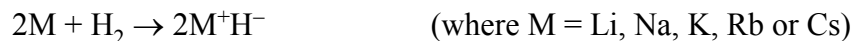
Reaction with halogens : All the alkali metals react vigorously with halogens to form their respective ionic crystalline halides of the general formula, M^+X^- where M = Li, Na, K, Rb or Cs and X = F, Cl, Br or I.

$$2M + X_2 \xrightarrow{\Delta} 2M^+X^-$$
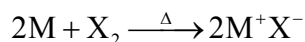
With the exception of LiF, all other lithium halides are covalent. Being covalent, LiCl, LiBr and LiI are insoluble in water but are soluble in organic solvents like pyridine, benzene, alcohols and ethers.

Reaction with nitrogen : Only lithium reacts with nitrogen to form lithium nitride (Li_3N).

$$6Li + N_2 \xrightarrow{\Delta} 2Li_3N$$
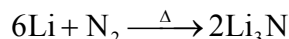
Solubility in liquid ammonia : All the alkali metals dissolve in liquid ammonia giving deep blue paramagnetic solutions when dilute, due to the presence of ammoniated electrons in the solution, blue colour changes to bronze & solution becomes diamagnetic

$$M + (x + y)NH_3 \rightarrow [M(NH_3)x]^+ + [e^-(NH_3)]^{-1}$$
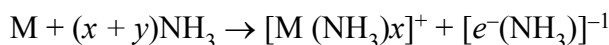
These ammoniated electrons absorbs energy in the visible region of light and in imparts blue colour to the solution. The solutions on standing liberate hydrogen resulting in the formation of an amide.

$$\left[e^-\left(NH_3\right)_y\right] \rightarrow NH_2^- + \left(y-1\right)NH_3 + \frac{1}{2}H_2$$
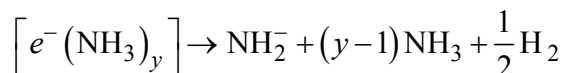
Nature of carbonates and bicarbonates : Li_2CO_3 is much less stable and decomposes on heating to red heat to give Li_2O and CO_2.

$$Li_2CO_3 \xrightarrow{red\ heat} Li_2O + CO_2$$
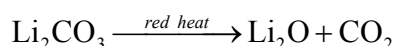
Nature of nitrates : $LiNO_3$ on heating decomposes to give NO_2 and O_2 while the nitrates of the other alkali metals decompose on heating to form nitrites and O_2.

$$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$

$$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$$
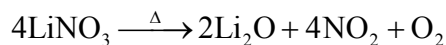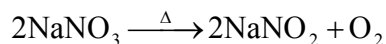
All nitrates are very soluble in water.

Diagonal relationship

Lithium shows diagonal relationship with magnesium (i) Similar atomic and ionic raddi (ii) Similar polarizing power

$$r(Li^+) = r(Mg^{2+})$$

Alkaline Earth Metals

Flame colouration : Like alkali metal salts, alkaline earth metal salts also impart characteristic flame colouration. As we move down the group from Ca to Ba, the ionization energy decreases, hence the energy or the frequency of the emitted light increases. Consequently, the colour imparted to the flame shows a gradual shift from red to violet. Thus,

Ca : Brick red   **Sr :** Crimson red   **Ba :** Apple green   **Ra :** Crimson

Be and Mg because of their high ionization energies, however, do not impart any characteristic colour to the Bunsen flame.

Chemical properties of alkaline earth metals

(1) Reaction with water. They react with H_2O evolving H_2 gas.

$$M + 2H_2O \rightarrow 2M(OH)_2 + H_2 \qquad \text{where } M = Mg, Ca, Sr \text{ or } Ba$$

(2) Reaction with oxygen. The affinity for oxygen increases down the group.

$$2M + O_2 \xrightarrow{\Delta} \underset{\text{Metal oxide}}{2MO} \qquad (M = Be, Mg \text{ or } Ca)$$

$$M + O_2 \xrightarrow{\Delta} \underset{\text{Metal peroxide}}{MO_2} \qquad (M = Be, Sr \text{ or } Ra)$$

(3) Reaction with hydrogen. All the alkaline earth metals except Be, combine with H_2 directly on heating to form metal hydrides of the general formula, MH_2. BeH_2 can be prepared by the reaction of

$$2BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$$
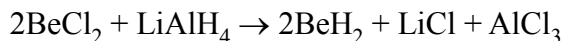
(4) Solubility in liquid ammonia. Like alkali metals, all alkaline earth metals dissolve in liquid ammonia giving bright solutions (when dilute) due to solvated electrons but concentrated solutions are bronze coloured due to the formation of metal clusters. These solutions decompose very slowly forming amides and evolving MH_2.

$$M + (x + 2y)NH_3 \rightarrow [M^{2+} (NH_3)_x]^{2+} + 2 [e(NH_3)_y]$$
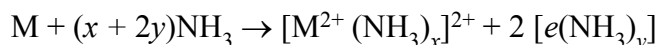
(5) Reaction with nitrogen. When heated with N_2, alkaline earth metals

form their respective nitrides (M_3N_2).

These nitrides react with water to evolve NH_3, *e.g.*,

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$$
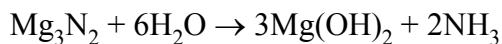
(6) Reaction with halogens. When heated with halogens (F_2, Cl_2, Br_2 or I_2), all the alkaline earth metals form halides of the general formula (MX_2).

Except for beryllium halides, all other halides of alkaline earth metals are ionic in nature. Beryllium halides are essentially covalent and soluble in organic solvent.

1. Oxides and Hydroxides :

    The enthalpies of the formation of the oxides are quite high, So they are very stable to heat. Beo is amphoteric while oxides of other elements are ionic and basic in nature as they form sparingly soluble hydroxides with water

    $$MO + H_2O \rightarrow M(OH_2)$$
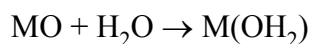
    The solubility, thermal stability and the basic character of hydroxides increase with increasing atomic number from $Mg(OH)_2$ to $Ba(OH)_2$

2. **Carbonates :** The solubility of the carbonates in water decreases as the atomic number of the metal in increases.

    $BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$. But the thermal stabilities of the carbonates increases in the order $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$ and these decompose on heating forming metal oxide and carbon dioxide.

    $$MCO_3 \xrightarrow{\Delta} MO + CO_2$$
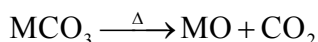
3. **Sulphate :** The solubilities of the sulphates of alkaline earth metals decreases as we move down the group from Be to Ba. Because the hydration enthalpies decreases down the group.

4. **Nitrates :** The nitrates of the alkaline earth metals decompose on heating to give their oxides like lithium nitrate.

    $$2M(MO_3)_2 \rightarrow 2MO + 4NO_2 + O_2$$

<div style="text-align:center">

ONE MARK QUESTIONS

</div>

1. Write general electronic configuration of alkali and alkaline earth metals ?
2. Among the alkali metals, which element has :

(a) Strongest reducing character in aqueous medium.

(b) Lowest size of ion in aqueous medium.

3. Why sodium metal is kept in kerosene ?

4. Why alkali metals are highly reactive ?

5. What is the oxidation state of K in KO_2 ?

6. State one use of liquid sodium metal.

7. LiCl is soluble in organic solvent. Explain why?

   [**Hint :** Li^+ has very high polarising power, thus LiCl is covalent in nature.]

8. Name the alkali metal which forms superoxide when heated in excess of air.

9. Write the average composition of Portland cement.

10. How plaster of paris is obtained from gypsum ?

11. Li_2CO_3 has lower thermal stability than that of Na_2CO_3, why ?

12. Why do group 1 elements known as alkali-metals?

13. Lithium is a less reactive alkali-metal yet it is the best reducing agent! why?

14. Name the hormone responsible for the regulation of calcium concentration in blood-plasma.

2- MARK QUESTION

1. Draw the structure of Beryllium chloride in (i) solid state (ii) vapour phase.

2. Write the significance of sodium and potassium in biological fluids.

3. The Solvay process cannot be used for the manufacture of K_2CO_3. Why ?

4. State two uses of sodium carbonate.

5. Account for the following :

   (a) Alkali metals reacts vigorously with halogens to form ionic halide M^+X^-, however lithium halides are somewhat covalent.

   (b) Lithium shows similarities to magnesium and similarly beryllium to aluminium in many of their properties, name this relationship and give its cause.

6. Explain why alkali metals are never found in free state ?

7. When alkali metals dissolves in liquid ammonia, the solution give blue colour which is conducting in nature. Why ? What happens to the magnetic nature of the solution when the concentrated solution of NH_3 is added to the blue coloured solution ?

8. (a) What property makes caesium and potassium useful as electrodes in photoelectric cell ?

   (b) All the alkali metals and their salts imparts characteristic flame colouration. Explain the reason.

   [**Hint :** Bunsen burner flame is sufficient to excite the electrones of alkali metals to higher energy level. This excited state is quite unstable and therefore when these excited electrons come back to its original level, they emit extra energy which fall in the visible region.]

9 Complete the following equations –

   (a) $CaCO_3 + CO_3 + H_2O \longrightarrow$

   (b) $CO_3^{2-} + H_2O \longrightarrow$

10. What happens when –

    (a) Potassium metal burns vigorously in oxygen.

    (b) Gypsum is heated above 393 k.

11. Give reasons of the following–

    (a) Sodium metal can't be used as electrode in photo-chemical cells.

    (b) Be and Mg are not detected by flame.

12. Arrange the following accordingly –

    (a) NaI, NaF, NaCl, NaBr (increasing order of melting point).

    (b) Na_2CO_3, K_2CO_3, Cs_2CO_3, Li_2CO_3 (increasing order of thermal stability.

3 - MARK QUESTIONS

1. Assign the appropriate reason for the following :
   (a) Solubility of alkaline earth metal hydroxides increases down the group.
   (b) The solubility of alkaline earth metal carbonates and sulphates decreases down the group.
   (c) Lithium salts are commonly hydrated.

2. Write balanced chemical equation for the reactions between :

(a) Ammonium chloride and calcium hydroxide.

(b) Ammonium hydrogen carbonate and sodium chloride.

(c) Calcium chloride and sodium carbonate.

3. List three properties of lithium in which it differs from the rest of the alkali metals.

4. State as to why :

(a) KO_2 is paramagnetic.

(b) An aqueous solution of sodium carbonate gives alkaline test.

(c) Sodium peroxide is widely used as an oxidising agent.

[Hint :

(a) O_2^- contains one unpaired electrons, hence paramagnetic.

(b) Carbonate part of Na_2CO_3 get hydrolysed by water to form an alkaline solution. $\quad HCO_3^- + H_2O \rightarrow H_2CO_3 + OH^-$

5. Arrange the following in order of property mentioned against each :

(a) $BaCl_2$, $MgCl_2$, $BeCl_2$, $CaCl_2$ – increasing ionic character

(b) $Mg(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$, $Ca(OH)_2$ – increasing solubility in water

(c) BeO, MgO, BaO, CaO – increasing basic character

6. Write chemical equation for the following :

(a) Quick lime is heated with silica.

(b) Chlorine reacts with slaked lime.

(c) Calcium carbonate reacts with hydrochloric acid.

7. Sodium hydroxide is generally prepared by the electrolysis of brine solution in the Castner-Kellner cell :

(a) Write the reactions that occur in the cell.

(b) Write any two uses of sodium hydroxide.

8. Complete the following reactions :

(a) $NaCl + NH_3 + H_2O + CO_2 \rightarrow$ .... + ...

(b) $Na_2SO_4 + CaCO_3 + C \rightarrow$ .... + ... + CO

(c) $Na_2CO_3 + SiO_2 \rightarrow$ .... + ...

9. Identify the compound A, B, C in the following reactions :

$\qquad 2NH_3 + H_2O + A \rightarrow (NH_4)_2CO_3$

$\qquad (NH_4)_2CO_3 + H_2O + B \rightarrow 2NH_4HCO_3$

$\qquad 2NH_4HCO_3 + NaCl \rightarrow NH_4Cl + C$

---

10. Write balanced chemical equation of hydrolysis of sodium oxide, sodium peroxide, sodium superoxide.

11. Comment on the following :

    (a) Lituim is the only alkali metal to form nitride directly.

    (b) Thee mobilities of the alkali metal ions in aqueous solution are

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

    (c) $E°$ for the reaction

    M^{2+} (aq) $+ 2e^- \rightarrow M(s)$ (where $M = Ca$, Sr or Ba) is nearly constant.

12. Choose the correct answer :

    (a) when of the alkali metal is having the least melting point.

    (i) Na   (ii) K   (iii) Rb   (iv) Cs.

    (b) Which one of the alkali metal give hydrated salts.

    (i) Li   (ii) Na   (iii) K   (iv) Cs.

    (c) Which one of the alkali earth metal carbonates is thermally the most stable ?

    (i) $MgCO_3$ (ii) $CaCO_3$ (iii) $SrCO_3$ (iv) $BaCO_3$

5 - MARK QUESTIONS

Explain why :

(a) The following reaction :

$$-\overset{|}{\underset{|}{C}} - Cl + MF \rightarrow -\overset{|}{\underset{|}{C}} - F + MCl, \text{proceed better with KF than with NaF.}$$

(b) Sodium wire is used to remove moisture from benzene but cannot be used for drying alcohol.

(c) Li metal is kept wrapped in paraffin wax and not stored in kerosene.

(d) The crystalline salts of alkaline earth metals contain more water of crystallization than corresponding alkali metals.

(e) LiCl is more covalent than NaCl.

[**Hint :** (a) KF is more ionic than NaF because Na^+ ion is smaller in size than K^+. Thus KF will undergo above nucleophilic substitution.

(b) Sodium removes moisture from benzene by reacting with H_2O, however, C_2H_5OH reacts with sodium.

(c) Due to small size and high nuclear charge alkaline earth metal ions have higher tendency of hydration.]

2. Explain the following observations :

(a) LiI is more soluble than KI in ethanol

(b) BeO is almost insoluble but $BeSO_4$ is soluble in water

(c) Sodium reacts with water less vigorously than potassium

(d) Halides of alkaline earth metals form halide hydrates such as

$MgCl_2, 8H_2O, CaCl_2, 6H_2O$

$SrCl_2, 6H_2O$ and $BaCl_2 . 2H_2O$

(e) The solubilities of alkaline earth metal carbonates and sulphates in water decreases down the group.

[**Hints :**

(a) High polarising capabvility of Li^+ ion

(b) Greater hydration enthalpy of Be^{2+} in $BeSO_4$ overcome the lattice enthalpy

(c) Increase in the electropositive character down the group.

(d) Metal halides of group 2 are hydroscopic in nature.

(e) Hydration enthalpy decreases down the group.

p-BLOCK ELEMENTS

Group-13 Elements

- **Inert pair effect :** It is the reluctance of the *s*-electrons of the valence shell to take part in bonding. It arises due to poor or ineffective shielding of the ns^2 electrons of the valence shell by the intervening *d*- and/or *f*-electrons. Inert pair effect increases down a group and thus the elements present in the lower part of the group show lower oxidation states which is two units less than the highest group oxidation state. In group 13 elements, inert pair effect is more pronounced in Tl.

- **Oxidation states :** B and Al show an oxidation state of +3 only while Indium and thallium show oxidation states of both +1 and +3. Further due to inert pair effect, as we move down the group, the stability of +3 oxidation state decreases while that of +1 oxidation state increases. For Tl, it is the +1 oxidation state which is more stable than +3 as shown by the redox potential data :

$$Tl^{3+} (aq) + 2e^- \rightarrow Tl^+ (aq); \quad E° = +1.25 \text{ V}$$
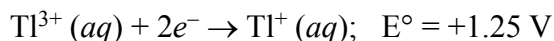
The decrease in stability of +3 oxidation state with increasing atomic number is due to decrease in bond energy with increase in size from Al to Tl. As a result, the energy required to unpair the ns^2 electrons is not compensated by the energy released in forming two additional bonds.

Stability of +1 oxidation state follows the trend : Ga < In < Tl

- **Halides :** All the elements of group 13 (except thallium which preferably forms thallous monohalides) form trihalides of the general formula MX_3 where X = F, Cl, Br and I.

All the boron trihalides, *i.e.,* BF_3, BCl_3, BBr_3 and BI_3 and aluminium trihalides *i.e.,* $AlCl_3$, $AlBr_3$ and AlI_3 (AlF_3 being ionic) are covalent compounds. Whereas boron trihalides exist as only monomers, aluminium trihalides exist as dimers.

- **Nature of Trihalides :** The trihalides of group 13 elements have only six electrons in the valence shell and hence have a strong tendency to accept a pair of electrons to acquire the nearest inert gas configuration. Consequently trihalides of group 13 elements behave as Lewis acids.

Group-14 Elements

- **Oxidation states :** All the elements show an oxidation state of +4. However, as we move down the group from C to Pb, the stability of +4 oxidation state decrease while that of +2 oxidation state increases due to inert pair effect. Thus, +4 oxidation state is important for C and Si while +2 state becomes increasingly important for Ge, Sn and Pb. The stability of the divalent state increases in the sequence Ge < Sn < Pb.

- **Catenation :** The propoerty of self-linking of an atoms of an element through covalent bonds to form straight or branched chains and rings of different sizes is called **catenation**. The tendency of an element to form chains depends upon the strength of the element-element bond. Amongst the group 14 elements, $C-C$ bond strength (348 KJ mol^{-1}) is maximum, therefore, carbon shows maximum tendency for catenation. As we move down the group, the element-element bond strength decreases very rapidly, *i.e.,*

Element-Element	$C-C$	$Si-Si$	$Ge-Ge$	$Sn-Sn$
Bond strength (kJ mol^{-1})	348	297	260	240

Therefore, the tendency for catenation decreases in the order $C >>> Si > Ge \approx Sn >> Pb$.

Lead however, do not show any tendency for catenation.

$p\pi$-$p\pi$ **and** *$p\pi$-$d\pi$* **multiple bonding :** Amongst group 14 elements, carbon shows a pronounced ability to form *$p\pi$-$p\pi$* multiple bonds with itself (*e.g.,* in graphite) and with other elements especially nitrogen and oxygen. Silicon and other heavier elements of this group show negligible tendency of this type. This is the reason that silicon exists only in the diamond structure.

$p\pi$-$d\pi$ multiple bonding has been observed particularly in case of silicon linked to oxygen and nitrogen. Thus trimethylamine, $N(CH_3)_3$ is pyramidal (N is sp^3-hybridized) and is more basic whereas similar silicon compound trisilylamine, $N(SiH_3)_3$ is planar (N is sp^2-hybridized) and is less basic. In this case, the lone pair of nitrogen atom is transferred to the empty *d*-orbital of silicon (*$p\pi$-$d\pi$* overlapping) leading to the planar structure.

- **Chemical Properties**

Nature of bonding : The compounds of group 14 elements which show an oxidation state of +4 are covalent while those which show an oxidation of +2 are ionic in nature. Further, as we move down the group, the tendency of the elements to form covalent compounds decreases but the tendency to form ionic compounds increases.

Formation of halides :

(i) **Tetrahalides :** All the elements of group 14 form tetrahalides of the general formula, MX_4 where $X = F, Cl, Br$ or I. All these tetrahalides are covalent compounds and have tetrahedral structures. The stability of these tetrahalides decreases as we move from C to Pb, *i.e.,*

$$CCl_4 > SiCl_4 > GeCl_4 > SnCl_4 > PbCl_4$$

Or $\quad CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$
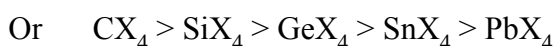
(ii) **Dihalides :** All the elements of group 14 form dihalides of the formula, MX_2 where $X = F, Cl, Br$ or I. The stability of these dihalides increases as we move down the group from C to Pb. Thus, the dihalides of tin and Pb, *i.e.,* $SnCl_2$ and $PbCl_2$ are quite stable. Dihalides are generally ionic in nature and behave as reducing agents, the reducing character (of M^{2+} species) decreases in the order *e.g.,* $GeCl_2 > SnCl_2 > PbCl_2$.

• **Formation of oxides :** All the elements of this group form two types of oxides : (i) monoxides and (ii) dioxide.

(i) **Monoxides :** All the elements of group 14 form monoxides of the general formula MO, *i.e.,* CO, SiO, GeO, SnO and PbO. These oxides except SiO and GeO are quite stable. CO is neutral while SnO and GeO are amphoteric.

(ii) **Dioxides :** All these elements form dioxides of the general formula, MO_2 *i.e.,* CO_2, SiO_2, GeO_2, SnO_2 and PbO_2. All these dioxides can be prepared by heating the elements in oxygen except lead which forms lead monoxide. CO_2 is a monomeric, linear molecule and hence exists as a gas while the dioxides of all other elements are crystalline solids with high melting points due to the formation of three dimentional network of bond.

• **Silicones :** Silicones are synthetic organosilicon compounds containing repeated R_2SiO units held by $Si - O - Si$ linkages. Since the empirical formula R_2SiO (where $R = CH_3$ or C_6H_5 group) is similar to that of a ketone (R_2CO), the name silicones have been given to these materials.

Short chains silicones are oily liquids, medium chains silicones behave as viscous oils, jellies and greases and those with very long chains behave as rubbery elastomers and resins.

Silicones are water repellent, heat resistant, chemically inert, resistant to oxidation and attack by organic acids and good electrical insulators.

Silicones are used for making water proof papers, wool, textiles, wood, etc., as lubricants at high and low temperatures, as antifoaming agents, as sealants. Being biocompatible they are also used in surgical and cosmetic plants.

1 - MARK QUESTIONS

1. Write the general electronic configuration of *p*-block elements.

2. Mention two important ores of boron.

3. Write the resonance structure of CO_3^{2-}.

4. Write the chemical formula of inorganic benzene.

5. Mention the hybridisation state of carbon in diamond and graphite.

6. Why boric acid (H_3BO_3) is a monobasic acid ?

7. Diamond is covalent, yet it has high melting point. Why ?

8. White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.

9. Why does boron trifluoride behave as a Lewis acid ?

10. Atomic radius of gallium (135 pm) is less than that of aluminium (143 pm). Why ?

11. Boron cannot form B^{3+} ions. Why ?

12. The +1 oxidation state gets progressively stabilized from Ga to Tl. Give chemical reaction in support of this observation.

13. Why is anhydrous $AlCl_3$ used as catalyst in several organic reactions ?

14. Aluminium is highly electropositive metal but nitric acid renders it passive. Why ?

15. Name the element of group 13 which forms only covalent compounds.

16. Draw the structure of Al_2Cl_6.

17. Mention an industrial application of silicones.

18. Name a zeolite catalyst used to convert alcohols directly into gasoline.

19. Electronegativity of group 13 elements is in the order B > Al > Ga > In > Tl. Explain this trend.

20. Why is boric acid considered as a weak acid ?

21. Write the isotopes of Boron.

22. Write the general electronic comfiguration of group 13 and group-14 elements.

23. Boron is a non-metal yet it has very high melting point why?

24. $AlCl_3$ exist in dimeric form in solid state and vapour phase. Why?

25. Boron can't show covalency more than 4. Why ?

2 - MARK QUESTIONS

1. How is diborane prepared in the laboratory ? Give its structure.

2. Account for the following :

   (a) BCl_3 exist but BH_3 does not.

   (b) Aluminium alloys are used to make aircraft body.

3. Mention two similarities and two dissimilarities between B and Al.

4. What happens when :

   (a) Borax is heated strongly.

   (b) Boric acid is added to water.

5. B – Cl bond has a dipole moment. Explain why BCl_3 molecule has zero dipole moment ?

6. Write balanced chemical equations for :

   (a) $BF_3 + LiH \rightarrow$

   (b) $B_2H_6 + NH_3 \rightarrow$

7. Write chemical reactions to justify amphoteric nature of aluminium.

8. The +1 oxidation state in group 13 and +2 oxidation state in group 14 become more and more stable with increasing atomic number. Explain why ?

9. Arrange the hydrides of group 14 elements in increasing order of :

   (a) thermal stability   (b) reducing power

10. $[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ not. Give appropriate reason.

11. Account for the following :

    (a) CO_2 is a gas while SiO_2 is a solid at room temperature.

    (b) Solid CO_2 is known as dry ice.

12. Write the composition of water gas. How it can be synthesized ?

13. How do you agree with phenomenon concept of inert pair effect ? Justify your answer.

14. What are silicones ? How are they manufactured ? Give the chemical equation involved.

15. Explain with suitable reasons :

    (a) CCl_4 is resistant to hydrolysis but $SiCl_4$ is readily hydrolysed.

    (b) In group 14, the tendency for catenation decreases with increasing atomic number.

3 - MARK QUESTIONS

1. List two important properties in which boron differs from the rest of the members of group. Mention the main reasons for the difference.

2. Write balanced chemical equations for :

    (a) $BF_3 + NaH \xrightarrow{450\,K}$

    (b) $Fe_2O_3 + 3CO \xrightarrow{\Delta}$

    (c) $CaCO_3 + 2HCl \rightarrow$

3. Identify X, Y and Z in the following chemical equations :

    $$Z + 3LiAlH_4 \rightarrow X + 3LiF + 3AlF_3$$
    $$X + 6H_2O \rightarrow Y + 6H_2$$
    $$X + 3O_2 \xrightarrow{\Delta} B_2O_3 + 3HO_2$$

    [**Ans.** $Z = BF_3$, $X = B_2H_6$, $Y = H_3BO_3$]

4. Select the member(s) of group 14 that :

    (a) forms the most acidic dioxide.

    (b) is commonly found in +2 oxidation state.

    (c) used as semiconductor.

5. (a) What are allotropes ? Sketch the structure of two allotropes of carbon namely diamond and graphite.

    (b) List two main differences in the properties of diamond and graphite on the basis of their structure.

6. Write one method for industrial preparation and one for laboratory preparation of CO. Suggest a reason as to why CO is poisonous.

7. Give suitable reasons for the following :

(a) CO_2 turns lime water milky, but if passed for a long time, the solution becomes clear again.

(b) Graphite is used as a lubricant but diamond is used as an abrasive.

(c) Graphite is a good conductor of electricity but diamond is insulator.

8. A salt A, gives the following results :

(a) It aqueous solution is alkaline to litmus

(b) It swells up to a glassy material B on strong heating.

(c) When conc. H_2SO_4 is added to a hot solution of A, white crystals an acid C separates out. Write equations for all the above reactions and identify A, B and C.

9. Suggest reasons for the following observations :

(a) Excessive content of CO_2 is responsible for global warming

(b) Boron is unable to form BF_6^{3-} ion.

(c) A boron carbide rod is used in nuclear reactor.

10. (i) How orthoboric acid is prepared? Give its structure.

(ii) What happens when—

(a) It is dissolved in water.   (b) It is heated.

11. Give reasons of the following –

(a) In diborane, two B–H–B bonds are different from common covalent bonds.

(b) Aluminium metal shows amphoteric behaviour.

(c) Quarts is used to develop extremely accurate clocks.

5 - MARK QUESTIONS

1. (a) Draw the structure of diborane.

(b) Define the term inert pair effect. Explain your answer with the help of lead chlorides.

(c) (i)   Which is more ionic, $SnCl_2$ or $SnCl_4$?

(ii) PbO_2 is a strong oxidising agent. Assign a reason for this.

2. (a) Account for the following :

(i) The first ionization enthalpy of carbon is greater than that of boron but the reverse is true for second ionization enthalpy.

(ii) $PbCl_4$ is less stable than $SnCl_4$ but $PbCl_2$ is more stable than $SnCl_2$.

(iii) Gallium has higher ionization enthalpy than aluminium.

(b) Identify the compounds X and Y in the following reactions :

(i) $Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + X$

(ii) $X \xrightarrow[370\ K]{\Delta} HBO_2 \xrightarrow[>\ 370\ K]{\Delta} Y$

3. Compare the general trends in the following properties of the elements in groups 13 and 14 :

(a) Atomic size

(b) Ionization enthalpy

(c) Metallic character

(d) Oxidation states

(e) Nature of halides

4. When metal 'X' is treated with sodium hydroxide, a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound (A) is soluble in dilute HCl to form compound (C). The compound (A) when heated strongly gives (D), which is used to extract metal. Identify (X), (A), (B), (C) and (D). Write chemical equations to support their identities.

5. Assign reasons :

(a) Aluminium alloyes are used to make body.

(b) Conc. HNO_3 can be transported in aluminium countainens.

(c) Aluminium utensils should not be kept overnight.

(d) Aluminium wire is used to make transmission cables.

(e) A mixture of diture NaOH and aluminium pieces is ased to open drain.

6. Name the following —

(a) The crystalline form of silica used in modern-radio and T.V. broadcasting and mobile-radio communication!

(b) The oxide of carbon which forms a complex with haemoglobin 300 times more faster than O_2.

(c) The allotrope of Carbon which has $\Delta_f H° = 0$.

(d) Group 13 element which is used to measure high temperature !

(e) A type of polymer which is semiorganic in nature !

UNIT-12

IUPAC NOMENCLATURE

(1) Longest Chain Rule :

Longest chain in molecule is selected.

$$\overset{1}{C}-\overset{2}{C}-\overset{3}{C}-\overset{4}{C}-\overset{5}{C}-\overset{6}{C}-\overset{7}{C}-\overset{8}{C}-\overset{9}{C}$$

with C below C2, and 7C, 8C below C6.
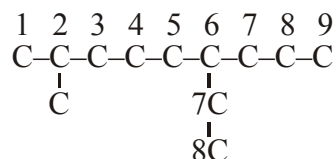
(2) Lowest Sum Rule :

The numbering is done is such a way that the branched carbon atoms of the parent chain get the lowest possible number or locant.

$$\overset{1}{C}-\overset{2}{C}-\overset{3}{C}-\overset{4}{C}-\overset{5}{C}-\overset{6}{C}-\overset{7}{C}-\overset{8}{C}-\overset{9}{C}$$

Case (I)

$$\overset{9}{C}-\overset{8}{C}-\overset{7}{C}-\overset{6}{C}-\overset{5}{C}-\overset{4}{C}-\overset{3}{C}-\overset{2}{C}-\overset{1}{C}$$
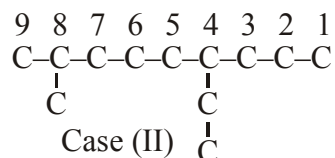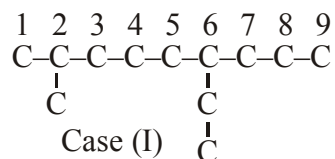
Case (II)

In case (I), the sum of locants (2 + 6) is lower than the sum of locants (4 + 8) in case (II). Hence, the numbering done in case (I) is **"right."**

(3) The names of side chains and the substituents are then prefixed to the name of parent alkane and position of substituents is indicated by appropriate numbers. The numbers are separated from the prefixes by hyphens (–).

(4) Alphabetical arrangement of side chains/substituents :

Thus, the name for compound shown above is : 6–ethyl–2–methyl nonane. Note that there is no break between methy and nonane, i.e., the name is always written as a single word.

(5) We write di, tri, tetra, penta for two, three, four, five identical subtituents and so on. The numbers (locants) are separated by commas. Note that di, tri,

tetra, penta, hexa etc do not determine the alphabetical order of the subtituents.

$$\overset{2}{CH_3}-\overset{}{CH}-CH_2-\overset{4}{CH}-\overset{6}{CH}-CH_2-CH_3$$

with substituents: CH_3 (below position 2), CH_3 and CH_2CH_3 (below positions 4, 6)
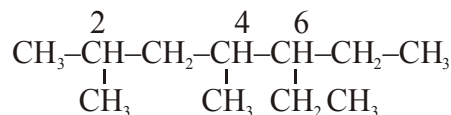
6 - Ethyl -2, 4 - dimethyl heptane

(6) **(a)** If two substituents are found in equivalent positions, the lower number (locant) is given to the one that comes first in alphabetical order.

$$\overset{6}{CH_3}-\overset{5}{CH_2}-\overset{4}{CH}-\overset{3}{CH}-\overset{2}{CH_2}-\overset{1}{CH_3}$$

with $\overset{1}{} \overset{2}{} | \overset{3}{} | \overset{4}{} \overset{5}{} \overset{6}{}$ and substituents CH_3 C_2H_5
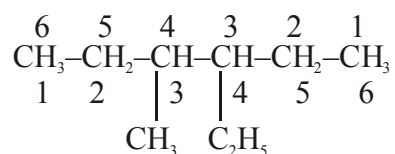
3- Ethyl - 4 - methyl hexane and not 4- ethyl - 3- methyl hexane

(b) The name of complex chains (substitued substituents) are enclosed in parentheses and numbering of C-atoms is carried such that the C-atom of substituted substituent attached to main chain is given number 1.

$$CH_3CH_2CH_2CH_2\overset{5}{C}HCH_2CH_2CH_2CH_2CH_3$$

with substituent $\overset{1}{} | \overset{2}{} \overset{3}{}$: $H_3C-CH-CH_2CH_3$
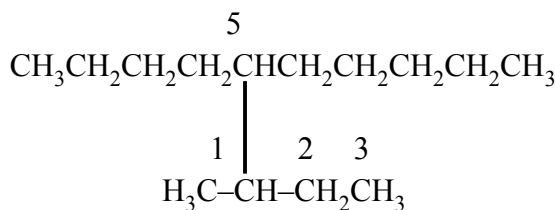
5-(1-Methylpropyl) decane, in place of 5-Isobutyldecane

(c) Composite or complex groups are represented by prefixing bis for 2, tris for 3, tetrakis for 4, pentakis for 5 identical composite groups and so on, and entire group is enclosed in parentheses (brackets). For example,

$$\begin{array}{c} CH_2Cl \\ | \\ Cl-CH_2-C-CH_2-Cl \\ | \\ CH_2Cl \end{array}$$
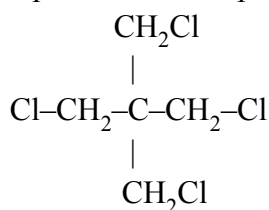
1, 3-Dichloro-2, 2-bis (chloromethyl) propane and IUPAC name of DDT is
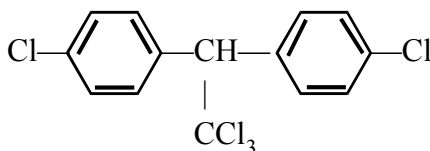
-1, 1,1-trichloroethane 2, 2-bis (4-Chlorophenyl)

(d) Name of a substituted substituent is considered to begin with the first letter of its complete name.

$$\underset{\displaystyle \text{7-(1, 2-Diflurobutyl)-5-ethyltridecane}}{}$$

$$\overset{\displaystyle \quad\quad\quad F\ \ F}{\underset{\displaystyle CH_3-[CH_2]_4-CH_2-CH-CH_2-CH-[CH_2]_3-CH_3}{H_3C-H_2C-HC-CH \qquad CH_2-CH_3}}$$

7-(1, 2-Diflurobutyl)-5-ethyltridecane
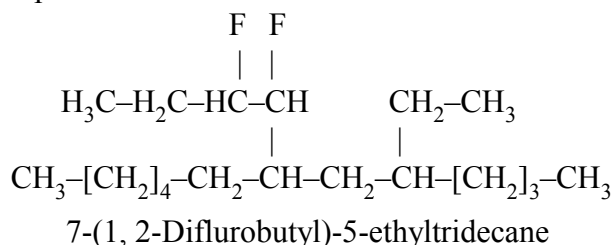
IUPAC Nomenclature for alkenes and alkynes :

(a) Multiple bond is preferred for numbering and represented by lowest number of C-atoms.

$H_2C = CH - CH_2CH_3$: But-1-ene **and not** 1-Butene

$H_3C - C \equiv C - CH_2CH_3$: Pent-2-yne **and not** 2-pentyne

(b) When two or more similar multiple bonds are present, suffix 'a' to the root word.

$CH_2 = CH - CH = CH_2 \qquad H_2C = CH - CH = CH - CH = CH_2$

Buta-1, 3-diene $\qquad$ Hexa-1, 3, 5-triene
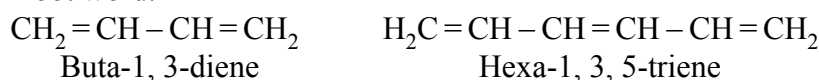
(c) When double and triple bonds are present on the same position from the ends in an organic compound, then double bond is preferred for naming and the compound is named as alkenyne, *e.g,*

$CH_2 = CH - CH \equiv CH$: But-1-en-3-yne

(d) When double and triple bonds are present on different positions, lowest sum rule will be followed and the compound is named as alkenyne *e.g.,*

$HC \equiv C - CH_2CH = CHCH_2CH_2CH_3$ $\quad$ Oct-4-en-1-yne
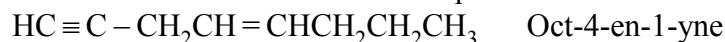
Functional groups : The groups which determine the properties and functions of an organic compound are known as functional groups.

When a functional group is present, a secondary suffix for functional group is added by replacing ending 'e' of the parent name if the name of functional groups starts from vowels y i.e., a, e, i, o and y.

CHARACTERISTICS (FUNCTIONAL) GROUPS

Suffixes and prefixes for some important characteristic groups in IUPAC nomenclature (in alphabetical order). (C) designates a carbon atom included in the name of the parent hydride and does not belong to a group designated by a suffix or a prefix.

Class	Formula	Prefix	Suffix
Acid halides	– CO-halogen	halodarbonyl-	carbonyl halide
	– (C)O-halogen	–	-oyl halide

Alcohols, Phenols	$-OH$	hydroxy-	-ol
Aldehydes	$-CHO$	formyl-	-carbaldehyde
	$-(C)HO$	oxo-	-al
Amides	$-CO-NH_2$	carbamoyl-	-carboxamide
	$-(C)O-NH_2$	–	-amide
Amines	$-NH_2$	amino-	-amine
Carboxylates	$-COO^-$	carboxylato	-carboxylate
	$-(C)OO^-$	–	-oate
Carboxylic acids	$-COOH$	carboxy-	-carboxylic acid
	$-(C)OOH$	–	-oic acid
Ethers	$-OR$	(R)-oxy-	–
Ester (of carboxylic acids)	$-COOR$	(R)oxycarbonyl-	(R).....Carboxylate
	$-(C)OOR$	–	(R)......oate
Ketones	$>(C)=O$	oxo-	-one
Nitriles	$-C\equiv N$	cyano-	-carbonitrile
	$-C\equiv N$	–	-nitrile
Salts (of carboxylic acids)	$-COO^-M^+$	–	(cation)..... carboxylate
Sulphonic acids	$-SO_2-OH$	sulpho	-sulphonic acid

Important Notes :

- When the name of suffix starts with a consonent (except a, e, i, o, u and y), ending 'e' of the parent hydride is retained.

  CH_3CH_2OH :   ethanol

  $HOCH_2CH_2OH$:   ethane-1, 2-diol

  Here 'e' is retained since first letter of diol, *i.e.,* 'd' is a consonent.

- When a functional group and a side chain/substituent is present, then functional group is preferred for naming and numbering.

  $$\underset{\displaystyle BrCH_2CH_2CH_2\overset{\displaystyle OH}{\overset{\displaystyle |}{C}}HCH_3}{}$$: 5-bromopentan-2-ol
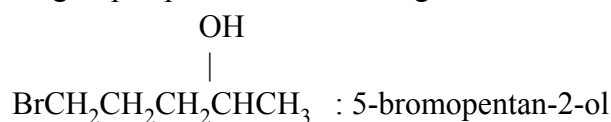
- When two or more functional groups are present, the order of preference is :

  $-COOH > -SO_3H > (-CO)_2O > -COOR' > -COX > -CONH_2 > -CN$

  $$> -CHO > -\overset{\displaystyle O}{\overset{\displaystyle ||}{C}} - > OH > -NH_2 > C=C > C\equiv C$$
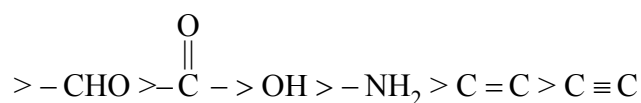
- When two or more functional groups are present, name of higher order functional group is suffixed and the rest are prefixed. Examples are :

$HOCH_3CH_2CH_2COOH$:   4-hydroxybutanoic acid

$$CH_3 - \overset{\overset{\textstyle O}{\|}}{C} - CH_2 - CH = CH - CHO \;:\;$$ 5-Oxohex-2-enol

$CH_3COCH_2COOC_2H_5$:   Ethyl 3-oxobutanoate

:   5-Hydroxycyclopent-2-enecarbaldehyde

$$NC-CH_2-\underset{\underset{\textstyle CN}{|}}{\overset{\overset{\textstyle OH}{|}}{C}}-CH_2-CN$$
:   2-Hydroxypropane-1, 2, 3-tricarbonitrile

$$HOOC-CH-\underset{\underset{\textstyle COOH}{|}}{\overset{\overset{\textstyle CHO}{|}}{C}}-CH-COOH$$
:   3-Formylpropane-1, 2, 3-tricarboxylic acid

:   N, 2-Dimethylcyclopentanecarboxamide

:   Ethyl 2-methylcyclopentanecarboxylate

$$\underset{\underset{\underset{COCl}{|}}{\overset{\overset{NO_2}{|}}{|}}{COCl-CH_2-C-CH_2-COCl}} \quad : \quad \text{2-Nitropropane-1, 2, 3-tricarbonyl chloride}$$

- $-\overset{\overset{O}{\|}}{C}-OH, -\overset{\overset{O}{\|}}{C}-H, -\overset{\overset{O}{\|}}{C}-NH_2, -\overset{\overset{O}{\|}}{C}-X, -\overset{\overset{O}{\|}}{C}-OR$ and $-CN$ are chain terminators.

- In cyclic compound, the word **'cyclo'** is prefixed and lowest sum rule is applied for prefixing the side chains/substituents.
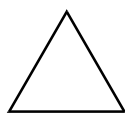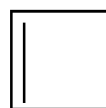
Cyclopropane   Cyclobutene
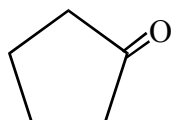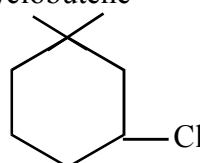
Cyclopentanone   3-Chloro-1, 1-dimethylcyclohexane

- In aromatic compounds, the following trival names have been retained by IUPAC system.

Benzene   Toluene

Benzyl   Benzyl alcohol

Benzyl chloride   Benzaldehyde

COOH

Benzoic acid

CH$_3$

CH$_3$

o-/p-/m-xylenes

COCH$_3$

Acetophenone

O
‖
C

Benzophenone

OH

Phenol

NH$_2$

Aniline

CN

Benzonitrile

OCH$_3$
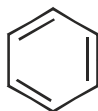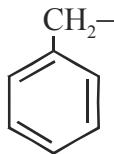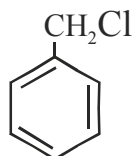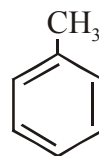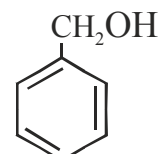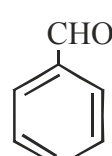
Anisole
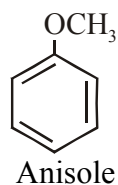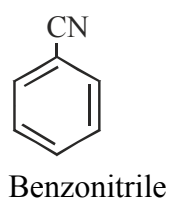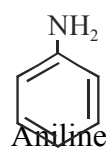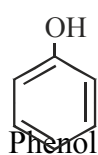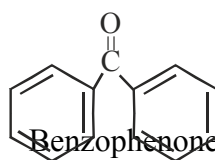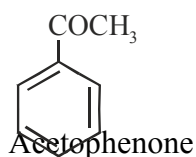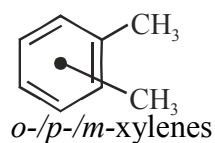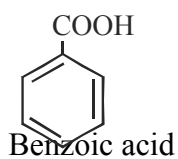
•   When a chain of two or more carbon atoms having a functional group or a multiple bond is attached with the benzene ring, then ring is taken as substituent and is names as phenyl group, *e.g.,*

CH$_2$CH$_2$OH

2-Phenylethan-1-ol

CH$_2$CH$_2$CHO

3-Phenylpropanal
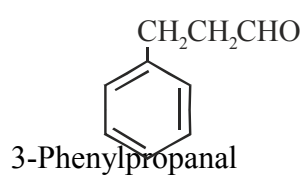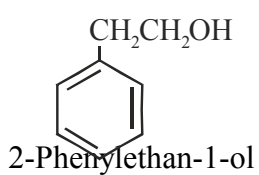
When the benzene ring is further substituted, then the name of the substituted phenyl group is enclosed in parentheses for example :

CH$_2$CH$_2$OH

Br

2-(3-Bromophenyl) ethan-1-ol

CH$_2$CH$_2$CHO

Br

3-(4-Bromophenyl) propanal
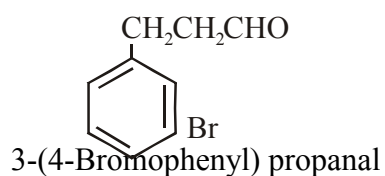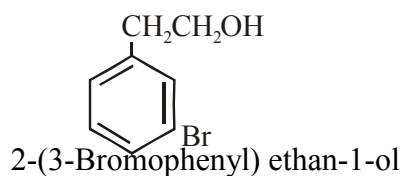
Purification and Characterization of Organic Compounds

(1) **Lassaigne's test for nitrogen :** Lassiagne's extract is heated with $FeSO_4$ solution in presence of alkali, the solution is cooled and acidified with dil. H_2SO_4. If a green or blue colouration is obtained, it confirms the presence of N in the organic compound. The chemisty of the test is :

$$Na + \underset{\text{From organic compound}}{C + N} \xrightarrow{\Delta} NaCN$$

$$2NaCN + FeSO_4 \rightarrow Fe[CN]_2 + Na_2SO_4; \qquad Fe[CN]_2 + 4NaCN \rightarrow \underset{\text{Sod. ferrocyanide}}{Na_4\left[Fe(CN)_6\right]}$$

$$3Na_4\left[Fe(CN)_6\right] + 4Fe^{3+} \rightarrow \underset{\text{Ferric ferrocyanide (Prussian Blue)}}{Fe_4\left[Fe(CN)_6\right]_3} + 12Na^+$$
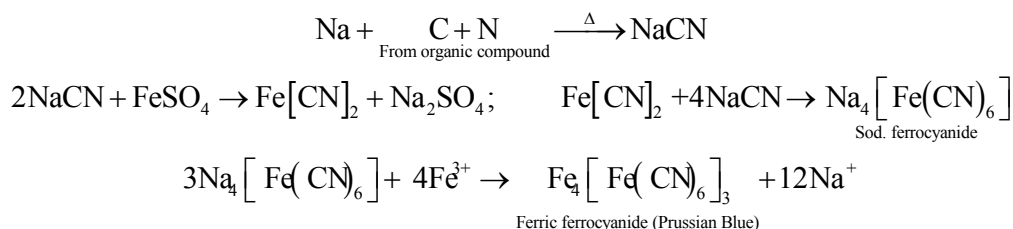
This test is very delicate and is given by all compounds containing C and N. As such NH_2NH_2, NH_4Cl, $NaNO_3$ etc. do not respond to this test since they do not contain carbon.

Formation of blood red colour indicates the presence of both N and S.

$$Na + \underset{\text{From organic compound}}{C + N + S} \xrightarrow{\Delta} \underset{\text{Sod. thiocyanate or Sod. sulphocyanide}}{NaSCN}$$

$$Fe^{3+} + N\overset{+}{a}SC\overset{-}{N} \rightarrow \underset{\text{Ferric thiocyanate (blood red colour)}}{\left[Fe(SCN)\right]^{2+}} + Na^+$$
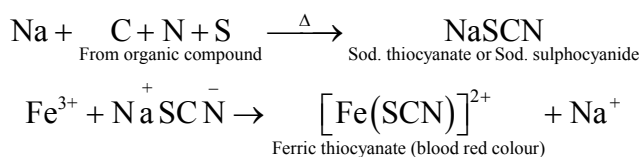
(2) **Detection of sulphur :** If S is present, during fusion with Na metal, Na_2S is formed which may be tested as follows :

(i) With sodium nitroprusside, violet colouration is produced.

$$Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2\left[Fe(CN)_5NO\right]} \rightarrow \underset{\text{(Violet colour)}}{Na_4\left[Fe(CN)_5NOS\right]}$$
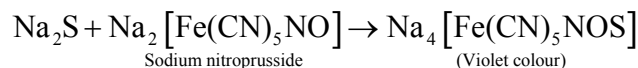
(ii) With lead acetate, black ppt. of PbS is formed.

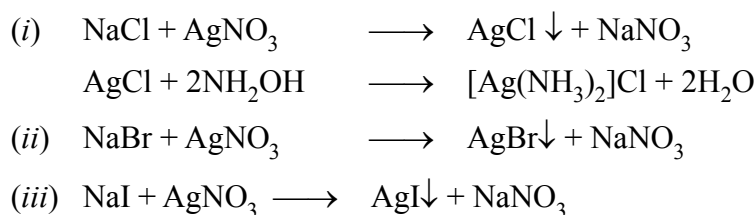$$Na_2S + \left(CH_3COO\right)_2Pb \rightarrow \underset{\text{(Black ppt.)}}{PbS} + 2CH_3COONa$$
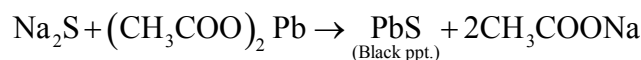
(3) **Detection of halogens :**

   (a) **Lassaigne's test :** When the organic compounds is fused with Na metal, the halogens combine with Na to form sodium halides.

   The presence of these halides is tested with $AgNO_3$ solution.

   (i) A white ppt. soluble in NH_4OH and insoluble in dil. HNO_3 indicates chlorine.

$$Na + X \xrightarrow{\Delta} NaX$$

(*i*) $NaCl + AgNO_3$ $\longrightarrow$ $AgCl \downarrow + NaNO_3$

$AgCl + 2NH_2OH$ $\longrightarrow$ $[Ag(NH_3)_2]Cl + 2H_2O$

(*ii*) $NaBr + AgNO_3$ $\longrightarrow$ $AgBr \downarrow + NaNO_3$

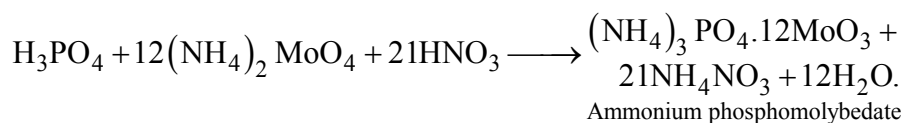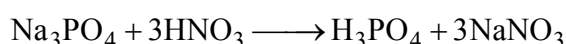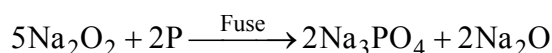(*iii*) $NaI + AgNO_3 \longrightarrow$ $AgI \downarrow + NaNO_3$
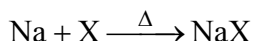
(ii) A pale yellow ppt. partially soluble in ammonia indicates bromine.

(iii) A yellow ppt. insoluble in ammonia indicates iodine.

If the organic compound also contain N or S, the sodium extract is first boiled with dil. HNO_3 to decompose any cyanides or sulphides, otherwise these will form ppt. with $AgNO_3$ solution.

(4) Detection of phosphorus : Phosphorus is detected by fusing the organic compound with sodium peroxide when phosphorus is converted into sodium phosphate.

$$5Na_2O_2 + 2P \xrightarrow{\text{Fuse}} 2Na_3PO_4 + 2Na_2O$$

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + 12(NH_4)_2 MoO_4 + 21HNO_3 \longrightarrow \begin{array}{l}(NH_4)_3 PO_4.12MoO_3 + \\ 21NH_4NO_3 + 12H_2O.\end{array}$$

Ammonium phosphomolybedate

The fused mass is extracted with H_2O and then boiled with conc. HNO_3 and then ammonium molybdate is added. Appearance of yellow ppt. or colouration due to the formation of ammonium phosphomolybdate indicates the presence of phosphorus.

(5) Estimation of Carbon and Hydrogen : Liebig's method : A known mass of the organic compound is heated strongly with excess of dry copper oxide in a current of dry air or oxygen (free from CO_2) when carbon present in the organic compound is oxidised to CO_2 and hydrogen to H_2O.
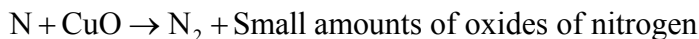
$$C + 2CuO \xrightarrow{\Delta} CO_2 + 2Cu; \qquad 2H + CuO \xrightarrow{\Delta} H_2O + Cu$$

Percentage of carbon $= \dfrac{12}{44} \times \dfrac{\text{Mass of } CO_2 \text{ formed}}{\text{Wt. of substance taken}} \times 100$

Perentage of hydrogen $= \dfrac{2}{18} \times \dfrac{\text{Mass of } H_2O \text{ formed}}{\text{Wt. of substance taken}} \times 100$
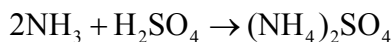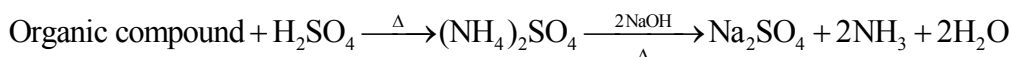
(6) Estimation of Nitrogen :

(a) Dumas method :

$$C + 2CuO \xrightarrow{\Delta} CO_2 + 2Cu; \qquad 2H + CuO \xrightarrow{\Delta} H_2O + Cu$$

$$N + CuO \rightarrow N_2 + \text{Small amounts of oxides of nitrogen}$$

$$\text{Oxides of nitrogen} + Cu \xrightarrow{\Delta} CuO + N_2$$
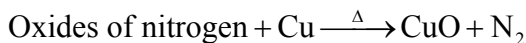
Percentage of nitrogen $= \dfrac{28}{22400} \times \dfrac{\text{Vol. of } N_2 \text{ (in cm}^3) \text{ at STP}}{\text{Wt. of substance taken}} \times 100$

(b) KJELDAHL's Method :

$$\text{Organic compound} + H_2SO_4 \xrightarrow{\Delta} (NH_4)_2SO_4 \xrightarrow[\Delta]{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

Percentage of nitrogen

$$= \dfrac{1.4 \times \text{Molarity of the acid} \times \text{Vol. of acid used} \times \text{Basicity of the acid}}{\text{Mass of substance taken}}$$

(7) Estimation of Halogens : Carius method :

Percentage of chlorine $= \dfrac{35.5}{143.5} \times \dfrac{\text{Mass of AgCl formed}}{\text{Mass of substance taken}} \times 100$

Percentage of bromine $= \dfrac{80}{188} \times \dfrac{\text{Mass of AgBr formed}}{\text{Mass of substance taken}} \times 100$

Percentage of iodine $= \dfrac{127}{235} \times \dfrac{\text{Mass of AgI formed}}{\text{Mass of substance taken}} \times 100$

Percentage of sulphur $= \dfrac{32}{233} \times \dfrac{\text{Mass of BaSO}_4 \text{ formed}}{\text{Mass of substance taken}} \times 100$

(8) Estimation of Phosphorus : A known mass of the organic compound is heated with fuming HNO_3 in a Carius tube when P of the organic compound is oxidized to H_3PO_4. Phosphoric acid thus formed is precipitated as magnesium ammonium phosphate by adding magnesia mixture (a solution containing $MgCl_2$, NH_4Cl and NH_4OH).
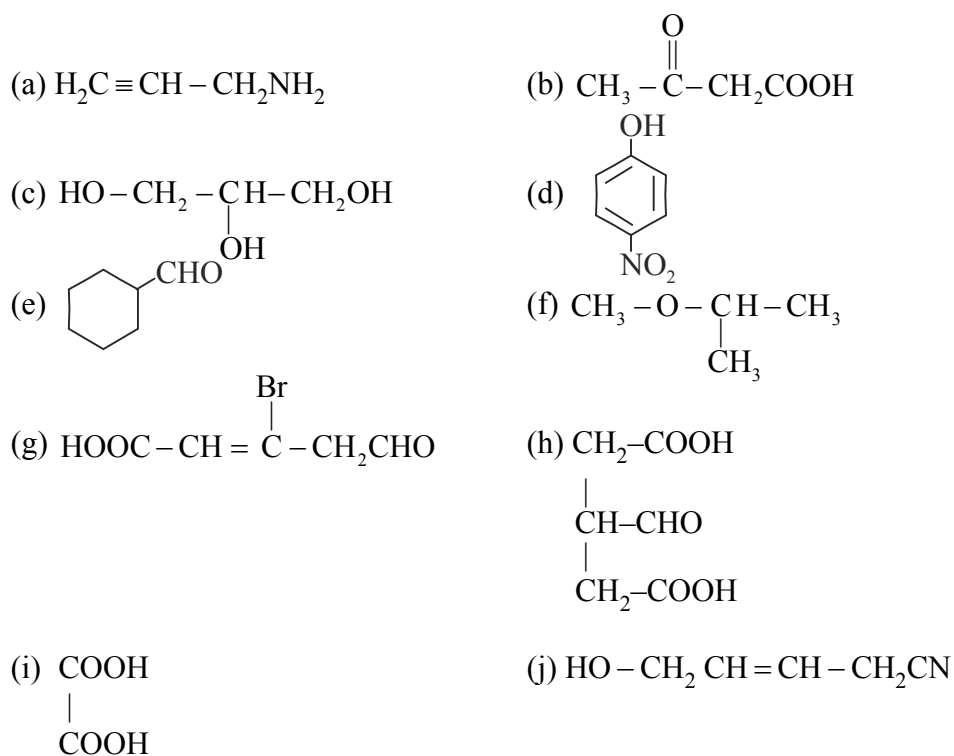
Percentage of phosphorus $= \dfrac{62}{222} \times \dfrac{\text{Mass of Mg}_2P_2O_7 \text{ formed}}{\text{Mass of substance taken}}$
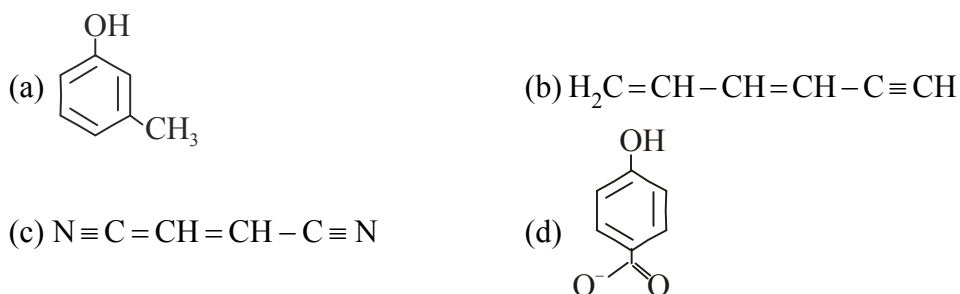
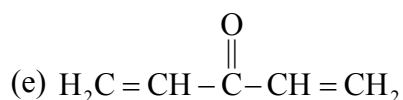## ORGANIC CHEMISTRY

1. Write IUPAC names of the following :

   (a) [structure] (b) [structure with Cl Br] (c) [structure with CN]

   (d) [structure with Br and O, H] (e) [structure with Br and CHO] (f) [structure]

2. Write IUPAC names of the following organic compounds :

   (a) $H_2C \equiv CH - CH_2NH_2$

   (b) $CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2COOH$

   (c) $HO - CH_2 - \underset{\underset{\displaystyle OH}{|}}{CH} - CH_2OH$

   (d) [benzene ring with OH and NO$_2$]

   (e) [cyclohexane with CHO]

   (f) $CH_3 - O - \underset{\underset{\displaystyle CH_3}{|}}{CH} - CH_3$

   (g) $HOOC - CH = \overset{\overset{\displaystyle Br}{|}}{C} - CH_2CHO$

   (h) CH_2-COOH
       $|$
       $CH-CHO$
       $|$
       CH_2-COOH

   (i) $COOH$
       $|$
       $COOH$

   (j) $HO - CH_2 \, CH = CH - CH_2CN$
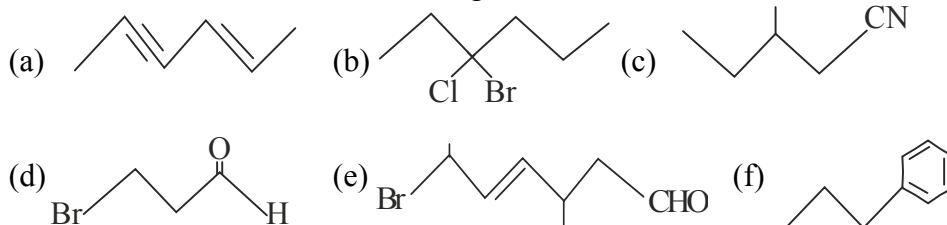
3. How many σ and π bonds are present in the following organic compounds :

   (a) [benzene ring with OH and CH$_3$]

   (b) $H_2C = CH - CH = CH - C \equiv CH$

   (c) $N \equiv C = CH = CH - C \equiv N$

   (d) [benzene ring with OH and O$^-$ C=O]

$$(e) \ H_2C = CH - \overset{\overset{\displaystyle O}{\displaystyle \|}}{C} - CH = CH_2$$

4. Draw the structures of the following organic compounds :

   (a) 2,2-dimethylhexane   (b) 4-methylpentanal

   (c) 2-methylpropan-2-ol   (d) cyclohexylcarbaldehyde

   (e) pent-3-enoic acid   (f) 4-nitrobenzoic acid

   (g) ethylproponoate   (h) ethoxybenzene

   (i) 4-hydroxybutanenitrile   (j) 4-phenylbut-1-ene

5. Mention the states of hybridisation of each carbon atom in the following compounds :

   (a) $CH_2 = C = O$

   (b) $CH_3 - C \equiv CH$

   (c) $\begin{array}{c} H_3C \\ \\ H_3C \end{array} \hspace{-0.5em} {>} C = O$

   (d) C_6H_6

   (e) $H_2C = CH - CH_2 - C \equiv CH$

6. Define the following terms with suitable examples :

   (a) Nucleophile   (b) Electrophile

   (c) Free radicals   (d) Carbocation

   (e) Carbanion

7. Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles :

   (a) $CH_3COOH + \mathbf{H\overset{-}{O}} \rightarrow CH_3COO^- + H_2O$

   (b) $CH_3COCH_3 + \mathbf{\overset{-}{C}N} \rightarrow (CH_3)_3 C(CN)(O^-)$

   (c) $C_6H_5 + \mathbf{CH_3 \overset{+}{C}O} \rightarrow C_6H_5COCH_3 + H^+$

   (d) $CH_3CH_2Cl + \mathbf{HC \equiv \overset{-}{C}} \rightarrow CH_3CH_2C \equiv CH + Cl^-$

   (e) $C_6H_5 + \mathbf{\overset{\oplus}{N}O_2} \rightarrow C_6H_5NO_2 + H^+$

8. Which of the following carbocation is most stable :

(a)
$$\underset{\text{(triphenylmethyl cation)}}{(C_6H_5)_3\overset{\oplus}{C}}$$

(b) $(CH_3)_3 C\overset{\oplus}{C}H_2$

(c) $(CH_3)_3 \overset{\oplus}{C}$

(d) $CH_3CH_2 \overset{\oplus}{C}H_2$

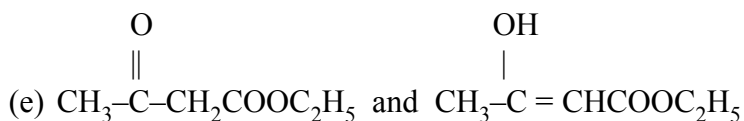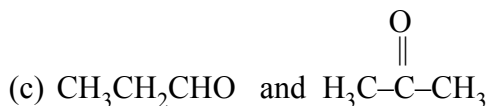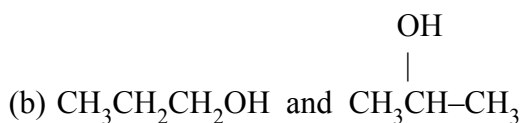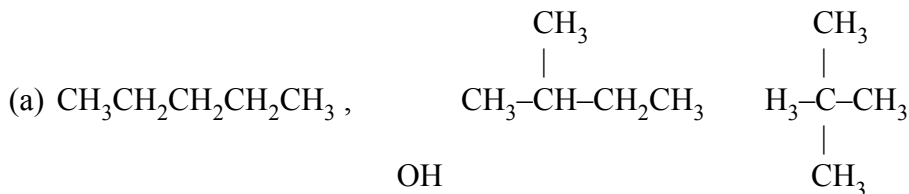(e) $H_3C - \overset{\oplus}{C}H - CH_2CH_3$
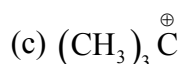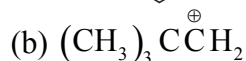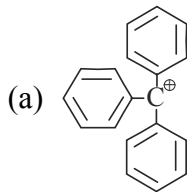
Arrange the above carbocations in the decreasing order of their stability.

9. Explain the following technique of separation of organic compounds with suitable examples :

(a) Crystallization

(b) Distillation

(c) Sublimation

(d) Chromatography

(e) Differential extraction

10. Discuss the chemistry of Lassaigne's test. Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur and halogens.

11. Name a suitable technique of separation of the components from a mixture of :

(a) calcium sulphate and camphor

(b) water and aniline

(c) a mixture of dyes

(d) copper sulphate and sodium chloride

(e) a mixture of amino acids

(f) glycerol and spentlye in soap industry.

12. Explain the terms inductive effect and electromeric effect. Arrange the following compounds in the increasing order of their acidic and basic strength :

(a) $ClCH_2COOH$, Cl_3CCOOH and $Cl_2CHCOOH$

(b) CH_3CH_2COOH, $(CH_3)_2CHCOOH$ and $(CH_3)_3CCOOH$

(c) CH_3NH_2, CH_3NHCH_3, $(CH_3)_3N$, $C_6H_5NHCH_3$

13. Write the isomerism among the following compounds :

$$\text{(a) } CH_3CH_2CH_2CH_2CH_3, \quad CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_2CH_3 \quad H_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

(b) $CH_3CH_2CH_2OH$ and $CH_3\underset{\underset{OH}{|}}{C}H-CH_3$

(c) CH_3CH_2CHO and $H_3C-\overset{\overset{O}{\|}}{C}-CH_3$

(b) $CH_3-O-CH_2CH_2CH_2CH_3$ and $CH_3CH_2OCH_2CH_3$

(e) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2COOC_2H_5$ and $CH_3-\overset{\overset{OH}{|}}{C}=CHCOOC_2H_5$

14. An organic compound was found to contain C = 39.13%, H = 8.64% and remaining is oxygen. Calculate the empirical formula of the compound.

[**Ans.** $C_3H_8O_3$]

15. An organic compound gave the following results on analysis :

C = 17.39%, H = 1.45%, Br = 57.97%, O = 23.19%. Molar mass of the compound was found to be 276 g m ol^{-1}. Calculate its molecular formula.

[**Ans.** $C_4H_4Br_2O_4$]

16. 0.185 g of an organic compound when treated with concentrated nitric acid and then silver nitrate in Carius method gave 0.320 g of silver bromide. Calculate the percentage of bromine in the compound. [**Ans.** 73.6%]

17. A sample of 0.50 g of an organic compound was treated to Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.5M H_3SO_4. The residual acid required 60mL of 0.5M NaOH for neutralisation. Find the percentage composition of nitrogen in the compound. [**Ans.** 56%]

18. A welding fuel gas contain carbon and hydrogen only. Burning a small sample of it in oxygen, gives 3.38 carbondioxide, 0.690 g water and no other

products. A volume of 10.0 L (measured at STP) of this welding gas found to weigh 11.6 g. Calculate :

(a) Empirical formula

(b) Molar mass of the gas

(c) Molecular formula

19. An organic compound on analysis gave following data

   (i) 0.25g of compound on complete combustion gave 0.37g CO_2 and 0.2g of water.

   (ii) 0.25g of compound on analysis by Duma's method gave 32 ml of nitrogen at N.T.P.
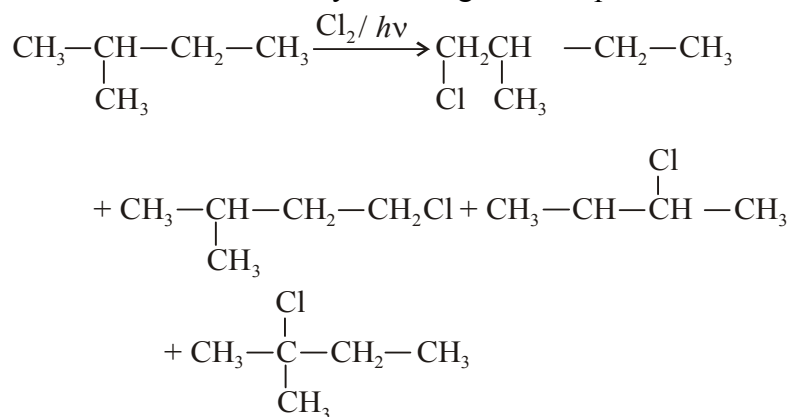
       Calculate the parcentage of C, H and N in compound.

HYDROCARBONS

Preparations

- **Hydrogenation :** Addition of H_2 to alkenes and alkynes in presence of catalyst to form alkanes.

- **Wurtz reaction :** Treatment of alkyl halides (X = Cl, Br, I) with sodium in dry ethereal solution to form symmetrical alkanes having double the number of carbon atoms as present in parent alkyl halide.

- **Decarboxylation** is the process of removal of CO_2 from the carboxylic acid to form an alkane having one carbon atom less than the parent carboxylic acid.

- **Kolbe's electrolysis** of sodium or potassium salt of carboxylic acid produces alkane having one carbon atom less than the parent acid.

- Halogenation of alkanes proceeds through free radical chain mechanism.

  Monochlorination of 2-methyl butane gives four products.

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3 \xrightarrow{Cl_2/\,h\nu} \underset{\underset{Cl}{|}}{CH_2}\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$$

$$+\ CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2Cl + CH_3-CH-\underset{\overset{|}{Cl}}{CH}-CH_3$$

$$+\ CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2-CH_3$$

- **Mechanism of Halogenation**
  (i) Reaction is initiated by homolysis of chlorine molecule in presence of light or heat

$$Cl-Cl \xrightarrow{h\nu} \dot{C}l + \dot{C}l$$

  (ii) $H_3C-H+\dot{C}l \longrightarrow \dot{C}H_3 + H-Cl$

$$H_3\overset{\bullet}{C} + Cl - Cl \longrightarrow H_3C - Cl + \overset{\bullet}{Cl}$$

(iii) $\overset{\bullet}{Cl} + \overset{\bullet}{Cl} \longrightarrow Cl - Cl$

$H_3\overset{\bullet}{C} + \overset{\bullet}{Cl} \longrightarrow H_3C - Cl$

$H_3\overset{\bullet}{C} + \overset{\bullet}{C}H_3 \longrightarrow H_3C - CH_3$
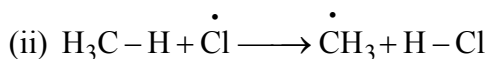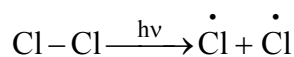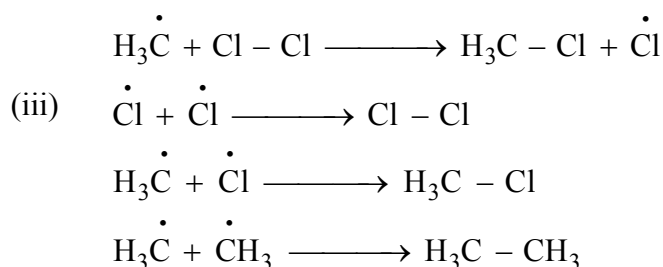
- **Lindlar's catalyst** is the partially deactivated palladised charcoal which converts unsymmetrical alkynes having no acidic terminal hydrogen to form cis-alkene.
- Unsymmetrical alkynes having no terminal hydrogen is reduced by Na/liquid NH_3 to form trans-alkene.
- **Saytzeff Rule** is used in dehydrohalogenation of alkyl halide which is a β-elimination reaction since hydrogen is eliminated from β-carbon having lesser number of hydrogen atoms. (β-carbon is the carbon atom which is next to carbon to which halogen is attached) to form more stable alkene having more substituted double bond.
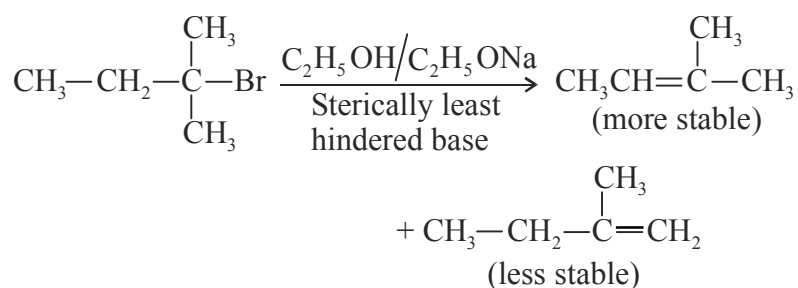
An exception to Saytzeff Rule : The most sterically hindered base $(CH_3)_3 C\overset{-}{O}\overset{+}{K}$ in tert-butyl alcohol cannot attack at the β-carbon atom having lesser number of hydrogen atoms because of greater crowding at the site of attack. Therefore, the base, tert-butoxide remove more exposed 1° hydrogen atom from β-carbon.
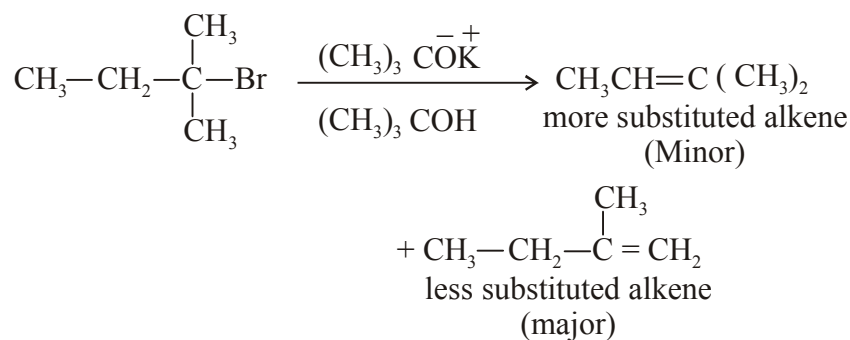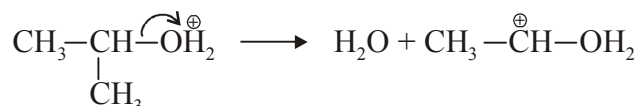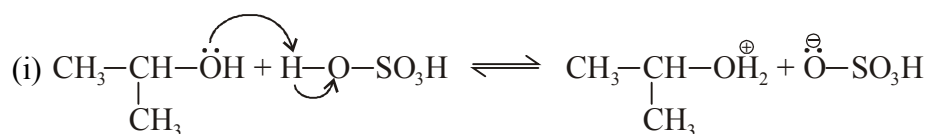
An Exception to Saytzeff Rule

(i) If leaving group is poor like F, then also least substituted albene is formed as major product.

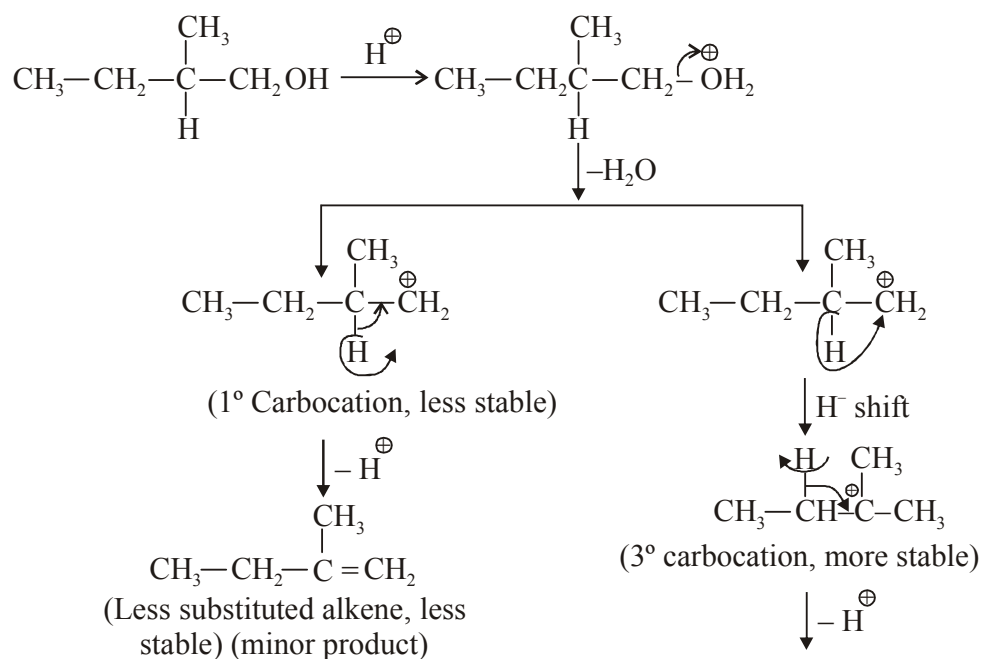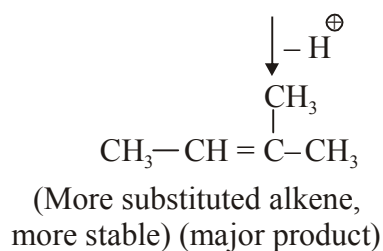$$H_3C-CH_2-\underset{\underset{F}{|}}{CH}-CH_3 \xrightarrow[\Delta]{KOH(alc)} H_3C-CH_2-CH=CH_2$$
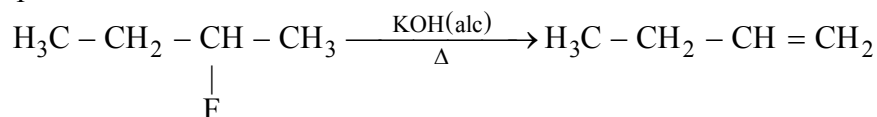
Acid Catalysed Dehydration of Alcohols : Dehydration of 1° alcohols is an Elimination reaction.

Mechanism :

(i) $CH_3-\underset{\underset{CH_3}{|}}{CH}-\ddot{O}H + H-O-SO_3H \rightleftharpoons CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\oplus}{O}H_2 + \overset{\ominus}{\ddot{O}}-SO_3H$

$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\oplus}{O}H_2 \longrightarrow H_2O + CH_3-\overset{\oplus}{C}H-OH_2$

(ii) $CH_3-\overset{\oplus}{C}H-\underset{\underset{H}{|}}{CH_2} \longrightarrow CH_3-CH=CH_2 + H^+$
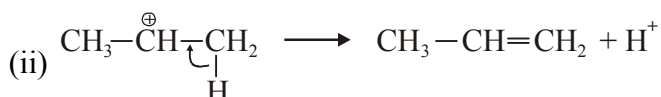
Rearrangement of carbocations obtained from 2° or 3° alcohols may occur by hydride (H^-) or methanide CH_3^- shift (both are 1, 2-shifts) to form more stable carbocations.

$$CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2OH \xrightarrow{H^\oplus} CH_3-CH_2\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\overset{\oplus}{O}H_2$$

$\downarrow -H_2O$

$CH_3-CH_2-\underset{\underset{H}{(\!H\!)}}{\overset{\overset{CH_3}{|}}{C}}\!\!-\overset{\oplus}{C}H_2$

(1° Carbocation, less stable)

$\downarrow -H^\oplus$

$CH_3-CH_2-\underset{}{\overset{\overset{CH_3}{|}}{C}}=CH_2$

(Less substituted alkene, less stable) (minor product)

$CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\oplus}{C}H_2$

$\downarrow H^-$ shift

$CH_3-\overset{H}{\underset{}{CH}}\!\!-\overset{\overset{CH_3}{|}}{\underset{}{\overset{\oplus}{C}}}-CH_3$

(3° carbocation, more stable)

$\downarrow -H^\oplus$

$$\downarrow -\overset{\oplus}{H}$$

$$\underset{CH_3-CH=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_3}{}$$

(More substituted alkene,
more stable) (major product)

Similarly acid catalysed dehydration of 2-methylbutan-2-ol forms 2-methylbut-2-ene as major product and 2-methylbut-1-ene as a major product.
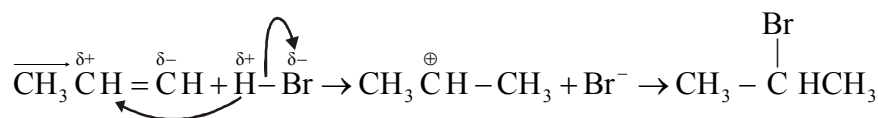
$$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_3 \xrightarrow{\overset{\oplus}{H}} CH_3-CH=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_3 + CH_3CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$$

(minor product)   (major product)
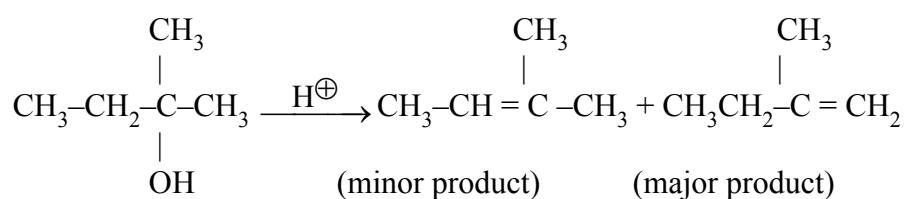
Markownikov Rule

Addition of hydrogen bromide to unsymmetrical alkanes

$$CH_3CH = CH_2 + HBr \rightarrow \underset{\text{major}}{CH_3CH(Br)-CH_3} + \underset{\text{minor}}{CH_3CH_2Br}$$
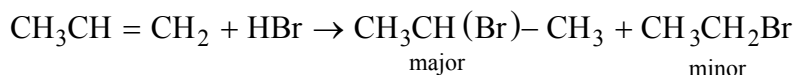
Mechanism : Markownikov rule proceed via carbocation formation :

1. Larger alkyl group polarise the π-bond.

$$\overset{\longrightarrow}{CH_3}\overset{\delta+}{C}H = \overset{\delta-}{C}H + \overset{\delta+}{H}-\overset{\delta-}{Br} \rightarrow CH_3\overset{\oplus}{C}H-CH_3 + Br^- \rightarrow CH_3 - \overset{\overset{\displaystyle Br}{|}}{C}HCH_3$$

2. $\overset{\oplus}{H}$ attacks first and generate more stable carbocation.
3. Br⁻ attacks to carbocation to form product.

    Another example is :

$$CH_3CH_2\overset{\delta+}{C}H = \overset{\delta-}{C}HCH_3 + \overset{\delta+}{H}-\overset{\delta-}{Br} \rightarrow CH_3CH_2\overset{\oplus}{C}HCH_2CH_3 + Br^{\ominus} \rightarrow$$

$$CH_3-CH_2-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_2-CH_3$$
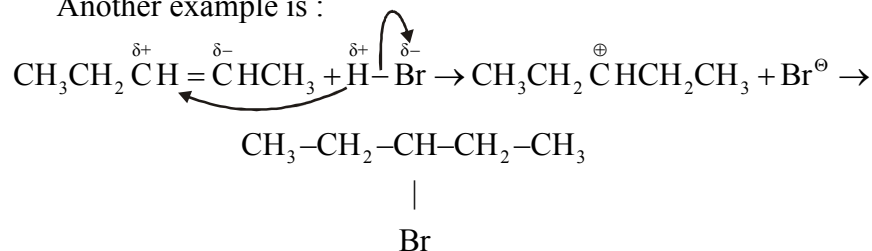
Addition of HBr to unsymmetrical alkanes in presence of peroxide

$$CH_3CH = CH_3 \xrightarrow[\text{Benzoyl Peroxide}]{HBr} \underset{\text{major}}{CH_3CH_2 - CH_2 - Br} + \underset{\text{minor}}{CH_3CH(Br)CH_3}$$
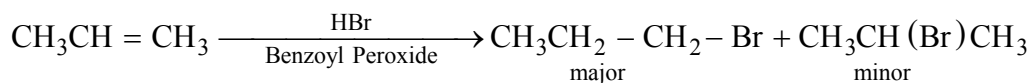
Mechanism of Peroxide effect :

Peroxide effect (Antimarkownikov rule) proceeds via free radical mechanism.

$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 \xrightarrow{h\nu} 2C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\bullet}{O} \rightarrow 2\overset{\bullet}{C}_6H_5+CO_2$$
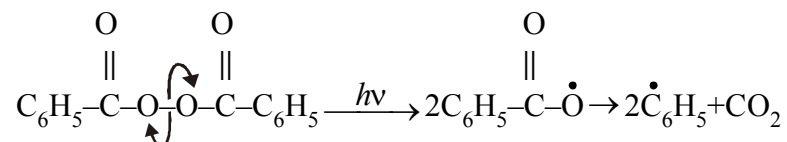
One free radical always generate another free radical.

$$\dot{C}_6H_5 + HBr \rightarrow C_6H_6 + \dot{Br}$$

$$CH_3CH=CH_2 + \dot{Br} \rightarrow CH_3\underset{\text{(More stable radical)}}{\dot{C}HCH_2Br} \xrightarrow{HBr} CH_3CH_2CH_2Br + \dot{Br}$$
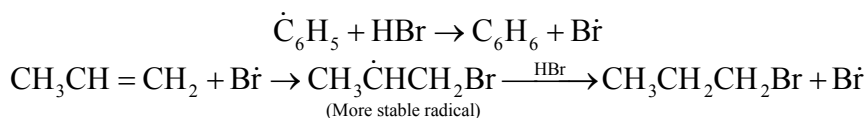
Friedel-Crafts Reaction :

Introduction of alkyl (R) or acyl group (COR) to benzene nucleus in presence of anhydrous $AlCl_3$ (Lewis acid) is called Friedel-Crafts rection.

Mechanism :

Step 1. Generation of electrophile, $AlCl_3$ is a Lewis acid and generate electrophile.

$$CH_3Cl + AlCl_3 \rightarrow Al\overset{\ominus}{C}l_4 + \overset{\oplus}{C}H_3$$
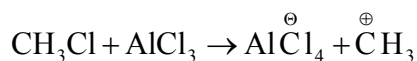
Step 2. Attack of electrophile on the ring
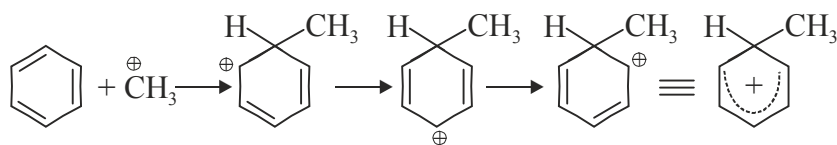
Step 3. Abstraction of H⁺ by the nucleophile
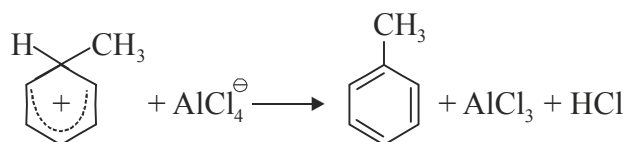
Some special cases of friedel-crafts reaction

(1) More stable carbocation will form the major product, *e.g.,*

$$CH_2CH_2CH_2Cl + AlCl_3 \longrightarrow A\overset{\ominus}{l}Cl_4 + CH_3CH\overset{\oplus}{C}H_2 \xrightarrow[\text{shift}]{H^-} CH_3-\overset{\oplus}{C}H-CH_3$$

1° carbocation   2° carbocation
(Less stable)   (more stable)

$$(CH_3)_2\ CHCH_2Cl \xrightarrow{AlCl_3} A\overset{\ominus}{l}Cl_4 + CH_3-\overset{CH_3}{\underset{H}{C}}-\overset{+}{C}H_2 \xrightarrow[\text{shift}]{H^{\ominus}} (CH_3)_3\ \overset{\oplus}{C}$$
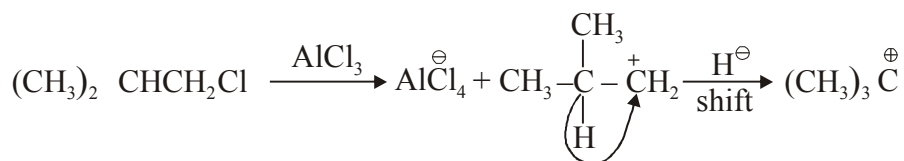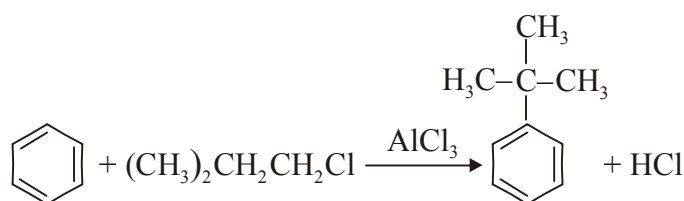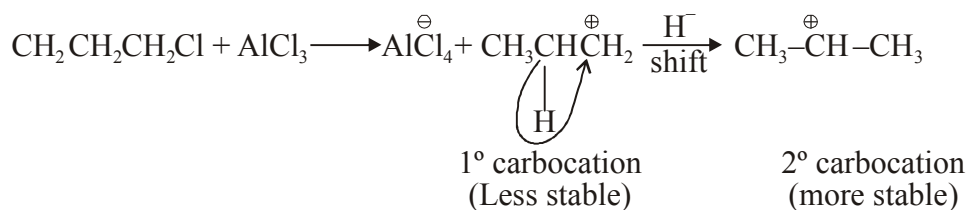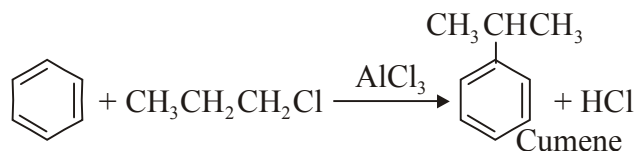
Directive influence of a functional group in monosubstituted benzene :

Activating groups like $- NH_2$, $- NHR$, $- NR_2$, $- NHCOCH_3$, $- OCH_3$, $- CH_3$, $- CH_2CH_3$ are *o-/p*-directors.

Halogen atoms deactivates the ring by electron withdrawing inductive effect. But the halogen atom increase the electron availability at *o-and/or/p*-positions by electron donating resonance effect. Hence halogens act also as *o-and/or/p*-directors.

Deactivating groups such as $- NO_2$, $- CN$, $- CHO$, $- COOH$, $- COR$, $-CONH_2$, $- COOR$ and $- SO_3H$ are *m*-directing groups.

HYDROCARBONS

1. Write IUPAC names of the following organic compounds :
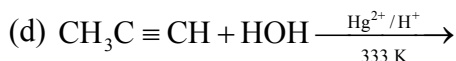
(a)   (b) $(CH_3)_4C$

(c) $\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown\!\!\diagup$ OH (d) $(CH_3)_2 CH \underset{\underset{O}{\|}}{C} CHC(CH_3)_3$

(e) $CH_3CH_2 - \underset{\underset{|}{OH}}{C} H - CH_2 - CH_2OH$ (f) $\underset{COOH}{\overset{COOH}{|}}$

(g)

$\overset{COOH}{\underset{CH_3}{\bigcirc}}$

(g) $CH_2 = CH - CH_2 - C \equiv CH$

(h) $CH_3 - C(CH_3)_2 - CH = CH_2$ (i) $CH_3 - CH = CH - CH_2COOH$

2. Complete the following equations :

(a) $HC \equiv CH \xrightarrow{Na} A \xrightarrow{CH_3Br} B$

(b) $HC \equiv CH + H_2O \xrightarrow[333 \text{ K}]{Hg^{2+}/H^+}$

(c) $HC \equiv CH \xrightarrow[873 \text{ K}]{\text{red hot iron tube}}$

(d) $CH_3C \equiv CH + HOH \xrightarrow[333 \text{ K}]{Hg^{2+}/H^+}$

(e) $HC \equiv CH + H + Br \rightarrow A \xrightarrow{HBr} B$

(f) $HC \equiv CH + Br_2 \rightarrow$

(g) $HC \equiv CH + O_2 \rightarrow$

(h) $CH_3C \equiv CH + H - Br \rightarrow$

(i) $CaC_2 + H_2O \rightarrow$

(j) $BrCH_2 - CH_2Br \xrightarrow[KOH]{\text{alcohol}} A \xrightarrow{NaNH_2} B$
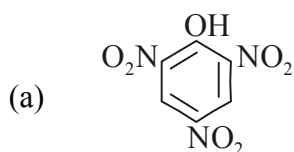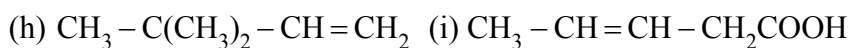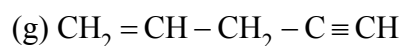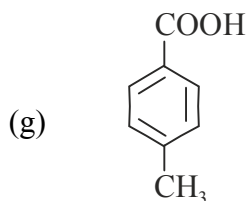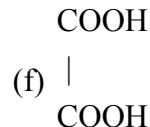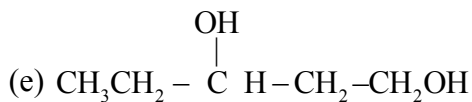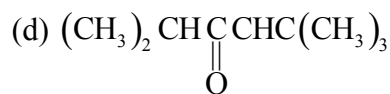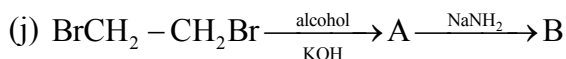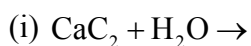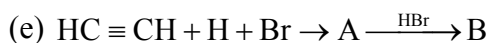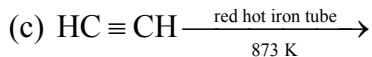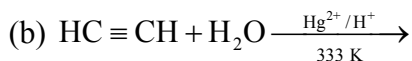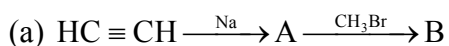
3. Explain the following reactions with suitable examples :
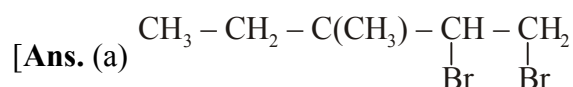(a) Wurtz reaction
(b) Kolbe's electrolysis
(c) Friedal Craft reaction

4. Define conformations. Write the conformations of ethane. Draw the structures of various conformers of ethane according to Newman projection formula. Name the most stable conformer of ethane.

5. State Markovnikov rule. Explain the mechanism of Markovnikov rule. Write the product when the same reaction is carried with HBr in presence of Benzoyl peroxide. Explain the mechanism of this reaction also.

6. Complete the following reactions :

(a) $CH_2CH_2CH = CHCH_3 + HBr \rightarrow$

(b) $CH_3CH = CH_2 + HBr \xrightarrow[\text{Peroxide}]{\text{Benzyl}}$

(c) $H_2C = CH_2 + O_3 \rightarrow A \xrightarrow{Zn/H_2O} B + C$

(d) $\begin{matrix} CH_3 \\ CH_3 \end{matrix} C = CH_2 + O_3 \rightarrow A \xrightarrow{Zn/H_2O} B + C$

(e) $CH_3CH = CH_2 + O_3 \rightarrow A \xrightarrow{Zn/H_2O} B + C$

(f) $CH_3 - C = CH_2 \xrightarrow{KMnO_4/H^+}$
$\qquad \qquad | $
$\qquad \quad CH_3$

(g) $CH_3CH = CHCH_3 \xrightarrow{MnO_4^-/OH^-}$

(h) $CH_2 = CH_2 + H_2O \xrightarrow[273\ K]{\text{dil KMnO}_4}$

(i) ⬡ $+ 3Cl_2 \xrightarrow[500\ K]{UV}$

(j) $CH_2 = CH_2 + Br_2(aq) \rightarrow$

7. How will you carry out following conversions :
   (a) Ethyne into propyne
   (b) Ethyne into benzene
   (c) Benzene into 4-nitrobromobenzene
   (d) Benzene into *n*-nitrochlorobenzene
   (e) But-2-ene into ethanol
   (f) Benzene into acetophenone
   (g) Benzene into 4-nitrotoluene
   (h) Ethane into ethyne

(i) Ethanoic acid into methane

(j) Methane into ethane

8. Illustrate by drawing resonance structures that $-OH$ attached to benzene ring, is ortho-and para-directing.

9. Illustrate by drawing resonance structure that $-NO_2$ attached to benzene ring is meta-directing.

10. Benzene undergo electrophilic substitution reaction. Explain the mechanism of electrophilic substitution in the following steps :

    (a) Generation of electrophile

    (b) Formation of carbocation intermediate

    (c) Removal of proton from carbocation intermediate

11. Give reasons :

    (a) $AlCl_3$ is used as catalyst in Friedal-Craft reaction.

    (b) Wurtz reaction is carried in dry ether.

    (c) Wurtz reaction is not preferred for the preparation of alkanes containing odd number of carbon atoms.

    (d) C-C bond length in benzene ring is 139 pm which is in between C-C single bond 154 pm and C=C double bond 133 pm.

    (e) Benzene is extra ordinarly stable although it constants three double bonds.

    (f) trans-2-butene has higher m.p. than cis-isomer.

    (g) Chlorobenene is less reactive towards electrophilic aromatic substitution than benzene.

    (h) Ethyne is more acidic than ethene and ethane.

    (i) Kharasch effect is spontaneous with HBr only.

    (j) $-OH$ is activating group while halogens are deactivating group, however, both are *o-/p*-director.

12. Give one chemical test to distinguish between compounds of the following pairs:

    (a) Ethane and ethene

    (b) Ethene and ethyne

(c) Benzene and cyclohexene

(d) But-1-yne and But-2-yne

(e) But-1-yne and Buta-1, 3-diene

13. An alkyl dihalide A, $C_6H_{12}Br_2$ on dehydrobromination with $NaNH_2$ gave compound $B.C_6H_{10}$. 'B' on hydration gave 3-methylpentan-2-one. Suggest suitable structural formulae for compound A and B.

[**Ans.** (a) $\underset{\displaystyle \overset{|}{Br}\ \ \overset{|}{Br}}{CH_3 - CH_2 - C(CH_3) - CH - CH_2}$

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

14. An alkene C_8H_{16} on ozonolysis form ozonide which on hydrolysis with Zn dust form an aldehyde and pentan-2-one as products. Draw the structure of alkene and write the chemical reaction involved.

[**Ans.** $\underset{\displaystyle H_2}{\overset{\displaystyle CH_3CH_2CH_2}{>}} C = CH - CH_2 - CH_3$]
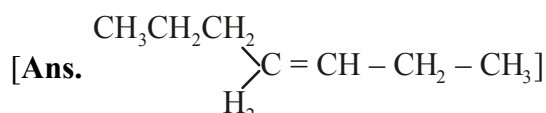
15. According to Huckel's rule what are the necessary conditions for any system to be aromatic? Explain why the following systems are aromatic or non-aromatic.

(i)   (ii) $= CH_2$ (iii)
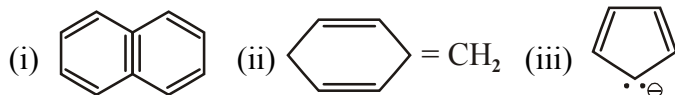
16. A hydrocarbon 'A' adds on mole of hydrogen in presence of Pt catalyst to form n-hexane. When 'A' is oxidised with $KMnO_4$, a single carboxylic acid 'B' containing three carbon atoms is obtained. Identity 'A' and 'B'.

[**Ans.** A : $CH_3CH_2CH = CHCH_2CH_3$
B : $CH_3 CH_2COOH$]
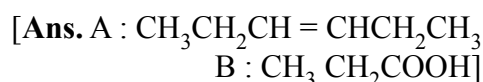
17. Write the structures of all possible position and chain isomers of hex-1-yne.

18. Show the formation of sigma and pi bonds in ethyne.

19. A hydrocarbon C_5H_{10} does not react with chorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

20. Draw the structures of geometrical isomers of but-2-ene. Which of them is more polar and why ?

ENVIRONMENTAL CHEMISTRY

(1) Main regions of the atmosphere are (i) troposphere, (ii) stratosphere, (iii) mesosphere and (iv) thermosphere.

(2) The addition of any undesirable material in air, water and soil by natural source or due to human activity to such a level of concentration which adversely affects the environment is called environmental pollution.

(3) Pollutants can be (i) gaseous air pollutants (*e.g.,* SO_2, NO_2, CO_2, H_2S, hydrocarbons, ozone etc.) and (ii) particulate pollutants (*e.g.,* dust, mist, fumes, smoke, smog etc.)

(4) **Green House Effect :** Warming of the earth by absorption and re-emission of solar radiations is called green house effect. Gases responsible for the green house effect are CO_2, CH_4, N_2O, CFCs, O_3 and water vapours.

(5) The word **smog** is a combination of smoke and fog. Classical smog occurs in cool humid climate and photochemical smog occurs in warm, dry and sunny climate. Classical smog is a mixture of smoke, fog and sulphur dioxide. It is reducing in nature whale photochemical smog is oxidising in nature. The common components of photochemical smog are O_3, NO, acrolein, formaldehyde and peroxyacetyl nitrate (PAN). Both O_3 and PAN act as powerful eye irritants. O_3 and NO irritate the nose and throat and their high concentration causes headache, chest pain, dryness of the throat, cough and difficulty in breathing. It also causes corrosion of metals, stones, building materials, rubber and painted surfaces.

(6) In 1980, Ozone hole was detected over south pole. The ozone layer is depleting because of the presence of certain chemicals like CFC's in the stratosphere. The most serious effect of the depletion of ozone layer is that the ultraviolet radiation coming from the sun can pass through the stratosphere and reach the surface of the earth and can lead to ageing of skin, cataract, sunburn, skin cancer, killing of many phytoplanktons, damage to fish productivity etc.

(7) Water pollution is defined as the contamination of water by substance which make it harmful for health of animals, plants or aquatic life and make it unfit for domestic, industrial and agricultural use.

(8) The amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water is called **BIOCHEMICAL OXYGEN DEMAND (BOD).** Clean water would have BOD value of less than 5ppm and highly polluted water could have a BOD value of 17ppm or more.

(9) The International standards for drinking water are given below and these must be followed :

Ions	Maximum limit	Harmful Effects
F^-	1 ppm	72 ppm causes brown mottling of teeth.
Pb	50 ppb	Can damage kidney, liver, reproductive system
SO_4^{2-}	500 ppm	Laxative effect
NO_3^-	50 ppm	Methemoglobinemia(blue-baby syndrome)

(10) Green chemistry is a way of thinking and is about utilising the existing knowledge and principles of chemistry and other sciences to reduce the adverse impact on environment.

1 - MARK QUESTIONS

1. Define environmental pollution.

2. Define the term pollutant.

3. Carbon monoxide is more harmful pollutant than carbondioxide. Explain.

4. Name the pollutant gas that causes stiffness and fall off flower buds in plants.

5. Name the gas responsible for irritant red haze in the traffic and congested places.

6. Mention the effect of increased concentration of carbondioxide in atmosphere.

7. Define Biochemical Oxygen Demand.

8. Name the compound responsible for ozone layer depletion in the stratosphere.

9. Why classical smog is also called reducing smog.

10. Describe 'blue baby' syndrome.

2 - MARK QUESTIONS

1. List the gases responsible for green house effect.

2. Mention the reasons how acid rain affect the ancient statues and monuments.

3. Write the chemical reaction involved in the formation of photochemical smog.

4. Write the reaction involved for ozone layer depletion in the stratosphere.

5. Discuss the effects if green house gases were totally missing in the earth's atmosphere.

6. Define pesticides and herbicides with examples.

7. Domestic waste can be used as manure. Explain in detail giving examples.

8. Write maximum concentration of the following species in drinking water :
    Fluoride, Lead sulphate and Nitrates

9. Write the effect of the following gases on human being :
    SO_2, NO_2, CO, CO_2

10. Define particulate pollutant. Classify the following particulate pollutants as viable or non viable : Smoke, dust, mist, moulds.

3 - MARK QUESTIONS

1. Mention the causes of water pollution. Suggest the measures to control water pollution.

2. Discuss the major causes of soil pollution. Suggest the effort you will make for controlling soil pollution.

3. Explain the term green chemistry. How will it help decrease environmental pollution ?

4. Discuss waste management. How will biodegradable and non-biodegradable wastes disposed off ?

5. Write the use of green chemistry in the following day to day life processes for decrease in pollution :

    (a) Dry cleaning of clothes

    (b) Bleaching of paper

    (c) Synthesis of chemicals

6. Define the following

    (a) Global warming

    (b) Eutrophication

    (c) Acid rain

SAMPLE PAPER - I (SOLVED)

(ACCORDING TO CBSE CURRICULUM : 2012-13)

CHEMISTRY - XI

Time : 3 hours   **Class : XI**   **Maximum Marks : 70**

General Instructions :

1. *All questions are compulsory.*

2. *Question no.1 to 8 are very short answer questions and carry 1 mark each.*

3. *Question no.9 to 18 are short answer questions and carry 2 marks each.*

4. *Question no.19 to 27 are also short answer questions and carry 3 marks each.*

5. *Question no. 28 to 30 are long answer questions and carry 5 marks each.*

6. *Use log tables it necessary, use of calculators is not allowed.*

QUESTIONS

1. What happens when sodium metal is dropped in water?   **(1 Mark)**

2. For an isolated system $\Delta U = 0$, What will be ΔS?   **(1 Mark)**

3. Explain why BeH_2 molecule has zero dipole moment although the Be-H bonds are polar?   **(1 Mark)**

4. Predict the shape of the NH_3 molecule according to VSEPR theory.
        (1 Mark)

5. Which isotope of hydrogen is radioactive?   **(1 Mark)**

6. Write the correct IUPAC name of the compound given below:

    $CH_2 = CH - C \equiv CH$ **(1 Mark)**

7. What type of hybridisation of carbon is involved in Benzene?
   (1 Mark)

8. Name any two gases responsible for greenhouse effect. **(1 Mark)**

9. Arrange the following ions in order of increasing ionic radius:

   K^+, P^{3-}, S^{2-}, Cl^-. Give reason. **(2 Marks)**

10. Why ionisation energy of Be is greater than Boron? **(2 Marks)**

11. A sample of gas occupies 3.00 L at 760 torr. Calculate the volume the gas will occupy if the pressure is changed to 1.45 atm and the temperature remains constant. **(2 Marks)**

12. Write the units of vanderWaals constant *a* and *b*. **(2 marks)**

13. Complete the following reactions: **(2 Marks)**

    (*i*) $Al + NaOH + H_2O \rightarrow$

    (*ii*) $SiCl_4(l) + H_2O(l) \rightarrow$ **(2 Marks)**

14. Explain : **(2 Marks)**

    (*i*) Alkali metals are soft and can be cut with help of a knife.

    (*ii*) Potassium is more reactive than sodium.

15. (*a*) Explain why Be and Mg do not give colour to the flame whereas other alkaline earth metals do. **(1 Mark)**

    (*b*) Why alkali and alkaline earth metals cannot be prepared by chemical reduction methods? **(1 Marks)**

16. Why $SiCl_4$ can be easily hydrolysed buy CCl_4 cannot be hydrolysed easily? Explain with reaction. **(2 Marks)**

17. Arrange benzene, hexane and ethyne in decreasing order of acidic behaviour. Also give reasons for this behaviour. **(2 Marks)**

18. 50 kg of $N_2(g)$ & 10.0 kg of $H_2(g)$ are mixed to produce $NH_3(g)$, identify the limiting reagent. Also, calculate the amount of NH_3 formed. **(3 Marks)**

19. Mohan was going with his friend Soham on a motorcycle. Their motorcycle was producing a lot of smoke. On the way, a Policeman stopped them and asked them to show pollution check certificate.

They did not have that certificate and the Policeman challan their vehicle. After reading this passage answer the following questions :

(i) Why did Policeman Challan their vehicle?

(ii) What human values do you associate with the act of Policeman?

20. **(3 Marks)**

(i) Calculate the wavelength in nanometers, of visible light having a frequency of 4.37×10^{14} S^{-1}.

(ii) What are frequency and wavelength of a photon emitted during a transition from n = 6 to $n = 1$ state in the hydrogen atom.

21. (i) Explain why the following electronic configuration is not possible:

$$n = 1, l = 0, m_l = +1, m_s = +\frac{1}{2}$$

(ii) Write electric configurations of Cu^{2+}.(Z=29)   **(3 Marks)**

22. (i) Draw the reasonating structures of O$_3$.

(ii) Why is NF$_3$ trigonal pyramidal while BF$_3$ is trigonal planar, though both are tetra atomic molecules?

(iii) State the hybridization of 3rd & 4th Carbon atom   **(3 Marks)**

$$HC\equiv C-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

23. Consider the reason: **(3 Marks)**

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 189.4kJ$$

Indicate the direction in which the equilibrium will shift when:

(i) Concentration of SO$_2$ is increased.

(ii) Concentration of SO$_3$ is increased.

(iii) Temperature is increased.

24. Define :   **(3 Marks)**

(i) Common ion effect

(ii) Buffer Solution

(iii) pH

25. Write the balanced equation by half-reaction method: **(3 Marks)**

$H_2S + Cl_2 \rightarrow S + Cl^-$ (in acidic medium)

26. Explain why: **(3 Marks)**

(*i*) $(CH_3)_3 C^+$ is more stable than $CH_3CH_2^+$ and CH_3^+ is the least stable cation.

(*ii*) On adding $AgNO_3$ to CCl_4 solution white precipitate of AgCl is not obtained.

(*iii*) Nitric acid is added to sodium extract before adding $AgNO_3$ for testing halogens.

27. (*i*) 0.2475 g of an organic compound gave on combustion 0.4950 g of carbon dioxide and 0.2025 g of water. Calculate the percentage of C and H in it.

(*ii*) What will happen during Lassaigne's test for nitrogen if the compound also contains sulphur? **(3 Marks)**

28. (*i*) In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change internal energy for the process?

(*ii*) The equilibrium constant for the reaction is 10. Calculate the value of ΔG^θ. Given R = 8.0 J mol^{-1} K^{-1}; T = 300 K**(5 Marks)**

OR

(*i*) Calculate lattice energy for the change

$Li^+(g) + Cl^-(g) \rightarrow LiCl(s)$
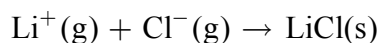
Given that:

$\Delta_{sub}H^\theta$ of Li = 160.67 kJ/mol

$\Delta_{diss}H^\theta$ of Cl_2 = 244.34 kJ/mol

$\Delta_{ie}H^\theta$ of Li(g) = 520.07 kJ/mol

$\Delta_{eg}H^\theta$ of Cl(g) = –365.26 kJ/mol

$\Delta_f H^\theta$ of LiCl(s)= –401.66 kJ/mol

(*ii*) For a reaction; $2A(g) + B(g) \rightarrow 2D(g)$

$$\Delta U^{\theta} = -10.5 \text{ kJ } \& \Delta S^{\theta} = -34.1 \text{ J}$$

Calculate $\Delta G°$ for the reaction and Pledict whether the reaction is spontaneous or not at 298 K.

29. (*i*) What happen when borax solution is acidified. Write the chemical reactions for the reaction.

(*ii*) Lead(IV) chloride is highly unstable towards heat. Why?

(*iii*) Boric acid is not protic acid. Why?

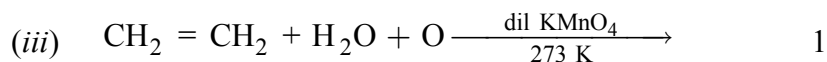(*iv*) SiO_2 is solid but CO_2 is a gas at room temperature. Why?

(5 Marks)

OR

When a metal X is treated with NaOH a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B) Compound (A) is soluble in dilute HCl to form compound (C). The compound (A) when heated strongly gives D which is used to extract metal. Identity (X), (A), (B), (C) & (D). Write suitable equations to support their identities.

30. (*a*) How will you convert: **(3 Marks)**

(*i*) Benzene to acetophenone

(*ii*) Benzene to *p*-nitrophenone

(*iii*) Ethanoic acid to methane

(*b*) Write the name of product obtained by the HBr with hex-1 ene in the presence of a peroxide. 1

(*c*) Hydrogen atoms of ethyme are acidic in nature, why? 1

OR

(*a*) Complete the following reactions:

(*i*) $+ H_2SO_4 \rightarrow$ (fuming) 1

(*ii*) $CaCO_2 + H_2O \rightarrow$ 1

(iii)　$CH_2 = CH_2 + H_2O + O \xrightarrow[\text{273 K}]{\text{dil } KMnO_4}$　　　1

(b)　$-NO_2$ group attached to benzene is meta directing but $-OH$ group is ortho and para directing. Explain why?　　2

SOLUTIONS OF SAMPLE PAPER

Ans 1. When sodium metal is dropped in water, hydrogen gas is evolved which catches fire　　**(½ Marks)**

$2Na + 2H_2O \rightarrow 2NaOH + H_2$　　**(½ Marks)**

Ans 2. $\Delta S = O$　　**(1 Marks)**

Ans 3. BeH_2 is a linear molecule with H-Be-H bond angle as 180°. Although the Be-H bonds are polar, the bond polarities cancel each other and the net dipole moment is zero.　　**(1 Marks)**

Ans 4. Trigonal pyramidal　　**(1 Marks)**

Ans 5. Tritium　　**(1 Marks)**

Ans 6. But-1-en-3-yne　　**(1 Marks)**

Ans 7. Sp^2　　**(1 Marks)**

Ans 8. Carbon dioxide and methane　　**(1 Marks)**

Ans 9. $K^+ < Cl^- < S^{2-} < P^{3-}$　　**(1 Marks)**

Reason : All the ions are isoelectronic with 18 electrons. If the number of electrons is the same, as the number of protons increase, the nuclear charge increase and hence the outermost electrons will experience a greater force of attraction towards the nucleus. This results in the decrease in lonic radii. Since the nuclear charge decreases from K^+ to P^{3-}, the ionic radii increase from K^+ to P^{3-}.　　**(1 Marks)**

Ans 10. The I.E of Be is greater than Born of because of :-　**(2×1 Marks)**

(1)　**Electronic configuration :** Be have fully filled stable configuration, so difficult to remove electron

$_4Be \rightarrow 1s^2 2s^2$

$_5B \rightarrow 1s^2 2s^2 2p^1$
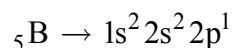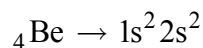
(*2*) **Penetration effect :** In case of Be, electron is to be removed from s-subshell while in Boron from p-subshell penetration effect of *s* is greater than p so difficult to remove electron from Be.

(1 Mark)

Ans 11. The given question is based on Boyle's Lao. Therefore,

$$P_1 V_1 = P_2 V_2 \qquad \text{(2×1 Marks)}$$

$$\Rightarrow \quad \frac{760 \text{ torr}}{760 \text{ torr/atm}} \times 3L = 1.45 \text{atm} \times V_2 L$$

$$\Rightarrow \quad V_2 = 2.07L \qquad \text{(1 Mark)}$$

Ans 12. Unit of a is atm lit^2 mol^{-2} and of b is lit mol^{-1} **(2×1 Marks)**

Ans 13. (*i*) $2AL + 2NaoH + 6H_2O \rightarrow 2Na[AL(OH)_4] + 3H_2$ **(1 Mark)**

(*ii*) $SiCl_4 (I) + 2H_2O(I) \rightarrow SiO_2(s) + 4HCl(aq)$ **(1 Mark)**

Ans 14. (*i*) Alkali metals have large atomic size with only one valence electron. Thus, they have weak metallic bonding between the atoms of the metal. Because of weak metallic bonding, alakli metals are soft and can be cut with a knife. **(1 Mark)**
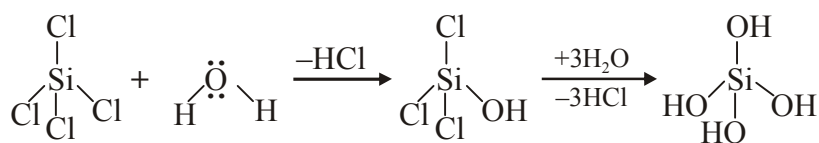
(*ii*) Reactivity of metals depends on ionization enthalpy. Smaller is the ionization enthalpy, greater is the reactivity. Potassium has a larger atomic size than sodium. Thus, the ionization enthalpy of potassium is less than sodium. Hence, potassium is more reactive than sodium. **(1 Mark)**

Ans 15. (*a*) Be and Mg both have high Ionisation enthalphy **(1 Mark)**

(*b*) Alkali metals and alkaline earth metals are good reducing agents and have high negative $E^0_{m^{n+}}/m$ values, therefore they can not be reduced by chemical Methods. **(1 Mark)**

Ans 16. In $SiCl_4$, Si atom has empty d-orbitals in its valence shell.

These empty d orbitals of Si can accept lone pair of electrons from water molecule. Eventually this leads to hydrolysis of $SiCl_4$ and $Si(OH)_4$ is formed. **(½ Mark)**

$$
\underset{\underset{Cl}{\overset{Cl}{|}}{Cl}\!-\!\overset{Cl}{\underset{|}{Si}}\!-\!Cl}{} \; + \; \overset{\cdot\cdot}{H}\overset{\cdot\cdot}{\underset{}{O}}{}\diagdown{}H \xrightarrow{\;-HCl\;} \underset{\underset{Cl}{\overset{Cl}{|}}{Cl}\!-\!\overset{Cl}{\underset{|}{Si}}\!-\!OH}{} \xrightarrow[-3HCl]{+3H_2O} \underset{\underset{HO}{}{HO}\diagup\overset{OH}{\underset{|}{Si}}\diagdown OH}{}
$$

(½ Mark)

Carbon atom on the other hand does not have any vacant d-orbitals in its valence shell. Hence, it cannot accept the electron pair from water molecule. Thus, CCl_4 dose not hydrolyse. **(1 Mark)**

Ans 17. The decreasing order of acidic behaviour is:

Ethyne > benzene > n-pentane **(1 Mark)**

The C–H bond in ethyne, benzene and n-pentane are formed by sp–s, sp^2–s and sp^3–s overlap. Now, greater the percentage s character, greater is the electronegativity. Therefore, sp-hybridised carbon in ethyne is more electronegative then sp^2 hybridised carbon of benzene which in turn is more electronegative than sp^3 hybridised carbon of n-pentane. Therefore, the polarity of the C-H bond is in order of:

Ethyne > benzene > pentane

Hence the acidity order is:

Ethyne > benzene > pentane **(1 Mark)**

Ans 18. Moles of $N_2 = \dfrac{Mass}{Molar\ mass}$

$$
= \frac{50 \times 10^3\,g}{28\ g/mol}
$$

$$
= 1.786 \times 10^3\ mol
$$

Moles of $H^2 = \dfrac{Mass}{Molar\ mass}$ **(½ Mark)**

$$
= \frac{10 \times 10^3\,g}{2\ g/mol}
$$

$$= 5.0 \times 10^3 \text{ mol}$$

$$N_2 \text{ (g)} + 3H_2 \text{ (g)} = 2NH_3 \text{ (g)} \hspace{3cm} \text{(Eqn 1)}$$

According to equation (1),

1 mole of N_2 (g) reacts with = 3 moles of H_2 (g)

Therefore 1.786×10^3 mol of N_2 (g) will react with

$$= \frac{3 \times 1.786 \times 10^3}{1} \text{ moles of } H_2 \text{ (g)}$$
$$= 5.36 \times 10^3 \text{ mol}$$

But we are having 5.0×10^3 mol of H_2 (g) only.

Hence, H_2 (g) is the limiting reagent. **(½ Mark)**

To calculate the amount of NH_3 formed,

3 moles of H_2 (g) give = 2 moles of NH_3 (g)

Therefore,

$$5.0 \times 10^3 \text{ moles of } H_2 \text{ will give } = \frac{2}{3} \times 5 \times 10^3 \text{ moles of } NH_3$$

$$= 3.3. \times 10^3 \text{ moles of } NH_3$$
(½ Mark)

Mass of NH_3 produced = $3.3 \times 10^3 \times 17$ g of NH_3

$$= 56.1 \text{ Kg} \hspace{3cm} \text{(½ Mark)}$$

Ans 19. (*i*) The exhaust of motorcycle was producing smoke which causes air pollution. The smoke is due to incomplete combustion of fuel producing CO and unburnt carbon. The are very harmful air pollutants. **(1 Mark)**

(*ii*) The act of policeman shows his Sincerity towards his duty and concern for mankind. He was not only doing his duty but was helping to maintain clean environment which is the need of the hour. We all should get our vehicles checked for air pollution timely to save our environment or out life. **(½ Mark)**

Ans 20. (*i*) $\quad v = \dfrac{c}{\lambda}$ **(½ Mark)**

$$\lambda = \frac{c}{v} = \frac{3 \times 10^8 \text{ m/s}}{4.37 \times 10^{14} \text{ s}^{-1}}$$

$$\therefore \lambda = 0.686 \times 10^{-6} \text{ m}$$

$$\therefore \lambda = 686 \text{ nm} \qquad \text{(½ Mark)}$$

(ii) Here $n_1 = 6$ & $n_2 = 1$

The energy gap between two orbits for a hydrogen atom is given as

$$\Delta E = 2.18 \times 10^{-18} \left(\frac{1}{n_1^2} \frac{-1}{n_2^2} \right) \qquad \text{(½ Mark)}$$

$$= 2.18 \times 10^{-18} \text{J} \left(\frac{1}{6^2} - \frac{1}{1^2} \right)$$

$$= 2.18 \times 10^{-18} \text{J} \left(\frac{1 - 36}{36} \right)$$

$$\Delta E = -2.11 \times 10^{-18} \text{J} \qquad \text{(½ Marks)}$$

Since ΔE is negative energy is emitted, frequency of photon is given by

$$v = \frac{\Delta E}{h} \qquad \text{(½ Mark)}$$

$$= \frac{2.11 \times 10^{-18} \text{J}}{6.626 \times 10^{-34} \text{Js}}$$

$$= 3.18 \times 10^{15} \text{ s}^{-1}$$

$$= 3.18 \times 10^{15} \text{ Hz} \qquad \text{(½ Mark)}$$

Ans 21. (i) For $n = 1$,

Value of $l = n - 1$

$$= 1 - 1$$

$$= 0$$

For each value of l,

Value of $m_l = -1, \ldots\ldots\ldots, 0, \ldots\ldots\ldots\ldots, +1$ **(1 Mark)**

Therefore,

For n = 1, l = 0,

$m_l = 0$

Thus the value of $m_l = 1$ is not possible. **(1 Mark)**

(ii) Electronic configuration of Cu^{2+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

(1 Mark)

Ans 22. (i) Resonating structure of O_3 molecule **(1 Mark)**

(ii) In NF_3, N atom involves Sp^3 hybridization and one position is occupied by a lone pair. Therefore the molecule is trigonal pyramidal. But in BF_3, B in involves SP^2 hybridization having trigonal planar geometry. Thus NF_3 is trigonal pyramidal while BF_3 is trigonal planar, even though both are tetra atomic molecules. **(1 Mark)**

(iii) $C_3 \rightarrow Sp^3$

$C_4 \rightarrow SP$ **(½ × 2 Marks)**

Ans 23. (i) If the concentration of SO_2 is increased the equilibrium will shift in the forward direction to consume the reactant SO_2.

(1 Mark)

(ii) If the concentration of SO_3 increased the equilibrium will shift in the backward direction to consume the product SO_3. **(1 Mark)**

(iii) If the temperature is increased, the equilibrium will shift in the backward direction as the increase in temperature will be compensated by absorbing heat. **(1 Mark)**

Ans 24. (i) **Common ion effect :** The suppression in degree of dissociation of weak electrolyte by adding in it a strength electrolyte having the common ion is called common ion effect. **(1 Mark)**

(ii) **Buffer Solution :** Buffer solution is that which resist the change in pH on addition of small amount of acid or base in it.

(1 Mark)

(*iii*) **pH :** It is the negative logarithm of hydronium ion concentration.

(1 Mark)

Ans 25. Step 1 : Write the oxidation numbers and separate the reaction into oxidation half and reduction half reactions.

$$\overset{-2}{H_2S} + \overset{0}{Cl_2} \rightarrow \overset{0}{S} + \overset{-1}{Cl^-}$$ **(½ Mark)**
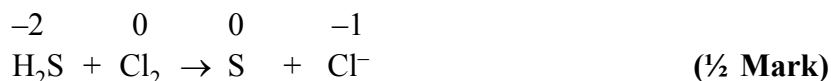
Step 2 : The half reaction are :

Oxidation half reaction : $H_2S \rightarrow S$

Reduction half reaction : $Cl_2 \rightarrow 2Cl^-$ **(½ Mark)**

Step 3 : Balance oxidation number by adding electrons.

Oxidation half reaction : $H_2S \rightarrow S + 2e^-$

Reduction half reaction : $Cl_2 + 2e^- \rightarrow 2Cl^-$ **(½ Mark)**

Step 4 : There are no oxygen atoms. So, balance the hydrogen atoms. Since the reaction takes place in acidic medium, the balancing of hydrogen atoms is done by adding the appropriate number of hydrogen ions to the deficient side.

Oxidation half reaction : $H_2S \rightarrow S + 2e^- + 2H^+$

Reduction half reaction : $Cl_2 + 2e^- \rightarrow 2Cl^-$ **(½ Mark)**

**Step 5 :** Add the two reactions to get a balanced redox reaction.

Balanced reaction :

$$H_2S + Cl_2 \rightarrow S + 2 H^+ + 2 Cl-$$ **(1 Mark)**
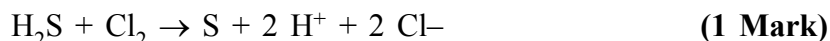
Ans 26. (*i*) $(CH_3)_3 C^+$ is stable due to hyperconjugation but CH_3^+ lacks hyperconjugation stability. **(1 Mark)**

(*ii*) In CCl_4 the C–Cl bonds are covalent which do not furnish Cl^- in solutions. **(1 Mark)**

(*iii*) Conc. HNO_3 is added to the sodium extract to decompose cyanide or sulphide of sodium if present. **(1 Mark)**

$$Na_2S + H^+ \rightarrow Na^+ + H_2S$$

$$NaCN + H^+ \rightarrow Na^+ + NCN$$
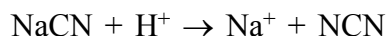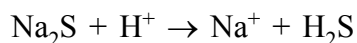
Ans 27. (*i*)   Mass of organic compound = 0.2457 g

Mass of CO_2 produced = 0.4950 g

Mass of H_2O produced = 0.2025 g

$$\% \text{ of C} = \frac{12}{44} \times \frac{\text{Mass of } CO_2}{\text{Mass of compound taken}} \times 100$$

$$\% \text{ of H} = \frac{2}{18} \times \frac{\text{Mass of } H_2O}{\text{Mass of compound taken}} \times 100$$

$$= \frac{2}{18} \times \frac{0.2025}{0.2475} \times 100$$

$$= 9.09$$

$$= \frac{12}{44} \times \frac{0.4950}{0.2475} \times 100 = 54.54 \qquad \textbf{(1 Mark)}$$

(*ii*)   Blood red colouration due to Fe (CNS) will be produced.

(1 Mark)

Ans 28. (*i*)   Heat absorbed by the system (q) = + 701 J   **(½ Mark)**

Work done by the system (w) = –394 J   **(½ Mark)**

Change in internal energy (ΔU) = q + w   **(½ Mark)**

$$= 701 - 394$$

$$= + 307 \text{ J} \qquad \textbf{(½ Mark)}$$

(*ii*) $\Delta G^\theta = -2.303 \ RT \log K$ **(1 Mark)**

R   = 8.0 $JK^{-1} mol^{-1}$

T   = 300 K

K   = 10

$\Delta G^\theta = - 2.303 \ RT \log K$

$$= - 2.303 \times 8.0 \times 300 \times \log 10 \qquad \textbf{(1 Mark)}$$

$$= 5527.\ 2 \ Jmol^{-1} \qquad \textbf{(1 Mark)}$$

OR

Ans 28. (*i*) $\Delta_f h^\theta = \Delta_{sub} H^\theta + \Delta_{ie} H^\theta + \frac{1}{2} \Delta_{diss} H^\theta + \Delta_{eg} H^\theta + \Delta_{lattice} H^\theta$

(½ Mark)

$\Delta_{lattice} H^\theta = -401.66 - (160.67) - (520.07) - \frac{1}{2}(244.34) - (-365.26)$

$\Delta_{lattice} H^\theta = -839.31\, kJ/mol$ **(½ Mark)**

(*ii*) $\Delta U^\theta = -10.5\, kJ, \quad \Delta n\,(g) = -1mol, \quad T = 298\, K$

$R = 8.314 \times 10^{-3}\, kJ\, K^{-1}\, mol^{-1}$

$\Delta H^\theta = \Delta H^\theta + \Delta n\,(g)\, RT$ **(½ Mark)**

$\Delta H^\theta = -10.5 + \left[-1mol \times 8.314 \times 10^{-3}\, 298 \right]$

$= -10.5\, kJ - 2.478\, kJ$

$= -12.978\, kJ$ **(½ Mark)**

$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$ **(½ Mark)**

$= -12978\, J - 298\,(-34.1\, J)$ **(½ Mark)**

$= -12978 + 10161.8$

$= -2816.2\, J$ **(½ Mark)**

Since the value of ΔG^θ is negative, the reaction is spontaneous.

(½ Mark)

Ans 29. (*i*) Borax solution on acidification forms boric acid.

$Na_2 B_4 O_7 + 2HCl + 5H_2O \rightarrow 2\, NaCl + 4H_3BO_3$ **(1 Mark)**
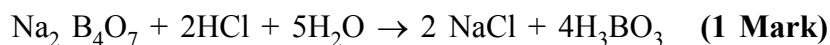
(*ii*) Pb (IV) state is unstable due to inect pair effect. **(1 Mark)**

(*iii*) Basic acid $(B(OH)_3$ accept OH from water and H^+ is released by H_2O molecule. **(1 Mark)**
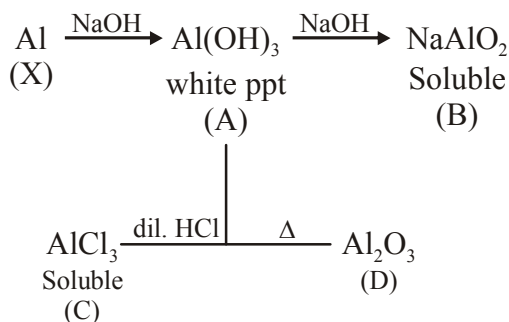
(*iv*) Carbon is able to form pπ-pπ bond with O atom and constitute a stable non-polar molecule $O = C = O$. Due to weak inter particle force its boiling point is low and it is gas at room temperature. **(1 Mark)**

Si on the other hand is not able to from pp-pp bond with O atoms because of its relatively large size. In order to complete

its octet Si is linked to four O atoms around it by sigma bond & these constitutes network structure, which is responsible for its solid state. **(1 Mark)**
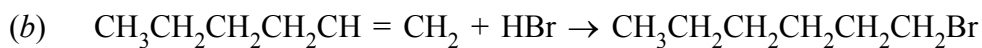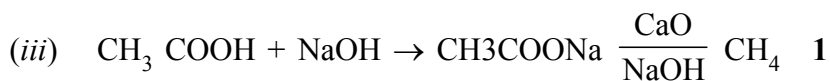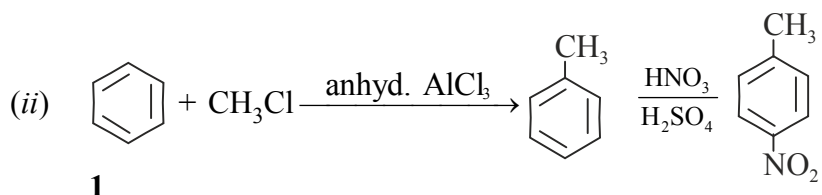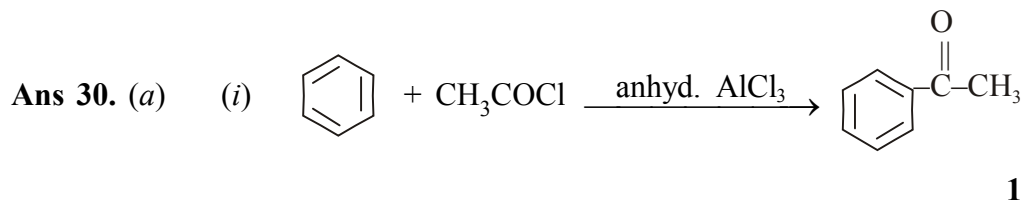
OR

Ans 29.

$$Al \xrightarrow{NaOH} Al(OH)_3 \xrightarrow{NaOH} NaAlO_2$$

Al — (X)

Al(OH)₃ — white ppt (A)

NaAlO₂ — Soluble (B)

$$AlCl_3 \xleftarrow{dil.\ HCl} \quad \xrightarrow{\Delta} Al_2O_3$$

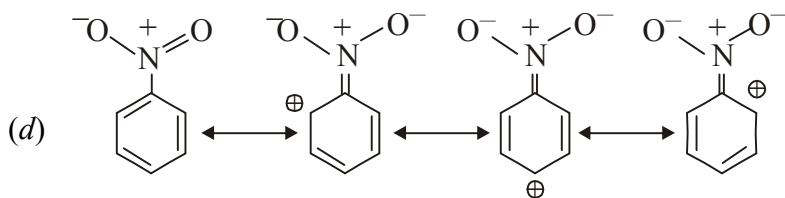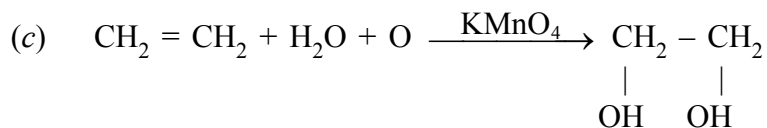AlCl₃ — Soluble (C)

Al₂O₃ — (D)

2 Marks for writing reactions

1 Marks for identifying X

½ mark each for correctly identifying A, B, C and D.

Ans 30. (*a*) (*i*)

$$\bigcirc + CH_3COCl \xrightarrow{anhyd.\ AlCl_3} \text{(acetophenone)}$$

1

(*ii*)

$$\bigcirc + CH_3Cl \xrightarrow{anhyd.\ AlCl_3} \xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3}$$

1

(*iii*) $CH_3 COOH + NaOH \rightarrow CH3COONa \xrightarrow[NaOH]{CaO} CH_4$ **1**

(*b*) $CH_3CH_2CH_2CH_2CH = CH_2 + HBr \rightarrow CH_3CH_2CH_2CH_2CH_2CH_2Br$

(*c*)   The H attached to *sp* hybrid carbon becomes acidic due to high electronegativity of (*sp* hybridised). C

OR

(a) + H_2SO_4 →

       (fuming)   (Benzene sulphonic acid)

(b) $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$

(c) $CH_2 = CH_2 + H_2O + O \xrightarrow{KMnO_4}$ $\underset{\underset{OH}{|}}{CH_2} - \underset{\underset{OH}{|}}{CH_2}$

(d)
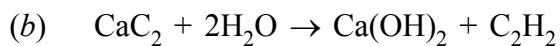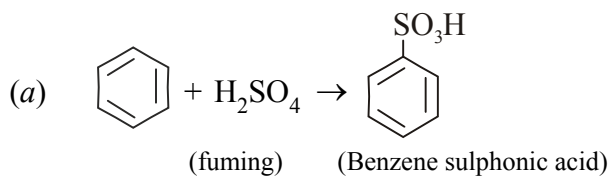
The electron density decreases on *o*- and *p*- positions as a result the electrophile attacks on *m*- position.
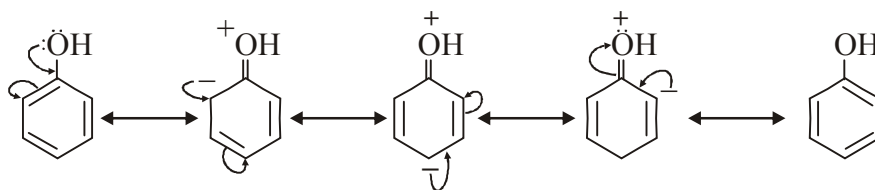
The electron density increase on *o*- and *p*- positions, therefore electrophile attacks on *o*- and *p*- positions.

SAMPLE PAPER - I (UNSOLVED)

(ACCORDING TO CBSE CURRICULUM : 2013-14)

CHEMISTRY - XI

Time : 3 hours   **Class : XI**   **Maximum Marks : 70**

General Instructions :

1. *All questions are compulsory.*

2. *Question no. 1 to 5 are very short answer questions and carry 1 mark each.*

3. *Question no. 6 to 10 are short answer questions and carry 2 marks each.*

4. *Question no. 11 to 22 are also short answer questions and carry 3 marks each.*

5. *Question no. 23 is value based question carrying 4 marks.*

6. *Question no. 24 to 26 are long answer questions and carry 5 marks each.*

7. *Use log tables it necessary, use of calculators is not allowed.*

QUESTIONS

1. How many atoms of helium are present in 64 u of helium?

   (1 Mark)

2. Write IUPAC name and symbol of element having atomic no. 110?

   (1 Mark)

3. What is absolute zero? **(1 Mark)**

4. What is the designation of an orbital having n = 3, l = 2? **(1 Mark)**

5. Define residual entropy. **(1 Mark)**

6. Commercially available sulphuric acid contains 93% acid by mass and has density of $1.84 mL^{-1}$. Calculate its molarity. **(2 Marks)**

7. Which out of NH_3 and NF_3 has higher dipole moment and why?

(2 Marks)

8. (*a*) State Hess's law of constant heat summation?

(*b*) For a reaction:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \Delta_r H\theta = -92.4 \, KJ$$

What is the standard enthalphy of formation of NH_3?

9. Balance the following redox reaction in acidic medium by ion electron method–

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

10. (*i*) Write IUPAC name of $CH_3 - CH_2 - CO - CH_2 - CHO$.

(*ii*) How many sigma and pi bonds are present in $CH_3CH=CHCH_2Cl$.

11. Why ethyne is acidic in nature? Give a chemical test to distinguish between ethene and ethyne.

12. (*a*) Why does boron triflouride behave as lewis acid?

(*b*) What are fullerenes?

13. An electron has a speed of 600 m/s with uncertainty of .025%. What is the uncertainty in locating its position?

OR

(*a*) Which atom is indicated by following configuration $[Ne]3s^23p^4$?

(*b*) How many odes are present in 3d orbital?

(*c*) Give an example of disproportionate reaction.

14. Of the following species which one is most stable and why–

$(CH_3)_3C+$, $(CH_3)_2CH+$, CH_3CH_2+, CH_3+

15. What happens when–

(*a*) Sodium Metal is heated in free supply of air.

(*b*) Gypsum is heated to 393 K.

(*c*) Why are group of 2 elements harder than group 1 elements.

16. (*a*) Assign the position to the element having outer electronic configuration $(n-1)d^2ns^2$ for n=4.

(b) Explain why cations are smaller and anions are bigger in radii than their parents?

17. (a) Why H_2O is a liquid and H_2S is a gas?.

(b) On the basis of MOT explain why Ne_2 molecule does not exist?

18. A sample of a gas contains

15 molecules with a speed of 3 ms^{-1},

25 molecules with a speed of 5 ms^{-1} and

30 molecules with a speed of 8 ms^{-1}

Calculate root mean square speed of these molecules.

19. Give reason Why?

(a) Be and Mg do not give colour to flame whereas other alkaline earth metal do so?

(b) A solution of Na_2CO_3 is alkaline.

(c) Solution of alkali metal in ammonia is soloured?

20. In Dumas method for estomation of nitrogen .03g of an organic compound gave 50 ml of nitrogen collected at 300K temperature and 715 mm pressure. Calculate the percentage composition of nitrogen in the compound? (Aqueous tension at 300K = 15mm)

21. (a) What is biochemical oxygen demand?

(b) Write down the reactions involved in ozone layer depletion?

22. (a) Name the series of hydrogen spectrum which lies in visible region?

(b) Calculate the kinetic energy of an electron emitted when radiation of frequency 1.1×10^{15} s^{-1} hits the metal. Threshold frequency of metal is 7.0×10^{14} s^{-1}?

23. Rashmi observed that whenever her mother washes clothes, the soap does not produce leather. Instead the water became cloudy. Her mother even changed the soap brand but was not able to get good lather. As a student of chemistry.

(*i*) How would you analyse the problem of Rashmi's mother and help her?

(*ii*) What are the values associated with your suggestion?

24. (*a*) Balance and complete the following reactions–

(*i*) $Al + NaOH + H_2O \rightarrow$ _____

(*ii*) $H_3BO_3 \xrightarrow{\Delta}$ _____

(*b*) What is Inorganic Benzene?

(*c*) Name the compound used as catalyst in petrochemical industry for cracking of hydrocarbons?

(*d*) Conc.HNO_3 can be transported in aluminium container why?

OR

A certain salt X gives the following results–

(*i*) Its aqueous solution is alkaline to litmus.

(*ii*) It swells up to glassy material Y on strong heating.

(*iii*) When conc.H_2SO_4 is added to a hot solution of X, white crystal of an acid Z separate out.

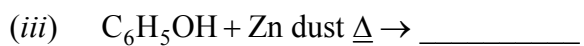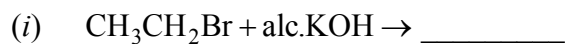Identify X, Y, Z and write equation for all the above reactions.

25. (*a*) Why does the dissociation of PCl_5 decreases in presence of Cl_2?

(*b*) State Le Chatelier's principle?

(*c*) 3.00 moles of PCl_5 kept in one litre closed reaction vessel was allowed to attain equilibrium at 380 K. Calculate composition of the mixture at eq.(Equilibrium constant = 1.80)

OR

(*a*) What is Buffer Solution?

(*b*) Write difference between Ionic Product and Solubility product?

(*c*) Calculate pH of a solution formed by dissolving 0.3g of NaOH in water to make 200 ml of solution?

26. (*a*) Which one is having high dipole moment and why.

cis-but-2-ene and trans-but-2-ene.

(*b*) Complete the following reactions:

(*i*) $CH_3CH_2Br + alc.KOH \rightarrow$ _____

(*ii*) $CH_3 - CH = CH_2 + HBr \xrightarrow{\text{PEROXIDE}}$ _____

(*iii*) $C_6H_5OH + Zn\ dust\ \underline{\Delta} \rightarrow$ _____

OR

(*b*) Draw Sawhorse projections of ethane?

(*c*) An alkene 'A' contains three C–C, eight C–H σ bonds and one C–C π bond. 'A' an ozonolysis gives two moles of an aldehyde of molar mass 44u. Write IUPAC name of 'A'.

SAMPLE PAPER - II (UNSOLVED)

(ACCORDING TO CBSE CURRICULUM : 2013-14)

CHEMISTRY - XI

Time : 3 hours   Class : XI   Maximum Marks : 70

General Instructions :

1. *All questions are compulsory.*

2. *Question no.1 to 5 are very short answer questions and carry 1 mark each.*

3. *Question no. 6 to 10 are short answer questions and carry 2 marks each.*

4. *Question no. 11 to 22 are also short answer questions and carry 3 marks each.*

5. *Question no. 23 is value based question carrying 4 marks.*

6. *Question no. 24 to 26 are long answer questions and carry 5 marks each.*

7. *Use log tables it necessary, use of calculators is not allowed.*
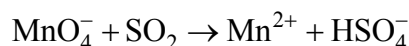
QUESTIONS

1. Which series of lines of the hydrogen spectrum lie in the ultra violet region.

2. What would be the IUPAC name and symbol for the element with atomic number 114?

3. Which of the following has maximum bond angle?

   H_2O, CO_2, NH_3, CH_4

4. Write van der Waals equation for one mole of a gas.
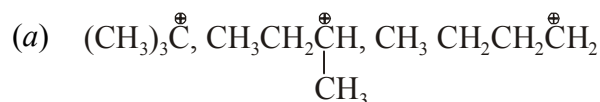
5. Predict the sign of $\Delta S°$ for the following reaction:

$$2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(g) + 2SO_2(g)$$
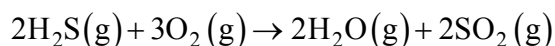
6. Identify 'A' and 'B' in the following:

$$\boxed{A} \xleftarrow{\text{Na}} CH \equiv CH \xleftarrow[873]{\text{Red hot iron tube}} \boxed{B}$$

7. The mass of an electron is 9.1×10^{-31} kg. If its K.E. (kinetic energy) is 3×10^{-25} J. Calculate its velocity.

8. Give two differences between σ and π bonds.

9. Compare the relative stability of the following species on the basis of molecular orbital theory and indicate their magnetic properties:

$$N_2^+ \text{ and } N_2^-$$

10. Balance the following equation in acidic medium by ion electron method:

$$MnO_4^- + SO_2 \rightarrow Mn^{2+} + HSO_4^-$$

11. Arrange the following:

    (a) $(CH_3)_3\overset{\oplus}{C}$, $CH_3CH_2\overset{\oplus}{C}H$, CH_3 $CH_2CH_2\overset{\oplus}{C}H_2$
    $\overset{|}{C}H_3$

    [Increasing order of stability]

    (b) I, –Br, –Cl, –F [Decreasing order of –1 effect]

    (c) Write structural formula of 3, 4, 4, 5, 5-tetramethylheptane

12. Compare the alkali metals and alkaline earth metals with respect to:

    (a) Ionization enthalpy

    (b) Basicity of oxides.

    (c) Electronic configuration

13. Give a brief account on the following:

    (a) KO_2 is paramagnetic in nature.

    (b) Sodium is stored under kerosene oil.

(c) Name the alkali metal which shows diagonal relationship with magnesium.

14. In carius method of estimation of halogen, 0.15 g of an organic compound gave 0.12 g of AgBr. Find out the percentage of bromine in the compound.

[Molar mass of AgBr = 188 mol^{-1}, At mass of Br = 80 g mol^{-1}]

15. Dinitrogen and dihydrogen react with each other produce ammonia according to the chemical equation:

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

(a) Calculate the mass of ammonia produced if 2×10^3 g dinitrogen reacts with 1×10^3 g dihydrogen.

(b) Will any of the two reactant remain unreacted?

(c) If yes, which one and what would be its mass?

16. (a) What causes the temporary and permanent hardness of water?

(b) Compare the structures of H_2O and H_2O_2.

17. (a) Write the conjugate acids for the Bronsted base NH_2^- and HCOO-?

(b) The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3} M. What is its pH? [log 3.8 = 0.5798]

(c) Equilibrium constant for a reaction is 4.0, what will be the equilibrium constant for the reverse reaction.

18. Explain the following:

(a) Boyle's law

(b) Avogadro's law

(c) Critical Temperature

OR

(a) In terms of Charles' law explain why –273°C is the lowest temperature.

(b) Calculate the total pressure in a mixture of 8 g of oxygen and

4 g of hydrogen. Confined in a vessel of 1 dm^3 at 27°C. R = 0.083 bar dm^3 K^{-1} mol^{-1}.

19. (*a*) How many electrons in an atom can have n + l = 6?

(*b*) Write the electronic configuration of CR$^+$ [Atomic number of Cr = 24]

(*c*) Define Hund's rule of Maximum multiplicity.

20. Give a brief account for the following:

(*a*) Anions are bigger in size than their parent atom.

(*b*) Oxygen has lesser first ionization enthalpy than nitrogen.

(*c*) Fluorine has less negative electron gain enthalpy than chlorine.

21. (*a*) The reaction quotient of a reversible reaction is Q$_c$ and the equilibrium constant is K$_c$. What do you conclude for the reaction if Q$_c$< K$_c$?

(*b*) State Le Chatelier's principle.

(*c*) In qualitative analysis, NH$_4$Cl is added before adding NH$_4$OH solution for testing of III group radicals [Fe^{3+}, Cr^{3+} and Al^{3+}]. Explain by using concept of common ion effect.

22. (*a*) What type of isomerism is shown by pentane and 2-Methyl (isopentane).

(*b*) Why is an organic compound fused with sodium for testing halogen, nitrogen, sulphur and phosphorus?

(*c*) Write the I.U.P.A.C name of $CH_2 = CHCH_2CH(OH)CH_3$

23. Cloroflurocarbons commonly known as Freons have the properties such as low boiling points, odourless, non-toxic, non-flammable, least chemical reactivity an thermally stable. These have been extensively used in air-conditions, refrigerators, spraycans, etc. In the group discussion in a school, Rakesh strongly supported the use of freons for making our life comfortable. However Rajnish strongly opposed the excessive use of these freons for their ill effects on the environment on the basis of the passage, answer the following questions:

(*i*) In this situation, whom will you support, Rakesh or Rajnish?

(*ii*) What are the valves associated with your decision or support.

24. (*a*) How can you convert the following:

(*i*) Methane into Ethane

(*ii*) Benzene into acctopherone

(*b*) Give a chemical test to distinguish between ethene and Ethyne.?

(*c*) Give a brief account for the following statements:

(*i*) *n*-pentane has greater boiling point that isopentane.

(*ii*) CH_4 cannot be synthesized by Wurtz reaction.

OR

(*a*) An alkyl halide (X) of formula $C_6H_{13}Cl$ on treatment with alcoholic KOH or potassium tert-butoxide give two isomeric alkenes Y and Z (C_6H_{12}). Both alkenes on hydrogenation give 2, 3-dimethylbutane. Predict the structure of X, Y and Z.
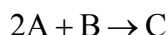
(*b*) Give the main products of the reactions:

(*i*) $\xrightarrow[\text{CH}_3\text{Cl}]{\text{Anhy, AlCl}_3}$

(*ii*) $CH-C=CH_2 + H_2O \xrightarrow{H^+}$
$\qquad \overset{|}{CH_3}$
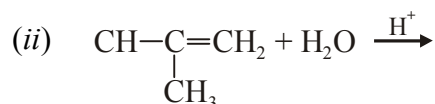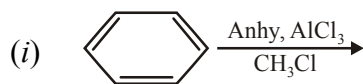
25. (*a*) State Hess's law.

(*b*) When $\Delta H > O$ and $\Delta S < O$, a reaction is never spontaneous. Explain.

(*c*) For the reaction:

$2A(g) + B(g) \rightarrow 2D(g)$

$\Delta U° = -10.kJ$ and $\Delta S° = -44.1\,JK^{-1}\,mol^{-1}$.

Calculate $\Delta G°$ for the reaction and predict whether the reaction may occur spontaneously.

OR

(*a*) For the reaction at 298 K

$$2A + B \rightarrow C$$

$\Delta H = 400$ kJ mol^{-1} and $\Delta S = 0.2$ kJ mol^{-1} K^{-1}

At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range.

(*b*) State first law of thermodynamics.

(*c*) Give one point to differentiate the following thermodynamic terms:

    (*i*) Extensive properties and intensive properties.

    (*ii*) Isothermal process and adiabatic process.

26. (*a*) Account for the following:

    (*i*) Boron trihalides (BX_3) act as Lewis acids.

    (*ii*) $PbCl_4$ is a powerful oxidising agent.

    (*iii*) Graphite acts as a good lubricant.

(*b*) Complete the following reactions:

    (*i*) $Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow$

    (*ii*) $B_2H_6 + 6NH_3 \xrightarrow{\Delta}$
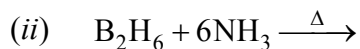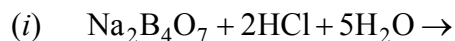
OR

(*a*) Draw the shape of B_2H_6 molecule.

(*b*) Give suitable reasons for the following:

    (*i*) $[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ not

(*ii*) diamond is covalent, yet it has high melting point.

(*c*) Complete the reactions: (5)

(*i*) $BF_3 + LiH \rightarrow$

(*ii*) $H_3BO_3 \xrightarrow{\Delta}$