

CHEMISTRY WRITING TEAM

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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 Chemistry : Some Basic Principles and Techniques	7
Unit XIII	Hydrocarbons	8
Unit XIV	Environmental Chemistry	3
Total		70

UNIT-1

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.

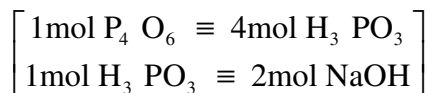
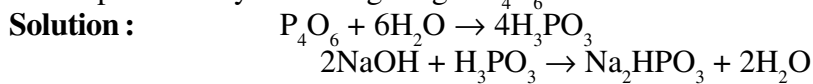
Gram molecular mass or the molar mass of molecular substances is the mass of 1 mol of molecules or molecular mass expressed in grams. For example, molecular mass of CO₂ is 44 u, therefore, molar mass of CO₂ is 44 grams/mol.

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.

Example : Calculate the volume of 0.1 M NaOH solution required to neutralise the solution produced by dissolving 1.1 g of P₄O₆ in water.



$$\text{mol of P}_4\text{O}_6 = 1.1\text{g P}_4\text{O}_6 \times \frac{1\text{ mol P}_4\text{O}_6}{220\text{g P}_4\text{O}_6} = 0.5 \times 10^{-2}\text{ mol P}_4\text{O}_6$$

$$\begin{aligned} \text{mol of NaOH} &= 0.5 \times 10^{-2}\text{ mol P}_4\text{O}_6 \times \frac{4\text{ mol H}_3\text{PO}_3}{1\text{ mol P}_4\text{O}_6} \times \frac{2\text{ mol NaOH}}{1\text{ mol H}_3\text{PO}_3} \\ &= 4 \times 10^{-2}\text{ mol NaOH} \end{aligned}$$

$$\begin{aligned} \therefore \text{Volume of NaOH solution in litres} &= 4 \times 10^{-2} \text{ mol NaOH} \times \frac{1 \text{ L NaOH solution}}{0.1 \text{ mol NaOH}} \\ &= 4 \times 10^{-1} \text{ L} = 0.4 \text{ L} \end{aligned}$$

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

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

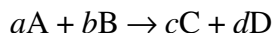
For binary solutions :

$$\text{Mole fraction (X}_B\text{) of solute} = \frac{n_B}{n_A + n_B}$$

$$X_A = 1 - X_B$$

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

For a general chemical equation :



Molarity relationship is :

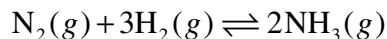
$$\text{mol of B} = \text{mol of A} \times \frac{b \text{ mol of B}}{a \text{ mol of A}}$$

Dilution Formula :

$$M_1 V_1 = M_2 V_2$$

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 CO₂.
6. Write the SI unit of temperature.
7. Define law of multiple proportions.
8. N₂ and H₂ combine according to the following equation :



If 100 mL of N₂ gas combines with 300 mL of H₂ gas, calculate the volume of NH₃ produced at same temperature and pressure.

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) $\frac{0.025 \times 298.15 \times 0.1155}{0.5785}$

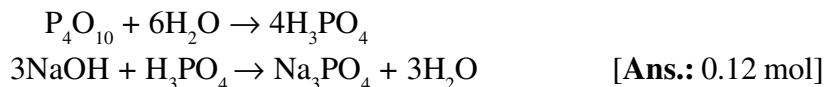
8. Which of the following samples has the largest number of atoms :
 (a) 1.0 g H_2 (g) (b) 1.0 Na (s)
 (c) 1.0 g CH_3OH (l) (d) 1.0 g Br_2 (l)
9. Determine the molecular formula of an oxide of iron in which the mass percent of iron and oxygen are 69.9 and 30.1 respectively. Molar mass of this oxide is 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 $g = 9.8 \text{ ms}^{-2}$, $1 \text{ Pa} = 1 \text{ Nm}^{-2}$) [Ans. : $1.01332 \times 10^5 \text{ Pa}$]
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.
16. Use the following data to calculate the molar mass of naturally occurring argon :

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

[Ans.: 39.948 g/mol]

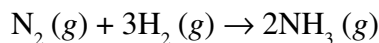
17. If the speed of light is $3.0 \times 10^8 \text{ ms}^{-1}$, calculate the distance covered by light in 2.00 ns. [Ans.: 0.600 m]
18. State the law of definite proportions. Explain it with the help of an example.
19. Burning a sample of a hydrocarbon gas gives 3.38 g CO_2 and 0.690 g H_2O . A volume of 10L (measured at STP) of this hydrocarbon weighs 11.6 g. Calculate the molecular formula of this hydrocarbon. [Ans.: C_2H_2]

20. Calculate the number of mol of 0.1 M NaOH solution produced by dissolving 2.84 g of P_4O_{10} in water. The reactions that occur are :



3 - MARK QUESTIONS

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 :

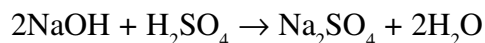


- (a) Calculate the mass of ammonia gas formed if 2.0 kg of nitrogen gas reacts with 1.0 kg of hydrogen gas.
- (b) Which of the two reactants is the limiting reagent and why ?
- (c) Which of the two reactants will remain unreacted and what will be the amount left unreacted ? [Ans.: m (NH_3) = 2.571 kg,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

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.

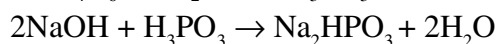
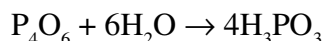
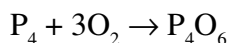
NaOH reacts with H_2SO_4 according to the following equation :



(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 $^{11}_5\text{B}$ and $^{10}_5\text{B}$ 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 M solution ?
3. (a) Define molality of a solution. How is it different from molarity ?
- (b) 1.24 g white phosphorus was allowed to react with oxygen to produce P_4O_6 , an acidic oxide. The solution of P_4O_6 in water is acidic and is neutralised with NaOH. How many moles of NaOH are required to neutralise H_3PO_4 generated in above case.

[Hint : The chemical reactions mentioned in above case are :



Moles of NaOH (n_{NaOH}) can be calculated as :

$$1 \text{ mol P}_4 \equiv 1 \text{ mol P}_4\text{O}_6 \equiv 4 \text{ mol H}_3\text{PO}_3$$

$$1 \text{ mol H}_3\text{PO}_3 \equiv 2 \text{ mol NaOH}$$

$$\begin{aligned} n_{\text{NaOH}} &= 1.24 \text{ g P}_4 \times \frac{1 \text{ mol P}_4}{124 \text{ g P}_4} \times \frac{1 \text{ mol P}_4\text{O}_6}{1 \text{ mol P}_4} \times \frac{4 \text{ mol H}_3\text{PO}_3}{1 \text{ mol P}_4\text{O}_6} \times \frac{2 \text{ mol NaOH}}{1 \text{ mol H}_3\text{PO}_3} \\ &= 0.01 \times 4 \times 2 = 0.08 \end{aligned}$$



UNIT-2

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

$$c = v\lambda \quad \text{where } c = \text{velocity in light} = 3.0 \times 10^8 \text{ m/s}$$
$$v = \text{frequency of } s^{-1} \text{ or Hz}$$
$$\lambda = \text{wavelength in metres}$$

- Wave number ($\bar{\nu}$) is the reciprocal of wavelength $\left(\bar{\nu} = \frac{1}{\lambda}\right)$.
- 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 $E = h\nu$, where h = Planck's constant, ν = 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 :

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

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

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

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

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

Brackett series : $n_1 = 4$ and $n_2 = 5, 6, 7, \dots$

Pfund series : $n_1 = 5$ and $n_2 = 6, 7, 8, \dots$

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

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

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

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

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

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 n^{th} orbit is given by $r_n = \frac{(0.529 \text{ \AA}) n^2}{z}$.
- **Photoelectric effect** : When radiation with certain minimum frequency (ν_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 $\nu > \nu_0$, the difference of energy ($h\nu - h\nu_0$) is converted into kinetic energy of the photoelectrons *i.e.*, $\frac{1}{2}mv^2 = h\nu - h\nu_0$. The minimum energy $h\nu_0$ required for emission of photoelectrons is called **threshold energy** or **work function**. No photoelectric effect is shown if incident frequency is less than ν_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 v is called **de Broglie equation**. It is given by

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

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 $\frac{h}{4\pi}$."

ways equal to or greater than $\frac{h}{4\pi}$."

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

where

Δx = uncertainty in position,

Δp = 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)**

$$n = 1, 2, 3, 4, \dots, \infty$$

It identifies shell, determines sizes and energy of orbitals and number of orbitals in the n^{th} 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 $+1/2$ or $-1/2$ 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). 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 :

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s$$

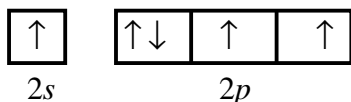
Exception of Aufbau principle : Extra stability is associated with the exactly half-filled and fully-filled orbitals. Thus the $p^3, p^6, d^5, d^{10}, f^7, f^{14}$ etc. have extra stability, *i.e.*, lower energy and therefore, more stable.

1 - MARK QUESTIONS

1. Indicate the number of electrons, protons and neutrons in the element ${}_{92}^{238}\text{U}$.
[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. Define threshold frequency (ν_0).
6. Write the dimensions of Planck's constant. Mention some other physical quantity, which has the same dimension.
7. Name the element which was discovered in the sun by spectroscopic method.
[Ans. Helium (He)]

8. Arrange the following type of radiations in increasing order of wavelength :
- (a) radiation from microwave oven (b) amber light from traffic signal
 (c) radiation from FM radio (d) cosmic rays from outer space
 (e) X-rays
- [Ans. cosmic rays < X-rays < amber light < microwaves < FM]
9. 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.]
10. Out of electron and proton, which one will have a higher velocity to produce matter waves of the same wavelength ?
- [Hint : $\lambda = \frac{h}{mv}$, For same wavelength, m_e is very small as compared to m_p .
 Therefore v_e will be higher as compared to v_p .]
11. An anion A^{3-} has 18 electrons. Write the atomic number of A. [Ans. 15]
12. What is the value of orbital angular momentum of 6s orbital ?
13. What physical meaning is attributed to the square of the absolute value of wave function $|\Psi^2|$?
14. Name two physical quantities which can be estimated by principal quantum number (n).
15. Which shell would be the first to have g -subshell ?
16. How many electrons in an atom can have $n + l = 6$? [Ans. 18]
17. Name three quantum numbers which arise as a result of the solution of Schrodinger wave equation.
18. What is the difference between the notations l and L ?
19. Write electronic configuration of the Cr^{3+} ion. [Atomic number of Cr = 24]
20. The ion of an element has configuration $[Ar]3d^4$ in +3 oxidation state. Write the electronic configuration of its atom.
21. State Pauli's exclusion principle.
22. How many nodes are there in 3s orbital ? [Ans. 2 nodes]
23. Why 1p, 2d and 3f subshells are not possible ?
24. How many unpaired electrons are present in Fe^{3+} ion ?
25. State Hund's rule of maximum multiplicity.
26. 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]

27. Which quantum number determines the orientation of atomic orbital ?
 28. Which orbital is non-directional ?
 29. Write the correct set of four quantum numbers for the valence electron (outermost electron) of potassium ($Z = 19$).
 30. Which principle is not obeyed in writing of electronic configuration :



2- MARK QUESTIONS

1. Give examples of each of the following :
- | | |
|--------------------------------------|--|
| (a) Isotope of $^{35}_{17}\text{Cl}$ | (b) Isobar of $^{40}_{18}\text{Ar}$ |
| (c) Isotone of $^{15}_7\text{N}$ | (d) Isoelectronic species of S^{2-} |
- [Ans. (a) $^{37}_{17}\text{Cl}$ (b) $^{40}_{20}\text{Ca}$ (c) $^{16}_8\text{O}$ (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% $^{22}_{10}\text{Ne}$]
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 Rutherford 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. $3.5 \times 10^{18} \text{ s}^{-1}$]
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 $\text{He}^+(g) \rightarrow \text{He}^{2+}(g) + e^-$

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

[Ans. $8.72 \times 10^{-18} \text{ J}$]

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}]

3 - MARK QUESTIONS

1. Differentiate between :

- Photon and quantum
- Orbit and orbital
- 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 a particle accelerator through a potential difference of 1 keV . [$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$]

[Ans. $3.87 \times 10^{-7} \text{ m}$]

4. The kinetic energy of a subatomic particle is $5.86 \times 10^{-25} \text{ J}$. Calculate the frequency of the particle wave.

[Ans. $1.76 \times 10^9 \text{ s}^{-1}$]

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 $1.312 \times 10^6 \text{ J mol}^{-1}$.

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.

5 - MARK QUESTIONS

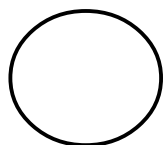
1. (a) Define photoelectric effect ? Mention its one practical application in daily life.
 (b) Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800 \AA . Calculate threshold frequency (ν_0) and work function (W_0) of the metal.

[Ans. $4.41 \times 10^{14} \text{ s}^{-1}$, $2.91 \times 10^{-19} \text{ J}$]
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 $5 \times 10^{-8} \text{ m}$. Calculate the wavelength associated with particle B, if its momentum is half of A.

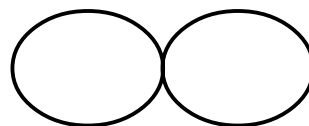
[Ans. $1 \times 10^{-7} \text{ m}$]
3. (a) What is the significance of the statement "Product of uncertainty in position and momentum is always constant." ?
 (b) Why is uncertainty principle not applicable to macroscopic and semimicro particles ?
 (c) An electron has a speed of 40 ms^{-1} accurate upto 99.99%. What is the uncertainty in locating its position ? ($m_e = 9.11 \times 10^{-31} \text{ kg}$)

[Ans. $1.45 \times 10^{-2} \text{ m}$]

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 :
- In potassium, the 19th electron enters in 4s subshell instead of 3d subshell.
 - Chromium has configuration $3d^5 4s^1$ and not $3d^4 4s^2$.
 - The three electrons present in 2p subshell of nitrogen (N) remain unpaired and have the parallel spins.



UNIT-3

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

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.

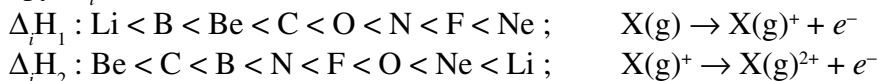
A cation is smaller but the anion is larger than the parent atom. In case of isoelectronic species, the cation with greater positive charge has smaller radius but anion with greater negative charge has the larger radius.

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

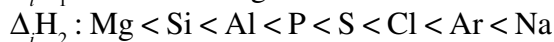
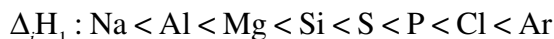
Second ionization enthalpy ($\Delta_i H_2$) is more than the first ionization enthalpy ($\Delta_i H_1$).

$$\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3 < \dots\dots\dots$$

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



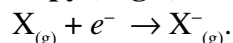
For the elements of third period, the correct increasing order of ionization enthalpy is :



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



Electron gain enthalpy ($\Delta_{eg}H$) is the enthalpy change for the reaction :



$\Delta_{eg}H$ for N atom is zero. All the elements except noble gases, have negative values of $\Delta_{eg}H$ whereas noble gases have positive values of $\Delta_{eg}H$.

***f*-block Elements (Inner-transition Series)**

Lanthanoids characterised by the filling of *4f* orbitals, are the elements following lanthanum from $_{58}\text{Ce}$ to $_{71}\text{Lu}$. Actinoids characterised by the filling of *5f* orbitals, are the elements following actinium from $_{70}\text{Th}$ to $_{103}\text{Lr}$. 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 $\Delta_{eg}H$: 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 $\Delta_{eg}H$ 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.

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 congeners. 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 *2s* and three *2p* orbitals) for bonding, whereas the second member of the group has nine valence orbitals (one *3s*, three *3p* and five *3d* orbitals). As a consequence of this, maximum covalency of first mem-

ber 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 $[\text{BF}_4]^-$ and Al, $[\text{AlF}_6]^{3-}$. In addition to this, the first member of each group of *p*-block elements displays greater ability to form *pπ-pπ* multiple bonds to itself (e.g. $\text{C} = \text{C}$, $\text{C} \equiv \text{C}$, $\text{N} = \text{N}$, $\text{N} \equiv \text{N}$, $\text{O} = \text{O}$) and to other second period elements (e.g., $\text{C} = \text{O}$, $\text{C} = \text{N}$, $\text{C} \equiv \text{N}$, $\text{N} = \text{O}$) 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 ?
7. How does ionization enthalpy vary in a period ?
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 :

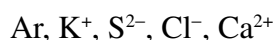
- (a) a non-metal.
- (b) an alkaline earth metal.

[Ans. II – alkaline earth metal, III – non-metal]

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 :



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 ?

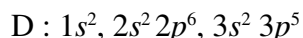
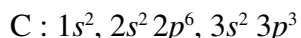
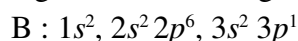
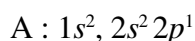
[Hint : Size of an anion is larger than the parent atom]

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 K₂O is a basic oxide.

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



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

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 3*d* series.
(b) To which block (*s*-, *p*-, *d*- or *f*-) does the element with atomic number 50 belong ?
5. Would you expect the first ionization enthalpies for two isotopes of the same element to be the same or different ? Justify your answer with an example.

6. 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.

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

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

7. An element belongs 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 ?
8. Write the atomic number and electronic configuration of the elements of fourth period which has maximum number of unpaired electrons ?
9. Why do the periodic properties such as ionization enthalpy, electron gain enthalpy and electronegativity show a decreasing trend down the group but an increasing trend along a period ? Explain your answer.
10. 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]
11. On the basis of quantum numbers, justify that fifth period of the periodic table should have eighteen elements.
12. Lanthanoids and actinoids are placed in separate rows at the bottom of the periodic table. Explain the reason for this arrangement.
13. The electronic configuration of three elements are given below :
- $$P = 1s^2, 2s^2, 2p_x^1, 2p_y^1$$
- $$Q = 1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$$
- $$R = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$$
- (a) Which element has the highest electron gain enthalpy ?
 (b) Which element has the lowest electron gain enthalpy ?
14. The element with atomic number 120 has not yet been discovered. In which group would you place this element ? Write its electronic configuration also.
15. 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.

16. Arrange the following species as stated, giving reasons :
- Increasing order of electronegativity (H, F, Cl)
 - Increasing order of ionic size : N^{3-} , Na^+ , F^- , O^{2-} , Mg^{2+}
17. Write the oxidation state and covalency of Al in $[\text{AlCl}(\text{H}_2\text{O})_5]^{2+}$.

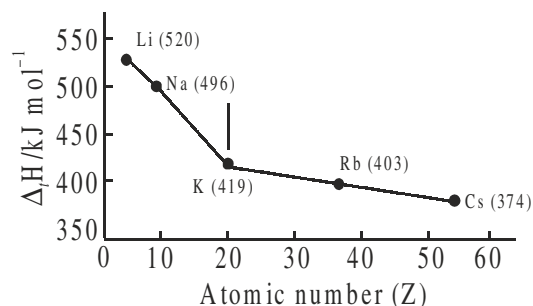
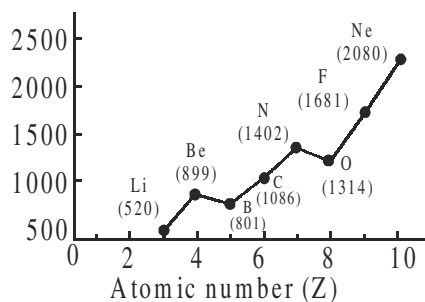
3 - MARK QUESTIONS

- Name the scientist who discovered that atomic number is the more fundamental periodic property of an element than its atomic mass.
 - Mention three main features of the modern periodic table.
- 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

- Name a transition metal.
 - Name an element whose oxide has very low melting point.
 - How many atoms of element 35 can combine with an element having atomic number 20 ? Write the formula of the compound.
 - 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 :
- highly electropositive
 - highly electronegative
 - a noble gas
- Give reason (s) for your choice.
4. (a) Define electronegativity.
- (b) Explain the following :
- LiF is less ionic than CsF .
 - Li salts are predominantly covalent while Na salts are predominantly ionic.

5. Justify the following statements :
- There are only fourteen lanthanoids and only fourteen actinoids.
 - There are 2, 8 and 8 elements in I, II and III period of the periodic table respectively.
 - 3d, 4d and 5d series consists of ten elements each.
6. Two elements P and Q have atomic numbers 16 and 19 respectively.
- Write the group numbers to which the elements belong to.
 - Name the element which is a powerful reducing agent.
 - Write the formula of the compound formed between P and Q.
7. Account for the following :
- Transition metals are less electropositive than group 1 and 2 metals.
 - In group 13, Boron forms $[\text{BF}_4]^-$ whereas Aluminium forms $[\text{AlF}_6]^{3-}$.
 - The increasing order of reactivity among group 1 elements is $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ whereas that among group 17 elements is $\text{F} > \text{Cl} > \text{Br} > \text{I}$.
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 :



- First ionization enthalpy generally increases as we go across a period and decreases as we descend a group.
 - Ionization enthalpy of boron is slightly less than that of beryllium.
 - 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 :
- Predict the groups of A and C.
 - 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 ($\Delta_f H_1$) and the second ($\Delta_f H_2$) ionization enthalpies (in kJ/mol) and the ($\Delta_{eg} H$) electron gain enthalpy (in kJ/mol) of a few elements are given below :

Elements	$\Delta_f H_1$	$\Delta_f H_2$	$\Delta_{eg} H$
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 :

- the least reactive element.
- the most reactive metal.
- the most reactive non-metal.
- the least reactive non-metal.
- the metal which can form a stable binary halide of the formula MX_2 (X = halogen).
- 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 $\Delta_f H$ 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.

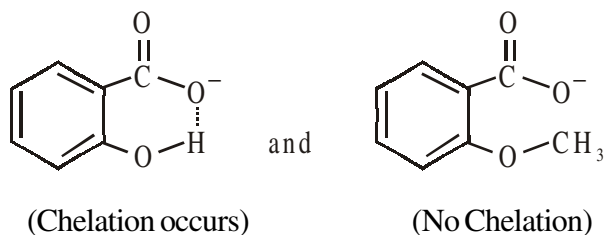
The strength of hydrogen bond depends on the electronegativity difference between H atom and the highly electronegative atoms like F, O and N having at least one lone pair of electron .

The strength of hydrogen bond decreases in the order :



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

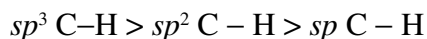
For example, 2-hydroxy benzoic acid is stronger than 2-methoxy benzoic acid because 2-hydroxybenzoate ion is stabilized by intramolecular hydrogen bonding (chelation).



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,



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 : 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 $\text{Ip-Ip} > \text{Ip-bp} > \text{bp-bp}$.

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	lp	Ip	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

Table 1
Arrangement of the electron pairs about a central 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	<i>sp</i>	BeF ₂
AB ₃	3	–	Trigonal planar	<i>sp</i> ²	BF ₃ , AlCl ₃
AB ₂ E	2	1	Bent	<i>sp</i> ³	SO ₂ , O ₃
AB ₄	4	–	Tetrahedral	<i>sp</i> ³	CH ₄ , NH ₄ ⁺
AB ₃ E	3	1	Pyramidal	<i>sp</i> ³	NH ₃ , PX ₃ (X = F, Cl, B, I)
AB ₂ E ₂	2	2	Bent (angular)	<i>sp</i> ³	H ₂ O, OF ₂ , NH ₂ ⁻
AB ₅	5	–	Trigonal bipyramidal	<i>sp</i> ³ <i>d</i>	PF ₅ , PCl ₅
AB ₄ E	4	1	See Saw/Irregular Tetrahedral	<i>sp</i> ³ <i>d</i>	SF ₄
AB ₃ E ₂	3	2	Bent T-shaped	<i>sp</i> ³ <i>d</i>	ClF ₃
AB ₂ E ₃	5	–	Linear	<i>sp</i> ³ <i>d</i>	XeF ₂ , ICl ₂ ⁻ , I ₃ ⁻
AB ₆	5	–	Octahedral	<i>sp</i> ³ <i>d</i> ²	SF ₆ , PF ₆
AB ₅ E	5	1	Square pyramidal	<i>sp</i> ³ <i>d</i> ²	BrF ₅ , XeOF ₄ , ClF ₅
AB ₄ E ₂	4	2	Square planar	<i>sp</i> ³ <i>d</i> ²	XeF ₄ , ICl ₄ ⁻
AB ₇	7	–	Pentagonal bipyramidal	<i>sp</i> ³ <i>d</i> 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	<i>sp</i>	[Ag(NH ₃) ₂] ⁺
Tetrahedral	<i>sp</i> ³	[Ni(CO) ₄], [NiCl ₄] ²⁻
Square planar	<i>dsp</i> ²	[Ni(CN) ₄] ²⁻ , [PtCl ₄] ²⁻
Trigonal bipyramidal	<i>dsp</i> ³	[Fe(CO) ₅]
Octahedral	<i>sp</i> ³ <i>d</i> ²	[CrF ₆] ³⁻ , [CoF ₆] ³⁻ , [FeF ₆] ³⁻
	<i>d</i> ² <i>sp</i> ³	[Fe(CN) ₆] ³⁻ , [Co(C ₂ O ₄) ₃] ³⁻

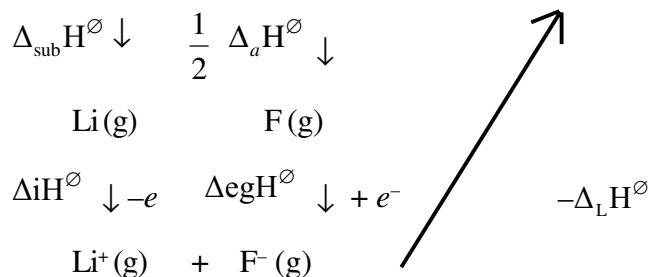
Molecular orbital theory was developed by F. Hund & R. S. Mulliken in 1932. This theory was able to explain the stability of the molecule, to calculate bond order, to find out the nature of the bond formed (*e.g.*, single, double or triple bonds), to calculate the bond length and predict the magnetic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

14. Arrange the repulsive interaction of electron pairs in the decreasing order as per the VSEPR theory :
lone pair-lone pair, lone pair-bond pair, bond pair-bond pair.
15. 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 $2s$
16. How is bond strength related to bond order ?
17. The H–P–H angle in PH_3 is smaller than the H–N–H angle in NH_3 . Why ?
18. What is percentage of s -character in sp and sp^3 hybrid orbitals ?
19. Which property is responsible for positive, negative or zero overlap of s - and p -atomic orbitals ?

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. Write two limitations of the octet rule.
5. Define electronegativity. How does it differ from electron gain enthalpy ?
6. Write the resonating structures of the following species :
(a) O_3 (b) CO_2
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. Using VSEPR theory, draw the shapes of SF_6 and BrF_5 molecules. Also write the state of hybridization of their central atoms.

4. Draw the Lewis structure of the species as mentioned below :
- in which the central atom has an incomplete octet.
 - in which the central atom has an expanded octet.
 - 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 :
- $CH_2=CH-C\equiv CH$
 - CH_3COOH
7. Calculate the lattice enthalpy of LiF given that the enthalpy of :
- Sublimation of lithium = 155.2 KJ/mol
 - Dissociation of $\frac{1}{2}$ mole of F_2 = 75.3 KJ
 - Ionization of Li = 520 KJ/mol
 - Electron gain enthalpy of 1 mole of F (g) = -333 KJ
 - $\Delta_f H^\circ$ overall = -594 KJ/mol



$$\Delta_f H^\circ = \Delta H^\circ + \frac{1}{2} \Delta_a H^\circ + \Delta_{eg} H^\circ - \Delta_L H^\circ$$

$$\Delta_L H^\circ = 1011.6 \text{ KJ / mol]}$$

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

[Hint : % 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%]

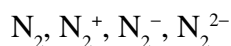
5 - MARKS QUESTIONS

1. (a) Write the electron dot structure of :



- (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 :



- (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 ?



UNIT-5

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-induced dipole forces

- **Boyle's Law :**

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

$$P_1 V_1 = P_2 V_2 \quad [\text{constant pressure}]$$

- **Charles's law :**

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

- **Gay Lussac's Law :**

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

- **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 of 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 :**

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

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

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

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

$$P_{total} = p_1 + p_2 + p_3 + \dots \quad [\text{constant T, V}]$$

$$P_{dry\ gas} = P_{total} - \text{Aqueous tension}$$

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

$$\text{as } Z = \frac{PV}{nRT}$$

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 than 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 ($T \geq 273\text{K}$), 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 $T \ll 273\text{ K}$, $Z < 1$.

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 :

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

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

a and b are constants called van der Waals constants.

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

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 meteorological 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. 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 $Z = \frac{pV}{nRT}$.

- (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.

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 . $R = 0.083\text{ bar dm}^3\text{ K}^{-1}\text{ mol}^{-1}$.

[Ans. 56.025 bar]



UNIT-6

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 boundary, real or imaginary separates 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.

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

$$= -2.303 nRT \log \frac{P_i}{P_f}$$

where P_i = Initial pressure; P_f = Final pressure

In free expansion of an ideal gas in vacuum, 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 loses nor gains 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 : $\Delta U = 0$

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

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

$$q = -W = -2.303 nRT \log \frac{V_f}{V_i}$$

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.

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 $T = \frac{\Delta H}{\Delta S}$.

Important formulas used in thermodynamics calculations

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

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

$$\Delta_r S^\ominus = \sum \nu_p \Delta S^\ominus (\text{products}) - \sum \nu_r \Delta S^\ominus (\text{reactants})$$

$$\Delta_r H^\ominus = \sum \nu_p \Delta_r H^\ominus (\text{products}) - \sum \nu_r \Delta_r H^\ominus (\text{reactants})$$

$$\Delta_r G^\ominus = \sum \nu_p \Delta_r G^\ominus (\text{products}) - \sum \nu_r \Delta_r G^\ominus (\text{reactants})$$

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 $-\Delta_r G^\ominus = -n E^\ominus$ cell F and in standard states $\Delta_r G^\ominus = -n E^\ominus$ 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.

$$\Delta_r H^\ominus = \Delta_r H_a^\ominus + \Delta_r H_b^\ominus + \Delta_r H_c^\ominus + \dots$$

(For definition of $\Delta_c H^\ominus$, $\Delta_a H^\ominus$, mean bond dissociation enthalpy (ΔH_{A-B}^\ominus), lattice enthalpy ($\Delta_L H^\ominus$), $\Delta_{fus} H^\ominus$, $\Delta_{vap} H^\ominus$, $\Delta_{sub} H^\ominus$, 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.*, $\Delta_r G = 0$.

$$0 = \Delta_r G^\ominus + 2.303 RT \log K$$

$$\text{and} \quad \Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$

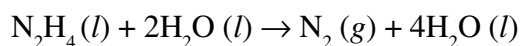
1- MARK QUESTIONS

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: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ $\Delta_r H^\theta = -92.4 \text{ kJ mol}^{-1}$
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 :
 $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g)$ $\Delta_f H^\theta = 90.0 \text{ kJmol}^{-1}$
[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

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) $\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g) \quad \Delta H_r = -184.62 \text{ kJ mol}^{-1}$
 - (b) $\text{CaO}(s) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s) \quad \Delta H_r = -178.3 \text{ kJ/mol}$
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 [$\text{N}_2\text{H}_4(l)$], hydrogen peroxide [$\text{H}_2\text{O}_2(l)$] and water [$\text{H}_2\text{O}(l)$] are -50.4 , -193.2 and -242.7 kJ/mol respectively. Calculate the standard enthalpy of formation for the following reaction :



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 ?

$$[\text{Ans. } q = + 701 \text{ J, } W = - 394 \text{ J, } \Delta U = 307 \text{ J}]$$

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.

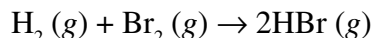
$$[\text{Ans. } 1.09 \text{ kJ}]$$

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 :



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 spontaneity ?

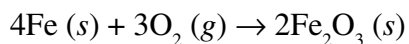
15. The equilibrium constant for a reaction is 10. What will be the value of ΔG^θ ?

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

16. Calculate the entropy change in surroundings when 1.0 mol of H₂O (l) is formed under standard conditions. Given : $\Delta_f H^\theta [\text{H}_2\text{O} (l)] = -286.0 \text{ KJ mol}^{-1}$, T = 298 K.

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

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



$$\Delta_r H^\theta = -1648 \times 10^3 \text{ J mol}^{-1} \quad \Delta_r S^\theta = -549.4 \text{ JK}^{-1} \text{ mol}^{-1}$$

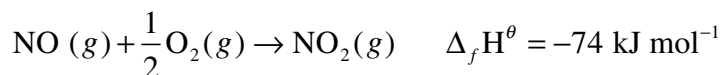
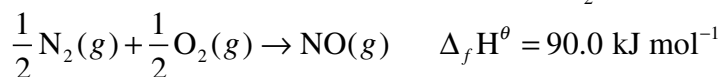
[Ans. $\Delta_r S_{total} = 4980.6 \text{ JK}^{-1} \text{ mol}^{-1}$. Hence the reaction is spontaneous]

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 NO₂ from the following data :



[Hint : Heat of formation of NO (g) is 90.0 kJ mol⁻¹ and the heat of formation of NO₂ (g) is [90.0 + (-74.0) = +16.0 kJ mol⁻¹]. Since enthalpy of formation of NO₂ is less positive than that of NO, therefore NO₂ is more stable than NO.]

3 - MARK QUESTIONS

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 MgBr₂, given that :

Enthalpy of formation of MgBr₂ = 524 kJ mol⁻¹

Sublimation enthalpy of Mg = 148 kJ mol⁻¹

Ionization enthalpy of Mg = 2187 kJ mol⁻¹

Vapourisation enthalpy of Br₂ (l) = 31 kJ mol⁻¹

Dissociation enthalpy of Br₂ (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.

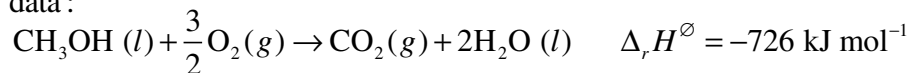
$$[\text{Ans. } \Delta U = 37.904 \text{ kJ/mol}]$$

- (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 ?

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

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 CH₃OH (l) from the following data :



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

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

$$\Delta_{\text{fus}} H = 6.03 \text{ kJ mol}^{-1} \text{ at } 0^\circ \text{ C}$$

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 risen from 298 K to 299 K. The heat capacity of bomb calorimeter is 20.7 kJ/K.

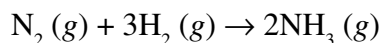
- (a) What is the amount of heat released ?
 (b) What are the values of ΔU and ΔH for the combustion of carbon ?

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

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 $\text{NaCl} (s)$.
12. State Hess's law of constant heat summation. What are its applications ?
13. (a) Define standard enthalpy change.
 (b) Why diamond does not have $\Delta_f H^\ominus = 0$ although it is an element ?

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 $\text{CH}_4 (g)$ at 298°K . You are given following data :
- (i) $\text{C} (\text{graphite}) + \text{O}_2 (g) \rightarrow \text{CO}_2 (g) \quad \Delta H_r^\ominus = -393.51 \text{ kJ mol}^{-1}$
 (ii) $\text{H}_2 (g) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{H}_2\text{O} (l) \quad \Delta H_r^\ominus = -285.8 \text{ kJ mol}^{-1}$
 (iii) $\text{CO}_2 (g) + 2\text{H}_2\text{O} (l) \rightarrow \text{CH}_4 (g) + 2\text{O}_2 \quad \Delta H_r^\ominus = +890.3 \text{ kJ mol}^{-1}$
- [Ans. -891 kJ/mol]
2. (a) Use the following data to determine ΔG^\ominus value for the following reaction :



Given data : $\Delta H_f^\ominus [\text{NH}_3 (g)] = -46.2 \text{ kJ mol}^{-1}$

$$S^\ominus [\text{N}_2 (g)] = 191.5 \text{ JK}^{-1} \text{ mol}^{-1}$$

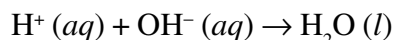
$$S^\ominus [\text{H}_2 (g)] = 130.6 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$S^\ominus [\text{NH}_3 (g)] = 192.5 \text{ JK}^{-1} \text{ mol}^{-1}$$

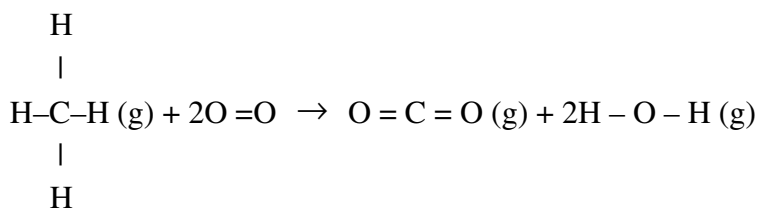
$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

- (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 $\text{H}_2\text{O} (l)$ 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 $\Delta_r H^\ominus$ for the following reaction ?



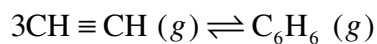
- (c) Calculate the enthalpy of formation of acetic acid (CH_3COOH) if its enthalpy of combustion is $-867.0 \text{ kJ mol}^{-1}$. The enthalpy of formation of $\text{CO}_2 (g)$ and $\text{H}_2\text{O} (l)$ are $-393.5 \text{ kJ mol}^{-1}$ and $-285.9 \text{ kJ mol}^{-1}$ respectively.
5. (a) State first 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 :



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) $2\text{Cl} (g) \rightarrow \text{Cl}_2 (g)$
 (b) $2\text{A} (g) + \text{B} (g) \rightarrow 2\text{C} (g)$
 (c) $2\text{CaCO}_3 (s) \rightarrow 2\text{CaO} (s) + 2\text{CO}_2 (g)$
 (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 $\Delta G = +ve$.
- (c) Using the data given below, calculate the value of $\Delta_r G^\circ$ and K_p for the following reaction at 298 K :



Assuming ideal gas behaviour, $\Delta_f G^\circ [\text{CH}\equiv\text{CH} (g)] = 2.09 \times 10^5 \text{ J mol}^{-1}$, $\Delta_f G^\circ [\text{C}_6\text{H}_6 (g)] = 1.24 \times 10^5 \text{ J mol}^{-1}$, $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$.



UNIT-7

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. $\Delta_r G^\ominus$ can never be zero because it is calculated from the $\Delta_r G^\ominus$ of the reactants and products. The $\Delta_r G^\ominus$ is related to equilibrium constant K_c or K_p as follows :

$$0 = \Delta_r G^\ominus - 2.303 RT \log K$$

$$\text{and } \Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus = -2.303 RT \log K$$

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.)

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

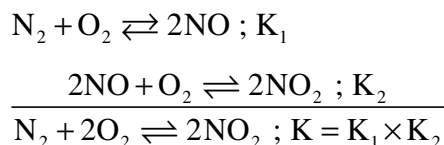
$$\Delta ng = [\text{sum of stoichiometric coefficients of gaseous products} \\ - \text{sum of stoichiometric coefficients of gaseous reactants}]$$

Predicting the direction of reaction : 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
$cC + dD \rightleftharpoons aA + bB$	$K_1 = \frac{1}{K}$
$naA + nbB \rightleftharpoons ncC + ndD$	$K_2 = K^n$
$\frac{a}{n}A + \frac{b}{n}B \rightleftharpoons \frac{c}{m}C + \frac{d}{n}D$	$K_3 = K^{1/n}$

When individual balanced equations are combined, multiply their equilibrium constants to obtain the equilibrium constant for the net reaction. For example,



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^+}) = $[\text{H}^+]/\text{mol L}^{-1}$

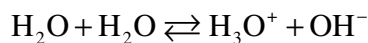
$$\text{pH} = -\log a_{\text{H}^+} = -\log \{[\text{H}^+]/\text{mol L}^{-1}\}$$

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

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

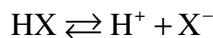
$$\therefore [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 298 \text{ K}$$

Ionisation constant of water and its ionic product



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

Ionisation constants of Acids and Bases (Acid-Base Equilibrium)



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

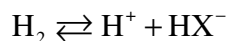
Similarly for base $\text{MOH} \rightleftharpoons \text{M}^+ + \text{OH}^-$

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

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 dibasic acid (H_2X) :



$$K_{a_1} = \frac{[\text{H}^+][\text{HX}^-]}{[\text{H}_2\text{X}]}$$



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

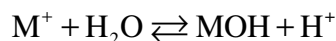
Higher order ionisation constants are smaller than lower order ionisation constants. Poly protic acid solution contain a mixture of acids like H_2X , HX^- and X^{2-} in case, of diprotic acids like H_2S , H_2CO_3 and oxalic acid.

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.

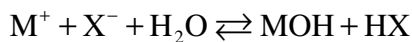
- Salts of strong acids and strong bases (e.g., NaCl) do not hydrolyse. The solution pH = 7.
- Salts of weak acids and strong bases (e.g., CH_3COONa) hydrolyse, pH > 7. (The anion acts as a base).
- Salt of strong acids and weak bases (e.g., NH_4Cl) hydrolyse, pH < 7. (The cation acts as an acid).
- Salt of weak acids and weak base (e.g., $\text{CH}_3\text{COONH}_4$) 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.
- The pH of solution of salts of weak acids and strong bases, *i.e.*, given by $\text{X}^- + \text{H}_2\text{O} \rightleftharpoons \underset{\text{(Weak acid)}}{\text{HX}} + \underset{\text{(Strong base)}}{\text{OH}^-}$

$$\text{pH} = 7 + \frac{1}{2}(\text{p}K_a + \log c)$$
- The pH of solution of salts of strong acid and weak base at 298 K is given by (MOH is weak base and H^+ , strong acid) :



$$\text{pH} = 7 - \frac{1}{2}(\text{p}K_b + \log c)$$

- The pH of solution of salts of weak acid and weak base at 298 K is given by



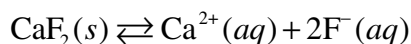
$$pH = 7 + \frac{1}{2}(pK_a - pK_b)$$

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.

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

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

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.



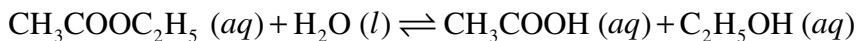
$$K_{sp} = [Ca^{2+}][F^-]^2$$

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 $K_{sp} = Q_{sp}$.

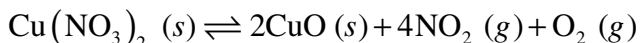
1- MARK QUESTIONS

- Define physical equilibrium. Give an example also.
- Justify the statement : 'Both physical and chemical equilibria are dynamic in nature.'
- At what temperature the solid and liquid phase of the same substance are in equilibrium with each other ?
- State the law of equilibrium.
- Name the indicator used for titration of strong acid versus strong base.
- Mention the effect of temperature on solubility of a gas in liquid.

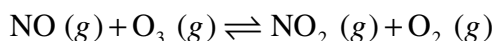
7. State Henry's law.
 8. Write the expression of K_c for the following reaction :



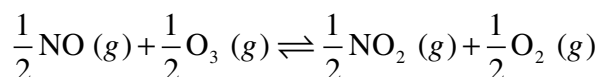
9. Write the expression of K_p for the following reaction :



10. For the following equilibrium $K_c = 6.3 \times 10$ at 1000 K :



Find the value of K_c for the following :



11. Equilibrium constant (K_c) for the reaction $\text{N}_2 (g) + 3\text{H}_2 (g) \rightleftharpoons 3\text{NH}_3 (g)$ 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. $\text{N}_2 (g) + 3\text{H}_2 (g) \rightleftharpoons 3\text{NH}_3 (g) + \text{Heat}$
 What is the effect of increasing temperature on the value of K .
 14. $\text{H}_2 (g) + \text{I}_2 (g) \rightleftharpoons 2\text{HI} (g)$
 Write the relationship between K_p and K_c .
 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.

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. $K_b (F^-) = 1.5 \times 10^{-11}$
32. Pure NaCl precipitates out when HCl gas is passed in brine solution. Name the phenomenon due to which it occurs.

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 solution of NH_4Cl in water shows pH less than 7.
 - 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 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.
13. (a) Write the conjugate acid and conjugate base of H_2O . [Ans. pH = 7.005]
 (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 :
- $$3\text{O}_2(g) \rightleftharpoons 2\text{O}_3(g)$$
- 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 ?

3 - MARK QUESTIONS

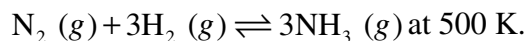
1. (a) Which of the following will act as Lewis acid :
 H_2O , BF_3 and H^+
 (b) Equal volumes of 0.02M CaCl_2 and 0.0004M Na_2SO_4 are mixed. Will a precipitate form ? Given : K_{sp} for $\text{CaSO}_4 = 2.4 \times 10^{-5}$.

2. (a) Assign reasons to the following :
- Pure liquids and solids can be ignored while writing the equilibrium constant expression.
 - 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 :

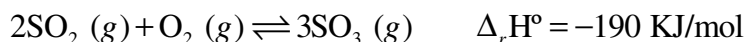


The value of $K_c = 3.75 \times 10^{-6}$ at 1069 K. Calculate K_p at this temperature.

4. (a) Define reaction quotient.
- (b) A mixture of H_2 , N_2 and NH_3 with molar concentrations of $3.0 \times 10^{-3} \text{ mol L}^{-1}$ and $2.0 \times 10^{-3} \text{ mol L}^{-1}$ 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 :



5. Consider the reaction :



Indicate the direction in which the equilibrium will shift when :

- temperature is increased.
 - pressure is decreased.
 - an inert gas is added at constant volume and (d) constant pressure ?
6. (a) Classify the following as homogeneous or heterogeneous equilibria :
- $2\text{NO} (g) + \text{O}_2 (g) \rightleftharpoons 2\text{NO}_2 (g)$
 - $\text{Mg} (s) + \text{O}_2 (g) \rightleftharpoons 2\text{MgO} (s)$
- (b) Consider the following transformations :

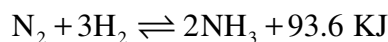


Calculate the value of K for $\text{A} \rightleftharpoons \text{D}$.

7. (a) Define K_w . Mention the effect of increasing temperature on the value of K_w .
- (b) All Lewis bases are also Bronsted bases. Explain.

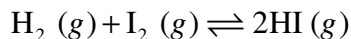
(c) K_b for NH_4OH is 1.8×10^{-5} , for CH_3NH_2 is 4.4×10^{-4} . Which of them is stronger base and why ?

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



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

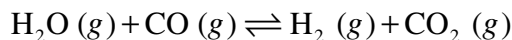
- (a) Increasing pressure
 - (b) Increasing temperature
 - (c) Use of a catalyst at an optimum temperature
9. Calculate the pH of following solution :
- (i) 0.3 g of $\text{Ca}(\text{OH})_2$ dissolved in water to give 500 mL of solution.
 - (ii) 1.0 mL of 13.6M HCl is diluted with water to give 1.0L solution.
 - (iii) 10 mL of 0.1M H_2SO_4 + 10 mL of 0.1M KOH.
10. At 700 K, equilibrium constant for the reaction :



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.

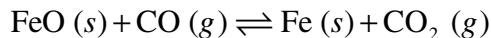
$$[\text{Ans. } [\text{H}_2] = [\text{I}_2] = 0.068\text{M}]$$

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 :



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 :



$$K_p = 0.265 \text{ atm at } 1050 \text{ K}$$

Calculate the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are $p_{\text{CO}} = 1.4 \text{ atm}$ and $p_{\text{CO}_2} = 0.80 \text{ atm}$.

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 $\text{Cu}(\text{IO}_3)_2$? For cupric iodate $K_{sp} = 7.4 \times 10^{-8}$.

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. $K_a = 2.09 \times 10^{-4}$, $\alpha = 4.57\%$]

15. The solubility of $\text{Sr}(\text{OH})_2$ 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 $\text{Sr}(\text{OH})_2 = 121.67 \text{ g/mol}$].

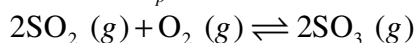
[Ans. $[\text{Sr}^{2+}] = 0.1581 \text{ M}$; $\text{pH} = 3.09$, $[\text{OH}^-] = 0.3162 \text{ M}$]

5 - MARK QUESTIONS

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 :

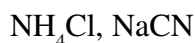


- (c) At 450 K, $K_p = 2.0 \times 10^{10} / \text{bar}^{-1}$ for the following reaction :



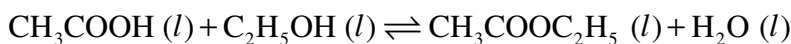
Calculate the value of K_c at this temperature.

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



- (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} .

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

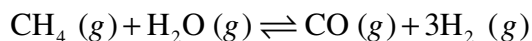


- (i) Write the reaction quotient, Q_c for this reaction .
(ii) At 293 K, if one starts with 1.0 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant. [Ans. $K_c = 22.9$]

(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 :



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, $(\text{CH}_3)_2\text{NH}$, is 5.4×10^{-4} . Calculate its degree of ionization in its 0.02 M solution.
 - (c) Calculate the percentage of dimethylamine ionized if the solution is also 0.1M in NaOH.



UNIT-8

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 valency 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 H₂, S in S₈, P in P₈, O in O₂ or O₃.
- (b) F has oxidation number -1.
- (c) Oxidation number of oxygen is -2 in all compounds except in peroxides, superoxides and oxygen fluoride. In O₂²⁻ ox. no. is -1, in O₂⁻ is -1/2, in OF₂ is +2, O₂F₂ 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 algebraic sum of oxidation numbers of all the atoms is equal to the net charge on the ion.

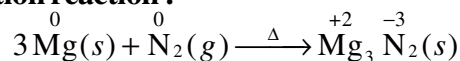
Stock notations : Cu₂O (Cuprous oxide)

Oxidation state of Copper = +1

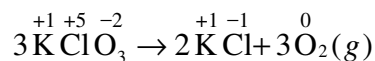
Stock notation of Cu₂O will be Cu₂(I)O.

Types of Redox reactions :

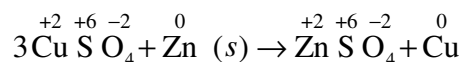
(a) **Combination reaction :**



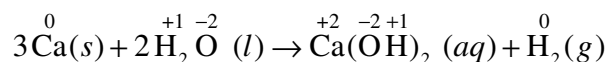
(b) Decomposition :



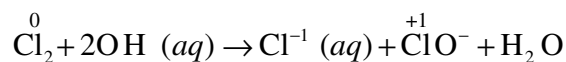
(c) Metal displacement :



(d) Non-metal displacement :



(e) Disproportionation :



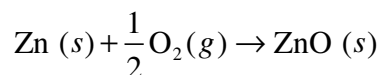
Salt bridge and its significance :

An inverted U-tube filled with concentrated solution of inert electrolyte like NH_4NO_3 , KCl .

- It connects the solution of two half-cells.
- It prevents the accumulation of charges in anodic as well as cathodic half-cells.

1 - MARK QUESTIONS

- Identify the oxidants and reductants in the following reaction :

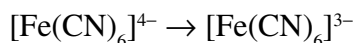


- Define oxidation number or oxidation state.
- Define the term oxidation and reduction in terms of oxidation number.
- Identify the strongest and weakest reducing agent from the following metals :
Zn, Cu, Ag, Na, Sn.

- Which one of the following is a case of reduction :

- | | |
|---|---|
| (a) $\text{Sn}^{4+} \rightarrow \text{Sn}^{2+}$ | (b) $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+}$ |
| (c) $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ | (d) $\text{Cl}^- \rightarrow \text{Cl}^0$ |

- The oxidation number of iron in reaction :



changes from :

- | | |
|--------------|--------------|
| (a) -4 to -3 | (b) -3 to -2 |
| (c) +2 to +3 | (d) +3 to +2 |

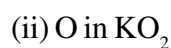
3 - MARK QUESTIONS

1. Explain why :
 - (a) The reaction $\text{FeSO}_4 + \text{Cu} \rightarrow \text{CuSO}_4 + \text{Fe}$ 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.

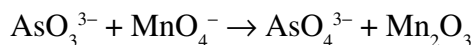
[Hint :

- (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 disproportionation reaction
 - (c) because it decompose to give nascent oxygen.]
3. Write the balanced ionic equation for the reaction of potassium dichromate (VI) $\text{K}_2\text{Cr}_2\text{O}_7$ with sodium sulphite in acid medium to give Cr (III) and sulphate ions.
 4. Balance the following equation by oxidation number method :
$$\text{P}(s) + \text{OH}^- (aq) \rightarrow \text{PH}_3 + \text{H}_2\text{PO}_2^- (aq)$$
 5. Write one example of each type of redox reactions :
 - (a) Combination reaction
 - (b) Decomposition reaction
 - (c) Metal displacement reaction

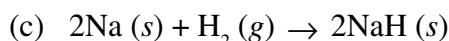
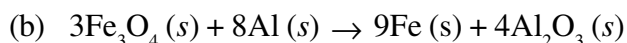
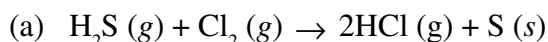
6. (a) Calculate the oxidation number of :



(b) Balance the following equation in basic medium by half reaction method :



7. Identify the species undergoing oxidation and reduction :



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.

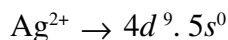
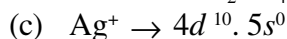
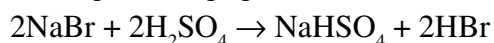
(b) When conc. H_2SO_4 is added to a inorganic mixture containing chloride, HCl is produced but if a mixture contains bromide, then we get red vapours of bromine.

(c) AgF_2 is unstable compound and a strong oxidising agent.

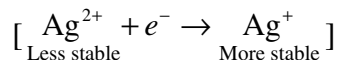
[Hint :

(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 .



Configuration shows that Ag^+ is more stable than Ag^{2+} , thus Ag^{2+} changes to Ag^+ and it acts as a oxidising agent.



UNIT-9

HYDROGEN

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.

Isotopes of Hydrogen :

- (a) Protium, 1_1H
- (b) Deuterium, 2_1H or D
- (c) Tritium, 3_1H 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 . They 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.

As its orbital is incomplete with $1s^1$ electronic configuration. It shows reactions by :

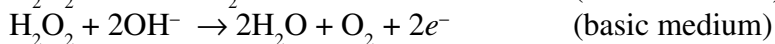
- (a) Loss of the only electron to give H⁺.
- (b) Gain of electron to form H⁻.
- (c) Sharing electrons to form a single covalent bond.

Hydrogen Peroxide (H₂O₂)

Oxidising action of H₂O₂ :



Reduction action of H₂O₂ :



H₂O₂ oxidises :

(a) Fe²⁺ to Fe³⁺ (acidic as well as basic medium)

(b) S²⁻ to SO₄²⁻ (acidic medium)

H₂O₂ reduces :

(a) MnO₄⁻ to Mn²⁺ (acidic medium)

(b) MnO₄⁻ to MnO₂ (basic medium)

(c) I₂ 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 H₂O₂ solution is expressed as percentage strength or as volume strength as given below :

$$\text{Molarity} \times 11.2 = \text{Volume strength of H}_2\text{O}_2$$

$$\text{Normality} \times 5.6 = \text{Volume strength of H}_2\text{O}_2$$

$$\text{Molarity} = \frac{\text{Percentage strength of H}_2\text{O}_2 \times 10}{\text{Molar mass of H}_2\text{O}_2}$$

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 CuSO₄.5H₂O ?
6. Give an example of 'non-stoichiometric 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.

2 - MARK QUESTIONS

1. Write two chemical reactions to show the atmospheric nature of water.
2. Complete the following reactions :
 - (a) $\text{NaH (s)} + \text{H}_2\text{O} \rightarrow$
 - (b) $\text{LiH} + \text{Al}_2\text{Cl}_3 \rightarrow$
3. Calculate the strength of 20 volume solution of hydrogen peroxide.
4. How can H_2O_2 be prepared by hydrated barium peroxide ($\text{BaO}_2 \cdot 8\text{H}_2\text{O}$) ?
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 congeners.
 - (b) Water is quite stable and does not dissociate in to its elements even at high temperature.

[Hint :

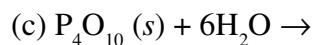
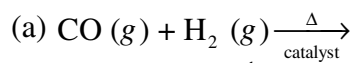
- (a) Due to the presence of intermolecular hydrogen bonding.
- (b) Due to its high negative enthalpy of formation ($\Delta_f H = -285.9 \text{ KJmol}^{-1}$)]
8. Write ionic equations for each of the following reactions :
 - (a) H_2O_2 reduces acidified potassium permanganate solution to colourless manganese 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 :
- Can phosphorus with electronic configuration $3s^2 3p^3$ form PH_5 ?
 - Water is responsible for moderation of body temperature. How?
 - Hard water is not suitable for boilers as well as for laundry.
- [Hint :**
- High $\Delta_a H$ 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.
 - High heat of vapourisation and high heat capacity.
 - Hard water form precipitate with soap and deposition of salts in the form of scales.]
3. Complete the following reactions :
- $\text{Ca}_3\text{H}_2 + \text{H}_2\text{O} \rightarrow$
 - $\text{AlCl}_3 (g) + \text{H}_2\text{O} \rightarrow$
 - $\text{CaO} (s) + \text{H}_2\text{O} \rightarrow$
4. How hydrogen peroxide is industrially prepared ? How is the conc. of H_2O_2 expressed ?
5. Explain the following terms :
- Hydrogenation
 - Syn gas
 - 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 :
- To remove the temporary hardness of water by boiling, the soluble $\text{Mg}(\text{HCO}_3)_2$ is converted to insoluble $\text{Mg}(\text{OH})_2$ and not to MgCO_3 .
 - In the Clark's method, only calculated amount of lime is added to hard water for removal of hardness.
 - Regeneration of sodium zeolite is essential by brine.

8. Complete the following reactions :



9. Comment on the reaction of dihydrogen with :

(a) Chlorine

(b) Sodium

(c) Copper(II) oxide

[Hint :

(a) H_2 reduces chlorine into chloride $[\text{Cl}^-]$ 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 in zero oxidation state and itself get oxidised to H_2O .]



UNIT-10

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.

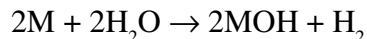
Reducing character : All the alkali metals are good reducing agents due to their low ionization enthalpies. Their reducing character in aq. medium, however, follows the order :



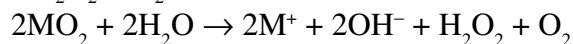
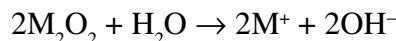
Mobility of ions in aqueous solution : The alkali metal ions exist as hydrated ions $\text{M}^+(\text{H}_2\text{O})_x$ in the aqueous solution. The degree of hydration, however, decreases with the increase in ionic size as we move from Li^+ to Cs^+ . In other words, Li^+ ion is most highly hydrated *e.g.*, $[\text{Li}(\text{H}_2\text{O})_6]^+$. 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.

Chemical properties of alkali metals

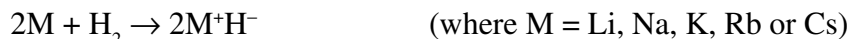
Reaction with water : All the alkali metals readily react with water evolving hydrogen.



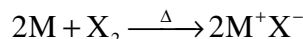
Reaction with oxygen : All the alkali metals when heated with oxygen form different types of oxides. For example, lithium forms mainly lithium oxide (Li_2O) and some Li_2O_2 , sodium forms sodium peroxide (Na_2O_2) and some NaO_2 , while K, Rb and Cs form their respective superoxides (MO_2 where $\text{M} = \text{K}, \text{Rb}$ or Cs). Superoxides are coloured and paramagnetic as these possess three electron bond ($:\text{O} \cdot \cdot \cdot \text{O}:$) where one unpaired electron is present. All oxides, peroxides and superoxides are basic in nature.



Reaction with hydrogen : All the alkali metals when heated with hydrogen form ionic crystalline hydrides of the general formula M^+H^- .

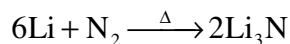


Reaction with halogens : All the alkali metals react vigorously with halogens to form their respective ionic crystalline halides of the general formula, M^+X^- where $M = \text{Li, Na, K, Rb or Cs}$ and $X = \text{F, Cl, Br or I}$.

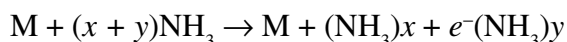


With the exception of LiF, all other lithium halides are covalent. Being covalent, LiCl, LiBr and LiI are insoluble in water but are soluble in organic solvents like pyridine, benzene, alcohols and ethers.

Reaction with nitrogen : Only lithium reacts with nitrogen to form lithium nitride (Li_3N).

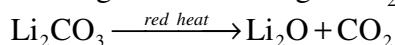


Solubility in liquid ammonia : All the alkali metals dissolve in liquid ammonia giving deep blue solutions when dilute, due to the presence of ammoniated (solvated) electrons in the solution.

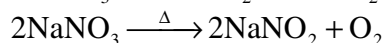
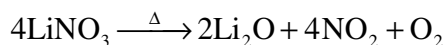


These electrons are excited to higher energy levels and the absorption of photons occurs in the red region of the spectrum. Thus, the solution appears blue.

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 .



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 .



All nitrates are very soluble in water.

Diagonal relationship

Lithium shows diagonal relationship with magnesium since they have almost the same ionic radii.

$$r(Li^+) = r(Mg^{2+})$$

Alkaline Earth Metals

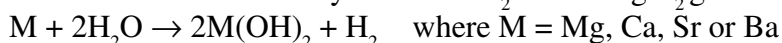
Flame colouration : Like alkali metal salts, alkaline earth metal salts also impart characteristic flame colouration. As we move down the group from Ca to Ba, the ionization energy decreases, hence the energy or the frequency of the emitted light increases. Consequently, the colour imparted to the flame 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

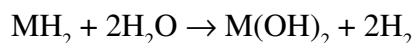
(1) **Reaction with water.** They react with H_2O evolving H_2 gas.



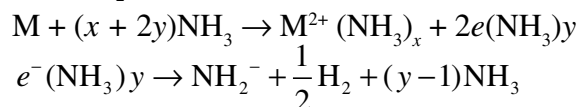
(2) **Reaction with oxygen.** The affinity for oxygen increases down the group.



(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 .

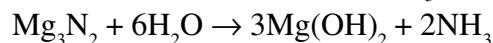


(4) **Solubility in liquid ammonia.** Like alkali metals, all alkaline earth metals dissolve in liquid ammonia giving bright solutions (when dilute) due to solvated electrons but concentrated solutions are bronze coloured due to the formation of metal clusters. These solutions decompose very slowly forming amides and evolving H_2 .

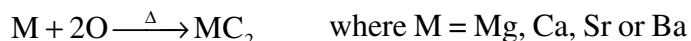


(5) **Reaction with nitrogen.** When heated with N_2 , alkaline earth metals form their respective nitrides (M_3N_2).

These nitrides react with water to evolve NH_3 , e.g.,



(6) **Reaction with carbon.** When heated with carbon, alkaline earth metals form their respective carbides of the general formula MC_2 (except beryllium) and are called acetylides containing the discrete C_2^{2-} anion.

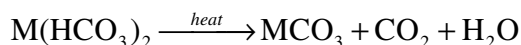


Beryllium, however, forms Be_2C called methanide containing the discrete C^{4-} anion.

(7) 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).

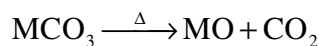
Solubility of sulphates : The solubilities of sulphates of alkaline earth metals decrease as we move down the group from Be to Ba.

Solubilities of bicarbonates and carbonates : The bicarbonates of the alkaline earth metals do not exist in the solid state but are known only in solution. On heating, these bicarbonates decompose forming carbonates with the evolution of CO_2 .



The solubilities of the carbonates decrease as we move down the group from Be to Ba, *i.e.*, $\text{BeCO}_3 > \text{MgCO}_3 > \text{CaCO}_3 > \text{SrCO}_3 > \text{BaCO}_3$.

Thermal stabilities of carbonates : The carbonates of alkaline earth metals decompose on heating forming metal oxide and carbon dioxide.



Thermal stabilities increase in the order



Thermal stabilities of sulphates : Like carbonates, thermal stabilities of sulphates also increase as the basic character of the metal hydroxide increases. This is shown by the temperature at which decompositions occur :

BeSO_4	MgSO_4	CaSO_4	SrSO_4
773 K	1168 K	1422 K	1647 K

ONE MARK QUESTIONS

- Write general electronic configuration of alkali and alkaline earth metals ?
- Among the alkali metals, which element has :
 - Strongest reducing character in aqueous medium.
 - Lowest size of ion in aqueous medium.
- Why sodium metal is kept in kerosene ?
- Why alkali metals are highly reactive ?
- What is the oxidation state of K in KO_2 ?
- State one use of liquid sodium metal.
- Name the oxoacid formed by carbon.
- LiCl is soluble in organic solvent. Explain why?

[**Hint** : Li^+ has very high polarising power, thus LiCl is covalent in nature.]

9. Name the alkali metal which forms superoxide when heated in excess of air.
10. Write the average composition of Portland cement.
11. How plaster of paris is obtained from gypsum ?
12. Li_2CO_3 has lower thermal stability than that of Na_2CO_3 , why ?

2- MARK QUESTION

1. Draw the structure of Beryllium chloride in solid state.
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 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 photo-electric 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.]

3 - MARK QUESTIONS

- Assign the appropriate reason for the following :
 - Solubility of alkaline earth metal hydroxides increases down the group.
 - The solubility of alkaline earth metal carbonates and sulphates decreases down the group.
 - Lithium salts are commonly hydrated.
- Write balanced chemical equation for the reactions between :
 - Ammonium chloride and calcium hydroxide.
 - Ammonium hydrogen carbonate and sodium chloride.
 - Calcium chloride and sodium carbonate.
- List three properties of lithium in which it differs from the rest of the alkali metals.
- State as to why :
 - KO_2 is paramagnetic.
 - An aqueous solution of sodium carbonate gives alkaline test.
 - Sodium peroxide is widely used as an oxidising agent.

[Hint :

 - It contains one unpaired electrons, hence paramagnetic.
 - Carbonate part of Na_2CO_3 get hydrolysed by water to form an alkaline solution.]
- Arrange the following in order of property mentioned against each :
 - BaCl_2 , MgCl_2 , BeCl_2 , CaCl_2 – increasing ionic character
 - $\text{Mg}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$ – increasing solubility in water
 - BeO , MgO , BaO , CaO – increasing basic character
- Write chemical equation for the following :
 - Quick lime is heated with silica.
 - Chlorine reacts with slaked lime.
 - Calcium carbonate reacts with hydrochloric acid.
- Sodium hydroxide is generally prepared by the electrolysis of brine solution in the Castner-Kellner cell :
 - Write the reactions that occur in the cell.
 - Write any two uses of sodium hydroxide.

8. (a) Write the various reactions that occur in the Solvay process.
 (b) Explain biological significance of Na and K.
9. Complete the following reactions :
- (a) $\text{NaCl} + \text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \dots + \dots$
 (b) $\text{Na}_2\text{SO}_4 + \text{CaCO}_3 + \text{C} \rightarrow \dots + \dots + \text{CO}$
 (c) $\text{Na}_2\text{CO}_3 + \text{SiO}_2 \rightarrow \dots + \dots$
10. Identify the compound A, B, C in the following reactions :
- $$2\text{NH}_3 + \text{H}_2\text{O} + \text{A} \rightarrow (\text{NH}_4)_2\text{CO}_3$$
- $$(\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O} + \text{B} \rightarrow 2\text{NH}_4\text{HCO}_3$$
- $$2\text{NH}_4\text{HCO}_3 + \text{NaCl} \rightarrow \text{NH}_4\text{Cl} + \text{C}$$
11. Write balanced chemical equation of hydrolysis of sodium oxide, sodium peroxide, sodium superoxide.

5 - MARK QUESTIONS

Explain why :

- (a) The following reaction :
- $$-\overset{\overset{|}{\text{C}}}{\underset{\underset{|}{|}}{\text{C}}} - \text{Cl} + \text{MF} \rightarrow -\overset{\overset{|}{\text{C}}}{\underset{\underset{|}{|}}{\text{C}}} - \text{F} + \text{MCl}, \text{ proceed better with KF than with NaF.}$$
- (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, $\text{C}_2\text{H}_5\text{OH}$ reacts with sodium.
 (c) Due to small size and high nuclear charge alkaline earth metal ions have higher tendency of hydration.]

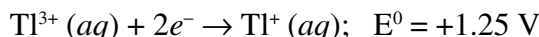


UNIT-11

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 :



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 thallos 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 $\text{Ge} < \text{Sn} < \text{Pb}$.
- **Catenation :** The property 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 (355 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})	355	215	165	152

Therefore, the tendency for catenation decreases in the order $\text{C} \gg \text{Si} > \text{Ge} \approx \text{Sn} \gg \text{Pb}$.

Tin and 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.

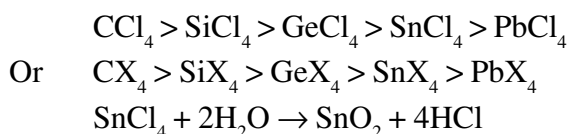
$p\pi$ - $d\pi$ multiple bonding has been observed particularly in case of silicon linked to oxygen and nitrogen. Thus trimethylamine, $\text{N}(\text{CH}_3)_3$ is pyramidal (N is sp^3 -hybridized) and is more basic whereas similar silicon compound trisilylamine, $\text{N}(\text{SiH}_3)_3$ is planar (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 $\text{X} = \text{F}, \text{Cl}, \text{Br}$ 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.*,



(ii) **Dihalides** : All the elements of group 14 form dihalides of the formula, MX_2 where $\text{X} = \text{F}, \text{Cl}, \text{Br}$ 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.*, $\text{GeCl}_2 > \text{SnCl}_2 > \text{PbCl}_2$.

• **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.*, $\text{CO}, \text{SiO}, \text{GeO}, \text{SnO}$ 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.*, $\text{CO}_2, \text{SiO}_2, \text{GeO}_2, \text{SnO}_2$ 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 dimensional network of bond.

• **Silicones** : Silicones are synthetic organosilicon compounds containing repeated R_2SiO units held by $\text{Si}-\text{O}-\text{Si}$ linkages. Since the empirical formula R_2SiO (where $\text{R} = \text{CH}_3$ 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, as surgical and cosmetic implants.

1 - MARK QUESTIONS

1. Write the general electronic configuration of *p*-block elements.
2. Mention two important ores of boron.
3. Name the elements present in boranes.
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 $\text{B} > \text{Al} > \text{Ga} > \text{In} > \text{Tl}$.
Explain this trend.
20. Why is boric acid considered as a weak acid ?

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) $\text{BF}_3 + \text{LiH} \rightarrow$
 - (b) $\text{B}_2\text{H}_6 + \text{NH}_3 \rightarrow$
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. $[\text{SiF}_6]^{2-}$ is known whereas $[\text{SiCl}_6]^{2-}$ 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

- List two important properties in which boron differs from the rest of the members of group. Mention the main reasons for the difference.
- Write balanced chemical equations for :
 - $\text{BF}_3 + \text{NaH} \xrightarrow{450\text{ K}}$
 - $\text{Fe}_2\text{O}_3 + 3\text{CO} \xrightarrow{\Delta}$
 - $\text{CaCO}_3 + 2\text{HCl} \rightarrow$
- Identify X, Y and Z in the following chemical equations :
$$\text{Z} + 3\text{LiAlH}_4 \rightarrow \text{X} + 3\text{LiF} + 3\text{AlF}_3$$
$$\text{X} + 6\text{H}_2\text{O} \rightarrow \text{Y} + 6\text{H}_2$$
$$\text{X} + 3\text{O}_2 \xrightarrow{\Delta} \text{B}_2\text{O}_3 + 3\text{HO}_2$$

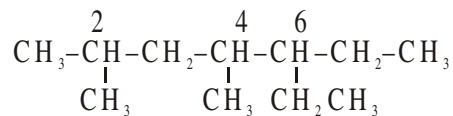
[Ans. Z = BF_3 , X = B_2H_6 , Y = H_3BO_3]
- Select the member(s) of group 14 that :
 - forms the most acidic dioxide.
 - is commonly found in +2 oxidation state.
 - used as semiconductor.
- What are allotropes ? Sketch the structure of two allotropes of carbon namely diamond and graphite.
 - List two main differences in the properties of diamond and graphite on the basis of their structure.
- Write one method for industrial preparation and one for laboratory preparation of CO. Suggest a reason as to why CO is poisonous.
- Give suitable reasons for the following :
 - CO_2 turns lime water milky, but if passed for a long time, the solution becomes clear again.
 - Graphite is used as a lubricant but diamond is used as an abrasive.
 - Graphite is a good conductor of electricity but diamond is insulator.
- 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 - MARK QUESTIONS

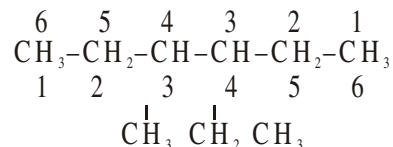
1. (a) Draw the structure of diborane.
(b) Define the term inert pair effect. Explain your answer with the help of lead chlorides.
(c) (i) Which is more ionic, SnCl_2 or SnCl_4 ?
(ii) PbO_2 is a strong oxidising agent. Assign a reason for this.
2. (a) Account for the following :
 - (i) The first ionization 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) $\text{Na}_2\text{B}_4\text{O}_7 + 2\text{HCl} + 5\text{H}_2\text{O} \rightarrow 2\text{NaCl} + \text{X}$
 - (ii) $\text{X} \xrightarrow[370 \text{ K}]{\Delta} \text{HBO}_2 \xrightarrow[> 370 \text{ K}]{\Delta} \text{Y}$
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





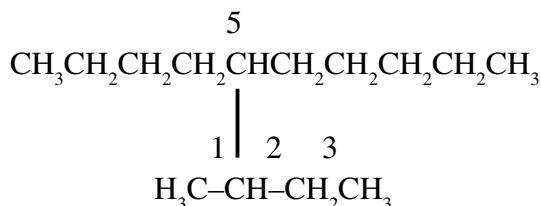
6 - Ethyl -2, 4 - dimethyl heptane

- (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.



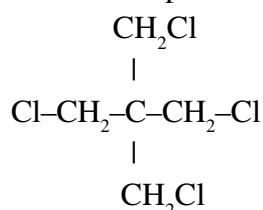
3- Ethyl - 4 - methyl hexane and not 4- ethyl - 3- methyl hexane

- (b) The name of complex chains (substituted 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.

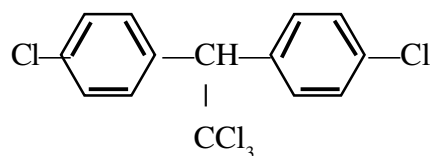


5-(1-Methylpropyl) decane, in place of 5-Isobutyldecane

- (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,

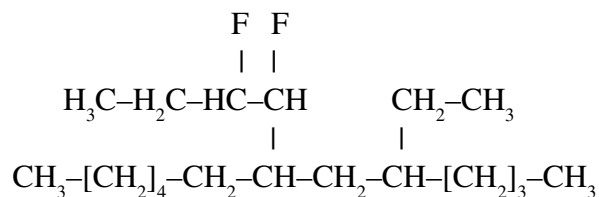


1, 3-Dichloro-2, 2-bis (chloromethyl) propane and IUPAC name of DDT is



-1, 1,1-trichloroethane 2, 2-bis (4-Chlorophenyl)

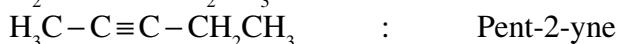
- (d) Name of a substituted substituent is considered to begin with the first letter of its complete name.



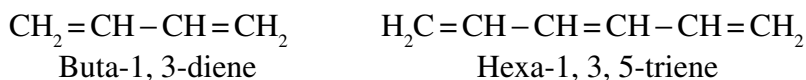
7-(1,2-Difluorobutyl)-5-ethyltridecane

IUPAC Nomenclature for alkenes and alkynes :

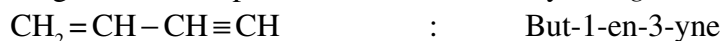
- (a) Multiple bond is preferred for numbering and represented by lowest number of C-atoms.



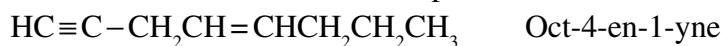
- (b) When two or more similar multiple bonds are present, suffix 'a' to the root word.



- (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.*,



- (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.*,



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, u 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 -(C)HO	formyl- oxo-	-carbaldehyde -al
Amides	-CO-NH ₂ -(C)O-NH ₂	carbamoyl- -	-carboxamide -amide
Amines	-NH ₂	amino-	-amine
Carboxylates	-COO ⁻ -(C)OO ⁻	carboxylato -	-carboxylate -oate
Carboxylic acids	-COOH -(C)OOH	carboxy- -	-carboxylic acid -oic acid
Ethers	-OR	(R)-oxy-	-
Ester (of carboxylic acids)	-COOR -(C)OOR	(R)oxycarbonyl- -	(R).....Carboxylate (R).....oate
Ketones	> (C)=O	oxo-	-one
Nitriles	-C≡N -C≡N	cyano- -	-carbonitrile -nitrile
Salts (of carboxylic acids)	-COO ⁻ M ⁺	-	(cation)..... carboxylate
Sulphonic acids	-SO ₂ -OH	sulpho	-sulphonic acid

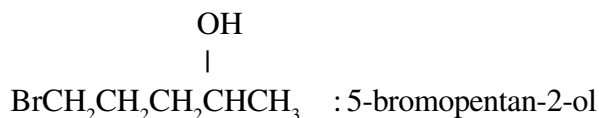
Important Notes :

- When the name of suffix starts with a consonant (except a, e, i, o, u and y), ending 'e' of the parent hydride is retained.

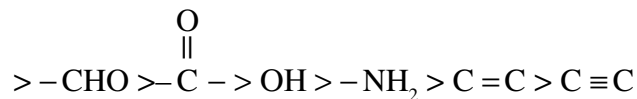


Here 'e' is retained since first letter of diol, *i.e.*, 'd' is a consonant.

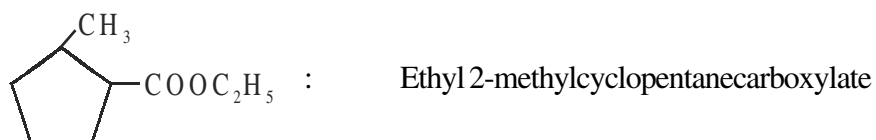
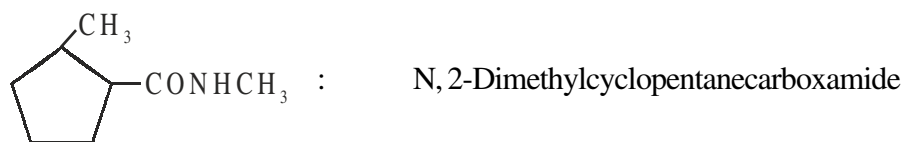
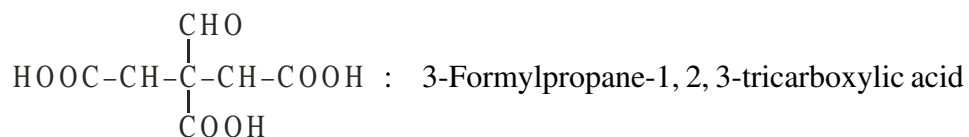
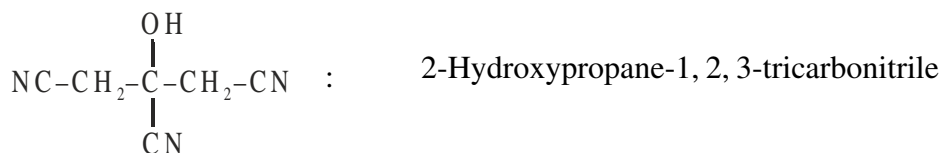
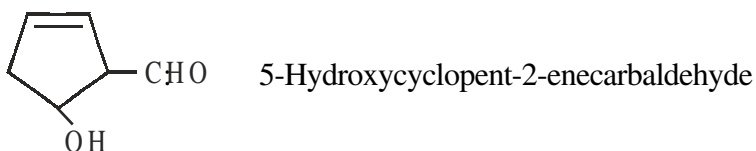
- When a functional group and a side chain/substituent is present, then functional group is preferred for naming and numbering.

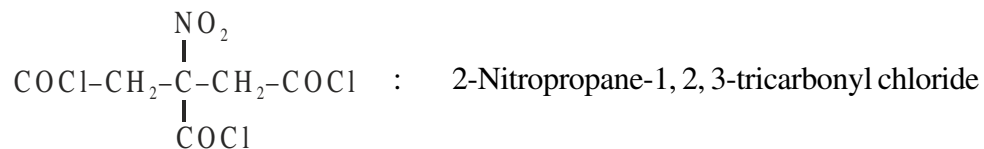


- When two or more functional groups are present, the order of preference is :
-COOH > -SO₃H > (-CO)₂O > -COOR' > -COX > -CONH₂ > -CN

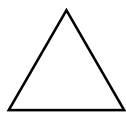


- When two or more functional groups are present, name of higher order functional group is suffixed and the rest are prefixed. Examples are :

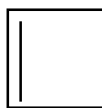




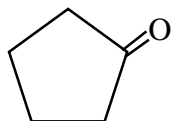
- $\overset{\text{O}}{\parallel}-\text{C}-\text{OH}, \overset{\text{O}}{\parallel}-\text{C}-\text{H}, \overset{\text{O}}{\parallel}-\text{C}-\text{NH}_2, \overset{\text{O}}{\parallel}-\text{C}-\text{X}, \overset{\text{O}}{\parallel}-\text{C}-\text{OR}$ and $-\text{CN}$ are chain terminators.
- In cyclic compound, the word '**cyclo**' is prefixed and lowest sum rule is applied for prefixing the side chains/substituents.



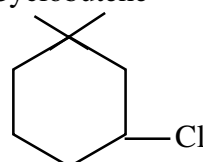
Cyclopropane



Cyclobutene

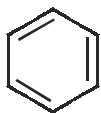


Cyclopentanone

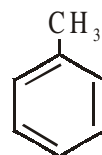


3-Chloro-1, 1-dimethylcyclohexane

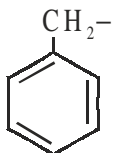
- In aromatic compounds, the following trival names have been retained by IUPAC system.



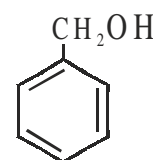
Benzene



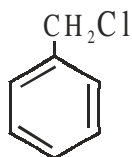
Toluene



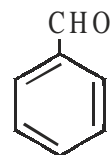
Benzyl



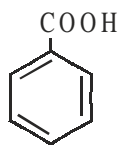
Benzyl alcohol



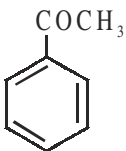
Benzyl chloride



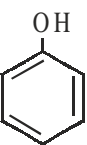
Benzaldehyde



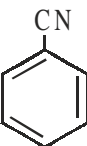
Benzoic acid



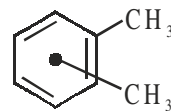
Acetophenone



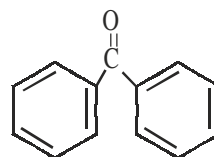
Phenol



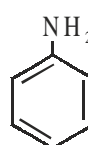
Benzonitrile



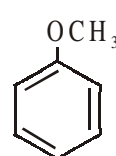
o-/p-/m-xylenes



Benzophenone

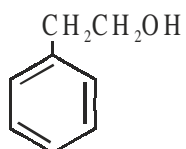


Aniline

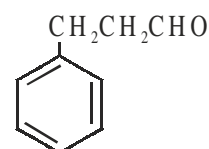


Anisole

- 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.*,

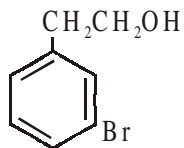


2-Phenylethan-1-ol

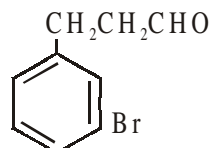


3-Phenylpropanal

When the benzene ring is further substituted, then the name of the substituted phenyl group is enclosed in parentheses for example :



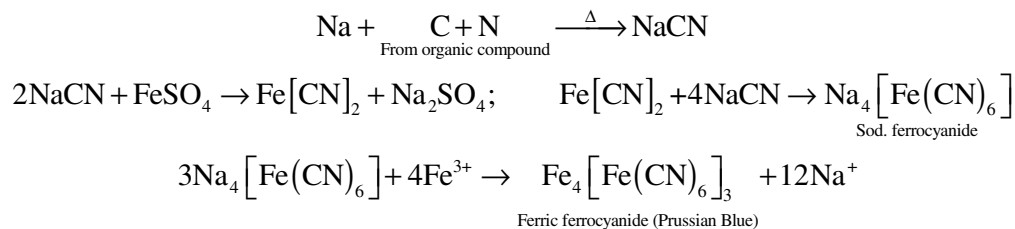
2-(3-Bromophenyl) ethan-1-ol



3-(4-Bromophenyl) propanal

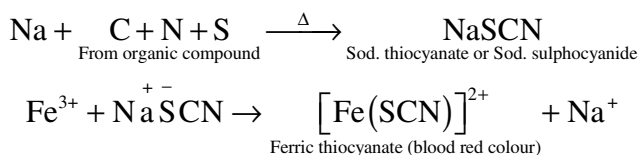
Purification and Characterization of Organic Compounds

- (1) **Lassaigne's test for nitrogen** : Lassaigne'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 chemistry of the test is :



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.

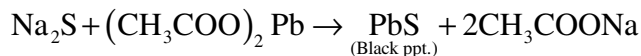


- (2) **Detection of sulphur** : If S is present, during fusion with Na metal, Na_2S is formed which may be tested as follows :

(i) With sodium nitroprusside, violet colouration is produced.



(ii) With lead acetate, black ppt. of PbS is formed.



- (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.

(ii) A pale yellow ppt. partially soluble in ammonia indicates bromine.

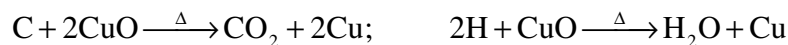
(iii) A yellow ppt. insoluble in ammonia indicates iodine.

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.

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 .

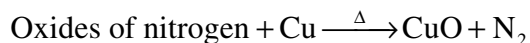
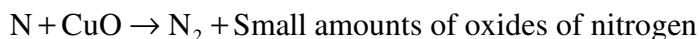
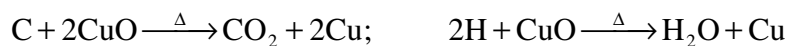


$$\text{Percentage of carbon} = \frac{12}{44} \times \frac{\text{Mass of CO}_2 \text{ formed}}{\text{Wt. of substance taken}} \times 100$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times \frac{\text{Mass of H}_2\text{O formed}}{\text{Wt. of substance taken}} \times 100$$

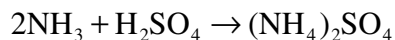
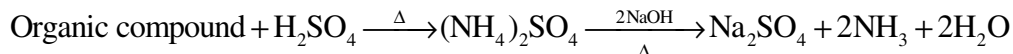
(6) Estimation of Nitrogen :

(a) Dumas method :



$$\text{Percentage of nitrogen} = \frac{28}{22400} \times \frac{\text{Vol. of N}_2 \text{ (in cm}^3\text{) at STP}}{\text{Wt. of substance taken}} \times 100$$

(b) KJELDAHL's Method



Percentage of nitrogen

$$= \frac{1.4 \times \text{Molarity of the acid} \times \text{Vol. of acid used} \times \text{Basicity of the acid}}{\text{Mass of substance taken}}$$

(7) Estimation of Halogens : Carius method :

$$\text{Percentage of chlorine} = \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl formed}}{\text{Mass of substance taken}} \times 100$$

$$\text{Percentage of bromine} = \frac{80}{188} \times \frac{\text{Mass of AgBr formed}}{\text{Mass of substance taken}} \times 100$$

$$\text{Percentage of iodine} = \frac{127}{235} \times \frac{\text{Mass of AgI formed}}{\text{Mass of substance taken}} \times 100$$

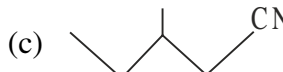
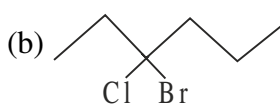
$$\text{Percentage of sulphur} = \frac{32}{233} \times \frac{\text{Mass of BaSO}_4 \text{ formed}}{\text{Mass of substance taken}} \times 100$$

- (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).

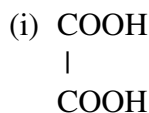
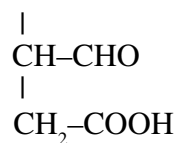
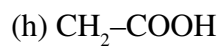
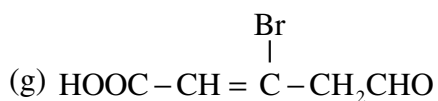
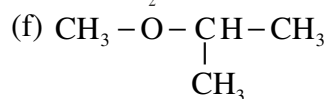
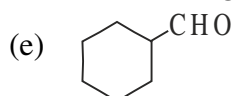
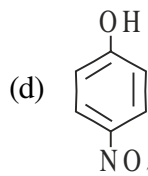
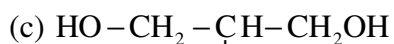
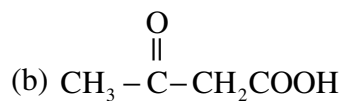
$$\text{Percentage of phosphorus} = \frac{62}{222} \times \frac{\text{Mass of Mg}_2\text{P}_2\text{O}_7 \text{ formed}}{\text{Mass of substance taken}}$$

ORGANIC CHEMISTRY

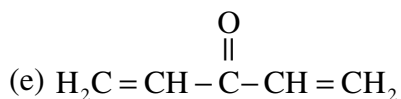
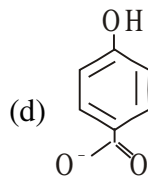
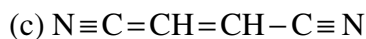
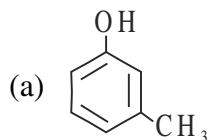
1. Write IUPAC names of the following :



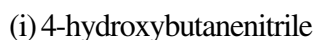
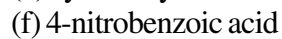
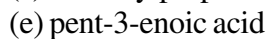
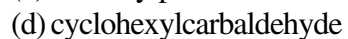
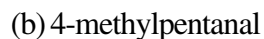
2. Write IUPAC names of the following organic compounds :



3. How many σ and π bonds are present in the following organic compounds :

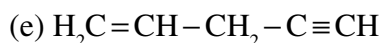
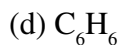
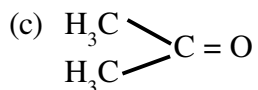
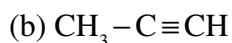
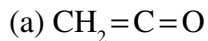


4. Draw the structures of the following organic compounds :



5. Mention the states of hybridisation of each carbon atom in the following compounds

:



6. Define the following terms with suitable examples :

(a) Nucleophile

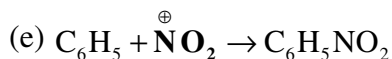
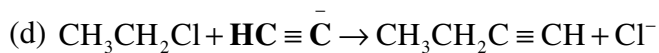
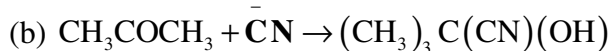
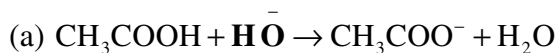
(b) Electrophile

(c) Free radicals

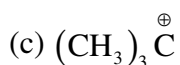
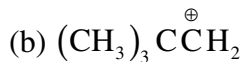
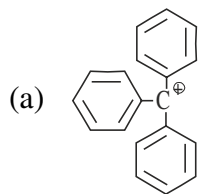
(d) Carbocation

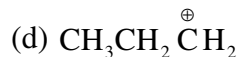
(e) Carbanion

7. Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles :



8. Which of the following carbocation is most stable :





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) Chloroform and aniline

(c) A mixture of dyes

(d) Copper sulphate and sodium chloride

(e) Benzoic acid and cane sugar

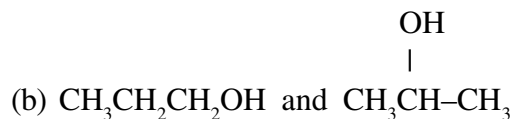
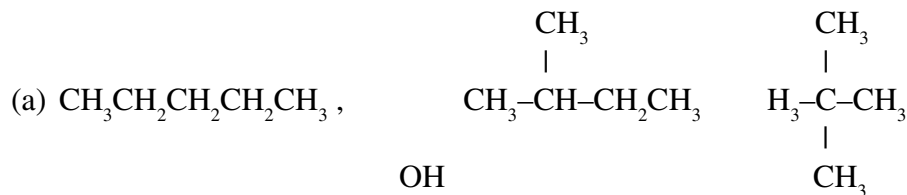
12. Explain the terms inductive effect and electromeric effect. Arrange the following compounds in the increasing order of their acidic and basic strength :

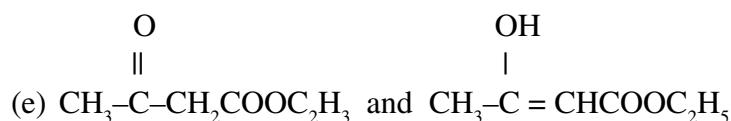
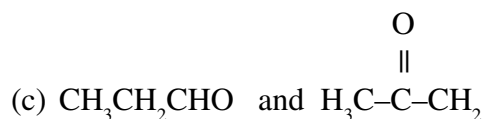
(a) ClCH_2COOH , Cl_3CCOOH and Cl_2CHCOOH

(b) $\text{CH}_3\text{CH}_2\text{COOH}$, $(\text{CH}_3)_2\text{CHCOOH}$ and $(\text{CH}_3)_3\text{CCOOH}$

(c) CH_3NH_2 , CH_3NHCH_3 , $(\text{CH}_3)_3\text{N}$, $\text{C}_6\text{H}_5\text{NHCH}_3$

13. Write the isomerism among the following compounds :





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. $\text{C}_3\text{H}_8\text{O}_3$]

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 mol^{-1} . Calculate its molecular formula.

[Ans. $\text{C}_4\text{H}_4\text{Br}_2\text{O}_4$]

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



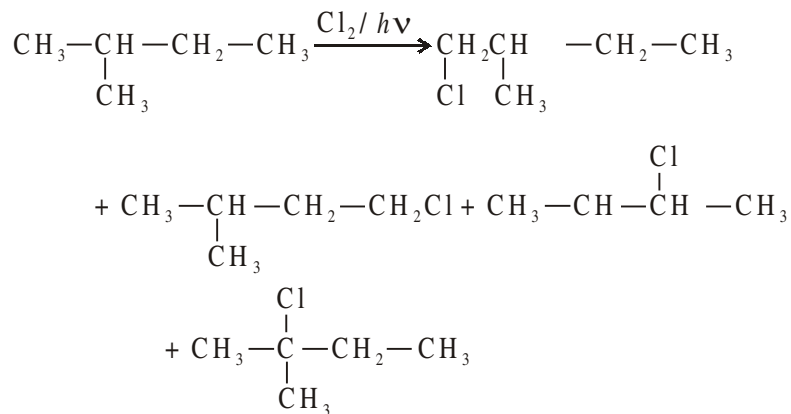
UNIT-13

HYDROCARBONS

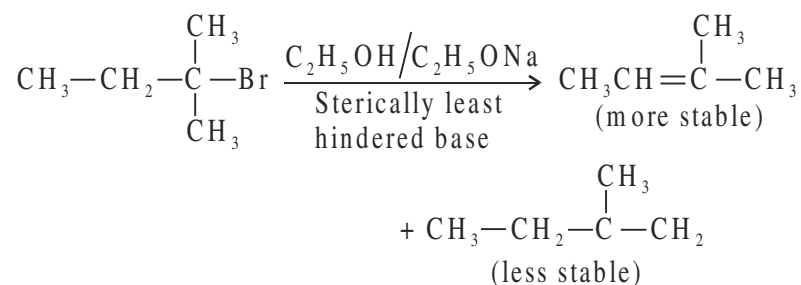
Preparations

- **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.

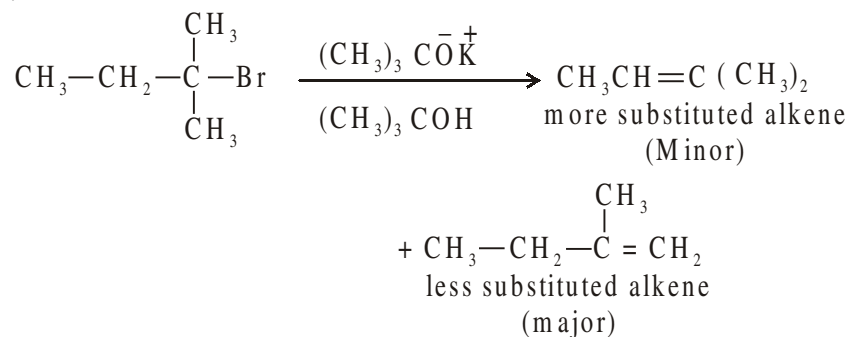
Monochlorination of 2-methyl butane gives four products.



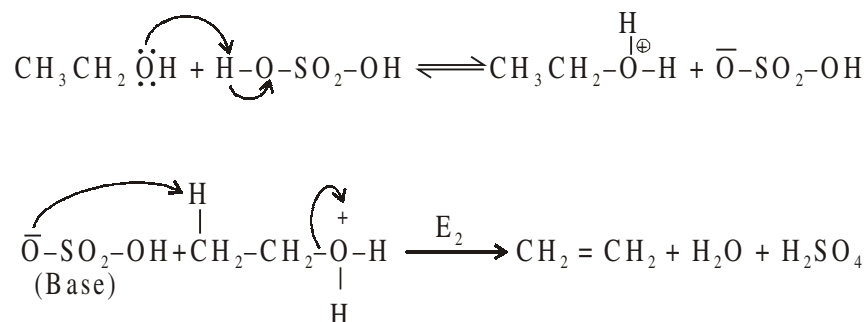
- **Lindlar's catalyst** is the partially deactivated palladised charcoal which converts unsymmetrical alkynes having no acidic terminal hydrogen to form cis-alkene.
- Unsymmetrical alkynes having no terminal hydrogen is reduced by Na/liquid NH_3 to form trans-alkene.
- **Saytzeff Rule** is used in dehydrohalogenation 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.



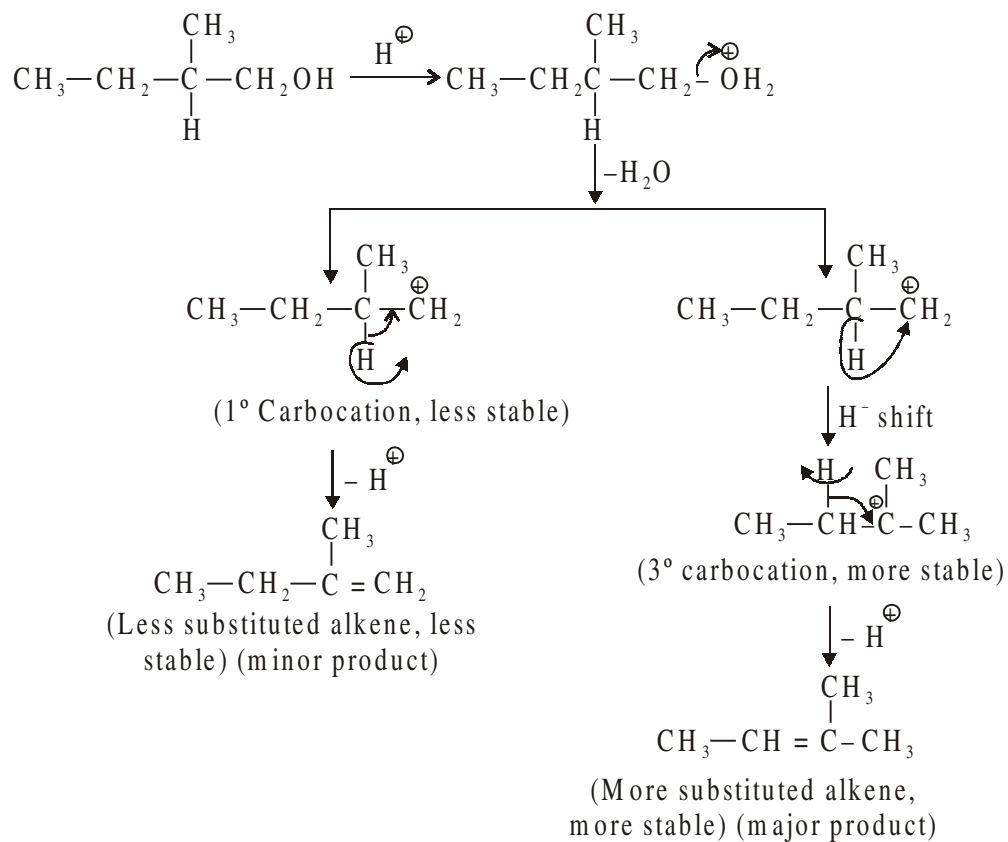
An exception to Saytzeff Rule : The most sterically hindered base $(\text{CH}_3)_3\text{C}\overset{-}{\text{O}}\overset{+}{\text{K}}$ in tert-butyl alcohol cannot attack at the β -carbon atom having lesser number of hydrogen atoms because of greater crowding at the site of attack. Therefore, the base, tert-butoxide remove more exposed 1° hydrogen atom from β -carbon.



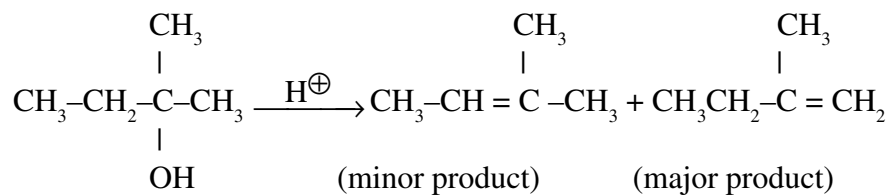
Acid Catalysed Dehydration of Alcohols : Dehydration of 1° alcohols is an E_2 reaction while dehydration of 2° and 3° alcohols is an E_1 reaction.



Rearrangement of carbocations obtained from 2° or 3° alcohols may occur by hydride (H⁻) or methanide CH₃⁻ shift (both are 1, 2-shifts) to form more stable carbocations.

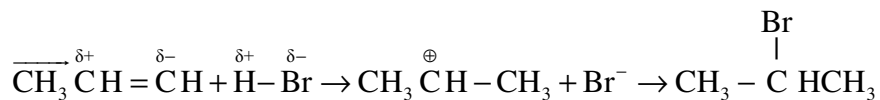


Similarly acid catalysed dehydration of 2-methylbutan-2-ol forms 2-methylbut-2-ene as major product and 2-methylbut-1-ene as a major product.



Mechanism : Markownikov rule proceed via carbocation formation :

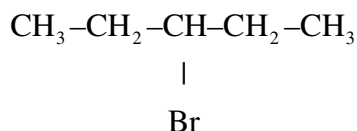
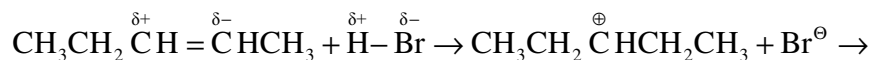
1. Larger alkyl group polarise the π -bond.



2. H attacks first and generate more stable carbocation.

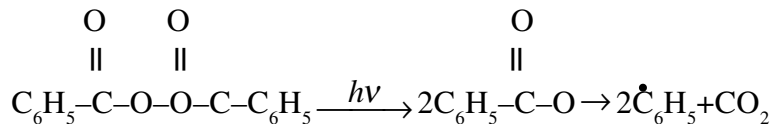
3. Br^- attacks to carbocation to form product.

Another example is :

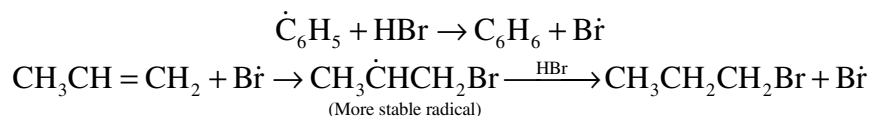


Mechanism of Peroxide effect :

Peroxide effect (Antimarkownikov rule) proceeds via free radical mechanism.



One free radical always generate another free radical.

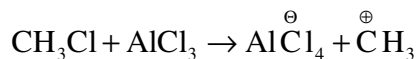


Friedel-Crafts Reaction :

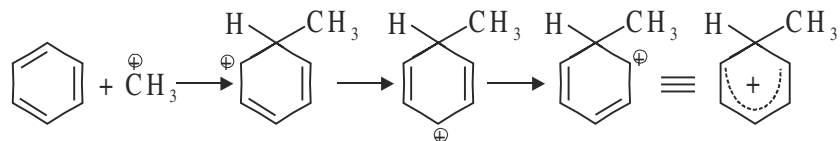
Introduction of alkyl (R) or acyl group (COR) to benzene nucleus in presence of anhydrous AlCl_3 (Lewis acid) is called Friedel-Crafts reaction.

Mechanism :

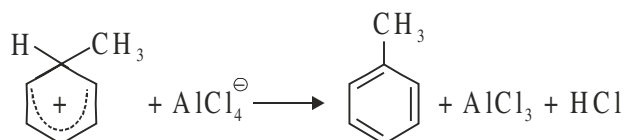
Step 1. Generation of electrophile, AlCl_3 is a Lewis acid and generate electrophile.



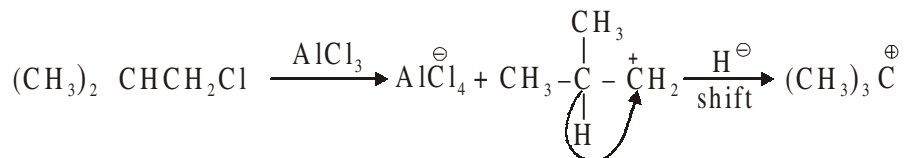
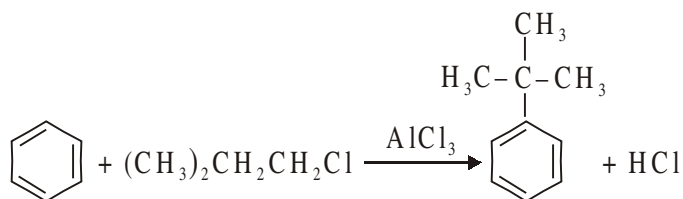
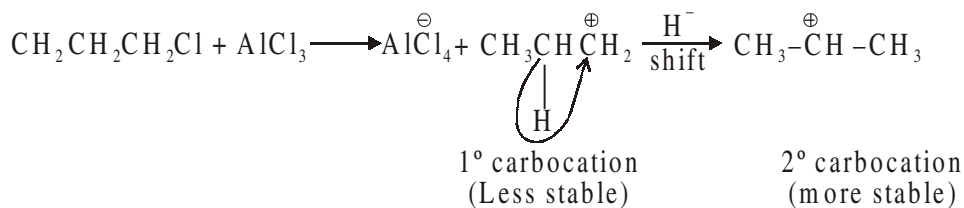
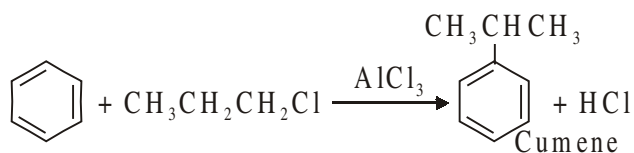
Step 2. Formation of intermediate.



Step 3.



(1) More stable carbocation will form the major product, *e.g.*,



Directive influence of a functional group in monosubstituted benzene :

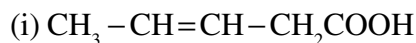
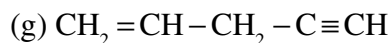
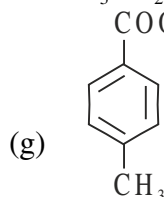
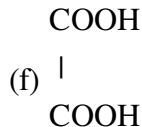
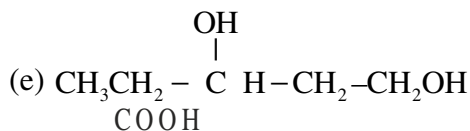
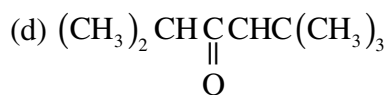
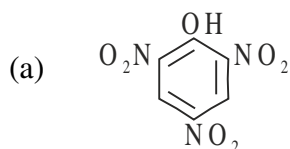
Activating groups like $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$, $-\text{NHCOCH}_3$, $-\text{OCH}_3$, $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$ are *o/p*-directors.

Halogen atoms deactivate the ring by electron withdrawing inductive effect. But the halogen atom increases the electron availability at *o*- and/or *p*-positions by electron donating resonance effect. Hence halogens act also as *o*- and/or *p*-directors.

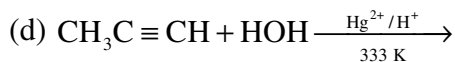
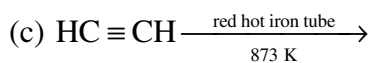
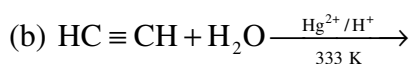
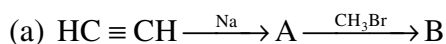
Deactivating groups such as $-\text{NO}_2$, $-\text{CN}$, $-\text{CHO}$, $-\text{COOH}$, $-\text{COR}$, $-\text{CONH}_2$, $-\text{COOR}$ and $-\text{SO}_3\text{H}$ are *m*-directing groups.

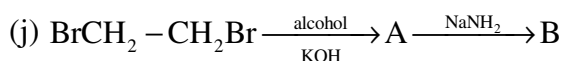
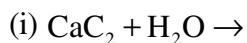
HYDROCARBONS

1. Write IUPAC names of the following organic compounds :



2. Complete the following equations :





3. Explain the following reactions with suitable examples :

(a) Wurtz reaction

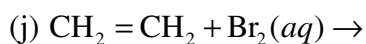
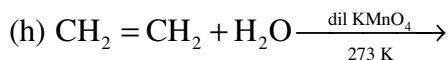
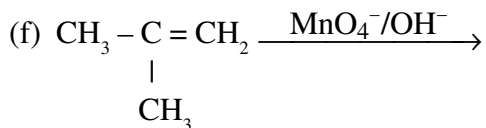
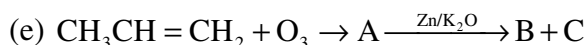
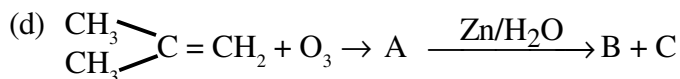
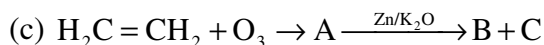
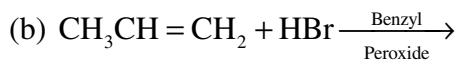
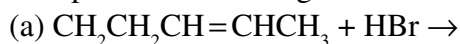
(b) Kolbe's electrolysis

(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 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 :



7. How will you carry out following conversions :
- Ethyne into propyne
 - Ethyne into benzene
 - Benzene into 4-nitrobromobenzene
 - Benzene into *n*-nitrochlorobenzene
 - But-2-ene into ethanol
 - Benzene into acetophenone
 - Benzene into 4-nitrotoluene
 - Ethane into ethyne
 - Ethanoic acid into methane
 - 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 –NO₂ attached to benzene ring is meta-directing.
10. Benzene undergo electrophilic substitution reaction. Explain the mechanism of electrophilic substitution in the following steps :
- Generation of electrophile
 - Formation of carbocation intermediate
 - Removal of proton from carbocation intermediate
11. Give reasons :
- AlCl₃ is used as catalyst in Friedal-Craft reaction.
 - Wurtz reaction is carried in dry ether.
 - Wurtz reaction is not preferred for the preparation of alkanes containing odd number of carbon atoms.
 - 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.
 - Aromaticity of benzene ring and higher members.
 - trans*-2-butene has higher m.p. than *cis*-isomer.
 - Alkynes on reduction with Lindlars catalyst (Pd/C) form *cis*-alkene and with Na in liquid NH₃ form *trans*-alkene.

- (h) Ethyne is more acidic than ethene and ethane.
 - (i) Kharasch effect is spontaneous with HBr only.
 - (j) $-\text{OH}$ 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, $\text{C}_6\text{H}_{12}\text{Br}_2$ 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.
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.



UNIT-14

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 and O_3 .
- (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. 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) 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 forming substances 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. Write your answer in one sentence.
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 gas responsible for ozone layer depletion.
9. Define smog and 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. How the following particulate pollutants are formed :
Smoke, dust, mist and fumes

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 you manage to dispose off biodegradable and non-biodegradable waste.
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



SAMPLE PAPER – I (SOLVED)

CHEMISTRY – XI

Time : 3 hrs.

M. M. : 70

General Instructions :

- (i) All questions are compulsory.
- (ii) Marks for each question are indicated against it.
- (iii) Question number 1 to 8 are very short answer questions carrying **one** mark each. Answer these in one word or about one sentence.
- (iv) Question number 9 to 18 are short answer questions carrying **two** marks each. Answer these in about 30 words.
- (v) Question number 19 to 27 are also short answer questions carrying **three** marks each. Answer them in about 40 words.
- (vi) Question number 28 to 30 are long answer questions carrying **Five** marks each. Answer them in about 70 words.
- (vii) Use log tables, if necessary. Use of calculator is not allowed.

1. The following set of quantum numbers is not possible. Explain, why ? 1
 $n = 2, l = 3, m = -3, m = +1/2$
2. Name a species which is isoelectronic with the following ions : 1
 Mg^{2+}, N^{3-}, O^{2-}
3. For an isolated system $\Delta U = 0$, what will be ΔS ? 1
4. Explain the structure of CO_2 in terms of resonance. 1
5. What are the conditions under which gases deviate from ideality. 1
6. Justify that the following reaction is a redox reaction : 1
 $H_2O (s) + F_2 (g) \rightarrow HF (g) + HOF (g)$
7. Write the IUPAC name of following : 1
 $CH_2=CH-C\equiv CH$
8. What is the oxidation state of K in KO_2 . 1

9. Write balanced equation for reaction between : 1 × 2 = 2
(a) Na_2O_2 and water
(b) Ca metal with HCl

OR

Describe the hybridisation in case of PCl_5 . Why are the axial bonds longer as compared to equatorial bonds ? 2

10. (a) Use molecular orbital theory to explain why Be_2 molecule does not exist. 1
(b) Explain the formation of σ and π bonds in C_2H_4 with the help of diagram. Mention the hybrid state of two carbon atoms. 1
11. Calculate the mass of a photon with wavelength 3.6 \AA . ($h = 6.26 \times 10^{-34} \text{ JS}$) 2
12. Predict the products of electrolysis of an aqueous solution of AgNO_3 with silver electrodes. Write reaction that occurs at each electrode. 2
13. Write all the reactions involved in the preparation of sodium carbonate from sodium chloride in Solvay Process. 2
14. Complete the following equations : 2
(a) $\text{Al} + \text{NaOH} + \text{H}_2\text{O} \rightarrow$
(b) $\text{H}_3\text{BO}_3 \xrightarrow{\Delta} \text{A} \xrightarrow{\Delta} \text{B}$
15. A polluted water sample has been found to have 15 ppm CHCl_3 in it.
(a) Express this value in percent by mass.
(b) Determine the molality of chloroform in the water sample. 2
16. An alkene 'A' on ozonolysis gives a mixture of ethanal and pentan-3-one. Write the structure and IUPAC name of A. 2
17. What is the basic principle involved in the following process :
(a) Partition chromatography 1
(b) Distillation under reduced pressure 1
18. (a) Explain why Be and Mg do not give colour to the flame whereas other alkaline earth metals do. 1
(b) Why alkali and alkaline earth metals cannot be prepared by chemical reduction methods ? 1

19. (a) Calculate the concentration of nitric acid in moles per litre in a sample which has a density 1.41 gmL^{-1} and the mass percent of HNO_3 in it being 69%. 2
- (b) How many atoms are present in 48u of C ? 1
20. (a) What are degenerate orbitals ? Give example. 1
- (b) Show that the circumference of the Bohr's orbit for H atom is an integral multiple of de Broglie's wavelength associated with the electron revolving around the orbit. 2

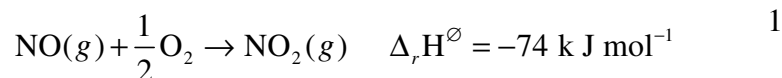
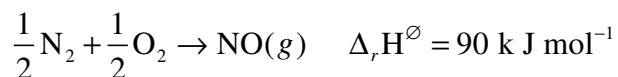
OR

- (a) Mention the difference between electromagnetic wave theory and Planck's quantum theory. 2
- (b) How many electrons can have quantum number values $n = 4, m_s = 1/2$. 1
21. (a) Write the general outer electronic configuration of *f*-block elements. 1
- (b) Predict the formula of a compound formed between silicon and oxygen. 1
- (c) N has higher ionisation enthalpy than O and why? 1
22. (a) Calculate the total pressure in a mixture of 8 g O_2 and 4 g H_2 confined in a vessel of volume 1 dm^3 at 27°C . ($R = 0.083 \text{ bar dm}^{-3} \text{ K}^{-1} \text{ mol}^{-1}$). 2
- (b) In terms of Charles's law explain why -273.15°C is the lowest possible temperature. 1
23. (a) The species H_2O and NH_3 can act both Bronsted acids and Bronsted Bases. For each give the corresponding conjugate acid and conjugate base. 2
- (b) What will be the pH of 0.002 M HCl ? 1
24. (a) Write the expression for K_p for the following reaction : 1
- $$\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g)$$
- (b) How will the values of K_p and composition of equilibrium mixture be affected by : 1
- (i) increasing the pressure
- (ii) using a catalyst

25. (a) Out of NH_3 , H_2O and HF which would you expect to have highest magnitude of hydrogen bonding and why ? 1
- (b) Write chemical equations to justify that H_2O_2 can act as an oxidising agent as well as a reducing agent. 2
26. Give reasons : 3
- (a) Why CO is a poisonous gas ?
- (b) Lead(IV) chloride is highly unstable towards heat.
- (c) Boric acid is not protic acid.
27. Explain the following terms : 3
- (a) Ozone hole
- (b) BOD
- (c) Green chemistry
28. (a) Derive the relationship between C_p and C_v for an ideal gas.
- (b) Given $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$ $\Delta H = -92.4 \text{ kJ/mol}$.
- What is the standard enthalpy of formation of NH_3 gas ?
- (c) The equilibrium constant for a reaction is 10. What will be sign of ΔG ? Will this reaction be spontaneous ?

OR

- (a) Compare the thermodynamic stabilities of NO and NO_2 from the following data :



- (b) Write the Born Haber Cycle for the formation of $\text{CaCl}_2(s)$. 2
- (c) For the reaction at 298 K : $2A + B \rightarrow C$

$$\Delta H = 400 \text{ kJ mol}^{-1} \text{ and } \Delta S = 0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

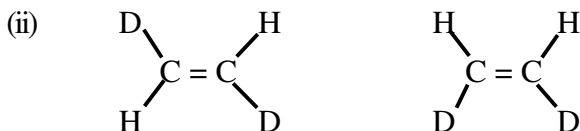
Determine the temperatures at which the reaction would be spontaneous.

[4]

29. (a) Give the reactions involved in the estimation of N and Cl by Lassaigne's test. 2
- (b) Explain the following with examples : 3
- Electrophiles
 - Nucleophiles
 - Inductive effect

OR

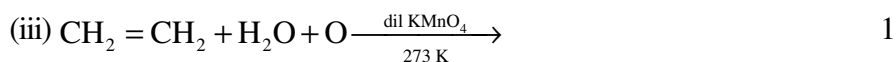
- (a) Explain why :
- $(\text{CH}_3)_3\text{C}^+$ is more stable than CH_3CH_2^+ and CH_3^+ is the least stable cation.
 - On adding AgNO_3 to CCl_4 solution, white precipitate of AgCl is not obtained.
 - Nitric acid is added to sodium extract before adding AgNO_3 for testing halogens.
- (b) What is the relationship between the members of following pairs of structures ?



30. (a) How will you convert :
- Benzene to acetophenone 1
 - Benzene to *p*-nitrophenone 1
 - Ethanoic acid to methane 1
- (b) Write IUPAC name of the product obtained by addition reaction of HBr to hex-1-ene in the presence of a peroxide. 1
- (c) Hydrogen atoms of ethyne are acidic in nature, why ? 1

OR

(a) Complete the following reactions :



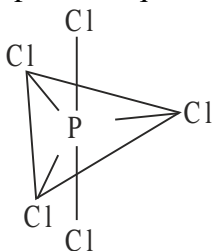
(b) -NO₂ group attached to benzene is meta directing but -OH group is ortho and para directing. Explain why? 2

ANSWERS

1. The value of $l = 3$ is not possible for $n = 3$. Permissible values of l is 0 to $n - 1$.
2. Na⁺ or F⁻ or Ne. 1
3. $\Delta S = +ve$ e.g. mixing of two gases separated by a partition at constant temperature. 1
4. $\ddot{O} = C = \ddot{O} \longleftrightarrow \ddot{O}^- - C \equiv \overset{+}{O} : \quad : \overset{+}{O} \equiv C - \ddot{O}^-$ 1
5. Low temperature and high pressure. 1
6. The reaction involve oxidation of fluorine (F₂ to F⁺) in HOF and reduction of Fluorine(F₂) to F⁻ in HF . 1
7. But-1-en-3-yne 1
8. K(+1) 1
9. (a) Na₂O₂ + H₂O → H₂O₂ + 2NaOH 1
(b) Ca + 2HCl → CaCl₂ + H₂ 1

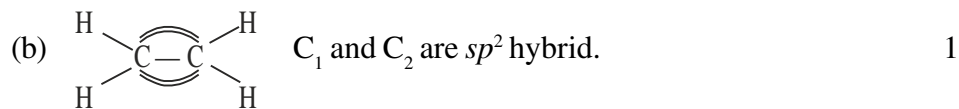
OR

*sp*³*d* hybridisation. The axial bonds are longer because axial bond pairs suffer more repulsion as compared to equatorial bond pairs.



[6]

10. (a) $\text{Be}_2 : \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2$ and $\text{B.O.} = \frac{1}{2}(4 - 4) = 0$
 Since B. O. is zero, molecule does not exist. 1

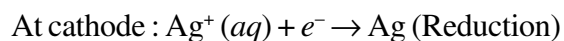
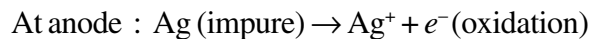


11.
$$\lambda = \frac{h}{mv}$$

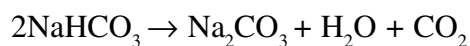
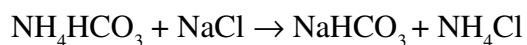
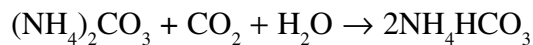
$$3.6 \times 10^{-10} = \frac{6.626 \times 10^{-34}}{m \times 3 \times 10^8}$$

$$m = 6.135 \times 10^{-29} \text{ kg}$$
 2

12. Products of electrolysis Ag and AgNO_3 . 2



13. $\text{H}_2\text{O} + \text{NH}_3 + \text{CO}_2 \rightarrow (\text{NH}_4)_2\text{CO}_3$ 2

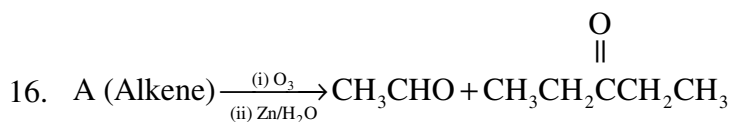


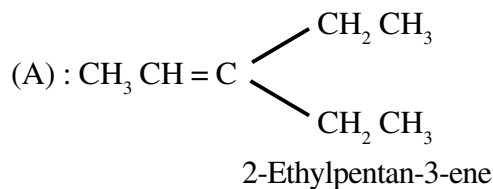
14. (a) $2\text{Al} + 2\text{NaOH} + 6\text{H}_2\text{O} \rightarrow 2\text{Na}[\text{Al}(\text{OH})_4] + 3\text{H}_2$ 2



15. (a) % by mass = $\frac{15}{106} \times 100 = 15 \times 10^{-4} \%$ 1

(b) Molality = $\frac{15}{119.5} \times \frac{1000}{10^6} = 1.25 \times 10^{-4} \text{ m}$ 1





17. (a) Partition chromatography is based on continuous differential partitioning of components of a mixture between the stationary and mobile phases. 1
- (b) Distillation under reduced pressure involves distillation at temperature lower than the normal boiling point of the liquid by reducing air pressure on the surface of liquid.
18. (a) Be and Mg both having high ionisation enthalpy. 1
- (b) Alkali metals and alkali earth metals are good reducing agents and have high -ve $E_{\text{M}^{n+}/\text{M}}^0$ values, therefore they can not be reduced by chemical methods. 1

19. (a)
$$M = \frac{W_B \times 1000}{M_B \times V}$$

Density of solution = $\frac{1.41 \text{ g}}{1 \text{ m}}$ $M_B(\text{HNO}_3) = 1 + 14 + 48 = 63 \text{ g/mol}$

Mass of 1 mL solution = 1.41 g

Mass of $\text{HNO}_3 = W_B = \frac{69}{100} \times 1.41 = 0.97 \text{ g}$

$V = 1 \text{ mL}$

$M = \frac{0.97}{63} \times 1000 = 10 \text{ mol L}^{-1}$ 2

(b) No. of C atoms = $\frac{48u}{12u} = 4$ 1

20. (a) The orbitals of a subshell having same energy are called degenerate orbitals, e.g., $2p_x, 2p_y, 2p_z$ are degenerate orbitals.
- (b) According to Bohr, the orbital angular momentum is quantized.

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

$$2\pi r = \frac{nh}{mv} = n\lambda \quad (\text{de Broglie wavelength, } \lambda = \frac{h}{mv}) \quad 2$$

OR

(a) According to electromagnetic wave theory energy is emitted in form of electrical and magnetic waves in continuous manner whereas Plank suggested energy cannot be emitted or absorbed continuously but in the form of small packets called quanta.

(b) Maximum No. of electrons in $n = 4 = 2 \times 4^2$

But only half of them have $m_s = +\frac{1}{2}$

No. of electrons with $n = 4, m_s = +\frac{1}{2}$ are 16. 1

21. (a) f -block elements configuration $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

(b) SiO_2

(c) It is easier to remove one electron from $2p^4$ configuration of O than from extra stable half-filled $2p^3$ configuration of N. 1

22. (a) $n_{\text{O}_2} = -\frac{8}{32} = 0.25$

$$n_{\text{H}_2} = \frac{4}{2} = 2$$

$$n_{\text{T}} = n_{\text{O}_2} + n_{\text{H}_2} = 0.25 + 2 = 2.25$$

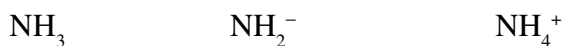
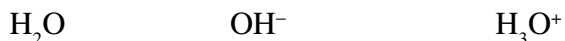
$$V = 1 \text{ dm}^3 = 1\text{L}, T = 300 \text{ K}$$

$$P = \frac{nRT}{V} = 2.25 \times 0.082 \times 300$$

$$= 55.35 \text{ atm} \quad 2$$

(b) Volume of gas becomes zero at -273.15°C , therefore the lowest possible temperature becomes -273.15° . 1

23. (a) **Species Conjugate base Conjugate acid**



2

- (b) $\text{pH} = -\log [\text{H}^+] / \text{mol L}^{-1}$ 1
 $= -\log (2 \times 10^{-3})$
 $= -(-3 + 0.3010) = 2.7$
24. (a) $K_p = \frac{P_{\text{CO}}}{P_{\text{CH}_4} P_{\text{H}_2\text{O}}}$ 1
- (b) (i) K_p is not affected by increasing the pressure but the forward reaction is favoured. 1
- (ii) K_p is not affected by a catalyst and the equilibrium composition also remains the same. 1
25. (a) HF has highest magnitude of hydrogen bonding because F is the most electronegative atom. 1
- (b) H_2O_2 as oxidising agent :
 $2\text{Fe}^{2+} (\text{aq}) + 2\text{H}^+ (\text{aq}) + \text{H}_2\text{O} (\text{aq}) \rightarrow 2\text{Fe}^{3+} (\text{aq}) + 2\text{H}_2\text{O}$
- Reducing action of H_2O_2 :
 $\text{HOCl} + \text{H}_2\text{O}_2 \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- + \text{O}_2$
26. (a) CO bonds with haemoglobin and reduces its ability to bind with oxygen. 1
- (b) Pb(IV) state is unstable due to inert pair effect. 1
- (c) Boric acid, $\text{B}(\text{OH})_3$ accept $\bar{\text{O}}\text{H}$ from water and H^+ is released by water molecule. 1
27. (a) **Ozone hole** - Depletion of ozone layer present over the south pole. 1
- (b) **BOD** - The amount of oxygen required by the bacteria to break down the organic matter in a certain volume of a sample of water is called Biochemical Oxygen Demand. 1
- (c) **Eutrophication** - The process in which nutrient enriched water bodies support a dense plant population which kills animal life due to less availability of oxygen is called Eutrophication. 1
28. (a) At constant volume $q_v = C_v \Delta T = \Delta U$
 At constant pressure $q_p = C_p \Delta T = \Delta H$
 For 1 mol of an ideal gas :

$$\Delta H = \Delta V + \Delta(PV)$$

$$\Delta H = \Delta V + \Delta(RT)$$

$$\Delta H = \Delta U + R\Delta T$$

$$C_p\Delta T = C_v\Delta T = R\Delta T$$

$$C_p - C_v = R \quad 2$$

$$(b) \Delta_f H^\ominus (\text{NH}_3) = \frac{\Delta_r H^\ominus}{2} = \frac{-94.2}{2} = 47.1 \text{ kJmol}^{-1} \quad 1$$

$$(c) \Delta G = -2.303 RT \log K_c$$

When $K_c = 10$,

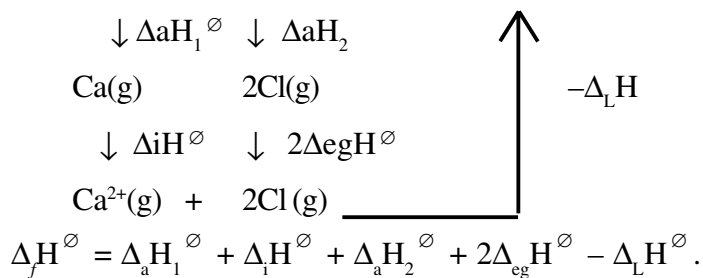
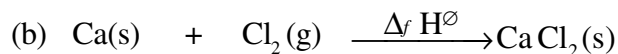
$$\Delta G = -ve. \text{ The reaction will be spontaneous.} \quad 2$$

OR

(a) NO is an endothermic compound whereas NO₂ is an exothermic compound, i.e.,

$$\Delta H^\ominus(\text{NO}) > \Delta_r H^\ominus(\text{NO}_2)$$

Hence, NO is less stable than NO₂.



(c) At equilibrium $\Delta G = \Delta H - T\Delta S = 0$

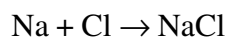
$$T = \frac{\Delta H}{\Delta S}$$

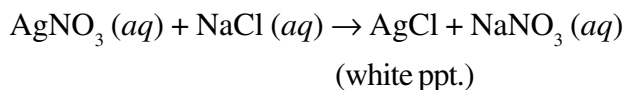
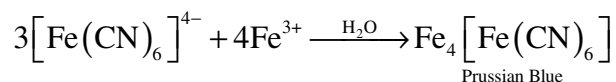
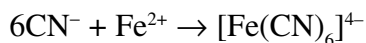
$$T = \frac{400 \text{ kJ mol}^{-1}}{0.2 \text{ kJ mol}^{-1}}$$

$$T = 2000 \text{ K}$$

Above this temperature $T\Delta S > \Delta H$ and the reaction will be spontaneous. 2

29. (a) $\text{Na} + \text{C} + \text{N} \rightarrow \text{NaCN}$

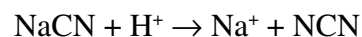
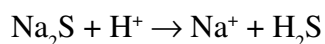




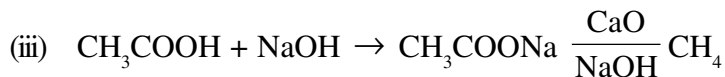
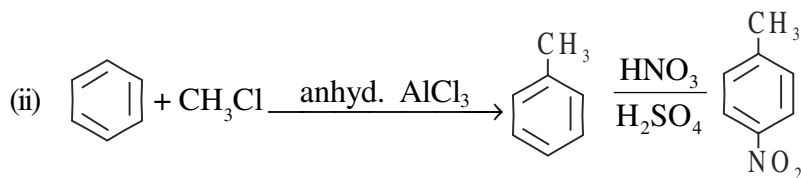
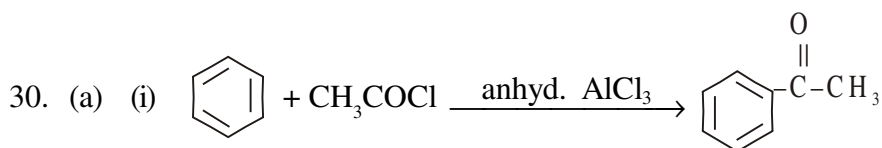
- (b) (i) Electrophile takes away an electron pair *e.g.*, NO_2^+ .
(ii) Nucleophile accepts an electron pair *e.g.*, OH^- . 1
(iii) **Inductive Effect** : The polarisation of a sigma bond due to the polarisation of adjacent sigma bond is called inductive effect. 1

OR

- (a) (i) $(\text{CH}_3)_3\text{C}^+$ is stable due to hyperconjugation but CH_3^+ lacks hyperconjugation stability. 1
(ii) In CCl_4 the C-Cl bonds are covalent which do not furnish Cl^- in solution. 1
(iii) Conc. HNO_3 is added to the sodium extract to decompose cyanide or sulphide of sodium if present. 1

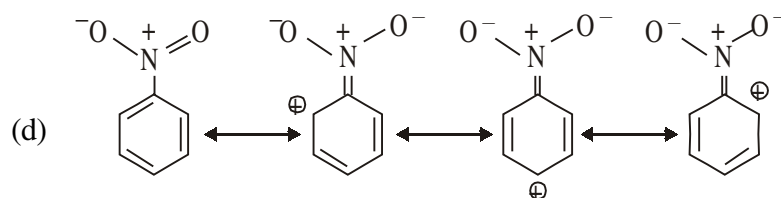
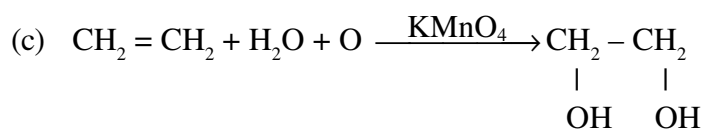
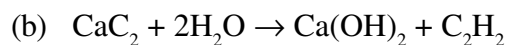
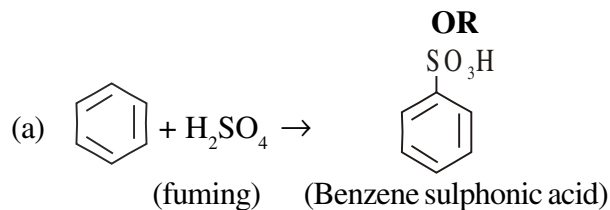


- (b) (i) Position isomers 1
(ii) Geometrical isomers 1

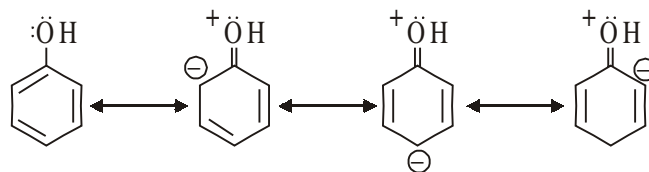


- (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ 1
1-Bromohexane

- (c) The H attached to *sp* hybrid carbon becomes acidic due to high electronegativity of C (*sp* hybridised). 1



The electron density decreases on *o*- and *p*- positions as a result the electrophile attacks on *m*-position.



The electron density increases on *o*- and *p*- positions, therefore electrophile attacks on *o*- and *p*- positions.



SAMPLE PAPER – II

CHEMISTRY – XI

Time allowed : 3 hrs.

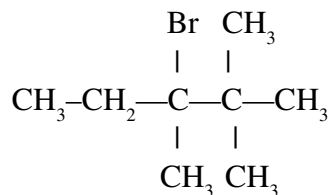
M. M. : 70

General Instructions :

- (i) All questions are compulsory.
 - (ii) Marks for each question are indicated against it.
 - (iii) Question number 1 to 8 are very short answer questions carrying one mark each. Answer these in one word or about one sentence.
 - (iv) Question number 9 to 18 are short answer questions carrying 2 marks each. Answer these in about 30 words.
 - (v) Question number 19 to 27 are also short answer questions carrying 3 marks each. Answer them in about 40 words.
 - (vi) Question number 28 to 30 are long answer questions carrying 5 marks each. Answer them in about 70 words.
 - (vii) Use log tables, if necessary. Use of calculator is not allowed.
-

1. Write the electronic configuration of Cu^+ ($Z = 29$). 1
2. State modern periodic law. 1
3. Give one example of intensive property. 1
4. What would you observe when HCl gas is passed into the saturated solution of NaCl ? 1
5. Calculate oxidation state of Mn in K_2MnO_4 . 1
6. Draw the structure of C_2H_5^+ . 1
7. Which reactive intermediate is formed when the covalent bond in $\text{CH}_3\text{-Li}$ undergoes hetrolytic cleavage ? 1

8. Predict the alkene as a major product obtained by the dehydrohalogenation of : 1



9. A sample of NaOH weighing 0.38 g is dissolved in water and solution is made 50.0 mL in a volumetric flask. Calculate the molarity of the resulting solution. (Molar mass of NaOH = 40 g mol⁻¹) 2
10. Electromagnetic radiation of wavelength of 242 nm is just sufficient to ionise sodium atom. Calculate the ionization enthalpy of sodium in kJ/mol. 2
11. Draw the energy level diagram of molecular orbitals in N₂ molecule. 2
12. On the basis of kinetic theory of gases explain why : 2
- (a) Gases exert pressure.
- (b) The volume of fixed amount of gas at constant pressure increases with the rise in temperature.
13. A student forgot to add the reaction mixture to a flask at 27° C and placed on the flame and heated it to 477° C. What fraction of air has been expelled out ? 2
14. State Le Chatelier principle. Predict the direction of the reaction : 2
- $$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$$
- when noble gas is added to the reaction mixture at constant pressure.
15. Balance the following chemical equation in alkaline medium : 2
- $$\text{I}^- + \text{MnO}_4^- \rightarrow \text{IO}_3^- + \text{MnO}_2$$
16. Contrast the action of heat on the following and explain your answer : 2
- (a) Na₂CO₃ and CaCO₃
- (b) Ca(NO₃)₂ and NaNO₃
17. Write the chemical equations for the following reactions : 2
- (a) Markownikov's rule (b) Friedel-Crafts reaction

OR

Explain the following technique of separation of organic compounds with suitable examples : 2

- (a) Chromatography (b) Differential extraction

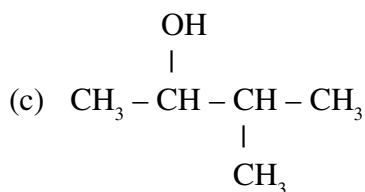
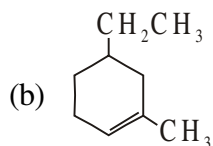
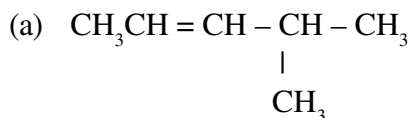
18. (a) Why is fusion of organic compound with sodium metal is essential before performing tests for detection of extra elements in the organic compounds ?
- (b) Write the chemistry involved in the test used for detection of nitrogen.
- 2
19. State Gay-Lussac's law combining volume of gas and Avogadro's law. Standard molar volume of any ideal gas is 22.7 L. Give the values of standard temperature and pressure. 3
20. (a) State Pauli's exclusion principle.
- (b) Which rule will be disobeyed by the following electronic configurations :
- (i) $2s^3$ (ii) $2s^2 2p_x^2 2p_y^1 2p_z^0$ 3
21. Account for the following : 3
- (a) Ionization enthalpy of nitrogen ($Z = 7$) is more than that of oxygen ($Z = 8$).
- (b) Electron gain enthalpy of chlorine ($Z = 17$) is more negative than that of fluorine ($Z = 9$).
- (c) Noble gases have high positive values of electron gain enthalpy.
22. (a) How many sigma (σ) and pi (π) bonds are there in $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$?
- (b) Using VSEPR model to predict the geometrical shapes of the following species :
- (i) ClF_3 (ii) XeF_2 3
23. (a) If water molecules were linear instead of angular, would water (H_2O) be a good solvent as it is ? Why or why not ?
- (b) How is H_2O_2 prepared by hydrated barium peroxide ? Show by chemical reactions that H_2O_2 acts both as oxidising and reducing agent. 3
24. Comment on each of the following observations :
- (a) The mobilities of the alkali metal ions in aqueous solution are $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$.
- (b) Lithium is only alkali metal to form a nitride directly.
- (c) Alkaline earth metals are harder than alkali metals. 3

OR

What happens when : 3

- (a) Sodium metal is dropped in water.
- (b) Sodium metal is heated in free supply of air.
- (c) Sodium peroxide dissolves in water.

25. Write the IUPAC name of the following organic compounds : 3

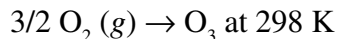


26. K_a for an acid (HA) is 5×10^{-6} . What is the pH of 0.2M solution of HA. Find also the molar concentration of A^- . 3

27. Write the use of green chemistry in the following day to day life processes for decrease in pollution : 3

- (a) Dry cleaning of clothes
- (b) Bleaching of paper
- (c) Synthesis of chemicals

28. (a) Calculate $\Delta_r G^\theta$ for conversion of oxygen to ozone :



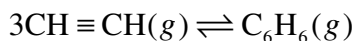
K_p for this conversion is 2.47×10^{-29} .

- (b) State the second law of thermodynamics. How is Gibbs energy change is related with spontaneity of a process ? 5

OR

- (a) Define Gibbs energy.
- (b) Predict the direction in which a reversible reaction will move when $\Delta G = +ve$.

- (c) Using the data given below, calculate the value of $\Delta_r G^\ominus$ and K_p for the following reaction at 298 K :



Assuming ideal gas behaviour, $\Delta_f G^\ominus [\text{CH}\equiv\text{CH}(g)] = 2.09 \times 10^5 \text{ J mol}^{-1}$, $\Delta_f G^\ominus [\text{C}_6\text{H}_6(g)] = 1.24 \times 10^5 \text{ J mol}^{-1}$ and $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. 5

29. (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 and why ?
(ii) PbO_2 is a strong oxidising agent. Assign a reason for this. 5

OR

- (a) Account for the following :
(i) AlCl_3 is a Lewis acid.
(ii) CO_2 is a gas while silicon dioxide is a solid.
(iii) Carbon shows catenation property but Pb does not.
(b) Write the balanced chemical equations for the following reactions :
(i) $\text{NaH} + \text{B}_2\text{H}_6 \rightarrow$
(ii) $\text{BF}_3 + \text{LiH} \rightarrow$
30. (a) Make the following conversions :
(i) Propene to propanal
(ii) 2-Bromopropane from propene
(b) A hydrocarbon 'A' adds one mole of hydrogen in presence of Pt catalyst to form *n*-hexane. When 'A' is oxidised with hot KMnO_4 solution (alkaline), a single carboxylic acid containing three carbon atoms is isolated. Give the structure of 'A' and write chemical equation of reactions involved. 5

OR

- (a) Give one chemical test to distinguish the following pairs :
(i) Ethene and Ethyne (ii) Ethane and Ethene
(b) An alkene $\text{C}_{18}\text{H}_{16}$ on ozonolysis form ozonide which on hydrolysis with Zn dust form an aldehyde and pentan-2-one as products. Draw the structures of alkene and write the chemical reaction involved. 5

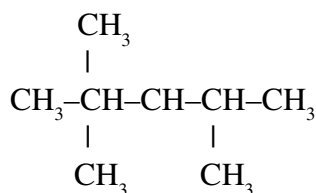
SAMPLE PAPER – III

CHEMISTRY – XI

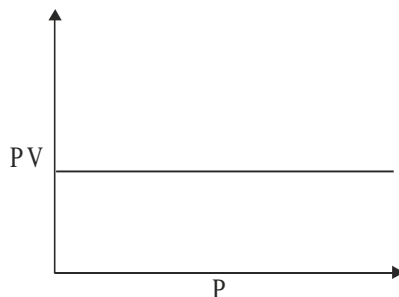
Time allowed : 3 hrs.

M. M. : 70

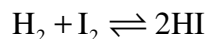
1. Define Avogadro's Law. 1
2. Write the electronic configuration of Cr (At. no. 24). 1
3. Give the IUPAC name of the following : 1



4. Which gas law is proved by the following graph ? 1



5. The equilibrium constant of the following reaction is K_1 . 1



Predict the equilibrium constant of the reverse reaction.

6. Product of the sign of ΔS for the following reaction : 1



7. Can we store CuSO_4 in a zinc vessel ?

Given: $E^0_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$; $E^0_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$ 1

8. How are 0.50M Na_2CO_3 and 0.50 mol Na_2CO_3 different ? 1

9. What do you understand by state functions ? Neither q nor w is a state function but $q + w$ is a state function. Explain. 2

10. (a) Draw the shape of B_2H_6 molecule. What is the hybridisation of B-atoms.
 (b) Why two different B–H bond lengths are observed for this molecule ?
11. Which of the following will have the most negative electron gain enthalpy and which will have the least value ? 2

P, S, Cl, F.

Explain your answer.

12. Balance the following reaction in basic medium : 2



OR

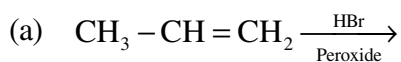
Predict the products of electrolysis in each of the following : 2

- (a) An aqueous solution of $AgNO_3$ with silver electrodes.
 (b) A dilute solution of H_2SO_4 with Pt electrodes.
13. What happens when : 2
- (a) Sodium metal is dropped in water.
 (b) $BaCl_2$ solution is added to sodium sulphate solution.
14. Which method of separation of components of a mixture should be used for the following mixtures : 2
- (a) Mixture of *o*- and *p*-nitrophenol
 (b) A mixture containing two compounds with different solubilities in water.
15. There are four elements named A, B, C and D with atomic numbers $z - 1, z, z + 1, z + 2$ respectively. B is a noble gas. Predict : 2
- (a) Which element possesses the lowest first ionisation enthalpy ?
 (b) Which element possesses the highest electronegativity ?

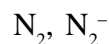
16. Explain the following : 2

- (a) NF_3 has lower dipole moment than that of NH_3 .
 (b) O_2 is paramagnetic in nature.

17. Complete the following reactions : 2



18. (a) Categorise the following as electrophile or nucleophile :
 SO_3 , OH^-
- (b) Write the resonating structures of CH_3COO^- ion. 2
19. (a) Calculate the bond order of the following species and predict their magnetic behaviour :



- (b) According to VSEPR theory, deduce the shape of XeF_4 . 3
20. (a) Write Van der Waal's equation for 1 mole of a gas.
- (b) Pressure of 1g of an ideal gas at 27°C is found to be 2 bar. When 2g of another ideal gas B is introduced in the same flask at same temperature, the pressure becomes 3 bar. Find a relationship between their molecular masses. 3

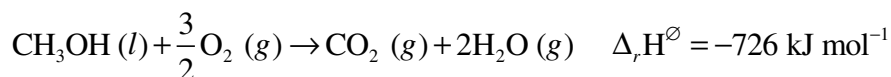
OR

- (a) Calculate the temperature of 4.0 mol of a gas occupying 5dm^3 at 3.32 bar. ($R = 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$). 2
- (b) The Van der Waal's constant of two gases A and B are :

Gas	a ($\text{atm L}^2 \text{ mol}^{-2}$)	b (L mol^{-1})
A	1.6	0.03
B	3.7	0.05

Which of the two gases is more easily liquefied ? 1

21. (a) For an isolated system $\Delta U = 0$, what will be ΔS ? 1
- (b) Calculate the standard enthalpy of formation of $\text{CH}_3\text{OH} (l)$ from the following data :



22. Complete the following reactions : 3
- (i) $\text{PbS} + \text{H}_2\text{O}_2 \rightarrow$
- (ii) $\text{K}_4[\text{Fe}(\text{CN})_6] + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow$
- (iii) $\text{KMnO}_4 + \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow$

23. Arrange the following in increasing order of property indicated against each : 3

(i) BaSO_4 , SrSO_4 , CaSO_4 (Solubility in water)

(ii) Li^+ , Na^+ , K^+ , Rb^+ (Ionic mobility)

(iii) LiCl , NaCl , KCl , RbCl (Ionic character)

24. Explain the following : 3

(a) Graphite is used as a lubricant.

(b) $[\text{SiF}_6]^{2-}$ is known but $[\text{SiCl}_6]^{2-}$ is not.

(c) Ga has smaller atomic radius than Al.

25. A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g CO_2 , 0.690 g H_2O and no other products. A volume of 10.0L (measured at STP) of this welding gas is found to weigh 11.6 g. Calculate :

(a) Empirical formula of welding gas.

(b) Molar mass of the gas.

(c) Its molecular formula.

26. (a) Why 3° Carbocation is more stable than 2° carbocation ?

(b) 0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine present in the compound. (At. mass of Ag = 108u, At. mass of Cl = 35.5u) 3

27. (a) What is the cause of acid rain ?

(b) Define Eutrophication.

(c) What do you mean by Green Chemistry ? 3

28. (a) Carry out the following conversions : 3

(i) Ethanoic acid to Methane

(ii) Benzene to Acetophenone

(b) Why is Wurtz reaction not preferred for preparation of alkanes having odd number of carbon atoms ?

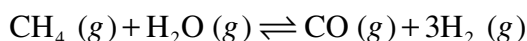
(c) Complete the following reaction :



- (d) Give a chemical test to distinguish between ethane and ethyne. 5

OR

- (a) Give one example of :
(i) Nucleophilic substitution reaction
(ii) Electrophilic aromatic substitution
- (b) Out of staggered and eclipsed conformations on *n*-butane, which is more stable and why ?
- (c) A hydrocarbon 'X' adds one mole of hydrogen in presence of Pt catalyst to form *n*-hexane. When 'X' is oxidised with KMnO_4 , a single carboxylic acid Y containing three carbon atoms is obtained. Identify X and Y. 5
29. (a) Hydrogen gas is obtained from the natural gas by the partial oxidation of natural gas by steam. The reaction is endothermic and can be represented as :



How will the composition of equilibrium mixture affected by :

- (i) Increase in pressure
(ii) Increase in temperature
(iii) Using a catalyst
- (b) Equal volumes of 0.002M solution of NaCl and AgNO_3 are mixed. Will it lead to the precipitation of AgCl ? (K_{sp} of AgCl is 7.4×10^{-8}) 5

OR

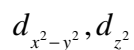
- (a) Classify the following species as Lewis acid or Lewis base :
(i) OH^- (ii) NH_4^+
- (b) A solution of 0.2M sodium nitrite is basic in nature. Give reasons for this observation.
- (c) A 0.2 M solution of formic acid is 3.2% ionised. What is its ionisation constant ?
30. (a) List the quantum numbers (*m* and *l*) for electrons in 3*d* orbitals ?
(b) Write the rule due to which the following electronic configuration for nitrogen is not possible :



- (c) An electron is moving with kinetic energy of 2.275×10^{-25} J. Calculate its de Broglie wavelength. ($h = 6.626 \times 10^{-34}$ JS; $m_e = 9.1 \times 10^{-31}$ kg) 5

OR

- (a) How many sub-shells are associated with $n = 4$? 1
- (b) Give the boundary surface diagrams for the following orbitals: 2



- (c) Calculate the wavelength of a photon emitted during a transition from $n = 5$ state to the $n = 2$ state in the hydrogen atom. The ground state electron energy for H atom is 2.18×10^{-18} J/atom.

