

*PM SHRI KV NO 1 SALT LAKE
SESSION: 2024-25
STUDY MATERIAL
SUBJECT: CHEMISTRY
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STUDY MATERIAL OF CLASS XI CHEMISTRY: SESSION 2023-24

1. Some basic concepts of chemistry

What is chemistry?

Chemistry is the science of molecules and their properties which deals with the study of matter, its composition, the changes that matter undergoes and the relation between changes in composition and changes in energy..

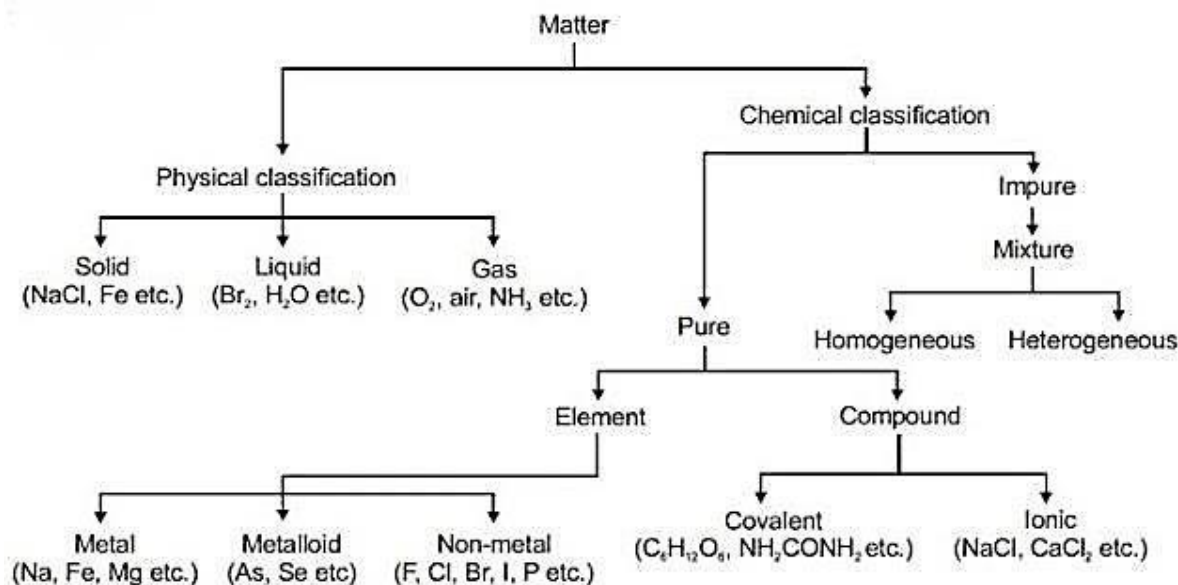
Importance of Chemistry:

Principles of chemistry are applicable in diverse areas, such as weather patterns, functioning of brain and operation of a computer, production in chemical industries, manufacturing **fertilisers, alkalis, acids, salts, dyes, polymers, drugs, soaps, detergents, metals, alloys**, etc., including new material. It also plays an important role in meeting human needs for **food, healthcare products and other material aimed at improving the quality of life.**

Few such examples: **Cisplatin** and **taxol** are effective against cancer therapy whereas **AZT** (Azydithymidine) used against AIDS.

Matter and its nature:

Anything that occupies space, has mass, and can be felt directly by our senses are all matters.

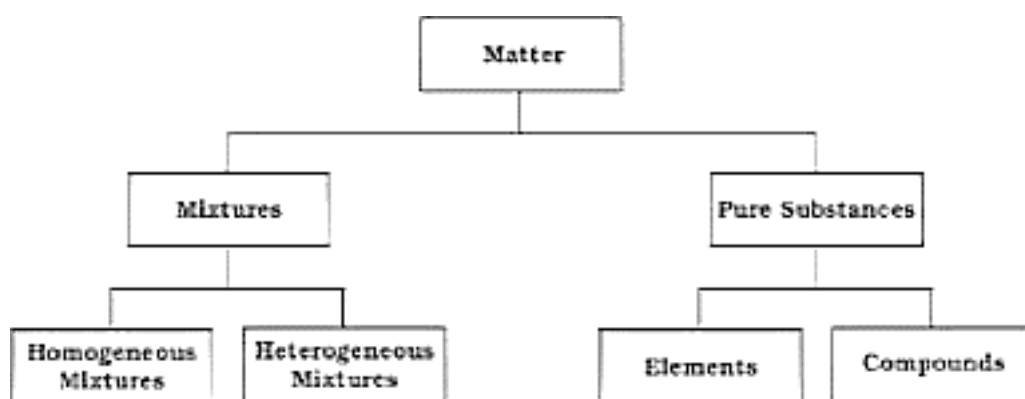


Physical Classification of Matter :

Properties	Solid	Liquid	Gas
1. volume	Definite	Definite	Indefinite
2. Shape	Definite	Indefinite	Indefinite

3. Intermolecular force of attraction	Very high force of attraction	Moderate	Negligible / Very low
4. Arrangement of Molecules	Orderly arranged	Free To move within the volume	Free to move every where
5. Inter molecular Space	Very small Space	Slightly greater	Very great
7. Compressibility	Not compressible	Not compressible	Highly compressible
8. Expansion on Heating	Very little	Very little	Highly expand
9. Rigidity	Very rigid	Not rigid known as fluid	Not rigid known as fluid
9. Fluidity	Can't flow	Can flow	Can flow
10. Diffusion	Hardly	Can diffuse rate of diffusion is rate very fast	Can diffuse rate of diffusion is rate very fast

Chemical Classification of matter---



Elements

An element is the simplest form of matter that cannot be split into simpler substances or built from simpler substances by any ordinary chemical or physical method. There are 118 elements known to us, out of which 92 are naturally occurring. After atomic no. 92, elements are known as synthetic elements, or trans-uranic elements. Elements are further classified into metals, non-metals and metalloids.

Compounds

A compound is a pure substance made up of two or more elements combined in a definite proportion by mass, which could be split by suitable chemical methods.

Characteristics of compound

- Compounds always contain a definite proportion of the elements by mass.
- The properties of compounds are totally different from the elements from which they are formed.
- Compounds are homogeneous.
- Compounds are broadly classified into inorganic and organic compounds. Inorganic compounds are those, which are obtained from non-living sources such as minerals. For example, common salt, marble and limestone. Organic compounds are those, which occur in living sources such as plants and animals. They all contain carbon. Common organic compounds are oils, wax, fats etc.

Mixtures

A mixture is a combination of two or more elements or compounds in any proportion so that the components do not lose their identity. Air is an example of a mixture. Mixtures are of two types, homogeneous and heterogeneous.

Homogeneous mixtures have the same composition throughout the sample. The components of such mixtures cannot be seen under a powerful microscope. They are also called solutions. Examples of homogeneous mixtures are air, sea water, gasoline, brass etc.

Heterogeneous mixtures consist of two or more parts (phases), which have different compositions. These mixtures have visible boundaries of separation between the different constituents and can be seen with the naked eye e.g., sand and salt, chalk powder in water etc.

LAWS OF CHEMICAL COMBINATIONS

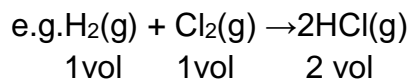
Law of Conservation of Mass (Given by Antoine Lavoisier in 1789). It states that matter (mass) can neither be created nor destroyed.

Law of Definite Proportions or Law of Constant Composition: This law was proposed by Louis Proust in 1799, which states that: 'A chemical compound always consists of the same elements combined together in the same ratio, irrespective of the method of preparation or the source from where it is taken'.

Law of Multiple Proportions Proposed by Dalton in 1803, this law states that:

'When two elements combine to form two or more compounds, then the different masses of one element, which combine with a fixed mass of the other, bear a simple ratio to one another'.

Gay Lussac's Law of Gaseous Volumes (Given by Gay Lussac in 1808.) It states when gases combine or are produced in a chemical reaction they do so in a simple ratio by volume provided all gases are at same temperature and pressure.



All reactants and products have simple ratio 1 : 1 : 2 by volume.

Avogadro Law (In 1811, Given by Avogadro) :According to this law equal volumes of gases at the same temperature and pressure should contain equal number of molecules.

Dalton's Atomic Theory: Postulates

- *All substances are made up of tiny, indivisible particles called atoms. *Atoms of the same element are identical in shape, size, mass and other properties.
- *Atoms of different elements are different in all respects.
- *Atom is the smallest unit that takes part in chemical reactions.
- *Atoms combine with each other in simple whole number ratios to form molecules.
- *Atoms cannot be created, divided or destroyed during any chemical or physical change.

Atoms and Molecules

The smallest particle of an element, which may or may not have independent existence, is called an atom, while the smallest particle of a substance which is capable of independent existence is called a molecule.

Molecules are classified as homoatomic and heteroatomic. Homoatomic molecules are made up of the atoms of the same element and heteroatomic molecules are made up of the atoms of the different element having different atomicity (number of atoms in a molecule of an element) like monoatomic, diatomic, triatomic and polyatomic.

Atomic Mass Unit

One atomic mass unit is defined as a mass exactly equal to one twelfth the mass of one carbon -12 atom. And $1 \text{ amu} = 1.66056 \times 10^{-24} \text{ g}$.

Today, amu 'has been replaced by u' which is known as unified mass.

Atomic Mass

Atomic mass of an element is defined as the average relative mass of an atom of an element as compared to the mass of an atom of carbon -12 taken as 12.

$$\text{Atomic mass} = \frac{\text{mass of an atom}}{1/12 \text{ mass of a carbon atom}(^{12}\text{C})}$$

Gram Atomic Mass

The quantity of an element whose mass in grams is numerically equal to its atomic mass. In simple terms, atomic mass of an element expressed in grams is the gram atomic mass or gram atom.

For example, the atomic mass of oxygen = 16 amu (1 atom)

Therefore gram atomic mass of oxygen = 16 g (1 mole of atoms)

Molecular Mass

Molecular mass of a substance is defined as the average relative mass of its molecule as compared to the mass of an atom of C-12 taken as 12. It expresses as to how many times the molecule of a substance is heavier than 1/12th of the mass of an atom of carbon.

For example, a molecule of carbon dioxide is 44 times heavier than 1/12th of the mass of an atom of carbon. Therefore the molecular mass of CO₂ is 44 amu. It is obtained by adding the atomic masses of all the atoms present in one molecule.

Gram Molecular Mass

A quantity of substance whose mass in grams is numerically equal to its molecular mass is called gram molecular mass. In simple terms, molecular mass of a substance expressed in grams is called gram molecular mass.

e.g., the molecular mass of oxygen = 32 amu

Therefore, gram molecular mass of oxygen = 32 g

Formula Mass

Sum of atomic masses of the elements present in one formula unit of a compound. It is used for the ionic compounds.

Mole Concept

Mole is defined as the amount of a substance, which contains the same number of chemical units (atoms, molecules, ions or electrons) as there are atoms in exactly 12 grams of pure carbon-12.

A mole represents a collection of 6.022×10^{23} (Avogadro's number) chemical units.

The mass of one mole of a substance in grams is called its molar mass.

Molar Volume

The volume occupied by one mole of any substance is called its molar volume. It is denoted by V. One mole of all gaseous substances at 273 K and 1 atm pressure occupies a volume equal to 22.4 litre or 22,400 mL. The unit of molar volume is litre per mol or millilitre per mol.

PERCENTAGE COMPOSITION—

The mass percentage of each constituent element present in any compound is called its percentage composition

$$\text{Mass \% of the element} = \frac{\text{Mass of element in 1 molecule of compound} \times 100}{\text{Molecular mass of the compound}}$$

Empirical Formula and Molecular Formula:

An **empirical formula** represents the simplest whole number ratio of various atoms present in a compound. E.g. CH is the empirical formula of benzene C₆H₆.

The **molecular formula** shows the exact number of different types of atoms present in a molecule of a compound. E.g. C₆H₆ is the molecular formula of benzene.

Relationship between empirical and molecular formulae

The two formulas are related as Molecular formula = n x empirical formula

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

Reactions in Solutions-- The concentration of a solution can be expressed in any of the following ways.

- 1. Mass Percent** is the mass of the solute in grams per 100 grams of the solution.

$$\text{Mass \% of the solute} = \frac{\text{Mass of the solute}}{\text{Mass of the solution}} \times 100$$

A 5 % solution of sodium chloride means that 5 g of NaCl is present in 100g of the solution.

2. Volume percent is the number of units of volume of the solute per 100 units of the volume of solution.

$$\text{Volume \% of the solute} = \frac{\text{Volume of the solute}}{\text{Volume of the solution}} \times 100$$

A 5 % (v/v) solution of ethyl alcohol contains 5 cm³ of alcohol in 100 cm³ of the solution.

3. Molarity of the solution is defined as the number of moles of solute dissolved per litre (dm³) of the solution. It is denoted by the symbol M. Measurements in Molarity can change with the change in temperature because solutions expand or contract accordingly.

$$\text{Molarity of the solution} = \frac{\text{No. of moles of the solute}}{\text{Volume of the solution in litre } V} = \frac{n}{V}$$

In terms of weight, molarity of the substance can be expressed as:

$$\text{Molarity} = \frac{W_g}{M \text{ g mol}^{-1} \times V \text{ litre}} = \frac{W}{M \times V} \text{ mol/L}$$

Molarity equation

To calculate the volume of a definite solution required to prepare solution of other molarity, the following equation is used:

$$M_1V_1 = M_2V_2,$$

where M₁= initial molarity, M₂= molarity of the new solution, V₁= initial volume and V₂= volume of the new solution.

4. Molality- Molality is defined as the number of moles of solute dissolved per 1000 g (1 kg) of solvent. Molality is expressed as 'm'.

$$\text{Molality} = \frac{\text{Moles of the solute}}{\text{Wt. of Solvent (in gm)}} \times 1000$$

5. Mole Fraction is the ratio of number of moles of one component to the total number of moles (solute and solvents) present in the solution. It is expressed as 'x'.

$$\text{Mole fraction of the solute} = \frac{\text{Moles of the solute}}{\text{Moles of solute} + \text{Moles of solvent}}$$

$$\text{Mole fraction of the solvent} = \frac{\text{Moles of the solvent}}{\text{Moles of solute} + \text{Moles of solvent}}$$

$$\text{Mole fraction of the solute} + \text{Mole fraction of solvent} = 1$$

ASSERTION-REASON TYPE QUESTIONS OF 1 MARK EACH

In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question:

(a) Assertion and Reason both are correct and Reason is the correct explanation of Assertion.

(b) Assertion and Reason both are correct statements but Reason is not the correct explanation of Assertion.

(c) Assertion is correct but Reason is wrong.

(d) Assertion is wrong but Reason is correct.

(1) **Assertion:** 1 mole O₂ and N₂ contain have same volume at a same temperature and pressure.

Reason: 1 mole of any gas at STP occupy 22.4 L at STP.

Correct Answer: (b)

(2) **Assertion:** Equal moles of different substances contain same number of constituent particles.

Reason: Equal weights of different substances contain the same number of constituent particles.

Correct Answer: (c)

(3) **Assertion:** The empirical formula of Ethanoic acid is CH_2O .

Reason: Empirical formula gives us exact no. of atoms present in a molecule.

Correct Answer: (c)

(4) **Assertion:** When 2 g hydrogen reacts with 32 g Oxygen to form water, Oxygen is the limiting reagent.

Reason: Limiting reagent is present in lesser amount than stoichiometric amount.

Correct Answer: (d)

(5) **Assertion:** One atomic mass unit is defined as one-twelfth of the mass of one carbon-12 atom.

Reason: Carbon-12 isotope is the most abundant isotope of carbon and has been chosen as the standard.

Correct Answer: (a)

VERY SHORT ANSWER TYPE QUESTIONS OF 1 MARK EACH

(1) Define one mole?

Ans. One mole is the amount of a substance that contains as many particles as there are atoms in exactly 12 g of the carbon-12.

(2) What is the limiting reagent?

Ans. The reactant which gets consumed first or limits the amount of product formed is known as limiting reagent.

(3) Write the empirical formula of the following:

(a) N_2O_4 (b) $\text{C}_6\text{H}_{12}\text{O}_6$ (c) H_2O (d) H_2O_2

Ans. (a) NO_2 (b) CH_2O (c) H_2O (d) HO

(4) Why the atomic masses of most of the elements are fractional?

Hints: Due to isotopic abundance/

(5) Which of the following have largest no. of atoms?

(i) 1 g Au (ii) 1 g Na (iii) 1 g Li (iv) 1 g Cl_2

Hints: 1 g Li as its gram atomic mass is least.

(6) Calculate the molecular mass of the of the following (i) H_2SO_4 (ii) NaOH

Ans: Molar mass of $\text{H}_2\text{SO}_4 = 2 + 32 + 4 \times 16 = 98$ amu

Molar mass of $\text{NaOH} = 23 + 16 + 1 = 40$ amu

(7) What do mean by Mole fraction?

Ans. Mole Fraction is the ratio of number of moles of one component to the total number of moles (solute and solvents) present in the solution. It is expressed as 'x'

(8) Define the law of multiple proportions. Explain it with one example.

Ans. When two elements combine to form two or more compounds, then the different masses of one element, which combine with a fixed mass of the other, bear a simple ratio to one another. For example- carbon combines with oxygen to form two compounds CO and CO_2 .

Compound CO CO_2

Mass of C 12 : 12 So, Mass of O = 16 : 32

Masses of oxygen which combine with a fixed mass of carbon (12g) bear a simple ratio of 16 : 32 or 1 : 2.

(9) How are 0.50 mol Na_2CO_3 and 0.50 M Na_2CO_3 different?

Ans. Molar mass of $\text{Na}_2\text{CO}_3 = 2 \times 23 + 12 + 3 \times 16 = 106$ g / mol

0.50 mol Na_2CO_3 and $0.50 \times 106 = 53$ g

0.50 M Na_2CO_3 means 0.50 mol i.e. 53 g of Na_2CO_3 are present in 1 L of the solution.

(10) What is the law called which deals with the ratios of the volumes of the gaseous reactants and products?

Ans. Gay Lussac's law of gaseous volumes.

(11) What is the difference between molality and molarity?

Ans: Molality is the number of moles of solute present in 1 kg of solvent, whereas molarity is the number of moles of solute dissolved in 1 litre of a solution.

Molality is independent of temperature, whereas molarity depends on temperature

(12) State Avogadro's law.

Ans: According to Avogadro's law, equal volumes of gases at the same temperature and pressure should contain equal number of molecules.

(13) Define one atomic mass unit (amu).

Ans: One atomic mass unit (amu) is defined as a mass exactly equal to one – twelfth the mass of one carbon – 12 atom

(14) At NTP, what will be the volume of molecules of 6.022×10^{23} H_2 ?

Ans: 22.4 Litres

(15) Calculate the number of molecules present in 0.5 moles of CO_2 ?

Ans: The number of molecules in 0.5 moles of O_2 is $6.022 \times 10^{23} \times 0.5 = 3.011 \times 10^{23}$.

MULTIPLE CHOICE QUESTIONS OF ONE MARK EACH

Question No.

1) A chemical equation is balanced according to the law

- (a) Definite proportion (b) Multiple proportion
(b) Avogadro Law (d) Conservation of mass [Correct Response (d)]

2) 1 amu is equal to

- (a) 1.008 g (b) 0.00059 g
(c) 1.66×10^{-24} g (d) 6.023×10^{23} g [Correct Response (c)]

3) Which of the following contain highest number of molecules

- (a) 7 g N_2 (b) 4 g H_2 (c) 8 g O_2 (d) 71 g Cl_2 [Correct Response (b)]

4) The empirical formula and molecular mass of a compound are CH_2O and 180 g respectively. What will be the molecular formula of the compound?

- (a) CH_3COOH (b) HCHO (c) CH_3OH (d) $\text{C}_6\text{H}_{12}\text{O}_6$ [Correct Response (d)]

5) Which of the following is dependent on temperature?

- (a) Molarity (b) Molality
(c) Mole fraction (d) Mass percentage [Correct Response (a)]

6) Which one of the following is not equal with 1 mol O_2

- (a) 16 g Oxygen (b) N_A no of molecules of O_2
(c) 22.4 L of Oxygen gas (d) None of these [Correct Response (a)]

7) One Gram Molecule of Benzene is equal to

- (a) 72 g Benzene (b) 18 g Benzene
(c) 76 g of Benzene (d) 78 g Benzene [Correct Response (d)]

8) A compound was found to contain Nitrogen and Oxygen in the ratio 28 g and 80 g. The formula of the compound is

- (a) NO (b) NO_2 (c) N_2O_5 (d) N_2O_3 Correct Response (c)

9) If the concentration of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in blood is 0.9 g/L, molarity of glucose in blood?

a) 5M b) 50 M c) 0.005 M d) 0.5 M [Correct Response(c)]

10) What is the mass percent of carbon in carbon dioxide?

SHORT ANSWER TYPE QUESTIONS OF 2 MARKS EACH

(1) Differentiate between molarity and molality.

(Hints: Any two differences (i) Unit of Molarity is mol L⁻¹ whereas molality is mol kg⁻¹

(ii) Molarity is temperature dependent whereas molality is independent of temperature

(iii) Definition of molarity and molality

(2) Convert into mole.

(i) 5.6 L of CO₂ at STP

(ii) 10²³ atoms of Na

(Hints (i) 5.6/22.4

(ii) 10²³/6.02x10²³)

(3) Give one example each of a molecule in which empirical formula and molecular formula are (i) same (ii) Different.

Ans:(i) Same molecular formula and empirical formula. Carbon dioxide, both is CO₂.

(ii) When molecular formula and empirical formula are different –

Hydrogen peroxide: molecular formula is H₂O₂ and empirical formula is HO.

(4) How many moles of methane are required to produce 22g CO₂ (g) after combustion?

Ans: According to the chemical equation, CH₄ (g) + 2O₂ (g) → CO₂(g) + 2H₂O (g)

44g CO₂ (g) is obtained from 16 g CH₄ (g).

[∴ 1 mol CO₂(g) is obtained from 1 mol of CH₄(g)]

Number of moles of CO₂ (g) = 22 g CO₂ (g) × 1 /44

= 1/2 mol CO₂ (g) = 0.5 mol CO₂ (g).

Hence, 0.5 mol CO₂ (g) would be obtained from 0.5 mol CH₄ (g) or 0.5 mol of CH₄ (g) would be required to produce 22 g CO₂ (g).

(5) Calculate the molarity of NaOH in the solution prepared by dissolving its 4 g in enough water to form 250 mL of the solution.

Ans: M = 3 mol L⁻¹ Mass of NaCl in 1 L solution = 3 × 58.5 = 175.5 g

Mass of 1L solution = 1000 × 1.25 = 1250 g (since density = 1.25 g mL⁻¹)

Mass of water in solution = 1250 – 175.5 = 1074.5 g

Molality = No. of moles of solute/Mass of solvent in kg = 3 mol/1.0745 kg = 2.79 m

LONG ANSWER TYPE QUESTIONS CARRYING THREE MARKS EACH

(1) A compound on analysis was found to contain C = 34.6%, H = 3.85% and O = 61.55%. Calculate the empirical formula.

(Hints: Step 1 Calculating relative no. in moles for each atom e.g., C=34.6/12=2.88

H = 3.85 / 1 = 3.85 O = 61.55 / 16 = 3.85

Step-2 Relative whole No. of atoms **C:H:O = 2.88:3.85:3.85 = 1:1.33:1.33=3:4:4**

Hence Empirical formula of the compound **C₃H₄O₄**

(2) What is the percentage of carbon, hydrogen and oxygen in ethanol?

Ans. Molecular formula of ethanol is : C₂H₅OH

Molar mass of ethanol is : (212.01 + 61.008 + 16.00) g = 46.068 g Mass per cent of

carbon = (24.02g / 46.068g) × 100 = 52.14%

Mass per cent of hydrogen = (6.048g / 46.068 g) × 100 = 13.13%

Mass per cent of oxygen = (16.00 g / 46.068g) × 100 = 34.73%

(3) What do mean by molarity. Calculate the molarity of NaOH in the solution prepared by dissolving its 4 g in enough water to form 250 mL of the solution.

Ans. The number of moles of solute dissolved per litre (dm³) of the solution is called molarity.

Since molarity (M) = No. of moles of solute / Volume of solution in litres
= (Mass of NaOH / Molar mass of NaOH) / 0.250 L

= (4g / 40g 0.1 mol) / 0.250L = 0.1 mol / 0.250 L = 0.4 mol L⁻¹ = 0.4 M

2. STRUCTURE OF ATOM

Atomic Number: The number of protons present in the nucleus is equal to the atomic number (z). In order to keep the electrical neutrality, the number of electrons in an atom is equal to the number of protons (atomic number, z)

Atomic Number (z) = Number of protons in the nucleus of an atom = Number of electrons in a neutral atom

Mass Number: Number of protons and neutrons present in the nucleus are collectively known as nucleons. The total number of nucleons is termed as mass number (A) of the atom.

Mass Number (A) = Number of protons (p) + Number of neutrons (n).

Isotopes: Atoms with identical atomic number but different atomic mass number are known as Isotopes. Isotopes of Hydrogen: protium 1_1H , deuterium 2_1H and tritium 3_1H .

Isobars: Isobars are the atoms with same mass number but different atomic number for Example: ${}^{14}_6C$, ${}^{14}_7N$

(i) **Dual character of the electromagnetic radiation** which means that radiations possess both wave like and particle like properties.

(ii) Experimental results regarding atomic spectra which can be explained only by assuming quantized electronic energy levels in atoms.

Characteristics of a Wave

(i) **Wavelength (λ):** It is defined as the distance between any two consecutive crests or troughs. It is represented by λ and its S.I. unit is metre (m).

(ii) **Frequency (ν):** Frequency of a wave is defined as the number of waves passing through a point in one second. It is represented by ν (nu) and is expressed in Hertz (Hz). 1 Hz = 1 cycle/sec.

(iii) **Velocity:** Velocity of a wave is defined as the linear distance travelled by the wave in one second. It is represented by c and is expressed in cm/sec or m/sec.

$$c = \nu \lambda$$

(v) **Amplitude:** Amplitude of a wave is the height of the crest or the depth of the trough. It is represented by V and is expressed in the units of length.

(vi) **Wave Number :** It is defined as the number of waves present in 1 metre length. Evidently it will be equal to the reciprocal of the wavelength. It is represented by $\bar{\nu}$ (read as nu bar).
$$\bar{\nu} = \frac{1}{\text{wave length}}$$

Electromagnetic Spectrum: When electromagnetic radiations are arranged in order of their increasing wavelengths or decreasing frequencies, the complete spectrum obtained is called electromagnetic spectrum.

Limitations of Electromagnetic Wave Theory Electromagnetic wave theory was successful in explaining properties of light such as interference diffraction etc; but it could not explain the following:

- (i) The phenomenon of black body radiation.
- (ii) The photoelectric effect.
- (iii) The variation of heat capacity of solids as a function of temperature.

Atomic spectrum: When a ray of white light is passed through a prism, we get a series of colored bands called spectrum. This spectrum is called continuous spectrum, because here violet merges into blue, blue into green and so on.

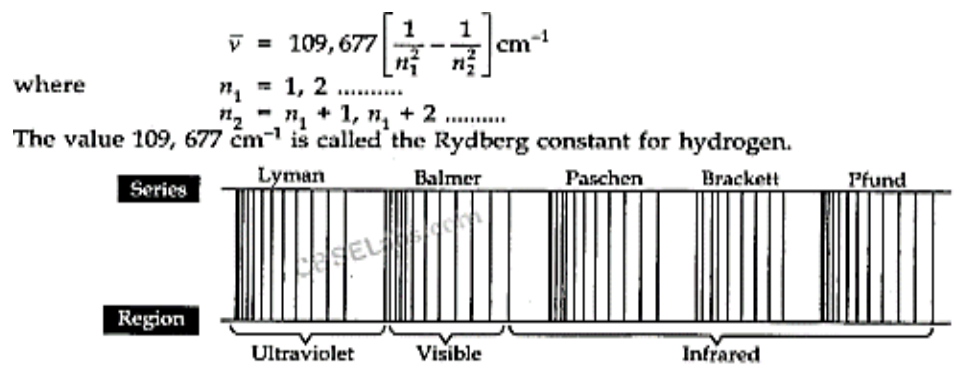
Emission and Absorption Spectra

Emission Spectra: Emission Spectra is noticed when the radiations emitted from a source are passed through a prism and then received on the photographic plate. Radiations can be emitted in a number of ways such as: (i) from sun or glowing electric bulb. (ii) by passing electric discharge through a gas at low pressure. (iii) by heating a substance to high temperature. The emission spectra of atoms in the gas phase do not form a continuous spectrum.

Absorption Spectra: When white light is passed through the vapours of a substance and the transmitted light is then allowed to strike a prism, dark lines appear in the otherwise continuous spectrum. The dark lines indicate that the radiations corresponding to them were absorbed by the substance from the white light. This spectrum is called absorption spectrum. Dark lines appear exactly at the same positions where the lines in the emission spectra appear.

Each element has a unique line emission spectrum. So, line emission spectra are also called finger print of atoms.

Line Spectrum of Hydrogen: When electric discharge is passed through hydrogen gas enclosed in discharge tube under low pressure and the emitted light is analyzed by a spectroscope, the spectrum consists of a large number of lines which are grouped into different series. The complete spectrum is known as hydrogen spectrum.



On the basis of experimental observations, Johannes Rydberg noted that all series of lines in the hydrogen spectrum could be described by the following expression: where Z is the atomic number of the species.

Here R_H = constant, called Rydberg constant for hydrogen and n_1, n_2 are integers from which electrons jumps ($n_2 > n_1$) For any particular series, the value of n_1 is constant while that of n_2 changes. For example,

Name of series	Region	n_1	n_2
Lyman series	Ultra violet	1	2, 3, 4, 5.....∞
Balmer series,	Visible	2	3, 4, 5, 6.....∞
Paschen series	Infrared	3	4, 5, 6, 7.....∞
Brackett series	Infrared	4	5, 6, 7, 8.....∞
Pfund series	Infrared	5	6, 7, 8,∞

Thus, by substituting the values of n_1 and n_2 in the above equation, wavelengths and wave number of different spectral lines can be calculated. When $n_1 = 2$, the

expression given above is called Balmer's formula.

Rydberg Equation

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

$R_H = 109,678 \text{ cm}^{-1}$ = Rydberg constant
 λ = wavelength of light emitted
 n_1 & n_2 = whole numbers (integers) from 1 to ∞ where $n_2 > n_1$
 If $n_1 = 1$, then $n_2 = 2, 3, 4, \dots$

} Corresponds to allowed energy levels for atom

the maximum no. of lines of H atom from n^{th} orbit = $\frac{n(n-1)}{2}$ (For $n = 6$ no. of H lines = 15)

$$E = h\nu = \frac{hc}{\lambda} \text{ (for 1 quantum or 1 photon)}$$

$$\& E = n h\nu = \frac{nhc}{\lambda} \text{ (for } n \text{ quanta or } n \text{ photons) where } h = \text{Planck's constant} = 6.6 \times 10^{-31} \text{ Js}$$

Bohr's Model of Atom

Niels Bohr in 1913, proposed a new model of atom on the basis of Planck's Quantum Theory.

The main postulates of this model are as follows:

- (i) In an atom, the electrons revolve around the nucleus in certain definite circular paths called orbits.
- (ii) Each orbit is associated with definite energy and therefore these are known as energy levels or energy shells. These are numbered as 1, 2, 3, 4,..... or K, L, M, N,.....
- (iii) As long as electron is present in a particular orbit, it neither absorbs nor loses energy and its energy, therefore, remains constant.
- (iv) When energy is supplied to an electron, it absorbs energy only in fixed amounts as quanta and jumps to higher energy state away from the nucleus known as excited state. The excited state is unstable, the electron may jump back to the lower energy state and in doing so, it emits the same amount of energy.

The energy change $\Delta E = E_2 - E_1 = h\nu = \frac{hc}{\lambda}$ or, $\lambda = \frac{hc}{\Delta E}$

- (v) Those orbits are permitted for the electron in which angular momentum of the electron is a whole number multiple of $\frac{h}{2\pi}$. Angular momentum of electron, $mvr = \frac{nh}{2\pi}$ ($n = 1, 2, 3, 4$ etc).

Dual Behavior of Matter (de Broglie Equation) de Broglie in 1924, proposed that matter, like radiation, should also exhibit dual behavior i.e., both particle like and wave like properties. This means that like photons, electrons also have momentum as well as wavelength.

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

Heisenberg's Uncertainty Principle It states that,

"It is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron".

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}, \quad \Delta x \cdot m\Delta v \geq \frac{h}{4\pi}, \quad \Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$$

Significance of Uncertainty Principle (i) It rules out existence of definite paths or trajectories of electrons and other similar particles.

(ii) The effect of Heisenberg's uncertainty principle is significant only for microscopic objects and is negligible for macroscopic objects.

Reasons for the Failure of Bohr Model (i) The wave character of the electron is not considered in Bohr Model. (ii) According to Bohr Model an orbit is a clearly defined path and this path can completely be defined only if both the position and the velocity of the electron are known exactly at the same time. This is not possible according to the Heisenberg's uncertainty principle.

Quantum Mechanical Model of Atom Quantum mechanics: Quantum mechanics is a theoretical science that deals with the study of the motions of the microscopic objects that have both observable wave like and particle like properties.

Quantum Numbers Atomic orbitals can be specified by giving their corresponding energies and angular momentums which are quantized (i.e., they have specific values). The quantized values can be expressed in terms of quantum number. These are used to get complete information about electron i.e., its location, energy, spin etc.

The principal quantum number (n) gives us the following information:

1. It gives the size the orbit.
2. It gives the energy of electron in an orbit.
3. It gives the shell in which the electron is found.
4. It also gives the average distance between the electron and the nucleus. As the value of n increases, the distance between the electron and the nucleus also increases. The possible values of n are 1, 2, 3, 4, 5 etc. If $n = 1$ the electron is in K shell $n = 2$ the electron is in L shell $n = 3$ the electron is in M shell and so on.
5. The maximum number of electrons in the shell with principal quantum number n is equal to $2n^2$.

Azimuthal or Subsidiary or Orbital Angular Quantum Number (l) The following information's are obtained from l .

1. It gives the shape of the orbital.
2. It gives the sub shell or sub level in which the electron is located.
3. It also gives the orbital angular momentum of the electron.
4. the values of $l = 0$ to $(n-1)$ The number of sub shells in a principal shell is equal to the value of n . For example,
When $n = 1, l = 0$. i.e. K shell contains only one sub shell : 1s sub shell
when $n = 2, l = 0$ and 1. i.e. L shell contains two sub shells: 2s and 2p sub shells
when $n = 3, l = 0, 1$ and 2. i.e. M shell contains three sub shells: 3s, 3p and 3d sub shells
when $n = 4, l = 0, 1, 2$ and 3. i.e. N shell contains four sub shells : 4s, 4p, 4d and 4f sub shells
5. the number of electrons that can be accommodated in sub-energy level is equal to $2(2l+1)$.

If $l = 0$ for s orbital then $= 2(2 \times 0 + 1) = 2$ electrons

If $l = 1$ for p orbital then $= 2(2 \times 1 + 1) = 6$ electrons

If $l = 2$ for d orbital then $= 2(2 \times 2 + 1) = 10$ electrons

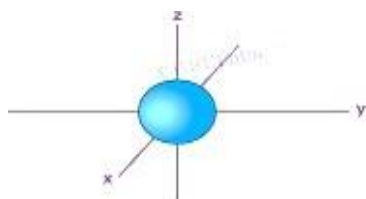
if $l = 3$ for f orbital then $= 2(2 \times 3 + 1) = 14$ electrons

Magnetic Orbital Quantum Number (m or m_l)

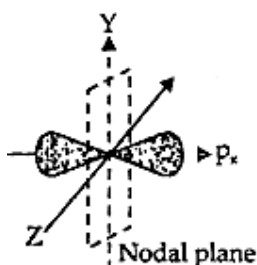
1. The magnetic orbital quantum number determines the number of preferred orientations of the electrons present in a sub-shell.
2. The magnetic quantum number is denoted by letter m and for a given value of l , it can have all the values ranging from $-l$ to $+l$ including zero. Thus, for energy value of l , m has $2l + 1$ values. For example, For, $l = 0$ (s-sub-shell), m can have only one value i.e., $m = 0$. This means that s-sub-shell has only one orientation in space. In other words, s-subshell has only one orbital called s-orbital.

Spin Quantum Number (S or m_s) This quantum number helps to explain the magnetic properties of the substances. A spinning electron behaves like a micro-magnet with a definite magnetic moment. If an orbital contains two electrons, the two magnetic moments oppose and cancel each other.

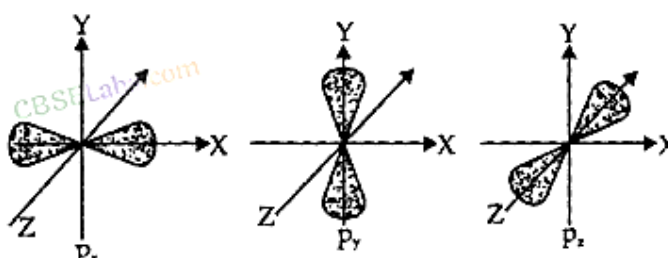
- **Shapes of s-orbitals** s-orbital with only one orientation has a spherical shape with uniform electron density along all the three axes.



Shapes of p-orbitals p-orbitals are present in the p-subshell for which $l = 1$ and m_l can have three possible orientations $-1, 0, +1$. Thus, there are three orbitals in the p-subshell which are designated as p_x, p_y and p_z orbitals depending upon the axis along which they are directed. The general shape of a p-orbital is dumb-bell consisting of two portions known as lobes. Moreover, there is a plane passing through the nucleus along which finding of the electron density is almost nil. This is known as nodal plane as shown in the fig.

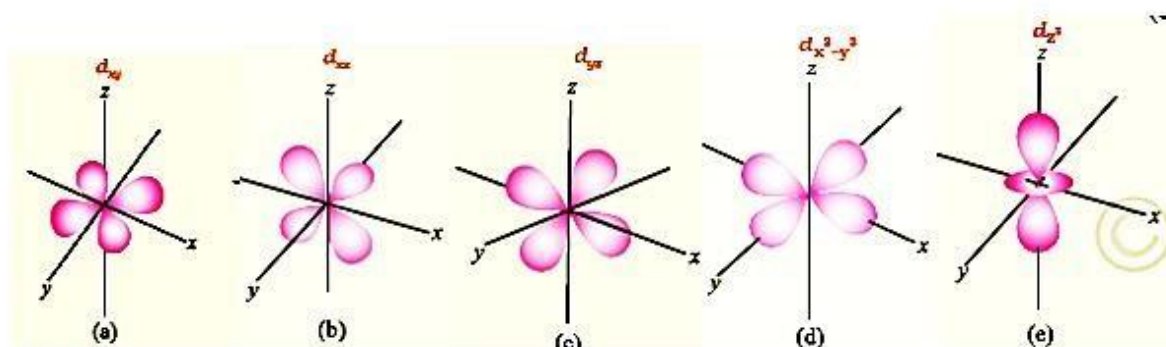


General shape of p-orbital



Shapes of $2p_x, 2p_y$ and $2p_z$ orbitals.

- **Shapes of d-orbitals** For d-orbitals, $l = 2$ and $m_l = -2, -1, 0, +1$ and $+2$. i.e., there are five possible orientations for d orbitals. So there are 5 types of d orbitals. They are $d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}$ and d_{z^2} . The shapes of the first four d orbitals are double dumb-bell and that of the fifth one, d_{z^2} , is dumb-bell having a circular collar in the XY plane. The five d-orbitals have equivalent energies. For d orbitals the number of radial nodes is 2 and the total number of nodes is $n-1$. Boundary surface diagrams for d-orbitals are as follows.



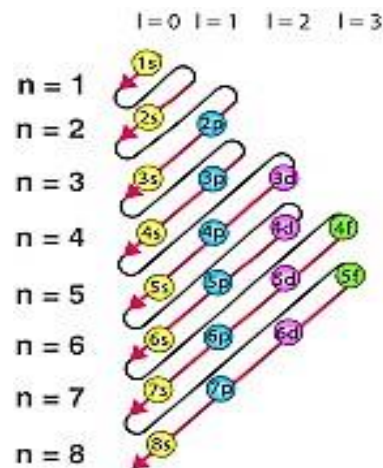
Number of radial nodes = $n - l - 1$ Number of angular nodes = l
 Total number of nodes = $n - 1$

Electronic Configuration of Atoms The distribution of electrons into orbitals of an atom is called its electronic configuration. The electronic configuration is explained

based on Aufbau principle, Hund's rule, Pauli's exclusion principle and stability concept.

- Aufbau principle:** The principle states: In the ground state of the atoms, the orbitals are filled in order of their increasing energies. In other words, electrons first occupy the lowest energy orbital available to them and enter into higher energy orbitals only after the lower energy orbitals are filled. This rule has two sub rules: a) The various orbitals are filled in the increasing order of their $(n+l)$ value. b) If two orbitals have the same $(n+l)$ values, the orbital with the lower n value is filled first. The increasing order of orbitals is as follows.

The order in which the energies of the orbitals increase and hence the order in which the orbitals are filled is as follows:
 $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p...$



(2) Pauli Exclusion Principle: According to this principle, **no two electrons in the orbitals of an atom can have the same set of four quantum numbers.**

Pauli exclusion principle can also be stated as: "Only two electrons may exist in the same orbital and these electrons must have opposite spins".

Example: Let e_1 and e_2 are two atoms of an atom

Let, for e_1 , $n = 4, l = 0, m_l = 0$ & $m_s = +\frac{1}{2}$

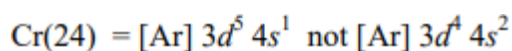
For e_2 , $n = 4, l = 0, m_l = 0$ & $m_s = -\frac{1}{2}$. i.e., here m_s cannot be $+\frac{1}{2}$ otherwise the two electrons will be of same spin & will repel each other & cannot exist in an orbital.

(3) Hund's rule of maximum multiplicity: It states that: pairing of electrons in the orbitals belonging to the same sub-shell (p, d or f) does not take place until each orbital belonging to that sub-shell has got one electron each with parallel spin. For example the electronic configuration of N is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ and not $1s^2 2s^2 2p_x^2$.

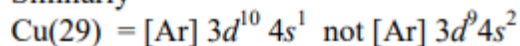
$2p_y^1$. Example:



Stability of Completely Filled and Half-Filled Subshells: For atoms having half-filled or completely filled electronic configurations have extra stability compared to other atoms. This is due to their symmetrical distribution of electrons and greater exchange energy. For example, the electronic configuration of Cr is $[\text{Ar}] 3d^5 4s^1$ and not $3d^4 4s^2$. This is because d^5 represents a half filled configuration and has extra stability. Similarly for Cu the electronic configuration is $[\text{Ar}] 3d^{10} 4s^1$ and not $3d^9 4s^2$.



Similarly



Example: Copper: ${}_{29}\text{Cu}$ (29e) \rightarrow Expected Elect. Conf. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$
(Partially filled $3d^9$)

Copper: Cu (Correct Elect. Conf.) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$ (Fully filled elec. conf.) → more stable.

So, the correct electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

Assertion - Reason Questions

In the following questions (1 to 5), a statement of assertion is followed by a corresponding statement of reason. Of the following statements, choose the correct one:

- A. Both assertion and reason are correct statements and reason is the correct explanation of the assertion.
- B. Both assertion and reason are correct statements and reason is not the correct explanation of the assertion.
- C. Assertion is correct but reason is incorrect statement.
- D. Assertion is incorrect but reason is correct statement.

1 Assertion: Bohr model of atom fails in case of multi electron species.
Reason: It does not mention electron-electron repulsion.

Answer B

2 Assertion: Both position and momentum of an electron cannot be determined simultaneously with maximum accuracy.

Reason: The path of an electron in an atom is clearly defined.

Answer C

3 Assertion: According to Thomson model of atom, mass of the atom is assumed to be uniformly distributed over the atom.

Reason: According to Thomson model of atom, positive charge is concentrated in the centre of the atom.

Answer C

4 Assertion: Electronic configuration of helium is $1S^2$.

Reason: Hund's rule demands that the configuration should display maximum stability.

Answer B

5 Assertion: The outer electronic configuration of Cr and Cu are $3d^5 4s^1$ and $3d^{10} 4s^1$ respectively.

Reason: Electrons are filled in orbitals in order of increasing energies given by (n+l) rule.

Answer B

Very Short Answer Questions(one word or one sentence)(One mark questions)

1 In the multi-electronic atoms, indicate the orbital which has lower energy? 4s or 3d?

Answer: 4s

2 How many unpaired electrons are present in zinc?

Answer: It has no unpaired electrons.

3 Write the electronic configuration of an element having atomic number 25.

Answer Mn- $[Ar]^{18} 4s^2 3d^5$

4 Write de Broglie relation.

Answer: $\lambda = h/mv$ (symbols have their usual significance).

5 Write the mathematical form of Heisenberg Uncertainty Principle.

Answer: $\Delta x \cdot \Delta p \geq h/4\pi$ (symbols have their usual significance).

6 State one defect of Bohr model of atom.

Answer: It can not explain Stark effect.

7 Is an electron stationary in stationary energy state?

Answer: No, the electron is not stationary. Only the energy associated with it is stationary.

8: State one point of Planck's Quantum theory.

Answer: Atoms and molecules could emit or absorb energy only in discrete quantities and not in a continuous manner.

OR

The energy (E) of a quantum of radiation is proportional to its frequency and is given by : $E = h\nu$ ($h = \text{planck constant} = 6.626 \times 10^{-34} \text{Js}$), $\nu(\text{neu}) = \text{frequency}$.

9 State Pauli's exclusion principle.

Answer: No two electrons can have all the four quantum numbers same.

10 State all the four quantum numbers.

Answer: Principal quantum numbers, Azimuthal quantum numbers, magnetic quantum number and spin quantum number.

11 Explain why atoms with half-filled and completely filled orbitals have extra stability?

Answer: Due to exchange energy and symmetry.

12 Which quantum number specifies the shape of an orbital?

Answer: Azimuthal quantum number.

13 Which of the following orbitals are not possible?

2s, 2p, 3f, 3d.

Answer: 3f

14 What do you understand by Hund's rule?

Answer: For the orbitals like p, d, f which have degenerate states, the pairing of electrons take place after all the orbitals getting singly filled.

15 What are the shapes of the following orbitals: d_{xy} and d_{z^2} .

Answer: d_{xy} has clover leaf shape (double dumb-bell) and d_{z^2} has dough-nut shape.

Multiple Choice Questions (Single correct option)

1 A p-orbital can accommodate up to :

- A) four electrons B) six electrons
C) two electrons with parallel spin D) two electrons with opposite spins

Answer: B

2 Principal quantum number of an atom is related to the:

- A) size of the orbital B) spin angular momentum
C) orientation of the orbital in space D) orbital angular momentum

Answer: A

3 Quantum numbers $n = 2, l = 1$ represent:

- A) 1s orbital B) 2s orbital C) 2p orbital D) 3d orbital

Answer: C

4 For principal quantum number $n = 4$, the total number of orbitals having $l = 3$ is : A) 3 B) 7 C) 5 D) 9

Answer: B

5 The electronic configuration of titanium is :

- A) $[\text{Ar}]^{18}4s^23d^1$ B) $[\text{Ar}]^{18}4s^23d^3$ C) $[\text{Ar}]^{18}4s^23d^2$ D) $[\text{Ar}]^{18}4s^24p^2$

Answer C

- 6 Which expression represents de Broglie relationship:
 A) $h/mv = p$ B) $\lambda = h/mv$ C) $\lambda = h/mp$ D) $\lambda m = v/p$

Answer: B

- 7 Which of the following series of transitions in the spectrum of hydrogen falls in visible region ?

- A) Paschen series B) Lyman series C) Balmer series D) Brackett series

Answer: C

- 8 Which one of the following statements rules out the existence of definite paths of electrons and other similar particles?

- A) Pauli's exclusion principle B) de Broglie relationship
 C) Aufbau principle D) Heisenberg Uncertainty Principle

Answer: D

- 9 Rutherford's gold foil experiment drew the following conclusion:

- A) mass of the atom is assumed to be uniformly distributed over the atom
 B) an atom possesses a spherical shape in which the positive charge is uniformly distributed
 C) most of the space in the atom is empty
 D) none of these

Answer: C

- 10 Half-filled and completely filled shells have extra stability due to :

- A) Pauli's exclusion principle B) Hund's rule
 C) Symmetrical distribution of electrons and exchange energy
 D) Aufbau principle

Answer: C

Section-C: Two Marks Questions

- 1 State two postulates of Bohr model of atom.

Answer: Bohr's postulates of hydrogen atom:

- a. The electrons revolve around the nucleus in some selected permissible orbits called stationary orbits.
 b. The angular momentum of an electron in a stationary state is an integral multiple of $h/2\pi$ ($mvr = nh/2\pi$). The symbols have their usual significances.

- 2 Explain Pauli's exclusion principle with an example.

Answer: Pauli's exclusion principle: No two electrons can have all the four quantum numbers same.

Example: For Helium the three quantum numbers are same but fourth quantum number (spin quantum number) is different.

E.C. of He: $1s^2$

For 1st electron, $n=1, l=0, m=0$ and $s=+1/2$.

For 2nd electron $n=1, l=0, m=0$ and $s=-1/2$.

- 3 Which one of the following electronic configurations is correct for chromium? a) $[Ar]^{18} 4s^2 3d^4$ or b) $[Ar]^{18} 4s^1 3d^5$?

Justify your answer.

Answer: b) $[Ar]^{18} 4s^1 3d^5$ is correct as half-filled orbitals are more stable than nearly half-filled orbitals due to exchange energy and more symmetry.

- 4 Out of the following, which electronic configurations is correct for nitrogen?

Give reason in support of your answer.
 a) $1s^2 2s^2 2p_x^1 2p_y^2 2p_z^0$ b) $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^0$

c) $1s^2 2s^2 2p_x^1 2p_y^2 2p_z^0$
 Answer: a) $1s^2 2s^2 2p_x^1 2p_y^2 2p_z^0$ is correct.

Reason: According to Hund's rule, for the orbitals like p,d,f which have degenerate states, the pairing of electrons take place after all the orbitals getting singly filled.

5 Designate the orbitals using s, p, d and f notations which are applicable:

a) $n=4, l=2$ b) $n=5, l=1$

Answer a) 4d b) 5p.

6 Write the electronic configuration of the following ions?

a) Na^+ b) O^{2-}

Answer: a) Configuration of $\text{Na} = 1s^2 2s^2 2p^6 3s^1$ and $\text{Na}^+ = 1s^2 2s^2 2p^6$

b) Configuration of $\text{O} = 1s^2 2s^2 2p^4$ and $\text{O}^{2-} = 1s^2 2s^2 2p^6$

Three marks Questions

1a) Write de Broglie equation.

b) What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 meter per second. Given : Planck's constant (h) = 6.626×10^{-34} Js.

Answer a): de Broglie equation: $\lambda = h/mv$ (symbols have usual significances).

b) According to de Broglie equation: $\lambda = h/mv$

Given: $h = 6.626 \times 10^{-34}$ Js, $m = 0.1$ kg, $v = 10$ m s^{-1}

$\lambda = h/mv = (6.626 \times 10^{-34}) / (0.1 \times 10) = 6.626 \times 10^{-34}$ m.

2 Write the significance (one point) of each of the following:

a) Principal quantum number b) Azimuthal quantum number

c) Magnetic quantum number.

Answer: Significance of principal Quantum number(n): The principal quantum number determines the size and to large extent the energy of the orbital. It also identifies the shell.

Significance of azimuthal Quantum number(l): It defines the 3-dimensional shape of the orbital.

Significance of magnetic Quantum number(m): It gives information about the spatial orientation of the orbital with respect to standard set of co-ordinate axis.

3 State the following: a) Aufbau principle, b) Hund's rule of maximum multiplicity c) Heisenberg Uncertainty principle.

Answer: a) Aufbau principle: In the ground state of the atoms, the orbitals are filled with electrons in order of their increasing energies.

It means the lower energy orbitals are filled first followed by higher energy orbitals.

b) Hund's rule of maximum multiplicity:

In the orbitals like p, d, f etc which have degenerate states, the pairing of electrons takes place after all the orbitals getting singly filled.

c) Heisenberg Uncertainty principle: It is impossible to determine simultaneously the exact position and exact momentum or velocity of subatomic particles like electrons.

4a) The uncertainty in the position of a moving bullet of mass 10 g is 10^{-5} m.

Calculate the uncertainty in its velocity.

(Given : $h = 6.626 \times 10^{-34}$ Js).

Answer: According to Heisenberg Uncertainty principle :

$$\Delta x \cdot \Delta p \geq h/4\pi$$

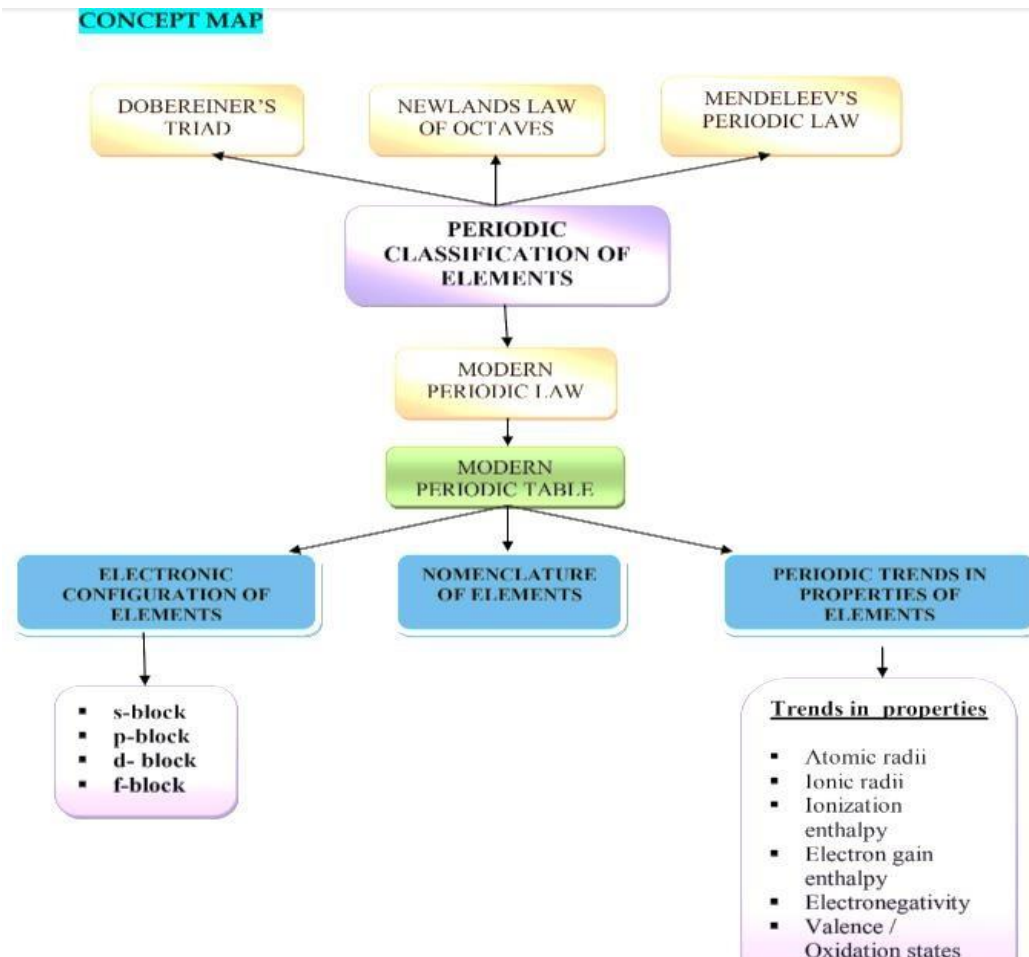
$$\Delta x \cdot m(\Delta v) \geq h/4\pi$$

Given: $h = 6.626 \times 10^{-34}$ Js, $\Delta x = 10^{-5}$ m, $m = 10$ g = 10^{-2} kg .

$$\Delta v = h / 4\pi m(\Delta x)$$

$$\Delta v = (6.626 \times 10^{-34}) / (4 \times 3.14 \times 10^{-2} \times 10^{-5}) = 5.27 \times 10^{-28} \text{ ms}^{-1} \text{ (Ans)}$$

3: CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES



1. INTRODUCTION

'Periodic table may be defined as the table which classifies all the known elements in accordance with their properties in such a way that elements with similar properties are grouped together in the same vertical column and dissimilar elements are separated from one another'.

2. DEVELOPMENT OF THE PERIODIC TABLE

All the earlier attempts of classification of elements were based upon their atomic weights.

J.W. Dobernier in 1829 classified the known elements in groups of three on the basis of similarities in their properties. These groups were called triads. In the triads:

- > Properties of elements in each triad were similar
- > Elements in the triad were arranged in the order of increasing atomic weights such that the atomic-mass of middle element was approximately equal to the arithmetic mean of the other two elements

Elements	Li	Na	K	
At.mass	7	23	39	$7 + 39 / 2 = 23$

New Lands Law of octaves: When elements were arranged in order of their increasing relative atomic masses. The properties of every eight elements were similar to the first one, like the eighth note of a musical scale. This repetition in the properties of elements is just like the repetition of eighth note in an octave of music. This arrangement of elements is called as Newland's law of Octave.

Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K	Ca					

This classification worked quite well for the lighter elements but it failed in case of heavier elements and therefore, discarded.

MENDELEEV'S PERIODIC LAW:

The law states that "The properties of elements are periodic function of their atomic weights."

Features of Mendeleev's periodic law are as follows:

- All 63 elements then known were arranged in an increasing order of their atomic masses; in such a way that elements with similar properties come under the same vertical column. Horizontal rows were called as Periods and vertical columns as groups.
- There were eight groups and a zero group and seven periods.
- Group I to group VII were further divided into two sub-groups A and B. Group VIII had nine elements in three sets containing three elements each.
- There were 7 periods in the table which were numbered as 1,2, 3, 4, 5, 6 and 7.
- The first 6 periods were complete while the seventh was incomplete.

• Merits of Mendeleev's periodic classification:-

- Properties of elements could be easily studied because elements present in same sub-group showed similar properties.
- Mendeleev considered similarities in properties of elements rather than atomic masses. So he corrected the atomic mass of some elements.
- Prediction of the existence and properties of new elements – Mendeleev left some gaps in his periodic table and he also predicted the properties of new elements which were undiscovered. E.g. Gaps were left below Aluminium and Silicon for the undiscovered elements. They were named as Eka-Aluminium and Eka-Silicon. These elements were further discovered as Gallium and Germanium.
- The inert gases when discovered were placed as a separate group without upsetting the order of other elements.

Demerits of Mendeleev's periodic Classification:-

- Position of Hydrogen – Position of Hydrogen was not clear in the Mendeleev's periodic table, because it has properties similar to alkali metals of first group and halogens of seventh group.
- Position of Isotopes – Isotopes of an element have different atomic masses, so according to increasing order of atomic masses, they should be placed in different groups .
- Some elements with higher atomic masses were placed before elements with lower atomic masses. e.g. (i) Ar⁴⁰, K³⁹ (ii) Co^{59.9}, Ni^{58.6}
All these pairs of elements got placed in wrong order of their atomic masses.

MODERN PERIODIC LAW: The modern periodic law states that "The physical and chemical properties of the elements are periodic functions of their atomic numbers".

MODERN PERIODIC TABLE

- The present form of the periodic table is the modern periodic table. It is based on the modern periodic law.
- It is also known as the Long Form of Periodic Table
- The elements are arranged in horizontal rows referred as 'periods' and vertical columns known as 'groups'.
- There are seven periods and 18 groups in the long form of the periodic table.

IUPAC NOMENCLATURE- Nomenclature of elements with Atomic Nos. > 100

The IUPAC has made recommendation that until a new elements discovery is proved, and its name is officially recognized, a systematic nomenclature is derived from the atomic number of the elements $Z > 100$. The nomenclature is as follows:

Table: Notation for IUPAC Nomenclature of Elements

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

Atomic Number	Name	Symbol	IUPAC official Name	IUPAC symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununilium	Uun	Darmstadtium	Ds
111	Unununium	Uuu	Röntgenium	Rg
112	Ununbium	Uub	Copernicium	Cn
113	Ununtrium	Uut	-	-
114	Ununquadium	Uuq	-	-
115	Ununpentium	Uup	-	-
116	Ununhexium	Uuh	-	-
117	Ununseptium	Uus	-	-
118	Ununoctium	Uuo	-	-

Example: At. no. $Z = 109 \rightarrow$ Un + nil + enn + ium = Unnilennium Symbol = Une

3. ELECTRONIC CONFIGURATION OF ELEMENTS & THE PERIODIC TABLE

- There is a close relationship between electronic configuration of elements and their position in the periodic table.
- Each period begins with the filling up of a new principle quantum no; 'n'.
- The period number indicates the value of n (principle quantum number) for the valence shell.

The elements are further classified into 4 blocks.

s-block elements (Groups 1 & 2)

Elements in which the last electron enters the s-orbital of their outermost energy level are called s-block elements. Their general valance shell electronic configuration is ns^{1-2}

. It consists of Group -1 (ns^1) and Group -2 (ns^2) elements.

p-block elements

The elements in which the last electron enters the p-orbital of their outermost energy level, are called p-block elements. Their general valance shell electronic configuration is $ns^2 np^{1-6}$

. It consists of Groups 13 to 18 of periodic table.

"The elements of group 1, 2 and 13 to 18 are called representative elements."

d-block elements or transition metals:

The elements consist of group 3 to 12 and have general valance shell electronic configuration $(n-1)d^{1-10} ns^{1or2}$. The valence electron enters the d-orbital of penultimate shell (n-1).

f-block elements or inner transition elements

The elements in which last electron enters f orbital the anti-penultimate energy level and have general valance shell electronic configuration $(n-2)f^{0-14}(n-1)d^{0or1} ns^2$

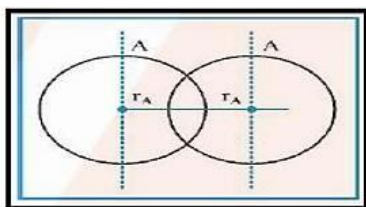
PERIODIC TRENDS IN PROPERTIES

1. ATOMIC RADII

Atomic radius is defined as the distance from the center of nucleus of the atom to the outer most shell of electrons.

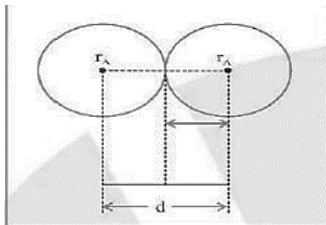
a) Covalent Radius

It is defined as one half of the distance between the centers of the nuclei of two similar atoms in a molecule bonded by a single covalent bond.

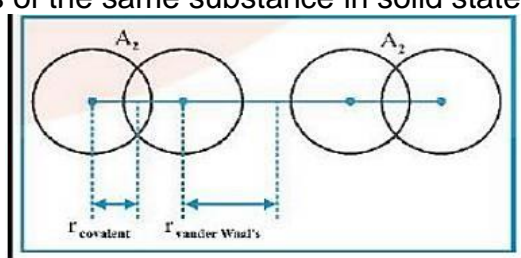


$$r_A = \frac{d_{A-A}}{2}$$

b) **Metallic radius:** It is defined as half inter nuclear distance between two adjacent atoms in metallic lattice.



c) **Van Der Waal's Radius:** It is defined as one half of the inter nuclear distance between two adjacent atoms of the same element belonging to two nearest neighbouring molecules of the same substance in solid state.



Note : $r_{\text{vander waal's}} > r_{\text{metallic}} > r_{\text{covalent}}$

VARIATION IN ATOMIC RADII

a) Along the period:

- Atomic radii decrease from left to right in a period.
- Reason: Along a period, nuclear charge increases progressively by one unit but the electrons are added to the same principal shell. As a result the electron cloud is pulled closer to the nucleus and atomic size decreases.

b) Down the group:

- The atomic radii increase from top to bottom in-group.
- Reason: On moving down the group, nuclear charge increases and also there is a progressive increase in the principal energy level. The increase in number of principal shell is more pronounced than the increase in nuclear charge. So the distance of the outer most electrons from the nucleus gradually increases down the group & the size increases.

2. IONIC RADII

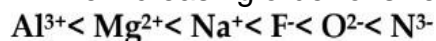
- Radius of cation is smaller than radius of parent atom. In a cation, the number of electrons is less but nuclear charge remain the same. The effective nuclear charge per electron increases which pulls the electron cloud more strongly towards the nucleus & hence the size decreases.
- Radius of anion is larger than the parent atom. In an anion, number of electrons increases, and the effective nuclear charge per electron decreases & the size increases.

3. ISOELECTRONIC IONS

Isoelectronic ions are ions of different elements which have same number of electrons but differ in magnitude of nuclear charge. E.g. Na^+ , Mg^{2+} , Al^{3+} , F^- , O^{2-} , N^{3-} . All have 10 electrons.

The size of iso electronic ions decreases with increases in magnitude of nuclear charge.

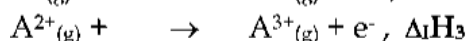
➤ The increasing order of size of the following isoelectronic species are as follows:



IONIZATION ENTHALPY ($\Delta_i H$)

It is defined as the amount of energy required to remove the most loosely bound electron from an isolated gaseous atom.

The amount of energies required to remove most loosely bound electron from unipositive, dipositive, tripositive ... ions of the element in gaseous state are called 2nd, 3rd Ionization enthalpies respectively. Or successive ionization enthalpy.



2. FACTORS GOVERNING IONIZATION ENTHALPY

(i) **Size of atom** – Smaller the size, greater is the I.E. (electrons are closer to the nucleus and so more energy is required to remove it)

(ii) **Charge on nucleus** – Greater the charge on nucleus, greater will be I.E. (Greater the nuclear pull more energy needed to remove the electron)

(iii) **Screening effect of inner electron** – In multi electron atoms, the outer most electrons are shielded from the nucleus by the inner electrons.

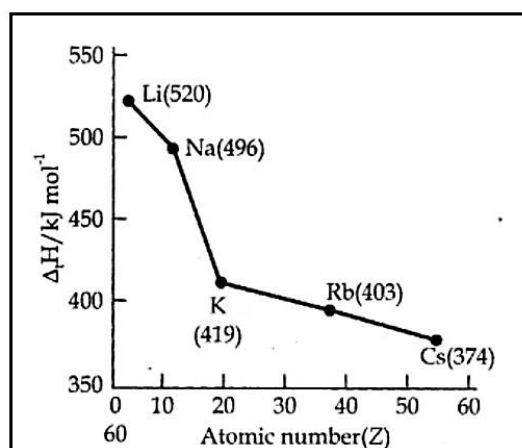
The effective nuclear charge felt on these electrons is less than the total nuclear charge. This is known as screening effect.

VARIATION IN IONIZATION ENTHALPY

Along a group

- The I.E decreases along a group as we move from top to bottom.
- Reason: In a group atomic size increases and also the shielding effect on the outermost electrons increases. As a result, electrons become less & less firmly held to the nucleus as we move down the group & the I.E. decreases, i.e. tendency to lose electron increases.

First $\Delta_i H$ of alkali metals as a function of nuclear charge Z



Along a period: The I.E increases along a period

- Along a period nuclear charge increases and the atomic size decreases, as a result the electrons are more tightly held to the nucleus & the I.E. increases, i.e, tendency to lose electron decreases.

IRREGULARITIES IN IONIZATION ENTHALPIES OF DIFFERENT ELEMENTS:

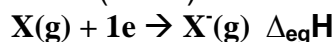
(l) Be & B: B is having less I.E. than Be.

Reason: (a) The electronic configuration of B ($1s^2 2s^2 2p^1$) is less stable than Be ($1s^2 2s^2$) which has completely filled orbital.

(b) In B, last electron enters the 2p orbital which has lesser penetrating power than 2s electron of Be and so it can be easily removed.

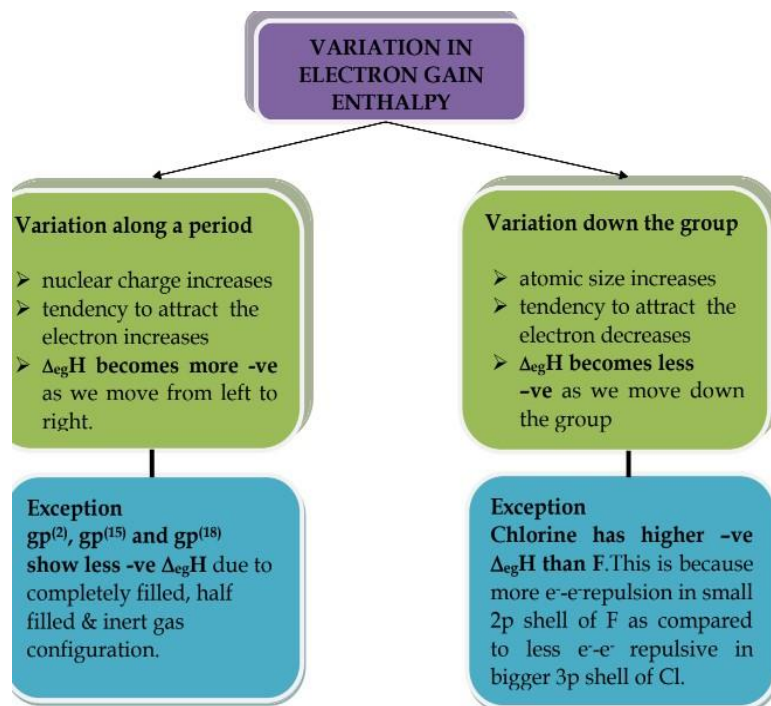
ELECTRON GAIN ENTHALPY ($\Delta_{eg}H$)

It is amount of energy associated when an electron is added to a neutral isolated gaseous atom to convert it into a negative ion (anion).



If an atom has high tendency to add an electron, energy is released & electron gain enthalpy is negative, exothermic.

If an atom has no tendency to add an electron, energy is required for this process & its electron gain enthalpy is positive, endothermic.



ELECTRONEGATIVITY: “Electro-negativity is the ability of an atom in a chemical compound to attract the shared pair of electrons to itself.”

FACTORS AFFECTING MAGNITUDE OF ELECTRONEGATIVITY

➤ Atomic radius: As the atomic radius of the element increases the electro-negativity value decreases.

➤ Effective nuclear charge: The electro-negativity value increases as the effective nuclear charge on the atomic nucleus increases.

ANOMALOUS BEHAVIOR OF FIRST ELEMENT OF EACH GROUP OF 2ND PERIOD:

The first element of each group shows property different from the rest of the elements in a group.

• This is due to (i) their small size (ii) large charge/radius ratio (iii) high ionization enthalpy. (iv) Absence of d orbital.

(The first member of each group has only 2s and 2p orbitals available for bonding whereas the rest of the elements also have d orbitals for bonding.)

DIAGONAL RELATIONSHIP

It has been observed that some elements of the second period show similarities in properties with the elements of the third period placed diagonally to each other, though belonging to different groups. This similarity in properties of elements placed diagonally to each other is called diagonal relationship.

• This is because diagonally situated elements have almost same size, ionization enthalpy, electronegativity etc.

For example, lithium (of group 1) resembles magnesium (of group 2) and

beryllium (of group 2) resembles aluminium (of group 13) and so as.

Group 1	Group 2	Group 13	Group 14
Li	Be	B	C
Na	Mg	Al	Si

QUESTION & ANSWERS

ASSERTION REASON QUESTIONS

For questions below, two statements are given one labelled Assertion (A) and the other labelled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) given below :

- (a) **Both A and R are correct and R is the correct explanation of A.**
(b) **Both A and R are correct but R is not the correct explanation of A.**
(c) **A is correct but R is wrong.**
(d) **A is wrong but R is correct.**

1. Assertion. Helium and beryllium have similar outer electronic configuration of the type ns^2 .

Reason. Both are chemically inert.

2. Assertion: Electron gain enthalpy becomes less negative as we go down a group.

Reason: Size of the atom increases on going down the group and the added electron would be farther from the nucleus.

3. Assertion: Generally, ionization enthalpy increases from left to right in a period.

Reason: When successive electrons are added to the orbitals in the same principal quantum level, the shielding effect of inner core of electrons does not increase very much to compensate for the increased attraction of the electron to the nucleus.

4. Assertion. Zinc is a s-block element.

Reason. The last electron in zinc goes to s-orbital.

5. Assertion: Of all the halogens, fluorine is most electronegative element.

Reason. Fluorine has the most negative electron gain enthalpy

Answer: 1-c, 2-a, 3- a, 4-d, 5-c

VERY SHORT ANSWER QUESTIONS 1 MARK EACH

1. What is meant by periodicity in properties of elements?

Ans: The recurrence of similar properties of the elements after certain regular intervals when they are arranged in the order of increasing atomic numbers is called periodicity.

2. What is the basic difference in approach between Mendeleev's Periodic Law and the Modern Periodic Law?

Answer: The basic difference in approach between Mendeleev's Periodic Law and Modern Periodic Law is the change in basis of classification of elements from atomic weight to atomic number.

3 Arrange (Increasing order of electron gain enthalpy) .

F, Cl, Br, I

Ans: $I < Br < F < Cl$.

4. Write the IUPAC name & symbol of an element having atomic no. 109.

Ans: Unnilennium Symbol: Uue

5.) Consider the following species: N^{3-} , O^{2-} , F^- , Na^+ , Mg^{2+} and Al^{3+} . What is common in them?

Ans: They are isoelectronic, having same number of electrons.

6. Arrange the following elements in the increasing order of their metallic character
Mg, Ca, K, Ge, Ga

Ans: $Ge < Ga < Mg < Ca < K$.

7. Where would you locate the following element in the periodic table?
A soft metal stored under kerosene

Ans: Group -1

8. Alkali metals do not form dipositive ions. Why?

Ans: They have only one valency electron.

9. Oxygen has lower ionization enthalpy than nitrogen. Give reason.

Ans: In Oxygen by removing one electron from 2p orbital, it acquire stable configuration whereas nitrogen has half-filled 2p orbitals, it difficult to remove electron.

10. Write the atomic number of the element present in the third period and seventeenth group of the periodic table.

Answer: The element is chlorine (Cl) with atomic number (Z) = 17.

11. Chlorine can be converted to its chloride more easily when compared to conversion of Fluorine to fluoride ion. Give reason.

Ans: Chlorine has more negative electron gain enthalpy than Fluorine, more energy is released when Chlorine gains electron to form Chloride ion, than flourine.

12. In terms of period and group where will you locate the element with $z = 114$?

Answer: Period – 7 and Group -14, Block-p.

13. Why do elements in the same group have similar physical and chemical properties?

Ans: Elements in the same group have similar physical and chemical properties same electronic configuration of outer shell.

14 How do atomic radius vary in a period and in a group? How do you explain the variation?

Ans: In group- atomic size increases on moving from top to bottom. In period- atomic size decreases on moving left to right in a period.

15. Which of the following pairs of elements would have a more negative electron gain enthalpy? (i) O or F (ii) F or Cl

Ans: (i) F (ii) Cl.

16. Write the general electronic configuration of d-, and f-block elements?

Answer: d-Block elements: $(n - 1) d^{1-10} ns^{0-2}$ where $n = 4-7$.

f-Block elements: $(n - 2) f^{0-14} (n - 1) d^{0-1} ns^2$ where $n = 6 - 7$

17. Assign the position of the element having outer electronic configuration,
(i) $ns^2 np^4$ for $n = 3$ (ii) $(n - 1) d^2 ns^2$ for $n = 4$ and (iii) $(n - 2) f^7 (n - 1) d^1 ns^2$ for $n = 6$ in the periodic table?

Answer: (i) $n = 3$ Thus element belong to 3rd period, p-block element.

Since the valence shell contains = 6 electrons, group No = $10 + 6 = 16$ configuration = $1s^2 2s^2 2p^6 3s^2 3p^4$ element name is sulphur.

Multiple Choice Questions 1 MARK EACH

1. Which set of triads doesn't fit into Dobereiner's Law of Triads?

a) lithium, sodium, potassium b) calcium, strontium, barium

c) phosphorus, arsenic, antimony d) iron, cobalt, nickel

Ans: (d)

2. In Mendeleev's Periodic Table, gaps were left for the elements to be discovered later. Which of the following elements found a place in the periodic table later?

a) Germanium b) Chlorine c) Oxygen d) Silicon

Ans: (a)

3. Which of the following statements about the Modern Periodic Table is correct:

(a) It has 18 horizontal rows known as Periods

(b) It has 7 vertical columns known as Periods

(c) It has 18 vertical columns known as Groups

(d) It has 7 horizontal rows known as Groups

Ans: (c)

4. An element which is an essential constituent of all organic compounds belongs to

(a) group 1 (b) group 14 (c) group 15 (d) group 16

Ans: (b)

5. Which among the following elements has the largest atomic radii?

(a) Na (b) Mg (c) K (d) Ca

Ans: (c)

6. The anion O^{2-} is isoelectronic with

(a) Ne (b) N^{2-} (c) N^{3-} (d) F^{-}

Ans: (b)

7. The correct order of radii of three species Ca, Ca^{+} and Ca^{2+} is

(a) $Ca > Ca^{+} > Ca^{2+}$ (b) $Ca^{2+} > Ca^{+} > Ca$

(c) $Ca^{+} > Ca > Ca^{2+}$ (d) $Ca^{+} > Ca^{2+} > Ca$

Ans: (a)

8. The family of elements with the highest ionization enthalpy

(a) alkaline earth metals (b) halogens

(c) noble gases (d) alkali metals

Ans: (c)

9. The correct order in which the first ionization enthalpy increases is

(a) K, Be, Na (b) Be, Na, K

(c) Na, K, Be (d) K, Na, Be

Ans: (d)

10. Which of the following property increases down the group?

a) electronegativity b) electropositive nature of element

c) atomic size d) both b and c

Ans: (d)

11. The size of isoelectronic species F^{-} , Ne and Na^{+} is affected by

(a) nuclear charge (Z) (b) valence principal quantum number (n)

(c) electron-electron interaction in the outer orbitals

(d) none of the factors because their size is the same

Answer: (a) Nuclear charge (Z).

12. Which of the following statements is incorrect in relation to ionization enthalpy?

(a) ionization enthalpy increases for each successive electron.

(b) The greatest increase in ionization enthalpy is experienced on removal of electrons from core noble gas configuration.

(c) End of valence electrons is marked by a big jump in ionization enthalpy.

(d) Removal of electron from orbitals bearing lower n value is easier than from orbital

having higher n value.

Answer: (d) is incorrect.

13. The elements in which 4f orbitals are progressively filled are called
(a) Actinides (b) Transition elements (c) Lanthanides (d) Halogens.

Answer: (c)

14. Which of the following has least electron affinity?

(a) Oxygen (b) Argon (c) Nitrogen (d) Boron

Answer: (b)

15. The general outer electronic configuration of transition elements is

(a) ns^2nd^{1-10} (b) $ns^2np^1(n-1)d^{1-10}$ (c) $ns^2np^6(n-1)d^{1-10}$ (d) $ns^{0-2}(n-1)d^{1-10}$

Answer: (d)

16. Total number of elements present in the 3rd period is

(a) 6 (b) 32 (c) 18 (d) 8

Answer: (d)

SHORT ANSWER QUESTION

2 MARKS EACH

1. Write 2 achievements of Mendeleev's periodic table.

Ans: i) Mendeleev considered similarities in properties of elements rather than atomic masses. So he corrected the atomic mass of some elements.

ii) Prediction of the existence and properties of new elements –Mendeleev left some gaps in his periodic table and he also predicted the properties of new elements which were undiscovered. E.g. Gaps were left below Aluminium and Silicon for the undiscovered elements. They were named as Eka-Aluminium and Eka-Silicon. These elements were further discovered as Gallium and Germanium.

2. Why is atomic number a better basis for classification of the elements than atomic mass?

Ans: The atomic mass of the element relates to the nucleus which is present in the centre of the atom. But the properties of the elements depend upon the electronic configuration which is linked with atomic number. As the atomic number or electronic configuration atom changes, the properties of the element involved also change.

3. What are the differences between electron gain enthalpy and electro-negativity?

Ans: Electron gain enthalpy : It is amount of energy associated when an electron is added to a neutral isolated gaseous atom to convert it into a negative ion (anion).

Electro-negativity : If an atom has high tendency to add an electron, energy is released. If an atom has no tendency to add an electron, energy is required for this process. $X(g) + 1e \rightarrow X^-(g) \Delta_{eg}H$

4. Name the factors which affect the ionisation enthalpy of an element.

Ans: (i) Size of atom or ion (ii) Nuclear charge (iii) Electronic configuration (iv) Screening effect (v) Penetration effect of the electrons.

5. What do you understand by the term diagonal relationship? Explain with the help of an example.

Ans: some elements of the second period show similarities in properties with the elements of the third period placed diagonally to each other, though belonging to different groups. This similarity in properties of elements placed diagonally to each other is called diagonal relationship.

For example, lithium (of group 1) resembles magnesium (of group 2) and beryllium (of group 2) resembles aluminium (of group 13)

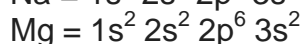
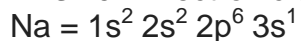
Short answer type questions:

6. Explain why cations are smaller and anions larger in radii than their parent atoms?

Answer: A cation is smaller than the parent atom because it has fewer electrons while its nuclear charge remains the same. The size of anion will be larger than that of parent atom because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge.

7. How would you explain the fact that the first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium?

Answer: Electronic configuration of Na and Mg are



First electron in both cases has to be removed from 3s-orbital but the nuclear charge of Na (+ 11) is lower than that of Mg (+ 12) therefore first ionization energy of sodium is lower than that of magnesium. After the loss of first electron, the electronic configuration of $\text{Na}^+ = 1s^2 2s^2 2p^6$ $\text{Mg}^+ = 1s^2 2s^2 2p^6 3s^1$

Here electron is to be removed from inert (neon) gas configuration which is very stable and hence removal of second electron requires more energy in comparison to Mg. Therefore, second ionization enthalpy of sodium is higher than that of magnesium.

8).

The first ($\Delta_i H_1$) and the second ($\Delta_i H_2$) ionization enthalpies (in kJ mol^{-1}) and the ($\Delta_{eg} H$) electron gain enthalpy (in kJ mol^{-1}) of a few elements are given below:

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

Which of the above elements is likely to be:

- (a) the least reactive element
- (b) the most reactive metal
- (c) the most reactive non-metal
- (d) the least reactive non-metal
- (e) the metal which can form a stable binary halide of the formula MX_2 (X = halogen)
- (f) the metal which can form a predominantly stable covalent halide of the formula MX (X = halogen)?

Answer: (a) The element V has highest first ionization enthalpy ($\Delta_i H_1$) and positive electron gain enthalpy ($\Delta_{eg} H$) and hence it is the least reactive element. Since inert gases have positive $\Delta_{eg} H$, therefore, the element-V must be an inert gas. The values of $\Delta_i H_1$, $\Delta_i H_2$ and $\Delta_{eg} H$ match that of He.

(b) The element II which has the least first ionization enthalpy ($\Delta_i H_1$) and a low negative electron gain enthalpy ($\Delta_{eg} H$) is the most reactive metal. The values of $\Delta_i H_1$, $\Delta_i H_2$ and $\Delta_{eg} H$ match that of K (potassium).

(c) The element III which has high first ionization enthalpy ($\Delta_i H_1$) and a very high negative electron gain enthalpy ($\Delta_{eg} H$) is the most reactive non-metal. The values of $\Delta_i H_1$, $\Delta_i H_2$ and $\Delta_{eg} H$ match that of F (fluorine).

(d) The element IV has a high negative electron gain enthalpy ($\Delta_{eg} H$) but not so high first ionization enthalpy ($\Delta_i H_1$). Therefore, it is the least reactive non-metal. The values of $\Delta_i H_1$, $\Delta_i H_2$ and $\Delta_{eg} H$ match that of I (Iodine).

(e) The element VI has low first ionization enthalpy ($\Delta_i H_1$) but higher than that of alkali metals. Therefore, it appears that the element is an alkaline earth metal and hence will form binary halide of the formula MX_2 (where X = halogen). The values of $\Delta_i H_1$, $\Delta_i H_2$ and $\Delta_{eg} H$ match that of Mg (magnesium).

(f) The element I has low first ionization ($\Delta_i H_1$) but a very high second ionization enthalpy ($\Delta_i H_2$), therefore, it must be an alkali metal. Since the metal forms a predominantly stable covalent halide of the formula MX (X = halogen), therefore, the alkali metal must be least reactive. The values of $\Delta_i H_1$, $\Delta_i H_2$ and $\Delta_{eg} H$ match that of Li (lithium).

LONG ANSWER TYPE QUESTIONS

1. **Nitrogen has positive electron gain enthalpy whereas oxygen has negative. However, oxygen has lower ionization enthalpy than nitrogen explain.**

Sol: The outermost electronic configuration of nitrogen is $2s^2 2p_x^1 2p_y^1 2p_z^1$. It is stable because it has exactly half filled 2p-subshell. Therefore, it has no tendency to accept extra electron and energy has to be supplied to add additional electron. Thus, electron gain enthalpy of nitrogen is slightly positive. On the other hand, the outermost electronic configuration of O is $2s^2 2p_x^2 2p_y^1 2p_z^1$. It has higher positive charge (+8) than nitrogen (+7) and lower atomic size than N. Therefore, it has a tendency to accept an extra electron. Thus, electron gain enthalpy of O is negative. However, oxygen has four electrons in the 2p subshell and can lose one electron to acquire stable half filled configuration and therefore, it has low ionization enthalpy. Because of stable configuration of N, it cannot readily lose electron and therefore, its ionization enthalpy is higher than that of O.

2. **Arrange the elements N, P, O and S in the order of (i) increasing first ionisation enthalpy. (ii) increasing non-metallic character.**

Give reason for the arrangement assigned.

Sol: (i) $S < P < O < N$

Ionisation enthalpy increases from left to right in a period and decreases down the group. N has higher ionisation enthalpy than O due to extra stability of half-filled orbitals. Similarly, P has higher ionisation enthalpy than S due to half-filled orbitals.

(ii) $P < S < N < O$

Non-metallic character decreases down the group and increases from left to right in a period.

3. **Explain the following:**

(a) **Electronegativity of elements increases on moving from left to right in the periodic table.**

(b) **Ionisation enthalpy decreases in a group from top to bottom.**

Sol: (a) The electronegativity generally increases on moving across a period from left to right (e.g., from Li to F in the second period). This is due to decrease in atomic size and increase in effective nuclear charge. As a result of increase in effective nuclear charge, the attraction for the outer electron and the nucleus increases in a period and therefore, electronegativity also increases.

(b) On moving down a group there is a gradual decrease in ionisation enthalpy. The decrease in ionisation enthalpy down a group can be explained in terms of net effect of the following factors:

(i) In going from top to bottom in a group, the nuclear charge increases.

(ii) There is a gradual increase in atomic size due to an additional main energy shell (n).

(iii) There is increase in shielding effect on the outermost electron due to increase in the number of inner electrons.

The effect of increase in atomic size and the shielding effect is much more than the effect of increase in nuclear charge. As a result, the electron becomes less and less firmly held to the nucleus as we move down the group. Hence, there is a gradual decrease in the ionization enthalpies in a group.

3. CHEMICAL BONDING AND MOLECULAR STRUCTURE

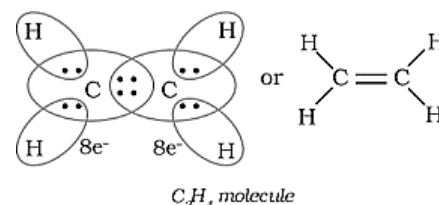
CHEMICAL BOND: The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.

Lewis Symbols: A Lewis Symbol is constructed by placing dots representing electrons in the outer energy around the symbol for the element

Table 4.1 The Lewis Representation of Some Molecules

Molecule/Ion	Lewis Representation	Lewis Representation
H ₂	H : H*	H - H
O ₂	:Ö::Ö:	:Ö=Ö:
O ₃	$\begin{array}{c} \text{O}^+ \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O}^- \end{array}$	$\begin{array}{c} \text{O}^+ \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O}^- \end{array}$
NF ₃	$\begin{array}{c} \text{F} \quad \text{N} \quad \text{F} \\ \\ \text{F} \end{array}$	$\begin{array}{c} \text{F} - \text{N} - \text{F} \\ \\ \text{F} \end{array}$
CO ₃ ²⁻	$\left[\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} - \text{C} - \text{O} \\ \diagdown \quad \diagup \end{array} \right]^{2-}$	$\left[\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} - \text{C} - \text{O} \\ \diagdown \quad \diagup \end{array} \right]^{2-}$
HNO ₃	$\begin{array}{c} \text{O}^+ \\ \diagup \quad \diagdown \\ \text{O} \quad \text{N} \quad \text{O} \quad \text{H} \\ \\ \text{O}^- \end{array}$	$\begin{array}{c} \text{O}^+ \\ \diagup \quad \diagdown \\ \text{O} = \text{N} - \text{O} - \text{H} \\ \\ \text{O}^- \end{array}$

* Each H atom attains the configuration of helium (a duplet of electrons)



Octet Rule: The tendency of atoms to have eight electrons in the valence shell is known as the "Octet rule".

Formal Charge: The formal charge is the difference in the number of valence electrons in the atom and the number of valence electrons in the Lewis structure.

$$\text{Formal charge (F.C.) on an atom in a Lewis structure} = \left[\begin{array}{l} \text{total number of valence} \\ \text{electrons in the free} \\ \text{atom} \end{array} \right] - \left[\begin{array}{l} \text{total number of non} \\ \text{bonding (lone pair)} \\ \text{electrons} \end{array} \right] - (1/2) \left[\begin{array}{l} \text{total number of} \\ \text{bonding (shared)} \\ \text{electrons} \end{array} \right]$$

It does not indicate the real charge. Let us consider the Ozone molecule (O_3). The Lewis structure of O_3 may be drawn as:



The atoms have been numbered as 1, 2 and 3. The formal charge on:

The central O atom marked 1

$$= 6 - 2 - \frac{1}{2} (6) = +1$$

The end O atom marked 2

$$= 6 - 4 - \frac{1}{2} (4) = 0$$

The end O atom marked 3

$$= 6 - 6 - \frac{1}{2} (2) = -1$$

Resonance: According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately.

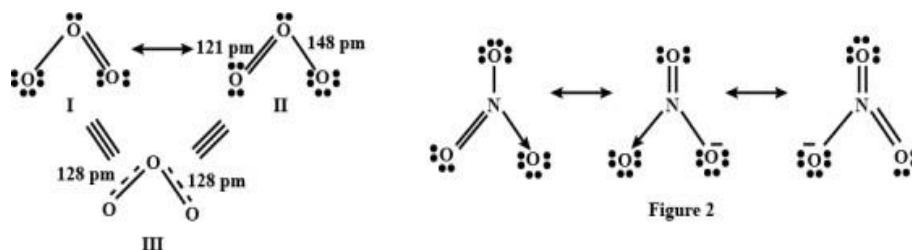
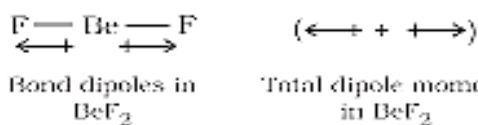


Figure 2

Dipole moment (μ) = charge (q) \times distance of separation (d)

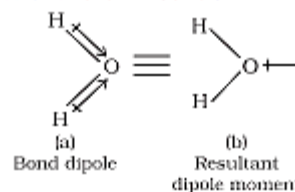
Unit: Debye units (D). The conversion factor is $1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m}$ where C is coulomb and m is meter.

The dipole moment in case of BeF_2 is zero. This is because the two equal bond dipoles point in opposite directions and cancel the effect of each other.



Bond dipoles in BeF_2

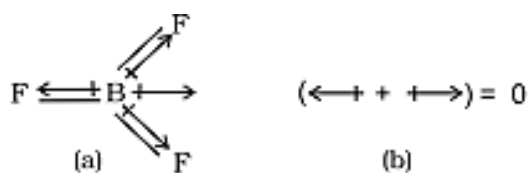
Total dipole moment in BeF_2



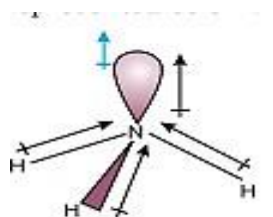
Bond dipole

Resultant dipole moment

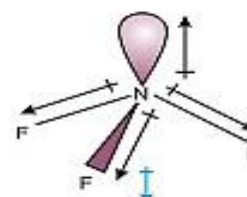
$$\text{Net Dipole moment, } \mu = 1.85 \text{ D} \\ = 1.85 \times 3.33564 \times 10^{-30} \text{ C m} = 6.17 \times 10^{-30} \text{ C m}$$



BF_3 molecule; representation of (a) bond dipoles and (b) total dipole moment



Resultant dipole moment in $\text{NH}_3 = 4.90 \times 10^{-30} \text{ C m}$



Resultant dipole moment in $\text{NF}_3 = 0.80 \times 10^{-30} \text{ C m}$

Table 4.5 Dipole Moments of Selected Molecules

Type of Molecule	Example	Dipole Moment, μ (D)	Geometry
Molecule (AB)	HF	1.78	linear
	HCl	1.07	linear
	HBr	0.79	linear
	HI	0.38	linear
	H ₂	0	linear
Molecule (AB ₂)	H ₂ O	1.85	bent
	H ₂ S	0.95	bent
	CO ₂	0	linear
Molecule (AB ₃)	NH ₃	1.47	trigonal-pyramidal
	NF ₃	0.23	trigonal-pyramidal
	BF ₃	0	trigonal-planar
Molecule (AB ₄)	CH ₄	0	tetrahedral
	CHCl ₃	1.04	tetrahedral
	CCl ₄	0	tetrahedral

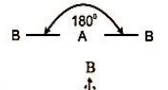
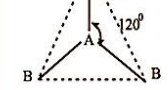
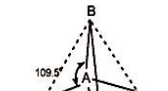
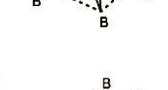
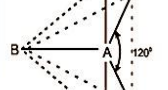
THE VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

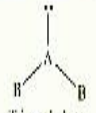
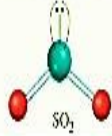
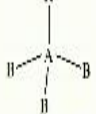
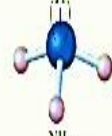


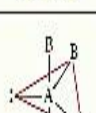
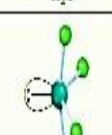
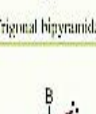
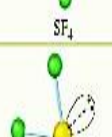
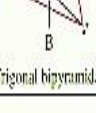
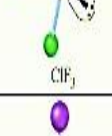
Main Postulates are the following::

- (i) The exact shape of molecule depends upon the number of electron pairs (bonded or non-bonded) around the central atoms.
- (ii) The electron pairs have a tendency to repel each other since they exist around the central atom and the electron clouds are negatively charged.
- (iii) Electron pairs try to take such position which can minimize the repulsion between them.
- (iv) The valence shell is taken as a sphere with the electron pairs placed at maximum distance.
- (v) A multiple bond is treated as if it is a single electron pair and the electron pairs which constitute the bond as single pairs.
- (vi) Where two or more resonance structures can represent a molecule, the VSEPR theory is applicable to any such structure.

The repulsive interaction of electron pairs decreases in the order:

Lone pair (lp)-Lone pair (lp) > Lone pair (lp) – bond pair (bp) > Bond pair (bp) – Bond pair (bp)

No. of shared electron pairs around central atom.	Geometry of the molecules	Shape of the molecule	Examples
2.		Linear	BeF ₂ , BeCl ₂ MgF ₂ , MgCl ₂
3.		Trigonal planar	BF ₃ , BCl ₃ AlF ₃ , AlCl ₃
4.		Tetrahedral	CH ₄ , CCl ₄ , SH ₄ , SCl ₄
5.		Trigonal Bipyramidal	PF ₅ , PCl ₅ SbF ₅
6.		Octahedral	SF ₆ , TeF ₆

Class of Molecule	Total Number of Electron Pairs	Number of Bonding Pairs	Number of Lone Pairs	Arrangement of Electron Pairs*	Geometry of Molecule or Ion	Examples
AB ₂ E	3	2	1		Bent	 SO ₂
AB ₃ E	4	3	1		Trigonal pyramidal	 NH ₃
AB ₂ E ₂	4	2	2		Bent	 H ₂ O
AB ₅ E	5	4	1		Distorted tetrahedron (or seesaw)	 SF ₄
AB ₃ E ₂	5	3	2		T-shaped	 ClF ₃
AB ₅ E ₂	5	2	3		Linear	 I ₃ ⁻

Types of Orbital Overlap:

Depending upon the type of overlapping, the covalent bonds are of two types, known as sigma (σ) and pi (π) bonds.

(i) Sigma (σ bond): Sigma bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis. The extent of overlap is more so, sigma bond is a strong bond. The axial overlap involving these orbitals is of three types:

(a) s-s overlapping: In this case, there is overlap of two half-filled s-orbitals along the internuclear axis as shown below:

(b) s-p overlapping: This type of overlapping occurs between half-filled s-orbitals of one atom and half filled p-orbitals of another atoms.

(c) p-p overlapping: This type of overlapping takes place between half-filled p-orbitals of the two approaching atoms. Generally, p_z orbitals are taken in inter nuclear axis.

(ii) pi (π bond): π bond is formed by the atomic orbitals when they overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbital formed is due to lateral overlapping or side wise overlapping. The extent of overlap is less, so pi bond is a weak bond. It can be p π - p π or p π - d π or d π - d π overlap.

Hybridisation: The process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape.

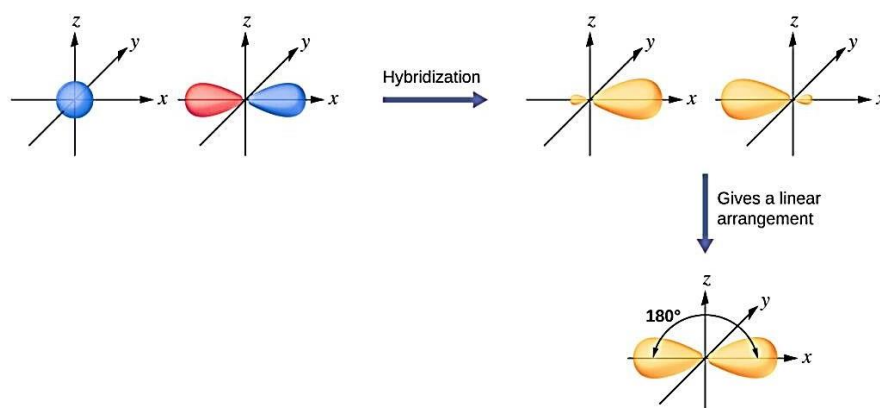
The important hybridisation schemes involving s,p and d orbitals are summarised below:

Shape of molecules/ions	Hybridisation type	Atomic orbitals	Examples
Square planar	dsp^2	$d+s+p(2)$	$[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Pt}(\text{Cl})_4]^{2-}$
Trigonal bipyramidal	sp^3d	$s+p(3)+d$	PF_5 , PCl_5
Square pyramidal	sp^3d^2	$s+p(3)+d(2)$	BrF_5
Octahedral	sp^3d^2 d^2sp^3	$s+p(3)+d(2)$ $d(2)+s+p(3)$	SF_6 , $[\text{CrF}_6]^{3-}$ $[\text{Co}(\text{NH}_3)_6]^{3+}$

Types of Hybridisations: (sp , sp^2 , sp^3 , sp^3d , sp^3d^2)

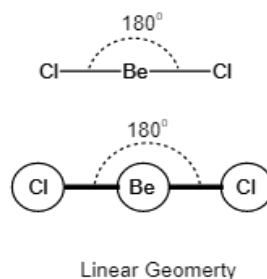
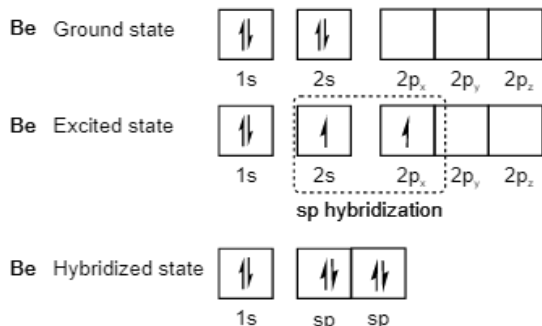
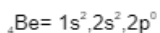
(i) **sp hybridisation:** When one s and one p-orbital hybridise to form two equivalent orbitals, the orbital is known as sp hybrid orbitals, and the type of hybridisation is called sp hybridisation.

Each of the hybrid orbitals formed has 50% s-character and 50% p-character. This type of hybridisation is also known as diagonal hybridisation having linear structure & bond angle = 180° .

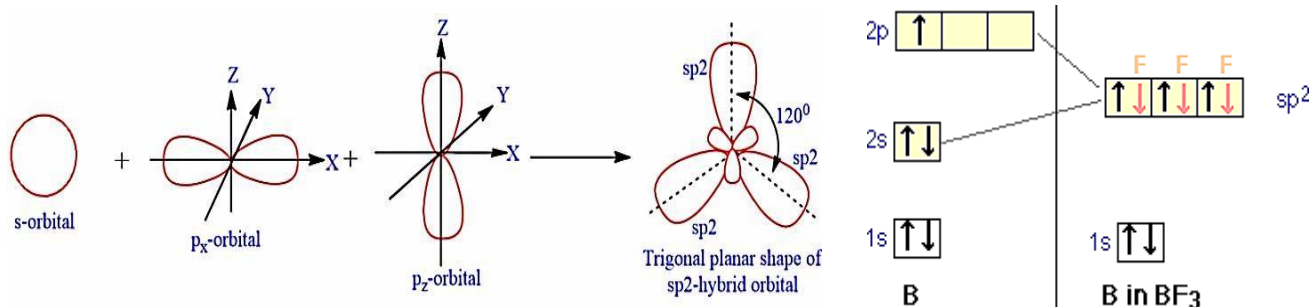


Example: BeCl_2 , BeF_2 , C_2H_2 etc.

Electronic configuration of beryllium is

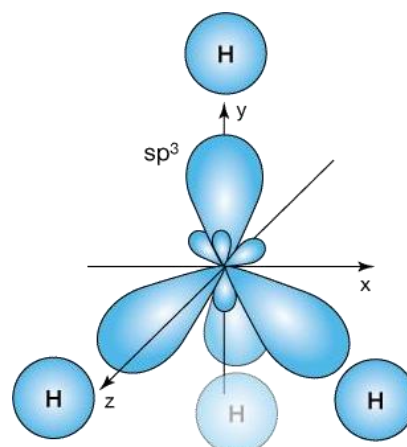
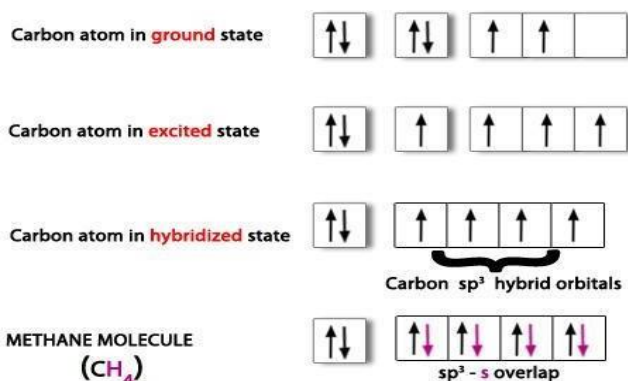


(ii) sp^2 hybridisation: In this type, one s and two p-orbitals hybridise to form three equivalent sp^2 hybrid orbitals in the same plane making an angle of 120° & trigonal planar shape. Each of the hybrid orbitals formed has 33.3 % s-character and 66.7 % p-character. Example: A few compounds in which sp^2 hybridisation takes place are BF_3 , BCl_3 carbon compounds containing double bond (C_2H_4) etc.

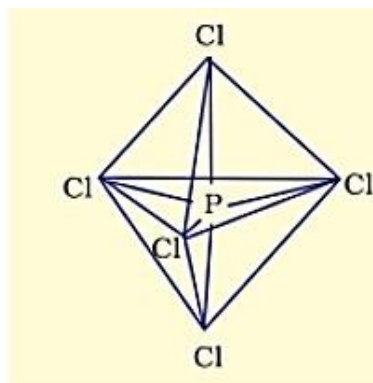
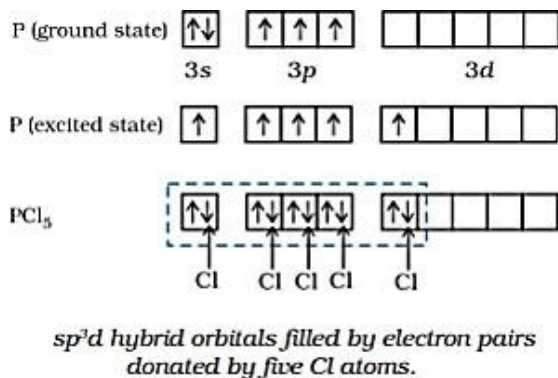


(iii) sp^3 hybridisation: In this type, one s and three p-orbitals in the valence shell of an atom get hybridised to form four equivalent sp^3 hybrid orbitals. Each orbital has 25% s-character and 75% p-character. With tetrahedral structure & bond angle 109.5° The four sp^3 orbitals are directed towards four corners of the tetrahedron.

A compound having sp^3 hybridisation is CH_4 , CCl_4 , NH_4^+ etc. The structures of NH_3 and H_2O molecules can also be explained with the help of sp^3 hybridisation.



Hybridisation in PCl_5



Molecular Orbital Theory: According to this theory, the atomic orbitals combine to form the molecular orbitals. The number of molecular orbitals formed is equal to the number of atomic orbitals involved. According to this theory.

The molecular orbitals are formed by LCAO (Linear combination of atomic orbitals) method, i.e., by addition or subtraction of wave functions of individual atoms, thus $\Psi_{MO} = \Psi_A \pm \Psi_B$

$$\Psi_b = \Psi_A + \Psi_B$$

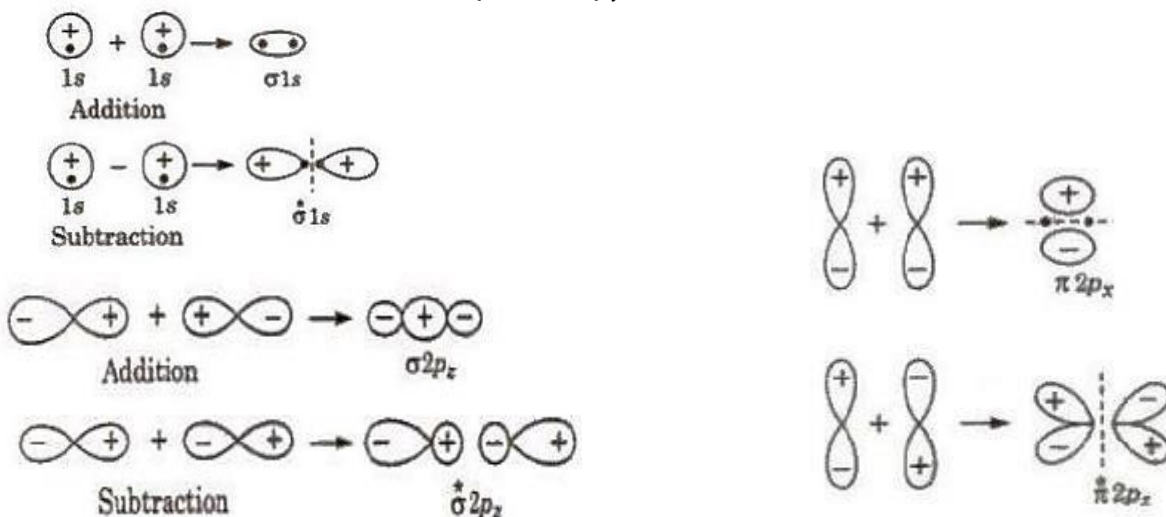
$$\Psi_a = \Psi_A - \Psi_B$$

2. Molecular orbital of lower energy is known as bonding molecular orbital and that of higher energy is known as anti-bonding molecular orbital.

3. Aufbau rule, Pauli's exclusion principle and Hund's rule are all applicable for molecular orbitals.

4. The shape is governed by the shape of atomic orbitals, e.g., s-s and p-p overlapping.

(i) Combination between s-atomic orbitals (ii) Combination between p-atomic orbitals (iii) Combination between 2p_x and 2p_y atomic orbitals



Electronic Configuration and Bond Order (BO) of Molecular Species: The order of energy of molecular orbitals has been determined experimentally by spectroscopy for the elements of the second period. The increasing order of energies of the molecular orbitals in homonuclear diatomic molecules is

(A) For (O₂, F₂ & Ne₂ (hypothetical)) :

Electronic configuration: σ_{1s} σ^*_{1s} σ_{2s} σ^*_{2s} σ_{2p_z} ($\pi_{2p_x} = \pi_{2p_y}$) ($\pi^*_{2p_x} = \pi^*_{2p_y}$) $\sigma^*_{2p_z}$

(B) For B₂, C₂, N₂

Electronic configuration: $\sigma 1s \ \sigma^* 1s \ \sigma 2s \ \sigma^* 2s \ (\pi 2p_x = \pi 2p_y) \ \sigma 2p_z \ (\pi^* 2p_x = \pi^* 2p_y) \ \sigma^* 2p_z$

Bond Order (BO) : Bond order is defined as half of the difference between the number of electrons present in bonding molecular orbitals (N_b) and antibonding molecular orbitals (N_a).
Bond order (B.O.) = $\frac{1}{2} [N_b - N_a]$ where N_b & N_a are no. of bonding electrons & anti bonding electrons.

(i) **Stability**: If $BO > 0$ or positive, $N_b > N_a \rightarrow$ the molecular species is stable & exists in nature.

If $BO \leq 0$ (i.e. zero or negative) : $N_b \leq N_a \rightarrow$ the molecular species is unstable & does not exist in nature.

(ii) The integral value of BO corresponds to the no. of covalent bonds.

(iii) Higher the BO, the molecular species is more stable.

(iv) Bond order a stability of molecular species

Bond order a bond dissociation enthalpy of molecular species.

Bond order a $\frac{1}{\text{bond length of molecular species}}$

(v) BO is fractional \rightarrow the molecular species is paramagnetic. (having one or more unpaired electrons & is weakly attracted in a magnetic field.

Bonding in Homonuclear

(Diatomic) Molecules:

(1) **Hydrogen molecule (H_2)**: It is formed by the combination of two hydrogen atoms. Each hydrogen atom has one electron in $1s$ orbital, so, the electronic configuration of hydrogen molecule ($2e^-$) is $\sigma 1s^2 \ \sigma^* 1s$

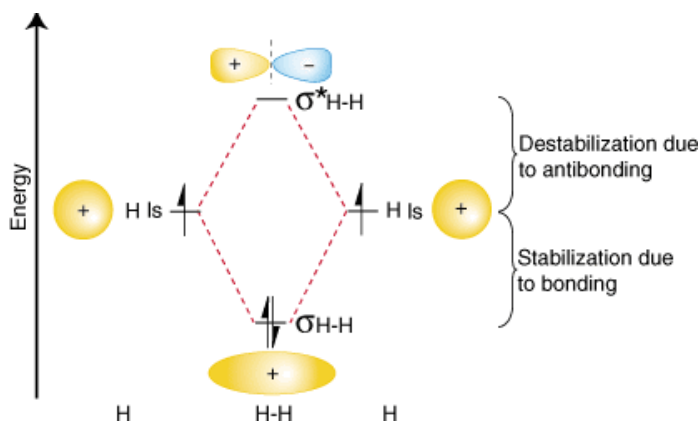
$$BO = \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1 \text{ Hence, two}$$

hydrogen atoms are bonded by a

single covalent bond. Bond dissociation energy of hydrogen has been found = 438 kJ/mole.

Bond-Length = 74 pm

No unpaired electron is present therefore, it is diamagnetic.

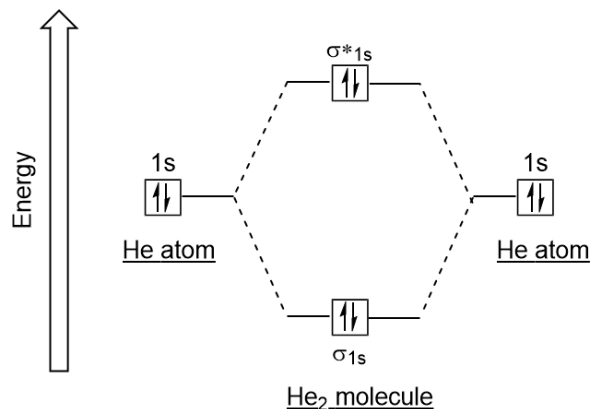


(2) **Helium molecule (He_2)**: Each helium atom contains 2 electrons ($1s^2$), thus in He_2 molecule has 4 electrons.

He_2 : electronic configuration is $\sigma 1s^2 \ \sigma^* 1s^2$

$$BOND \ ORDER = \frac{N_b - N_a}{2} = \frac{2 - 2}{2} = 0 \quad \text{So, } He_2 \text{ does not}$$

exist.



(3) **Lithium molecule (Li_2)**

$$E.C. \text{ of } Li = 1s^2 2s^1$$

There are 6 electrons in Li_2

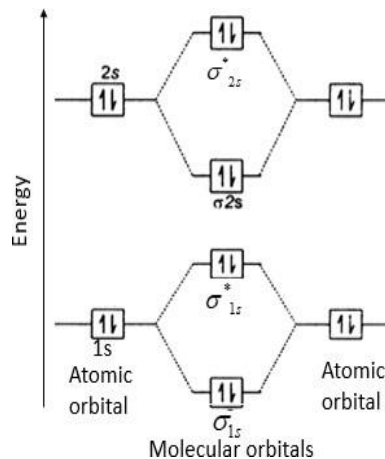
$$E.C. \text{ of } Li_2 = (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2$$

It can also be represented as KK $[\sigma 2s]^2$

$$\text{Bond order} = \frac{1}{2} [N_b - N_a]$$

$$= \frac{1}{2} [4 - 2] = 1$$

Nature = Diamagnetic, since molecular orbitals are completely filled.



(4) Explain: Be₂ does not exist in nature:

Be₂ has 8 electrons

Its electronic configuration: $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2$

So, bond order = $\frac{N_b - N_a}{2} = \frac{4 - 4}{2} = 0$ So, Be₂ does not exist.

The energy level diagram of Be₂ is →

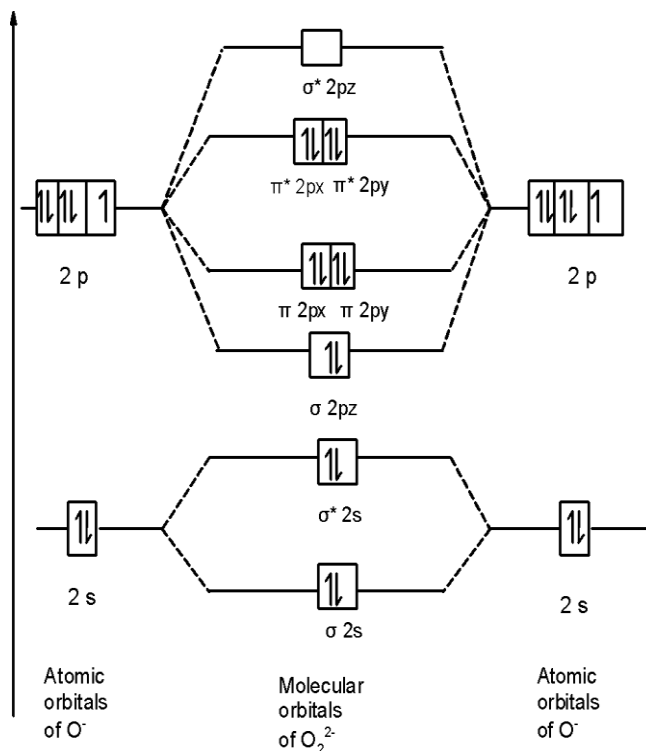
(5) Explain: Dioxygen molecule is paramagnetic. Draw its energy level diagram.

Ans. Atomic no. of oxygen atom is 8 so, O₂ has 16 electrons.

Molecular orbital electronic configuration of O₂ is $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$

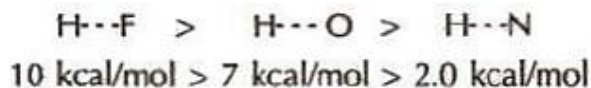
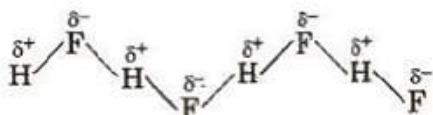
Due to the presence of unpaired electrons in $\pi^* 2p_x^1 = \pi^* 2p_y^1$ O₂ molecule is paramagnetic

(Bond order = $\frac{N_b - N_a}{2} = \frac{10 - 6}{2} = 2$. It has 2 covalent bonds.)



Hydrogen Bond

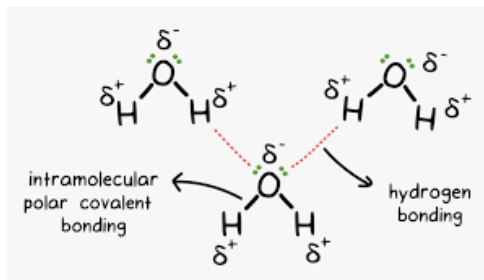
It is defined as the electrostatic force of attraction existing between hydrogen atom covalently bonded to highly electronegative atom (N, O or F) and the electronegative atom belonging to another molecule of the same or different substance. It is represented by dotted lines. The chains possess a zig – zag structure.



Types of hydrogen bonds are

- (i) Intermolecular H-bonding: H-bonding involving two or more molecules.
- (ii) Intramolecular H-bonding: H-bonding within a molecule.

Water is a liquid due to inter molecular H bonds.



Applications of Intermolecular H-bonding

- (i) Melting point and boiling point of water has the lowest molecular weight among the hydrides of group 16 elements yet it has the highest melting and boiling points. It is due to intermolecular H Bonding in H_2O .
- (ii) Melting point and boiling point of alcohols the marked difference between the melting and boiling points of alcohols is also due to H-bonding.

Strength of bonds: Ionic bond > covalent bond > metallic bond > H-bond.

Assertion & Reason Questions

Directions: Each of these questions contain two statements, Assertion and Reason. Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below.

- (a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.
- (b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion
- (c) Assertion is correct, reason is incorrect
- (d) Assertion is incorrect, reason is correct.

Q.1. Assertion : The bond order of helium is always zero.

Reason : The number of electrons in bonding molecular orbital and antibonding molecular orbital is equal.

Ans- A

Q.2. Assertion : The lesser the lattice enthalpy more stable is the ionic compound.

Reason : The lattice enthalpy is greater, for ions of highest charge and smaller radii.

Ans- D

Q.3. Assertion : pi bonds are weaker than σ bonds.

Reason : pi bonds are formed by the overlapping of p-p orbitals side wise.

Answer- A

Q.4. Assertion : BF_3 molecule has zero dipole moment.

Reason : F is electronegative and B-F bonds are polar in nature.

Answer- B

Q.5. Assertion : CH_2Cl_2 is non-polar and CCl_4 is polar molecule.

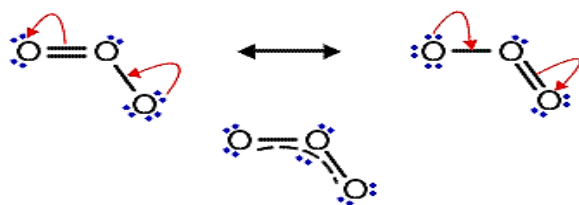
Reason : Molecule with zero dipole moment is non-polar in nature.

Answer- D

Q.6. Assertion : Lone pair-lone pair repulsive interactions are greater than lone pair-bond pair and bond pair-bond pair interactions.

Reason : The space occupied by lone pair electrons is more as compared to bond pair electrons.

The resonance forms of ozone



The 'averaged' structure of ozone showing the delocalised molecular orbital.

14. Arrange O_2 , O_2^- , O_2^{2-} , O_2^+ in increasing order of bond energy.

Answer: $O_2^{2-} < O_2^- < O_2 < O_2^+$

15. Arrange the following, according to increasing covalent nature.

NaCl, MgCl₂, AlCl₃

Answer: NaCl < MgCl₂ < AlCl₃

17. Out of sigma and Π bonds, which one is stronger and why?

Answer: sigma-bond is stronger. This is because sigma-bond is formed by head-on overlapping of atomic orbitals and Π bond is formed by side wise overlapping.

18. What type of bond are formed due to orbital overlap?

Ans - Covalent bond

19. Define bonding & antibonding molecular orbital.

Ans - When two atomic orbitals combine, two molecular orbitals are formed. One is known as bonding molecular orbital while the other is called antibonding molecular orbital.

The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.

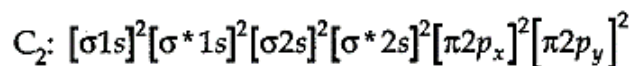
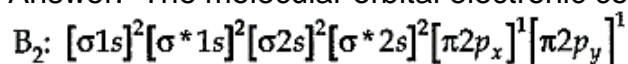
20. Define bond order.

Ans - Bond order (B.O.) is defined as one half the difference between the number of electrons present in the bonding and the antibonding Orbitals

Bond order: = $\frac{1}{2}(N_b - N_a)$

21. Why B₂ is paramagnetic in nature while C₂ is not?

Answer: The molecular orbital electronic configuration of both B₂ and C₂ are-



Since, B₂ has two unpaired electrons, B₂ is paramagnetic. C₂ has no unpaired electron. Thus, C₂ is diamagnetic.

22. What are the types of H-bonding? Which of them is stronger?

Ans - Intramolecular H-bonding & Intermolecular H-bonding. Intermolecular H-bonding is stronger.

Multiple Choice Questions (MCQs) 1 mark each:

Question 1. A co-ordinate bond is formed by:

- (a) sharing of electrons contributed by both the atoms
- (b) complete transfer of electrons
- (c) sharing of electrons contributed by one atom only
- (d) none of these.

Question 2. The species CO, CN and N₂ are:

- (a) isoelectronic
- (b) having coordinated bond
- (c) having polar bond
- (d) having low bond energies.

Question 3. The axial overlap between the two orbitals leads to the formation of a:

- (a) sigma bond
- (b) pi bond
- (c) multiple bond
- (d) none of these.

Question 4. In SO_2 molecule, S atom is:

- (a) sp^3 hybridized (b) sp hybridized (c) sp^2 hybridized (d) d sp^2 hybridized.

Question 5 MX_6 is a molecule with octahedral geometry. How many X – M – X bonds are at 180° ?

- (a) four (b) two (c) three (d) six.

Question 6. The molecule Ne_2 does not exist because

- (a) $N_b > N_a$ (b) $N_b = N_a$ (c) $N_b < N_a$ (d) None of these.

Question 7 Which of the molecules does not have a permanent dipole moment?

- (a) SO_3 (b) SO_2 (c) H_2S (d) CS_2

Question 8. In sp^3 , sp^2 and sp hybridized carbon atom, the p character is maximum in: (a) sp^3 (b) sp^2 (c) sp (d) all of the above have same p-character.

Question 9. Out of the following, intramolecular hydrogen bonding exists in:

- (a) water (b) H_2S (c) 4-nitrophenol (d) 2-nitrophenol.

Question 10. The outer orbitals of C in ethene molecule can be considered to be hybridized to give three equivalent sp^2 orbitals. The total number of sigma (s) and pi (p) bonds in ethene molecule is

- (a) 1 sigma (s) and 2 pi (p) bonds (b) 3 sigma (s) and 2 pi (p) bonds
(c) 4 sigma (s) and 1 pi (p) bonds (d) 5 sigma (s) and 1 pi (p) bonds.

MCQs Answer: 1. (c) 2. (a) 3. (a) 4. (c) 5. (c) 6. (b) 7. (d) 8. (a) 9. (d) 10. (d)

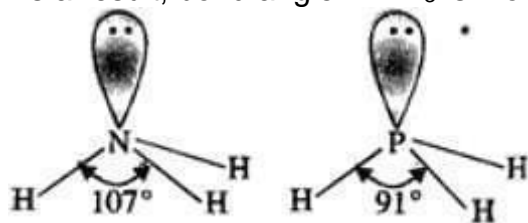
SA 2 marks

Q.1 A molecule of H_2 exists while that of the He_2 does not. Explain.

Ans- Hydrogen atom ($Z = 1$) has only one electron present in the s-orbital ($1s^1$). The two such half-filled atomic orbitals combine to form a molecular orbital which contains both these electrons. But helium ($Z = 2$) has already a filled orbital ($1s^2$). Therefore, the atomic orbitals of the helium atoms do not combine. Thus, a molecule of H_2 exists while that of He_2 does not. (BO of $\text{H}_2 = 1$ but BO of $\text{He}_2 = 0$)

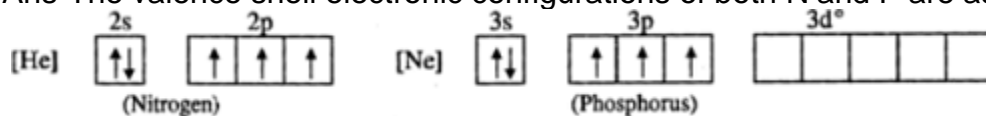
Q.2 Bond angle in NH_3 is more than in PH_3 . Explain.

Ans- Both NH_3 and PH_3 are the hydrides of nitrogen and phosphorus which are present in group 15. Nitrogen is more electronegative (3.0) as compared phosphorus (2.1). As a result, the shared electron pairs lie closer to the nitrogen atom in NH_3 than to the phosphorus atom in PH_3 . Therefore, the electron density around the nitrogen atom is more than around the phosphorus atom. This results in greater repulsion in the electron pairs around nitrogen atom than around phosphorus atom. As a result, bond angle in NH_3 is more than in PH_3 .



Q. 3 A molecule of PCl_5 exists while that of NCl_5 does not.

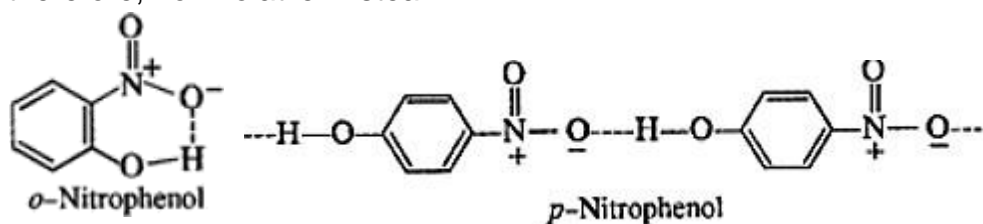
Ans-The valence shell electronic configurations of both N and P are as follows :



Since nitrogen atom has no vacant 2d orbitals, it cannot extend its covalency to five. Therefore, a molecule of NCl_5 does not exist. But in case of phosphorus, an electron can be promoted from 3s filled orbital to 3d vacant orbitals. Therefore, phosphorus can extend its covalency to five. Thus, a molecule of PCl_5 can exist.

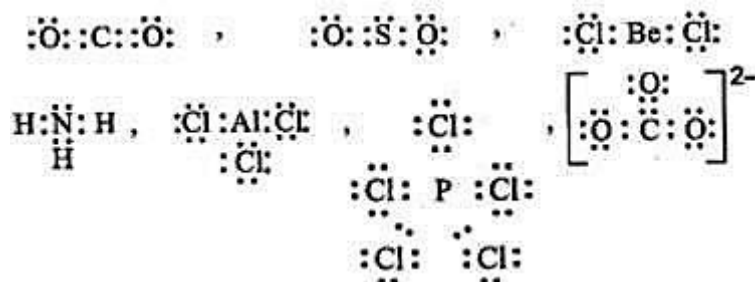
Q. 4 o-nitrophenol is steam volatile while p-nitrophenol is not. Discuss.

Answer: In o-nitrophenol, intra molecular hydrogen bonding is present while inter molecular hydrogen is present in the molecules of p-nitrophenol. Energy is needed to overcome attractive forces in the molecules of p-nitrophenol but no such energy is required in case of molecules in o-nitrophenol. This means that the boiling point of o-nitrophenol is less and is steam volatile while that of p-nitrophenol is more and is, therefore, non-volatile in steam.



Q. 5 Draw the Lewis structures of the following molecules and ions and tell in which case/cases the octet rule is violated CO_2 , SO_2 , BeCl_2 , NH_3 , AlCl_3 , PCl_5 , CO_3^{2-}

Answer:



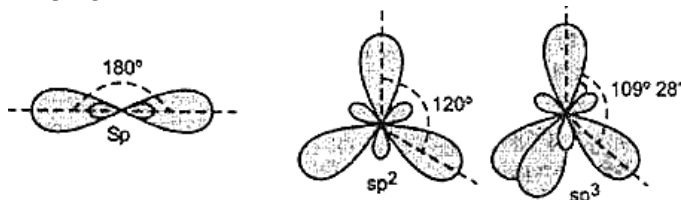
The octet rule is violated in case of BeCl_2 , AlCl_3 and PCl_5 .

Q.6 On the basis of VSEPR theory, predict the shapes of the following molecules / ions? (i) SiF_4 (ii) NH_2^- (iii) NH_4^+ (iv) C_2H_2 (v) H_3O^+ (vi) F_2O (vii) PCl_3 (viii) PF_5 .

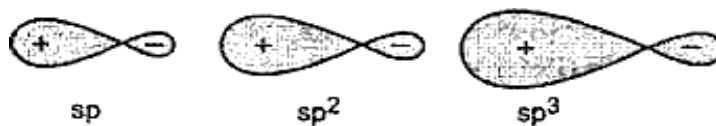
Answer: (i) Tetrahedral (ii) V-shape (iii) Tetrahedral (iv) Cylindrical (v) Trigonal pyramidal (vi) V-shape (vii) Trigonal pyramidal (viii) Trigonal bipyramidal.

Q. 7 Draw the shapes of the following hybrid orbitals ; sp , sp^2 and sp^3

Answer:



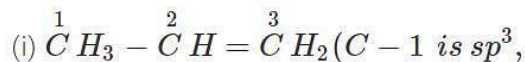
All the hybrid orbitals have same shape. However, their sizes are in the order



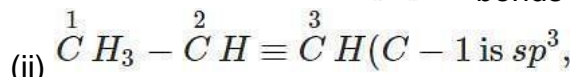
$$sp < sp^2 < sp^3$$

Q. 8. Name the type of hybridisation of each C-atom in a molecule of (i) propylene (propene) (ii) propyne. How many σ and π -bonds are present in each case?

Answer:



$\text{C} - 2$ and $\text{C} - 3$ are sp^2), σ - bonds = 8, π -bonds = 1.



$\text{C} - 2$ and $\text{C} - 3$ are sp), σ - bonds = 6, π -bonds = 2.

Q. 9. Which out of CH_3F and CH_3Cl has a higher dipole moment and why?

Answer: The dipole moment of CH_3Cl is greater than that of CH_3F . The C-F bond length in CH_3F is smaller than the C-Cl bond length in CH_3Cl . The charge separation in the C-F bond is more than in the Cl-C bond- fluoride being more electronegative than chlorine. The bond length has a greater effect than the charge separation. Hence the dipole moment of CH_3Cl is greater than that of CH_3F .

Q. 10. Why HCl is polar whereas the Cl_2 molecule is non-polar?

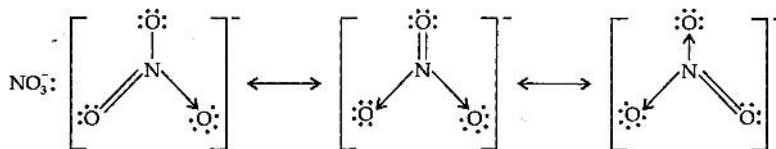
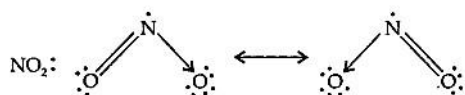
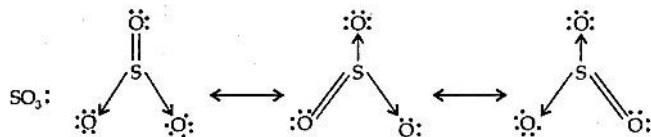
Answer: In Cl_2 both atoms have the same electronegativity. Hence the shared pair of electrons is attracted equally by both and remains exactly in the center.

In HCl, chlorine is more electronegative than H. Hence shared pair of electrons is more attracted towards chlorine, which, therefore acquires a negative charge while H acquires a positive charge.

SA 3MARKS

Q.1 Write the resonance structures for SO_3 , NO_2 and NO_3^- .

Answer:



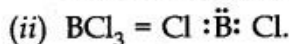
Q. 2 Discuss the shape of the following molecules using the VSEPR model:

BeCl_2 , BCl_3 , SiCl_4 , AsF_5 , H_2S , PH_3

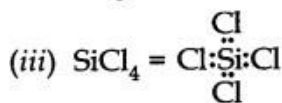
Answer:



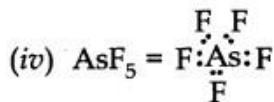
The central atom has only two bond pairs and there is no lone pair. Hence, shape is **linear**.



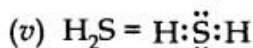
The central atom has only 3 bond pairs and no lone pair, *i.e.*, AB_3 . Hence, shape is **triangular planar**.



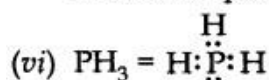
Bond pairs = 4, lone pairs = 0, *i.e.*, it is of the type AB_4 . Hence, shape is **Tetrahedral**.



Bond pairs = 5, lone pairs = 0, *i.e.*, it is of the type AB_5 . Hence, shape is **Trigonal bipyramidal**.



Bond pairs = 2, lone pairs = 2, *i.e.*, it is of the type AB_2L_2 . Hence, shape is **Bent/V-shaped**.



Bond pairs = 3, lone pair = 1, *i.e.*, it is of the type AB_3L . Hence, shape is **Trigonal**.

Q.3 Compare the relative stability of the following species and indicate their magnetic properties: O_2 , O_2^+ , O_2^- (Superoxide), O_2^{2-} (peroxide)

Answer: O_2 : Bond order = 2, paramagnetic

O_2^+ : Bond order = 2.5, paramagnetic

O_2^- : Bond order = 1.5, paramagnetic

O_2^{2-} : Bond order = 1, diamagnetic

Order of relative stability is $\text{O}_2^+ > \text{O}_2 > \text{O}_2^- > \text{O}_2^{2-}$ as bond order of O_2^+ , O_2 , O_2^- , O_2^{2-} are (2.5) (2.0) (1.5) (1.0) respectively.

Q.4 Account for the following:

(i) Water is a liquid while H_2S is a gas

(ii) NH_3 has higher boiling point than PH_3 .

Answer: (i) In case of water hydrogen bonding causes association of the H_2O molecules. There is no such hydrogen bonding in H_2S , that's why it is a gas.

(ii) There is hydrogen bonding in NH_3 but not in PH_3 .

Q 5. (a) Define dipole moment. What are the units of dipole moment?

(b) Dipole moment values help in predicting the shapes of covalent molecules. Explain.

Answer: (a) Dipole moment: In a polar molecule, one end bears a positive charge and the other has a negative charge. Thus, the molecule has two poles with equal magnitude of the charges. The molecule is known as dipolar molecule and possesses dipole moment.

It is defined as the product of the magnitude of the positive or negative charge and the distance between the charges. μ (dipole moment) = $q \times d$

SI unit of dipole moment is coulomb metre (m) or Debye.

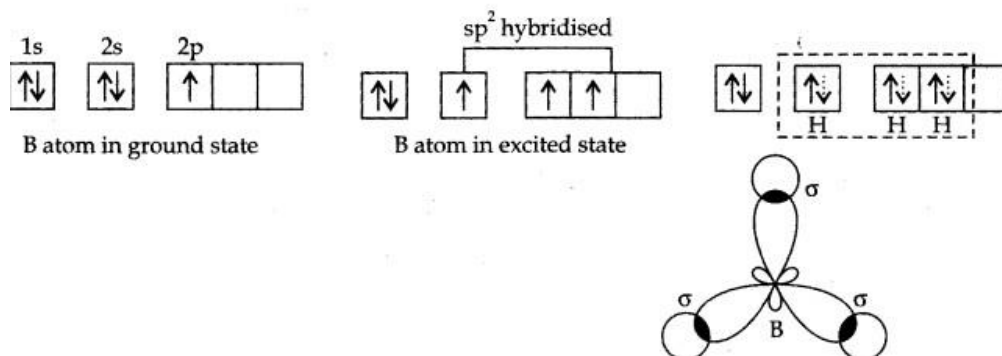
(b) The dipole moment values are quite helpful in determining the general shapes of molecules.

For molecules with zero dipole moment, shapes will be either linear or symmetrical. For Example. BeF_2 CO_2 etc. Molecules that possess dipole moments, their shape will not be symmetrical.

Q 6. Discuss the orbital structures of the following molecules on the basis of hybridisation, (i) BH_3 (ii) C_2H_2

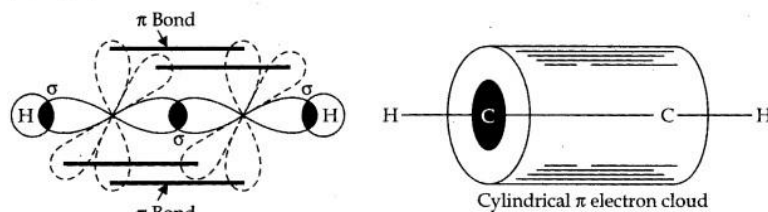
Answer:

(i) **Formation of BH_3** (atomic No. of B is 5.)



B atom gets hybridised to form three equivalent hybrid orbitals directed towards three corners of equilateral triangle with B atoms in the centre. Bond angle = 120° .

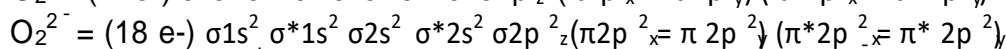
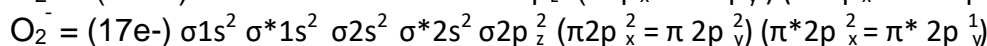
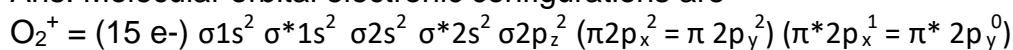
(ii) C_2H_2



Both the carbon atoms are sp hybridised. Both the carbon atoms have also two unhybridized orbitals which overlap sidewise with the similar orbitals of the other carbon atom to form two pi bonds.

3) Which is most stable out of O_2^+ , O_2^- & O_2^{2-} ? Explain. Arrange them in increasing order of bond length & bond dissociation energy.

Ans. Molecular orbital electronic configurations are



$$\text{Bond order of } \text{O}_2^+ = \frac{N_b - N_a}{2} = \frac{10 - 5}{2} = 2.5 \quad \text{Bond order of } \text{O}_2^- = \frac{N_b - N_a}{2} = \frac{10 - 7}{2} = 1.5$$

$$\text{Bond order of } \text{O}_2^{2-} = \frac{N_b - N_a}{2} = \frac{10 - 8}{2} = 1$$

So, Bond order increases $\text{O}_2^{2-} < \text{O}_2^- < \text{O}_2^+$ Hence, O_2^+ is most stable.

Bond length: $\text{O}_2^+ < \text{O}_2^- < \text{O}_2^{2-}$

Bond dissociation energy: $\text{O}_2^+ > \text{O}_2^- > \text{O}_2^{2-}$

4. Thermodynamics

[MLL: System, Surroundings, Types of system, State function, Extensive and intensive properties, Isothermal and adiabatic process, Internal Energy and Internal Energy change, First Law of thermodynamics and its mathematical formula, Enthalpy and enthalpy change, relation between heat of reaction at const pressure and

constant volume ($\Delta H = \Delta U + \Delta n_{(g)} RT$), simple numerical based on this formula, Heat capacity, Gibbs' Free energy, Entropy, Second law of thermodynamics, Hess's law, numerical based on this law and simple numerical based on the formula

$\Delta G^\circ = -2.303RT \log K$, $\Delta G = \Delta H - T\Delta S$, $\Delta S = q_{rev}/T$ & NCERT Text Book Question No. 6.1 to 6.6 MCQ, 6.14, 6.17, 6.19, 6.20]

MLL THERMODYNAMICS CLASS XI

System: The part of universe in which observations are made.

Surroundings: The part of universe other than the system is known as surroundings.

Types of Systems:

Open system: The system in which energy and matter both can be exchanged with the surroundings.

Closed system : The system in which only energy can be exchanged with the surroundings.

Isolated system: The system in which neither energy nor matter can be exchanged with the surroundings.

Intensive Properties: Properties which do not depend on the quantity of matter. e.g., pressure, temperature, specific heat, molar heat capacity etc

Extensive Properties: Properties which are dependent on the quantity of matter e.g., internal energy, volume, enthalpy, heat capacity etc.

State functions: Properties of a system which are independent of path followed and depend only on initial and final state e.g., U, H, G etc.

Path functions: Properties which depend upon the path followed e.g., work, heat, etc.

Thermodynamic Process: It is the operation which brings change in the state of the system. Thermodynamic processes are as follows:-

Isothermal process: In which temperature remains constant, i.e., ($\Delta T = 0$, $\Delta U = 0$).

Isochoric process: In which volume remains constant, i.e., ($\Delta V = 0$).

Isobaric process: In which pressure remains constant, i.e., ($\Delta p = 0$).

Adiabatic process: In which heat is not exchanged between the system and the surroundings ($q = 0$).

First Law of Thermodynamics:

Energy can neither be created nor destroyed although it can be converted from one form to the other. Mathematically, $\Delta U = q + W$

Sign conventions: q is +ve = heat is supplied to the system

q is -ve = heat is lost by the system

W is +ve = work done on the system (eg during compression of a gas)

W is -ve = work done by the system (eg during expansion of a gas)

Enthalpy (H): $H = U + PV$

At constant volume $\Delta V = 0$, $q_v = \Delta U$

So $\Delta H = \Delta U + p\Delta V$, $q_p = H_2 - H_1 = \Delta H = \Delta U + P\Delta V$

Exothermic reaction: Reaction accompanied by release of energy. $q = \Delta H = -ve$

Endothermic reactions: Reaction accompanied by release of energy. $q = \Delta H = +ve$

Specific heat capacity: Specific heat, also called specific heat capacity is the quantity of heat required to raise the temperature of unit mass of a substance by one degree Celsius (or one kelvin).

Standard Enthalpy of Reactions: The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states. The standard state of a substance at a specified temperature is its pure form at 1 bar

Standard enthalpy of fusion: The enthalpy change that accompanies melting of one mole of a solid substance in standard state.

Standard enthalpy of vaporization: The enthalpy change that accompanies vaporization one mole of a liquid at constant temperature and under standard pressure.

Standard enthalpy of sublimation: $\Delta_{\text{sub}}H^0$ is the change in enthalpy when one mole of a solid substance sublimates at a constant temperature and under standard pressure (1bar).

Standard enthalpy of formation: The enthalpy change for the formation of one mole of a compound from its elements in their standard states.

Bond enthalpy (B.E. or $\Delta_{\text{bond}}H$): It is amount of energy released when gaseous atoms combines to form one mole of bonds between them or heat absorbed when one mole of bonds between them are broken to give free gaseous atoms. Further

$$\Delta_r H = \text{B.E.}(\text{Reactants}) - \text{B.E.}(\text{Products})$$

Lattice Enthalpy $\Delta_{\text{lattice}}H$: The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

Enthalpy of Solution ($\Delta_{\text{sol}}H^0$): Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent.

Hess's Law of constant heat summation: The total enthalpy change in a reaction is same whether the reaction takes place in one step or in several steps.

i.e. $\Delta H = H_1 + H_2 + H_3 + \dots$

Entropy (S): It is measure of randomness or disorder in a system.

$$\text{Entropy change } (\Delta S) = q_{(\text{rev.})}/T$$

Order of entropy: Gas > Liquid > Solid.

Crystallization of a solid: Entropy decrease ($\Delta S = -ve$)

$H_2 \rightarrow 2H$: Entropy increases ($\Delta S = +ve$)

Melting of a solid : Entropy increases ($\Delta S = +ve$)

Vaporization of a liquid: Entropy increases ($\Delta S = +ve$)

Dissolution of a solid : Entropy increases ($\Delta S = +ve$)

Spontaneity in term of (ΔS)

$$\Delta S(\text{total}) = \Delta S(\text{universe}) = \Delta S(\text{system}) + \Delta S(\text{surrounding})$$

If $\Delta S(\text{total})$ is +ve, the process is spontaneous.

If $\Delta S(\text{total})$ is -ve, the process is non spontaneous

Second Law of thermodynamics: In any spontaneous process, the entropy of the universe always increases. $\Delta S_{\text{total}} = \Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$

Gibb's energy (G): $G = H - TS$

$$\Delta G = \Delta H - T\Delta S \text{ (Gibb's equation)}$$

Spontaneity in term of (ΔG) If $\Delta G = -ve$ the process is spontaneous.

If $\Delta G = +ve$ the process is non-spontaneous If $\Delta G = 0$ for Equilibrium

ΔH	ΔS	ΔG	Reaction will be spontaneous / non spontaneous
-ve	+ve	-ve	Spontaneous at all temp
+ve	-ve	+ve	Non spontaneous
-ve	-ve	-ve (at low temp) +ve (at high temp)	Spontaneous at low temp Non spontaneous at high temp
+ve	+ve	+ve (at low temp) -ve (at high temp)	Non spontaneous at low temp Spontaneous at high temp

SOME IMPORTANT FORMULAE

$\Delta U = q + w$
$\Delta U = q_v$

$\Delta H = q_p$
$\Delta H = \Delta U + P\Delta V$
$\Delta H = \Delta U + \Delta n_g RT$
$Q = c m \Delta T$ (c is specific heat capacity)
$Q = C \Delta T$ (C is heat capacity)
$Q = c_m n \Delta T$ (c_m is molar heat capacity and n is no. of moles)
$\Delta_r H = \text{B.E. (Reactants)} - \text{B.E. (Products)}$
$\Delta_r H = \sum \Delta_f H (\text{Products}) - \sum \Delta_f H (\text{Reactants})$
Hess's Law $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \dots$
$\Delta H_{\text{sol}} = \Delta H_{\text{lattice}} + \Delta H_{\text{hydration}}$
$\Delta G = \Delta H - T\Delta S$
$\Delta_r G^0 = -RT \ln K$
$\Delta_r G^0 = -2.303 RT \ln K$

Assertion Reasoning Type Question:

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

- Both A and R are true and R is the correct explanation of A.**
- Both A and R are true but R is not the correct explanation of A.**
- A is true but R is false.**
- A is false but R is true.**

1. Assertion (A): Combustion of all organic compounds is an exothermic reaction.

Reason (R): The enthalpies of all elements in their standard state are zero.

(Answer) a) Both A and R are true but R is not the correct explanation of A.

2. Assertion (A): Spontaneous process is an irreversible process and may be reversed by some external agency.

Reason (R): Decrease in enthalpy is a contributory factor for spontaneity

(Answer) (b) Both A and R are true but R is not the correct explanation of A.

3. Assertion (A) : A liquid crystallises into a solid and is accompanied by decrease in entropy.

Reason (R) : In crystals, molecules organise in an ordered manner

(Answer) (a) Both A and R are true and R is the correct explanation of A.

4. Assertion (A): The thermodynamic factor which determines the spontaneity of a process is the free energy. For a process to be spontaneous the free energy must be -ve.

Reason (R) The change in free energy is related to the change in enthalpy and change in entropy. The change in entropy for a process must always be positive if it is spontaneous.

(Answer) (c) A is true but R is false.

5. Assertion: The sum of $q + w$ is a state function.

Reason: Work and heat are state functions.

(Answer)(c) A is true but R is false.

6. Assertion: A reaction in which randomness of the system increases, will always be spontaneous.

Reason: According to second law of thermodynamics, spontaneous reaction is accompanied by increase in randomness of the universe.

(Answer): (d) A is false but R is true.

7. Assertion: Standard enthalpy of formation of diamond is zero.

Reason: Standard enthalpy of formation of substance is the enthalpy change for formation of one mole of the substance from its elements in their standard states.

(Answer): (d) A is false but R is true

8. Assertion : The sum of $q + w$ is a state function.

Reason : Work and heat are state functions.

(Answer): (c) A is true but R is false.

C. Short Answer Type : 1 mark each.

1. $\Delta G^\circ = -2.303RT \log K$, for $K = 1$ what is the value of ΔG° ?

Ans: Zero $\because \log 1 = 0$

2. Identify intensive properties out of the following :Mass, density, heat capacity, Temperature, specific heat capacity

Answer: density, Temperature, specific heat capacity

3. At what condition of a chemical change, the value of ΔH and ΔU will be equal?

$\Delta H = \Delta U$ when $\Delta n(g) = 0$ i.e. no of moles of reactants and products are equal

4. State Hess's Law

Ans: The Enthalpy change for a particular reaction is always constant and is independent of path in which the reaction takes place $\Delta H = \Delta H_1 + \Delta H_2 + \dots$

5. What is the value of entropy change (ΔS) at equilibrium state?

Ans: $\Delta S = 0$

6. For an isolated system $\Delta U = 0$; what will be ΔS ? Ans: $\Delta S > 0$

7. Calculate the value of $\Delta n_{(g)}$

(i) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ (ii) $CO_{(g)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{2(g)}$

Ans; (i) $\Delta n(g) = 0$ (ii) $\Delta n(g) = 1 - (1 + \frac{1}{2}) = -\frac{1}{2}$

8. State 3rd law of thermodynamics.

Ans: The entropy of perfectly crystalline substances at absolute zero is taken as zero.

9. State the second law of thermodynamics.

Ans: In any spontaneous process, the entropy of the universe always increases.

10. Define the term Heat Capacity.

Ans; The amount of heat required to raise the temperature of a substance by 1° is called Heat Capacity.

11. For a reaction both ΔH and ΔS , under what condition the reaction will be occurred spontaneously?

Ans; $\Delta G = \Delta H - T\Delta S$, If ΔG is -ve then the reaction will be spontaneous, at higher temperature the term $T\Delta S$ will be large and ΔG value will be -ve.

12. What is meant by an adiabatic process?

Answer: A process in which there is no transfer of heat between the system and surroundings.

13. Define Lattice enthalpy.

Answer: Enthalpy change when one mole of an ionic solid changes into its ions in gaseous state.

14. Define standard enthalpy of formation of a substance.

Answer: Enthalpy change when one mole of a substance is formed from its elements in their standard states.

15. For the reaction, $2 \text{Cl(g)} \rightarrow \text{Cl}_2(\text{g})$, what are the signs of ΔH and ΔS ?

Answer: ΔH and ΔS are negative.

16. Identify state functions out of the following H, q, U, w

Answer: H, U.

17. Predict whether the entropy increases/decreases in the following changes-

(i) dissolution of a solid to form aqueous solution

(ii) Temperature of a crystallize solid raised from OK to 115K

Answer: i) increases ii) increases.

18. Given: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$, $\Delta H^0 = -92.4 \text{KJ.mol}^{-1}$ What is the standard Enthalpy of formation of $\text{NH}_3(\text{g})$?

Answer: standard enthalpy of formation of $\text{NH}_3(\text{g}) = -92.4/2 = -46.2 \text{ kJ/mol}$.

19. The enthalpy of atomisation for the reaction $\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{g}) + 4\text{H}(\text{g})$ is 1665 kJ mol^{-1} . What is the bond energy of C–H bond?

Answer: The bond energy of C–H bond = $1665/4 = 416.2 \text{ kJ/mol}$

20. For the reaction $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ Which out of Enthalpy change and internal energy change will have a larger value?

Answer: Since $\Delta n_g = -\frac{1}{2}$, using formula $\Delta H = \Delta U + \Delta n_g RT$
 $\Delta H < \Delta U$

Multiple Choice Questions Type: 1 mark each

1. Which of the following statements is correct?

- (i) The presence of reacting species in a covered beaker is an example of open system.
- (ii) There is an exchange of energy as well as matter between the system and the surroundings in a closed system.
- (iii) The presence of reactants in a closed vessel made up of copper is an example of a closed system
- (iv) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system

Ans: (iii)

2. The volume of gas is reduced to half from its original volume. The specific heat will be _____.

- (i) reduce to half
- (ii) be doubled
- (iii) remain constant
- (iv) increase four times

Ans: (iii)

3. The entropy change can be calculated by using the expression $\Delta S = q_{\text{rev}} / T$. When water freezes in a glass beaker, choose the correct statement amongst the following

- (i) ΔS (system) decreases but ΔS (surroundings) remains the same.
- (ii) ΔS (system) increases but ΔS (surroundings) decreases.
- (iii) ΔS (system) decreases but ΔS (surroundings) increases.
- (iv) ΔS (system) decreases and ΔS (surroundings) also decrease.

Ans: (iii)

4. The work done in case of isothermal free expansion is

a) maximum b) minimum c) zero d) positive

(Answer) c) zero.

5. Which of the following statement is not correct?

- (i) ΔG is positive for a spontaneous reaction
- (ii) ΔG is negative for a spontaneous reaction
- (iii) ΔG is positive for a non-spontaneous reaction
- (iv) ΔG is zero for a reversible reaction

Ans: (i)

6. $\Delta_f U^\circ$ of formation of CH_4 (g) at certain temperature is -393 kJ mol^{-1} . The value of $\Delta_f H^\circ$ is (i) zero (ii) $< \Delta_f U^\circ$ (iii) $> \Delta_f U^\circ$ (iv) equal to $\Delta_f U^\circ$

Ans: (ii)

7. Which of the following is an extensive property

i) Molar heat capacity ii) Temperature iii) Enthalpy iv) All of these

Answer: iii) Enthalpy.

8. The q iswhen heat is transferred from the surroundings to the system and w is..... When a gas undergoes expansion

- i) positive, negative ii) negative, positive
- iii) positive, positive iv) negative, negative

Answer: i) positive, negative.

9. ΔH for the reaction $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$

(i) $\Delta U - 2RT$ (ii) $\Delta U + 2RT$ (iii) $\Delta U - RT$ (iv) $\Delta U = RT$

Ans: (i)

10. In bomb calorimeter which quantity is kept constant to measure ΔU ?

(i) volume (ii) pressure (iii) temperature (iv) all of these

Ans: (i) volume

Short Answer Type : 2 mark each

1. State whether the entropy increases or decreases in the following transformation

- (i) $2\text{H}_2\text{O} (\text{l}) \rightarrow 2 \text{H}_2 (\text{g}) + \text{O}_2 (\text{g})$
- (ii) $\text{CaCO}_3 (\text{s}) \rightarrow \text{CaO} (\text{s}) + \text{CO}_2 (\text{g})$
- (iii) $2\text{SO}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2 \text{SO}_3 (\text{g})$
- (iv) $\text{H}_2\text{O} (\text{ice}) \rightarrow \text{H}_2\text{O} (\text{l})$

Ans i) Entropy increases ii) Entropy increases

2. The equilibrium constant for the reaction is 10. Calculate the value of ΔG . Given $R = 8 \text{ J/k/mol}$; $T = 300\text{K}$

$$\begin{aligned} \text{Ans: } \Delta G^\circ &= -2.303RT \log K \\ &= -2.303 \times 8 \times 300 \times \log 10 = -2.303 \times 8 \times 300 \quad [\because \log 10=1] \\ &= -5.527 \text{ kJ/mol} \end{aligned}$$

3. Identify the state functions and path functions out of the following: enthalpy, entropy, heat, temperature, work, free energy.

Ans: State function: enthalpy, entropy, heat, temperature

Path function: work, free energy

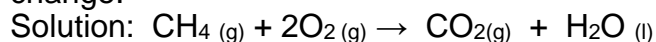
4. Calculate the entropy change in surroundings when 1.0 mol of water H_2O_0 is formed under standard condition. Given $\Delta H^\circ = -286 \text{ kJ/mol}$

Ans.

$$q_{\text{rev}} = (-\Delta_f H^\ominus) = -286 \text{ kJ mol}^{-1} = 286000 \text{ J mol}^{-1}$$

$$\Delta S_{(\text{Surroundings})} = \frac{q_{\text{rev}}}{T} = \frac{(286000 \text{ J mol}^{-1})}{298 \text{ K}} = 959 \text{ J K}^{-1} \text{ mol}^{-1}.$$

6. The heat of combustion of gaseous CH₄ at const. volume is measured in a bomb calorimeter at 298 K and it is found to be - 885.4 kJ/mol. Find the value of enthalpy change.



$$\Delta n_{(g)} = 1 - (1+2) = -2 \text{ moles}$$

$$\Delta U = -885.4 \text{ kJ / mol} = -885400 \text{ J / mol}$$

$$\Delta H = \Delta U + \Delta n_{(g)} RT \text{ or, } \Delta H = -885400 - 2 \times 8.314 \times 298 = -890355 \text{ J}$$

$$= -890.355 \text{ kJ}$$

6. For a reaction at 298 K, 2A + B → C

ΔH = 40 kJ / mol and ΔS = 0.2 kJ / K / mol. At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range?

Answer: As per the Gibbs Helmholtz equation: ΔG = ΔH - TΔS For equilibrium, ΔG = 0 ; ΔH = TΔS or T = ΔH / ΔS

$$T = (400 \text{ KJ mol}^{-1}) / (0.2 \text{ KJ K}^{-1} \text{ mol}^{-1}) = 2000 \text{ K}$$

Thus, reaction will be in a state of equilibrium at 2000 K and will be spontaneous above this temperature.

7. During a change, 5 kJ of heat is supplied to the system and 200J of work is done by the system. Calculate the change in internal energy of the system.

Answer: ΔU = q + w

Heat is supplied to the system. So, q = +5kJ = +5000J

Work is done by the system. So, w = -200J

Putting values in the equation

$$\Delta U = 5000\text{J} - 200\text{J}$$

$$\Delta U = 4800 \text{ J}$$

8. Calculate the heat necessary to raise the temperature of 54 g of aluminium from 10°C to 30°C. Molar heat capacity of Al is 24 J mol⁻¹ K⁻¹

Answer: C = 24 J mol⁻¹ K⁻¹

$$\Delta T = T_2 - T_1 = 30 - 10 = 20^\circ\text{C} = 20 \text{ K}$$

Number of mole of Aluminium = 54/27 = 2 mole

$$Q = n C_m \Delta T$$

$$Q = 2 \text{ mole} \times 24 \text{ J mol}^{-1} \text{ K}^{-1} \times 20 \text{ K}$$

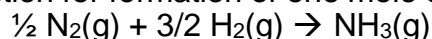
$$Q = 960 \text{ KJ}$$

9. Enthalpy of fusion and enthalpy of vaporisation of sodium metal are 2.6 and 98.2kJ/mol respectively. What is the enthalpy of sublimation of sodium?

Answer: Δ_{sub}H = Δ_{fus}H + Δ_{vap}H = 2.6 + 98.2 = 100.8 kJ/mol

10. Given: N₂(g) + 3H₂(g) → 2NH₃(g), ΔH⁰ = -92.4KJ.mol⁻¹ What is the standard enthalpy of formation of NH₃(g).

Answer: The reaction for formation of one mole of ammonia is



The standard enthalpy of formation of ammonia is

$$\Delta_f H^0 \text{ NH}_3(\text{g}) = -\frac{92.4}{2} = -46.2 \text{ KJmol}^{-1}$$

Long Answer Type Questions:

1. For the reaction $2A(g) + B(g) \rightarrow 2D(g)$ $\Delta U^{\circ} = -10.5 \text{ kJ}$ and $\Delta S^{\circ} = -44.1 \text{ JK}^{-1}$. Calculate ΔG° for the reaction, and predict whether the reaction may occur spontaneously.

Ans. $2A(g) + B(g) \rightarrow 2D(g)$ $\Delta U^{\circ} = -10.5 \text{ kJ}$ and $\Delta S^{\circ} = -44.1 \text{ J K}^{-1}$

$$\Delta n_g = 2 - (2 + 1) = -1 \text{ mole}$$

$$\Delta H^{\circ} = \Delta U^{\circ} + \Delta n_g RT$$

$$= (-10.5 \text{ kJ}) - (-1) (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) (298 \text{ K})$$

$$= -10.5 \text{ kJ} - 2.48 \text{ kJ}$$

$$\Delta H^{\circ} = -12.98 \text{ kJ}$$

Substituting the values of ΔH° and ΔS° in the expression of ΔG°

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$= -12.98 \text{ kJ} - (298 \text{ K}) (-44.1 \text{ J K}^{-1})$$

$$= -12.98 \text{ kJ} + 13.14 \text{ kJ}$$

$$\Delta G^{\circ} = +0.16 \text{ kJ}$$

Since ΔG° for the reaction is positive, the reaction will not occur spontaneously.

3. From the following bond energies:

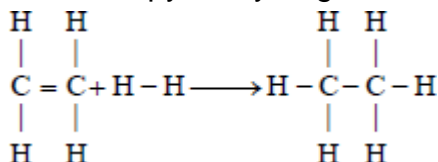
H – H bond energy: $431.37 \text{ kJ mol}^{-1}$

C = C bond energy: $606.10 \text{ kJ mol}^{-1}$

C – C bond energy: $336.49 \text{ kJ mol}^{-1}$

C – H bond energy: $410.50 \text{ kJ mol}^{-1}$

Calculate Enthalpy for hydrogenation of Ethene involving the reaction,



Answer:

Enthalpy of reaction

$$= \text{B.E.}_{(\text{Reactant})} - \text{B.E.}_{(\text{Product})}$$

$$= [\text{B.E.}_{(\text{C}=\text{C})} + 4\text{B.E.}_{(\text{C}-\text{H})} + \text{B.E.}_{(\text{H}-\text{H})}]$$

$$- [\text{B.E.}_{(\text{C}-\text{C})} + 6\text{B.E.}_{(\text{C}-\text{H})}]$$

$$= [606.1 + (4 \times 410.5) + 431.37] - [336.49 + (6 \times 410.5)]$$

$$= -120.0 \text{ kJ mol}^{-1}$$

3. Enthalpies of formation of $\text{C}_2\text{H}_4(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ at 25°C and 1atm pressure are 52, – 394 and – 286 kJ/mol respectively. Calculate Enthalpy of combustion of Ethene.

Answer:

The reaction is $\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$.

$$\text{Enthalpy of reaction } \Delta_r H = \Delta_f H(\text{products}) - \Delta_f H(\text{reactants}) \quad \{\Delta_f H(\text{O}_2) = 0\}$$

$$= [2 \times (-394) + 2 \times (-286)] - [52 + 0]$$

$$= -1412 \text{ kJ/mol.}$$

4. Define the following terms: i) Enthalpy (ii) Entropy (iii) Gibb's Free energy

Ans: i) Enthalpy may be defined as the "sum of the internal energy and pressure-volume energy of the system" $H = U + P.V$

ii) Entropy is measure of randomness or disorder of a system.

i.e. Gas > Liquid > Solid.

(iii) Gibbs energy (G) It is a measure of capacity of a system to do maximum useful work. $G = H - T.S$

5. State the First Law of Thermodynamics. Established the mathematical formula of First Law of Thermodynamics.

Ans: Energy can neither be created nor be destroyed; it may be converted from one form into another.

Mathematically $\Delta U = q + w$,

Let us consider a system whose internal energy is U_1 , now if the system are supplied q amount of heat, the energy of the system become $U_1 + q$.

Due to supply of heat the system do some work (expansion) i. e. w .

Hence, the final energy of the system U_2 become $U_1 + q + w$

Therefore, $U_2 = U_1 + q + w$

Or $U_2 - U_1 = q + w$

Or, $\Delta U = q + w$

$$\Delta U = q + w$$

$w = -P \Delta V$ (work of expansion)

6. Calculate the standard enthalpy of formation of CH_3OH . from the following

data: (i) $\text{CH}_3\text{OH}(\text{l}) + 3/2 \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}); \Delta_r H^\ominus = -726 \text{ kJ mol}^{-1}$

(ii) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}); \Delta_c H^\ominus = -393 \text{ kJ mol}^{-1}$

(iii) $\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l}); \Delta_f H^\ominus = -286 \text{ kJ mol}^{-1}$

Answer:

The equation we aim at; $\text{C}(\text{s}) + 2\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{CH}_3\text{OH} \quad \Delta_f H^\ominus = ? \dots$

Multiply eqn. (iii) by 2 and add to eqn. (ii)

$\text{C}(\text{s}) + 2\text{H}_2(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l});$

$$\Delta H = - (393 + 522) = -965 \text{ kJ mol}^{-1} \dots \text{(iv)}$$

Subtract eqn. (iv) from eqn. (i)

$\text{CH}_3\text{OH}(\text{l}) + 3/2 \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \quad \Delta H = -726 - (-965) \text{ kJ mol}^{-1}$

$\text{C}(\text{s}) + 2\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{CH}_3\text{OH}(\text{l}) \quad ; \Delta_f H^\ominus = -239 \text{ kJ mol}^{-1}$

8. The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are given in the following reactions. Calculate the Enthalpy of formation of $\text{CH}_4(\text{g})$

i) $\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad ; \quad \Delta_c H^\ominus = -890.3 \text{ kJ/mol}$

ii) $\text{C}(\text{s}) + \text{O}_2 \longrightarrow \text{CO}_2 \quad ; \quad \Delta_c H^\ominus = -393.5 \text{ kJ/mol}$

iii) $\text{H}_2 + 1/2 \text{O}_2 \longrightarrow \text{H}_2\text{O} \quad ; \quad \Delta_c H^\ominus = -285.8 \text{ kJ/mol}$

Answer:

Multiplying equation (iii) by 2 and add equation (ii) we get

$\text{C}(\text{s}) + \text{O}_2 + 2 \text{H}_2 + \text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad ; \quad \Delta_c H_1 = -393.5 + 2x - 285.8$ Or,

$\text{C}(\text{s}) + 2\text{O}_2 + 2 \text{H}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta_c H_2 = -965.1 \text{ kJ/mol} \dots \text{(iv)}$

Now, subtract eqn (iv) from (i)

$\text{CH}_4 + 2\text{O}_2 - \text{C}(\text{s}) - 2\text{O}_2 - 2 \text{H}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O} - \text{CO}_2 - 2\text{H}_2\text{O}$

$\Delta H^\ominus = -890.3 - (-965.1) \text{ kJ/mol}$

Or, $\text{CH}_4 + 2\text{O}_2 - \text{C}(\text{s}) - 2\text{O}_2 - 2\text{H}_2 = 0 \quad ; \quad \Delta H^\ominus = 74.8 \text{ kJ/mol}$

Or, $-\text{C}(\text{s}) - 2 \text{H}_2 = -\text{CH}_4 \quad ; \quad \Delta H^\ominus = 74.8 \text{ kJ/mol}$

Or $\text{C}(\text{s}) + 2 \text{H}_2 = \text{CH}_4 \quad ; \quad \Delta H^\ominus = -74.8 \text{ kJ/mol}$

Equilibrium

KEY POINTS

- Equilibrium in physical processes:
- Solid-liquid equilibrium
- Liquid-vapour equilibrium
- Dynamic equilibrium
- law of chemical equilibrium and equilibrium constant

- homogeneous equilibrium
- Equilibrium constant in gaseous systems
- Factors affecting equilibrium-Le Chateliers principle
- Ionic equilibrium-ionisation of acids and bases
- Strong and weak electrolytes
- Degree of ionisation
- Ionisation of polybasic acids
- Acid strength –pH
- Hydrolysis of salt, buffer solution
- Henderson equation
- Solubility product
- Common ion effect:

1. Equilibrium in chemical process – At equilibrium the concentration of each reactant and product becomes constant.

At equilibrium the rate of forward reaction becomes equal to the rate of backward reaction and hence dynamic in nature.

2. Equilibrium Constant – The product of molar concentration of products raised to power their molar coefficient divided by molar concentration of the reactants raised to the power their molar coefficient is constant at constant temperature and is called equilibrium constant.

3. Relationship between K_p and K_c.

$$K_p = K_c (RT)^{\Delta n}$$

4. Relationship between equilibrium constant and reaction quotient.

- If $Q_c < K_c$, the reaction proceeds in forward direction.
- If $Q_c > K_c$, the reaction proceeds in backward direction.
- If $Q_c = K_c$, the reaction is in equilibrium.

5. Different acid- base concepts.

According to Arrhenius an acid is a substance that gives H⁺ ion on dissociation and base is a substance that gives OH⁻ ion on dissociation.

6. According to Lowry Bronsted concept acid is an proton donor and base is an proton acceptor.

7. According to Lewis concept a base is an electron donor and acid is an electron acceptor.

8. Le Chatliers principle – When an equilibrium is subjected to change in temperature pressure or concentration, the equilibrium will shift in that direction to undo the effect.

9. (i) pH = - log [H⁺]

(ii) K_w = [H₃O⁺] [OH⁻], where K_w = ionic product of water.

Ionic product of water increases with increase in temperature because dissociation of water into H_3O^+ & OH^- increases with increase in the temperature.

11. Solubility product is the product of molar concentration of ions in a saturated solution but ionic product is the product in any solution.

12. The common ion effect is an effect that suppresses the ionization of an electrolyte when another electrolyte (which contains an ion which is also present in the first electrolyte, i.e. a common ion) is added.

$$1. aA + bB \rightleftharpoons cC + dD, K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

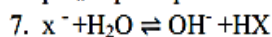
$$2. K_p = K_c (RT)^{\Delta n}$$

$$3. \Delta G^0 = -RT \ln K = -2.303RT \log K$$

$$4. K_a \times K_b = K_w$$

$$5. \text{pH} = -\log[\text{H}^+], \text{pOH} = -\log[\text{OH}^-]$$

$$6. \text{p}K_w = \text{pH} + \text{pOH} = 14$$



Degree of hydrolysis $h = \sqrt{k_w/k_a} \times c$ (for salts of strong acid and weak base)

$$\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_a + \log c)$$

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

Degree of hydrolysis $h = \sqrt{K_w/K_a \times K_b}$ (for salts of weak acid and weak base)

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

pH of buffer solution of salt of weak acid and its salt:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{Base}]}$$

[Base]

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{Base}]}$$

[Base]

Salt type	Relation between K_{sp} and S	Example
AB	$K_{sp} = s \times s = s^2$	AgCl, ZnS
AB ₂	$K_{sp} = s \times (2s)^2 = 4s^3$	PbCl ₂ , HgCl ₂
A ₂ B	$K_{sp} = (2s)^2 \times (s) = 4s^3$	Ag ₂ SO ₄
AB ₃	$K_{sp} = (s) \times (3s)^3 = 27s^3$	Fe(OH) ₃

ASSERTION-REASON TYPE QUESTIONS

(A) Both Assertion and reason are true and reason is correct explanation of assertion.

(B) Assertion and reason both are true but reason is not the correct explanation of assertion.

(C) Assertion is true, reason is false.

(D) Assertion is false, reason is true

1. Assertion (A): For any chemical reaction at a particular temperature, the equilibrium constant is fixed and is a characteristic property.

Reason (R) : Equilibrium constant is independent of temperature

Ans – C.

2. Assertion (A): Chemical equilibrium is in a state of dynamic equilibrium.

Reason (R): At equilibrium the forward and backward reactions are proceeding at the same rate

and no macroscopic change is observed.

Ans – A.

3. Assertion (A): If Q_c (reaction quotient) < K_c (equilibrium constant) reaction moves in direction of reactants.

Reason (R): Reaction quotient is defined in the same way as equilibrium constant at any stage of the reaction.

Ans – D.

4. Assertion: When $Q_c = K_c$, reaction is at equilibrium.

Reason: At equilibrium, ΔG is 0.

Ans – B.

5. Assertion: An aqueous solution of ammonium acetate can act as buffer solution.

Reason: An aqueous solution of any pure liquid can act as buffer solution

Ans: C

SHORT QUESTIONS (1 Mark Each)

Q 1. Solubility of CO_2 decreases with rise in temperature Why?

Ans - The dissolution of CO_2 gas in water is exothermic in nature because the gas contracts in volume. Thus, on increasing the temperature, the speed of the endothermic or reverse process will increase according to Le Chatelier's principle.

Q 2. What is the relationship between K_p and K_c ?

Ans - $K_p = K_c (RT)^{\Delta n}$

Q 3. Define common ion effect.

Ans - The common ion effect is an effect that suppresses the ionization of an electrolyte when another electrolyte (which contains an ion which is also present in the first electrolyte, i.e. a common ion is added).

Q 4. Ammonia is termed as a base although it does not have OH^- ions in it. Why?

Ans - It is a Lewis base, as it can donate its lone pair of electrons.

Q 5. How does a catalyst affect the equilibrium constant?

Ans - It helps to attain the equilibrium faster.

Q 6 Write conjugate acid and conjugate base of H_2O ?

Ans - H_3O^+ & OH^- .

Q 7. Name one natural buffer solution.

Ans - Blood is an example of natural buffer solution.

Q 8. What is the expression for K_{eq} ? for the reaction $2\text{N}_2\text{O}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g})$

Ans - $K = \frac{[\text{NO}]^4}{[\text{N}_2\text{O}]^2 [\text{O}_2]}$

Q 10. How is ionic product of a salt different from its solubility product?

Ans: -- Solubility product is the product of molar concentration of ions in a saturated solution but ionic product is the product in any solution.

Q 11. When is a precipitate formed when solution of BaCl_2 and Na_2SO_4 are mixed?

Ans - A precipitate is formed when in the final solution after mixing, the ionic product of $[\text{Ba}^{2+}][\text{SO}_4^{2-}] > K_{sp}$ for BaSO_4 .

Q 12. Which of the following are Lewis acid? H_2O , BF_3 , H^+ , NH_4^+

Ans - BF_3 , H^+ , NH_4^+ .

Q 13. Explain why pure liquids and solids can be ignored while writing the value of equilibrium constants.

Answer: This is because molar concentration of a pure solid or liquid is independent of the amount present. Since density of pure liquid or solid is fixed and molar mass is also fixed. Therefore, molar concentration are constant

Q 14. Give one example of everyday life in which there is gas solution equilibrium.

Ans - Soda - water bottle.

Q 15. What happens to the dissociation of PCl_5 in a closed vessel if helium gas is introduced into it at the same temperature?

Answer: Volume is constant, molar concentration of all reactant & products are constant, so there is no change in the state of equilibrium.

MULTIPLE CHOICE QUESTIONS OF ONE MARK EACH

Q 1. According to Lewis concept, an acid is:

- (a) proton donor (b) electron pair donor
(c) electron pair acceptor (d) proton acceptor

Ans: (c)

Q 2. Ostwald's dilution law is applicable to:

- (a) Strong electrolytes only (b) Weak electrolyte only
(c) Non-electrolytes (d) Strong and weak electrolytes

Ans: (b) Weak electrolyte only

Q 3. The pH of a solution of hydrochloric acid is 4. The molarity of the solution is:

- (a) 4.0 (b) 0.4 (c) 0.0001 (d) 0.04

Ans: (c)

Q 4. The strong conjugate base is (a) NO_3^- (b) Cl^- (c) SO_4^{2-} (d) CH_3COO^-

Ans (d)

Q 5. Which of the following pairs constitutes a buffer?

- (a) NaOH and HCl (b) HNO_3 and NH_4NO_3 (c) HCl and KCl (d) HNO_2 and NaNO_2

Ans (d)

Q 6. Le Chatelier's principle is applicable to:

- (a) only homogeneous chemical reversible reactions
(b) only heterogeneous chemical reversible reactions
(c) only physical equilibria
(d) all systems, chemical or physical in equilibrium.

Ans (d)

Q 7. Which of the following is the weakest base?

- (a) NaOH (b) $\text{Ca}(\text{OH})_2$ (c) NH_4OH (d) KOH

Ans (c)

Q 8. For the reversible reaction: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3 + \text{Heat}$

The equilibrium shifts in forward direction

- (a) by increasing the concentration of $\text{NH}_3(\text{g})$ (b) by decreasing the pressure
(c) by decreasing the concentration of N_2 and H_2
(d) by increasing pressure and decreasing temperature

Ans (d)

Q 9. A base according to Bronsted concept is a substance which can:

- (a) lose pair of electrons (b) donate protons
(c) gain a pair of electrons (d) accept protons

Ans (d)

Q 10. When NH_4Cl is added to NH_4OH solution the dissociation of ammonium hydroxide is reduced. It is due to:

- (a) common ion effect (b) hydrolysis (c) oxidation (d) reduction

Ans (a)

Q 11. In the chemical reaction $\text{A} \rightarrow \text{B}$, the system will be known in equilibrium when?

- (a) A completely changes to B (b) 50% of A changes to B
(c) The rate of change of A to B and B to A on both the sides are same
(d) Only 10% of A changes to B

Ans (c)

Q 12. The reaction $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D} + \text{heat}$ has reached equilibrium. The reaction may be made to proceed forward by:

- (a) Adding more C (b) Adding more D (c) Decreasing the temperature
 (d) Increasing the temperature

Ans (c)

Q 13. A reaction is $A + B \rightleftharpoons C + D$. Initially we start with equal concentration of A and B. At equilibrium we find the moles of C are two times of A. What is the equilibrium constant of the reaction?

- a. 4 b. 2 c. 1 / 4 d. 1 / 2

Ans (a)

Q 14. An acidic buffer solution can be prepared by mixing solution of

- (a) Ammonium acetate and acetic acid
 (b) Ammonium chloride and hydrochloric acid
 (c) Sulphuric acid and sodium sulphate
 (d) Acetic acid and sulphuric acid

Ans (a)

Q 15. The expression for the solubility product of $Al_2(SO_4)_3$ is

- (a) $K = [Al^{3+}] (SO_4^{2-})$ (b) $K = [Al^{3+}]^3 [SO_4^{2-}]^2$
 (c) $K = [Al^{3+}]^2 [SO_4^{2-}]^3$ d. $K = [Al^{3+}]^2 [SO_4^{2-}]^2$

Ans (c)

SHORT QUESTIONS (2 Marks each)

Q 1. Write down the characteristics of buffer solution

Ans. Characteristics of buffer solution

- (i) It has a definite pH.
 (ii) Its pH does not change on standing for long periods of time.
 (iii) Its pH does not change on dilution.
 (iv) Its pH is slightly changed by the addition of small quantity of an acid or base.

Q 2. What is the effect of temperature on ionic product of water and why?

Ans;- Ionic product of water increases with increase in temperature because dissociation of water into H_3O^+ & OH^- increases with increase in the temperature.

Q 3. What are pH & pOH values of a neutral solution at a temperature at which $K_w = 10^{-13}$. What happens to the ionic product of water if some acid is added into water?

Ans - $pK_w = pH + pOH$. But $pK_w = 13$

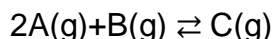
For neutral solution $pH = pOH$. Hence, $pH = pOH = 6.5$.

So, ionic product of water remains unchanged.

Q 4. The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3} M. What is its pH?

Ans - $pH = -\log [H^+]$
 $= -\log (3.8 \times 10^{-3}) = 3 - 0.5798$
 $= 2.42$.

Q 5 How are K_p and K_c related with for the following equilibrium?



Ans. $\Delta n_g = 1 - 3 = -2$

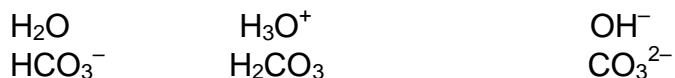
$$K_p = K_c (RT)^{\Delta n_g}$$

$$= K_c (RT)^{-2}$$

Therefore, $K_c = K_p (RT)^2$

Q 6 The species: H_2O and HCO_3^- can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and conjugate base.

Species	Conjugate acid	Conjugate base
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At 450 K, $K_p = 2.0 \times 10^{10}$ / bar for the given reaction at equilibrium.

$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ What is K_c at this temperature?

Ans: $K_p = K_c(RT)^{\Delta n}$

$$K_c = K_p / (RT)^{\Delta n} = (2 \times 10^{10}) / (.0831)(450) = 7.48 \times 10^{11} \text{ L / mol}$$

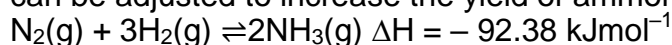
Short Answer type questions: 3 MARKS each.

Q 1. How can you predict the following stages of a reaction by comparing the value of K_c and Q_c ?

- (i) Net reaction proceeds in the forward direction.
- (ii) Net reaction proceeds in the backward direction.
- (iii) No net reaction occurs.

Ans: i) If $Q_c < K_c$ ii) If $Q_c > K_c$ iii) If $Q_c = K_c$.

Q 2. On the basis of Le-Chatelier principle explain how temperature and pressure can be adjusted to increase the yield of ammonia in the following reaction.



What will be the effect of addition of argon to the above reaction mixture at constant volume?

Ans - According to Le- Chateliers principle, decrease in temperature and increase in pressure will increase the yeild of ammonia.

It is an exothermic process as ΔH is negative.

Effect of temperature According to Le-Chatelier's principle, low temperature is favourable for high yield of ammonia, but practically very low temperatures slow down the reaction. So, optimum temperature 700 K is favourable in attainment of equilibrium.

Effect of pressure Similarly, high pressure about 200 atm is favourable for high yield of ammonia. On increasing pressure, reaction goes in the forward direction because the number of moles decreases in the forward direction.

Addition of argon At constant volume addition of argon does not affect the equilibrium because it does not change the partial pressures of the reactants or products involved in the reaction and the equilibrium remains undisturbed.

Q 3. The value of K_c for the reaction $2A \rightleftharpoons B + C$ is 2×10^{-3} . At a given time, the composition of reaction mixture is $[A] = [B] = [C] = 3 \times 10^{-4}$ M. In which direction the reaction will proceed?

Ans. For the reaction the reaction quotient Q_c is given by, $Q_c = [B][C] / [A]^2$

as $[A] = [B] = [C] = 3 \times 10^{-4}$ M

$$Q_c = (3 \times 10^{-4}) (3 \times 10^{-4}) / (3 \times 10^{-4})^2 = 1$$

as $Q_c > K_c$ so the reaction will proceed in the reverse direction.

Q 4. What do you understand by buffer solutions? Classify them and give one example of each.

Ans. A solution that resists change in its pH due to addition of small amount of strong acid or small amount of strong base

They are classified in two categories: Acidic Buffer and Basic buffer solutions

(i) Acidic Buffer: $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$

(ii) Basic Buffer: $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$

REDOX REACTION

KEY POINTS :

The chemical changes that occur when electrons are transferred between reactants are called oxidation – reduction reactions.

OXIDATION	REDUCTION
1. Addition of oxygen	1. Removal of oxygen
2. Removal of hydrogen	2. Addition of hydrogen
3. Addition of an electronegative element	3. Removal of an electronegative element
4. Removal of an electropositive element	4. Addition of an electropositive element
5. Loss of electron	5. Gain of electron

Oxidation number denotes the charge assigned to an atom of a compound or an ion according to some arbitrary rules. It is equal to the number of electrons in the valence shell of an atom, that are gained or lost while forming a bond in a compound.

Calculation of oxidation number:

1. Oxidation number (O.N) of all the elements in their elemental form (in standard state) is taken as zero. Ex: O. N. of elements in Cl_2 , F_2 , O_2 , P_4 , O_3 , $\text{Fe}_{(s)}$, H_2 , N_2 , C (graphite) is zero.
2. Common O. N. of elements of group 1 is one. Common O.N. of elements of group 2 is two.
3. For ions composed of only one atom, the oxidation number is equal to the charge on the ion.
4. The oxidation number of oxygen in most compounds is -2 . While in peroxides (e.g., H_2O_2 , Na_2O_2), O.N. -1 , in super oxides (e.g., KO_2 , RbO_2) each oxygen atom has O.N. of $-(\frac{1}{2})$.
5. In oxygen difluoride (OF_2) and dioxygen difluoride (O_2F_2), the oxygen is assigned an oxidation number of $+2$ and $+1$, respectively.
6. The oxidation number of hydrogen is $+1$ but in metal hydride its O.N. is -1 .
7. In all its compounds, fluorine has an O.N. of -1 .
8. The algebraic sum of the O.N. of all the atoms in a compound must be zero.
9. In polyatomic ion, the algebraic sum of all the O.N. of atoms of the ion must equal the charge on the ion.

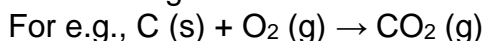
Oxidising agent: A reagent which can increase the oxidation number of an element in a given substance. These reagents are also called as oxidants. It itself gets reduced.

Reducing agent: A reagent which lowers the oxidation number of an element in a given substance. These reagents are also called as reductants. It itself gets oxidised.

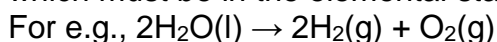


Types of redox reactions

1. Combination reactions: A reaction in which two atoms or molecules combine together form molecule or compound.



2. Decomposition reactions: They are the opposite reactions of combination reactions. or breakdown of a compound into two or more components at least one of which must be in the elemental state.



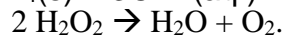
3. Displacement reactions: In a displacement reaction, an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element.

For e.g. (i) Metal displacement: $\text{CuSO}_4(\text{aq.}) + \text{Zn}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{ZnSO}_4(\text{aq.})$

(ii) Non-metal displacement: $2\text{Na}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaOH}(\text{aq.}) + \text{H}_2(\text{g})$

4. Disproportionation reactions: In a disproportionation reaction an element in one oxidation state is simultaneously oxidized and reduced in the same reaction.

For e.g., $\text{P}_4(\text{s}) + 3\text{OH}^-(\text{aq.}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow \text{PH}_3(\text{g}) + 3\text{H}_2\text{PO}_2^-(\text{aq.})$



SECTION A: ASSERTION AND REASON (1 MARK)

In the following questions a statement of assertion (A) followed by a statement of reason (R) is given. Choose the correct option out of the choices given below each question.

(i) Both A and R are true and R is the correct explanation of A.

(ii) Both A and R are true but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) Both A and R are false.

Assertion (A) : Among halogens fluorine is the best oxidant.

Reason (R) : Fluorine is the most electronegative atom.

Ans: (ii) Both A and R are true but R is not the correct explanation of A.

2. Assertion (A): In the reaction between potassium permanganate and potassium iodide, permanganate ions act as oxidising agent.

Reason (R) : Oxidation state of manganese changes from +2 to +7 during the reaction.

Ans: (iii) A is true but R is false.

3. Assertion (A) : The decomposition of hydrogen peroxide to form water and oxygen is an example of disproportionation reaction.

Reason (R) : The oxygen of peroxide is in -1 oxidation state and it is converted to zero oxidation state in O_2 and -2 oxidation state in H_2O .

Ans: (i) Both A and R are true and R is the correct explanation of A.

4. Assertion (A) : Redox couple is the combination of oxidised and reduced form of a substance involved in an oxidation or reduction half-cell.

Reason (R) : In the representation $E_{\text{Fe}^{+3}/\text{Fe}^{+2}}^0$, $E_{\text{Cu}^{2+}/\text{Cu}}^0$, Fe^{+3}/Fe and Cu^{2+}/Cu are redox couples.

Ans: (ii) Both A and R are true but R is not the correct explanation of A.

5. Assertion (A): HgCl_2 and SnCl_2 cannot stay together.

Reason (R): HgCl_2 is an oxidising agent but SnCl_2 is reducing agent.

Ans: (i) Both A and R are true and R is the correct explanation of A.

SECTION B: VERY SHORT ANSWER (1 MARK)

1. What is Oxidation in terms of electron transfer.

Ans: Loss of electrons.

2. What is Reduction in terms of electron transfer.

Ans: Gain of electrons.

3. What is Oxidant in terms of electron.

Ans: Substance which can accept one or more electron.

4. What is Reductant in terms of electron.

Ans. Substance which can donate one or more electron.

5. Give two examples of Oxidant.

Ans: KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$.

6. Give two examples of Reductant.

Ans. HCl and SnCl_2 .

7. Calculate Oxidation number of the metal in the compound BaO_2 .

Ans: +2.

8. Give example of an element whose Oxidation number is zero.

Ans. Cl_2 (Any Pure Element)

9. Give example of a compound of Nitrogen where its Oxidation number is negative.

Ans: NH_3

10. Give example of a compound of Carbon where its Oxidation number is zero.

Ans: CH_2Cl_2 or $\text{C}_6\text{H}_{12}\text{O}_6$

11. Write the Disproportionation Reaction of ClO^- .

Ans: $\text{ClO}^- \rightarrow 2\text{Cl}^- + \text{ClO}_3^-$ (Any other example)

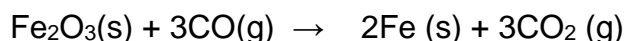
12. Iron undergo Oxidation more readily than Copper. Why?

Ans: Electrode potential of Iron is lower than that of copper.

13. What is the Oxidation number of Chlorine in Bleaching Powder.

Ans: Zero.

14. Identify the substances reduced in the following reaction:



Ans: Substance reduced is Fe_2O_3 .

15. Give an example of disproportionation reaction.

Ans: $\text{Cl}_2 + 2\text{NaOH} \rightarrow \text{NaCl} + \text{NaClO} + \text{H}_2\text{O}$



Chlorine is getting oxidised as well as reduced.

\therefore It is disproportionation reaction.

16. What is the oxidation number of Mn in KMnO_4

Ans: Let oxidation number of Mn be x.

$$\therefore +1 + x - 8 = 0 \Rightarrow x = +7.$$

17. Which is best reducing agent and best oxidising agent?

Ans: (i) Li is best reducing agent due to lowest standard reduction potential.

(ii) F_2 is best oxidising agent due to highest standard reduction potential.

18. Can we store copper sulphate in an iron vessel? Why?

Ans: No, because iron is more reactive than copper, and therefore, it will displace copper from its salt solution.

19. An electrochemical cell consist of two electrodes i.e. anode and cathode. What is direction of flow of electrons in the cell?

Ans: Electrons flow from anode to cathode because electron density is more at anode due to loss of electron and less at cathode due to gain of electrons.

20. A freshly cut apple is almost white but turns brown after some time, why?

Ans: Apple contains Fe^{2+} which get oxidised to Fe^{3+} which is brown in colours. Apple turns brown due to oxidation of Fe^{2+} to Fe^{3+}

21. Represent a galvanic cell in electrode and ions contain Cu electrode dipped in 1 molar solution of copper sulphate and silver electrode dipped in 1 molar solution of silver nitrate.

Given = $E_{\text{Cu}^{2+}/\text{Cu(s)}} = + 0.34 \text{ V}$, $E_{\text{Ag}^+/\text{Ag(s)}} = + 0.80 \text{ V}$
 Ans: $\text{Cu(s)} \mid \text{Cu}^{2+}(1 \text{ M}) \parallel \text{Ag}^+(1 \text{ M}) \mid \text{Ag(s)}$

SECTION C: MULTIPLE CHOICE QUESTION (1 MARK)

1. Which of the following is not an example of redox reaction?

- (i) $\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$ (ii) $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$
 (iii) $2\text{K} + \text{F}_2 \rightarrow 2\text{KF}$ (iv) $\text{BaCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2\text{HCl}$

Ans: (iv) $\text{BaCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2\text{HCl}$

2. The more positive the value of E^0 , the greater is the tendency of the species to get reduced. Using the standard electrode potential of redox couples given below find out which of the following is the strongest oxidising agent. The E^0 values:

$\text{Fe}^{3+}/\text{Fe}^{2+} = + 0.77\text{V}$; $\text{I}_2(\text{s})/\text{I}^- = +0.54\text{V}$; $\text{Cu}^{2+}/\text{Cu} = +0.34\text{V}$; $\text{Ag}^+/\text{Ag} = +0.80\text{V}$

- (i) Fe^{3+} (ii) $\text{I}_2(\text{s})$ (iii) Cu^{2+} (iv) Ag^+

Ans: (iv) Ag^+

3. E^0 values of some redox couples are given below. On the basis of these values choose the correct option. The E^0 values: $\text{Br}_2/\text{Br}^- = + 1.90\text{V}$;

$\text{Ag}^+/\text{Ag(s)} = +0.80\text{V}$; $\text{Cu}^{2+}/\text{Cu(s)} = + 0.34\text{V}$; $\text{I}_2(\text{s})/\text{I}^- = + 0.54\text{V}$

- (i) Cu will reduce Br^- (ii) Cu will reduce Ag
 (iii) Cu will reduce I^- (iv) Cu will reduce Br_2

Ans: (iv) Cu will reduce Br_2

4. Using the standard electrode potential, find out the pair between which redox reaction is not feasible. E^0 values: $\text{Fe}^{3+}/\text{Fe}^{2+} = + 0.77$; $\text{I}_2/\text{I}^- = + 0.54$;

$\text{Cu}^{2+}/\text{Cu} = + 0.34$; $\text{Ag}^+/\text{Ag} = + 0.80 \text{ V}$

- (i) Fe^{3+} and I^- (ii) Ag^+ and Cu (iii) Fe^{3+} and Cu (iv) Ag and Fe^{3+}

Ans: (iv) Ag and Fe^{3+}

5. The oxidation number of an element in a compound is evaluated on the basis of certain rules. Which of the following rules is not correct in this respect?

- (i) The oxidation number of hydrogen is always +1.
 (ii) The algebraic sum of all the oxidation numbers in a compound is zero.
 (iii) An element in the free or the uncombine state bears oxidation number zero.
 (iv) In all its compounds, the oxidation number of fluorine is -1 .

Ans: (i) The oxidation number of hydrogen is always +1.

6. Which of the following arrangements represent increasing oxidation number of the central atom?

- (i) CrO^- , ClO^- , CrO^{2-} , MnO^-
 (ii) ClO^{2-} , CrO^{3-} , MnO^{4-} , CrO^{4-}
 (iii) CrO^{3-} , ClO^{4-} , MnO^{4-} , CrO^{2-}
 (iv) CrO_4^{2-} , MnO_3^- , CrO_2^{4-} , ClO_3^{4-}

Ans: (i) CrO_2^- , ClO_3^- , CrO_4^{2-} , MnO_4^-

7. The largest oxidation number exhibited by an element depends on its outer electronic configuration. With which of the following outer electronic configurations the element will exhibit largest oxidation number?

- (i) $3d^1 4s^2$ (ii) $3d^3 4s^2$ (iii) $3d^5 4s^1$ (iv) $3d^5 4s^2$

Ans: (iv) $3d^5 4s^2$

8. Identify disproportionation reaction

- (i) $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ (ii) $\text{CH}_4 + 4\text{Cl}_2 \rightarrow \text{CCl}_4 + 4\text{HCl}$
 (iii) $2\text{F}_2 + 2\text{OH}^- \rightarrow 2\text{F}^- + \text{OF}_2 + \text{H}_2\text{O}$ (iv) $2\text{NO}_2 + 2\text{OH}^- \rightarrow \text{NO}_2^- + \text{NO}_3^- + \text{H}_2\text{O}$

Ans: (iv) $2\text{NO}_2 + 2\text{OH}^- \rightarrow \text{NO}_2^- + \text{NO}_3^- + \text{H}_2\text{O}$

9. The oxidation number of Cl in Cl_2O_7 is

- (a) +7 (b) +5 (c) +3 (d) -7
 Ans. (a)

10. The oxidation number of Mn is maximum in
 (a) MnO_2 (b) K_2MnO_4 (c) Mn_3O_4 (d) KMnO_4
 Ans. (d)

SECTION D: SHORT ANSWER (2 MARKS)

1. Calculate the oxidation amount of phosphorus in the following species.

- (a) HPO_3^{2-} and (b) PO_4^{3-}

Ans: (a) +3 (b) +5.

2. Calculate the oxidation number of each sulphur atom in the following compounds:

- (a) $\text{Na}_2\text{S}_2\text{O}_3$ (b) $\text{Na}_2\text{S}_4\text{O}_6$ (c) Na_2SO_3 (d) Na_2SO_4

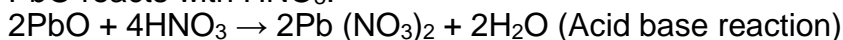
Ans: (a) +2 (b) +5,0,0, +5 (c) +4 (d) +6

3. MnO_4^{2-} undergoes disproportionation reaction in acidic medium but MnO_4^- does not. Give reason.

Ans: In MnO_4^- , Mn is in the highest oxidation state i.e. +7. Therefore, it does not undergo disproportionation. MnO_4^{2-} undergoes disproportionation as follows:
 $3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$

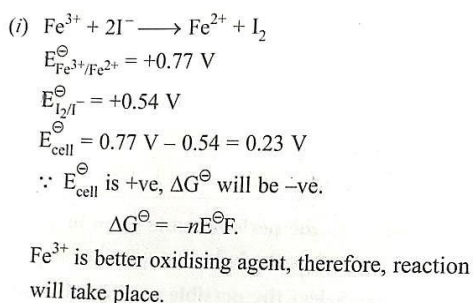
4. Nitric acid is an oxidising agent and reacts with PbO but it does not react with PbO_2 . Explain why?

Ans: PbO is a basic oxide and simple acid base reaction takes place between PbO and HNO_3 . On the other hand, in PbO_2 lead is in +4 oxidation state and cannot be oxidised further. Therefore, no reaction takes place. Thus, PbO_2 is passive, only PbO reacts with HNO_3 .

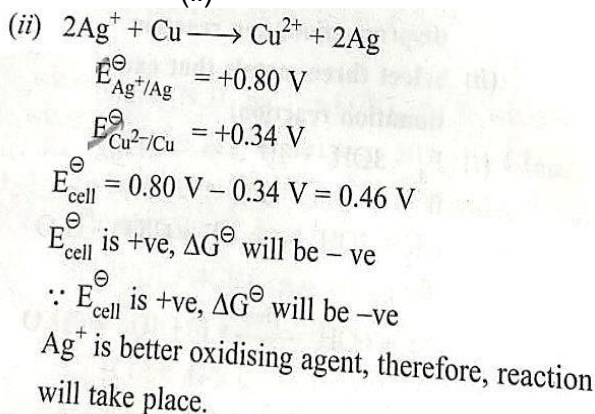


5. Using the standard electrode potentials given in the table, predict if the reaction between the following is feasible: (i) $\text{Fe}^{3+}(\text{aq})$ and $\text{I}^-(\text{aq})$ (ii) $\text{Ag}^+(\text{aq})$ and $\text{Cu}(\text{s})$
 ($E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.77\text{V}$, $E^\circ_{\text{I}_2/\text{I}^-} = +0.54\text{V}$) ($E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80\text{V}$, $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$)

Ans. (i)

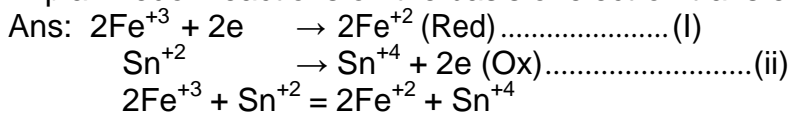


(ii)



SECTION E: LONG ANSWER (3 MARKS)

1. Explain redox reactions on the basis of electron transfer. Give suitable examples.



In the yellow colour Ferric Chloride solution white colour Stannous Chloride solution drop wise added and the mixture was stirred continuously with a glass rod. The yellow colour solution turns to light green colour because the above mentioned

chemical reaction occurs. Here Ferric Chloride is reduced to Ferrous Chloride by the gain of electron and Stannous Chloride is oxidized to Stannic Chloride by the loss of electron. So in the above process electron transfer is occurring.

2. Why does fluorine not show disproportionation reaction?

Ans: Disproportionation is a redox reaction in which one compound of intermediate oxidation state converts to two compounds, one of higher and one of lower oxidation states. So, to occur such type of redox reaction, the element should exist in at least three oxidation states. So that element present in the intermediate state and it can change to both higher and lower oxidation state during disproportionation reaction. Fluorine is the most electronegative element and a strong oxidizing agent and is the smallest in size of all the halogens. It does not show a positive oxidation state (shows only -1 oxidation state) and hence, does not undergo disproportionation reaction.

3. Write the balanced chemical equation corresponding to the reaction.

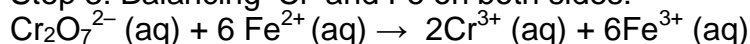


Ans. Step 1:

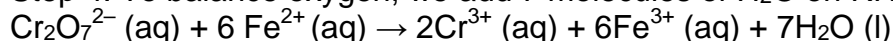


Step 2: The oxidation state of Cr decreases by 3 per chromium atom, total decrease is 6 for two chromium atoms, oxidation state of Fe changes from $+2$ to $+3$, i.e., increases by 1, therefore, to equalize the increase and decrease, we multiply Fe^{2+} by 6 and $\text{Cr}_2\text{O}_7^{2-}$ by 1.

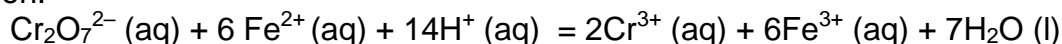
Step 3: Balancing 'Cr' and Fe on both sides:



Step 4: To balance oxygen, we add 7 molecules of H_2O on RHS.



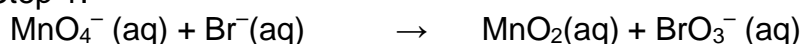
Step 5: To balance hydrogen, we add 14H^+ on LHS and we get balanced equation:



4. Permanganate ion reacts with bromide ion in basic medium to give manganese dioxide and bromate ion. Write the balanced chemical equation for the reaction.

3

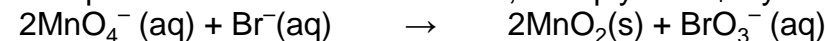
Ans: Step 1:



Step 2: MnO_4^- is oxidant because its oxidation state is decreasing. Br^- is reductant because its oxidation state is increasing.

Step 3: Oxidation state of Mn is decreasing by 3. Oxidation state of Br is increasing by 6.

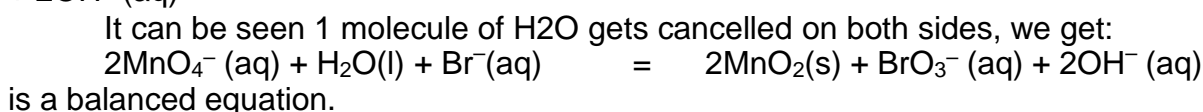
To equalise increase and decrease, multiply MnO_4^- by 2 and Br by 1 we get:



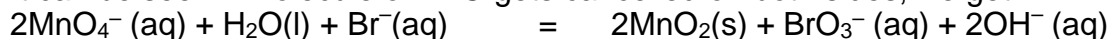
Step 4: Now for balancing oxygen, we add 1 molecule of H_2O on RHS.



Step 5: As the reaction is taking place in basic medium to balance hydrogen, add $2\text{H}_2\text{O}$ molecule on LHS and 2OH^- on RHS



It can be seen 1 molecule of H_2O gets cancelled on both sides, we get:



is a balanced equation.

1. Consider the following table of standard reduction potentials:

Reaction	E° (volts)
$A^{3+} + 2e^- \rightarrow A^+$	1.36
$B^{2+} + 2e^- \rightarrow B$	0.72
$C^{2+} + 2e^- \rightarrow C$	-0.28
$D^+ + e^- \rightarrow D$	-1.42

- (i) Which substance is (a) strongest oxidizing agent? (b) Strongest reducing agent
(ii) Which substances can be oxidized by B^{2+} ?
(iii) Which substance can be reduced by C?

Ans. (i) A^{3+} (ii) (D) (iii) C & D (iv) A^{3+} & B^{2+}

ORGANIC CHEMISTRY - SOME BASIC PRINCIPLES AND TECHNIQUES

Organic Chemistry Some basic principles and Techniques

Organic Chemistry – Organic chemistry is the study of carbon compounds that always contain carbon and it is limited to other elements. Compounds obtained from plants and animals were termed organic to indicate their ultimate source was a living organism.

Organic chemistry is one of the most important disciplines of science which deals with the study of carbon compounds especially hydrocarbons and their derivatives.

General Introduction:

- Catenation** – Catenation can be defined as the self-linking of atoms of an element to form chains and rings. This definition can be extended to include the formation of layers (two-dimensional catenation) and space lattices (three-dimensional catenation).
- Tetravalency and small size** – Carbon exhibits tetravalency. The tetravalency of carbon can be satisfied by forming bonds with carbon, hydrogen or other atoms. The carbon atom has 4 electrons in its valence shell. In order to account tetravalency it is believed during the process of bond formation which is energy-releasing process the two electrons in the 2s orbital get unpaired and out of them, one is promoted to empty orbital.

Structural Representations of Organic Compounds

- Complete Structural Formula** – Full structural equations show all the atoms in a molecule, the types of bonds that bind them, and how they are interconnected.
- Condensed Structural Formula** – The Condensed structural formula is used to save space, structural formulas are conveniently abbreviated as condensed structural formulas.
- Bond Line Structural Formula** – A bond-line structure is a less cluttered drawing than a condensed structural formula. However, to understand the simplified bond-line structure, the reader has to mentally add many more features to comprehend the overall structure.

Classification of Organic Compounds

- Acyclic or Open Chain Compounds & Alicyclic or Closed Chain or Ring Compounds** – Organic compounds are classified as open-chain compounds and closed chain compounds in terms of the carbon chain. Also termed as Organic

Compounds Acyclic or Open Chain or Aliphatic Compounds, Cyclic or Closed Chain or Ring Compounds.

2. **Aromatic Compounds** – Plants and micro-organisms have an exclusive route to benzene-ring compounds. The great majority of aromatic compounds in nature, therefore, are produced by plants and microorganisms, and animals are dependent upon plants for many aromatic compounds either directly or Indirectly.
3. **Heterocyclic Aromatic Compounds** – In the twentieth century it is witnessed that the first inorganic heteroaromatic compound produced in the laboratory. Some of these heterocyclic aromatic compounds are very important in biochemical processes, drugs, and agrochemicals.

Nomenclature: IUPAC Rules – Nomenclature of Organic Compounds follows recommendations of IUPAC in naming organic compounds, carbocations, etc. The International Union of Pure and Applied Chemistry (IUPAC) formulated rules for naming organic compounds.

Isomerism

1. **Structural Isomerism** – Structural Isomerism arises due to different arrangement of atoms within the molecule. Two molecules are structural isomers if they share the same molecular formula.
2. **Stereoisomerism** – Stereo-isomers are isomeric molecules having the same molecular formula and the same sequence of bonded atoms, but are only different in the 3D orientations of their atoms in space. Stereoisomerism may be of two types viz. geometrical (or cis-trans) isomerism and optical (or d-l or mirror-image) isomerism.

Fundamental Concepts

1. **The Shapes of Carbon Compounds** – Tetravalent carbon atom is the building block of structural organic chemistry. The four hydrogen atoms, with four carbon atoms, form a structure known as a tetrahedron.
2. **Functional Groups** – Functional groups were introduced as a useful method for organizing this vast number of compounds because chemical reactions occur at the functional group and compounds with the same functional group undergo similar reactions. Example: C_2H_6O has isomers: C_2H_5-OH & CH_3-O-CH_3 .
3. **Homologous Series** – A series of organic compounds in which every succeeding member differs from the previous one called Homologous Series.

These differ by $-CH_2-$

Methods of Purification

1. **Simple crystallization** – Crystallization is one of the most effective purification techniques for solids. Simple crystallization involves the selection of the solvent and preparation of the solution.
2. **Fractional crystallization** – Fractional crystallization is used for the purification of a single substance contaminated with small quantities of impurities.
3. **Sublimation** – Sublimation is an excellent method for purifying relatively volatile organic solids on scales ranging from a few milligrams to tens of grams.

- Simple distillation** – Simple distillation is the process of converting a liquid into its vapour, transferring the vapour to another place, and recovering the liquid by condensing the vapour.
- Fractional distillation** – Fractional distillation is the separation procedure of a mixture into sections or fractions of its material. By heating them to a temperature at which one or more parts of the mixture vaporize, chemical compounds are isolated.
- Steam distillation** – A steam distillation is simply a distillation in which steam is involved as a process component. Steam distillation and organic solvent extraction have both been widely used to extract compounds from spices.
 - Ortho nitro phenol is separated from its mixture with p-nitro phenol by steam dist.
 - Aniline is separated from aniline-water mixture by steam distillation.
- Azeotropic distillation** – Azeotropic distillation is accomplished by adding to the liquid phase, a volatile third component that changes the volatility of one of the two components more than the other so that the components are separated by distillation.
- Distillation under reduced pressure:** Glycerol is separated from spent-lye in soap industry by this technique.
- Chromatography** – The purpose of preparative chromatography is to separate the components of a mixture for further use (and is thus a form of purification).

Quantitative Analysis:

The elementary organic analysis is also considered, along with the development of the theory of analytical chemistry. Quantitative analysis refers to assessing how much is present in a sample of a given item. The quantity of any or all components of a sample can be expressed in terms of size, concentration, or relative abundance.

Nitrogen in organic compound is detected by Lassaigne's test. The compound formed is Prussian blue colouration; $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

ASSERTION AND REASONING QUESTIONS (Each question carry 1 mark)

In the following questions a statement of assertion (A) followed by a statement of reason (R) is given. Choose the correct option out of the choices given below each question.

- Both A and R are true and R is the correct explanation of A
- Both A and R are true but R is not the correct explanation of A.
- A is true but R is false.
- A is false but R is true.

1. ASSERTION (A): benzene shows resonating structures

REASON (R): Benzene has delocalised pi electrons

Ans. (a) Both A and R are true and R is the correct explanation of A.

2. ASSERTION(A): H_2O is a nucleophile

REASON (R): H_2O is an electron rich species

Ans. (a) Both A and R are true and R is the correct explanation of A.

3. ASSERTION(A): CH_3CH_2^+ is less stable than $(\text{CH}_3)_2\text{CH}^+$

REASON (R): CH_3CH_2^+ has more hyper conjugative forms than $(\text{CH}_3)_2\text{CH}^+$

Ans. (c) A is true but R is false.

4. ASSERTION(A): both the carbon atoms of ethene are sp^3 hybridised

REASON (R): it has C=C bond

Ans. (d) A is false but R is true.

5. ASSERTION(A) carbon shows catenation property

REASON (R): C-C single bond is very weak

Ans. (c) A is true but R is false

VERY SHORT TYPE QUESTIONS (1 mark for each question)

1. Identify the nucleophiles from the following:

CN^- , NO_2^+ , OH^- , Cl^+ , H_2O

Ans. CN^- , OH^- , H_2O

2. Write the IUPAC name of the following: $\text{CH}_3\text{-CH}_2\text{-COOH}$

Ans. Propanoic acid.

3. Define homolytic cleavage of covalent bond?

Ans. Breaking of covalent bond takes place in such a way, one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms.

4. Which bond is more polar in the following pair of molecules?

$\text{H}_3\text{C-NH}_2$, $\text{H}_3\text{C-OH}$

Ans. C-O bond is more polar than C-N bond as O is more electronegative than N.

5. Give two examples of organic compounds where resonance effect is possible.

Ans. a. Benzene b. chlorobenzene

6. Name the metal which is used in Lassaigne extract.

Ans. Sodium metal.

7. Name the chemicals which are used to detect nitrogen in organic compounds.

Ans. Freshly prepared ferrous sulphate and concentrated sulphuric acid.

8. How many sigma and pi bonds in the following molecule:

$\text{CH}_2=\text{CHCN}$.

Ans. Sigma bonds = 6 and pi bonds = 3.

9. Name a suitable technique of separation of the components from a mixture of calcium sulphate and camphor.

Ans. Sublimation process.

10. Arrange the following in order of decreasing priority in IUPAC system

$-\text{CONH}_2$, $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{CHO}$

Ans. $-\text{SO}_3\text{H} > -\text{COOH} > -\text{CONH}_2 > -\text{CHO}$

11. Draw the structure of Pent-4-en-2-ol.

Ans. $\text{CH}_3\text{-CH(OH)CH}_2\text{-CH=CH}_2$

12. Name the first synthesis organic compound.

Ans. Urea.

13. Write the IUPAC name of chloroform.

Ans. Trichloromethane

14. Name two methods for the estimation of nitrogen in organic compounds.

Ans. Dumas method and Kjeldahl method.

15. Identify the functional group present in the following compounds:

a. $\text{CH}_3\text{-CO-C}_2\text{H}_5$ b. $\text{CH}_3\text{-O-C}_2\text{H}_5$

Ans. a. ketonic functional group b. ether functional group

MCQ TYPE QUESTIONS (EACH CARRY 1 MARK)

1. The IUPAC name of $\text{CH}_3\text{COCH(CH}_3)_2$ is

(a) 3-Methyl-2-butanone

(b) Isopropyl methyl ketone

(c) 2-Methyl-3-butanone

(d) 4-Methyl isopropyl ketone

- What is the state of hybridization of carbon in carbanion
(a) sp (b) sp^2 (c) sp^3 (d) sp^3d
- Which of the following is the correct order regarding the $-I$ effect of the substituents?
(a) $-NR_2 < -OR < -F$ (b) $-NR_2 > -OR > -F$ (c) $-NR_2 < -OR > -F$ (d) $-NR_2 > -OR < -F$
- Which of the following carbocations has the least stability
(a) Methyl (b) Ethyl (c) tert-butyl (d) Isopropyl.
- Which of the following is not an electrophile?
(a) $:CH_2$ (b) $+CH_3$ (c) SO_3 (d) $:SH^+$
- Heterolytic cleavage of a C-X bond may result in the formation of
(a) a free radical (b) a carbocation (c) a carbene (d) a carbanion
- Of the five isomeric hexanes, the isomer that can give two monochlorinated compounds is (a) 2-methyl pentane (b) 2,2-dimethyl butane
(c) 2,3-Dimethyl butane (d) n-hexane.
- Consider the following compounds: A. chloroethene B. benzene
C. 1,3-butadiene D. 1,3,5-hexatriene.
All the carbon atoms are sp^2 -hybridised in
(a) A,C,D only (b) A,B only (c) B,C,D only (d) A,B,C and D.
- The Lassaigne's extract is boiled with dil. HNO_3 before testing for halogens because
(a) silver halides are soluble in HNO_3
(b) Na_2S and $NaCN$ are decomposed by HNO_3
(c) Ag_2S is soluble in HNO_3 (d) $AgCN$ is soluble in HNO_3 .
- Which of the following carbocation is most stable?
(a) $(CH_3)_3CC^+H_2$ (b) $(CH_3)_3C^+$ (c) $CH_3CH_2C^+H_2$ (d) $CH_3C^+HCH_2CH_3$.

Answer. 1.(a) 2.(c) 3.(a) 4.(a) 5.(d) 6.(a) 7.(c) 8.(d) 9.(b) 10.b

SHORT ANSWER TYPE QUESTIONS (2 MARKS FOR EACH QUESTION)

1. Explain, how is the electronegativity of carbon atoms related to their state of hybridisation in an organic compound?

Ans. Since s-electrons are more firmly attached by the nucleus than p-electrons, therefore, electronegativity increases as the s-character of the hybridised orbital increases, i.e., in the order $sp^3 < sp^2 < sp$.

2. Identify the most stable species in the following set of ions giving reasons CH_3^+ , CH_2^+Br , CH^+Br_2 , C^+Br_3

Ans. CH_3^+ is the most stable species because replacing H atom by Br (-Inductive effect) increases +ve charge on carbon atom and destabilised the species.

3. Write structural formulae for compounds named as-

(i) 1-Chloroheptane

(ii) 5-Bromoheptanoic acid

Ans. (i) $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2Cl$

(ii) $CH_3-CH_2-CH(Br)-CH_2-CH_2-CH_2-COOH$

4. Arrange the following in order of increasing stability

Ans. $CH_3^+ < CH_2^+ < CH^+ < (CH_3)_2C^+ < (CH_3)_3C^+$

5. Why does NH_3 act as a nucleophile?

Ans. N in NH_3 has lone pair electron. So, it is electron rich species and can donate these electrons.

LONG ANSWER QUESTIONS (EACH CARRY 3 MARKS)

1. Two liquids (A) and (B) can be separated by the method of fractional distillation. The boiling point of a liquid (A) is less than the boiling point of a liquid (B). Which of the liquids do you expect to come out first in the distillate? Explain.

Ans. Fractional distillation is used to separate the components of a mixture if their boiling points differ by 20° or less. In this method, a fractionating column is used in between the flask and the condenser. The fractionating column aims to provide hurdles for the ascending vapours and provide ample surface area for condensing the high boiling liquid. Consequently, the low boiling liquid (A) vapours will move up while those of the high boiling liquid will condense and fall back into the flask. As a result of this fractionation, liquid A with a lower boiling point will distil first, and liquid B with a higher boiling point afterwards.

2. Give three points of differences between inductive effect and resonance effect.

Ans. 1. Inductive Effect involves the displacement of electrons in saturated compounds. Resonance Effect involves displacing π electrons or lone pairs of electrons in unsaturated and conjugated compounds.

2. In the inductive Effect, a slight displacement of σ electrons and partial +ve or -ve charge develops. In the resonance effect, there is a complete transfer of π electrons, and as a result, a complete +ve or -ve charge develops.

3. The Inductive Effect can move only up to 3 to 4 carbons. In the resonance effect, the movement of electrons all along the length of the conjugated system takes place.

HYDROCARBON

Minimum Level of Learning (MLL):

Naming hydrocarbons according to IUPAC system of nomenclature;

Structures of isomers of alkanes, alkenes, alkynes and aromatic hydrocarbons,

Various methods of preparation of hydrocarbons;

Distinguish between alkanes, alkenes, alkynes and aromatic hydrocarbons on the basis of physical and chemical properties;

Draw and differentiate between various conformations of ethane;

The formation of the addition products of unsymmetrical alkenes and alkynes on the basis of electronic mechanism;

Structure of benzene, explain aromaticity and mechanism of electrophilic substitution reactions of benzene, the directive influence of substituents in monosubstituted benzene ring, carcinogenicity and toxicity.

ASSERTION AND REASON TYPE QUESTION (1M)

Choose the correct option from the following.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct

explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

Q.1) Assertion: Boiling point of alkanes increases with increase in molecular weight.

Reason: van der Waal's forces increase with increase in molecular weight.

Ans:(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

Q.2) Assertion: Methane cannot be obtained by Wurtz reaction.

Reason: Wurtz reaction leads to the formation of symmetrical alkane having an even number of carbon atoms.

Ans: a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

Q.3) Assertion: Trans-pent-2-ene is polar but trans-but-2-ene is non-polar.

Reason: The polarity of cis-isomer is more than trans which are either non-polar or less polar.

Ans: (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

Q.4) Assertion: All the hydrogen atoms in $\text{CH}_2 = \text{C} = \text{CH}_2$ are attached to sp^2 hybridised carbon atom.

Reason: All the carbon atoms in its are sp^2 hybridized.

Ans: (c) Assertion is correct statement but reason is wrong statement.

Q.5) Assertion: Acetylene is acidic in nature.

Reason: Acetylene is sp hybridised.

Ans: (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion

MULTIPLE CHOICE QUESTION (1M)

Q.1) In the compound $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2 \text{CH}_3$, the hybridisation of $\text{C}_2 - \text{C}_3$ bond is of the type

(a) $\text{sp}^2 - \text{sp}^2$ (b) $\text{sp}^3 - \text{sp}^3$ (c) $\text{sp} - \text{sp}^3$ (d) $\text{sp}^2 - \text{sp}^3$

Ans: (a) $\text{sp}^2 - \text{sp}^3$

Q.2) The number and type of bonds in benzene are

(a) twelve sigma (σ) and three pi (π) bonds (b) six sigma (σ) and two pi (π) bonds

(c) three sigma (σ) and one and a half pi (π) bonds

(d) One sigma (σ) bond

Ans: (a) twelve sigma (σ) and three pi (π) bonds.

Q.4) During addition of HBr across a double bond in unsymmetrical alkenes, the halogen atoms go to the carbon atom having lesser number of hydrogen atoms, according to:

(a) Markownikoff rule

(b) Peroxide effect

(c) Saytzeff rule.

(d) None of the above.

Ans(a) Markownikoff rule

Q.5) Benzene reacts with CH_3Cl in presence of anhydrous AlCl_3 for the preparation of

(a) Chlorobenzene

(b) Benzyl chloride

(c) xylene

(d) toluene

Ans: (d) toluene

Q.6) Methane, Ethane and propane to form a homologous series

Q.3) The Number of structural isomers for C_5H_{12} is

(a) 3 (b) 4 (c) 5 (d) 6

Ans: (a) 3

Q.6) Homologous series those _____

a) differ from each other by CH_2 group

(b) aliphatic compounds

(c) saturated compounds

(d) hydrocarbon.

Ans: (a) differ from each other by CH_2 group

Q.7) Sodium salt of carboxylic acids on heating with soda lime gives alkane containing _____ than the carboxylic acid

(a) one carbon less (b) one carbon more (c) two carbon less (d) two carbon more

Ans: (a) one carbon less.

Q.8) Which of the following compounds reacts with sodium to liberate hydrogen gas?

(a) Ethane (b) Propene (c) Acetylene (d) Benzene

Ans: (c) Acetylene.

Q.9) What is a general formula of alkynes?

(a) $\text{C}_n\text{H}_{2n-2}$

(b) C_nH_{n-2}

(c) C_nH_{2n}

(d) $\text{C}_n\text{H}_{2n+2}$

Ans: (b) C_nH_{n-2}

Q.10) An organic compound, ethane and ethene can be distinguish by

(a) Bromine water

(b) Tollen reagent

(c) Fehling solution

(d) Ammonical silver nitrate solution.

Ans: (a) Bromine water

Very short answer (1Mark Each)

Q.1) What effect does branching of an alkane chain on its boiling point?

Ans: Branching of carbon atom chain decreases the boiling point of alkane.

Q.2) Arrange the isomers of pentane in increasing order of their boiling points.

2-methylbutane, 2, 2-Dimethylpropane, pentane

Ans. 2, 2-Dimethylpropane < 2-methylbutane < pentane.

Q.3) What are conformations?

Ans: Conformations are spatial arrangements of atoms which are obtained by rotation around single bond.

Q.4) what are the two-extreme type of conformation in Ethane?

Ans: 1) Staggered 2) Eclipsed.

Q.5) Why alkyne do not show geometrical isomerism?

Ans: Alkyne have linear shape hence do not show geometrical isomerism.

Q.6) How would you distinguish between but-1-yne and but-2-yne.

Ans: On a reaction with Sodium metal, but-1-yne liberate Hydrogen gas where as but-2-yne does not reacts.

Q.7) How will you distinguish between propene and propyne?

Ans: Propyne react with sodium metal and liberate hydrogen gas. Propene do not react with sodium metal.

Q.8) How will you distinguish between propene and propane?

Ans: When we pass them through Br₂ in CCl₄ solution. Propene will decolourise the reddish orange colour of bromine solutions but propane does not react.

Q.9) Arrange the following in the increasing order of acidic character.

HC≡CH, CH₃CH₃, H₂C=CH₂

Ans: CH₃CH₃ < H₂C=CH₂ < HC≡CH

Q.10) Name the alkane that cannot be prepared by Wurtz reaction.

Ans: Methane.

Q.11) Arrange the following: HCl, HBr, HI, HF in order of decreasing reactivity towards alkenes.

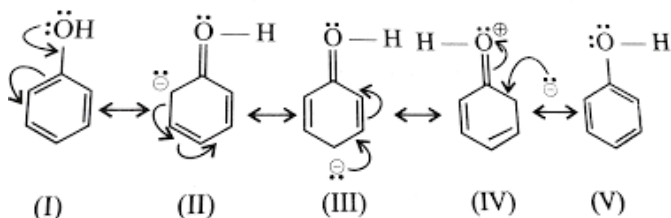
Ans: HI > HBr > HCl > HF

Q.12) What are ortho, para directing group in aromatic electrophilic substitution reactions.

Ans: Those group which increases electron density at ortho and para position are known as ortho-para directing group.

All the activating groups are ortho-para directing groups.

Q. 13. Show the canonical structures of phenol.

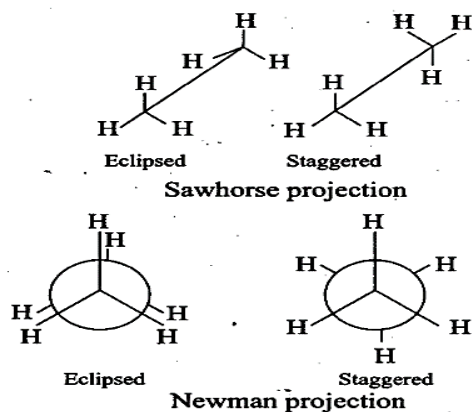


Q.14) Name the examples of ortho para directing group..

Ans: OH, -NH₂, -NHR, -NHCOCH₃, -OCH₃, -CH₃, -C₂H₅ etc.

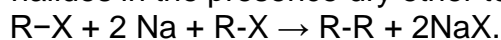
Q.15) Write IUPAC names of the following compounds: CH₃CH=C(CH₃)₂.

Sol.



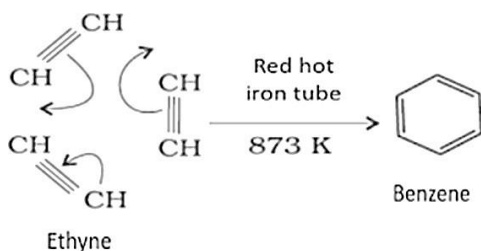
Q.4) Explain with example Wurtz reaction.

Ans: Wurtz reaction: In this reaction, sodium metal is reacted with two molecules alkyl halides in the presence dry ether to form a higher alkane. Higher alkane.

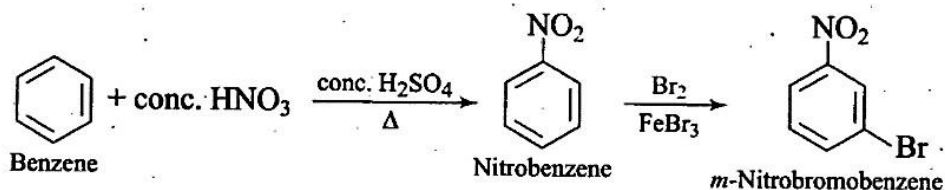
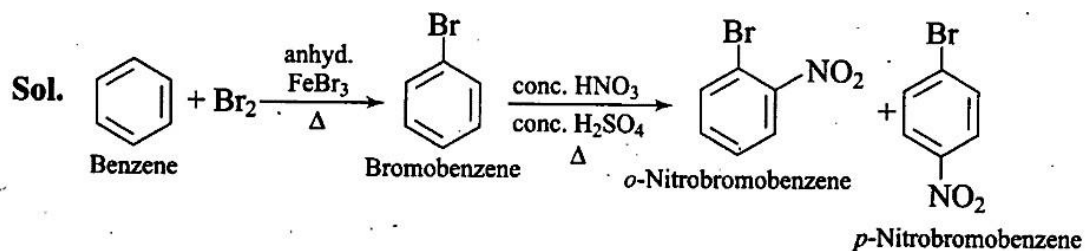


Q.5) How would you convert Acetylene to Benzene.

Ans: When acetylene(ethyne) gas is heated to 873 K in a red-hot iron tube, benzene is produced.



Q.6) How will you convert benzene into (i) p-nitrobromobenzene (ii) m-nitrobromobenzene?



Q27.

Long answer question (3M)

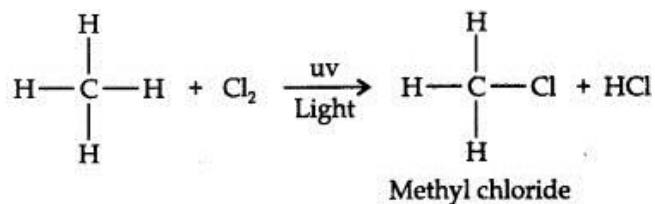
Q 1) (a) Define substitution reactions. Why do benzene undergo electrophilic substitution reactions even though they contain double bonds?

(b) What happens when benzene is treated with

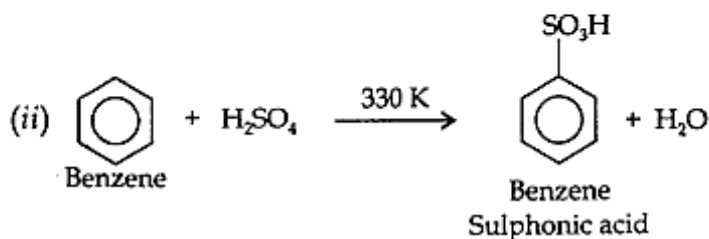
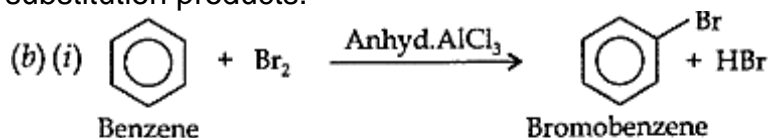
(i) Br₂ in presence of anhydrous AlCl₃

(ii) Conc. H₂SO₄ at 330 K.

Ans: (a) Substitution reactions are those reactions in which an atom or group of atoms directly attached to carbon in the substrate molecule is replaced by another atom or group of atoms, for example,

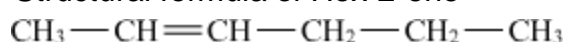


Benzene undergoes electrophilic substitution reactions because benzene ring has delocalized electrons is an electron-rich system. It is attacked by electrophiles giving substitution products.

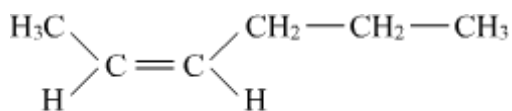


Q.2). Draw the cis and trans structures of hex-2-ene. Which isomer will have higher boiling point and why?

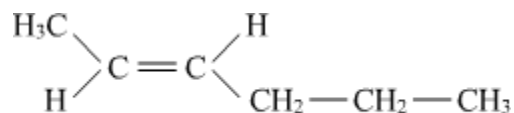
Structural formula of Hex-2-ene



Geometrical isomers of hex-2-ene are



cis-isomer



trans-isomer

The dipole moment of cis-compound is a sum of the dipole moments of C-CH₃ and C-CH₂CH₂CH₃ bonds acting in the same direction.

The dipole moment of trans-compound is the resultant of the dipole moments of C-CH₃ and C-CH₂CH₂CH₃ bonds acting in opposite directions.

Hence, cis-isomer is more polar than trans-isomer.

The higher the polarity, the greater is the intermolecular dipole-dipole interaction and the higher will be the boiling point. Hence, cis-isomer will have a higher boiling point than trans-isomer.