केन्द्रीय विद्यालय संगठन

KENDRIYA VIDYALAYA SANGATHAN

STUDY MATERIAL

2015-16

CHEMISTRY

CLASS XI

PREFACE

Kendriya Vidyalaya Sangathan is a pioneer organization which caters to the all round development of the students. Time to time various strategies have been adopted to adorn the students with academic excellence.

This support material is one such effort by Kendriya Vidyalaya Sangathan, an empirical endeavour to help students learn more effectively and efficiently. It is designed to give proper platform to students for better practice and understanding of the chapters. This can suitably be used during revision. Ample opportunity has been provided to students through master cards and question banks to expose them to the CBSE pattern. It is also suggested to students to keep in consideration the time-management aspect as well.

I extend my heartiest gratitude to the Kendriya Vidyalaya Sangathan authorities for providing the support material to the students prepared by various Regions. The same has been reviewed by the Regional Subject Committee of Patna Region who have worked arduously to bring out the best for the students. I also convey my regards to the staff of Regional Office, Patna for their genuine cooperation.

In the end, I earnestly hope that this material will not only improve the academic result of the students but also inculcate learning habit in them.

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INDEX

Chemistry XI

UNIT 1

SOME BASIC CONCEPTS OF CHEMISTRY

Chemistry: Chemistry is the branch of science that deals with the composition, structure and properties of matter. Chemistry is called the science of atoms and molecule

Branches of Chemistry

Organic Chemistry -This branch deals with study of carbon compounds especially hydrocarbons and their derivatives.

Inorganic Chemistry-This branch deals with the study of compounds of all other elements except carbon. It largely concerns itself with the study of minerals found in the Earth's crust.

Physical Chemistry-The explanation of fundamental principles governing various chemical phenomena is the main concern of this branch. It is basically concerned with laws and theories of the different branches of chemistry.

Industrial Chemistry-The chemistry involved in industrial processes is studied under this branch.

Analytical Chemistry-This branch deals with the qualitative and quantitative analysis of various substances.

Biochemistry-This branch deals with the chemical changes going on in the bodies of living organisms; plants and animals.

Nuclear Chemistry-Nuclear reactions, such as nuclear fission, nuclear fusion, transmutation processes etc. are studied under this branch.

PROPERTIES OF MATTER AND THEIR MEASUREMENT--Every substancehas unique or characteristic properties. These properties can be classified into two categories – **physical properties** and **chemical properties**.

Physical properties are those properties which can be measured or observed without changing the identity or the composition of the substance. E.g. colour, odour, melting point, boiling point, density etc.

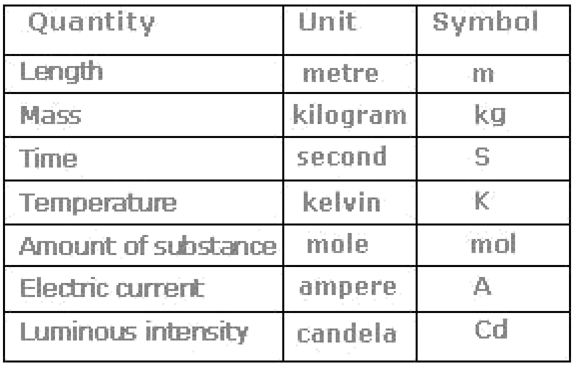
The measurement or observation of **chemical properties** requires a chemical change to occur. e.g. Burning of Mg-ribbon in air

Chemical properties are characteristic reactions of different substances; these include acidity or basicity, combustibility etc. Many properties of matter such as length, area, volume, etc., are quantitative in nature.

Metric System was based on the decimal system.

The International System of Units (SI)

The International System of Units (in French Le Systeme International d'Unites– abbreviated as SI) was established by the 11th General Conference on Weights and Measures (CGPM from *Conference Generale des Poids at Measures*). The SI system has seven *base units*



Quantity	Unit	Symbol
Length	metre	m
Mass	kilogram	kg
Time	second	S
Temperature	kelvin	K
Amount of substance	mole	mol
Electric current	ampere	A
Luminous intensity	candela	Cd

Prefixes in SI system

Multiple	Prefix	Symbol
10^{-12}	pico	p
10^{-9}	nano	n
10^{-6}	micro	µ
10^{-3}	milli	m
10^{-2}	centi	c
10^{-1}	deci	d
10	deca	da
10^{2}	hecto	h
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G
10^{12}	tera	T

Mass and Weight-- Mass of a substance is the amount of matter present in it while **weight** is the force exerted by gravity on an object. The mass of a substance is constant whereas its weight may vary from one place to another due to change in gravity. The mass of a substance can be determined very accurately by using an analytical balance

Volume-- Volume has the units of $(\text{length})^3$. So volume has units of m^3 or cm^3 or dm^3.A common unit, litre (L) is not an SI unit, is used for measurement of volume of liquids. 1 L = 1000 mL, 1000 cm^3 = 1 dm^3

Density: Density of a substance is its amount of mass per unit volume.SI unit of density = SI unit of mass/SI unit of volume = kg/m^3 or $kg\ m^{-3}$ This unit is quite large and a chemist often expresses density in $g\ cm^{-3}$.

Temperature--There are three common scales to measure temperature—°C (degree celsius), °F (degree Fahrenheit) and K (kelvin). Here, K is the SI unit.

$$°F = \frac{9}{5}(°C) + 32$$

K = °C + 273.15

Note—Temperature below 0 °C (i.e. negative values) are possible in Celsius scale but in Kelvin scale, negative temperature is not possible.

Scientific Notation

In which any number can be represented in the form N × 10^n (Where n is an exponent having positive or negative values and N can vary between 1 to 10).

e.g. We can write 232.508 as 2.32508 $x10^2$ in scientific notation. Similarly, 0.00016 can be written as 1.6 x 10^{-4}.

Precision refers to the closeness of various measurements for the same quantity. **Accuracy** is the agreement of a particular value to the true value of the result

Significant Figures

The reliability of a measurement is indicated by the number of digits used to represent it. To express it more accurately we express it with digits that are known with certainty. Meaningful digits are called as Significant figures. They contain all thecertain digits plus one doubtful digit in a number.

Rules for Determining the Number of Significant Figures

1. All non-zero digits are significant. For example, 6.9 has two significant figures, while 2.16 has three significant figures. The decimal place does not determine the number of significant figures.
2. A zero becomes significant in case it comes in between non zero numbers. For example, 2.003 has four significant figures, 4.02 has three significant figures.
3. Zeros at the beginning of a number are not significant. For example, 0.002 has one significant figure while 0.0045has two significant figures.
4. All zeros placed to the right of a number are significant. For example, 16.0 has three significant figures, while 16.00has four significant figures. Zeros at the end of a number without decimal point are ambiguous.
5. In exponential notations, the numerical portion represents the number of significant figures. For example, 0.00045 is expressed as 4.5 x 10^{-4} in terms of scientific notations. The number of significant figures in this number is 2, while in Avogadro's number (6.023 x 10^{23}) it is four.
6. The decimal point does not count towards the number of significant figures. For example, the number 345601 has six significant figures but can be written in different ways, as 345.601 or 0.345601 or 3.45601 all having same number of significant figures.

Retention of Significant Figures - Rounding off Figures

The rounding off procedure is applied to retain the required number of significant figures.

1. If the digit coming after the desired number of significant figures happens to be more than 5, the preceding significant figure is increased by one, 4.317 is rounded off to 4.32.
2. If the digit involved is less than 5, it is neglected and the preceding significant figure remains unchanged, 4.312 is rounded off to 4.31.
3. If the digit happens to be 5, the last mentioned or preceding significant figure

is increased by one only in case it happens to be odd. In case of even figure, the preceding digit remains unchanged. 8.375 is rounded off to 8.38 while 8.365 is rounded off to 8.36.

Dimensional Analysis During calculations generally there is a need to convert units from one system to other. This is called **factor label method** or **unit factor method** or **dimensional analysis**.

For example- 5 feet and 2 inches (height of an Indian female) is to converted in SI unit

1 inch = 2.54×10^{-2} m

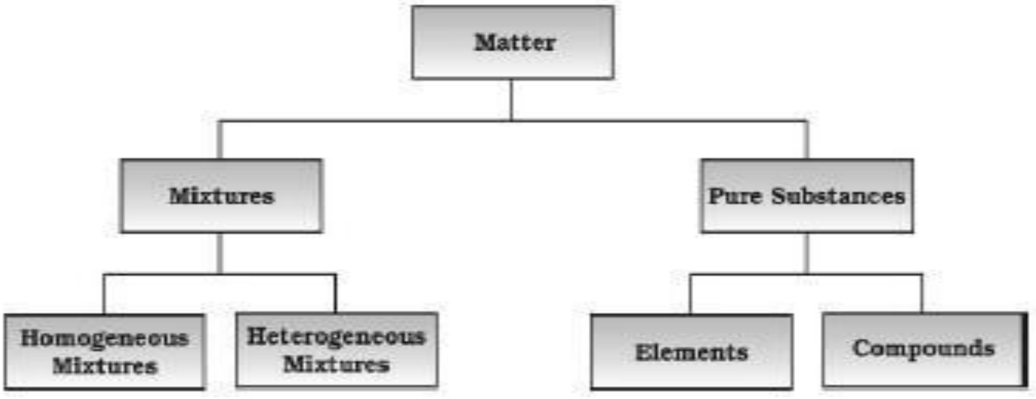
$1 = \frac{2.54 \times 10^{-2}\ \text{m}}{1\,\text{inch}}$ then, 5 feet and 2 inch = 62 inch

$= 62\ \text{inch} \times \frac{2.54 \times 10^{-2}\ \text{m}}{1\,\text{inch}} = 1.58\ \text{m}$

Physical Classification of Matter

Properties	**Solid**	**Liquid**	**Gas**
1. volume	Definite	Definite	Indefinite
2. Shape	Definite	Indefinite	Indefinite
3. Inter molecular force of attraction	Very high	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	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 knownas fluid	Not rigid and known as fluid
9. Fluidity	Can't flow	Can flow	Can flow
10. Diffusion	They can diffuse due to kinetic energy of liquid/gases	Can diffuse And rate of diffusion is very fast	Can diffuse And rate of diffusion is 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 114 elements known to us, out of which 92 are naturally occurring while the rest have been prepared artificially.

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 same 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, seawater, 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.)According to this law 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.

eg. $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$
1V 1V 2V (at same T,P)

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

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

- 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 combinations.
- Atoms combine with each other in simple whole number ratios to form compound atoms called 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 but is the reactive units of a reaction, 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 have 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 amu = 1.66056×10^{-24} 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.

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

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

Therefore gram atomic mass of oxygen = 16 g

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-

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

Mole Concept.

One 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 Vm. 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

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

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 (C_6H_6).

The **molecular formula** shows the exact number of different types of atoms present in a molecule of a compound. E.g. C_6H_6 is the molecular formula of benzene.

Relationship between empirical and molecular formulae

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

$$n = \frac{\text{Molecular mass}}{\text{empirical formula mass}}$$

Chemical Equation-

Shorthand representation of a chemical change in terms ofsymbols and formulae of the substances involved in the reaction is called chemical equation..

The substances that react among themselves to bring about the chemical changes are known as reactants, whereas the substances that are produced as a result of the chemical change, are known as products.

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 ofthe 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 unitsof 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 cm^3 of alcohol in 100 cm^3 of the solution

3. **Molarity** of the solution is defined as the number of moles of solute dissolved per litre (dm^3) 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.

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

The Molarity of the solution can also be expressed in terms of mass and molar mass

$$\text{Molarity of the solution} = \frac{\text{Mass of the solute}}{\text{Molar mass of the solute X volume of the solution in liter}}$$

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

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

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 M_1= initial molarity, M_2= molarity of the new solution, V_1= initial volume and V_2= 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'.

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

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

Mole fraction of the solute + Mole fraction of solvent = 1

One Mark questions with answers

1. What is the significant figures in 1.050×10^4?

Ans. Four

2. What is the S.I. unit of Density?

Ans. Kg m^{-3}

3. 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'.

4. Round off up to 3 significant figure (a) 1.235 (b) 1.225

Ans. (a) 1.24 (b) 1.22

5. What is AZT?

Ans. Azidothymidine.

6. What is limiting reagent?

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

7. What is the relation between temperature in degree Celsius and degree fahrenheit?

Ans.

$$^\circ F = \frac{9}{5}(^\circ C) + 32$$

8. 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.

9. Calculate the formula mass calcium chloride.

Ans. Formula mass of $CaCl_2$= 40+2 x35.5=40+71 = 111 u

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.

Two Marks questions with answers

1. Give the two points of differences between homogeneous and heterogeneous mixtures.

Ans.

Homogeneous mixture	Heterogeneous mixture
1. Homogeneous mixtures have the same composition throughout the sample. 2. The components of such mixtures cannot be seen under a powerful microscope.	1. Heterogeneous mixtures consist of two or more parts (phases), which have different compositions. 2. These mixtures have visible boundaries of separation between the different constituents and can be seen with the naked eye

2. Copper oxide obtained by heating copper carbonate or copper nitrate contains copper and oxygen in the same ration by mass. Which law is illustrated by this observation? State the law.

Ans. **Law of Definite Proportions** This law 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.

3. Write the empirical formula of the following:

(a) N_2O_4 (b) $C_6H_{12}O_6$ (c) H_2O (d) H_2O_2

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

4. Briefly explain the difference between precision and accuracy.

Ans. Precision refers to the closeness of various measurements for the same quantity. However, accuracy is the agreement of a particular value to the true value of the result.

5. 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
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.

6. Chlorine has two isotopes of atomic mass units 34.97 and 36.97. The relative abundance of the isotopes is 0.755 and 0.245 respectively. Find the average atomic mass of chlorine.

Ans. Average atomic mass = 34.97 x 0.755 +36.97 x 0.245 = 35.46 u

7. Calculate the percentage composition of water.

Ans. $\text{Mass \% of an element} = \frac{\text{mass of that element in the compound} \times 100}{\text{Molar mass of the compound}}$

Molar mass of water = 18.02 g

$\text{Mass \% of hydrogen} = \frac{2 \times 1.008 \times 100}{18.02}$

$= 11.18\ \%$

$\text{Mass \% of Oxygen} = \frac{16.00 \times 100}{18.02}\ \% = 88.79\ \%$

8. State the number of significant figures in each of the following:

(i) 208.91 (ii) 0.00456 (iii) 453 (iv) 0.346

Ans.

(i) 208.91 has five significant figures.

(ii) 0.00456 has three significant figures.

(iii) 453 has three significant figures.

(iv) 0.346 has three significant figures.

8. Express the results of the following calculations to the appropriate number of significant figures.

$$\text{(i)}\ \frac{3.24 \times 0.08666}{5.006} \quad \text{(ii)}\ \frac{(1.36 \times 10^{-4})(0.5)}{2.6}$$

Ans.

$$\text{(i)}\ \frac{3.24 \times 0.08666}{5.006}$$

= 0.05608 = 0.0561

$$\text{(ii)}\ \frac{(1.36 \times 10^{-4})(0.5)}{2.6}$$

= 0.2615 x 10-4 = 0.3 x 10^{-4}

9. How are 0.50 mol Na_2CO_3 and 0.50 M Na_2CO_3 different?

Ans. Molar mass of Na_2CO_3= 2 x 23 +12 + 3 x 16 = 106 g / mol

0.50 molNa_2CO_3means 0.50 x 106 = 53 g

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

Three Marks questions with answers-

1. What is unit factor method? Express the following in SI units - 93 million miles (distance between earth and sun)

Ans. Method to convert units from one system to other is called unit factor method.

93 million miles = 93 x 10^6 miles

1 mile = 1.60934 km = 1.60934 x 10^3 m

$$1 = \frac{1.60934 \times 10^3\ \text{m}}{1\ \text{mile}}$$

$$93\ \text{million mile} = 93 \times 10^6\ \text{mile} \times \frac{1.60934 \times 10^3\ \text{m}}{1\ \text{mile}}$$

= 1.5 x 10^{11} m

2. Write the three points of difference between compound and mixture.

Ans.

Compound	Mixture
Constituents are always present in a fixed ratio by mass	Constituents may be present in any Ratio
May or may not be homogeneous in nature	Always homogeneous in nature
Constituents can be easily separated	Constituents cannot be easily

by simple mechanical means	separated by simple mechanical means
Properties are midway between those of its constituents.	Properties are entirely different from those of its constituents.

3. What do mean bygram atomic mass.One million silver atoms weigh 1.79 x 10^{16} g. Calculate the gram atomic mass of silver.

Ans. Atomic mass of an element expressed in grams is the gram atomic mass
Number of silver atoms = 1 million = 1 x 10^{6}

Mass of one million Ag atoms = 1.79 x 10^{16} g

Mass of 6.023 x 10^{23} atoms of silver = $\frac{1.79 \times 10^{6} g}{10^{6}}$ x 6.023 x 10^{23} 1 x

= 107.8 g

4. What is the percentage of carbon, hydrogen and oxygen in ethanol?

Ans. Molecular formula of ethanol is : C_2H_5OH

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 / 46.068g)×100 = 13.13% Mass per cent of oxygen = (16.00 g / 46.068g)×100 = 34.73%

5. 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 (dm^3) 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

   = (4 g / 40 g 0.1 mol)/0.250L =0.1 mol/0.250 L

   = 0.4 mol L^{-1}
   = 0.4 M
6. Classify the following as pure substances or mixture-

   (a) ethyl alcohol (b) oxygen (c) blood (d) carbon (e) steel (f) distilled water

   Ans. Pure substance- ethyl alcohol , oxygen , carbon, distilled water
   Mixture- blood, steel
7. What are the rules for rounding off?

Ans.1. If the digit coming after the desired number of significant figures happens to be more than 5, the preceding significant figure is increased by one,

2. If the digit involved is less than 5, it is neglected and the preceding significant figure remains unchanged,

3.If the digit happens to be 5, the last mentioned or preceding significant figure is increased by one only in case it happens to be odd. In case of even figure, the preceding digit remains unchanged.

8. Define –(a) Average atomic mass (b) Molecular mass (c) Formula mass

Ans. (a) Average 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.

(b) Molecular mass- it is sum of atomic masses of the elements present in a molecule.

(c) Formula mass- it is sum of atomic masses of the elements present in a formula unit of a compound.

9. Express the following in the scientific notation with 2 significant figures-

(a) 0.0048 (b) 234,000 (c) 200.0

Ans. (a) 4.8×10^{-3} (b) 2.3×10^{5} (c) 2.0×10^{2}

10. Calculate the number of atoms in each of the following (i) 52 moles of Ar (ii) 52 u of He (iii) 52 g of He

Ans. **(i)** 1 mole of Ar = 6.022×10^{23} atoms of Ar

$\therefore$ 52 mol of Ar = $52 \times 6.022 \times 10^{23}$ atoms of Ar = 3.131×10^{25} atoms of Ar

(ii)1 atom of He = 4 u of He Or,

4 u of He = 1 atom of He

1 u of He = 1/4 atom of He

52u of He = 52/4 atom of He

= 13 atoms of He

(iii) Molar mass of He = 4 g/mol

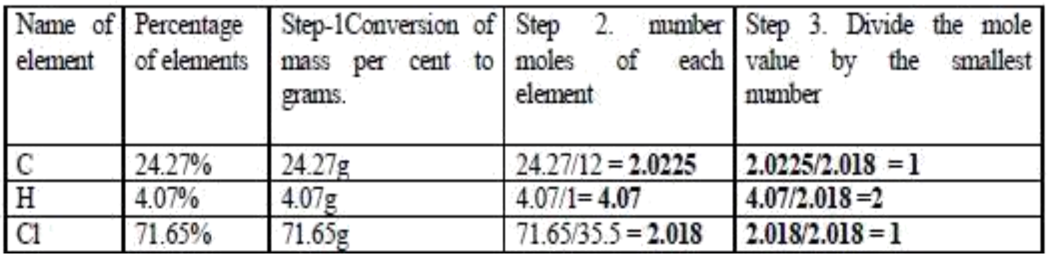
4 g of He contains = 6.022×10^{23} atoms of He

52 g of He contains = $\frac{6.022 \times 10^{23} \times 52}{4}$ = 78.286×10^{23} atoms of He

Five Marks questions with answers-

1. What is the difference between empirical and molecular formula? A compound contains 4.07 % hydrogen, 24.27 % carbon and 71.65 % chlorine. Its molar mass is 98.96 g. What are its empirical and molecular formulas?

Ans. An empirical formula represents the simplest whole number ration of various atoms present in a compound whereas the molecular formula shows the exact number of different types of atoms present in a molecule of a compound.



Name of element	Percentage of elements	Step-1Conversion of mass per cent to grams.	Step 2. number moles of each element	Step 3. Divide the mole value by the smallest number
C	24.27%	24.27g	24.27/12 = **2.0225**	**2.0225/2.018 = 1**
H	4.07%	4.07g	4.07/1= **4.07**	**4.07/2.018 =2**
Cl	71.65%	71.65g	71.65/35.5 = **2.018**	**2.018/2.018 = 1**

The empirical formula of the above compound is CH_2Cl.
empirical formula mass is 12 + (1x2) + 35.5 = 49.5
n= molecular mass/ empirical formula mass =98.96/49.5 =
2 Hence molecular formula is $C_2H_4Cl_2$

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

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

(i) Calculate the mass of ammonia produced if 2.00×10^3 g dinitrogen reacts with 1.00×10^3 g of dihydrogen.
(ii) Will any of the two reactants remain unreacted?
(iii) If yes, which one and what would be its mass?

Ans. (i) Balancing the given chemical equation, $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

From the equation, 1 mole (28 g) of dinitrogen reacts with 3 mole (6 g) of dihydrogen to give 2 mole (34 g) of ammonia.

⇒ 2.00×10^3g of dinitrogen will react with $\frac{6\text{ g}}{28\text{ g}} \times 2.00 \times 10^3$ g dihydrogen

i.e., 2.00×10^3 g of dinitrogen will react with 428.6 g of dihydrogen.

Given,

Amount of dihydrogen = 1.00×10^3 g

Hence, N_2 is the limiting reagent.

$\therefore$ 28 g of N_2 produces 34 g of NH_3.

Hence, mass of ammonia produced by 2000 g of N_2 $= \frac{34\text{ g}}{28\text{ g}} \times 2000$ g

= 2428.57 g

(ii) N_2 is the limiting reagent and H_2 is the excess reagent. Hence, H_2 will remain unreacted.

(iii) Mass of dihydrogen left unreacted = 1.00×10^3 g – 428.6 g

= 571.4 g

3. A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide, 0.690 g of water and no other products. A volume of 10.0 L (measured at STP) of this welding gas is found to weigh 11.6 g. Calculate (i) empirical formula, (ii) molar mass of the gas, and (iii) molecular formula.

Ans. **(i)** 1 mole (44 g) of CO_2 contains 12 g of carbon.

3.38 g of CO_2 will contain carbon $= \frac{12\text{ g}}{44\text{ g}} \times 3.38\text{ g}$
= 0.9217 g

18 g of water contains 2 g of hydrogen.

0.690 g of water will contain hydrogen $= \frac{2\text{ g}}{18\text{ g}} \times 0.690$ =
0.0767 g

Since carbon and hydrogen are the only constituents of the compound, the total mass of the compound is:= 0.9217 g + 0.0767 g= 0.9984 g

Percent of C in the compound $= \frac{0.9217\text{ g}}{0.9984\text{ g}} \times 100$ =
92.32%

Percent of H in the compound $= \frac{0.0767\text{ g}}{0.9984\text{ g}} \times 100$ =
7.68%

Moles of carbon in the compound $= \frac{92.32}{12.00}$ =
7.69

Moles of hydrogen in the compound = $\frac{7.68}{1}$ =
7.68

Ratio of carbon to hydrogen in the compound = 7.69: 7.68= 1: 1
Hence, the empirical formula of the gas is CH.

(ii) Given,
Weight of 10.0L of the gas (at S.T.P) = 11.6 g

Weight of 22.4 L of gas at STP $= \frac{11.6\text{ g}}{10.0\text{L}} \times 22.4\text{ L}$
= 25.984 g≈ 26 g

Hence, the molar mass of the gas is 26 g.

(iii) Empirical formula mass of CH = 12 + 1 = 13 g

$$n = \frac{\text{Molar mass of gas}}{\text{Empirical formula mass of gas}}$$

$$= \frac{26\,\text{g}}{13\,\text{g}}$$

$n = 2$

∴Molecular formula of gas = $(CH)_n = C_2H_2$

HOTS (Higher Order Thinking Skills)

1. What is the difference between 160 cm and 160.0 cm

Ans. 160 has three significant figures while 160.0 has four significant figures. Hence, 160.0 represents greater accuracy.

2. In the combustion of methane, what is the limiting reactant and why?

Ans. Methane is the limiting reactant because the other reactant is oxygen of the air which is always present in excess. Thus, the amounts of CO_2 and H_2O formed depend upon the amount of methane burnt.

3. A compound made up of two elements A and B has A= 70 %, B = 30 %. Their relative number of moles in the compound are 1.25 and 1.88. calculate
   a. Atomic masses of the elements A and B
   b. Molecular formula of the compound , if its molecular mass is found to be 160

Ans. Relative no. of moles of an element = $\frac{\text{\% of the element}}{\text{Atomic mass}}$

Or atomic mass = $\frac{\text{\% of the element}}{\text{Relative no. of moles}} = \frac{70}{1.25} = 56$

Atomic mass of B = 30/1.88 = 16

Calculation of Empirical formula

Element	Relative no. of moles	Simplest molar ratio	Simplestwhole no. molar ratio
A	1.25	1.25/1.25 = 1	2
B	1.88	1.88/1.25 = 1.5	3

Empirical formula = A_2B_3

Calculation of molecular formula-

Empirical formula mass = 2 x 56 + 3x 16 = 160

n= molecular mass / Empirical formula mass = 160/160 = 1

Molecular formula = A_2B_3

CHAPTER 2

STRUCTURE OF ATOM

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

PARTICLE	ELECTRON	PROTON	NEUTRON
Discovery	Sir. J. J. Thomson (1869)	Goldstein (1886)	Chadwick (1932)
Nature of charge	Negative	Positive	Neutral
Amount of charge	1.6 x 10^{-19}Coloumb	1.6 x 10^{-19}Coloumb	0
Mass	9.11 x 10^{-31}kg	1.672614 x 10^{-27}kg	1.67492 x10^{-27}kg

Electrons were discovered using cathode ray discharge tube experiment. Nucleus was discovered by Rutherford in 1911.

Cathode ray discharge tube experiment: A cathode ray discharge tube madeof glass is taken with two electrodes. At very low pressure and high voltage, current starts flowing through a stream of particles moving in the tube from cathode to anode. These rays were called cathode rays. When a perforated anode was taken, the cathode rays struck the other end of the glass tube at the fluorescent coating and a bright spot on the coating was developed

Results:

4. Cathode rays consist of negatively charged electrons.
5. Cathode rays themselves are not visible but their behaviour can be observed with help of fluorescent or phosphorescent materials.
6. In absence of electrical or magnetic field cathode rays travel in straight lines
7. In presence of electrical or magnetic field, behaviour of cathode rays is similar to that shown by electrons
8. The characteristics of the cathode rays do not depend upon the material of the electrodes and the nature of the gas present in the cathode ray tube.

Charge to mass ratio of an electron was determined by Thomson. The charge to mass ratio of an electron as 1.758820 x 10^{11} C kg^{-1}

Charge on an electron was determined by R A Millikan by using an oil drop experiment. The value of the charge on an electron is -1.6 x 10^{-19}C.

The mass on an electron was determined by combining the results of Thomson's experiment and Millikan's oil drop experiment. The mass of an electron was determined to be 9.1094 x 10^{-31}kg.

Discovery of protons and canal rays: Modified cathode ray tube experiment was carried out which led to the discovery of protons.

Characteristics of positively charged particles:

a. Charge to mass ratio of particles depends on gas from which these originate

b. The positively charged particles depend upon the nature of gas present in the cathode ray discharge tube

c. Some of the positively charged particles carry a multiple of fundamental of electrical charge.
d. Behaviour of positively charged particles in electrical or magnetic field is opposite to that observed for cathode rays

Neutrons were discovered by James Chadwick by bombarding a thin sheet of beryllium by α- particles. They are electrically neutral particles having a mass slightly greater than that of the protons.

Atomic number (Z) : the number of protons present in the nucleus (Moseley1913).

Mass Number (A) : Sum of the number of protons and neutrons present inthenucleus.

Thomson model of an atom: This model proposed that atom is considered as a uniform positively charged sphere and electrons are embedded in it. An important feature of Thomson model of an atom was that mass of atom is considered to be evenly spread over the atom. Thomson model of atom is also called as Plum pudding, raisin pudding or watermelon model Thomson model of atom was discarded because it could not explain certain experimental results like the scattering of α- particles by thin metal foils.

Observations from α- particles scattering experiment by Rutherford:

1. Most of the α- particles passed through gold foil un deflected
2. A small fraction of α- particles got deflected through small angles
3. Very few α- particles did not pass through foil but suffered large deflection nearly180^o

Conclusions Rutherford drew from α- particles scattering experiment:

1. Since most of the α-particles passed through foil undeflected, it means most of the space in atom is empty
2. Since some of the α-particles are deflected to certain angles, it means that there is positively mass present in atom
3. Since only some of the α-particles suffered large deflections, the positively charged mass must be occupying very small space
4. Strong deflections or even bouncing back of α-particles from metal foil were due to direct collision with positively charged mass in atom

Rutherford's model of atom: This model explained that atom consists of nucleus which is concentrated in a very small volume. The nucleus comprises of protons and neutrons. The electrons revolve around the nucleus in fixed orbits. Electrons and nucleus are held together by electrostatic forces of attraction.

Drawbacks of Rutherford's model of atom:

1. According to Rutherford's model of atom, electrons which are negatively charged particles revolve around the nucleus in fixed orbits.

2. The electrons undergo acceleration. According to electromagnetic theory of Maxwell, a charged particle undergoing acceleration should emit electromagnetic radiation. Thus, an electron in an orbit should emit radiation. Thus, the orbit should shrink. But this does not happen.
3. The model does not give any information about how electrons are distributed around nucleus and what are energies of these electrons

Isotopes: These are the atoms of the same element having the same atomic number but different mass number. e g $_1H^1$,$_1H^2$,$_1H^3$

Isobars: Isobars are the atoms of different elements having the same mass number but different atomic number. e g $_{18}Ar^{40}$, $_{20}Ca^{40}$

Isoelectronic species: These are those species which have the same number of electrons.

Electromagnetic radiations: The radiations which are associated with electrical and magnetic fields are called electromagnetic radiations. When an electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the form of waves. These waves are called electromagnetic waves or electromagnetic radiations.

Properties of electromagnetic radiations:

1. Oscillating electric and magnetic field are produced by oscillating charged particles. These fields are perpendicular to each other and both are perpendicular to the direction of propagation of the wave.
2. They do not need a medium to travel. That means they can even travel in vacuum.

Characteristics of electromagnetic radiations:

1. **Wavelength:** It may be defined as the distance between two neighbouring crests or troughs of wave as shown. It is denoted by λ.
2. **Frequency (ν):** It may be defined as the number of waves which pass through a particular point in one second.
3. **Velocity (v):** It is defined as the distance travelled by a wave in One second. In vacuum all types of electromagnetic radiations travel with the same velocity. Its value is 3×10^8 m $sec^{-1.}$ It is denoted by v
4. Wave number: Wave number $(\bar{\nu})$ is defined as the number of wavelengths per unit length.

Velocity = frequency x wavelength $c = \nu\lambda$

Planck's Quantum Theory-

- The radiant energy is emitted or absorbed not continuously but discontinuously in the form of small discrete packets of energy called ‘quantum’. In case of light , the quantum of energy is called a ‘photon’
- The energy of each quantum is directly proportional to the frequency of the radiation, i.e. $E \, \alpha \, \upsilon$ or $E= h\upsilon$ where h= Planck’s constant = 6.626×10^{-27} Js
- Energy is always emitted or absorbed as integral multiple of this quantum. $E=nh\upsilon$ Where n=1,2,3,4,.....

Black body: An ideal body, which emits and absorbs all frequencies, is called a black body. The radiation emitted by such a body is called black body radiation.

Photoelectric effect: The phenomenon of ejection of electrons from the surface of metal when light of suitable frequency strikes it is called photoelectric effect. The ejected electrons are called photoelectrons.

Experimental results observed for the experiment of Photoelectric effect-

- o When beam of light falls on a metal surface electrons are ejected immediately.

9. Number of electrons ejected is proportional to intensity or brightness of light

10. Threshold frequency (vo): For each metal there is a characteristic minimum frequency below which photoelectric effect is not observed. This is called threshold frequency.

- ➢ If frequency of light is less than the threshold frequency there is no ejection of electrons no matter how long it falls on surface or how high is its intensity.

Photoelectric work function (Wo): The minimum energy required to eject electrons is called photoelectric work function. $W_o = h\nu_o$

Energy of the ejected electrons :

$$h(\nu - \nu_0) = \frac{1}{2} m_e v^2$$

Dual behavior of electromagnetic radiation- The light possesses both particle and wave like properties, i.e., light has dual behaviour . Whenever radiation interacts with matter, it displays particle like properties.(Black body radiation and photoelectric effect) Wave like properties are exhibited when it propagates(interference an diffraction)

When a white light is passed through a prism, it splits into a series ofcoloured bands known as spectrum.

Spectrum is of two types: continuous and line spectrum

2. The spectrum which consists of all the wavelengths is called continuous spectrum.
3. A spectrum in which only specific wavelengths are present is known as a line spectrum. It has bright lines with dark spaces between them.

Electromagnetic spectrum is a continuous spectrum. It consists of a range of electromagnetic radiations arranged in the order of increasing wavelengths or decreasing frequencies. It extends from radio waves to gamma rays.

Spectrum is also classified as emission and line spectrum.

- o Emission spectrum: The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum.
- ➢ Absorption spectrum is the spectrum obtained when radiation is passed through a sample of material. The sample absorbs radiation of certain

wavelengths. The wavelengths which are absorbed are missing and come as dark lines.

The study of emission or absorption spectra is referred as spectroscopy.

- Spectral Lines for atomic hydrogen:

Series	n_1	n_2	Spectral Region
Lyman	1	2, 3, 4, 5 ...	Ultraviolet
Balmer	2	3, 4, 5 ...	Visible
Paschen	3	4, 5 ...	Infrared
Brackett	4	5, 6 ...	Infrared
Pfund	5	6, 7...	Infrared

Rydberg equation

$$\bar{\nu} = 109{,}677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{cm}^{-1}$$

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

Bohr's model for hydrogen atom:

3. An electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called orbits or energy levels. These orbits are arranged concentrically around the nucleus.
4. As long as an electron remains in a particular orbit, it does not lose or gain energy and its energy remains constant.
5. When transition occurs between two stationary states that differ in energy, the frequency of the radiation absorbed or emitted can be calculated

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

6. An electron can move only in those orbits for which its angular momentum is an integral multiple of h/2π

$$m_e \, vr = n.\frac{h}{2\pi} \qquad n = 1,2,3.....$$

The radius of the *n*th orbit is given byr_n =52.9 pm x $\underline{n^2}$ Z

energy of electron in *n*th orbit is :

$$E_n = -2.18\text{x}10^{-18} \left(\frac{Z^2}{n^2} \right) \text{J}$$

Limitations of Bohr's model of atom:

a. Bohr's model failed to account for the finer details of the hydrogen spectrum.
b. Bohr's model was also unable to explain spectrum of atoms containing more than one electron.

Dual behavior of matter: de Broglie proposed that matter exhibits dual behavior i.e. matter shows both particle and wave nature. de Broglie's relation is

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

Heisenberg’s uncertainty principle: It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron. The product of their uncertainties is always equal to or greater than h/4π.

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

where Δx = uncertainty in position,
Δp = uncertainty in momentum

Heisenberg’s uncertainty principle rules out the existence of definite paths or trajectories of electrons and other similar particles

Failure of Bohr’s model:

a. It ignores the dual behavior of matter.
b. It contradicts Heisenberg’s uncertainty principle.

Classical mechanics is based on Newton’s laws of motion. It successfully describes the motion of macroscopic particles but fails in the case of microscopic particles.

Reason: Classical mechanics ignores the concept of dual behaviour of matter especially for sub-atomic particles and the Heisenberg’s uncertainty principle.

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 mechanics is based on a fundamental equation which is called Schrodinger equation.

Schrodinger’s equation: For a system (such as an atom or a molecule whose energy does not change with time) the Schrödinger equation is written as:

$$\hat{H}\Psi = E\Psi$$

$\hat{H}$ is the Hamiltonian operator

E is the total energy of the system

Ψ represents the wave function which is the amplitude of the electron

Wave

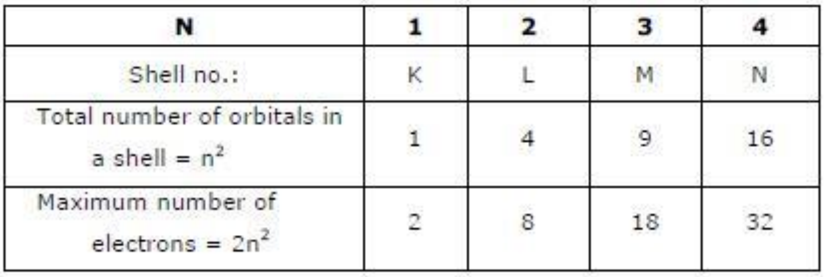
When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) of the electron associated with each energy level. Out of the possible values, only certain solutions are permitted. Each permitted solution is highly significant as it corresponds to a definite energy state. Thus, we can say that energy is quantized.

ψ gives us the amplitude of wave. The value of ψhas no physical significance. Ψ^2gives us the region in which the probability of finding an electron is maximum. It is called probability density.

Orbital: The region of space around the nucleus where the probability of finding an electron is maximum is called an orbital.

Quantum numbers: There are a set of four quantum numbers which specify the energy, size, shape and orientation of an orbital. To specify an orbital only three quantum numbers are required while to specify an electron all four quantum numbers are required.

Principal quantum number (n): It identifies shell, determines sizes and energy of orbitals



N	1	2	3	4
Shell no.:	K	L	M	N
Total number of orbitals in a shell = n^2	1	4	9	16
Maximum number of electrons = $2n^2$	2	8	18	32

Azimuthal quantum number (l): Azimuthal quantum number. 'l' is also known as orbital angular momentum or subsidiary quantum number. l. It identifies sub-shell, determines the shape of orbitals, energy of orbitals in multi-electron atoms along with principal quantum number and orbital angular momentum, *i.e.,* $\sqrt{l(l+1)}\frac{h}{2\pi}$. The number of orbitals in a subshell = 2*l* + 1. For a given value of *n,* it can have *n* values ranging from 0 to n-1. Total number of subshells in a particular shell is equal to the value of n.

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

Magnetic quantum number or Magnetic orbital quantum number (ml):

It gives information about the spatial orientation of the orbital with respect to standard set of co-ordinate axis.For any sub-shell (defined by 'l' value) 2l+1 values of ml are possible. For each value of l, m_l = – l, – (l –1), – (l–2)... 0,1... (l – 2), (l–1), l

Electron spin quantum number (ms): It refers to orientation of the spin of the electron. It can have two values +1/2 and -1/2. +1/2 identifies the clockwise spin and -1/2 identifies the anti- clockwise spin.

The region where this probability density function reduces to zero is called nodal surfaces or simply nodes.

Radial nodes: Radial nodes occur when the probability density of wave function for the electron is zero on a spherical surface of a particular radius.

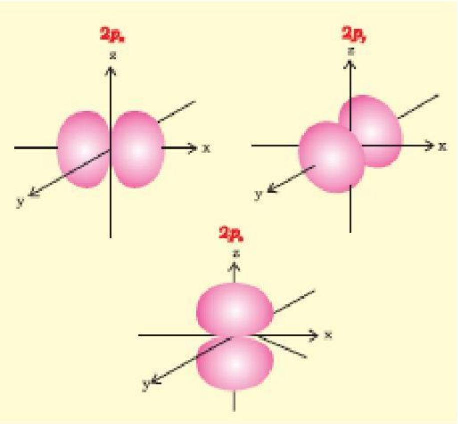
Number of radial nodes = n – l – 1

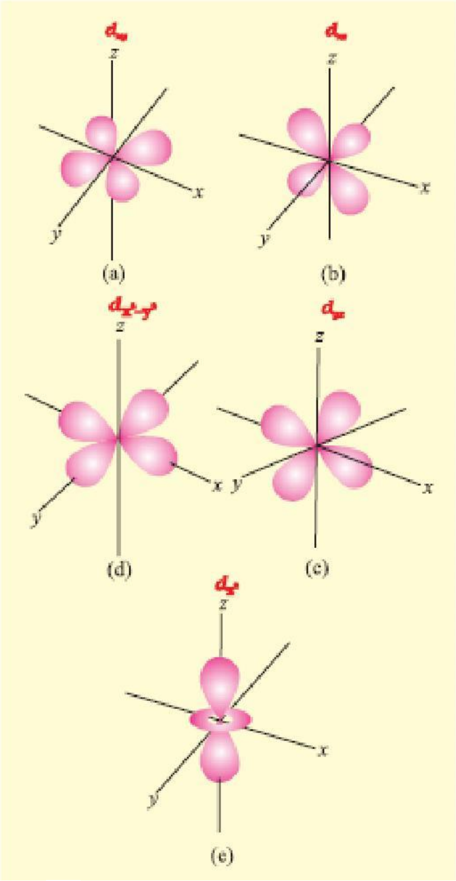
Angular nodes: Angular nodes occur when the probability density wave function for the electron is zero along the directions specified by a particular angle. Number of angular nodes = l

Total number of nodes = n – 1

Degenerate orbitals: Orbitals having the same energy are called degenerate orbitals.

Shape of p and d-orbitals





Shielding effect or screening effect: Due to the presence of electrons in the inner shells, the electron in the outer shell will not experience the full positive charge on the nucleus.

So, due to the screening effect, the net positive charge experienced by the electron from the nucleus is lowered and is known as effective nuclear charge. Effective nuclear charge experienced by the orbital decreases with increase of azimuthal quantum number (l).

Aufbau Principle: In the ground state of the atoms, the orbitals are filled in order of their increasing energies

n+l rule-Orbitals with lower value of (n+l) have lower energy. If two orbitals have the same value of (n+l) then orbital with lower value of nwill have lower energy.

The order in which the orbitals are filled is as follows:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d, 6p, 7s...

Pauli Exclusion Principle: No two electrons in an atom can have the same set of four quantum numbers. Only two electrons may exist in the same orbital and these electrons must have opposite spin.

Hund's rule of maximum multiplicity: Pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.

Electronic configuration of atoms: Arrangement of electrons in different orbitals of an atom. The electronic configuration of different atoms can be represented in two ways.

a. $s^a p^b d^c$...... notation.

b. Orbital diagram:, each orbital of the subshell is represented by a box and the electron is represented by an arrow (↑) a positive spin or an arrow (↓) a negative spin.

Stability of completely filled and half filled subshells:

9. Symmetrical distribution of electrons- the completely filled or half filled sub-shells have
symmetrical distribution of electrons in them and are more stable.
10. Exchange energy-The two or more electrons with the same spin present in the degenerate orbitals of a sub-shell can exchange their position and the energy released due to this exchange is called exchange energy. The number of exchanges is maximum when the subshell is either half filled or completely filled. As a result the exchange energy is maximum and so is the stability.

ONE MARK QUESTIONS

2 Neutrons can be found in all atomic nuclei except in one case. Which is this atomic nucleus and what does it consists of?

Ans. Hydrogen atom. It consists of only one proton.

2. Calculate wave number of yellow radiations having wavelength of 5800 A^0.

Ans. Wave number = 1/ wavelength

Wavelength = 5800 A^0 = 5800 x 10^{-10} m

Wave number = 1/5800 x 10^{-10} m = 1.72 x 10^6 m^{-1}

3. What are the values of n and l for 2p orbital? Ans. n=2 and l= 1

4. Which of the following orbitals are not possible? 1p, 2s, 3f and 4d

Ans. 1p and 3f are not possible.

5. Write the electronic configuration of the element having atomic number 24. Ans. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

6. What atoms are indicated by the following electronic configurations?

a. $1s^2\ 2s^2\ 2p^1$ b. $[Ar]4s^2\ 3d^1$

Ans. a. Boron b. Scandium

7. What is the relationship between frequency and wavelength of light?

Ans. velocity of light = frequency x wavelength. Frequency and wavelength are inversely proportional to each other.

8. State Pauli Exclusion Principle.

Ans. No two electrons in an atom can have the same set of four quantum numbers or an orbital can have maximum two electrons and these must have opposite spin.

9. When α- rays hit a thin foil of gold, very few α- particles is deflected back. What does it prove?

Ans. There is a very small heavy body present within the atom.

10. What is the difference between a quantum and a photon?

Ans. The smallest packet of energy of any radiation is called a quantum whereas that of light is called photon.

TWO MARKS QUESTIONS

1. Write the complete symbol for the atom with the given atomic number (Z) and mass number(A). (a) Z = 17, A = 35 (b) Z = 92 , A = 233

Ans. (a) ${}^{35}_{17}Cl$ (b) ${}^{233}_{92}U$

2. Using s,p,d and f notation, describe the orbital with the following quantum numbers-

(a) n=1,l=0 (b) n=3, l=1 (c) n=4, l=2 (d) n=4, l=3

Ans. (a) 1s (b) 3p (c)4d (d) 4f

3. How many electrons in an atom have the following quantum numbers?

a. n=4, m_s= -1/2 b. n =3 , l=o

Ans. (a) 16 electrons (b) 2 electrons.

4. An element with mass number 81 contains 31.7 % more neutrons as compared to protons. Assign the atomic symbol.

Ans. Mass number = 81, i.e., p + n = 81

If protons = x, then neutrons = $x + \frac{31.7}{100} \times x = 1.317\ x$

x+1.317x = 81 or 2.317x = 81 x=35

Thus proton = 35, i.e., atomic no. = 35 Hence symbol is ${}^{81}_{35}Br$

2. (i) The energy associated with the first orbit in the hydrogen atom is -2.18×10^{-18} J/atom. What is the energy associated with the fifth orbit

(ii) Calculate the radius of Bohr's fifth orbit for hydrogen atom.

Ans. (i) $E_n = -2.18 \times 10^{-18}/ n^2$ $E_5 = -2.18 \times 10^{-18}/ 5^2 = -8.72 \times 10^{-20}$ J

(ii) For H atom, $r_n = 0.529 \times n^2$ $r_5 = 0.529 \times 5^2 = 13.225\ A^0 = 1.3225$ nm

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

(a) n=0, l=0; m_l = 0, m_s= + ½ (c)n=1, l=0; m_l = 0, m_s= - ½

(b) n=1, l=1; m_l =- 0, m_s= + ½ (d) n=2, l=1; m_l = 0, m_s= + ½

Ans. (a) Not possible because n≠ 0 (c) Not possible because when n=1, l≠1

(b) Possible (d) Possible

3. (a)What is the lowest value of n that allows g orbitals to exist?

   (b)An electron is in one of the 3d orbitals, Give the possible values of n,l and $m_l$for this electron.

Ans.(a) minimum value of n= 5

(b)n=3, l=2, m_l = -2, -1, 0, +1, +2

8. Calculate the total number of angular nodes and radial nodes present in 30 orbitals.

Ans. For 3p orbitals, n=3, l= 1

Number of angular nodes = l= 1

Number of radial nodes = n-l-1 = 3-1-1= 1

(iv) Mention the draw backs of Rutherford's atomic model.

Ans. 1. It could not explain the stability of an atom.

It could not explain the line spectrum of H- atom.

(v) State de-Broglie concept of dual nature of matter. How do dual nature of electron verified?

Ans. Just as light has dual nature, every material particle in motion has dual nature (particle nature and wave nature). The wave nature has been verified by Davisson and Germer's experiment whereas particle nature by scintillation experiment.

THREE MARKS QUESTIONS

1. State (a)Hund's Rule of maximum Multiplicity (b) Aufbau Principle (c) n+l rule

Ans.(a) Pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.

(b)In the ground state of the atoms, the orbitals are filled inorder of their increasing energies

(c) Orbitals with lower value of (n+l) have lower energy. If two orbitals have the same value of (n+l) then orbital with lower value of n will have lower energy.

2. Write down the quantum numbers n and l for the following orbitals

   a. 2p b. 3d c. 5f

Ans. a. n=2, l= 1 b. n= 3, l=2 c. n= 5, l=3

3. Write the 3 points of difference between orbit and orbital.

Ans.

Orbit	orbital
1. An orbit is a well defined circular path around the nucleus in which the electrons revolve	1. An orbital is the three dimensional space around the nucleus within which the probability of finding an electron is maximum(upto 90 %)
2. It represents the planar motion of an electron around the nucleus	2. It represents the three dimensional motion of an electron around the nucleus
3. All orbits are circular and disc like	3. Different orbitals have different shapes, i.e., s-orbitals are spherically symmetrical, p-orbitals are dumb-bell

	shaped and so on.

4. State Heisenberg’s uncertainty principle. Calculate the uncertainty in the position of an electron if the uncertainty in its velocity is 5.7×10^{5} m/s.

Ans. It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron. The product of their uncertainties is always equal to or greater than h/4π.

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

$$\Delta x = h/4\pi \text{ x } m \text{ x } \Delta v = \frac{6.6 \text{ x } 10^{-34}}{4 \text{ x } 3.14 \text{ x } 9.1 \text{ x } 10^{-31} \text{ x } 5.7 \text{ x } 10^{5}} = 1.0 \text{ x } 10^{-10} \text{ m}$$

5. Write 3 points of differences between electromagnetic waves and matterwaves.

Electromagnetic waves	Matter waves
1. These are associated with electric and magnetic fields	1. These are not associated with electric and magnetic field.
2. They do not require any medium for propagation.	2. They require medium for propagation
3. They travel with the same speed a that of light	3. They travel with lower speeds not constanr for all matter waves

6. (i) Calculate the number of electrons which will together weigh one gram. (ii) Calculate the mass and charge of one mole of electrons

Ans. (i) Mass of one electron = 9.10939×10^{-31} kg

∴ Number of electrons that weigh 9.10939×10^{-31} kg = 1

Number of electrons that will weigh 1 g = $(1 \times 10^{-3}$kg)

$$= \frac{1}{9.10939 \times 10^{-31} \text{ kg}} \times \left(1 \times 10^{-3} \text{ kg}\right)$$

$= 0.1098 \times 10^{-3 + 31}$

$= 0.1098 \times 10^{28}$

$= 1.098 \times 10^{27}$

(ii) Mass of one electron = 9.10939×10^{-31} kg

Mass of one mole of electron = $(6.022 \times 10^{23}) \times (9.10939 \times 10^{-31}$

kg) = 5.48×10^{-7} kg

Charge on one electron = 1.6022×10^{-19} coulomb

Charge on one mole of electron = $(1.6022 \times 10^{-19} \text{C})(6.022 \times 10^{23})$

= 9.65×10^{4} C

7. Find energy of each of the photons which
   (i) correspond to light of frequency 3×10^{15} Hz.
   (ii) have wavelength of 0.50 Å.

   Ans.(i) Energy (E) of a photon is given by the expression,

   $E = h\nu$
   Where,
   h = Planck's constant = 6.626×10^{-34} Js ν = frequency of light = 3×10^{15} Hz
   Substituting the values in the given expression of E:
   $E = (6.626 \times 10^{-34})(3 \times 10^{15})$ $E = 1.988 \times 10^{-18}$ J

   (ii) Energy (E) of a photon having wavelength (λ) is given by the expression,

   $$E = \frac{hc}{\lambda}$$

   h = Planck's constant = 6.626×10^{-34} Js
   c = velocity of light in vacuum = 3×10^{8} m/s
   Substituting the values in the given expression of E:

   $$E = \frac{(6.626 \times 10^{-34})(3 \times 10^{8})}{0.50 \times 10^{-10}} = 3.976 \times 10^{-15} \text{ J}$$
   $$\therefore E = 3.98 \times 10^{-15} \text{ J}$$

8. What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with $n = 4$ to an energy level with $n = 2$?
   Ans. The $n_i = 4$ to $n_f = 2$ transition will give rise to a spectral line of the Balmer series. The energy involved in the transition is given by the relation,

   $$E = 2.18 \times 10^{-18}\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$

Substituting the values in the given expression of *E:*

$$E = 2.18\times10^{-18}\left[\frac{1}{4^2}-\frac{1}{2^2}\right]$$

$$= 2.18\times10^{-18}\left[\frac{1-4}{16}\right]$$

$$= 2.18\times10^{-18}\times\left(-\frac{3}{16}\right)$$

$E = -(4.0875 \times 10^{-19} \text{J})$

The negative sign indicates the energy of emission.

Wavelength of light emitted $(\lambda) = \frac{\text{hc}}{E}$

$\left(\text{since } E = \frac{\text{hc}}{\lambda}\right)$

Substituting the values in the given expression of λ:

$$\lambda = \frac{\left(6.626\times10^{-34}\right)\left(3\times10^{8}\right)}{4.0875\times10^{-19}}$$

$$\lambda = 4.8631\times10^{-7}\ \text{m}$$

$$= 486.3\times10^{-9}\,\text{m}$$

$$= 486\ \text{nm}$$

9. An atom of an element contains 29 electrons and 35 neutrons. Deduce **(i)**the number of protons and **(ii)** the electronic configuration of the element (iii) Identify the element .

Ans.**(i)**For an atom to be neutral, the number of protons is equal to the number of electrons.

∴ Number of protons in the atom of the given element = 29

(ii) The electronic configuration of the atom is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$(iii) Copper

10. Give the number of electrons in the species H_2^+, H_2 and O_2^+

Ans. Number of electrons present in hydrogen molecule (H_2) = 1 + 1 = 2

∴ Number of electrons in H_2^+ = 2 – 1 = 1 Number of electrons in H_2 = 1 + 1 = 2

Number of electrons present in oxygen molecule (O_2) = 8 + 8 = 16

∴ Number of electrons in O_2^+ = 16 – 1 = 15

FIVE MARKS QUESTIONS WITH ANSWERS

1. What are the draw backs of Bohr's atomic model? Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the de Broglie wavelength associated with the electron revolving around the orbit.

Ans.1.Bohr's model failed to account for the finer details of the hydrogen spectrum.

2. Bohr's model was also unable to explain spectrum of atoms containing more than one electron.
3. Bohr's model was unable to explain Zeeman effect and Stark effect i
4. Bohr's model could not explain the ability of atoms to form molecules by chemical bonds

Since a hydrogen atom has only one electron, according to Bohr's postulate, the angular momentum of that electron is given by:

$mvr = n\frac{h}{2\pi}$.........(1) Where, $n = 1, 2, 3, \ldots$

According to de Broglie's equation:

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

$$\text{or } mv = \frac{h}{\lambda}.........(2)$$

Substituting the value of 'mv' from expression (2) in expression (1):

$$\frac{hr}{\lambda} = n\frac{h}{2\pi}$$

$$\text{or } 2\pi r = n\lambda...........(3)$$

Since'$2\pi r$'represents the circumference of the Bohr orbit (r), it is proved by equation (3) that the circumference of the Bohr orbit of the hydrogen atom is an integral multiple of de Broglie's wavelength associated with the electron revolving around the orbit.

2. State photo electric effect. The work function for caesium atom is 1.9 eV. Calculate (a) the threshold wavelength and (b) the threshold frequency of the radiation. If the caesium element is irradiated with a wavelength 500 nm, calculate the kinetic energy and the velocity of the ejected photoelectron. Ans. Photoelectric effect: The phenomenon of ejection of electrons from the surface of metal when light of suitable frequency strikes it is called

photoelectric effect. The ejected electrons are called photoelectrons. It is given that the work function (W_0) for caesium atom is 1.9 eV.

(a) From the expression, $W_0 = \frac{hc}{\lambda_0}$, we get:

$$\lambda_0 = \frac{hc}{W_0}$$

Where,
λ_0 = threshold
wavelength h =
Planck’s constant
c = velocity of radiation
Substituting the values in the given expression of (λ_0):

$$\lambda_0 = \frac{\left(6.626\times10^{-34}\ \text{Js}\right)\left(3.0\times10^{8}\ \text{ms}^{-1}\right)}{1.9\times1.602\times10^{-19}\ \text{J}}$$

$$\lambda_0 =$$

$$6.53 \times 10^{-7}\ \text{m}$$

Hence, the threshold wavelength λ_0 is 653 nm.

(b) From the expression, $W_0 = h\nu_0$, we get:

$$\nu_0 = \frac{W_0}{h}$$

Where,
ν_0= threshold
frequencyh = Planck’s
constant
Substituting the values in the given expression ofν_0:

$$\nu_0 = \frac{1.9\times1.602\times10^{-19}\ \text{J}}{6.626\times10^{-34}\ \text{Js}}$$

(1 eV = 1.602×10^{-19}J)
ν_0= $4.593 \times 10^{14}\text{s}^{-1}$

Hence, the threshold frequency of radiation (ν_0) is $4.593 \times 10^{14}\text{s}^{-1}$.

(c) According to the question:
Wavelength used in irradiation (λ) = 500
nm Kinetic energy = h ($\nu - \nu_0$)

$$= hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)$$

$$= \left(6.626\times10^{-34}\ \text{Js}\right)\left(3.0\times10^{8}\ \text{ms}^{-1}\right)\left(\frac{\lambda_0 - \lambda}{\lambda\lambda_0}\right)$$

$$= \left(1.9878\times^{-26}\ \text{Jm}\right)\left[\frac{(653-500)10^{-9}\text{m}}{(653)(500)10^{-18}\ \text{m}^2}\right]$$

$$= \frac{\left(1.9878\times10^{-26}\right)\left(153\times10^{9}\right)}{(653)(500)}\text{J}$$

$$= 9.3149 \times 10^{-20}\ \text{J}$$

Kinetic energy of the ejected photoelectron = 9.3149×10^{-20} J Since K.E $= \frac{1}{2}mv^2 = 9.3149 \times 10^{-20}$ J

$$v = \sqrt{\frac{2(9.3149 \times 10^{-20}\ \text{J})}{9.10939 \times 10^{-31}\ \text{kg}}}$$

$$= \sqrt{2.0451 \times 10^{11}\ \text{m}^2\text{s}^{-2}}$$

$$v = 4.52 \times 10^{5}\ \text{ms}^{-1}$$

Hence, the velocity of the ejected photoelectron (v) is $4.52 \times 10^{5}\ \text{ms}^{-1}$.

3. (a)The quantum numbers of six electrons are given below. Arrange them in order of increasing energies. If any of these combination(s) has/have the same energy lists:

   1. $n= 4$, $l = 2$, $m_l=–2$, $m_s=–1/2$
   2. $n= 3$, $l = 2$, $m_l= 1$, $m_s= +1/2$
   3. $n= 4$, $l = 1$, $m_l= 0$, $m_s= +1/2$
   4. $n = 3$, $l= 2$, $m_l=–2$, $m_s=–1/2$
   5. $n = 3$, $l= 1$, $m_l=–1$,$m_s= +1/2$
   6. $n = 4$, $l= 1$, $m_l= 0$, $m_s= +1/2$

   (b)Among the following pairs of orbitals which orbital will experience the larger effective nuclearcharge? (i) 2*s* and 3*s*, (ii) 4*d* and 4*f*, (iii) 3*d* and 3*p*

Ans.(a)For$n = 4$ and $l = 2$, the orbital occupied is 4*d*. For $n = 3$ and $l = 2$, the orbital occupied is 3*d*. For $n = 4$ and $l = 1$, the orbital occupied is 4*p*.

Hence, the six electrons i.e., 1, 2, 3, 4, 5, and 6 are present in the 4*d*, 3*d*, 4*p*, 3*d*, 3*p*, and 4*p* orbitals respectively.

Therefore, the increasing order of energies is 5(3*p*) < 2(3*d*) = 4(3*d*) < 3(4*p*) = 6(4*p*) < 1 (4*d*).

(b)Nuclear charge is defined as the net positive charge experienced by an electron in the orbital of a multi-electron atom. The closer the orbital, the greater is the nuclear charge experienced by the electron (s) in it.

(i) The electron(s) present in the 2*s* orbital will experience greater nuclear charge (being closer to the nucleus) than the electron(s) in the 3*s* orbital.

(ii) 4*d* will experience greater nuclear charge than 4*f*since 4*d* is closer to the nucleus.

(iii) 3*p* will experience greater nuclear charge since it is closer to the nucleus than 3*f*.

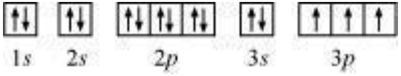
4. (i) The unpaired electrons in Al and Si are present in 3p orbital. Which electrons will experience more effective nuclear charge from the nucleus?

   (ii) Indicate the number of unpaired electrons in: (a) P, (b) Si, (c) Cr, (d) Fe Ans. (i) the electrons in the 3*p* orbital of silicon will experience a more effective nuclear charge than aluminium.

(ii) **(a)** Phosphorus (P):

Atomic number = 15

The electronic configuration of P is:$1s^2\ 2s^2\ 2p^6 3s^2\ 3p^3$ The orbital picture of P can be represented as:

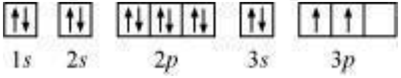


From the orbital picture, phosphorus has **three** unpaired electrons.

(b) Silicon (Si):

Atomic number = 14

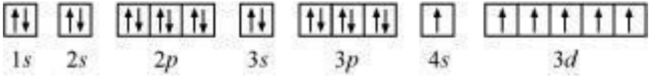
The electronic configuration of Si is:$1s^2\ 2s^2\ 2p^6\ 3s^2 3p^2$ The orbital picture of Si can be represented as:



From the orbital picture, silicon has **two** unpaired electrons.

(c) Chromium
(Cr):Atomic
number = 24

The electronic configuration of Cr is:$1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6\ 4s^1\ 3d^5$
The orbital picture of chromium is:

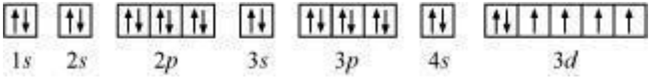


From the orbital picture, chromium has **six** unpaired electrons.

(d) Iron (Fe):

Atomic number = 26

The electronic configuration is:$1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6\ 4s^2\ 3d^6$ The orbital picture of chromium is:



From the orbital picture, iron has **four** unpaired electrons.

HOTS QUESTIONS WITH ANSWERS

1. Give the name and atomic number of the inert gas atom in which the total number of d-electrons is equal to the difference between the numbers of total p and total s electrons.

Ans. electronic configuration of Kr (atomic no.=36) =$1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6 3d^{10} 4s^2 4p^6$ Total no. of s-electrons = 8, total no. of p-electrons = 18.
Difference = 10
No. of d- electrons = 10

2. What is the minimum product of uncertainty in position and momentum of an electron?

Ans.h/4π

3. Which orbital is non-directional ? Ans. s- orbital

4. What is the difference between the notations *l* and L ? Ans. l represents the sub-shell and L represent shell.

5. How many electrons in an atom can have $n + l = 6$? Ans. 18

6. An anion A^{3+} has 18 electrons. Write the atomic number of A. Ans.15

7. Arrange the electron (*e*), protons (*p*) and alpha particle (α) in the increasing order for the values of *e/m* (charge/mass).

Ans.. $\alpha < p < e$

CHAPTER-3

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES OF ELEMENTS

Mandeleev's Periodic Law:- The properties of the elements are the periodic function of their atomic masses.

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

Modern Periodic Law: The physical and chemical properties of elements are theperiodic functions of their atomic numbers.

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

MAIN GROUP ELEMENTS/ REPRESENTATIVE ELEMENTS:

The s- and p- block elements are called main group elements or representative elements.

s- block elements: Group-1 (Alkali metals) and Group-2 elements (Alkalineearth metals) which respectively have ns^1 and ns^2 outermost electronic configurations.

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

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

f-**Block elements (Inner- transition Series)**

Lanthanoids charecterised by the filling of4 f-orbitals, are the elements following lanthanum from $_{58}Ce$ to $_{71}Lu$. Actinoids characterised by filling of 5f-orbitals, are the elements following actinium from $_{70}{}^{Th}$ to $_{103}Lr$. Characteristic outer electronic configuration is $(n-2)\ f^{1-14}\ (n-1)\ d^{0-1}\ ns^2$.

Noble Gases: The gaseous elements of group 18 are called noble gases. The general outermost electronic configuration of noble gases (except He) is ns^2 np^6. He exceptionally has $1s^2$ configuration. Thus the outermost shell of noble gases is completely filled.

PERIODICITY: The repetition of similar properties after regular intervals is called periodicity.

Cause of Periodicity: The properties of elements are the periodic repetition of similar electronic configuration of elements as the atomic number increases.

ATOMIC PROPERTIES: The physical characteristics of the atom of an element are called atomic properties. The properties such as atomic radius, ionic radius, ionisation energy, electro-negativity, electron affinity and valence etc., called atomic properties.

ATOMIC RADIUS- The distance from the centre of the nucleus to the outermost shell of the electrons in the atom of any element is called its atomic radius.

Periodicity- (a) In period- Atomic radius of elements decreases from left to rightin a period.

(b) In Group- Atomic radius of elements increases on moving top to bottom in a group.

COVALENT RADIUS- Half the inter-nuclear distance between two similar atoms of any element which are covalently bonded to each other by a single covalent bond is called covalent radius.

VAN DER WAALS' RADIUS: Half the inter-nuclear separation between two similar adjacent atoms belonging to the two neighbouring molecules of the same substance in the solid state is called the van der waals'radius of that atom.

METALLIC RADIUS: Half the distance between the nuclei of the two adjacent metal atoms in a close packed lattice of the metal is called its metallic radius.

Van der Waals'radius > Metallic radius > Covalent radius

IONIC RADIUS: The effective distance from the centre of the nucleus of an ion upto which it has an influence on its electron cloud is called its ionic radius.

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

IONISATION ENTHALPY: The ionisation enthalpy is the molar enthalpy change accompanying the removal of an electron from a gaseous phase atom or ion in its ground state. Thus enthalpy change for the reaction; $M_{(g)} \rightarrow M^{+}_{(g)} + e^{-}$

Is the ionisation enthalpy of the element M. Like ionisation energies for successive ionisation, the successive ionisation enthalpy may also be termed as 2nd ionisation enthalpy ($\Delta_r H_2$), third ionisation enthalpy ($\Delta_r H_3$) etc. The term ionisation enthalpy is taken for the first ionisation enthalpy, ($\Delta_r H_1$) is expressed in kg mol^{-} or in eV.

Periodicity:

i) Generally the ionisation enthalpies follow the order (there are few exceptions):

$(\Delta_r H_1) < (\Delta_r H_2) < (\Delta_r H_3)$

9. The ionisation enthalpy decreases on moving top to bottom in a group.
10. The ionisation enthalpy increases on moving from left to right in a period.

ELECTRON GAIN ENTHALPY: The electron gain enthalpy (($\Delta_{eg}H$) is the molar enthalpy change when an isolated gaseous atom or ion in its ground state adds an electron to form the corresponding anion thus the enthalpy change for the reaction; $X_{(g)} + e^{-} \rightarrow X^{-}_{(g)}$

is called the electron gain enthalpy (Δ_{eg} H) of the element X. The Δ_{eg} H may be positive or negative.

The successive values for the addition of second, third etc. Electron, these are called second, third etc. electron gain enthalpies. For example,

$X_{(g)} + e^{-} \rightarrow X^{-}_{(g)}$ $\Delta H = \Delta_{eg} H_1$ is called first electron gain enthalpy

$X^{-}_{(g)} + e^{-} \rightarrow X^{2-}_{(g)}$ $\Delta H = \Delta_{eg} H_2$ is called second electron gain enthalpy

$X^{2-}_{(g)} + e^{-} \rightarrow X^{3-}_{(g)}$ $\Delta H = \Delta_{eg} H_3$ is called third electron gain enthalpy Usually the term electron gain enthalpy ($\Delta_{eg}H$) means the first electron gain enthalpy.

Periodicity:

5. In period- The electron gain enthalpy increases from left to right in a period.
6. In group- The electron gain enthalpy decreases from top to bottom in a group.

ELECTRONEGATIVITY: “The relative tendency of an atom in a molecule to attract the shared pair of electrons towards itself is termed as its electro-negativity.”

Periodicity:

7. In period- The electro-negativity increases from left to right in a period.
8. In group- The electro-negativity decreases from top to bottom in a group.

VALENCE ELECTRONS: The electrons present in outermost shell are called as valence electron. Because the electrons in the outermost shell determine the valency of an element.

VALENCY OF AN ELEMENT: The number of hydrogen or halogen atom or double the number of oxygen atom, which combines with one atom of the element is taken as its valency. According to the electronic concept of valency, “ the number of electrons which an atom loses or gains or shares with other atom to attain the noble gas configuration is termed as its valency.”

Periodicity:

9. In period- The valency first increases then decreases from left to right in a period.
10. In group- The valency remains constant from top to bottom in a group.

ELECTROPOSITIVE OR METALLIC CHARACTER: The tendency of an element to lose electrons and forms positive ions (cations) is called electropositive or metallic character. The elements having lower ionisation energies have higher tendency to lose electrons, thus they are electropositive or metallic in their behaviour.

Alkali metals are the most highly electropositive elements.

Periodicity: In period- The electropositive or metallic characters decreases from left to right in a period.

In group- The electropositive or metallic characters increases from top to bottom in a group.

ELECTRO-NEGATIVE OR NON- METALLIC CHARACTERS: the tendency of an element to accept electrons to form an anion is called its non metallic or electronegative character. The elements having high electro-negativity have higher tendency to gain electrons and forms anion. So, the elements in the upper right hand portion of the periodic table are electro-negative or non-metallic in nature.

Periodicity:

3. In period- The electro-negative or non- metallic characters increases from left to right in a period.
4. In group- The electro-negative or non-metallic characters decreases from top to bottom in a group.

REACTIVITY OF METALS:

Periodicity:

11. In period- The tendency of an element to lose electrons decreases in a period. So the reactivity of metals decreases from left to right in a period.
12. In group- The tendency of an element to lose electrons increases in a period. So the reactivity of metals increases from top to bottom in a group.

REACTIVITY OF NON- METALS:

13. In period- The tendency of an element to gain electrons increases in a period. So the reactivity of non-metals increases from left to right in a period.
14. In group- The tendency of an element to gain electrons decreases in a group. So the reactivity of non-metals increases from top to bottom in a group.

SOLUBILITY OF ALKALI METALS CARBONATES AND BICARBONATES:

PERIODICITY IN GROUP: The solubility of alkali metal carbonates and bicarbonates in water increases down the group (From Lithium to Caesium).

SOLUBILITY OF ALKALINE EARTH METAL HYDROXIDES AND SULPHATES:

PERIODICITY IN GROUP: The solubility of alkaline earth metal hydroxide and sulphates in water increases down the group (From Beryllium to Barium).

BASIC STRENGTH OF ALKALINE EARTH METAL HYDROXIDES:

PERIODICITY IN GROUP: The basic strength of alkaline earth metal hydroxide in water increases down the group (From Beryllium to Barium), i.e.,

$$Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$$

$$\xrightarrow[\text{Basic strength increases}]{\hspace{10em}}$$

THERMAL STABILITY OF CARBONATES OF ALKALI AND ALKALINE EARTH METALS:

Except lithium carbonate, ($LiCO_3$), the carbonates of all other alkali metals are stable towards heat, i.e., carbonates of alkali metals (except $LiCO_3$) do not decompose on heating. $LiCO_3$ decomposes on heating to give lithium oxide ($LiCO_3$).

The carbonates of alkaline earth metals are relatively less stable. On heating, they decompose to give corresponding oxide and CO_2 gas. The decomposition temperature for alkaline earth metal carbonates increases as we go down the group.

Anomalous Properties of Second Period Elements

Their anomalous behaviour is attributed to their small size, large charge/radius ratio, high electro negativity, non- availability of d- orbitals in their valence shell. The first member of each group of p-Block elements displays greater ability to form pp-pp multiple bonds to itself (e.g. C=C, C≡C O=O, N≡N) and to other second period elements (e.g. C=O, C≡N, N=O) compared to subsequent member of the group.

ONE MARK QUESTIONS

Q1. Select the species which are iso-electronic (same number of electron) with each other.

(1) Ne (2) Cl^- (3) Ca^{2+} (4) Rb^+

Ans-The Cl^- and Ca^{2+}. Both have 18 e^- each.

Q.2. What the elements of a group have common among them?

Ans- They have same number of electrons in the valence shell.

Q.3. What the s- and p- block elements are collectively called?

Ans- Representative elements.

Q.4. Define atomic radius.

Ans- The one-half the distance between the nuclei of two covalently bonded atoms of the same element in a molecule is called as atomic radius.

Q.5. State the modern periodic law.

Ans- The physical and chemical properties of the elements are the periodic function of their atomic numbers.

Q.6. Name the groups of elements classified as s-, p- and d- blocks.

Ans- s- block= 1,2 (including He), p- block= 13 to 18 (except He), d- block= 3 to 12.

Q.7. Define the term ionisation enthalpy.

Ans- The energy required to remove the outer most electron from the valence shell of an isolated gaseous atom is called as ionisation enthalpy.

Q.8.In how many groups and periods the elements in modern periodic table are classified?

Ans- In 18 groups and 7 periods.

Q.9. What do you mean by electronic configuration of the elements?

Ans- The systematic distribution of the electrons among the orbitals of an atom of an element according to increasing order of their energies is called as electronic configuration of that element.

TWO MARKS QUESTIONS

Q.1. Describe the two merits of long form periodic table over the Mendeleev's periodic table?

Ans- 1. It removed the anomalies about the position of isotopes which existed in the Mendeleev's table.

2. It relates the position of an element in the periodic table with its electronic configuration.

Q.2. What is a period in the periodic table? How do atomic sizes change in a period with an increase in atomic number?

Ans- The horizontal rows in periodic table are called as periods. The atomic sizes decrease in a period with an increase in atomic number.

Q.3. The outer electronic configuration of some elements are:

(a) $3s^2\ 3p^4$ (b) $3d^{10}4s^2$ (c) $3s^2\ 3p^6\ 4s^2$ (d) $6s^2\ 4f^3$

To which block of elements in the periodic table each of these belongs?

Ans- (a) p- Block (b) d- Block (c) s- Block (d) f- Block

Q.4. What is meant by periodicity in properties of elements? What is the reason behind this?

Ans- The repetition of similar properties after regular intervals is called as periodicity. It is due to the similarity in the outer electronic configurations which gives rise to the periodic properties of the elements.

Q.5. How do atomic radii vary in a group and a period?

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.

Q.6. Arrange the following in the order of increasing radii:

(a) I, I^+, I^- (b) F, Cl, Br

Ans- (a) $I^+ < I < I^+$ (b) O < N< P

Q.7. 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

Q.8. How does ionisation enthalpy vary in a group and a period?
Ans- In Period- It increases from left to right
In group- It decreases down the group.

Q.9. Noble gases have zero electron gain enthalpy values. Explain.

Ans- Because the outer most shell of noble gases is completely filled and no more electrons can be added.

Q.10. Elements in the same group have equal valency. Comment on it.

Ans- Because the general outer most electronic configurations of the elements of a group remain same and they contain equal number of electrons in their respective outer most shells.

THREE MARKS QUESTIONS

Q.1. The first ionisation enthalpy of magnesium is higher than that of sodium. On the other hand, the second ionisation enthalpy of sodium is very much higher than that of magnesium. Explain.

Ans- The 1st ionisation enthalpy of magnesium is higher than that of Na due to higher nuclear charge and slightly smaller atomic radius of Mg than Na. After the loss of first electron, Na^+ formed has the electronic configuration of neon (2,8). The higher stability of the completely filled noble gas configuration leads to very high second ionisation enthalpy for sodium. On the other hand, Mg^+ formed after losing first electron still has one more electron in its outermost (3s) orbital. As a result, the second ionisation enthalpy of magnesium is much smaller than that of sodium.

Q.2. What are the major differences between metals and non-metals?Ans-

Property	Metal	Non- Metal
Nature	Electropositive	Electronegative
Type of ion formed	Cation (Positively Charged)	Anion (Negatively Charged)
Reaction with acids	Active metals displace hydrogen	Do not displace hydrogen
Oxides	Basic	Acidic

Q.3. Among the elements of the second period Li to Ne pick out the element:

(i) with the highest first ionisation energy(ii) with the highest electronegativity

(iii) with the largest atomic radius Give the reason for your choice.

Ans- (i) The ionisation energy increases on going from left to right. Therefore, the element with the highest ionisation energy is Ne.

15. The electro negativity is electron- accepting tendency. This increases on going from left to right and decreases down the group. Therefore, the element with the highest electro- negativity is F.

16. The atomic radius decreases across a period on going from left to right. Thus, the first element of any period should have the largest atomic radii. Here, Li has the largest atomic radii.

Q.4. Arrange the following as stated:

(i) N_2, O_2, F_2, Cl_2 (Increasing order of bond dissociation energy)
(ii) F, Cl, Br, I (Increasing order of electron gain enthalpy)
(iii) F_2, N_2, Cl_2, O_2 (Increasing order of bond length)

Ans- (i) $F_2 < Cl_2 < O_2 < N_2$
(ii) $I < Br < F < Cl$

(iii) $N_2 < O_2 < F_2 < Cl_2$

Q.5. Why does the first ionisation enthalpy increase as we go from left to right through a given period of the periodic table?

Ans- In a period, the nuclear charge (the number of protons) increases on going from left to right. The electron added to each element from left to right enters the same shell. This results in an increase of the effective nuclear charge across the period on moving from left to right. As a result, the electron get more firmly bound to the nucleus. This causes an increase in the first ionisation enthalpy across the period.

Q.6. Use the periodic table to answer the following questions.

(i) Identify the element with five electrons in the outer sub-shell.

p Identify an element that would tend to lose two electrons.

q Identify an element that would tend to gain two electrons.

Ans- (i) Chlorine (ii) Magnesium (iii) Oxygen

Q.7. Explain why are cations smaller and anions larger in size than their parent atoms?

Ans- (a) The cations are smaller than their parent atoms due to the following reasons:

Disappearance of the valence shell.

Increase of effective nuclear charge

(b) The anions are larger than their parent atoms due to the following reason:

An increase in the number of electrons in the valence shell reduces the effective nuclear charge due to greater mutual shielding by the electrons. As a result, electron cloud expands, i.e., the ionic radius increases.

Q.8. Describe the theory associated with the radius of an atom as it

(a) gains an electron (b) loses an electron

Ans- **(a)**When an atom gains an electron, its size increases. When an electron is added, the number of electrons goes up by one. This results in an increase in repulsion among the electrons. However, the number of protons remains the same. As a result, the effective nuclear charge of the atom decreases and the radius of the atom increases.

(b) When an atom loses an electron, the number of electrons decreases by one while the nuclear charge remains the same. Therefore, the interelectronic repulsions in the atom decrease. As a result, the effective nuclear charge increases. Hence, the radius of the atom decreases.

Q.9. How does atomic radius vary in a period and in a group? How do youexplain the variation?

Ans- Atomic radius generally decreases from left to right across a period. This is because within a period, the outer electrons are present in the same valence shell and the atomic number increases from left to right across a period, resulting in an increased effective nuclear charge. As a result, the attraction of electrons to the nucleus increases.

On the other hand, the atomic radius generally increases down a group. This is because down a group, the principal quantum number (*n*) increases which results in an increase of the distance between the nucleus and valence electrons.

Q.10. Consider the following species:

N^{3-}, O^{2-}, F^{-}, Na^{+}, Mg^{2+} and Al^{3+}

(a) What is common in them?

(b) Arrange them in the order of increasing ionic radii.

Ans- (a) the same number of electrons (10 electrons). Hence, the given species are isoelectronic.

(b) $Al^{3+} < Mg^{2+} < Na^{+} < F^{-} < O^{2-} < N^{3-}$

FIVE MARKS QUESTIONS

Q.1. What is the cause of the periodicity in the properties of the elements? How do the following properties vary in (a) a group and (b)in a period

(i) electronegativity (ii) ionisation enthalpy (iii) Atomic size

Ans- It is due to the similarity in the outer electronic configurations which gives rise to the periodic properties of the elements.

(a) In a group:
  (i) Electronegativity- It decreases down the group.
  (ii) Ionisation enthalpy- It decreases down the group.
  (iii) Atomic size- It increases down the group.

(b) In a period:
  (i) Electronegativity- Increases
  (ii) Ionisation enthalpy- Increases
  (iii) Atomic size- Dereases.

Q.2. The first $(\Delta_i H1)$ and the second $(\Delta_i H)$ ionization enthalpies (in kJ mol^{-1}) andthe $(\Delta_{eg} H)$ electron gain enthalpy (in kJ mol^{-1}) of a few elements are given below:

Elements	$_{i}H$	$_{i}H$	$_{eg}H$
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.

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

5. the metal which can form a predominantly stable covalent halide of the formula MX (X=halogen)?

Ans- **(a)**Element V is likely to be the least reactive element. This is because it hasthe highest first ionization enthalpy ($\Delta_i H_1$) and a positive electron gain enthalpy ($\Delta_{eg}H$).

- ➢ Element II is likely to be the most reactive metal as it has the lowest first ionization enthalpy ($\Delta_i H_1$) and a low negative electron gain enthalpy ($\Delta_{eg}H$).
- ➢ Element III is likely to be the most reactive non–metal as it has a high first ionization enthalpy ($\Delta_i H_1$) and the highest negative electron gain enthalpy ($\Delta_{eg}H$).
- ➢ Element V is likely to be the least reactive non–metal since it has a very high first ionization enthalpy ($\Delta_i H_2$) and a positive electron gain enthalpy ($\Delta_{eg}H$).
- ➢ Element VI has a low negative electron gain enthalpy ($\Delta_{eg}H$). Thus, it is a metal. Further, it has the lowest second ionization enthalpy ($\Delta_i H_2$). Hence, it can form a stable binary halide of the formula MX_2(X=halogen).
- ➢ Element I has low first ionization energy and high second ionization energy. Therefore, it can form a predominantly stable covalent halide of the formula MX (X=halogen).

CHAPTER-4

CHEMICAL BONDING AND MOLECULAR STRUCTURE

OCTET RULE- During a chemical reaction the atoms tend to adjust their electronic arrangement in such a way that they achieve 8 e^- in their outermost electron. This is called octet rule.

CHEMICAL BOND- the chemical force which keeps the atoms in any molecule together is called a chemical bond.

IONIC BOND- The columbic force of attraction which holds the oppositely charged ions together is called an ionic bond. An ionic bond is formed by the complete transfer of one or more electrons from the atom of a metal to an atom of non- metal.

LATTICE ENTHALPY- The molar enthalpy change accompanying the complete separation of the constituent particles that compose of the solids (such as ions for ionic solid, molecules for molecular solids) under standard conditions is called lattice enthalpy ($\Delta_l H^o$). The lattice enthalpy is a positive quantity.

ELECTRO VALENCY: The number of electrons lost or gain by an atom of an element is called as electrovalency.

The elements which give up electrons to form positive ions are said to have positive valency, while the elements which accept electrons to form negative ions are said to have negative valency.

FORMATION OF AN IONIC BOND: It is favoured by, (i) the low ionization enthalpy of a metallic element which forms the cations, (ii) High electron gain enthalpy of non- metallic element which forms the anions, (iii) Large lattice enthalpy i.e; the smaller size and the higher charge of the atoms.

COVALENCY: The number of electrons which an atom contributes towards mutual sharing during the formation of a chemical bond called its covalency in that compound.

SINGLE COVALENT BOND: A covalent bond formed by the mutual sharing of one pair of electrons is called a single covalent bond, or simply a single bond. A single covalent bond is represented by a small line (−) between the two atoms.

DOUBLE COVALENT BOND: A covalent bond formed by the mutual sharing oftwo pair of electrons is called a double covalent bond, or simply a double bond. A double covalent bond is represented by two small horizontal lines (=) between the two atoms. E.g. O=O, O=C=O etc.

TRIPLE COVALENT BOND: A covalent bond formed by the mutual sharing of three pair of electrons is called a triple covalent bond, or simply a triple bond. A triple covalent bond is represented by three small horizontal lines (≡) between the two atoms. E.g. N≡N, H-C≡C-H etc.

FORMATION OF A COVALENT BOND: Formation of a covalent bond is favoured by

11. High ionisation enthalpy of the combining elements.
12. Nearly equal electron gain enthalpy and equal electro-negativities of combining elements.
13. High nuclear charge and small atomic size of the combining elements.

POLAR COVALENT BOND: The bond between two unlike atoms which differ in their affinities for electrons is said to be polar covalent bond. E.g. H-Cl

COORDINATE BOND: The bond formed when one sided sharing of electrons take place is called a coordinate bond. Such a bond is also known as dative bond. It is represented by an arrow (→) pointing towards the acceptor atom. E.g. $H_3N \rightarrow BF_3$

Bond Length: Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule

Bond Angle: It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion

Bond Enthalpy: It is defined as the amount of energy required to break one moleof bonds of a particular type between two atoms in a gaseous state.

Bond Order: In the Lewis description of covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule

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

Dipole moment : The product of the magnitude of the charge and the distance between the centres of positive and negative charge. It is a vector quantity and is represented by an arrow with its tail at the positive centre and head pointing towards a negative centre. Dipole moment (μ) = charge (Q) × distance of separation (r)

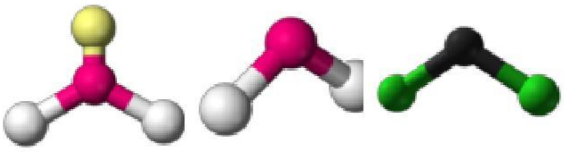
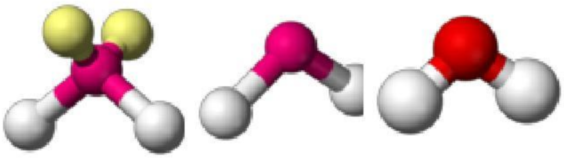
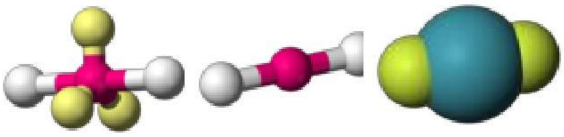
SIGMA BOND: A covalent bond formed due to the overlapping of orbitals of the two atoms along the line joining the two nuclei (orbital axis) is called sigma (σ) bond. For example, the bond formed due to s-s and s-p, p-p overlapping along the orbital axis are sigma bonds.

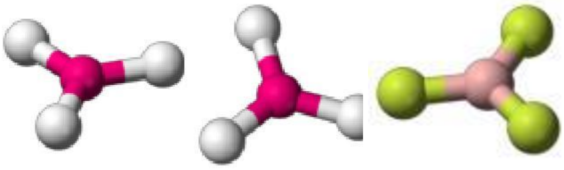
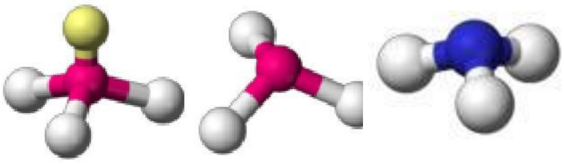
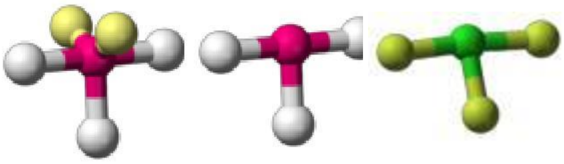
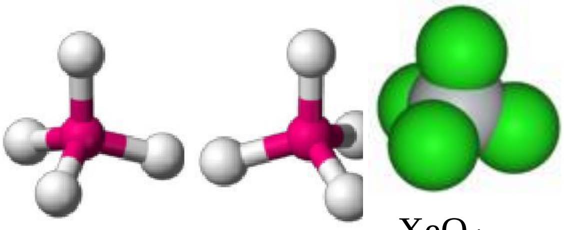
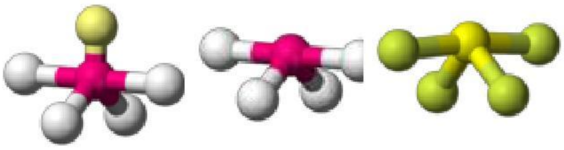
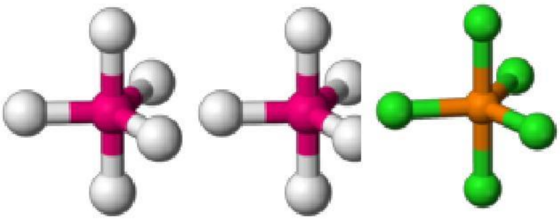
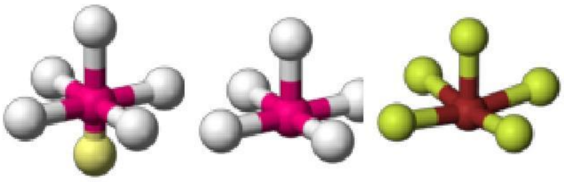
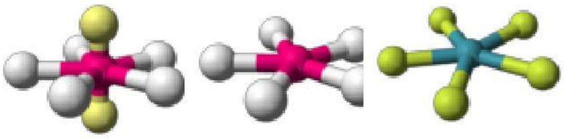
Pi- BOND: A covalent bond formed by the side wise overlapping of p- or d- orbitals of two atoms is called as pi (π) bond. For example, the bond formed due to the sideways overlapping of the two p- orbitals is a pi- bond.

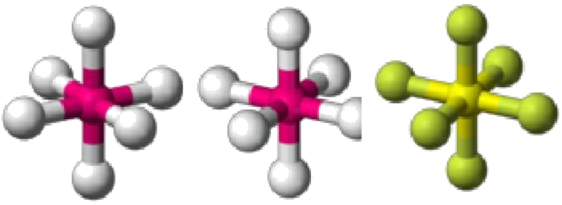
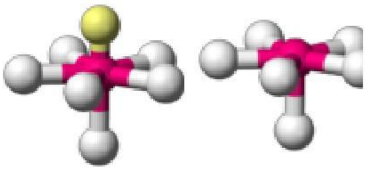
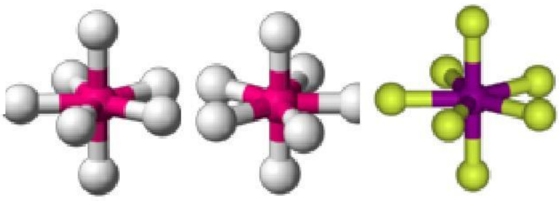
HYDROGEN BOND: The bond between the hydrogen atom of one molecule and a more electro- negative element of same or another molecule is called as hydrogen bond.

HYBRIDIZATION: The process of mixing of the atomic orbitals to form new hybrid orbitals is called hybridization. All hybrid orbitals of a particular kind have equal energy, identical shapes and are symmetrically oriented in shape.

The hybrid orbitals are designed according to the type and the atomic orbitals merging together, e.g.,

Molecule	**Shape/Hybridization**	**arrangeme nt† Geometry ‡**	**Examples**
AX_2E_0	sp Linear		$BeCl_2$, $HgCl_2$, CO_2
AX_2E_1	Sp^2 Bent		NO_2^-, SO_2, O_3, CCl_2
AX_2E_2	Sp^3 Bent		H_2O, OF_2
AX_2E_3	Sp^{3}d Linear		XeF_2, I_3^-, $XeCl_2$

AX_3E_0	Sp^2	Trigonal planar		BF_3, CO_3^{2-}, NO_3^{-}, SO_3
AX_3E_1	Sp^3	Trigonal pyramidal		NH_3, PCl_3
AX_3E_2	Sp^3d	T-shaped		ClF_3, BrF_3
AX_4E_0	Sp^3	Tetrahedral		CH_4, PO_4^{3-}, SO_4^{2-}, ClO_4^{-}, XeO_4
AX_4E_1	Sp^3d	Seesaw		SF_4
AX_4E_2	Sp^3d^2	Square planar		XeF_4
AX_5E_0	Sp^3d	Trigonal bipyramidal		PCl_5
AX_5E_1	Sp^3d^2	Square pyramidal		ClF_5, BrF_5, $XeOF_4$
AX_5E_2	Sp^3d^3	Pentagonal planar		XeF_5

AX_6E_0	Sp^3d^2 Octahedral		SF_6, WCl_6
AX_6E_1	Pentagonal pyramidal		$XeOF_5^-$, IOF_5^{2-}[7]
AX_7E_0	Pentagonal bipyramidal Sp^3d^3		IF_7

ONE MARK QUESTIONS

Q.1. What is the total number of sigma and pi bonds in the following molecules?

(a) C_2H_2 (b) C_2H_4

Ans- There are three sigma and two pi-bonds in C_2H_2.

there are five sigma bonds and one pi-bond in C_2H_4.

Q.2. Write the significance of a plus and a minus sign shown in representing the orbitals.

Ans- Molecular orbitals are represented by wave functions. A plus sign in an orbital indicates a positive wave function while a minus sign in an orbital represents a negative wave function.

Q.3. How do you express the bond strength in terms of bond order?

Ans- Bond strength represents the extent of bonding between two atoms forming a molecule. The larger the bond energy, the stronger is the bond and the greater is the bond order.

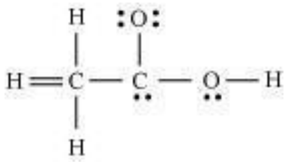
Q.5. Define the bond length.

Ans- Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule.

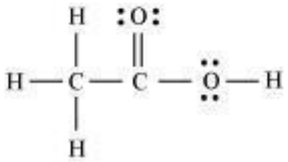
Q.6. Arrange the bonds in order of increasing ionic character in the molecules: LiF, K_2O, N_2, SO_2 and ClF_3.

Ans- $N_2 < SO_2 < ClF_3 < K_2O < LiF$.

Q.7. The skeletal structure of CH_3COOH as shown below is correct, but some of the bonds are shown incorrectly. Write the correct Lewis structure for acetic acid.



Ans- The correct Lewis structure for acetic acid is as follows:



Q.8. Define octet rule.

Ans- The elements tend to adjust the arrangement of their electrons in such a way that they (except H and He) achieve eight electrons in their outermost shell. This is called octet rule.

Q.9. Define lattice enthalpy.

Ans- The energy required when one mole of an ionic compound in crystalline form is split into the constituent ions is called lattice enthalpy.

Q.10. Which type of bond is formed when the atoms have zero difference in electronegativity?

Ans- Covalent bond.

TWO MARKS QUESTIONS

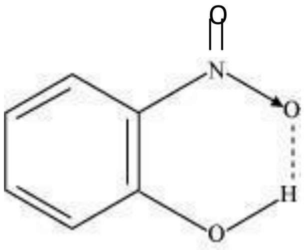
Q.1. Define hydrogen bond. Is it weaker or stronger than the van der Waals forces?

Ans- A hydrogen bond is defined as an attractive force acting between the hydrogen attached to an electronegative atom of one molecule and an electronegative atom of a different molecule (may be of the same kind).

There are two types of H-bonds:

17. Intermolecular H-bond e.g., HF, H_2O etc.

18. Intramolecular H-bond e.g., o-nitrophenol



Hydrogen bonds are stronger than Van der Waals' forces since hydrogen bonds are regarded as an extreme form of dipole-dipole interaction.

Q.2. Write the favourable factors for the formation of ionic bond.

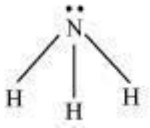
Ans-(i) Low ionization enthalpy of metal atom.

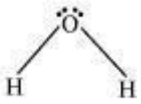
19. High electron gain enthalpy ($\Delta_{eg}H$) of a non-metal atom.

20. High lattice energy of the compound formed.

Q.3. Although geometries of NH_3 and H_2O molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. Discuss.

Ans- The molecular geometry of NH_3 and H_2O can be shown as:





The central atom (N) in NH_3 has one lone pair and there are three bond pairs.
In H_2O, there are two lone pairs and two bond pairs.

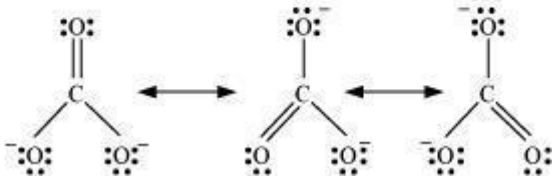
The two lone pairs present in the oxygen atom of H_2O molecule repel the two bond pairs. This repulsion is stronger than the repulsion between the lone pair and the three bond pairs on the nitrogen atom.

Since the repulsions on the bond pairs in H_2O molecule are greater than that in NH_3, the bond angle in water is less than that of ammonia.

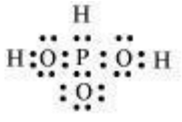
Q.4. Explain the important aspects of resonance with reference to the CO_3^{2-} ion.

Ans- According to experimental findings, all carbon to oxygen bonds in CO_3^{2-} are equivalent. Hence, it is inadequate to represent CO_3^{2-} ion by a single Lewis structure having two single bonds and one double bond.

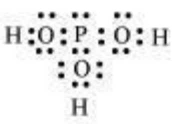
Therefore, carbonate ion is described as a resonance hybrid of the following structures:



Q.5. H_3PO_3 can be represented by structures 1 and 2 shown below. Can these two structures be taken as the canonical forms of the resonance hybrid representing H_3PO_3? If not, give reasons for the same.



(1)



(2)

Ans- The given structures cannot be taken as the canonical forms of the resonance hybrid of H_3PO_3 because the positions of the atoms have changed.

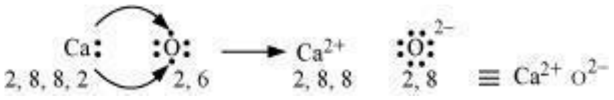
Q.6. Use Lewis symbols to show electron transfer between the following atoms to form cations and anions: (a) Ca and O (c) Al and N.

Ans**(a)**Ca and O:

The electronic configurations of Ca and O are as follows:

Ca: 2, 8, 8, 2 O: 2, 6

Oxygen requires two electrons more to complete its octet, whereas calcium has two electrons more than the nearest noble gas i.e., Argon. Hence, the electron transfer takes place as:

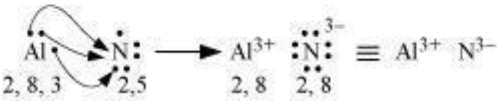


(b) Al and N:

The electronic configurations of Al and N are as follows:

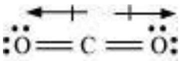
Al: 2, 8, 3 N: 2, 5

Nitrogen is three electrons short of the nearest noble gas (Neon), whereas aluminium has three electrons more than Neon. Hence, the electron transference can be shown as:



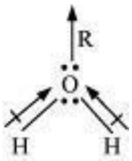
Q.7. Although both CO_2 and H_2O are triatomic molecules, the shape of H_2O molecule is bent while that of CO_2 is linear. Explain this on the basis of dipole moment.

Ans- According to experimental results, the dipole moment of carbon dioxide is zero. This is possible only if the molecule is linear so that the dipole moments of C– O bonds are equal and opposite to nullify each other.



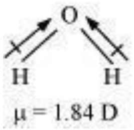
Resultant μ = 0 D

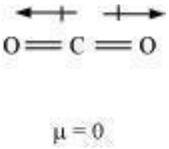
H_2O, on the other hand, has a dipole moment value of 1.84 D (though it is a triatomic molecule as CO_2). The value of the dipole moment suggests that the structure of H_2O molecule is bent where the dipole moment of O–H bonds are unequal.



Q.8. Write the significance/applications of dipole moment.

Ans- Dipole moment is the measure of the polarity of a bond. It is used to differentiate between polar and non-polar bonds since all non-polar molecules (e.g. H_2, O_2) have zero dipole moments. It is also helpful in calculating the percentage ionic character of a molecule.





Q.9. Use molecular orbital theory to explain why the Be_2 molecule does not exist.

Ans- The electronic configuration of Beryllium is $1s^2 2s^2$.

The molecular orbital electronic configuration for Be_2 molecule can be written as:

$\sigma_{1s}^2 \; \sigma_{1s}^{*2} \; \sigma_{2s}^2 \; \sigma_{2s}^{*2}$ Hence, the bond order for Be_2 is $\frac{1}{2}(N_b - N_a)$.

Where,

N_b= Number of electrons in bonding orbitals
N_a= Number of electrons in anti-bonding orbitals

$\therefore$ Bond order of $Be_2 = \frac{1}{2}(4-4) = 0$

A negative or zero bond order means that the molecule is unstable.
Hence, Be_2 molecule does not exist.

Q.10. Distinguish between a sigma and a pi bond.

Ans- The following are the differences between sigma and pi-bonds:

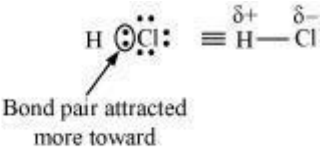
Sigma (σ) Bond	**Pi (π) Bond**
(a) It is formed by the end to end overlap of orbitals.	It is formed by the lateral overlap of orbitals.
(b) The orbitals involved in the overlapping are *s–s, s–p,* or *p–p*.	These bonds are formed by the overlap of *p–p*orbitals only.
(c) It is a strong bond.	It is weak bond.
(d) The electron cloud is symmetrical about the line joining the two nuclei.	The electron cloud is not symmetrical.
(e) It consists of one electron cloud, which is symmetrical about the internuclear axis.	There are two electron clouds lying above and below the plane of the atomic nuclei.
(f) Free rotation about σ bonds is possible.	Rotation is restricted in case of pi-bonds.

Q.11. Explain with the help of suitable example polar covalent bond.

Ans- When two dissimilar atoms having different electronegativities combine to form a covalent bond, the bond pair of electrons is not shared equally. The bond pair shifts towards the nucleus of the atom having greater electronegativity. As a result, electron distribution gets distorted and the electron cloud is displaced towards the electronegative atom.

As a result, the electronegative atom becomes slightly negatively charged while the other atom becomes slightly positively charged. Thus, opposite poles are developed in the molecule and this type of a bond is called a polar covalent bond.

HCl, for example, contains a polar covalent bond. Chlorine atom is more electronegative than hydrogen atom. Hence, the bond pair lies towards chlorine and therefore, it acquires a partial negative charge.



THREE MARKS QUESTIONS

Q.1. Write Lewis dot symbols for atoms of the following elements: Mg, Na, B, O, N, Br.

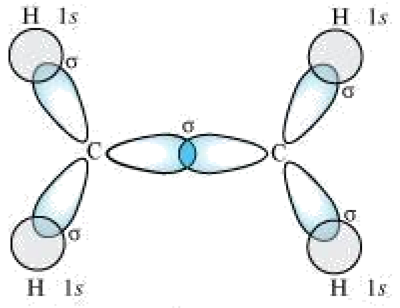
Ans- Mg: Na.  :   

Q.3. Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in C_2H_4 and C_2H_2 molecules.

Ans- **C_2H_4:**The electronic configuration of C-atom in the excited state is:

${}_6C = 1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$

In the formation of an ethane molecule (C_2H_4), one sp^2 hybrid orbital of carbon overlaps a sp^2hybridized orbital of another carbon atom, thereby forming a C-C sigma bond. The remaining two sp^2 orbitals of each carbon atom form a sp^2-*s* sigma bond with two hydrogen atoms. The unhybridized orbital of one carbon atom undergoes sidewise overlap with the orbital of a similar kind present on another carbon atom to form a weak π-bond.



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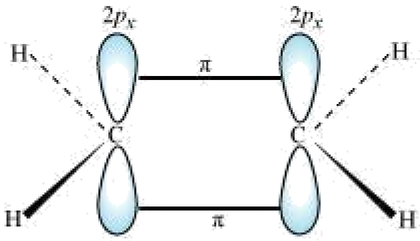

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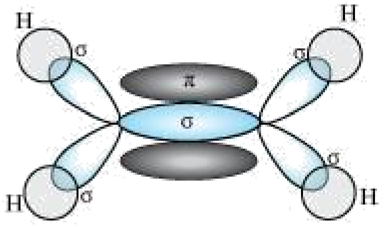

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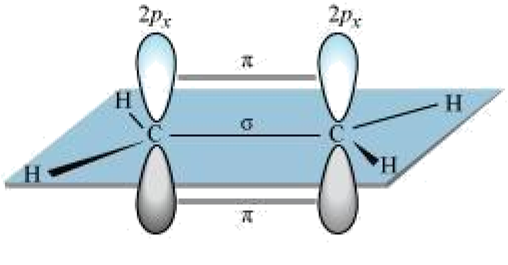


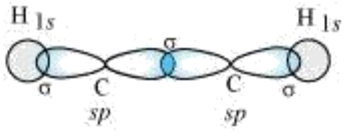
(d)

C_2H_2 :

In the formation of C_2H_2 molecule, each C–atom is *sp* hybridized with two 2*p*-orbitals in an unhybridized state.

One *sp* orbital of each carbon atom overlaps with the other along the internuclear axis forming a C–C sigma bond. The second *sp* orbital of each C–atom overlaps a half-filled 1*s*-orbital to form a σ bond.

The two unhybridized 2*p*-orbitals of the first carbon undergo sidewise overlap with the 2*p* orbital of another carbon atom, thereby forming two pi (π) bonds between carbon atoms. Hence, the triple bond between two carbon atoms is made up of one sigma and two π-bonds.



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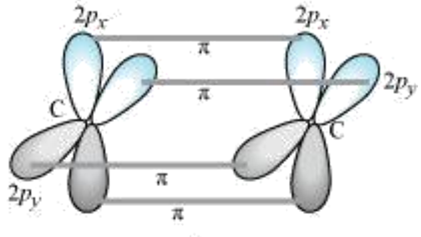

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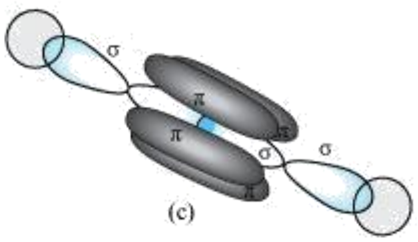


Q.4. Explain the formation of H_2 molecule on the basis of valence bond theory.

Ans- Let us assume that two hydrogen atoms (A and B) with nuclei (N_A and N_B) and electrons (e_A and e_B) are taken to undergo a reaction to form a hydrogen molecule. When A and B are at a large distance, there is no interaction between them. As they begin to approach each other, the attractive and repulsive forces start operating.

Attractive force arises between:

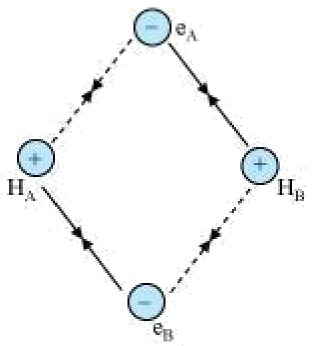
21. Nucleus of one atom and its own electron i.e., $N_A – e_A$ and $N_B – e_{B.}$

22. Nucleus of one atom and electron of another atom i.e., $N_A – e_B$ and $N_B – e_{A.}$

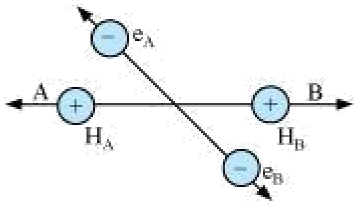
Repulsive force arises between:

5. Electrons of two atoms i.e., $e_A – e_{B.}$
6. Nuclei of two atoms i.e., $N_A – N_{B.}$

The force of attraction brings the two atoms together, whereas the force of repulsion tends to push them apart.



Attractive Forces



Repulsive Forces

The magnitude of the attractive forces is more than that of the repulsive forces. Hence, the two atoms approach each other. As a result, the potential energy decreases. Finally, a state is reached when the attractive forces balance the repulsive forces and the system acquires minimum energy. This leads to the formation of a dihydrogen molecule.

Q.5. Write the important conditions required for the linear combination of atomic orbitals to form molecular orbitals.

Ans- The given conditions should be satisfied by atomic orbitals to form molecular orbitals:

23. The combining atomic orbitals must have the same or nearly the same energy. This means that in a homonuclear molecule, the 1*s*-atomic orbital of an atom can combine with the 1*s*-atomic orbital of another atom, and not with the 2*s*-orbital.

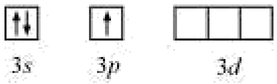
24. The combining atomic orbitals must have proper orientations to ensure that the overlap is maximum.

25. The extent of overlapping should be large.

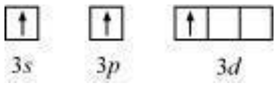
Q.6. Describe the hybridisation in case of PCl_5. Why are the axial bonds longer as compared to equatorial bonds?

Ans- The ground state and excited state outer electronic configurations of phosphorus (Z = 15) are:

Ground state:

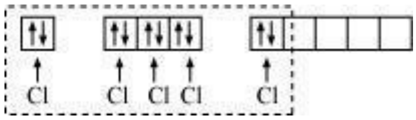


Excited state:

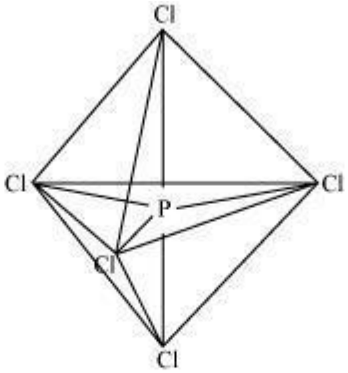


Phosphorus atom is sp^3d hybridized in the excited state. These orbitals are filled by the electron pairs donated by five Cl atoms as:

PCl_5



The five sp^3d hybrid orbitals are directed towards the five corners of the trigonal bipyramidals. Hence, the geometry of PCl_5 can be represented as:



There are five P–Cl sigma bonds in PCl_5. Three P–Cl bonds lie in one plane and make an angle of 120° with each other. These bonds are called equatorial bonds. The remaining two P–Cl bonds lie above and below the equatorial plane and make an angle of 90° with the plane. These bonds are called axial bonds.

As the axial bond pairs suffer more repulsion from the equatorial bond pairs, axial bonds are slightly longer than equatorial bonds.

Q.7. What is meant by the term bond order? Calculate the bond order of:

N_2, O_2, O_2^+ and O_2^-.

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

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

Bond order of N_2

$[\sigma(1s)]^2[\sigma^*(1s)]^2[\sigma(2s)]^2[\sigma^*(2s)]^2[\pi(2p_x)]^2[\pi(2p_y)]^2[\sigma(2p_z)]^2$

Number of bonding electrons, $N_b = 10$

Number of anti-bonding electrons, $N_a = 4$

Bond order of nitrogen molecule $= \frac{1}{2}(10-4)$ = 3

Bond order of O_2

$[\sigma-(1s)]^2[\sigma^*(1s)]^2[\sigma(2s)]^2[\sigma^*(2s)]^2[\sigma(1p_z)]^2[\pi(2p_x)]^2[\pi(2p_y)]^2[\pi^*(2p_x)]^1[\pi^*(2p_y)]^1$

Bond order $= \frac{1}{2}(N_b - N_a)$ $= \frac{1}{2}(8-4)$ = 2

Hence, the bond order of oxygen molecule is 2.

Similarly, the electronic configuration of O_2^+ can be written as:

$KK[\sigma(2s)]^2[\sigma^*(2s)]^2[\sigma(2p_z)]^2[\pi(2p_x)]^2[\pi(2p_y)]^2[\pi^*(2p_x)]^1$

Bond order of $O_2^+ = \frac{1}{2}(8-3)$ = 2.5

The electronic configuration of O_2^- ion will be:

$KK[\sigma(2s)]^2[\sigma^*(2s)]^2[\sigma(2p_z)]^2[\pi(2p_x)]^2[\pi(2p_y)]^2[\pi^*(2p_x)]^2[\pi^*(2p_y)]^1$

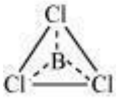
Bond order of O_2^- $= \frac{1}{2}(8-5)$ = 1.5

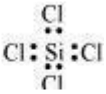
Q.8. Discuss the shape of the following molecules using the VSEPR model:

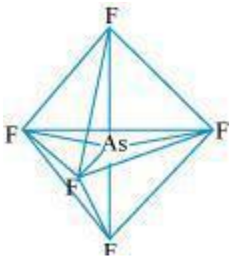
$BeCl_2$, BCl_3, $SiCl_4$, AsF_5, H_2S, PH_3

Ans- $BeCl_2$: Cl : Be : Cl The central atom has no lone pair and there are two bond pairs. i.e., $BeCl_2$ is of the type AB_2. Hence, it has a linear shape.

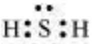
$\underline{BCl_3}$:  The central atom has no lone pair and there are three bond pairs.

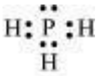
Hence, it is of the type AB_3. Hence, it is trigonal planar. 

$\underline{SiCl_4}$:  The central atom has no lone pair and there are four bond pairs. Hence, the shape of $SiCl_4$ is tetrahedral being the AB_4 type molecule.



$\underline{AsF_5}$: The central atom has no lone pair and there are five bond pairs. Hence, AsF_5 is of the type AB_5. Therefore, the shape is trigonal bipyramidal.

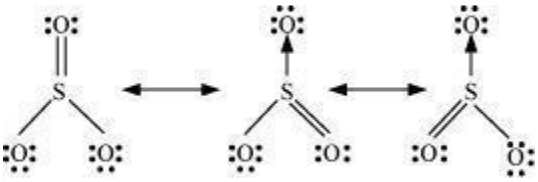
H_2S:  The central atom has one lone pair and there are two bond pairs. Hence, H_2S is of the type AB_2E. The shape is Bent.

$\underline{PH_3}$:  The central atom has one lone pair and there are three bond pairs. Hence, PH_3 is of the AB_3E type. Therefore, the shape is trigonal bipyramidal.

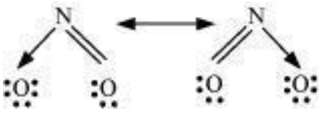
Q.9. Write the resonance structures for SO_3, NO_2 and NO_3^- .

Ans- The resonance structures are:

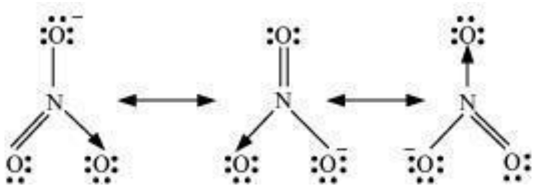
26. SO_3:



27. NO_2 :



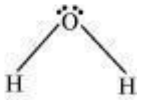
(c) NO_3^- :



Q.10. What do you understand by bond pairs and lone pairs of electrons? Illustrate by giving example.

Ans- The shared pairs of electrons present between the bonded atoms are called **bond pairs**. All valence electrons may not participate in bonding. The electron pairs that do not participate in bonding are called **lone pairs** of electrons.

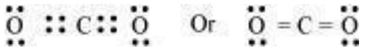
In H_2O, there are two bond pairs and two lone pairs on the central atom (oxygen).



FIVE MARKS QUESTIONS

Q.1. Define octet rule. Write its significance and limitations.

Ans-- The octet rule or the electronic theory of chemical bonding was developed by Kossel and Lewis. According to this rule, atoms can combine either by transfer of valence electrons from one atom to another or by sharing their valence electrons in order to attain the nearest noble gas configuration by having an octet in their valence shell.



The octet rule successfully explained the formation of chemical bonds depending upon the nature of the element.

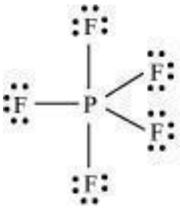
Limitations of the octet theory:

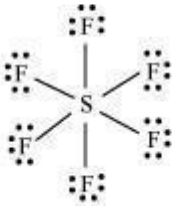
The following are the limitations of the octet rule:

28. The rule failed to predict the shape and relative stability of molecules.

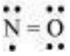
29. It is based upon the inert nature of noble gases. However, some noble gases like xenon and krypton form compounds such as XeF_2, KrF_2 etc.

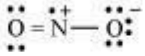
r The octet rule cannot be applied to the elements in and beyond the third period of the periodic table. The elements present in these periods have more than eight valence electrons around the central atom. For example: PF_5, SF_6, etc.



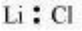


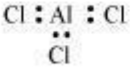
s The octet rule is not satisfied for all atoms in a molecule having an odd number of electrons. For example, NO and NO_2 do not satisfy the octet rule.

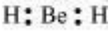




t This rule cannot be applied to those compounds in which the number of electrons surrounding the central atom is less than eight. For example, LiCl, BeH_2, $AlCl_3$ etc. do not obey the octet rule.



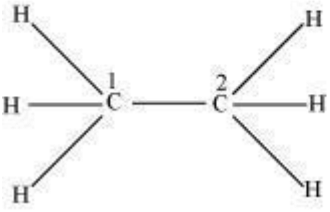




Q.2. Which hybrid orbitals are used by carbon atoms in the following molecules?

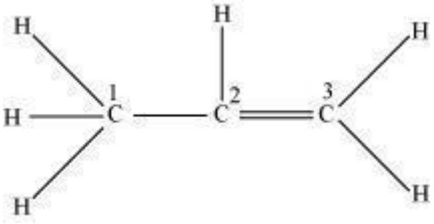
CH_3–CH_3; (b) CH_3–CH=CH_2; (c) CH_3-CH_2-OH; (d) CH_3-CHO (e) CH_3COOH

Ans- **(a)**



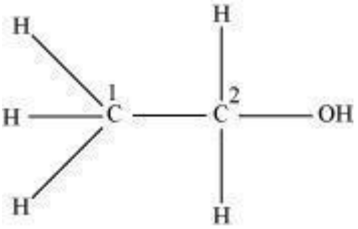
Both C_1 and C_2 are sp^3 hybridized.

(b)



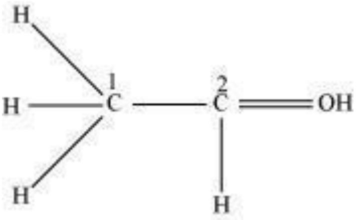
C_1 is sp^3 hybridized, while C_2 and C_3 are sp^2 hybridized.

(c)



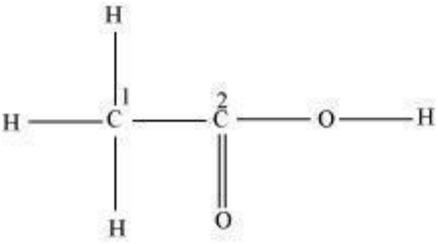
Both C_1 and C_2 are sp^3 hybridized.

(d)



C_1 is sp^3 hybridized and C_2 is sp^2 hybridized.

(e)



C_1 is sp^3 hybridized and C_2 is sp^2 hybridized.

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)

Ans- There are 16 electrons in a molecule of dioxygen, 8 from each oxygen atom. The electronic configuration of oxygen molecule can be written as:

$$[\sigma-(1s)]^2[\sigma^*(1s)]^2[\sigma(2s)]^2[\sigma^*(2s)]^2[\sigma(1p_z)]^2[\pi(2p_x)]^2[\pi(2p_y)]^2[\pi^*(2p_x)]^1[\pi^*(2p_y)]^1$$

Since the 1*s* orbital of each oxygen atom is not involved in boding, the number of bonding electrons = 8 = N_b and the number of anti-bonding orbitals = 4 = N_a.

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

$= \frac{1}{2}(8-4)$

= 2

Similarly, the electronic configuration of O_2^+ can be written as:

$$KK[\sigma(2s)]^2[\sigma^*(2s)]^2[\sigma(2p_z)]^2[\pi(2p_x)]^2[\pi(2p_y)]^2[\pi^*(2p_x)]^1$$

N_b= 8

N_a= 3

Bond order of $O_2^+ = \frac{1}{2}(8-3)$

= 2.5

Electronic configuration of O_2^- ion will be:

$$KK[\sigma(2s)]^2[\sigma^*(2s)]^2[\sigma(2p_z)]^2[\pi(2p_x)]^2[\pi(2p_y)]^2[\pi^*(2p_x)]^2[\pi^*(2p_y)]^1$$

N_b= 8

N_a= 5

Bond order of O_2^- = $\frac{1}{2}(8-5)$

= 1.5

Electronic configuration of O_2^{2-} ion will be:

$$KK[\sigma(2s)]^2[\sigma^*(2s)]^2[\sigma(2p_z)]^2[\pi(2p_x)]^2[\pi(2p_y)]^2[\pi^*(2p_x)]^2[\pi^*(2p_y)]^2$$

N_b= 8

$N_a = 6$

Bond order of O_2^{2-} = $\frac{1}{2}(8-6)$

= 1

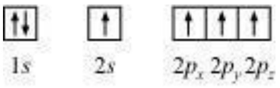
Bond dissociation energy is directly proportional to bond order. Thus, the higher the bond order, the greater will be the stability. On this basis, the order of stability is $O_2^+ > O_2 > O_2^- > O_2^{2-}$.

HOTS

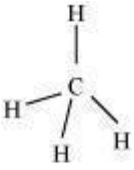
Q.1. Apart from tetrahedral geometry, another possible geometry for CH_4 is square planar with the four H atoms at the corners of the square and the C atom at its centre. Explain why CH_4 is not square planar?

Ans- Electronic configuration of carbon atom: $_6C: 1s^2 2s^2 2p^2$

In the excited state, the orbital picture of carbon can be represented as:



Hence, carbon atom undergoes sp^3 hybridization in CH_4 molecule and takes a tetrahedral shape.



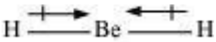
For a square planar shape, the hybridization of the central atom has to be dsp^2. However, an atom of carbon does not have *d*-orbitalsto undergo dsp^2 hybridization. Hence, the structure of CH_4 cannot be square planar.

Moreover, with a bond angle of 90° in square planar, the stability of CH_4 will be very less because of the repulsion existing between the bond pairs. Hence, VSEPR theory also supports a tetrahedral structure for CH_4.

Q.2. Explain why BeH_2 molecule has a zero dipole moment although the Be–H bonds are polar.

Ans- The Lewis structure for BeH_2 is as follows: $H : Be : H$

There is no lone pair at the central atom (Be) and there are two bond pairs. Hence, BeH_2 is of the type AB_2. It has a linear structure.

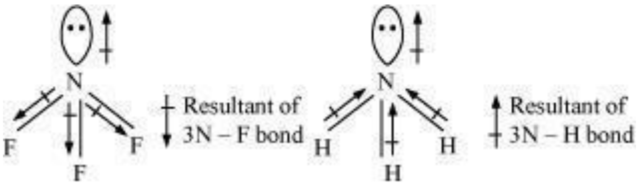


Dipole moments of each H–Be bond are equal and are in opposite directions. Therefore, they nullify each other. Hence, BeH_2 molecule has zero dipole moment.

Q.3. Which out of NH_3 and NF_3 has higher dipole moment and why?

Ans- In both molecules i.e., NH_3 and NF_3, the central atom (N) has a lone pair electron and there are three bond pairs. Hence, both molecules have a pyramidal shape. Since fluorine is more electronegative than hydrogen, it is expected that the net dipole moment of NF_3 is greater than NH_3. However, the net dipole moment of NH_3 (1.46 D) is greater than that of NF_3 (0.24 D).

This can be explained on the basis of the directions of the dipole moments of each individual bond in NF_3 and NH_3. These directions can be shown as:



Thus, the resultant moment of the N–H bonds add up to the bond moment of the lone pair (the two being in the same direction), whereas that of the three N – F bonds partly cancels the moment of the lone pair.

Hence, the net dipole moment of NF_3 is less than that of NH_3.

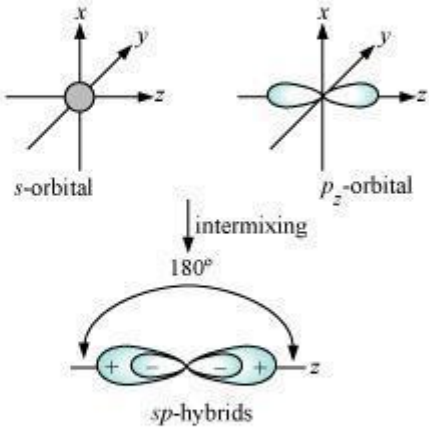
Q.4. What is meant by hybridisation of atomic orbitals? Describe the shapes of sp, sp^2, sp^3 hybrid orbitals.

Ans- Hybridization is defined as an intermixing of a set of atomic orbitals of slightly different energies, thereby forming a new set of orbitals having equivalent energies and shapes.

For example, one 2*s*-orbital hybridizes with two 2*p*-orbitals of carbon to form three new sp^2 hybrid orbitals.

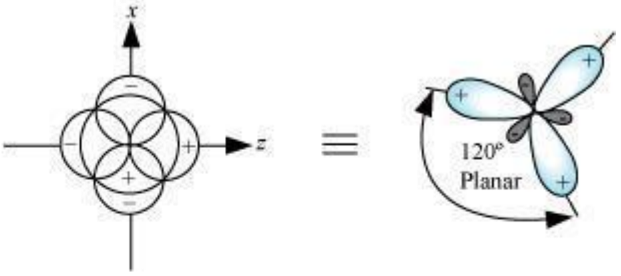
These hybrid orbitals have minimum repulsion between their electron pairs and thus, are more stable. Hybridization helps indicate the geometry of the molecule.

Shape of *sp* hybrid orbitals: *sp* hybrid orbitals have a linear shape. They are formed by the intermixing of *s* and *p* orbitals as:



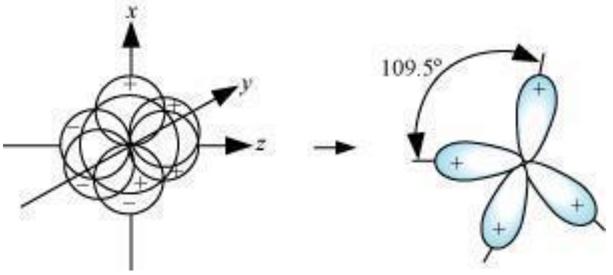
Shape of sp^2 hybrid orbitals:

sp^2hybrid orbitals are formed as a result of the intermixing of one *s*-orbital and two2*p*-orbitals. The hybrid orbitals are oriented in a trigonal planar arrangement as:



Shape of sp^3 hybrid orbitals:

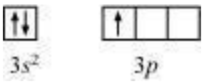
Four sp^3 hybrid orbitals are formed by intermixing one s-orbital with three *p*-orbitals. The four sp^3hybrid orbitals are arranged in the form of a tetrahedron as:



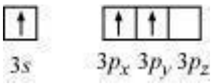
Q.5. Describe the change in hybridisation (if any) of the Al atom in the following reaction.

$AlCl_3 + Cl^- \longrightarrow AlCl_4^-$

Ans- The valence orbital picture of aluminium in the ground state can be represented as:



The orbital picture of aluminium in the excited state can be represented as:



Hence, it undergoes sp^2 hybridization to give a trigonal planar arrangement (in $AlCl_3$).

To form $AlCl_4^-$, the empty $3p_z$ orbital also gets involved and the hybridization changes from sp^2 to sp^3. As a result, the shape gets changed to tetrahedral.

CHAPTER 5

STATES OF MATTER

14. **Change in state** : It is over all effect of Intermolecular forces, molecular Interactional energy & thermal energy:

15. **Measurable properties of gases** : P,V, T, n, Viscosity, specific heat are some measurable properties.

16. **Gas Laws** : The quantitative relationship b/w any two ofthe variables (V, n, P,T) when other two are constant.

17. Boyle's Law : The pressure of fixed msss of gas varies inversely with the volume at constant T. P α 1/V(n,T const.)

$P_1V_1 = P_2 V_2$

30. **Charles' Law** : At constant P, the volume of fixed amount of gas varies directly with its absolute temperature.

V α T or $\frac{V}{T}$ $cons\tan t,$ $\frac{V_1}{T_1}$ $\frac{V_2}{T_2}$

31. **Gay lussac's Law :** At constant V, The pressure of fixed amount of gas varies directly with its absolute temperature.

P α T or $\frac{P}{T}$ $const,$ $\frac{P_1}{T_1}$ $\frac{P_2}{T_2}$

32. Ideal gas equation : The relationship b/w P, V and T by Gas Laws PV= nRT.

33. Avogadro's Law : At given T and P, the volume of gas varies directly to the amount of gas . V α n (P, T constant)

34. Dalton's Law of partial pressure : The pressure exerted by a mixture of non reacting gases is equal to the sum of their partial pressure at constant (V,T)

P (total) = P1 + P2 + P3 + ………. (T, V, constant)

7. Kinetic Molecular theory :

Gases consist of large number of identical particles (atoms or molecules) that are so small that the actual volume of the molecules is negligible in comparison to the empty space between them.

There is no force of attraction between the particles of a gas at ordinary temperature and pressure

Particles of a gas are always in constant and random motion

Pressure is exerted by the gas as a result of collision of the particles with the walls of the container

Collisions of gas molecules are perfectly elastic

At any particular time, different particles in the gas have different speeds and hence different kinetic energies

Average kinetic energy of the gas molecules is directly proportional to the absolute temperature

8. Real Gases : The gases which deviates from Ideal behavior at higher pressure and low temperature b/c of force of attraction b/w molecules increases .

9. Compressibility factor (Z) : It determine extent of devation of real gases from Ideal gas behavior : $Z = \frac{PV}{n.R.T.}$ for ideal gas Z=1, for Non ideal gas Z< 1, Z > 1

13. Vander waal's Equation : $(P + \frac{n^2 a}{V})(V - nb) = nRT.$

14. Critical Temperature : (Tc) The temperature above which a gas cannot be liquefied whatever high pressure may be

15. Critical Pressure : The minimum pressure required to liquity a gas at its critical temperature.

16. Critical Volume : The volume of 1 mole of gat at Tc, Pc.

17. Super cooled liquids : The liquids which are cooled to a temperature below its freezing point without freezing .

18. Elastic Collision : The collisions in which no loss of K.E. only there is transfer of energy.

19. Vapour pressure : The equilibrium pressure by vapour of liquid in a container at given temperature (T)

20. At higher altitude : The b.p. of water decreases b/c the atmospheric pressure is less than one atmosphere.

21. Surface Tension (V) : It is force acting per unit length perpendicular to the line drawn on the surface : (Nm^{-1}) : It decreases with increases in T, it increases with increase in external pressure, b/c of it falling drops of liquid are spherical, liquid in capillary tube rises.

22. Viscosity (η) : It is resistance offered to the flow of liquid due to friction b/w layer of fluids . $F \quad n.A.\frac{dv}{dn}$

23. Effect of T & P on viscosity: It decreases with increase in T, and increases with increase in P.

24. Low M.P. & B.P. of molecular liquids is due to low magnitude of molecular interaction energy.

One mark questions

ii At what condition surface tension vanishes ?

iii Why Helium is used in balloons in place of hydrogen?

iv At what temperature below which a gas does not obey ideal gas law?

v At what temperature the volume of a gas is supposed to be zero?

vi What is the molar volume at 0^{O}C and 1 bar pressure?

6. Name the temperature above which a gas cannot be liquefied by any amount of pressure.

7. What is the effect of increase of temperature on surface tension and viscosity in a liquid?

8. How is the partial pressure of a gas in a mixture related to the total pressure of the gaseous mixture?

9. Why vegetables are cooked with difficulty at hill station.

10. What is the value of Z (compressibility factor) for an Ideal gas?

Answers to One mark questions

Ans 1 At critical temperature, meniscus b/w liquid and vapours disappears.

Ans 2. He is incombustible , though heavier than H_2 .

Ans 3. Below Boyle Temperature.

Ans 4. At absolute zero (O K) temperature.

Ans 5. It 22400 ml.

Ans 6. It is critical temperature (Tc)

Ans 7. Both decreases with increase in temperature

Ans 8. $P_1 = X_1 \times P_{(total)}$

Ans 9. At hill station the atmospheric pressure is less and so boiling point decreases.

Ans10. For ideal gas Z=1.

Two Marks Questions

Q.1 How do you convert pressure in atmosphere in to SI unit.

Q.2 What type graph will you get when PV is plotted against P at constant temperature.

Q.3 What would have happened to the gas if the molecular collisions were not elastic?

Q.4 At a particular temperature, why is vapour pressure of acetone less than of ether?

Q.5 Why liquids diffuse slowly as compared to gases?

Q.6 What would be the SI unit for quantity $\frac{PV^2T^2}{n}$?

Q.7 In terms of Charles law explain why -273^{o} C is the lowest temperature?

Q.8 For real gases the relation b/w P,V,T is given by vander Waal's equation, write it for n moles?

Q.9 What correction is applied to obtain pressure of dry gas with the total pressure & aqueous tension?

Q.10 Name two phenomena that can be explained on the basis of surface tension.

Answers to two marks questions

Ans 1. 1atm = 101325 Pa or Nm^{-2}, 1 bar = 10^{5} Pa.

Ans 2 .A straight line parallel to pressure axis.

Ans 3. On every collision there is loss of energy, so molecules would have slowed down & settled down in vessel and pressure reduce to O.

Ans 4. b/c molecular force of attraction in acetone is stronger than those present in ether.

Ans 5. In liquids the molecules are less free than in a gas. i. e intermolecular forces in liquid are greater than in gas.

Ans 6. $$\frac{P.V^{2}.T^{2}}{n} = Nm^{-2}(m^{3})^{2}K^{2}mol^{-1} = Nm^{4}K^{2}mol^{-1}$$

Ans 7 At -273^{o} C, the Volume of gas becomes equal to zero i. e. gas ceases to exist.

Ans 8. Vander waal's equation

$$(P+\frac{n^{2}a}{V})(V-nb) = nRT.$$

Ans. 9. $P_{(dry\ gas)} = P_{(Total)}$ - Aqueous tension

Ans. 10. Surface tension can explain (i) capillary action, (ii) Spherical shape of small drops of liquid.

Three Marks Questions

Q.1 Calculate temperature of 4.0 moles of gas occupying 5dm^{3} volume at 3.32 bar. (R= 0.083 bar dm^{3} k^{-1} mol^{-1})

Ans $PV \quad nRT, or\ T \quad \frac{PV}{nR}$

$$\text{Or } T \quad \frac{3.32\ bar\ x\ 5dm^{3}}{4.0mol\ x\ 0.083bar\ dm^{3}\ K^{1}\ mol^{1}} \quad 50k.Ans$$

Q.2 34.05 ml of phosphorus vapours weight 0.0625g at 543^{o} C and 1 bar pressure what is molar mass of phosphorous?

Ans. $\frac{P_1V_1}{T_1} \quad \frac{P_2V_2}{T_2} \quad , \quad \frac{1\ x\ 34.05}{(54b\ \ 273\ )} \quad \frac{1\ x\ v_2}{273}\ at\ 0^{o}\ C$

Or V_2 = 11.35 ml

Now 11.35 ml of vapours at 0^{o}C and 1 bar pressure weight 0.0625 gm

Now 22700 ml of vapors at 0^{O} C and 1 bar pressure weight

$$\underline{\qquad\qquad} = \frac{0.0625}{11.35}\ x\ 22700$$

Q.3A mixture of dihydrogen and dinitrogen at 1 bar pressure contains 20% by weight of H_2. Calculate partial pressure of H_2.

AnsThe mixture of H_2 and O_2 contain 20% H_2 means 20 gm H_2& 80gm O_2

$$n_2\ (H_2) = \frac{20}{2} = 10\,moles,\ n(O_2) = \frac{80}{32} = 2.5\,moles.$$

$$P_{(H2)} = \frac{n(H_2)}{n\ (H_2)\quad n\ (V_2)}\ x\ P_{(total)} = \frac{10}{10\ \ +2.5}\ x\ 1bar = 0.8bar$$

Q.4 What will be minimum pressure required compressing $500dm^3$ of air at 1 bar to 200 dm^3 at 30^o C?

Ans. P_1 = 1bar. V_1 = $500dm^3$

P_2 = ? V_2 =200 dm^3& temp. constant 30^oC So by

Boyle's low $P_1V_1 = P_2\ V_2$

$$1 \text{ x } 500 = P_2 \text{ x } 200 \qquad \text{or } P_2 = \frac{500}{200} = 2.5\ bar$$

Q.5 Calcutate the total pressure in mixture of 4g of O_2 and 2gm. Of H_2 can fixed to a total volume of IL at 0^o C. (R = 0.0821) Latm. Mol^{-1}

Ans $$P = (n_{H2} - n_{O2)} \text{ x } \frac{RT}{V} = \left(\frac{4}{32} + \frac{2}{2}\right) \times \frac{0.0821 \times 273}{1} = \left(\frac{1}{8} + 1\right) \times \frac{22.4}{1} = 25.2 \text{ atm}$$

Q.6

Account for the following :

(i) The size of weather balloon becomes longer and larger as it ascend up into higher altitudes.

Ans (i) At higher altitudes atmospheric pressure decreases, but inside the balloon gas exerts pressure and size becomes larger.

Q.8 What do you mean by ideal gas and real gas? Why do real gases deviate from ideal behaviors?

Ans. Ideal gas follows gas laws at all P & T

Real gas donot " gas laws at all P & T.

Real gas deviate from ideal behaviour due to force of attraction and because of volume of molecules of gases are not negligible.

Q.9 Using the equation of state PV=nRT Show that at given T, density of gas proportional to gas pressure P.

Ans. $PV = n\,RT \Rightarrow P = \frac{n}{V} R\,T \Rightarrow P = \frac{m}{M\,V} R\,T \Rightarrow P = \frac{m}{V}\frac{R\,T}{M}$

$\Rightarrow P = \rho \frac{R\,T}{M}$ (Where $\rho = \frac{m}{V}$ = density = d)

$\Rightarrow P \propto \rho$ ($\because \frac{R\,T}{M}$ = constant)

$P \alpha d$

Q.10 Critical temperature of CO_2 and CH_4 gases are 31.1^0C and -81.9^0C respectively. Which of these has strong intermolecular forces & why?

Ans CO_2 has strong vander waal's forces of attraction than $CH_{4.}$ b/c of greater polarity and high molecular wt.

Hots Questions with Answers.

Q.1 (a)Why aerated water bottles kept under water during summer?

(b) Which property of liquid is responsible for spherical shape of drop?

(c) Why is moist air lighter than dry air?

(d) Define aqueous tension?

(e) What is units of a and b which are vander waal's constant?

Ans (a) To reduce temperature so to reduce pressure, other wise bottle may burst.

(b) Surface Tension.

(c) Moist air has water vapours which lowers vapour density, so it is lighter.

(d) It is pressure of water vapours at given T.

(e)Unit of a in atm. L^2 mol^{-2}, b is L $mol^{-1.}$

Q.2 Why does sharpened edge becomes smooth on heating up tomelting point?

Ans On heating the glass it melts and take up rounded shape at edges which has minimum surface area. b/c of surface tension. Q.3 Arrange following in order of increasing density:

$$d = \frac{PM}{RT},\ O_2 \text{ at } 25^0\ C, 1atm,\ O_2 \text{ at } O^0C, 2\ atm,\ O_2 \text{ at } 273^{'} C, 1atm.$$

Ans $d = \frac{PM}{RT}$, R, M are constant, so d depends upon $\frac{P}{T}$ so at 25^0C,

1Atm $\frac{P}{T} = \frac{1}{298}$, At 273^0C, 1atm $\frac{P}{T} = \frac{1}{546}$ Hence increasing order of

density will be: O_2 at 273^0 C, 1atm < O_2 at 25^0 C, 2atm.

Q.4 An O_2 cylinder has 10L O_2 at 200 atm. It patient takes 0.50ml of O_2 at 1 atm in one breath at 37^0C. How many breaths are possible?

Ans 10L at 200 atm = ? L at 1atm $P_,V_,\ P_2 V_2 \quad 200\ x10\ \ 1\ xV_2$or

V_2 = 2000 L, No of breathes = $\frac{Total\ Volume}{Volume\ for\ 1breath} = \frac{2000\ L}{0.5\ x10^3\ \ L} = 4\ x10^{\ 6}$

CHAPTER 6

THERMODYNAMICS

Brief Summary of the chapter:

1. Thermodynamics: Science which deals with study of different forms of energy and quantitative relationship.

2. System & Surroundings: The part of universe for study is called system and remaining portion is surroundings.

3. State of system & state function: State of system is described in terms of T, P, V etc. The property which depends only on state of system not upon path is called state function eg. P, V, T, E, H, S etc.

4. Extensive & Intensive Properties: Properties which depends on quantity of matter called extensive prop. eg. mass, volume, heat capacity, enthalpy, entropy etc. The properties which do not depend on quantity of matter present are called Intensive properties. eg. T, P, density, refractive index, viscosity, bp, pH, mole fraction etc.

5. Internal energy: It is the sum of all kinds of energy with a system.

   i.e. $U = E_e + E_n + E_c + E_p + E_k + $ ------

   $\Delta U = U_2 - U_1$ or $U_P - U_R$ & U is state function and extensive properly. If $U_1 > U_2$ energy is released.

Heat (q): It I a form of energy which is exchanged between system and surrounding due to difference of temperature. Unit is Joule (J) or Calorie

(1 Calorie = 4.18 kJ).

35. First Law of Thermodynamics: It is law of conservation energy. Energy can neither be created not destroyed, it may be converted from one from into another.

Mathematically $\Delta U = q + w$,
$w = -p.\ \Delta V$ (work of expansion)

$\Delta U = q - p\Delta V$ or $q = \Delta U + p.\Delta V$, q,w are not state function.

But ΔU is state function.

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

   At constant volume $V = 0$, $q_V = \Delta U$; $q_p = \Delta H$

   $\Delta H = \Delta U + \Delta PV = \Delta U + P \Delta V$ (at constant P)

   $q_p = q_V + P \Delta V$

9. Relationship between q_p, q_V i.e. ΔH & ΔU

   $\because PV = nRT$
   At constant Pressure and Temperature

$\Rightarrow P \Delta V = RT \Delta n_g$

$\Delta H = \Delta U + P \Delta V = \Delta U + RT \Delta n_g = \Delta U + (\Delta n_g) RT$ where Δn_g = Number of moles of gaseous products – Number of moles of gaseous reactants

$\Rightarrow q_p = q_V + P \Delta V = q_V + (\Delta n_g) RT$

10. Exothermic and Endothermic reactions: ΔH = –ve for exothermic and ΔH = +ve for endothermic reaction i.e. evolution and absorption of heat.

    E.g. (Exothermic)
    $C + O_2 \rightarrow CO_2 + 393.5\ kJ$ (i.e. $\Delta H = -393.5\ kJ$)
    E.g. (Endothermic)
    $N_2 + O_2 \rightarrow 2NO - 180.7\ kJ$, (i.e. $\Delta H = 180.7\ kJ$)

11. Enthalpy of reaction ($\Delta_r H$): The enthalpy change taking place during a reaction.

12. Standard Enthalpy of reaction ($\Delta_r H^0$): Enthalpy change of reaction taking place at 1 bar pressure and 298 K with reactants in their standard states.

13. Different types of Enthalpies of reactions:
    (i) Enthalpy of combustion ($\Delta_c H$) (ii) Enthalpy of formation ($\Delta_f H$)

    (iii) Enthalpy of neutralization ($\Delta_n H$) (iv) Enthalpy of solution ($\Delta_s H$)

    (v) Enthalpy of atomization ($\Delta_a H$) (vi) Enthalpy of Ionisation ($\Delta_i H$)

    (vii) Enthalpy of Hydration ($\Delta_h H$) (viii) Enthalpy of fusion ($\Delta_{fus} H$)

(ix) Enthalpy of vapourization ($\Delta_{vap}H$) (x) Enthalpy of sublimation ($\Delta_{sub}H$)

10. Hess's Law of constant heat summation: The total amount of heat change is same whether the reaction takes place in one step or in several steps.
    i.e. $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 +$ ----------

11. Bond enthalpy: 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 $\Delta_{bond}H$ = B.E. (Reactants) – B.E. (Products)

12. Spontaneous & Non Spontaneous Processes: A process which can take place by itself is called spontaneous process. A process which can neither take place by itself or by initiation is called non Spontaneous.

13. Driving forces for spontaneous process: (i) Tendency for minimum energy state. (ii) Tendency for maximum randomness.

14. Entropy (S): It is measure of randomness or disorder of system. i.e. Gas>Liquid>Solid.

    Entropy change (S) = $\frac{q_{(rev)}}{T}$ $JK^{-1} mol^{-1}$

    Spontaneity in terms of ΔS

    $\Delta S_{(total)} = \Delta S_{(universe)} = \Delta S_{(system)} + \Delta S_{(surroundings)}$

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

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

15. Second Law of thermodynamics: In any spontaneous process, the entropy of the universe always increases. A spontaneous process cannot be reversed.
16. Gibb's free energy (G): It is defined as G = H – TS
    $\Delta G = \Delta H - T \Delta S$
    It is Helmholtz equation. ΔG is equal to useful work.
    i.e. $\Delta G = W_{(useful)} = W_{(max.)}$
    If ΔG = - ve; the process is spontaneous.
    Effects of T on spontaneity of a process: $\Delta G = \Delta H - T \Delta S$

(i) For endothermic process may be non spontaneous at low temp.

(ii) For exothermic process may be non spontaneous at high temp. and spontaneous at law temp.

17. Calculation of $\Delta_r G^0$)

$\Delta_r G^0 = \Delta_r G^0(p) - \Delta_r G^0(r)$

18. Relationship between ($\Delta_r G^0$) & Equilibrium constant (K)

$\Delta_r G = \Delta_r G^0 + RT \ln Q = -2.303\, RT \log K$

19. Calculation of entropy change:

$\Delta_r S^0 = \Delta_f S^0(p) - \Delta_r S^0(r)$

ONE MARK QUESTIONS:

1. State First Law of thermodynamics.

2. What is a thermodynamic state function?

3. Give enthalpy (H) of all elements in their standard state.

4. From thermodynamic point to which system the animals and plants belong?
5. Predict the sign of Δ S for the following reaction:

$$CaCO_3(s) \xrightarrow{heat} CaO(s) + CO_2(g)$$

6. For the reaction, $Cl_2(g) \rightarrow 2\,Cl(g)$; What will be the sign of ΔH and Δ S?

7. State Hess's Law for constant heat summation?

8. What is Gibb's Helmhaltz equation?

9. Define extensive properties.

10. Give relationship between ΔH, Δ U for a reaction in gaseous state.

ANSWERS FOR ONE MARK QUESTIONS

1. Energy can neither be created nor destroyed. The energy of an isolated system is constant. $U = q + w$.
2. A function whose value is independent of path. eg. P, V, E, H
3. In standard state enthalpies of all elements is zero.
4. Open system.
5. ΔS is positive (entropy increases)
6. ΔH (-ve) because energy is released in bond formation and ΔS (-ve) because atoms combine to form molecules.
7. The change of enthalpy of reaction remains same, whether the reaction is carried out in one step or several steps.
8. $\Delta G = \Delta H - T \Delta S$
9. Properties which depends upon amount of substance called extensive properties. Volume, enthalpy, entropy.
10. $\Delta H = \Delta U + \Delta$ ng. RT.

TWO MARKS QUESTIONS:-

Q.1 In a process, 701J heat is absorbed and 394J work is done by system. What is change in Internal energy for process?

Q2. Given: $N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$; $\Delta_r H^0 = - 92.4\ kJmol^{-1}$. What is the standard enthalpy of formation of $NH_3(g)$?

Q.3 Calculate entropy change in surroundings when 1.0 mol of $H_2O(l)$ is formed under standard conditions? Given $\Delta H^0 = -286 KJmol^{-1}$.

Q.4 Give relationship between entropy change and heat absorbed/evolved in a reversible reaction at temperature T.

Q.5 What is spontaneous change? Give one example.

Q.6 A real crystal has more entropy than an Ideal Crystal. Why?

Q.7 Under what condition, the heat evolved/absorbed in a reaction is equal to its free energy change?

Q.8 Predict the entropy change in-

(i) A liquid crystallizes into solid

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

Q.9 What is bond energy? Why is it called enthalpy of atomization?

Q.10 Calculate entropy change for the following process.

$H_2O_{(s)} \longrightarrow H_2O_{(l)}$, is 6.0 KJ mol^{-1} at 0^0C.

ANSWER FOR TWO MARKS QUESTIONS:

1. q= 701 J, w = 394 J, so Δ U = q + w = 701 – 394 = 307 J
2. $\Delta_f H^0 (NH_3(g)) = \frac{92.4}{2} = 46.2$ kJ mol^{-1}
3. $q_{(rev.)} = -\Delta H^0 = -286$ $KJmol^{-1} = 286000Jmol^{-1}$

   $\Delta S = \frac{Q_{(rev)}}{T} = \frac{286000\ J/mol}{298\ K} = 959$ Jper K per mol
4. $\Delta S = \frac{Q_{(rev)}}{T}$
5. A process which can take place of its own or initiate under some condition. eg. Common salt dissolves in water of its own.
6. A real crystal has some disorder due to presence of defects in their structural arrangement, and Ideal crystal does not have any disorder.
7. In $\Delta G = \Delta H - T.\Delta S$, when reaction is carried out at O K or

$\Delta S = 0$, then $\Delta G = \Delta H$.

8. (i) Entropy decreases b/c molecules attain an ordered state.

(ii) entropy increase b/c from OK to 115K particles begin to move.

9. It is the amount of energy required to dissociate one mole of bonds present b/w atoms in gas phase. As molecules dissociates into atoms in gas phase so bond energy of diatomic molecules is called enthalpy of atomization.

10. $H_2O_{(s)} \rightarrow H_2O_{(l)}$ at 0^0C, $\Delta_{fus}H = 6KJ\ mol^{-1}$

$= 6000J\ mol^{-1}$

$\Delta T_f = 0^0\ C = 0 + 273 = 273\ K$

So $\Delta_{fus}\ S = \frac{\Delta fusH}{T} = \frac{6000\ J\ mol^{-1}}{273\ K} = 21.98\ JK^{-1}\ mol^{-1}$ –

THREE MARKS QUESTIONS:

Q.1 For oxidation of iron, $4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)}$
ΔS is –549.4J.K^{-1} mol^{-1}, at 298K. In spite of –ve entropy change of this reaction, why is the reaction spontaneous? ($\Delta_rH^0 = - 1648 \times 10^3\ J\ mol^{-1}$)

Q.2 Using the bond energy of H_2 = 435 KJ mol^{-1}, Br_2 = 192 KJ mol^{-1}, HBr = 368 $KJmol^{-1}$. Calculate enthalpy change for the reaction $H_{2(g)} + Br_{2(g)} \longrightarrow 2HBr_{(g)}$

Q.3 Enthalpies of formation of $CO_{(g)}$, $CO_{2(g)}$, $N_2O_{(g)}$ and $N_2O_{4(g)}$ and –110, –393, 81 and 9.7 KJ mol^{-1} respectively. Find value $\Delta\ _rH$ for the reaction
$N_2O_{4(g)} + 3CO_{(g)} \longrightarrow N_2O\ (g) + 3\ CO_2(g)$

Q.4 For the reaction at 298K, $2A+B \rightarrow C$, H = 400 KJ mol^{-1}, ΔS = 0.2 KJ mol^{-1} K^{-1}. At what temperature will the reaction become spontaneous, considering ΔH,
ΔS be constant at the temp.

Q.5 The equilibrium constant for a reaction is 10. What will be the value of ΔG^0? R = 8.314J.$K^{-1}mol^{-1}$ T = 300K.

Q.6 What do you understand by state function? Neither q nor w is a state function but q + w is a state function? Explain.

Q.7 Justify the following statements:

(i) An endothermic reaction is always thermodynamically spontaneous.

(ii) The entropy always increases on going from liquid to vapour state at any temperature T.

Q.8 Calculate the temperature above which the reduction reaction becomes spontaneous:

$PbO_{(s)} + C_{(s)} \rightarrow Pb_{(s)} + CO_{(g)}$, given [$\Delta H = 108.4$ KJ mol^{-1}, $\Delta S = 190$J.K^{-1} mol^{-1}].

Q.9 From the data given below at 298K for the reaction:

$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$ Calculate enthalpy of formation of $CH_{4(g)}$ at 298K. Given:[$\Delta_r H = -890.5$KJ, $\Delta_f H_{(CO_2)} = -393.3$ kJ/mol, $\Delta_f H_{(H_2O)} = -286.0$ kJ/mol

Q.10. For the reaction, $NH_4Cl\ (s) \rightarrow NH_3(g) + HCl(g)$ at 25^{0}C enthalpy change $\Delta H = 177$ kJ/mol and $\Delta S = 285$ JK^{-1} mol^{-1}. Calculate free energy change ΔG at 25^{0}C and predict whether the reaction is spontaneous or not.

ANSWER TO THREE MARKS QUESTIONS

Ans. 1. $\Delta S_{(surr)} = \frac{\Delta_f H^0}{T} = \frac{(-1648 \times 10^3 Jmol^{-1}}{298\ K} = 5530\ JK^{-1}mol^{-1}$

& $\Delta S_{(system)} = -549.4\ JK^{-1}mol^{-1}$

$\Delta S_{(total)} = 5530 - 549.4 = 4980.6\ JK^{-1}mol^{-1}$

Since $\Delta S_{(total)}$ is + ve, so the reaction is spontaneous.

Ans. 2. $\Delta_r H^0$ = Sum of bond enthalpies of reactants – Sum of bon enthalpies of products

$= [435 - 192] - [2 \times 368]$ KJ mol^{-1}

$= 627 - 736 = -109$ kJmol^{-1} Ans.

Ans. 3. $\Delta_r H = \Delta_r H^0_{(prod)} - \Delta_r H^0_{(react)}$

$= [81 + 3(-393)] - [9.7 + 3(-110)]$

$= -777.7$ kJ

Ans.4 $\Delta H = 400$ KJ mol^{-1}, $\Delta S = 0.2$ KJK^{-1} mol^{-1}.

$\Delta G = \Delta H - T.\ \Delta S$

O = 400 – 0.2 x T ($\Delta G = 0$ at equilibrium)

$T = \frac{400}{0.2}$ 2000K, so reaction will be spontaneous above 2000K.

Ans.5 $\Delta_r G^0 = -2.303$ RT logK

–2.303 x 8.314 x 300 x log10

–19.147 x 300 x 1

= –5744.1J

$\Delta_r G^0 = -5.7441 KJ.mol^{-1}$

Ans.6 The property whose value depends upon state of system and is independent ofpath. q + w = U, which is a state function as value of U does not depends upon path.

Ans.7 (a) It is false, exothermic reaction is not always spontaneous. If ΔS = +ve and T.ΔS> H. The process will be non spontaneous even it. It is endothermic.

(b) The entropy of vapour is more than that of liquid, so entropy increases during vaporization.

Ans. 8. Δ G = ΔH – T ΔS, at equilibrium ΔG = 0, ΔH = TΔS

$\Rightarrow \Delta$

$$T = \frac{\Delta H}{\Delta S} = \frac{108.4 \times 10^3\ J.mol^{-1}}{190\ J.K^{-1} mol^{-1}} = 570.526\ K$$

So the reaction will be spontaneous above 570.52K, as above this temperature

Δ G will be –ve.

Ans. 9. $\Delta_r H = \Delta_f H_{(CO2)}$ - 2 $\Delta_f H_{(CH4)} - \Delta_f H_{(O2)}$

$+ \Delta \qquad - \Delta$

$\Rightarrow -890.5 kJmol^{-1} = -393.5kJ + 2(-286\ kJmol^{-1}\quad) \quad - O\ kJmol^{-1}$

$\Delta H_f(CH_4) = -75.0\ KJ.mol^{-1}$.

4 $\Delta H_f(CH_4) = 75.0 KJ.mol^{1}$.

Ans.10 $\Delta H = 177$ KJ mol^{-1}, $\Delta S = 285$ JK^{-1} mol^{-1}

$\Delta G = \Delta H - T\Delta S$ = 177 kJ/mol - $\frac{298 \times 285}{1000}$ kJ/ mol

= 177 kJ/mol – 84.93 kJ/mol = 92.07 kJ.mol^{-1}.

Since

ΔG is +ve, so the reaction is non spontaneous.

FIVE MARKS QUESTIONS:-

Q.1 What is entropy? Why is the entropy of a substance taken as zero at 0K? Calculate the $\Delta_r G$ for the reaction?

$N_{2(g)} + 3H_{2(g)} \Rightarrow 2NH_{3(g)}$ at 298K

The value of equilibrium constant (K) is 6.6x10^{5}, R = 8.314JK^{-1}mol^{-1}.

Ans: It is measure of randomness or disorder of system.

Because at O K there is complete order in the system.

ΔG^0 = –2.303 RT logK = –2.303 x 8.314 x 298 x log6.6 x

105 = -5705.8[log6.6 + log 10^{5}]

= –5705.8[0.8195 + 5.0] = –5705.8 +

5.8195J = –33204.903J

ΔG^0 = –33.205 KJ mol^{-1}.

Q.2 (i) What are extensive property and intensive properties?

(ii)Calculate the value of equilibrium constant (K) at 400K for

$2\ NOCl_{(g)} \rightarrow 2NO_{(g)} + Cl_{2(g)}$.

ΔH^0 = 77.2KJ.mol^{-1}, ΔS^0 = 122J.K^{-1}mol^{-1} at 400K, R = 8.314 J.K^{-1}mol^{-1}.

Ans. (i) An **extensive property** is a property whose value depends on the quantity or size of matter present in the system Those properties which do not depend on the quantity or size of matter present are known as **intensive properties**

(ii) $\mathbf{\Delta G^0} = \Delta H^0 - T\Delta S^0 = 77.2\text{kJ} - \frac{400\text{x}122}{1000}\text{kJ.mol}^{1}$

$= 77.2 - 48.8 = 28.4 \text{ kJ mol}^{-1}$

and $\Delta G^0 = -2.303 \text{ RT logK}.$

$28400 = -2.303 \text{ x } 8.314 \text{ x } 400 \log K.$

$\text{logK} = \frac{7.1}{2.303\text{x}8.314} \quad 3.7081 \quad \bar{4}.2919\text{K}$

$\text{K} - \text{antilog } (\bar{4}.2919) \quad = 1.95\text{x}10^{-4}$

Q.3 Define standard enthalpy of formation. Calculate the enthalpy of formation of benzene from data

$C_6H_6(l) + \frac{15}{2} O_2 \rightarrow 6 CO_2(g) + 3 H_2O (l); \Delta_cH^0 (C_6H_6) = -3266.0$ kJ/mol

$C (s) + O_2 (g) \rightarrow CO_2(g);$ $\Delta_fH^0(CO_2) = -393.1$ kJ/mol

$H_2(g) + \frac{1}{2} O_2 (g) \rightarrow H_2O (l);$ $\Delta_fH^0 (H_2O) = -286.0$ kJ/mol

Ans. The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation**.**

$\Delta_fH^0 (C_6H_6) = - \Delta_cH^0 (C_6H_6) + 6 \text{ x } \Delta_fH^0(CO_2) + 3 \text{ x } \Delta_fH^0 (H_2O)$

$= 3266 + 6 (-393.1) + 3 (-286)$

$= 49.4$ kJ/mol

HOTS QUESTIONS

1. Why standard entropy of an elementary substance is not zero whereas standard enthalpy of formation is taken as zero?

   Ans. A substance has a perfectly ordered arrangement only at absolute zero. Hence , entropy is zero only at absolute zero. Enthalpy of formation is the heat change involved in the formation of one mole of the substance from its elements. An element formed from it means no heat change.
2. The equilibrium constant for a reaction is one or more if ΔG° for it is less than zero. Explain

   Ans. **—**ΔG° = RT ln K, thus if ΔG° is less than zero. i.e., it is negative, then ln K will be positive and hence K will be greater than one.

3. Many thermodynamically feasible reactions do not occur under ordinary conditions. Why?

   Ans. Under ordinary conditions, the average energy of the reactants may be less than threshold energy. They require some activation energy to initiate the reaction.

CHAPTER-7

EQUILIBRIUM

Equilibrium state- When rate of formation of a product in a process is in competition with rate of formation of reactants, the state is then named as "Equilibrium state" .

➢ Equilibrium in physical processes: solid ⇌ liquid ⇌ gas

$H_2O(s) \rightleftharpoons H_2O(l) \rightleftharpoons H_2O(vap)$

Law of chemical equilibrium: At a given temperature, the productof concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the Equilibrium Law or Law of Chemical Equilibrium.

$aA + bB \rightleftharpoons cC + dD$

$K_c = [C]^c [D]^d / [A]^a [B]^b$

Chemical equation	**Equilibrium constant**
$aA + bB \rightleftharpoons cC + D$	K
$cC + dD \rightleftharpoons aA + bB$	$K'c = (1/Kc)$
$naA + nbB \rightleftharpoons ncC + ndD$	$K'''c = (Kc^n)$

Concentrations or partial pressure of pure solids or liquids do not appear in the expression of the equilibrium constant. In the reaction,

$Ag_2O(s) + 2HNO_3(aq) \rightleftharpoons 2AgNO_3(aq) + H_2O(l)$

$$Kc = \frac{[AgNO3]^2}{[HNO3]2}$$

If $Qc > Kc$, the reaction will proceed in the direction of reactants (reverse reaction).If $Qc < Kc$, the reaction will proceed in the direction of the products (forward reaction)

Kp is equilibrium constant in terms of partial pressure of gaseous reactants and products.

Kc is equilibrium constant in terms of molar concentration of gaseous reactants and products.

➢ $Kp = Kc(RT)^{\Delta n}$ here **R** is gas constant, **T** is temperature at which the process is carried out &**Δn** is no. of moles of gaseous product minus no. of moles of gaseous reactants.

If $Kc > 10^3$; Kc is very high i.e. the reaction proceeds nearly to completion.

If $Kc < 10^{-3}$; Kc is very small i.e. the reaction proceeds rarely.

➢ If Kc is ranging in the range of 10^3 to 10^{-3}; i.e. reactants and products are just in equilibrium.

- $\Delta G^0 = -RT \ln K$ or $\Delta G^0 = -2.303RT \log K$

- Factors affecting equilibrium constant:- temperature, pressure, catalyst and molar ncentration of reactants and products. **<u>Le Chatelier's principle</u>**:-It states that a**change in any of the factorsthat determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.**

- Arrhenius acids are the substances that ionize in water to form **H^+**.

- Arrhenius bases are the substances that ionize in water to form **OH^-**.

- Lewis acids are lone pair (of e-) accepters while Lewis bases are lone pair donators.

- Proton donor are acids while proton accepters are bases(Bronsted-Lowry concept).

- The acid-base pair that differs only by one proton is called a **conjugate acid-base pair**. If Brönsted acid is a strong acid then **its -conjugate base is a weak base and *vice -versa*.**

- **Ionic product of water**.Kw = $[H^+][OH^-]$

- **pH = -log $[H^+]$; here $[H^+]$** is molar concentration of hydrogen ion.

- **pH + pOH =14**

- **pKa + pKb =14**

- **Ka x Kb = Kw =** ionic product of water**=1×10^{-14}**

- Buffer solution :The solutions which resist change in pH on dilution or withthe addition of small amounts of acid or alkali are called Buffer Solutions**.**

- **common ion effect**: It can be defined as a shift in equilibrium on adding asubstance that provides more of an ionic species already present in the dissociation equilibrium.

- Hydrolysis of Salts: process of interaction between water andcations/anions or both of salts is calledhydrolysis.

- Salts of weak NO^3acid and strong base e.g.,CH_3COONa are basic in nature.

- The cations (e.g., Na^+, K^+,Ca^{2+}, Ba^{2+}, etc.) of strong bases and anions(e.g., Cl^-, Br^-,ClO_4^- etc.) of strong acids simply get hydrated but do not hydrolyse, and therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7.

- Salts of strong acid and weak base e.g.,NH_4Cl, are acidic

- Salts of weak acid and weak base, e.g.,CH_3COONH_4. The pH is determined by the formula $pH = 7 + ½ (pK_a – pK_b)$

- Solubility product- product of the molar concentrations of the ions in a saturated solution, each concentration term raised to the power equal to the no. of ions produced.

ONE MARK QUESTIONS

Q.1. Mention the factors that affect equilibrium constant.
Ans. Temperature, pressure, and molar concentration of reactants andproducts,catalyst.
Q. 2. What is ionic product ofwater? Ans. Kw = $[H^+]$ $[OH^-]$

Q.3. Write conjugate acids of H_2O & NH_3.
Ans. H_3O^+& NH_4^+.

Q.4. Define Arrhenius acids.
Ans. Arrhenius acids are the substances that ionize in water to form$\mathbf{H^+}$.

Q.5. Define the term degree of ionization.
Ans.Extent up to which an acid/base/salt ionize to form ions.

Q.6. What are Buffer solutions?
Ans.The solutions which resist change in pH on dilution or with the addition of smallamounts of acid or alkali are called Buffer Solutions.
Q.7. Write Kc for the gaseous reaction- $N_2 + 3H_2 \rightleftharpoons 2NH_3$
Ans. $Kc=[NH_3]^2/[N_2]\ [H_2]^3$

Q.8. Out of H_2O & H_3O^+which is stronger acid?
Ans. H_3O^+.

Q.9. What is common ion effect?
Ans. Shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium.

Q.10. Write relationship between Kp and Kc for the gaseous reaction - $N_2 + O_2 \rightleftharpoons 2NO$
Ans.Kp = Kc(asΔn is zero for the above said reaction).

TWO MARKS QUESTIONS

1. What is effect of catalyst on equilibrium constant „Kc‟?

Ans . A catalyst does not affect equilibrium constant because it speeds up both forward and backward reactions to the same extent.

45. State Le Chatelier's principle.

    Ans.It states that a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.

46. What is meant by conjugate acid –base pairs?
Ans. The acid base pair that differs only by one proton is called conjugate acid base pair.

u Classify the following bases as strong and weak bases: $NaHCO_3$, NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$.
Ans:-strong base: NaOH, KOH ; weak bases: $NaHCO_3$,$Ca(OH)_2$, $Mg(OH)_2$.

v The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3}M. What is its pH ?
Ans:-pH = $-\log[3.8 \times 10^{-3}]$
$-\{\log[3.8] + \log[10^{-3}]\}$
$-\{(0.58) + (-3.0)\} = -\{-2.42\} = 2.42$

7. The species: H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Bronsted acids and bases.For each case give the corresponding conjugate acid and conjugate base.
Ans:-

Species	Conjugate acid	Conjugate base
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{2-}
HSO_4^-	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	NH_2^-

vii Explain Lewis acids and bases with suitable examples.
Ans:-Lewis acids are lone pair (of e-) acceptors while Lewis bases are lone pair donators.
$AlCl_3$ is a Lewis acid while NH_3 is a Lewis base.

viii What is difference between alkali and bases? Give examples.
Ans:- An alkali is a water soluble base. All the alkalis are bases but all the bases are not alkali. Ex- NaOH is an alkali/base. $Ca(OH)_2$ is a base but not an alkali.

(f) Explain homogeneous and heterogeneous equilibrium giving examples.

Ans:- If all the reactants and products present in an equilibrium mixture are in same phase→homogeneous equilibrium.

If all the reactants and products present in an equilibrium mixture are in different phase→ heterogeneous equilibrium.

$N_{2\,(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ homogeneous equilibrium

$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ heterogeneous equilibrium

THREE MARK QUESTIONS

1. The pH of some common substances is given bellow. Classify the substances as acidic/basic

Name of fluid	pH
Lime water	10
Milk of magnesia	10
Human saliva	6.4
Lemon juice	2.2
Sea water	7.8
Vinegar	3
milk	6.8

Ans.:- acidic-Human saliva, Lemon juice, milk, vinegar
Basic- Lime water, sea water, milk of magnesia.

2. Explain general characteristics of acids and bases.

Ans.:- Most of the acids taste sour.Acids are known to turn blue litmus paper into red and liberate dihydrogen on reacting with some metals.

Bases are known to turn red litmus paper blue, tastebitter and feel soapy. 3. Water is amphoteric in nature. Explain.

Ans.:- Water can react with acid as well as base

$H_2O + HCl \rightarrow H_3O^+ + Cl^-$ water is basic

$H_2O + NH_3 \rightarrow OH^- + NH_4^+$ water is acidic

3. Describe the effect of :

- addition of H_2

addition of CH_3OH

removal of CO

d) removal of CH_3OH

on the equilibrium of the reaction:

$2H_{2(g)} + CO_{(g)} \rightleftharpoons CH_3OH_{(g)}$

Ans.:- a) addition of H_2 equilibrium will shift on RHS

b) addition of CH_3OH equilibrium will shift on LHS
c) removal of CO equilibrium will shift on LHS
d) removal of CH_3OH equilibrium will shift on RHS

4. Classify the following species into Lewisacids and Lewis bases and showhow these act as such:

11. HO^- (b)F^- (c) H^+ (d) BCl_3

Solution

(iii) Hydroxyl ion is a Lewis base as it can donate a lone pair of electron ($:OH^-$).

(iv)Fluoride ion acts as a Lewis base as it can donate any one of its four lone pairs of electrons

A proton is a Lewis acid as it can accept a lone pair of electrons from bases like hydroxyl ion and fluoride ion.

BCl_3 acts as a Lewis acid as it can accept a lone pair of electrons from species like ammonia or amine molecules.

5. For the equilibrium,$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$ the value of the equilibrium constant, *Kc* is 3.75×10^{-6} at 1069 K. Calculate the *Kp*for the reaction at this temperature?

Solution

We know that,$K_p = K_c(RT)^{\Delta n}$

For the above reaction,$\Delta n = (2+1) - 2 = 1$

$K_p = 3.75 \times 10^{-6}(0.0831 \times 1069)$ $K_p = 0.033$.

6. Hydrolysis of sucrose gives Glucose and Fructose. Equilibrium constant *Kc* for the reaction is 2×10^{13} at 300K. Calculate ΔG^0 at 300K.

Solution

$\Delta G^0 = - RT \ln K_c$

$\Delta G^0 = - 8.314 J\ mol^{-1} K^{-1} J \times 300K \ln(2 \times 10^{13})$ $\Delta G^0 = - 7.64 \times 10^4\ J\ mol^{-1}$

7. Explain the following :

(i) Common ion effect (ii) solubility products (iii) pH

Ans. (i) Suppression of ionization of weak electrolyte by adding a strong electrolyte having an ion common.

(ii) Product of the molar concentrations of the ions in a saturated solution, each concentration term raised to the power equal to the no. of ions produced.

Negative logarithm of hydrogen ion concentration.

7. The values of *K*sp of two sparingly soluble salts $Ni(OH)_2$ and AgCN are 2.0×10^{-15} and 6×10^{-17} respectively. Which salt is more soluble? Explain.

Solution

$AgCN \rightleftharpoons Ag^+ + CN^-$

$K_{sp} = [Ag^+][CN^-] = 6 \times 10^{-17}$

$Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$

$K_{sp} = [Ni^{2+}][OH^-]^2 = 2 \times 10^{-15}$

Let $[Ag^+] = S_1$, then $[CN^-] = S_1$ Let

$[Ni^{2+}] = S_2$, then $[OH^{-}] = 2S_2$
$S_1^2 = 6 \times 10^{-17}$, $S_1 = 7.8 \times 10^{-9}$ $(S_2)(2S_2)^2 =$
2×10^{-15}, $S_2 = 0.58 \times 10^{-4}$

$Ni(OH)_2$ is more soluble than AgCN.

FIVE MARKS QUESTIONS

1. At 473 K, equilibrium constant *Kc*for decomposition of phosphorus pentachloride,PCl_5 is 8.3×10^{-3}. If decomposition is depicted as,

$PCl_5 (g) \rightleftharpoons PCl_3 (g) + Cl_2 (g)$ $\Delta rH^0 = 124.0$ kJ mol^{-1}

a) Write an expression for *Kc* for the reaction.

b) What is the value of *Kc* for the reverse reaction at the same temperature?

c)what would be the effect on *K*c if (i) more $PCl_5$is added (ii) pressure is increased(iii) the temperature is increased ?

Ans: (a) $Kc=\frac{[PCl_3][Cl_2]}{[PCl_5]}$

(b)120.48

(i) equilibrium will shift on RHS

(ii) equilibrium will shift on LHS

= equilibrium will shift on RHS

2. Dihydrogen gas is obtained from natural gas by partial oxidation with steam asper following endothermic reaction

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

a) Write as expression for *Kp* for the above reaction.

b) How will the values of *Kp* and composition of equilibrium mixture be affected by (i) increasing the pressure(ii) increasing the temperature(iii) using a catalyst?

Ans. (a) $K_p=p(CO).p(H_2)^3/ p(CH_4).p(H_2O)$

(b)(i) value of Kp will not change, equilibrium will shift in backward direction.

Value of Kp will increase and reaction will proceed in forward direction.

(iii)no effect.

3. What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species:HNO_2, CN^{-}, $HClO_4$, F^{-}, OH^{-}, CO_3^{2-}, and S^{2-}

Ans.The acid-base pair thatdiffers only by one proton is called a conjugate acid-base pair

Species	Conjugate

	acid/base
HNO_2	NO_2^-
CN^-	HCN
$HClO_4$	ClO_4^-
F^-	HF
OH^-	H2O
CO_3^{2-}	HCO_3^{2-}
S^{2-}	HS^-

HOTS QUESTIONS

1. The value of *Kc*for the reaction$2A \rightleftharpoons B + C$ is 2×10^{-3}. At a given time, the composition of reaction mixture is[A] = [B] = [C] = 3×10^{-4} M. In which irection the reaction will proceed?

Solution

For the reaction the reaction quotient *Qc* is given by, $Qc = [B][C]/[A]^2$ as $[A] = [B] = [C] = 3 \times 10^{-4}$M

$Qc = (3 \times 10^{-4})(3 \times 10^{-4}) / (3 \times 10^{-4})2 = 1$

As $Qc > Kc$ so the reaction will proceed in the reverse direction.

2. PCl_5, $PCl_3$and $Cl_2$are at equilibrium at500 K and having concentration 1.59MPCl_3, 1.59M Cl_2 and 1.41 M PCl_5. Calculate *Kc* for the reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Solution

The equilibrium constant *Kc* for the above reaction can be written

$$\text{as, } Kc = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= (1.59)^2 / 1.41 = 1.79$$

3. Why is ammonia termed as a base though it does not contain OH^- ions?

Ans. Ammonia is termed as a base on the basis of Lewis concept it can donate a lone pair of electrons.

CHAPTER-8
REDOX 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 oxidation state of an element in a compound ascertained according to a set of rules formulated on the basis that electron in a covalent bond belongs entirely to more electronegative element.

Calculation of oxidation number-

1. O. S. of all the elements in their elemental form (in standard state) is taken as zero O. S. of elements in Cl_2, F_2, O_2, P_4, O_3, Fe(s), H_2, N_2, C(graphite) is zero.
2. Common O. S. of elements of group one (1^{st}) is one. Common O. S. of elements of group two (2^{nd}) 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), each oxygen atom is assigned an oxidation number of –1, in superoxides (e.g., KO_2, RbO_2) each oxygen atom is assigned an oxidation number of (–½).
5. In oxygendifluoride (OF_2) and dioxygendifluoride (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 oxidation no. is–1.
7. In all its compounds, fluorine has an oxidation number of –1.
8. The algebraic sum of the oxidation number of all the atoms in a compound must be zero.
9. In polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion must equal the charge on the ion.

Stock-notation: The oxidation number is expressed by putting a Roman numeral representing the oxidation number in parenthesis after the symbol of the metal in the molecular formula. Thus aurous chloride and auric chloride are written as Au(I)Cl and Au(III)Cl_3. Similarly, stannous chloride and stannic chloride are written as Sn(II)Cl_2 and Sn(IV)Cl_4.

Oxidation:An increase in the oxidation number
Reduction: A decrease in the oxidation number

Oxidising agent: A reagent which can increase the oxidation number of an element in a given substance is called an O**xidant or Oxidising agent**.
Reducing agent: A reagent which lowers the oxidation number of an element in a given substance is called **reductant or reducing agent**.

Redox reactions: Reactions which involve oxidation and reduction simultaneously are called Redox reactions.

Balancing of redox reactions: <u>Oxidation Number Method:</u>

Write the net ionic equation for the reaction of potassium dichromate(VI), $K_2Cr_2O_7$ with sodium sulphite,Na_2SO_3, in an acid solution to give chromium(III) ion and the sulphate ion.

Step 1: The skeletal ionic equation is:

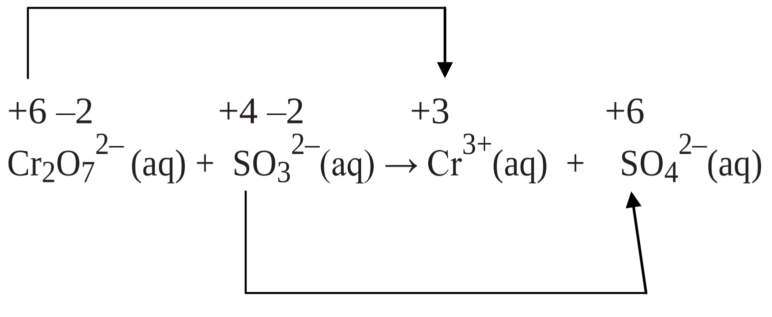
$$Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$$

Step 2: Assign oxidation numbers for Cr and S

$$\overset{+6\ -2}{Cr_2O_7^{2-}}(aq) + \overset{+4\ -2}{SO_3^{2-}}(aq) \rightarrow \overset{+3}{Cr^{3+}}(aq) + \overset{+6\ -2}{SO_4^{2-}}(aq)$$

Step 3: Calculate the increase and decrease of oxidation number, and make them equal:

Change in O.N.= [(+3) – (+6)] x 2 = - 3



$$\overset{+6\ -2}{Cr_2O_7^{2-}}(aq) + \overset{+4\ -2}{SO_3^{2-}}(aq) \rightarrow \overset{+3}{Cr^{3+}}(aq) + \overset{+6}{SO_4^{2-}}(aq)$$

Change in O.N. of S-atom = (+6) – (+4) = 2

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq)$$

Step 4: Balance the number of oxygen atoms by adding water molecule.

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + 4H_2O(l)$$

Step 5: Balance the number of hydrogen atoms by adding H^+as the reaction occurs in the acidic medium,

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) + 8H^+ \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq)$$

Half Reaction Method

balance the equation showing the oxidation of Fe^{2+} ions to Fe^{3+} ions by dichromate ions $(Cr_2O_7)^{2-}$ in acidic medium, wherein, $Cr_2O_7^{2-}$ ions are reduced to Cr^{3+} ions.

Step 1: Write unbalanced equation for the reaction in ionic form :

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

Step 2: Separate the equation into half reactions:

Oxidation half : $Fe^{2+}\,(aq) \rightarrow Fe^{3+}\,(aq)$

(increase in O.N of Fe from 2 to 3)

Reduction half : $Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}\,(aq)$

(Decrease in O.N. of Cr from 6 to 3)

Step 3: Balance the atoms other than O and H in each half reaction individually.

$$Cr_2O_7^{2-}\,(aq) \rightarrow 2Cr^{3+}\,(aq)\ ;\ \ Fe^{2+}\,(aq) \rightarrow Fe^{3+}\,(aq)\quad \text{(already balanced)}$$

Step 4: For reactions occurring in acidic medium, add H_2O to balance O atoms and H^+ to balance H atoms.

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

Step 5: Add electrons to one side of the half reaction to balance the charges. If need be, make the number of electrons equal in the two half reactions by multiplying one or both half reactions by appropriate coefficients.

$$Fe^{2+}\,(aq) \rightarrow Fe^{3+}\,(aq) + e^-\,]\ x\ 6$$

$$6Fe^{2+}\,(aq) \rightarrow 6\,Fe^{3+}\,(aq) + 6\,e^-$$

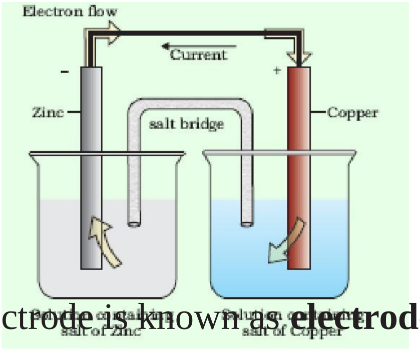
$$Cr_2O_7^{2-}\,(aq) + 14H^+\,(aq) + 6e^- \rightarrow 2Cr^{3+}\,(aq) + 7H_2O$$

Step 6: Add the two half reactions and cancel the electrons on each side. This gives the net ionic equation as :

$$6Fe^{2+}(aq) + Cr_2O_7^{2-}\,(aq) + 14H^+(aq) \rightarrow 6\,Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$$

A **redox couple** is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half reaction represented as Zn^{2+}/Zn and Cu^{2+}/Cu.

Electrochemical cells are the devices which are used to get electric current by using chemical reaction.



Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.

The potential associated with each electrode is known as **electrode potential**. If the concentration of each species taking part in the electrode reaction is unity (if any gas appears in the electrode reaction, it is confined to 1 atmospheric pressure) and further the reaction is carried out at 298K, then the potential of each electrode is said to be the **Standard Electrode Potential**.

SHE (Standard Hydrogen Electrode) is used to measure electrode potential and its standard electrode potential is taken as 0.00 V.

ONE MARK QUESTIONS

1. Define oxidation and reduction in terms of oxidation number.

   Ans Increase in Oxidation Number is Oxidation and decrease in Oxidation Number is called reduction.

2. What is meant by disproportionation? Give one example.

   Ans : In a disproportionation reaction an element simultaneously oxidized and reduced.

   0 -3 +1

   $P_4 + 3OH^- + 3H_2O \rightarrow PH_3 + 3H_2PO_2^-$

3. What is O.N. of sulphur in H_2SO_4?

   Ans: +6

4. Identify the central atom in the following and predict their O.S. HNO_3

   Ans: central atom:- N; O.S. +5

5. Out of Zn and Cu which is more reactive?

   Ans: Zn.

6. What is galvanization?

   Ans: Coating of a less reactive metal with a more reactive metal e.g.- coating of iron surface with Zn to prevent rusting of iron.

7. How is standard cell potential calculated using standard electrode potential?

   Ans: $E^0_{cell} = E^0_{cathode} - E^0_{anode}$

8. What is O.S. of oxygen in H_2O_2? Ans: - -1.

9. The formation of sodium chloride from gaseous sodium and gaseous chloride is a redox process justify.

   Ans: Na atom gets oxidized and Cl is reduced.

TWO MARKS QUESTIONS 1.

Write the balanced redox reaction .

(I) $MnO_4^-(aq) + Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + Fe^{3+}(aq)$ [acidic medium]

(II) (II) $Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$ [Acidic medium]

Ans:- (i) $MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$

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

48. Identify the strongest & weakest reducing agent from the following metals:

    Zn, Cu, Na, Ag, Sn

    Ans: Strongest reducing agent: Na, weakest reducing agent: Ag.

49. Determine the oxidation no. of all the atoms in the following oxidants: $KMnO_4$, $K_2Cr_2O_7$ and $KClO_4$

    Ans :

In $KMnO_4$, K = +1, Mn = +7, O = -2
In $K_2Cr_2O_7$, K = +1, Cr = +6, O = -2
In $KClO_4$, K = +1, Cl = =+7, O = -2

50. Determine the oxidation no. of all the atoms in the following species:Na_2O_2 and OF_2.

Ans: In Na_2O_2, Na = +1, O = -1
InOF$_2$, F = -1, O = +2

51. Is it possible to store :

(i) H_2SO_4 in Al container?(ii) $CuSO_s$ solution in Zn vessel?

Ans : (i) yes. (ii) No.

52. Calculate the standard e.m.f. of the cell formed by the combination of two electrodes having standard electrode potential 0.34 and - 0.76 respectively.

$Zn/Zn^{2+}||Cu^{2+}/Cu.$

Solution- : $E^0_{cell} = E^0_{cathode} - E^0_{anode}$
$=0.34 - (-0.76) = 1.10V.$

53. Identify the oxidizing and reducing agents in the following equations:

(i) $MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O_{(l)}$ (ii) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

Ans : (i) O.A. = MnO_4^- ; R.A.= Fe^{2+}
(ii)O.A.=$Cr_2O_7^{2-}$; R.A.= Fe^{2+}

w Predict all the possible oxidation states of Cl in its compounds. Ans:- 0, -1, +1, +3, +5, +7

x Formulate possible compounds of „Cl‟ in its O.S.is: 0, -1, +1, +3, +5, +7 Ans: Cl_2, HCl, HOCl, HOClO, $HOClO_2$, $HOClO_3$ respectively.

y List three measures used to prevent rusting of iron.

Ans: (i) galvanization(coating iron by a more reactive metal)
54. greasing/oiling
55. painting.

THREE MARK QUESTIONS

p Write short notes on :

(a) Electrochemical series(b) redox reactions (c) oxidizing agents

Ans :(a) Electrochemical series :- arrangement of metals(non-metals also) in increasing order of their reducing power or vice versa.

(b) Reactions in which both Oxidation and reduction take place simultaneously are REDOX REACTIONS.

(c)oxidizing agents : chemical specie which can oxidize the other one or can reduce itself.

10. Calculate O. S. of sulphur in the following oxoacids of „S‟ :

H_2SO_4 ,$H_2SO_3$$H_2S_2O_8$and $H_2S_2O_7$

Ans : +6, +4, +6 and +6 respectively.

(calculate by considering x of ‟S‟ and taking +1 of H, -2 0f “O” and -1 of “O” in peroxide bond.)

11. Explain role of salt bridge in Daniell cell.

Ans : (a) it completes the electric circuit in the cell.
it maintains the electric neutrality in the cell.

12. Account for the followings :

(i) sulphur exhibits variable oxidation states. Ans.
Due to the presence of vacant „d‟ orbitals in „S‟

(ii) Fluorine exhibits only -1 O.S.
Ans . It is most electronegative element

(iii) oxygen can’t extend its valency from 2.
Ans. Small size/unavailabilityof vacant d orbitals in O

5. Balance the equation $MnO_4^{-} + I^{-} \rightarrow Mn^{2+} + I_2 + H_2O$by ion electron method in acidic medium.

Ans :<u>Step-I</u> Balancing of reduction half reaction by adding protons and electrons on LHS and more water molecules on RHS: $8H^{+} + MnO_4^{-} + 5e^{-} \rightarrow Mn^{2+} + 4H_2O$

<u>Step-II</u> Balancing of oxidation half reaction by adding electrons on RHS:

$2I^{-} \rightarrow I_2 + 2e^{-}$

Step-III To multiply the OHR by 5; RHR by2 andto add OH & RH reactions to get overall redox reaction(cancellation of electrons of RH & OH reactions):

$$[8H^{+}(aq) + MnO_4^{-}(aq) + 5e^{-} \rightarrow Mn^{2+}(aq) + 4H_2O(l)] \times 2$$

$$[2I^{-} \rightarrow I_2 + 2e^{-}] \times 5$$

$MnO_4^{-}(aq) + 5Fe^{2+}(aq) + 8H^{+}(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O_{(l)}$

---

complete and balance the following equations:

` $H^{+} + Cr_2O_7^{2-} + Br^{-} \rightarrow 2Cr^{3+} + Br_2 +$ -----

10. $H_2O_2 + Cl^{-} \rightarrow OH^{-} + Cl_2$

11. $Zn + Cu^{2+} \rightarrow$?

Ans :(i) $14H^{+} + Cr_2O_7^{2-} + 6Br^{-} \rightarrow 2Cr^{3+} + 3Br_2 + 7H_2O$

5. $H_2O_2 + 2Cl^{-} \rightarrow 2OH^{-} + Cl_2$

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

= Identify the oxidizing and reducing agents in the following equations:

(i) $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$

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

(iii) $MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$

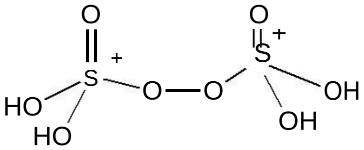
Ans :(i) O.A. =H_2SO_4 ; R.A.= Fe
(ii) O.A. = Cl_2; R.A.=H_2
(iii)O.A. = MnO_2; R.A. =HCl

8. . Arrange the following in increasing order of their reducing power:

Cu, Ag, Au, Zn, Fe, Al, Na, Mg, Pt(SHE), Hg, Ca, K

Ans : Au, Hg, Ag, Cu, Pt(SHE), Fe, Zn, Al, Mg, Na, Ca, K

9. Indicate O.S. of sulphur atom present in given structure of peroxodisulphuric acid.



Ans. Oxidation number of S atoms = + 6

10.What is SHE? What is its use?

Ans :Standard Hydrogen Electrode (SHE) has been selected to have zero standard potential at all temperatures. It consists of a platinum foil coated with platinum black (finely divided platinum) dipping partially into an aqueous solution in which the activity (approximate concentration 1M) of hydrogen ion is unity and hydrogen gas is bubbled through the solution at 1 bar pressure. The potential of the other half cell is measured by constructing a cell in which reference electrode is standard hydrogen electrode. The potential of the other half cell is equal to the potential of the cell.

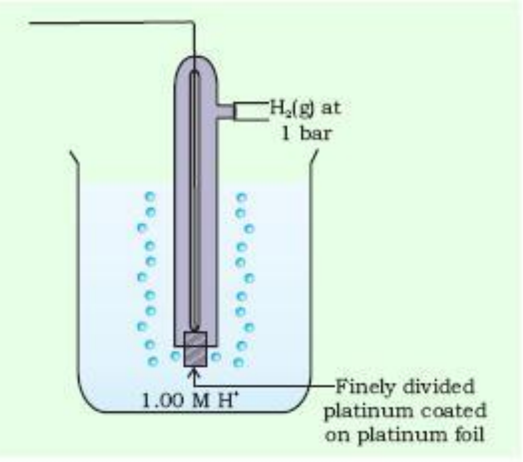


Fig: SHE

HOTS QUESTIONS

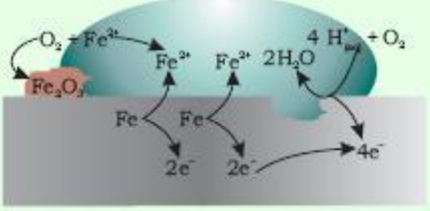
1. Is rusting of iron an electrochemical phenomenon? How ?explain.

Ans : Yes. Rusting of iron is an electrochemical phenomenon because this is possible due to formation of a small electrochemical cell over rough surface of iron and the following redox reaction takes place there in that cell-

Oxidation $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$] x 2

Reduction $O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$

$\frac{1}{2} O_2 + 2H_2O + 2Fe^{2+} \rightarrow Fe_2O_3 + 4H^{+}$



Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$

Reduction: $O_2(g) + 4H^{+}(aq) + 4e^{-} \rightarrow 2H_2O(l)$

Atomospheric oxidation : $2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2}O_2(g) \rightarrow Fe_2O_3(s) + 4H^{+}(aq)$

Fig. 5.14 *Corrosion of iron in atmosphere.*

c. We spend crores of Rupees to replace corroded materials and lose even thousands of lives every year due to corrosion. How can it be prevented? Explain.

Ans : (i) By Galvanization: Coating of a less reactive metal with a more reactive metal e.g.- coating of iron surface with Zn to prevent rusting of iron.

(ii) By greasing /oiling (to keep away the object from the contact of air & moisture.)

(iii)By painting (to keep away the object from the contact of air & moisture.)

CHAPTER 9

HYDROGEN ✪

Position of Hydrogen in Periodic Table : Group 1; Period : 1st

* Lightest element known having atomic number 1.
*Dihydrogen
*It resembles both alkali metals and halogens and therefore, its position is anomalous.
*In modern periodic table it is located separately

☆ Resemblance with alkali metals:-

1. Electronic configuration

$_1H = 1s^1$ $_{11}Na = 1s^2, 2s^2, 2p^6, 3s^1$ $_{19}K = 1s^2, 2s^2, 2p^6, 3s^2 3p^6, 4s^1$

10. Electropositive character: H^+, Na^+, K^+ etc.

11. Oxidation state: +1

12. Combination with electronegative elements: form binary compounds withelectronegative elements like alkali metals.

Halides: HCl, NaCl, KCl etc

Sulphides: H_2S Na_2S, K_2S etc

☆ Resemblance with halogens:-

1. Electronic configuration:

Both contain one electron less than the nearest noble gas configuration $_1H = 1s^1$ (near to $_2He$)

$_9F = 1s^2, 2s^2, 2p^5$ (near to $_8Ne$)

$_{17}K = 1s^2, 2s^2, 2p^6, 3s^2 3p^5$ (near to $_{18}Ar$)

a. **Non-metallic character:** like halogens, hydrogen is non-metallic in nature.

b. **Atomicity:** Diatomic molecules.

c. **Formation of similar types of compounds:**

i. Halides: CCl_4, $SiCl_4$, $GeCl_4$

ii. Hydrides: CH_4, SiH_4, GeH_4

5. Oxidation state: –1

$Na^{+1}H^{-1}$ $Na^{+1}Cl^{-1}$

☆ Difference from alkali metals:-

1) **Ionization enthalpy: -** the ionization enthalpy of hydrogen is very high in comparison to alkali metals.
2) **Non- metallic character:** alkali metals are typical metals while hydrogen is non-metal
3) **Atomicity**: hydrogen is diatomic while alkali metals are monoatomic.
4) **Nature of compounds:** the compounds of hydrogen are predominantly covalent while those of alkali metals are ionic. For example: HCl is covalent while NaCl is ionic.
   The oxides of alkali metals are basic while hydrogen oxide is neutral.

☆ Difference from halogens:-

1) **Less tendency for hydride formation:** Hydrogen has less tendency to take up electron to form hydride ion (H^-) as compared to the halogens which form halide ions (X^-) very easily.
2) **Absence of unshared pairs of electrons :**
3) **Nature of oxides:** The oxides of halogens are acidic while hydrogen oxide is neutral.

✪ Occurrence of Hydrogen:

➢ Hydrogen, the most abundant element in the universe and the third most abundant on the surface of the globe, is being visualised as the major future source of energy

✪ Isotopes of hydrogen:-

S.N.	**Property**	**Protium**	**Deuterium**	**Tritium**
1	Relative abundance	99.985 %	0.015 %	10^{-15}%
2	Relative atomic mass	1.007825	2.014102	3.016
3	Radioactive stability	Non-radioactive	Non-radioactive	Radioactive $t_{1/2}$ = 12.334 yrs

✪ Preparation:

☆ Methods for commercial production of dihydrogen

1. Electrolysis of water

$2H_20 \rightarrow 2H^+ + 2OH^-$

at cathode

→

$[2H^+ + 2e^- \rightarrow H_2]$

At anode

$4OH^- \rightarrow 2H_2O + O_2$

$2\,H_2O\,(l) \rightarrow 2\,H_2\,(g) + O_2\,(g)$

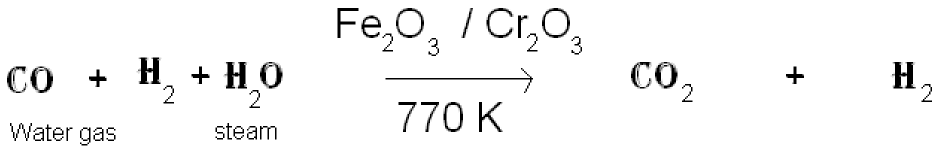
➢ The hydrogen prepared by this method is of very high purity. However, this method is not commonly used because it is very expensive. This method is can be used only at those places where the electricity is cheap.

2. By the reaction of steam on coke :-

$$C + H_2O(g) \xrightarrow{1270\,k} \underbrace{CO + H_2}_{\text{Water gas}}$$

Since the mixture of CO and H_2 is used for the synthesis of methanol and a number of hydrocarbons, it is also called synthesis gas or syn gas.

* The process of producing syn gas from coal or coke is called coal gasification.



$$\underset{\text{Water gas}}{CO + H_2} + \underset{\text{steam}}{H_2O} \xrightarrow[770\ K]{Fe_2O_3\ /\ Cr_2O_3} CO_2 + H_2$$

➢ This reaction is called water gas shift reaction.

✪ Properties of Hydrogen:-

☆ Physical Properties:-

1. It is slightly soluble in water (about 2 %)
2. It is highly combustible and therefore should be handled carefully.
3. It is the lightest substance. The mass of one litre hydrogen at NTP is only 0.0899 g.

☆ **Chemical properties:-**Not very reactive due to high bond dissociation energy (435.88 kJ mol^{-1} at 298.2 K)

(i)Combustion: - It burns with pale blue flame

$$2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O(l)$$

(ii) Reaction with metals:-Reactive metals like Na, K, Ca, Li and form hydrides.

$$Ca + H_2 \xrightarrow{525\ k} CaH_2$$

➢ Metals like Pt, Pd, Ni (elements of d block) form interstitial hydrides by absorbing large volume of hydrogen. Such hydrogen is called ‘occluded hydrogen and this property of adsorption of a gas by a metal is called occlusion.

(iii) Reaction with metal oxides:-Hydrogen reduces oxides of less active metals tocorresponding metal.

$$Fe_3O_4 + 4H_2 \xrightarrow{Heat} 3Fe + 4H_2O$$

$$CuO + H_2 \xrightarrow{Heat} Cu + H_2O$$

(iv) Reaction with non-metals:-

$$3H_2\,(g) + N_2\,(g) \xrightarrow[673k,200\ atm]{Fe,\ Mo} 2NH_3\ (g)$$ { Haber process}

$\triangle H = -\ 92.6$ kJ/mole

$$2H_2\,(g) + O_2\,(g) \xrightarrow{970\ k} 2H_2O \qquad \triangle H = -\ 285.9 kJ/mole$$

(v) Reaction with carbon monoxide:-

$$CO + 2H_2 \xrightarrow[700\ k,200\ atm]{ZnO,\ Cr2O3} CH_3OH$$

(vi) Reaction with unsaturated Hydrocarbons:-

(a) $H_2C = CH_2 + H_2 \xrightarrow[473\ K]{Ni,\ Pd\ or\ Pt} H_3C - CH_3$

(b) Hydroformylation of olefins to aldehydes: Hydroformylation or Oxo process

$$RCH = CH_2 + H_2 + CO \xrightarrow[\boxed{\text{High Temperature and pressure}}]{[Co(CO)_4]_2} RCH_2CH_2CHO$$

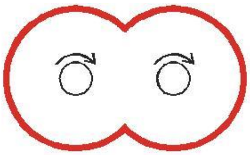
13. Hydrogenation of oils:- Vegetable oils are poly unsaturated in nature. The C=C bonds in oils can easily undergo oxidation and the oil becomes rancid i.e. unpleasant in taste. Hydrogenation of vegetable oil reduces the number of double bonds and solid fat (Vegetable ghee) is formed.

$$\text{Vegetable Oil} + H_2 \xrightarrow[473\ k,]{NI} \textit{Solid fat (Vegetable ghee)}$$

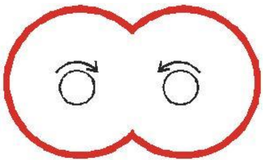
✪ **Uses of Hydrogen:-** it is used ..

1. As a reducing agent.
2. In the manufacture of vanaspati fat, ammonia, metal hydrides, methanol, fertilizers such as urea etc.
3. In the manufacture of synthetic petrol.
4. In the atomic hydrogen torch and oxy hydrogen torches for cutting and welding. Dihydrogen is dissociated with the help of an electric arc and the hydrogen atoms produced are allowed to recombine on the surface to be welded. High temperature of about 4000 K is generated.
5. In the fuel cell for generating electrical energy.

✪ **Ortho and parahydrogens:-** A molecule of dihydrogen …….



Ortho hydrogen



Para hydrogen

- They show different physical properties. For example :
  - The thermal conductivity of para hydrogen is about 50 % greater than that of ortho hydrogen.
  - The melting point of para hydrogen is 0.15 K below that of hydrogen containing 75% ortho hydrogen.
  - They show similar chemical properties.

✪ **Atomic hydrogen:-**

Because of high H—H bond enthalpy, atomic hydrogen is produced only at high temp in an electric arc or under ultraviolet radiation.

$$H_2(g) \xrightarrow{3270\ k} 2H(g); \qquad \Delta H = +435.9\ \text{kJ}$$

(Atomic hydrogen)

- Highly reactive.
  - Half life period is 0.3 sec and therefore, it immediately gets converted into the molecular form liberating a large amount of energy which is used for cutting and welding purposes.

✪ **Nascent hydrogen:-** Hydrogen produced in contact with the substance to be reduced is known as 'nascent hydrogen'. It is very reactive form of hydrogen and is better reducing agent than ordinary dihydrogen.

✪ **Hydrides:-**Under certain conditions H_2 combines with almost all the elements , except noble gases to form compounds called hydrides.

There are three types of hydrides ,they are

= Ionic or saline hydrides

= Covalent or molecular hydrides (iii) Metallic or non-stoichiometric hydrides

(i) Ionic or saline hydrides:- These are the compounds of H_2 formed with most of the s-block elements which are highly electro- positive.

(ii) Covalent or molecular hydrides:-These are the compounds of hydrogen formed with most of the p-block elements

[a]Electron deficient:- The hydrides which do not have sufficient number ofelectrons to form normal covalent bonds is called electron deficient hydride. For example, hydrides of group 13 elements (BH_3, AlH_3, etc.).They are known as Lewis acids i.e., electron acceptors. To make up their deficiency they generally exist in polymeric forms such as B_2H_6, Al_2H_6, etc.

6. **Electron precise:-**The hydrides which have sufficient number of electrons required for forming covalent bonds is called electron precise hydride. For example, hydrides of group 14 (CH_4, SiH_4, GeH_4, SnH_4, PbH_4 etc.) they have tetrahedral geometry.
7. **Electron rich hydrides:-**The hydrides which have excess electrons as required to form normal covalent bonds is called electron rich hydride. For example, hydrides of group 15 to 17 (NH_3, PH_3, H_2O, H_2S, H_2Se, H_2Te, HF etc.)

(iii) Metallic or non-stoichiometric hydrides:-

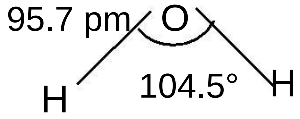
- *These are formed by many d-block and f-block elements*
- *These hydrides conduct heat and electricity though not efficient.*

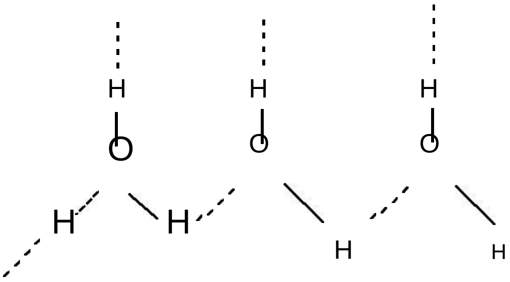
✪ **Water: -**Water! It is the major part of all living organisms. Water is also known as the river of life.

- Human body has about 65%and some plants have as much as 95%water.

❖ **STRUCTURE OF WATER:-**

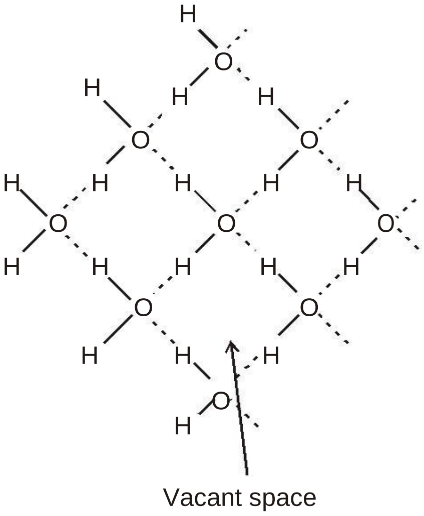
- In a gas phase water is bent molecule with a bond angle of 104.5 and O-H bond length of 95.7pm. It is highly polar molecule..





Solid state

❖ **Structure of ice**:-Ice has a highly ordered 3D hydrogen bonded structure. Each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 276 pm



☆ **Chemical Properties of water:-**

[i] AMPHOTERIC NATURE:-It has the ability to act as an acid with NH_3 and as a base with H_2S

$H_2O(l) + NH_3(aq) \rightarrow OH^-(aq) + NH_4^+(aq)$

$H_2O(l) + H_2S(aq) \rightarrow H_3O^+(aq) + HS^-(aq)$

[ii] REDOX REACTIONS INVOLVING WATER:-

- Water can be easily reduced to H_2 by highly electropositive metals

$2H_2O(l) + 2Na(s) \rightarrow 2NaOH(aq) + H_2(g)$

[iii] HYDROLYSIS REACTION:-Due to high dielectric constant, it has a very strong hydrating tendency. It dissolves many ionic compounds.

$P_4O_{10}(s) + 6H_20(l) \longrightarrow 4H_3PO_4(aq)$

$SiCl_4(l) + 2H_2O(l) \longrightarrow Si(OH)_4(s) + 4HCl(aq)$

[iv] HYDRATES FORMATION:-From the aqueous solutions many salts can be crystallized as hydrated salts. Hydrated salts have the following types of water.

(1) Coordinated water e.g., $[Cr(H_2O)_6]^{3+}\ 3Cl^-$

(2) Interstitial water e.g.,$BaCl_2.2H_2O$

(3) hydrogen-bonded water e.g. $[Cu(H_2O)_4]^{2+}SO_4^{2-}.H_2O$ in $CuSO_4.5H_2O$

.

✪ **Hard & Soft Water:-**

- The water which contains dissolved salts of bicarbonates, sulphates and chlorides of calcium and magnesium is called hard water. Hard water does not produce lather with soap solution.
- Soft water is free from bicarbonates, sulphates and chlorides of calcium and magnesium. It produces lather with soap solution easily. e.g., distilled water, rain water..

☆ **Types of hardness:-**The hardness of water is of two types

(i)Temporary hardness

- Due to presence of soluble bicarbonates of calcium and magnesium.
- Can be removed by simple boiling.

(ii)Permanent hardness

- Due to presence of chlorides and sulphates of calcium and magnesium.
- Requires treatment of water to remove this type of hardness.
- ***Do you know?***

  Temporary hardness is also called carbonate hardness &
  Permanent hardness is also called non-carbonate hardness

☆ **Softening of water:-**The process of removal of $Ca^{2+}$and Mg^{2+}ions from wateris called softening of water.

❖ **Removal of temporary hardness:-**

10. By boiling :

$M(HCO_3)_2 \xrightarrow{Heat} MCO_3 + H_2O + CO_2$(M = Ca or Mg)
(Soluble) (Insoluble)

3. **Clark's method or calcium hydroxide method**

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$
(Soluble) (Insoluble)

$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 + Mg(OH)_2 + 2H_2$
(Soluble) (Insoluble) (Insoluble)

❖ **Removal of permanent hardness:-**

(i) By washing soda ($Na_2CO_3.10H_2O$) treatment:

$CaCl_2 + Na_2CO_3 \rightarrow 2CaCO_3 + 2NaCl$
(Insoluble)

$MgSO_4 + Na_2CO_3 \longrightarrow MgCO_3 + Na_2SO_4$
(Insoluble)

(ii) By using inorganic cation exchanger (permutit method or Zeolite method):

$Na_2Al_2Si_2O_8 + CaCl_2 \rightarrow Ca(Al_2Si_2O_8)_2 + 2NaCl$
Zeolite Settles at bottom

The zeolite can be regenerated by treatment with sodium chloride solution. $Ca(Al_2Si_2O_8)_2 + 2NaCl \rightarrow Na_2Al_2Si_2O_8 + CaCl_2$

2 By organic ion exchanger or synthetic resins (ion exchange resins):-

- Synthetic resins are the insoluble polymeric solids having giant hydrocarbon network containing reactive acidic or basic groups. These are superior to Zeolite because they can remove all types of cations as well as anions present in water. This resulting water is known as demineralised or deionised water.
- These are two types:

2. **Cation exchanger resins**: They have acidic groups such as COOH or SO_3H.they may be represented as **resin—H^+**

$Mg^{2+} + 2H-resin \rightarrow Mg(resin)_2 + 2H^+$
In hard water Cation exchanger

$Ca^{2+} + 2H-resin \longrightarrow Ca(resin)_2 + 2H^+$
Hard water Cation exchanger

5. **Anion exchanger resins:** they have basic groups such as–OH^-or–NH_2.they may be represented as **resin—OH^-** or **resin—$NH_3^+OH^-$**

$$\underset{\text{Hard water}}{SO_4^{2-}} + \underset{\text{Anion exchanger}}{2HO-resin} \longrightarrow SO_4-resin_2 + 2OH^-$$

$$\underset{\text{Hard water}}{Cl^-} + \underset{\text{Anion exchanger}}{HO-resin} \longrightarrow Cl-re\ sin + OH^-$$

Regeneration of resins:

$$\underset{\text{Exhausted resin}}{Cl-resin} + NaOH \longrightarrow \underset{\text{Re generated resin}}{HO-resin} + NaCl$$

✪ **Hydrogen peroxide [H_2O_2]:-** discovered by French chemist J.L. Thenard

❖ **Methods of preparation**

1) From sodium peroxide (Merck's process):-

$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$

(20% ice cooled solution) (30% solution)

2. From Barium peroxide:-

Hydrogen peroxide was first prepared by J. L. Thenard in 1818 by acidifying barium peroxide and removal of excess water by evaporation under reduced pressure.

$BaO_2.8H_2O + H_2SO_4 \longrightarrow BaSO_4 + 8H_2O + H_2O_2$

➢ Barium sulphate is filtered off leaving behind H_2O_2.

Store of Hydrogen peroxide:-

(a) It must be kept in wax lined coloured bottles because the rough glass surface causes its decomposition.

(b) A small amount of phosphoric acid , glycerol or acetanilide is generally added to retard the rate of decomposition of H_2O_2. These substances act as negative catalysts.

Physical properties of Hydrogen peroxide:-

a. In the pure state H_2O_2 is an almost colourless(very pale blue) liquid.

b. H_2O_2 is miscible with water in all proportions and forms a hydrate $H_2O_2.H_2O$ (mp 221K).

c. A 30 % solution of H_2O_2 is marketed as '100 volume' hydrogen peroxide. It means that one millilitre of 30% H_2O_2 solution will give 100 mL of oxygen at STP. Commercially, H_2O_2 is marketedas 10 V, which means that the sample contains 3% H_2O_2.

Chemical properties of Hydrogen peroxide:-

Oxidising properties

(iv) $2K_4[Fe(CN)_6] + H_2SO_4 + H_2O_2 \longrightarrow$

$2K_3[Fe(CN)_6] + 2H_2O + K_2SO_4$

(v) $C_6H_6 + H_2O_2 \longrightarrow \underset{\text{Phenol}}{C_6H_5OH} + H_2$

(vii) $NaNO_2 + H_2O_2 \longrightarrow NaNO_3 + H_2O$

(viii) $K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \longrightarrow K_2SO_4 + CrO_5 + 5H_2O$

Reducing properties

(i) $H_2O_2 + O_3 \longrightarrow H_2O + O_2$

(ii) $Ag_2O_2 + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$

(iii) $PbO_2 + 2HNO_3 + H_2O_2 \longrightarrow Pb(NO_3)_2 + 2H_2O + O_2$

Reducing properties

(iv) $2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow$

$K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

(v) $Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2$

(vi) $6KAuCl_4 + 3H_2O_2 \longrightarrow 2Au + 2KCl + 6HCl + 3O_2$

Oxidising properties of H_2O_2

$HClO$ _+ $H_2O_2 \rightarrow HCl + H_2O + O_2$
$PbS + H_2O_2 \rightarrow PbSO_4 + H_2O$
Reducing property of H_2O_2

$2\,MnO_4^- + 6\,H^+$ _+ $5\,H_2O_2 \rightarrow 2\,Mn^{2+} + 8\,H_2O$

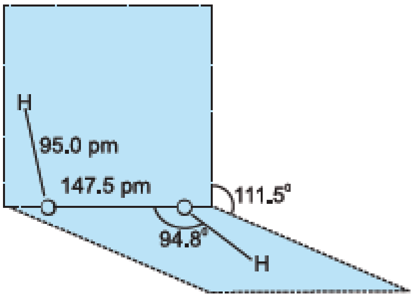
❖

Uses of hydrogen peroxide

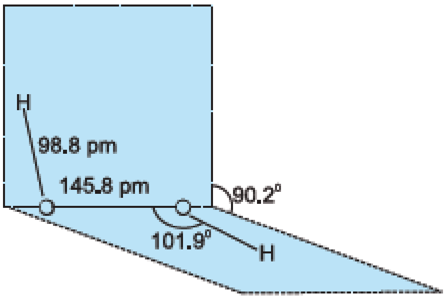
1) For bleaching silk, wool, hair and leather
2) As rocket fuel

❖

Structure of hydrogen peroxide



(a) Gas phase



(b) Solid phase

Hydrogen economy (Hydrogen as fuel)

- The electricity cannot be stored to run automobiles. It is not possible to store and transport nuclear energy. Hydrogen is an alternative source of energy and hence called as ‘hydrogen economy’. Hydrogen has some advantages as fuel
- Available in abundance in combined form as water.
- On combustion produces H_2O. Hence pollution free.
- H_2-O_2 fuel cell has high efficiency of about 70 %.
- Excellent reducing agent. Therefore can be used as substitute of carbon in reduction for processes in industry.

❖ **Obstacles in hydrogen economy**

- **Transportation:**
- Hydrogen gas is explosive and hence it is difficult to store and transport.
- Formation of hydrogen from H_2O:
- The cheaper production of the hydrogen is basic requirement of hydrogen economy which is not possible now.
- The main aim and advantage of hydrogen economy is to transmit energy in form of hydrogen.

One mark question:

1. What is meant by 10 volume hydrogen peroxide?
2. Why is dihydrogen gas not preferred in balloons?
3. Name the constituents of water gas.
4. Name one compound each in which hydrogen exists in (i) positive oxidation state, and (ii) Negative oxidation state.
5. What type of elements form interstitial hydrides?
6. How many hydrogen bonded water molecule(s) are present in $CuSO_4.5H_2O$?
7. What happens when heavy water is added to calcium carbide?
8. Concentrated sulphuric acid cannot be used for drying H_2. Why?
9. Complete the following reactions?

(i) $C_3H_8\,(g) + 3H_2O(\xrightarrow[\text{catalyst,}]{\text{heat}}$

(ii) $Zn(s) + NaOH(aq) \xrightarrow{\text{heat}}$

10. How is heavy water obtained from ordinary water?

Solutions:

1. It means that 1 ml of H_2O_2 will give 10 ml of oxygen at N.T.P.
2. Dihydrogen gas is combustible in nature. Therefore, it may react with oxygen highly violently. Thus, it is not used in balloons.
3. Carbon monoxide and hydrogen.
4. (i) HCl (ii) NaH
5. Elements of d-and f-block.
6. In $CuSO_4.5H_2O$, there is one hydrogen bonded water molecule which is outside the coordination sphere. The other four molecules of water are coordinated.
7. Deutero acetylene is formed.

$$CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + C_2D_2$$

8. Conc. H_2SO_4 on absorbing water from moist H_2 produces so much heat that H_2 catches fire.
9.

(i) $C_3H_8\,(g) + 3H_2O(\xrightarrow[\text{catalyst,}]{\text{heat}} 3CO + 7H_2(g)$

(ii) $Zn(s) + NaOH(aq) \xrightarrow{\text{heat}} Na_2ZnO_2(aq) + H_2(g)$

10. Heavy water is obtained from ordinary water by repeated electrolysis in the presence of 3% NaOH.

Two mark questions

1. Can we use concentrated sulphuric acid and pure zinc in the preparation of dihydrogen? Justify your answer.
2. Write the chemical reactions to show the amphoteric nature of water.
3. Why is hydrogen peroxide stored in wax-lined plastic coloured bottles?
4. H_2O_2 acts as an oxidizing agent as well as reducing agent. Why?
5. What causes the temporary and permanent hardness of water?

Solutions:

1. (a) Conc. H_2SO_4 cannot be used because it acts as oxidizing agent also and gets reduced to SO_2.

$$Zn + \text{dil } H_2SO \longrightarrow ZnSO_4 + 2H_2O + SO_2$$

(b) Pure Zn is not used because it is non-porous and reaction will be slow. The impurities in Zn help in constitute of electrochemical couple and speed up reaction.

2. Water is amphoteric in nature and it behaves both as an acid as well as a base. With acids stronger than itself (eg., H_2S) it behaves as a base and with bases

stronger than itself (eg. NH_3) it acts as an acid.

(i) As a base: $H_2O(l) + H_2S(aq) \rightarrow H_3O^+(aq) + HS^-(aq)$

(ii) As an acid: $H_2O(l) + NH_3(aq) \rightarrow OH^-(aq) + NH_4^+(aq)$

3. The decomposition of H_2O_2 occurs readily in the presence of rough surface (acting as catalyst). It is also decomposed by exposure of light. Therefore, wax-lined smooth surface and coloured bottles retard the rate of decomposition of H_2O_2.

In H_2O_2, oxygen has -1 oxidation state which lies between maximum (0 in O_2 or +2 in OF_2) and minimum -2 (in O_2F). Therefore, oxygen can be oxidized to O_2 (zero oxidation state) acting as reducing agent or can be reduced to H_2O or OH^- (-2 oxidation state) acting as an oxidizing agent.

$$\overset{-1}{H_2O_2} \rightarrow \overset{0}{O_2} + 2e^-$$

(Reducing agent)

$$\overset{-1}{H_2O_2} + 2e^- \rightarrow \overset{-2}{2OH^-}$$

(Oxidizing agent)

5. Temporary hardness is due to presence of soluble bicarbonates of calcium and magnesium. On the other hand, permanent hardness is due to presence of chlorides and sulphates of calcium and magnesium.

Three mark question:

1. Hard water is unsuitable for laundry, washing and dyeing. Explain.
2. What do you understand by (i) electron-deficient, (ii) electron-precise, and (iii) electron-rich compounds of hydrogen? Provide justification with suitable examples.
3. Compare the structures of H_2O and H_2O_2.

Solutions:

1. Ans: - We know that the soaps are the sodium salts of higher fatty acids like stearic acid ($C_{17}H_{35}COOH$), oleic acid ($C_{17}H_{33}COOH$) or palmitic acid ($C_{17}H_{31}COOH$). When soap is added to hard water, the anions of soap combine with Ca^{+2} and Mg^{+2} ions to form calcium and magnesium salt which are insoluble in water.

$$\underset{\text{From hard Water}}{M^{+2}} + \underset{\text{sodium stearate (Soap)}}{2C_{17}H_{35}COONa} \rightarrow \underset{\text{Metal stearate (precipitate)}}{(C_{17}H_{35}COO)_2M\downarrow} + 2Na$$

Therefore, no lather is produced until all the calcium and magnesium ions are precipitated. This also results into wastage of lot of soap. So hard water is unsuitable for laundry, washing and dyeing.

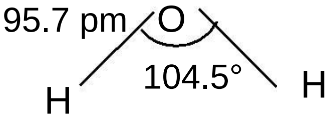
2. **[a]Electron deficient**:- The hydrides which do not have sufficient number of

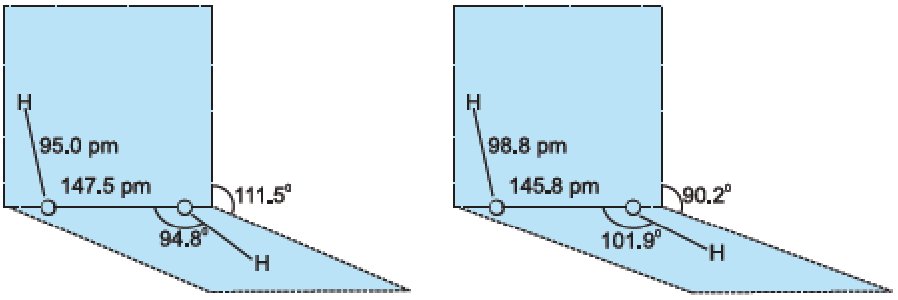
electrons to form normal covalent bonds is called electron deficient hydride. For example, hydride of group 13 elements (BH_3, AlH_3, etc.).

[b] Electron precise:-The hydrides which have sufficient number of electronsrequired for forming covalent bonds is called electron precise hydride. For example, hydrides of group 14 elements (CH_4, SiH_4, GeH_4, SnH_4, PbH_4 etc.) they have tetrahedral geometry.

[c] Electron rich hydrides:-The hydrides which have excess electrons asrequired to form normal covalent bonds is called electron rich hydride. For example, hydrides of group 15 to 17 (NH_3, PH_3, H_2O, H_2S, H_2Se, H_2Te, HF etc.)

3. In water, O atom is sp^3hybridised and there are two O—H bonds and two sp^3 hybrid orbitals occupy lone pairs of stronger lone pair-lone pair repulsions than bond pair-bond pair repulsions, the H-O-H bond decreases from 109.5 to 104.5^0. Therefore, water molecule is a bent or angular molecule. H_2O_2 has non-planar structure. In this structure, two O—O oxygen atoms are bonded to each other by a single covalent bond and each O atom is further bonded to a hydrogen atom by a single covalent bond. The two O—H bonds are in different planes in 111.50 in the gas phase.





(a) Gas phase

(b) Solid phase

Chapter 10

The s- Block Element

Important points

- Groups (1 & 2) belong to the s-block of the Periodic Table.
- Group 1 consists of : lithium, sodium, potassium, rubidium, caesium and francium and collectively known as the *alkali metals.*
- Group 2 include : beryllium, magnesium, calcium, strontium, barium and radium. Except Beryllium they are known as *alkaline*

Physical properties-

a) **Large atomic radii:** The atomic radii of alkali metals are the largest in their respective periods. These increase as we travel down the group.

b) **Large ionic radii:** The ionic radii increase as we move down the group due to theaddition of a new energy shell with each succeeding element.

c) **Low ionization enthalpy:** The ionization enthalpies decrease as we move down the group. The ionization enthalpies of the alkali metals are the lowest due to loosely held s- electron.

d) **Hydration enthalpy:** It decreases with the increase in ionic radii. The hydration enthalpy of Li ion is the maximum and the hydration enthalpy of Cs ion is the minimum.

e) **Oxidation state:** The alkali metals exhibit oxidation state of +1 in their compounds and are strongly electropositive in character. The electropositive character increases from Li to Cs.

f) **Metallic character:** The metallic character increases down the group.

g) **Melting point and boiling point::** The m p and b p of alkali metals are very low and decrease with increase in atomic number.

h) **Nature of bonds formed:** These metals form ionic bonds. The ionic character increases as we go down the group.

i) **Flame colouration:** All the alkali metals impart a charactersistic colour to the flame.

j) **Photoelectric effect:** Alkali metals (except Li) exhibits photoelectric effect.

❖ **Chemical features of alkali metals:**

a) **Reducing character:** As the ionization enthalpies of the alkali metals decrease down the group their reducing character or reactivity in the gaseous state increases down the group. i.e., Li < Na < K < Rb < Cs .

b) **Reaction with dihydrogen:** Alkali metals react with dry hydrogen at about673 K to form crystalline hydrides which are ionic in nature and have high melting points.

$$2\,M + H_2 \xrightarrow{\text{Heat}} 2M^{+}H^{-}$$

c) **Oxides and hydroxides:** Alkali metals when burnt in air form different compounds, for example the alkali metals on reaction with limited quantity of oxygen form normal oxides (M_2O) M= Li, Na, K, Rb, Cs

5) **Reaction with halogens:** The members of the family combine with halogento form corresponding halides which are ionic crystalline solids.
Reactivity of alkali metls with particular halogen increases from Li to Cs.
6) **Reaction with water:** Alkali metals react with water and other compoundscontaining acidic hydrogen atoms such as hydrogen halides, acetylene etc. to liberate hydrogen gas.
7) **Solubility in liquid ammonia:** All alkali metals dissolve in liquid ammoniagiving deep blue solutions which are conducting in nature.
8) **Reaction with sulphur and phosphorus:** Alkali metals react with sulphur andphosphorus on heating to form sulphides and phosphides respectively.

❖ Diagonal relationship between Li and Al

Li resembles Mg mainly due to similarity in sizes of their atoms and ions. The main points of similarity are:

4) Both are quite hard.
5) Both LiOH and $Mg(OH)_2$ are weak bases.
6) Carbonates of both on heating decompose to produce oxides and carbondioxide.
7) Both react with nitrogen to give ionic nitrides.
8) Nitrates of both decompose on heating to give oxides.
9) Both Li and Mg do not form solid bicarbonates.
10) Because of covalent character LiCl and $MgCl_2$ are soluble in ethanol.
11) The hydroxides, bicarbonates and fluorides of both Li and Mg are sparingly soluble in water.

❖ Biological importance of Na and K

- Sodium ions participate in the transmission of nerve signals.
- Sodium ions also regulate flow of water across the cell membranes and in transport of sugars and amino acids into the cells.
- Potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in oxidation of glucose to produce ATP.
- Potassium ions in combination with sodium ions are responsible for transmission of nerve signals.
- The functional features of nerve cells depend upon the sodium potassium ion gradient that is established in the cell.

❖ Group 2 elements: Alkaline earth metals

- **Atomic radii :** The atomic radii of alkaline earth metals are fairly large thoughsmaller than the corresponding alkali metals and they increase down the group. This is because on moving down the group, atomic radii increase primarily due to the addition of an extra shell of electrons in each succeeding element.

- **Ionic radii:** the atoms of these elements form divalent ions which show the sametrend of increase in their size down the group.

- **Ionization enthalpy:** The alkaline earth metals have fairly low Ionizationsenthalpies though greater than those of the corresponding elements of group 1 and this value decreases down the group.

(d) Hydration enthalpy: the Hydration enthalpies of alkaline earth metal ion decrease as the size of the metal ion increases down the

Group $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

(e) Oxidation State: All the members of the family exhibit +2 oxidation state in their compounds and form divalent cations (M^{2+})

(f) Electro negativity : The electro negativity values of alkaline earth metals arequite close to those of alkali metals, though slightly more.

(g) Metallic Character : Alkaline earth metals have stronger metallic bonds ascompared to the alkali metals present in the same period.

(h) Melting and boiling point : The melting and Boiling points of these metals arehigher than those of alkali metals present in the same period.

(i) Colouration to the flame : With the exception of beryllium and magnesium, therest of the elements impart characters in colour to the same flame. For example,

Be	Mg	Ca	Sr	Ba	Ra
-	-	Brick Red	Crimson	Grassy Green	Crimson

J) Complex formation: Generally the members do not form complexes. However,smaller ions (Be & Mg Ions) form complexes with the electron donor species

(v) **Formation of organo-metallic compounds:** Both beryllium and magnesiumform a number of organo-metallic compounds containing M-C bond with certain organic compounds. For example, magnesium reacts with alkyl halide in the presence of dry ether to give Grignard reagent.

(vi) **Reducing character:** Alkaline earth metals are weak reducing agent than thecorresponding alkali metals which have lower ionization enthalpies and comparatively bigger atomic sizes.

(vii) **Reaction with oxygen:** With the exception of Ba and Ra which form peroxides (MO_2) rest of the metals form normal oxides (MO) on heating with excess of oxygen.

(viii) **Reaction with halogen**s: The members of the family combine directly withhalogen at appropriate temperature to form corresponding halides.

(ix) **Reaction with water:** The members of this group are less reactive towards wateras compared to the corresponding alkali metals because these are less electropositive in nature.

(x) **Reaction with hydrogen:** The members except Be combine with hydrogendirectly upon heating to form metal hydrides.

Uses of some important compounds:-

(i) Caustic soda:

It is used: in soap, paper, textile, petroleum industry **ii) Sodium carbonate**

It is used:

a) in glass and soap industry
b) in paper making and textile manufacturing
c) in paint and dye stuffs
d) in metal refining

(e) in production of sodium compounds such as borax, caustic soda, sodium phosphate etc.

iii**) Quick lime:**

It is used:

(c) in the preparation of cement, glass and calcium carbide.

(d) In the purification of sugar

c. In softening of hard water d. As a flux in the extraction of metal

25. Lime stone: It is used

as building material

in the manufacture of quick lime

in Solvay process to prepare Na_2CO_3 as it is a source of CO_2

in metallurgy for the extraction of iron

in toothpaste and certain cosmetics

26. Cement: It is an important building material. It is used in concrete and reinforcedconcrete, in plastering and in the construction of bridges, dams and buildings.

27. Plaster of paris: It is used

in making moulds for pottery and ceramics etc.

in surgical bandages for setting broken bones of the body

for making statues, models, decorative materials and black board chalk.

➢ **Biological importance of Ca and Mg**

Magnesium ions are concentrated in animal cells and Calcium ions are concentrated in body fluids, outside the cell.

All enzymes that utilize ATP in phosphate transfer require magnesium ion as cofactor.

In green plants magnesium is present in chlorophyll.

Calcium and magnesium ions are also essential for the transmission of impulses along nerve fibres.

Calcium ions are important in blood clotting and are required to trigger the contraction of muscles.

Calcium ions also regulate the beating of the heart.

One mark questions:

1. Why are halides of beryllium polymeric?

Ans:- The halides of Be are electron deficient as their octets are incomplete. Therefore, to complete their octets, the halides polymerize.

2. Name the groups which constitute s-block elements. Ans:- group-1 and 2

3.Arrange the alkaline earth metal carbonates in the decreasing order of thermal stability.

Ans:- $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3 > BeCO_3$

4.Write the general electronic configuration of s-block elements. Ans:- [Noble gas] ns^{1-2}

5.What is the chemical formula of Plaster of Paris?

Ans:- $CuSO_4.1/2H_2O$

6.Name the compound which can be obtained by Solvay's process.

Ans:- Sodium carbonate

7.How does the basic character of hydroxides of alkali metals vary down the group? Ans:- Increases down the group

8.Which out of $MgSO_4$ or $BaSO_4$ is more soluble in water?

Ans:- $MgSO_4$

9.Name radioactive elements of group 1 and 2.
Ans:- Francium and Radium.

10.Which elements of alkaline earth metals family do not give characteristic flame colouration?
Ans:- Be and Mg

Two marks questions

1. Among the alkali metals which has
- (i) Highest melting point
- (ii) Most electropositive character
- (iii) Lowest size of ion
- (iv) Strongest reducing character.

Ans:- (i) Li (ii) Cs (iii) Li (iv) Li

(v) Complete the following reactions:

$Mg(NO_3)_2 \xrightarrow{Heat}$

(ii) $LiOH \xrightarrow{Heat}$

(iii) $Na_2O + H_2O \longrightarrow$
(iv) $Na + O_2 \longrightarrow$

Ans:-

(i) $2Mg(NO_3)_2 \xrightarrow{Heat} 2MgO + 4NO_2 + O_2$

(ii) $2LiOH \xrightarrow{Heat} Li_2O + H_2O$

(iii) $Na_2O + H_2O \longrightarrow 2NaOH$

(iv) $2Na + O_2 \longrightarrow Na_2O_2$

2. Name the chief factors responsible for anomalous behaviour or lithium.

Ans:- the anomalous behaviour of lithium is because of its:
- (i) Small size of atom and ion,
- (ii) High ionization enthalpy, and
- (iii) Absence of d-orbitals in its Valence shell.

3. Which out of Li and Na has greater value for the following properties:
- **(i) Hydration enthalpy**
- **(ii) Stability of hydride**
- **(iii) Stability of carbonate**
- **(iv) Basic character of hydroxide**

Ans:- (i) Li (ii) Li (iii) Na (iv)Na

4. **Why are alkali metals not found in nature?**

Ans. Alkali metals are highly reactive in nature due to low ionization enthalpy andstrong electropositive character. They do not occur in free state and are always combined with other elements. As a result alkali metals are not generally found in nature.

5. **Why are lithium salts commonly hydrated and those of the other alkali ions usually anhydrous?**

Ans. In the lithium salt, the Li^+ion due to very small size gets readily hydrated oncoming in contact with moisture (water). Therefore, lithium salts are commonly hydrated. But the other alkali metal ions are comparatively big in size. They have therefore, lesser tendency to get hydrated. These salts are usually anhydrous.

6. **Beryllium and magnesium do not give colour to flame whereas other alkaline earth metals do so why?**

Ans: Beryllium and magnesium atoms in comparison to other alkaline earth metals are comparatively smaller and their ionisation enthalpies are very high. Hence, the energy of the flame in not sufficient to excite their electrons to higher energy levels. These elements, therefore, do not give any colour in Bunsen flame.

7. **Why are alkali metals soft and have low melting points?**

Ans: Alkali metals have only one valence electron per metal atom. As a result, the binding energy of alkali metal ions in the close-packed metal lattices are weak. Therefore, these are soft and have low melting point.

8. **Which out of the following and why can be used to store an alkali metal?**

H_2O, C_2H_5OH and Benzene

Ans:- Benzene can be used to store an alkali metal because other substance react with alkali metal as:

$$Na + H_2O \longrightarrow NaOH + 1/2H_2$$

$$Na + C_2H_5OH \longrightarrow C_2H_5ONa + 1/2H_2$$

9. **Why are alkali metals not found free in nature?**

Ans:- Alkali metals are highly reactive. So they can react with air and moisture and therefore, are not found free in nature. They are present in the combined state in the form of halides, oxides, silicates, nitrates, etc.

Three marks questions

1. **When an alkali metal dissolves in liquid ammonia the solution can acquire different colours. Explain the reasons for this type of colour change.**

Ans. The dissolution of the metal in liquid ammonia is accompanied by theirformation of ammoniated electrons that give rise to dark colour. This is because ammoniated electrons absorb energy corresponding to the red region of the visible light. However, if the concentration increases above 3M, the colour changes to copper-bronze and the solution acquires metallic luster due to the formation of metal ion clusters.

$$M+(x+y)NH_3 \rightarrow [M(NH_3)x]^+ + [e(NH_3)_y]^-$$

2. In what ways lithium shows similarities to magnesium in its chemical behaviour?

Ans. Li resembles Mg mainly due to similarity in sizes of their atoms and ions. Themain points of similarity are:

Both are quite hard.

1 Both LiOH and $Mg(OH)_2$ are weak bases.

2 Carbonates of both on heating decompose to produce oxides and carbondioxide.

3 Both react with nitrogen to give ionic nitrides.

3. Discuss the various reactions that occur in the Solvay process.

Ans. In Solvay ammonia process.

When carbon dioxide is passed through a concentrated solution of brine saturated with NH_3, $NaHCO_3$ gets precipitated. $NaHCO_3$ on subsequent heating gives Na_2CO_3.

$$NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3 + NH_4Cl$$

$$2\,NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

CO_2 needed for the reaction is prepared by heating calcium carbonate and the quick lime, CaO is dissolved in water to form slaked lime, $Ca(OH)_2$

$$CaCO_3 \rightarrow CaO + CO_2$$

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

NH_3 needed for the purpose is prepared by heating NH_4Cl and $Ca(OH)_2$

$$2\,NH_4Cl + Ca(OH)_2 \rightarrow 2\,NH_3 + CaCl_2 + H_2O$$

4. What happens when (i) magnesium is burnt in air (ii) quick lime is heated with silica (iii) chlorine reacts with slaked lime (iv) calcium nitrate is heated?

Ans. (i) A mixture of magnesium oxide and magnesium nitride is formed

$$5Mg + \underset{\textbf{In air}}{\mathbf{O_2 + N_2}} \rightarrow 2\,MgO + Mg_3N_2$$

(ii) Calcium silicate is formed.

$$CaO + SiO_2 \rightarrow CaSiO_3$$

(iii) Calcium oxychloride (bleaching powder) is formed

$$Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O$$

(iv) Nitrogen dioxide is evolved.

$$Ca(NO_3)_2 \xrightarrow{Heat} CaO + 2\,NO_2 + O_2$$

5. Describe the importance of the following (i) limestone (ii) cement (iii) plaster of paris.

Ans. i) Lime stone: It is used

(ii) as building material

(iii) in the manufacture of quick lime

(iv) in Solvay process to prepare Na_2CO_3 as it is a source of CO_2

(v) in metallurgy for the extraction of iron

(vi) in toothpaste and certain cosmetics

ii) Cement: It is an important building material. It is used in concrete and reinforcedconcrete, in plastering and in the construction of bridges, dams and buildings.

iii) Plaster of paris: It is used

d) in making moulds for pottery and ceramics etc.

e) in surgical bandages for setting broken bones of the body

f) for making statues, models, decorative materials and black board chalk.

6. What happens when:

(iii) Sodium metal is dropped in water?

(iv) Sodium metal is heated in free supply of air?

(v) Sodium peroxide dissolves in water?

Ans. a) Sodium metal catches fire and hydrogen gas is evolved

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2 + Heat$$

b) Sodium peroxide is formed

$$2Na + O_2 \longrightarrow Na_2O_2$$

c) (i) Sodium peroxide reacts with water at ordinary temperature to liberate oxygen gas

$$Na_2O_2 + 2H_2O \longrightarrow 4\ NaOH + O_2$$

ii) With ice cold water, $H_2O\ _2$ is formed

$$Na_2O_2 + 2H_2O \longrightarrow 2\ NaOH + H_2\ O_2$$

7. **State as to why**

3 a solution of Na_2CO_3 is alkaline?

4 alkali metals are prepared by electrolysis of their fused chlorides?

5 sodium is found to be more useful than potassium?

Ans. (a) Sodium carbonate being a salt of strong base (NaOH) and weak acid(H_2CO_3) forms alkaline solution upon hydrolysis

$$Na_2CO_3 + 2H_2O \rightarrow 2NaOH + H_2CO_3$$

(b) Since the discharge potential of alkali metals is much higher than that of hydrogen, therefore, when the aqueous solution of any alkali metal chloride is subjected to electrolysis, H_2 instead of the alkali metal is produced at the cathode. Therefore, to prepare alkali metals, electrolysis of their fused chlorides is carried out.

(c) Sodium is relatively more abundant than potassium. At the same time, it is also less reactive and its reactions with other substances can be better controlled.

8. Why are potassium and cesium, rather than lithium used in photoelectric cells?

Ans. The ionization enthalpy of lithium is quite high. The photons of light are not ina position to eject electrons from the surface of lithium metal. Therefore photoelectric effect is not noticed. However, both potassium and cesium have comparatively low ionization enthalpies. This means that the electrons can quite easily be ejected from the surface of these metals when photons of certain minimum frequency (threshold frequency) strike against their surface

9. Why is Li_2CO_3 decomposed at a lower temperature whereas Na_2CO_3 at higher temperature?

Ans. Li^+ion is very small in size. It is stabilized more by smaller anions such asoxide ion rather than large anions such as carbonate. Therefore Li_2CO_3 decomposes into Li_2O on mild heating. On the other hand, Na^+ ion is larger in size. It is stabilized more by larger carbonate ion than smaller oxide ion. Hence, Na_2CO_3 does not undergo thermal decomposition easily.

10. Explain why can alkali and alkaline earth metals not be obtained by chemical reduction methods?

Ans. The metals belonging to both these families are very strong reducing agents. Itis therefore not possible to reduce their oxides by reacting with common reducing agents like carbon (coke), zinc etc. These are normally isolated by carrying out the electrolysis of the salts of these metals in the molten state.

Five marks questions:

- Compare the solubility and thermal stability of the following compounds of the alkali metals with those of the alkaline earth metals.(a) Nitrates (b) Carbonates (c) Sulphates.

Ans. Solubility:

In case of alkali metals: Nitrates, carbonates and sulphates of alkali metals are soluble in water. In alkali metals lattice energies decrease more rapidly than the hydration energies, therefore their solubility increases down the group.

In case of alkaline earth metals: Nitrates of all alkaline earth metals are soluble in water but their solubility decreases down the group because their hydration energies decrease more rapidly than their lattice energies.

Since the size of CO_3^{2-} and SO_4^{2-} anions is much larger than the cations, therefore lattice energies remain almost constant with in a particular group. Since, the hydration energies decrease as we move down the group, therefore the solubility of alkaline earth metal carbonates and sulphates decrease down the group. However, the hydration energy of Be^{2+} and Mg^{2+} ions overcome the lattice energy factor and therefore $BeSO_4$ and $MgSO_4$ are readily soluble in water while the solubility of other sulphates decreases down the group from $CaSO_4$ to $BaSO_4$.

Thermal Stability:

a) Nitrates: Nitrates of both alkali and alkaline earth metals decompose on heating. All alkaline earth metal nitrates decompose to form metal oxide, NO_2 and O_2.

$$2M(NO_3)_2 \longrightarrow 2MO + 4NO_2 + O_2$$

M= Be, Mg, Ca, Sr, or Ba

The nitrates of Na, K. Rb and Cs decompose to form metal nitrites and

O_2. $2MNO_3 \longrightarrow 2MNO_2 + O_2$

However, due to diagonal relationship between Li and Mg, lithium nitrate decomposes like $Mg(NO_3)_2$ to form metal oxide, NO_2 and O_2.

$$4LiNO_3 \xrightarrow{Heat} 2LiO_2 + 4NO_2 + O_2$$

3. Carbonates: Carbonates of alkaline earth metals decompose on heating to form metal oxide and carbon di oxide.

$$2MCO_3 \longrightarrow 2MO + CO_2 \quad M= Be, Mg, Ca, Ba$$

Further as the electropositive character of the metal increases down the group the stability of these metal carbonates increases or the temperature of their decomposition increases.

6. Sulphates: Sulphates of alkaline earth metals decompose on heating to form metal oxide and SO_3.

$$MSO_4 \xrightarrow{Heat} 2MO + SO_3 \quad M= Be, Mg, Ca, Ba$$

The temperature of decomposition of these sulphates increases as the electropositive character of the metal or the basicity of the metal hydroxide increases down the group.

Among the alkali metals due to diagonal relationship, Li_2SO_4 decomposes like $MgSO_4$ to form the corresponding metal oxide and SO_3.

$$Li_2SO_4 \xrightarrow{Heat} Li_2O + SO_3$$

$$MgSO_4 \xrightarrow{Heat} 2MgO + SO_3$$

Other alkali metals are stable to heat and do not decompose easily.

2. Compare the alkali metals and alkaline earth metals with respect to (i) ionization enthalpy (ii) basicity of oxides and (iii) solubility of hydroxides..

Ans.

3 Ionization enthalpy (I E): I E of alkaline earth metals are higher than those of alkali metals of group 1. This is because the atoms of alkaline earth metals have smaller size (due to higher nuclear charge) as compared to the alkali metals.

4 Basicity of oxides: The oxides of alkali and alkaline earth metals dissolve in water to form their respective hydroxides. These hydroxides are strong bases. The hydroxides of alkaline earth metals are less basic than of alkali metals of the corresponding periods. This is due to their (i) high ionization enthalpy (ii) small ionic size and (iii) dipositive charge on the ions.

As a result M-O bond in these hydroxides is relatively stronger than that of corresponding alkali metals and therefore does not break.

5 Solubility of hydroxides: Because of smaller size and higher ionic charge, the lattice enthalpies of alkaline earth metals are much higher than those of alkali metals and hence the solubility of alkali metal hydroxides is much higher than that of alkaline earth metals. However the solubility of the hydroxides of both alkali and alkaline earth metals increase down the group due to large decrease in their lattice enthalpies as compared to their hydration enthalpies.

4. Explain the significance of sodium, potassium, magnesium and calcium in biological fluids.

Ans. Significance of sodium and potassium:

12. Sodium ions participate in the transmission of nerve signals.

13. Sodium ions also regulate flow of water across the cell membranes and in transport of sugars and amino acids into the cells.

14. Potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in oxidation of glucose to produce ATP.

(iv) Potassium ions in combination with sodium ions are responsible for transmission of nerve signals.

(v) The functional features of nerve cells depend upon the sodium potassium ion gradient that is established in the cell.

Significance of Magnesium and Calcium:

1. Magnesium ions are concentrated in animal cells and Calcium ions are concentrated in body fluids, outside the cell.
2. All enzymes that utilize ATP in phosphate transfer require magnesium ion as cofactor.
3. In green plants magnesium is present in chlorophyll.
4. Calcium and magnesium ions are also essential for the transmission of impulses along nerve fibres.
5. Calcium ions are important in blood clotting and are required to trigger the contraction of muscles.
6. Calcium ions also regulate the beating of the heart.

HOTS QUESTIONS

1. Potassium carbonate cannot be prepared by Solvay process. Why?

Ans. This is due to the reason that potassium bicarbonate ($KHCO_3$) formed as an intermediate (when CO_2 gas is passed through ammoniated solution of potassium chloride) is highly soluble in water and cannot be separated by filtration.

2. The hydroxides and carbonates of sodium and potassium are easily soluble in water while the corresponding salts of magnesium and calcium are sparingly soluble in water. Explain.

Ans. All the compounds are crystalline solids and their solubility in water is guided by both lattice enthalpy and hydration enthalpy. In case of sodium and potassium compounds, the magnitude of lattice enthalpy is quite small as compared to hydration enthalpy since the cationic sizes are large. Therefore, the compounds of sodium and potassium that are mentioned, readily dissolve in water. However, in case of corresponding magnesium and calcium compounds, the cations have smaller sizes and more magnitude of positive charge. This means that their lattice enthalpies are more as compared to the compounds of sodium and potassium. Therefore, the hydroxides and carbonates of these metals are only sparingly soluble in water.

3. Why is LiF almost insoluble in water whereas LiCl soluble not only in water but also in acetone?

Ans. The low solubility of LiF in water is due to its very high lattice enthalpy (F^- ion is very small in size). On the other hand, in lithium chloride (LiCl) the lattice enthalpy is comparatively very small. This means that the magnitude of hydration enthalpy is quite large. Therefore lithium chloride dissolves in water. It is also soluble in acetone due to dipolar attraction. (Acetone is polar in nature)

CHAPTER11

Thep-blockelements

Elements in which the last electron enters in the any one of the three p-orbitals of their outermost shells–p-block elements

- Gen. electronic configuration of outer shell is ns^2np^{1-6}

The inner core of e- config. May differ which greatly influences their physical & to some extent chemical properties.

- The block of elements in the periodic table consisting of the main groups:
- Group13 (B toTl)
- Group14 (C to Pb)
- Group15 (N toBi)
- Group16 (O to Po)
- Group17 (F toAt)
- Group18 (He toRn)

(1) Members at the top and on the right of the *p*-block are nonmetals (C,N, P, O, F, S, Cl, Br, I, At).

(2)Those on the left and at the bottom are metals (Al,Ga,In,Tl, Sn, Pb, Sb, Bi,Po).

(3) Between the two from the top left to bottom right lie an ill-defined group of metalloid elements (B, Si, Ge, As,Te)

GROUP13 :The boron group

- Outer Electronic Configuration:-ns^2np^1
- group members: boron (B), aluminum (Al), gallium (Ga), indium (In)& thallium(Tl). All, except boron, are metals.
- Boron show diagonal relationship with Silicon; both are semiconductors metalloids & forms covalent compounds.
- Boron compounds are electron deficient, they are lack of an octet of electrons about the B atom.
- diborane B_2H_6, is simplest boronhydride

- Structure:three-centre two-electron: the H atoms are simultaneously bonded to two B atoms the B-H bridging bond lengths are greater than B-H terminal.
- -Boronoxide is acidic (it reacts readily with water to form boric acid)
- aluminium compounds: aluminiumoxide is amphoteric
- aluminum halides, e.g., $AlCl_3$ is dimer, an important catalyst in organic chemistry have an incomplete octet, acts as Lewis acid by accepting lonepairs from Lewis bases, forming adduct
- aluminum hydride, e.g., $LiAlH_4$, a reducing agent
- Atomic Properties-Electronic Configurations

Element	Symbol	Atomic No.	Electronic Configuration	Abundance in Earth's Crest (in ppm)
Boron	B	5	$[He]2s^2 2p^1$	8
Aluminium	Al	13	$[Ne]3s^2 3p^1$	81,300
Galium	Ga	31	$[Ar]3d^{10} 4s^2 4p^1$	15
Indium	In	49	$[Kr]4d^{10} 5s^2 5p^1$	1
Thallium	Tl	81	$[Xe]5d^{10} 6s^2 6p^1$	0.3

.Atomic and ionic radii

- The atomic and ionic radii of group 13 elements are compared to corresponding elements of group2. From left to right in the period, the magnitude of nuclear charge increases but the electrons are added to, the same shell. These electrons do not screen each other, therefore, the electrons experience greater nuclearcharge.
- In other words, effective nuclear charge increases and thus, size decreases. Therefore, the elements of this group have smaller size than the corresponding elements of second group.
- On moving down the group both atomic and ionic radii are expected to increase due to the addition of new shells. However, the observed atomic radius of Al (143pm) is slightly more than that of Ga (l35pm).

Ionization energies

The first ionization energies of group13elements are less than the corresponding members of the alkaline earths.

The sharp decrease in I.E. from B to Al is due to increase in size. In case of Ga, there are ten d-electrons in its inner electronic configuration.

The very high value of 3rd I.E. of thallium indicates that +3 O.N. state is not stable, rather +1 is more stable for thallium.

Electropositive (or metallic) character

The elements of group13 are less electropositive as compared to elements of group2. On moving down the group the electropositive (metallic) character increases because ionization energy decreases. For e.g., Boron is a non-metal while the other elements are typical metals.

Oxidation states

The common oxidation states of group13 elements are +3 and +l. The stability of the +1 oxidation state increases in the sequence Al<Ga<In<Tl due to Inert pair effect.

Element	B	Al	Ga	In	Tl
Oxidation state	+3	+3	+3,+1	+3,+1	+3,+1

Chemical reactivity of Gr.13 Elements

All elements in their compounds exhibit the oxidation state of +3 and +1.

Hydrides

- None of the group13 elements reacts directly with hydrogen. However, a no. of hydrides of these elements have been prepared by indirect methods. The boron hydrides are called boranes &classified in twos eries:

  (a)B_nH_{n+4} called nidoboranes (b) B_nH_{n+6} called arachnoboranes

- INUDUSTRIAL PREPARATION:-

  $2BF_3(g) + 6LiH(s) \rightarrow B_2H_6(g) + 6LiF(s)$

- Laboratory method:

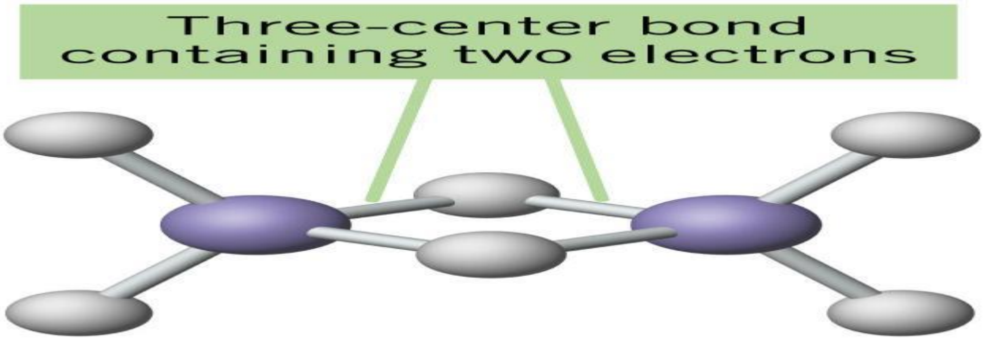
  (i) By the reaction of iodine with sodium borohydride in a high boiling solvent.

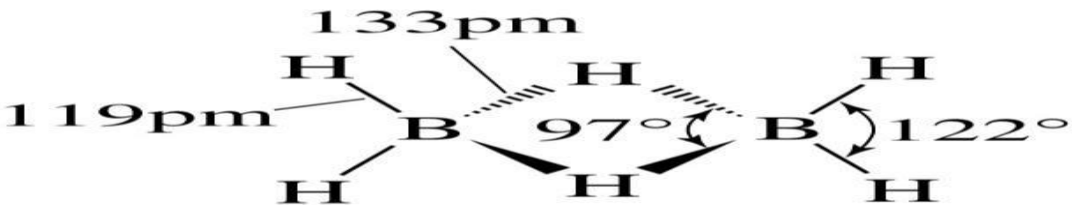
  $2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$

  (ii) By reduction of BCl_3 with $LiAlH_4$

  $4BCl_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$

Structure of Diborane, B_2H_6





Some important characteristics of boranes:

i) Lower boranes are colourless gases while higher boranes are volatile liquids or solids.

ii) They undergo spontaneous combustion in air due to strong affinity of boron for oxygen.

$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O + Heat$

iii) Boranes react with alkali metal hydrides in diethyl ether to form borohydride complexes.

$B_2H_6 + 2MH \rightarrow 2M^+[BH_4]^-$ (M=LiorNa)

Metalborohydride

- (iv)Diborane reacts with ammonia to give borazine at 450K.

  $B_2H_6 + 6NH_3 \rightarrow 3B_3N_3H_6 + 12H_2$

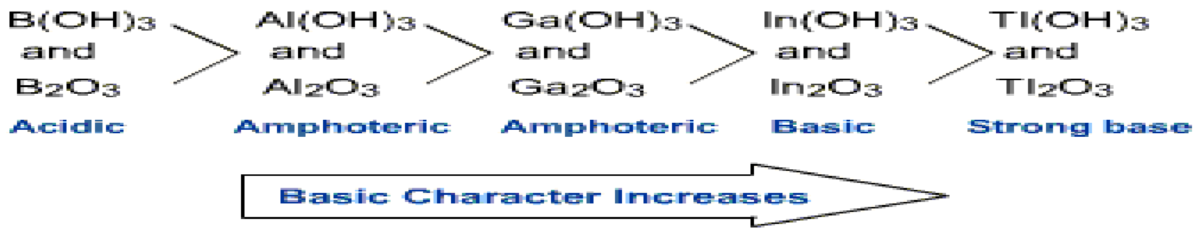
- Borazine has a cyclic structure similar to benzene and thus is called inorganic benzene
- The other elements of this group form only a few stable hydrides. The thermal stability decreases as we move down the group.

- AlH_3 is a colourlesss solid polymerized viaAl-H-Al bridging units. These hydrides are weak Lewis acids and readily form adducts with strong Lewis base (B:) to give compounds of the type MH_3 (M=AlorGa). They also form complex-tetrahydridoanions, [MH4]-. The most important tetrahydridocompound is $Li[AlH_4]$

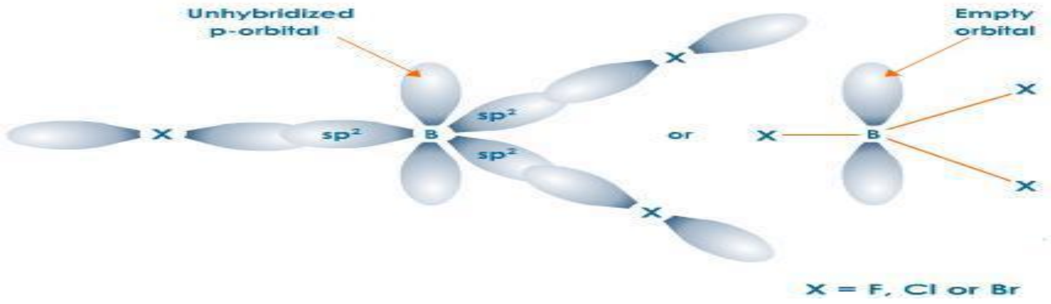
$$4LiH+AlCl_3 \xrightarrow{\text{ether}} LiAlH_4 \quad +3LiCl$$

OXIDES & HYDROXIDES

- M_2O_3 & $M(OH)_3$

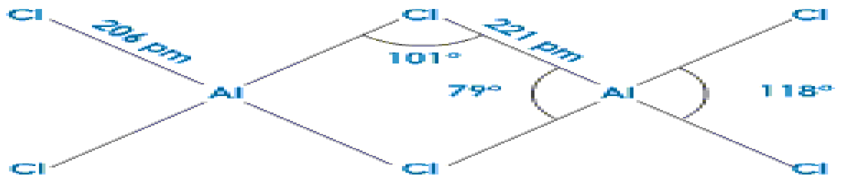


HALIDES:Structureofborontrihalides



Dimeric structure of aluminium chloride

– Boron halides do not form dimmers because the size of boron is so small that it is unable to coordinate four large-sized halide ions.



- Anomalous properties of boron

1. Boron is a non-metal & bad conductor of electricity where as aluminium is a metal & good conductor. B is hard but Al is a soft metal.
2. Boron exists in two forms-crystalline and amorphous. But Al does not exist in different forms.

3.The melting and boiling point of boron are much higher than that of Al.

4.Boron forms only covalent compounds where as Al forms even some ionic compounds.

5.The hydroxides and oxides of boron are acidic in nature where as those of aluminium are amphoteric.

6.The trihalides of boron exist as monomers. On the other hand, aluminium halides exist as dimers.

7.The hydrides of boron are quite stable while those of aluminium are unstable

- Boron and silicon exhibit the typical properties of non-metals. These donot form cations. Both exist in amorphous as well as crystalline forms.
- Boron oxide (B_2O_3) and silica (SiO_2) both are acidic and dissolve in alkali solutions to form borates and silicates respectively.

  $B_2O_3 + 6NaOH \rightarrow 2Na_2BO_3 + 3H_2O$

  $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$
- The chlorides of both B and Si get hydrolyzed by water to boric acid and silicic acid respectively.

  $BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$ $SiCl_4 + 3H_2O \rightarrow H_2SiO_3 + 4HCl$
- The hydrides of Boron and Silicon are quite stable. Numerous volatile hydrides are also known which catch fire on exposure to air and are easily hydrolyzed.
- Both elements are semiconductors.

Behaviour in Aqueous Solutions

1 Al, Ga, In and Tl exhibit a well-defined aqueous chemistry in their tripositive states. Species like $[M(OH)_4]^-$,$[M(H_2O)_2(OH)_4]^-$,$[M(OH_2)_6]^{3+}$ for M=Al, Ga, in exist in aqueous solution.

2. Al, Ga. In and T1 ions exist as octahedral aqua ions, $[M(OH_2)_6]^{3+}$ in aqueous solution and many salts like halides, sulphates, nitrates and perchlorates exist as hydrates.

3.Aluminium sulphate forms double salts- called alum, having the general formula

$M_2SO_4.Al_2(SO_4)_3.12H_2O$, where M=$Na^+orK^+$.

USES OF BORON & ALUMINIUM

- Aluminium is used extensively in industry and everyday life. It forms many useful alloys with Cu, Mn, Mg, Si and Zn. Hence, aluminium and its alloys find use in packaging, utensil making, construction, aerospace and other transportation industries. It is used as a conductor for transmission of electricity. Aluminium is also used in the alumino-thermite process for production of chromium and manganese from their ores.

Group 14 Elements:- The Carbon Family

Group 14 includes carbon(C), silicon(Si), germanium(Ge), tin(Sn) and lead (Pb).

General electronic configuration of carbon family is ns^2np^2.

Covalent radius:-Covalent radius expected to increase from C to

Si, From Si to Pb small increase is found.

Ionization Enthalpy:-The first ionization enthalpies of group 14 elements are higher than those of the corresponding group13 elements.

Electronegativity:-Group 14 elements are smaller in size as compared to group 13 elements that's why this group elements are slightly more electronegative than group 13

Chemical properties:-

Carbon and silicon mostly show +4 oxidation state. Germanium forms stable compounds in +4 state and only few compounds in +2 state.

Tin forms compounds in both oxidation states. Lead compounds in +2 state are stable and in +4 state are strong oxidizing agents.

Exception:-PbF_4 and SnF_4 are ionic in nature.

Except CCl_4 other tetrachlorides are easily hydrolysed bywater.

Since carbon does not have d-orbitals and hence cannot expand its coordinationnumber beyond 4

$$CCl_4 + H_2O \rightarrow \text{No Reaction}$$

$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$$

Silicicacid

Allotropes of Carbon:-The three types of allotropes are–

1-Diamond 2-Graphite 3-Fullerence

Diamond:-In diamond each carbon atom under goes SP^3hybridisation. Each carbon is tetrahedrally linked to four other carbon atoms.

Graphite:-In graphite, carbon is SP^2-hybridized graphite has a two-dimensional sheet like structure consisting of a number of hexagonal rings fused together.

Graphite conducts electricity along the sheet. It is very soft and Slippery

Fullerene was discovered collectively by three scientists namely R.ESmalley, R.FCurl andH.WKroto

Some Important Compounds Of Carbon and Silicon

Carbon monoxide:-It is prepared by direct oxdisation of C in limited supply of oxygen.

$$2C+O_2(g) \rightarrow 2CO(g)$$

Commercially it is prepared by the passage of steam over hot coke

Carbon dioxide:-It is prepared by complete combustion of carbon and carbon fuels in excess of air.

$$C(s)+O_2(g) \rightarrow CO_2(g)$$

Laboratory method:-

In laboratory it is prepared by the treatment of dil HCl on $CaCO_3$

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

Silicon dioxide:-Silicon dioxide is a COVALENT THREE DIMENSIONAL NETWORK SOLID.

Each silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms.

Silicones:-Silicones are the synthetic organo-silicon polymers having general formulae $(R_2SiO)_n$ in which R=alkyl (methyl, ethyl or phenyl)

Silicates:-Silicates exist in nature in the form of feldspar, zeolites, mica and asbestos etc.

The basic structure of silicates is SiO_4^{4-}

Zeolites:-Zeolites is a alumino-silicate of metal. Metal cations participating in formation of Zeolite are usually Na^+,K^+,or Ca^{2+}.

Zeolites are used to remove permanent hardness of water.

ONE MARK QUESTIONS

1. Why is boron used in nuclear reactions ?

Ans:-Because Boron can absorb neutrons.

2.By giving a balanced equation show how $B(OH)_3$ behaves as an acid in water.

Ans:-$B(OH)_3+2H_2O \longrightarrow [B(OH)_4]^-+H_3O^+$

3.Name the element of group 14 which exhibits maximum tendency for catenation?

Ans:-Carbon

4.What is the basic building unit of all silicates?

Ans:-$SiO_4^{4-}$is the basic unit of all silicates.

5.What happens when $NaBH_4$ reacts with iodine?

Ans:-$2NaBH_4+I_2 \longrightarrow B_2H_6+2NaI+H_2$.

6.What happens when boric acid is heated?

Ans:-$4H_3BO_3 \longrightarrow 4HBO_2 \longrightarrow H_2B_4O_7$.

7.What is producer gas?

Ans:-Producer gas is a mixture of CO and N_2 in the ratio of 2:1.

8. Write the state of hybridization of 'B' in BF_3.

ANS:-Hybridisation of 'B' in BF_3 is Sp^2.

9. Mention the state of hybridization in B in BH_4^-.

Ans:-Sp^3.

10.Which oxide of carbon is regarded as an hydride of carbonic acid.

Ans:-CO_2 is regarded as a hydride of carbonicacid.

Because $H_2CO_3 \rightarrow H_2O+CO_2$

TWO MARKS QUESTIONS

1.Give the chemical reaction as an evidence for each of the following observations.

(i) Tin (II) is a reducing agent where as lead(II) isnot.

(ii)Gallium (I) undergoes disproportionation reaction.

Ans:-(i) Due to inert pair effect Pb^{2+} is more stable than Pb^{4+}. Whereas Sn^{4+} is more stable than Sn^{2+}.

(ii)$3Ga^{+} \rightarrow 2Ga + Ga^{3+}$

This is because Ga^{3+} is more stable than Ga^{+}.

2.What happens when

(i) Quick lime is heated with coke ?

(ii) Carbon monoxide reacts with Cl_2

Ans:-(i) $CaO+3C \rightarrow CaC_2+CO$

(iii) $CO+Cl_2 \rightarrow COCl_2$

3.Give reason

(i)C and Si are always tetravalent but Ge, Sn,Pb show divalency.

(ii) Gallium has higher ionization enthalpy than Al. Explain.

Ans:-(i)Ge, Sn,Pb show divalency due to inert pair effect, Pb^{2+} is more stable than Pb^{4+}.

(ii)Due to poor shielding effect of d-electrons in Ga effective nuclear charge increases as compared toAl thus the I.E is higher than Al.

4.Give reason why boron and aluminium tend to form covalent compounds.

Ans:-Sum of three ionization of both the element are very high. Thus they have no tendency to lose electrons to form ionic compound. Instead they form covalent compounds.

5.If B-Cl bond has a dipole moment, Explain why BCl_3 molecule has zero dipole moment.

Ans:-B-Cl bond has dipole moment because of polarity. In BCl_3 since the molecule is symmetrical thus the polarities cancel out.

6.Suggest a reason as to why CO is poisonous.

Ans:-CO reacts with haemoglobin to form carboxy-haemoglobin which can destroy the oxygen carrying capacity of haemoglobin and the man dies of suffocation.

6. What do you understand by-

(a)Inert pair effect:-The pair of electron in the valence shell does not take part in bond formation it is called inert pair effect.

(b)Allotropy:-It is the property of the element by which an element can exists in two forms which have same chemical properties but different physical properties due to thei rstructures.

8.How is excessive content of CO_2 responsible for global warming?

Ans:-Excess of CO_2 absorbs heat radiated by the earth. Some of it dissipates in the atmosphere while the remaining heat is radiated back to the earth. Temperature of the earth increases.

9. Describe two similarities and two dissimilarities between B and

Al. Ans:-Similarities:-

(i) Both have same number of valence electrons.
(ii) Both have similar electronic configuration.

Dissimilarities:-

(i) B is a non-metal where Al is a metal.
(ii) B forms acidic oxide whereas Al forms amphoteric oxides.

10.What are fullerenes? How were they prepared?

Ans:-Fullerene is the allotrope ofcarbon. Its structure is like a soccerball.

Fullerenes are prepared by heating graphite in electric arc in presence of inert gases such as helium or argon.

THREE MARKS QUESTIONS

1. What happens when

(a)Borax is heated strongly

(b)Boric acid is added to water

(c) Aluminium is treated with dilute NaOH

Ans:-(a)$Na_2B_4O_7.10H_20 \rightarrow Na_2B_4O_7 \rightarrow 2NaBO_2+B_2O_3$

(b)$B(OH)_3+H_2O \rightarrow [B(OH)_4]^-+H^+$

(C)$2Al+2NaOH+H_2O \rightarrow 2NaAlO_2+3H_2$

2.Explain the following reactions.

(a)Silicon is heated with methyl chloride at high temperature in the presence of copper.

(b)Silicon dioxide is treated with hydrogen fluoride.

(c) CO is heated with ZnO.

Ans:-(a)A mixture of mono-,di-and trimethyl chloro silianes along with a small amount of tetra methyl silane is formed.

$CH_3Cl+Si \rightarrow CH_3SiCl_3+(CH_3)_2SiCl_2+(CH_3)_3SiCl+(CH_3)_4Si$

(b) The initially formed silicon tetra fluroide dissolves in HF to form hydro fluoro silicic acid

$SiO_2+2HF \rightarrow SiF_4+2H_2O$

$SiF_4+2HF \rightarrow H_2SiF_6$

(c) ZnO is reduced to zinc metal

$ZnO +CO \rightarrow Zn+CO_2$

3.Give reasons:-

(a)Diamond is used as an abrasive.

(b)Aluminium alloys are used to make aircraft body.

(c)Aluminium utensils should not be kept in water overnight.

Ans:-(a) Diamond is used as an abrasive because it is an extremely hard substance.
(b)Alloys of alumimium like duralium is used to make aircraft body due to some of its property.

(d) Generally aluminium metal doesnot react with water quickly but when it is kept overnight. It reacts slowly with water in presence of air.

$$2Al(s)+O_2(g)+H_2O(l) \rightarrow Al_2O_3(s)+H_2(g)$$

4.A certain salt X, give the following results. (i) Its aqueous solution is alkaline to litmus.

(ii)It swells up to a glassy material Y on strong heating.

(iii) when conc.H_2SO_4 is added to a hot solution of X, white crystal of an acid Z separates out.

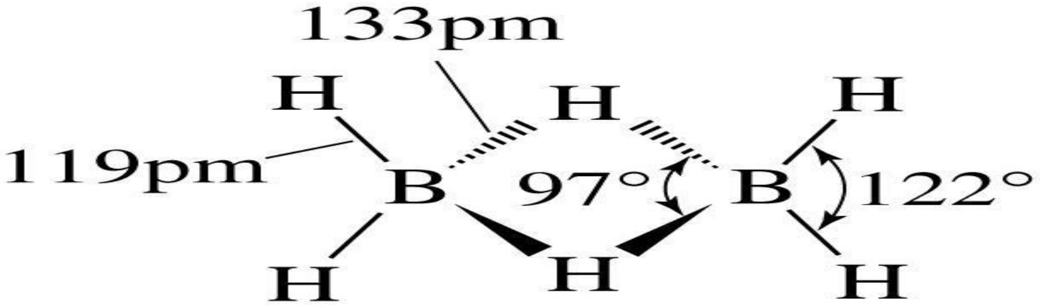
Ans:-(i) $Na_2B_4O_7+10H_2O \rightarrow 2NaOH+H_2B_4O_7+8H_2O$

(ii) $Na_2B_4O_7 \rightarrow 2NaBO_2+B_20_3$

(iii)$Na_2B_4O_7.10H_2O+H_2SO_4 \rightarrow 4H_3BO_3+Na_2SO_4+5H_2O$

5. Draw structure of diborane.

Ans.



FIVE MARKS QUESTIONS

1 Explain the formation of (i) Watergas (ii) Producergas. Give their uses. What happens when CO_2 is passed through lime water (i) for short duration (ii) fo long duration.

Ans:-(i)$C(s)+H_2O(g) \rightarrow CO(g)+H_2(g)$
(Watergas)

(ii) $2C(s)+ O_2+4N_2(g) \rightarrow 2CO(g)+4N_2(g)$
(Producergas)

Water gas and Producer gas are used asfuel.

$Ca(OH)_2+CO_2 \rightarrow CaCO_3+H_2O$

(Whiteppt.)

(i) $CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$
(Soluble)

2 (a)Why do Boron halides form addition compound with NH_3?
(b)Assign appropriate reason for each of the following observations:-

(i) Anhydrous $AlCl_3$ is used as a catalyst in many organic reactions.
(ii) No form of elemental silicon is comparable to graphite.

Ans:- (a) It is because BX_3 is electron deficient whereas NH_3 is electron rich.

(b) (i) It is Lewis acid.

(ii) It cannot form pπ–pπ bond due to large size.

3.(i) Give reason for the following observations:-
(a)The tendency for catenation decreases down the group in Group14.
(b)The decreasing stability of +3 oxidation state with increasing atomic number in group 13.
(c) PbO_2 is a stronger oxidizing agent than SnO_2.
(d) Molten aluminium bromide is a poor conductor of electricity.

Ans:- (i) (a) It is due to decrease in bond dissociation energy which is due to increase in atomic size.

C-C>Si-Si>Ge-Ge>Sn-Sn>Pb-Pb.

(b) It is due to inert pair effect.

(c) PbO_2 is stronger oxidizing agent than SnO_2 because Pb^{2+} is more stable than Pb^{4+} whereas $Sn^{4+}$is more stable than Sn^{2+}.

(d) Molten $AlBr_3$ is poor conductor of electricity because it is covalent compound.

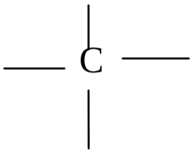
CHAPTER12

Organicchemistry: Some Basic Principles and Techniques

Organic compounds are the hydrocarbons and their derivativesand organic chemistry is that branchof chemistry that deals with the study of these compounds

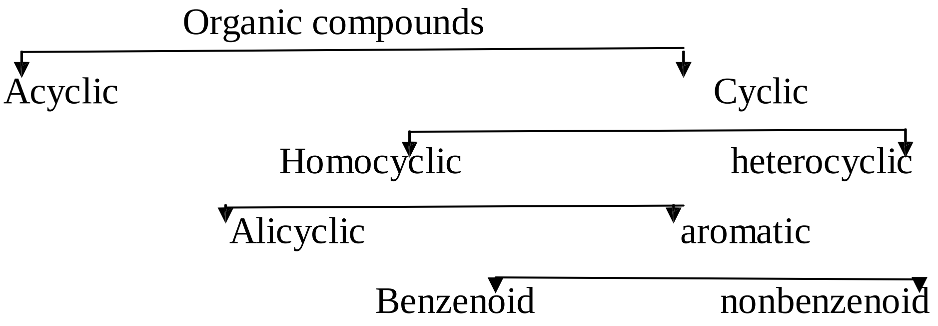
Tetravalency of carbon

The atomic number of Carbon is 6 and its electronic configuration is 2, 4 i.e.it has 4 valence electrons. Thus carbon is always tetracovalent, i.e.it forms 4 covalent bonds with other atoms



Catenation –The self linking property of carbon is known as catenation. This is the main reason of existence of such large number of compounds

Classification of organic compounds



Functional groups: A functional group may be defined as an atom or a group of atoms present in a molecule which largely determines the chemical properties.

CLASS OF ORGANIC COMPOUNDS	NAME OF FUNCTIONAL GROUP	STRUCTURE
Alkenes	double bond	-C=C-
Alkynes	triple bond	-CΞC-
Halogens	halogen	-X(F,Cl,Br,I)
Alcohols	hydroxyl	-OH
Aldehydes	aldehydic (formyl)	-CHO
Carboxylic acids	carboxyl	-COOH
Acid amides	amides	$-CONH_2$
Primary amines	amino	$-NH_2$

HOMOLOGOUS SERIES

Homologous series is defined as a family or group of structurally similar organic compounds all members of which contain the same functional group, show a gradation in physical and similarity in chemical properties and any two adjacent members of which differ by -CH_2 group. The individual members of this group are called homologues and the phenomenon is called homology.

NOMENCLATURE OF ORGANIC COMPOUNDS

Organic chemistry deals with millions of compounds. In order to clearly identify them, a systematic method of naming known as IUPAC system of nomenclature is adopted. The names are such that the listener can deduce the structure from it. The IUPAC name consists of three parts:

	Prefix	Word root	Suffix
EX:	3methyl	oct	ane

NOMENCLATURE OF ALKANES Straight chain alkanes:

The names of such compounds is based on their chain structure, and end with suffix ‘-ane’and carry a prefix indicating the number of carbon atoms present in the chain.

Branched chain hydrocarbons:

1.)The longest carbon chain in the molecule is identified.
2.)The numbering is done in such a way that the branched carbon atoms get the lowest possible value.
3.)The names of the alkyl groups attached as a branch are then prefixed to the name of the parent alkane and its position is indicated bynumbers.
4.)The lower number is given to the first in alphabetical order.
5.) The carbon atom of the branch that attaches to the root alkane is numbered 1.

Organic compounds having Functional Groups:

The longest chain of carbon atoms containing the functional groups is numbered in such a way that the functional group attached to the carbon atom gets the lowest possible number in the chain.

When there are more functional groups then a priority order is followed as:

-COOH,-SO_3H,-COOR,COCl,-$CONH_2$,-CN,-HC=O,=C=O,-OH,-NH_2,=C=C=, -CΞ C-.

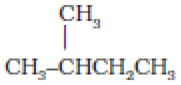
ISOMERISM

Two or more compounds having the same molecular formula but different physical and chemical properties are called isomers and this phenomenon is called isomerism.

Chain isomerism: When two or more compounds having same molecular formula but different carbon skeletons are referred to as chain isomers.

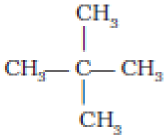
Pentane

$CH_3CH_2CH_2CH_2CH_3$



Isopentane
(2-Methylbutane)

$CH_3-CH(CH_3)CH_2CH_3$



Neopentane
(2,2-Dimethylpropane)

$CH_3-C(CH_3)_2-CH_3$

Position Isomerism: Compounds which have the same structure of carbon chain but differ in position of double or triple bonds or functional group are called position isomers and this phenomenon is called Position Isomerism. e g

$CH_3\text{-}CH_2\text{-}CH{=}CH_2$ $\qquad$ $CH_3\text{-}CH{=}CH\text{–}CH_3$

Functional Isomerism: Compounds which have the same molecular formula but different functional group are called functional isomers and this phenomenon is called functional Isomerism.e g

$CH_3\text{–}CH_2\text{–}OH$ $\qquad$ $CH_3\text{–}O\text{–}CH_3$

Metamerism: It is due to the presence of different alkyl groups on either side of functional group in the molecule. Ex. $C_4H_{10}O$ represents $C_2H_5OC_2H_5$ and $CH_3OC_3H_7$.

FISSION OF COVALENT BOND

Heterolytic cleavage: In this cleavage the bond breaks in such a way that the shared pair of electron remains with one of the fragments.

$H_3C\text{–}Br \longrightarrow {}^{+}CH_3 + Br^{-}$

Homolytic Cleavage: In this cleavage the shared pair of electron goes with each of the bonded atom.

$R\text{–}X \longrightarrow R^{\cdot} + X^{\cdot}$

Alkyl free radical

Nucleophiles: A reagent that brings an electron pair is called nucleophile i.e. nucleus seeking eg -OH,-CN

Electrophiles: A reagent that takes away electron pair is called electrophile
i.e. electron seeking eg>C=O, $R_3C\text{–}X$, CH_3^{+}

Inductive Effect: The displacement of the electron along the chain of the carbon atoms due to presence of an atom or group at the end of the chain.

$$\overset{\delta+++}{CH_3} \rightarrow \overset{\delta++}{CH_2} \rightarrow \overset{\delta+}{CH_2} \rightarrow Cl$$

Resonance Effect: The polarity produced in the molecule by the interaction of two pi bonds or between a pi bond and lone pair of electron present on an adjacent atom.

There are two types of resonance effect:

1)Positive resonance effect: In this effect the transfer of electrons is away from an atom or substituent group attached to the conjugated system.

The atoms or groups which shows +R effect are halogens, -OH, -OR,-NH_2

2) Negative resonance effect:In this effect the transfer of electrons is towards the atom or substituent group attached to the conjugated system.

The atoms or groups which shows – R effect are –COOH,-CHO,-CN

METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

:Sublimation : This method is used to separate the sublimable compounds from non sublimable compounds.

Crystallisation: This method is based on the difference in the solubilities of compound and impurities in a suitable solvent. The impure compound is dissolved in solvent and heated at higher temp. On cooling, from the hot and conc solution pure compounds crystallize out.

Distillation: This method is used to separate volatile liquids from non volatile liquids and liquids having sufficient difference in their boiling points.

Fractional distillation: If the boiling points of two liquids is not much, they are separated by this method.

Distillation under reduced pressure: This method is used to purify liquids having high boiling points and decomposes at or below their boiling points.

Steam distillation: This method is used to separate substances which are steam volatile and are immiscible with water.

Differential Extraction: When an organic compound is present in an aqueous medium it is separated by shaking it with organic solvent in which it is mores oluble than in water.The aqueous solution is mixed with organic solvent in a separating funnel and shaken for sometimes and then allowed to stand for sometime. When organic solvent and water form two separate layers the lower layer is run out by opening the tap of funnel and organic layer is separated. The process is repeated several times and pure organic compound is separated.

Chromatography : This technique is used to separate mixtures into their components, purify the compounds and test the purity of compounds. It is classified as
Adsorption Chromatography: It is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Silica gel or alumina is used as

adsorbents.

Partition Chromatography:It is based on the continuous differential partitioning of components of a mixture between stationary and mobile phase.

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Detection of Carbon and Hydrogen: The Carbon and Hydrogen present in the Organic compound is detected by heating the compound with Copper (II) oxide in a hard glass tube when carbon present in the compound is oxidized to CO_2 which can be tested with lime Water and Hydrogen is converted to water which can be tested with anhydrous copper sulphate which turns blue.

$C+CuO \longrightarrow 2Cu+ CO_2$
$2H+CuO \rightarrow Cu+ H_2O$
$CO_2 +Ca(OH)_2 \longrightarrow CaCO_3 +H_2O$
$5H_2O+ CuSO_4 \longrightarrow CuSO_4.5H_2O$

DETECTION OF OTHER ELEMENTS

Sodium Fusion Extract: A small piece of dry Sodium metal is heated with an organic compound in a fusion tube for 2-3 minutes and the red hot tube is plunged into distilled water contained in a china dish. The content of the china dish is boiled ,cooled and filtered. The filtrate is known as Sodium fusion extract.

Test for Nitrogen: The sodium fusion extract is boiled with iron (II) sulphate and then acidified with Conc sulphuric acid, the formation of Prussian blue colour confirms the presence of nitrogen.

$6CN^{-}+Fe^{2+} \longrightarrow [Fe(CN)_6]^{4-}$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3.xH_2O}$$

Testfor Sulphur: The sodium fusion extract is acidified with aceticacid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur. $S^{2-}+Pb^{2+} \longrightarrow \underset{\text{Black}}{PbS}$

Test for halogens: The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish ppt. sparingly soluble in ammonium hydroxide shows the presence of bromine, a yellowish ppt. insoluble in ammonium hydroxide shows the presence of iodine.

$X^{-} +Ag^{+} \longrightarrow AgX$

QUANTITATIVEANALYSIS(Carbonand Hydrogen)

Let the mass of organic compound be m g.Mass of water and carbon di oxide produced be m_1 and m_2 g respectively;

$$\%\text{ofcarbon} = \frac{12 \times m_2 \times 100}{44 \times m}\ \%$$

$$\%\text{ofhydrogen} = \frac{2 \times m_1 \times 100}{18 \times m}\ \%$$

Nitrogen

DUMAS METHOD: A known mass of organic compound is heated with excess of CuO in an atmosphere of CO_2, when nitrogen of the organic compound is converted into N_2 gas.The volume of N_2 thus obtained is converted into STP and the percentage of nitrogen determined by applying the equation:

$$\text{Volume of Nitrogen at STP} = \frac{P_1V_1 \times 273}{760 \times T_1}$$

$$\%N = \frac{28 \times \text{vol of } N_2 \text{ at STP} \times 100}{22400 \times \text{mass of the substance taken}}$$

KJELDAHL'S METHOD: A known mass of organic compound is heated with conc. H_2SO_4 in presence of K_2SO_4 and little $CuSO_4$ or Hg in along necked flask called Kjeldahl's flask when nitrogen present in the organic compound is quantitatively converted into $(NH_4)_2SO_4$. $(NH_4)_2SO_4$ thus obtained is boiled with excess of NaOH solution to liberate NH_3 gas which is absorbed in a known excess of a standard acid such as H_2SO_4 or HCl.

The volume of acid unused is found by titration against a standard alkali solution. From the volume of the acid used, the percentage of nitrogen is determined by applying the equation,

$$\%N = \frac{1.4 \times \text{Molarityoftheacid} \times \text{Basicityoftheacid} \times \text{Voloftheacidused}}{\text{Massofthe substancetaken}}$$

Halogens

Carius method:

A known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass test tube known as carius tube in a furnace. Carbon and hydrogen present in the compound are oxidized to carbon di oxide and water. The halogen present forms the corresponding silver halide. It is filtered, dried, and weighed.

Let the mass of the organic compound taken = m g

Mass of AgX formed =m_1 g

1 mol of AgX contains 1 mol of X

Mass of halogen in m_1 g of AgX

$$= \frac{\text{at mass of X} \times m_1 \text{ g}}{\text{Molecular mass of AgX}}$$

% of halogen

$$= \frac{\text{at mass of X} \times m_1 \text{ g} \times 100\ \%}{\text{Molecularmassof AgX} \times m}$$

Sulphur

Let the mass of the organic compound taken = m g

Mass of $BaSO_4$ formed = m_1 g

% of sulphur $= \frac{32 \times m_1 \times 100}{233 \times m}$ %

Phosphorous

Let the mass of the organic compound taken = m g

Mass of ammonium phosphomolydate = m_1 g

% of phosphorous = $\frac{31 \times m_1 \times 100}{1877 \times m}$ %

Oxygen

Let the mass of the organic compound taken = m g

Mass of CO_2 = m_1 g

% of oxygen = $\frac{32 \times m_1 \times 100}{44 \times m}$ %

One Mark Questions

Q1 Suggest a method to purify a liquid which decomposes at its boiling point.

A1 The process Distillation Under reduced pressure is used to purify a liquid which decomposes at its boiling point.

Q2 How will you separate a mixture of O-nitrophenol and p-nitrophenol ?

A2 o-nitrophenol is steam volatile therefore it can be separated by Steam distillation.

Q3 Lassaigne'stest is not shown by diazonium Salt. Why?

A3 On heating diazonium Salts loses Nitrogen and cannot fuse with the Sodium metal therefore diazonium Salts do not show Positive Lassaigne's test for nitrogen.

Q4 Alcohols are weaker acids than Water, Why ?

A4 The alkyl group in alcoh~~ols~~ has + I effect due to which electron density is increased on Oxygen atom which makes the release of hydrogen ion more difficult from alcohol. $R \rightarrow O \rightarrow H$

Q5 Why is nitric acid added to Sodium extract before adding Silver nitrate for testing halogens?

A5.Nitric acid is added to decompose NaCN and Na_2S

$NaCN + HNO_3 \rightarrow NaNO_3 + HCN$

$Na_2S + 2HNO_3 \rightarrow 2NaNO_3 + H_2S$

Q6 Which of the two $O_2NCH_2CH_2^-$ or $CH_3CH_2O^-$ is expected to be more stable and why?

A6. NO_2 group has–I effect and disperse the negative charge on Oxygen atom

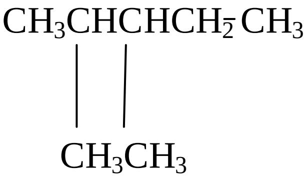
$O_2N \leftarrow CH_2 \leftarrow CH_2O^-$

Q7. Arrange the following in increasing Order of Stability;

$(CH_3)_3C^+$, $CH_3CH_2CH_2C^+H_2$, $CH_3CH_2C^+HCH_3$, $CH_3C^+H_2$, $CH_3CH_2C^+H_2$

A7. $CH_3C^+H_2 < CH_3CH_2C^+H_2 < CH_3CH_2CH_2C^+H_2 < CH_3CH_2C^+HCH_3 < (CH_3)_3C^+$

Q8 Write the IUPAC name of the following



$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$

A8 2,3-Dimethylpentane

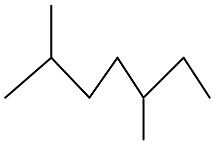
Q9 Write the hybridized state of C atoms in the following

$CH_2 = CH - C \Xi N$

A9 sp^2 sp^2 sp

$CH_2=CH-C\Xi N$

Q10 Give the IUPAC name of the following compound.



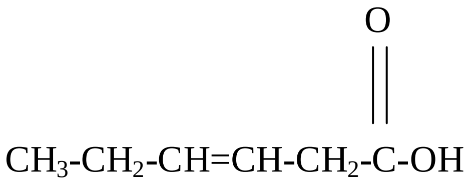
A10 2,5Dimethylheptane

Two Marks Questions

Q1Draw the Structures of the following compounds.

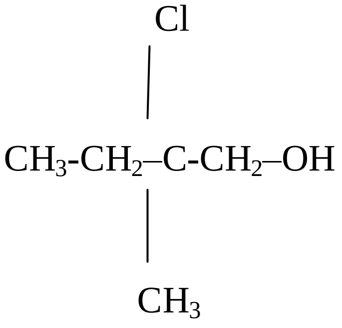
A) Hex-3-enoicacid b)2-Chloro-2-methylbutan-1-ol

A1 a)



$CH_3-CH_2-CH=CH-CH_2-\overset{\overset{O}{\|}}{C}-OH$

b



$CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2-OH$

Q2. Explain Inductive effect withexample.

A2 Inductive Effect:The displacement of the electron along the chain of the carbon atoms due to presence of an atom or group at the end of the chain.

$\delta+++$ $\delta++$ $\delta+$

$CH_3\rightarrow$ $CH_2 \rightarrow$ CH_2 $\rightarrow Cl$

Q3Explain why $(CH_3)_3C^+$is more stable than $CH_3C^+H_2$.

A3 $(CH_3)_3C^+$ has nine alpha hydrogen atoms and has nine hyperconjugation structures while $CH_3C^+H_2$has three alpha hydrogen atoms and has three hyperconjugation structures, therefore $(CH_3)_3C^+$ is more stable than $CH_3C^+H_2$

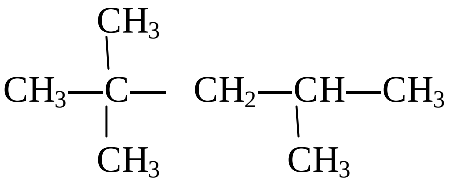
Q4 Give the number of Sigma and pi bonds in the following molecules

a) CH_3NO_2 b)$HCONHCH_3$

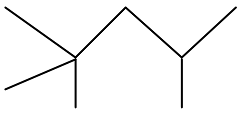
A4 a) 6 Sigma and 1 pi bond

b)8 Sigma and 1 pi bond

Q5 Write the condensed and bond line formula of 2,2,4-Trimethylpentane.
A5



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-\;CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$



Q6 How is Sodium fusion extract is prepared?

A6 A small piece of dry Sodium metal is heated with an organic compound in a fusion tube for 2-3 minutes and the red hot tube is plunged into distilled water contained in a china dish. The content of the chinadish is boiled, cooled and filtered. The filtrate is known as Sodium fusion extract.

Q7. Explain the principle of paper chromatography.

A7 Paper chromatography is based on the difference in the rates at which the components of a mixture are adsorbed. The material on which different components are adsorbed is called Stationary phase which is generally made up of alumina, silicagel or activated charcoal. The mixture to be separated is dissolved in a suitable medium and it is called moving phase. The moving phase is run on the Stationary phase, the different compounds are adsorbed on stationary phase at different rates.

Q8 Why is an organic compound fused with Sodium for testing nitrogen, halogens and sulphur?

A8 On fusing with sodium metal the elements present in an organic compounds are converted into sodium salts which are water soluble which can be filtered and detected by the respective tests.

Q9 It is not advisable to use sulphuric acid in place of acetic acid for acidification while testing sulphur by lead acetate test.Givereason.

A9. Lead acetate on reacting with sulphuric acid will give a white ppt of leadsulphate which interferes in the detection of sulphur.

$$(CH_3COO)_2Pb \quad + \quad H_2SO_4 \longrightarrow PbSO_4 + 2\ CH_3COOH$$

Q10 Under what conditions can the process of steam distillation be used?

A10 Steam distillation is used to purify the liquids which are steam volatile and water and the liquid are not miscible with each other.

Three Marks Questions

Q1 In an estimation of sulphur by carius method 0.468 g of an organic compound gave 0.668 g of barium sulphate. Find the percentage of sulphur in the compound.

A1 Mass of the compound=0.468g
Mass of the barium sulphate=0.668g

$$\% \text{ of sulphur} = \frac{32 \text{ X Massofbariumsulphate X}100}{233\text{XMassofthecompound}}$$

$$= \frac{32 \text{ x}0.668\text{x}100}{233\text{x}0.468}$$

=19.60 %

Q2 Which bond is more polar in the following pairs of molecules.

a) H_3C-H, H_3C-Br   b) H_3C-NH_2,H_2C-OH   c) H_3C-OH, H_3C-SH

A2 a) C-Br because Br is more electronegative than C

b) C-O because O is more electronegative than N
c) C-O because O is more electronegative than S

Q3 Define Isomerism .Explain position Isomerism and Functional Isomerism with examples.

A3 Two or more compounds having the same molecular formula but different physical and chemical properties are called isomers and this phenomenon is called isomerism.

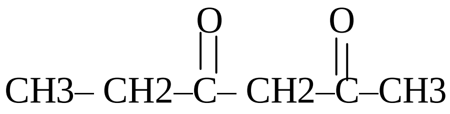
Position Isomerism : Compounds which have the same structure of carbon chain but differ in position of double or triple bonds or functional group are called position isomers and this phenomenon is called positionIsomerism. e g

CH_3-CH_2-CH=CH_2 CH_3-CH=CH–CH_3

Functional Isomerism :Compounds which have the same molecular formula but different functional group are called functional isomers and this phenomenon is called functional Isomerism.e g

CH_3–CH_2–OH CH_3–O–CH_3

Q4 Write the IUPAC names of the following compounds.

A.


$$\text{CH3– CH2–}\overset{\overset{\displaystyle O}{||}}{\text{C}}\text{– CH2–}\overset{\overset{\displaystyle O}{||}}{\text{C}}\text{–CH3}$$

B. HCΞC–CH=CH– CH–CH_2

C. Cl$CH_2CH_2CH_2CH_2$Br

A4 A hexane2,4dione

B hexa-1,3-dien-5-yne

C 1-bromo-4-chlorobutane

Q5 Define Homologous series.Write the general formula of alkane, alkene and alkynes.

A5Homologous Series: It is defined as group of similar organic compounds which contains the similar functional groups and the two adjacent members of the series is differ by a–CH_2 group.

Alkanes C_nH_{2n+2}

Alkenes C_nH_{2n}

Alkynes C_nH_{2n-2}

Q6. How many Sigma and pi bonds are present in the following molecules.

A $HC\ \Xi CCH=CHCH_3$

B $CH_2=C=CHCH_3$

A6 A Sigma bonds=10 pi bonds=3

B Sigma bonds=9 pi bonds=2

Q7 Define functional groups.Write the general formula of Carboxylic acids acid chlorides.

A7 Functional Groups:It is an atom or group of atoms bonded together in a unique manner which is usually the site of chemical reactivity in an organic molecule . eg CH_3OH

General formula of Carboxylic acids: $C_nH_{2n+1}COOH$

General formula of acid chlorides:RCOCl

Q8 Write a short note on differential extraction.

A8 When an organic compound is present in an aqueous medium it is separated by shaking it with organic solvent in which it is more soluble than in water. The aqueous solution is mixed with organic solvent in a separating funnel and shaken for sometimes and then allowed to stand for some time. When organic solvent and water form two separate layers the lower layer is run out by opening the tap of funnel and organic layer is separated. The process is repeated several times and pure organic compound is separated.

Q9. How are carbon and Hydrogen detected in an organic compounds?

A9. The Carbon and Hydrogen present in the Organic compound is detected by heating the compound with Copper (II) oxide in a hard glass tube when carbon present in the compound is oxidized to CO2 which can be tested with lime Water and Hydrogen is converted to water which can be tested with anhydrous copper sulphate which turns blue.

$C+CuO \rightarrow 2Cu+ CO_2$

$2H+CuO \rightarrow Cu+ H_2O$

$CO_2 +Ca(OH)_2 \rightarrow CaCO_3 +H_2O$

$5H_2O+ CuSO_4 \rightarrow CuSO_4.5H_2O$

Q10 Write a shortnoteonResonanceeffect .

Resonance Effect: The polarity produced in the molecule by the interaction of two pi bonds or between a pi bond and lone pair of electron present on an adjacent atom.

There are two types of resonance effect:

1)Positive resonance effect: In this effect the transfer of electrons is away from an atom or substituent group attached to the conjugated system.

The atoms or groups which shows +R effect are halogens, -OH, -OR,-NH_2

2) Negative resonance effect:In this effect the transfer of electrons is towards the atom or substituent group attached to the conjugated system.

The atoms or groups which shows – R effect are –COOH,-CHO,-CN

Five Marks Questions

Q1 Differentiate between the principle of estimation of nitrogen in anorganic Compound by i)Dumasmethod ii)Kjeldahl'smethod.

Ans: **DUMAS METHOD:** A known mass of organic compound is heated with excess of CuO in an atmosphere of CO_2, when nitrogen of the organic compound is converted into N_2 gas.The volume of N_2 thus obtained is converted into STP and the percentage of nitrogen determined by applying the equation:

$$\text{Volume of Nitrogen at STP} = \frac{P_1V_1x273}{760xT_1}$$

$$\%N = \frac{28 \text{ x vol of } N_2 \text{ at STPx100}}{22400 \text{ x mass of the substance taken}}$$

KJELDAHL'S METHOD: A known mass of organic compound is heated with conc. H_2SO_4 in presence of K_2SO_4 and little $CuSO_4$ or Hg in along necked flask called Kjeldahl's flask when nitrogen present in the organic compound is quantitatively converted into $(NH_4)_2SO_4$. $(NH_4)_2SO_4$ thus obtained is boiled with excess of NaOH solution to liberate NH_3 gas which is absorbed in a known excess of a standard acid such as H_2SO_4 or HCl.

The volume of acid unused is found by titration against a standard alkali solution. From the volume of the acid used, the percentage of nitrogen is determined by applying the equation,

$$\%N = \frac{1.4 \text{xMolarityoftheacidxBasicityoftheacidxVoloftheacidused}}{\text{Massofthe substancetaken}}$$

Q2A sample of 0.50 g of organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.5 M H_2SO_4. The residual acid required 60 mL of 0.5M solution of NaOH for neutralization. Find the percentage composition of nitrogen in the compound.

Ans:The volume of H_2SO_4 used.

Volume of acid taken=50 mL of 0.5 M H_2SO_4 = 25 mL of 1 M H_2SO_4

Volume of alkali used for neutralization of excess acid = 60 mLof 0.5 M NaOH = 30mL of 1MNaOH

Now 1mole of H_2SO_4 neutralizes 2 moles of NaOH

(i.e. $H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$)

…30 mLof 1 M NaOH=15 mL of 1 M H_2SO_4

Unused acid = 15 mL of 1 M H_2SO_4
Used acid in neutralizing NH_3 = (25 – 15) mL of 1 M H_2SO_4 =10 mL of 1 M H_2SO_4

% of nitrogen.

1 mole of H_2SO_4 neutralizes 2 moles of NH_3…
10 mL of 1M H_2SO_4=20mL of 1M NH_3

But1000 mL of 1 M NH_3 contains N = 14 g.

20 mlof 1M NH_3will contain nitrogen= $\frac{14 \times 20}{1000}$

But this amount of nitrogen is present in 0.5g of organic compound

$$\therefore \%\text{ofN} = \frac{14 \times 20 \times 100}{1000 \times 0.5} = 56.0\ \%$$

Q3You have a mixture of three liquids A, B, C. There is a large difference in the boiling point of A and the rest two liquids. Boiling points of liquids B and C are quite close. Liquid A boils at higher temperature than B and C and boiling point of B is lower than C. How will you separate the components of the mixture.

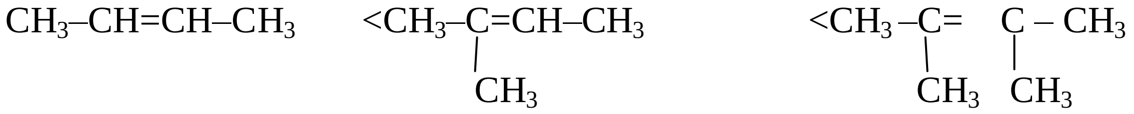
Ans. Since the boiling point of liquid A is much higher than those of liquids B and C, therefore separate liquid A by simple distillation. Since boiling points of liquids B and C are quite close but much lower than liquid A therefore mixture of B and C will distil together leaving behind A.

Now place the mixture of liquids B and C in a flask fitted with fractionating column. Since the b.p. of liquid B is lower than that of C, on fractional distillation first liquid B will distil over and then liquid C.

HOTS QUESTIONS

Q1 Explain hyper conjugation effect. How does hyperconjugation effect explain the stability of alkenes?

Ans. The relative stability of various classes of carbonium ions may be explained by the number of no-bond resonance structures that can be written for them. Such structures are obtained by shifting the bonding electrons from an adjacent C-H bond to the electron deficient carbon so the positive charge originally on carbon is dispersed to the hydrogen. This manner of electron release by assuming no bond character in the adjacent C-H bond is called Hyper conjugation. Greater the hyperconjugation greater will be the stability of alkenes.



$$CH_3–CH=CH–CH_3 \quad < CH_3–\underset{CH_3}{\underset{|}{C}}=CH–CH_3 \quad < CH_3–\underset{CH_3}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}–CH_3$$

Q2 In DNA and RNA nitrogen is present in the ring system. Can Kjeldahl method be used for the estimation of nitrogen present in these? Give reasons.

Ans In DNA and RNA nitrogen is present in hetrocyclic rings. Kjeldahl method cannot be used to estimate nitrogen present in the ring because here nitrogen cannot be completely converted into $(NH_4)_2SO_4$ during digestion. Therefore Kjeldahl method cannot be used to estimate nitrogen present in DNA and RNA.

Q3 1.216 g of an organic compound was Kjeldahlised and the ammonia evolved was absorbed in 100 mL1N H_2SO_4. The remaining acid solution was made up to 500 ml by addition of water. 20 ml of this dilute solution required 32 mL of N/10 caustic soda solution for complete neutralization. Calculate the percentage of nitrogen in the organic compound.

Ans 20 ml of dil.Unreacted H_2SO_4=32 mL of N/10 NaOH sol.

500 ml of dil unreacted H_2SO_4=$\frac{32\text{ x}500}{20}$mLof$\frac{N}{10}$NaOH=$\frac{\text{32x500mlof1NNaOH}}{\text{20 x10}}$

=80ml 1 N NaOH

But 80ml1 N NaOH=80ml 1NH_2SO_4

So, acid left unused =80ml1NH_2SO_4

Acid used =(100–80)= 20ml1NH_2SO_4

$$\%N= \frac{\text{1.4xNormality of the acid xVol of the acid used}}{\text{Mass of the substance taken}}$$

$$=\frac{1.4\text{x}1\text{x}20}{1.216} \qquad =23.026\ \%$$

CHAPTER13

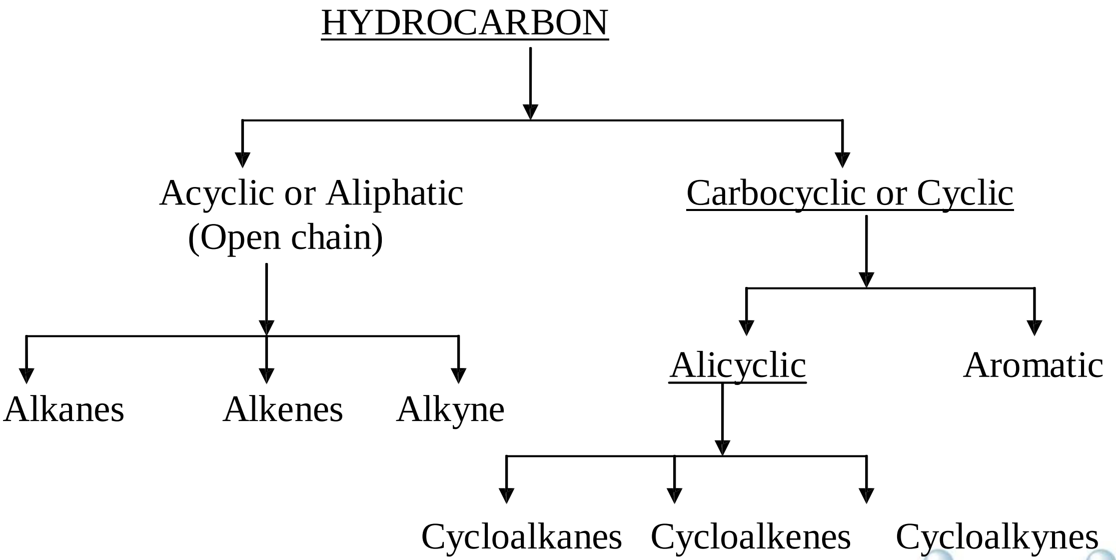
HYDROCARBON

- Hydrocarbons are composed of Carbon and hydrogen.
- The important fuels like Petrol, kerosene, coal gas, CNG, LPG etc. are all hydrocarbons or their mixture.

Sources:

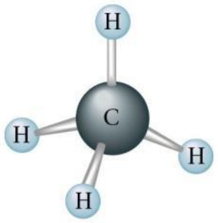
Petroleum and natural gas are the major sources of aliphatic hydrocarbon while coal is an important source of aromatic hydrocarbons. The oil trapped inside the rocks is known as petroleum. PETRA–ROCK, OLEUM–OIL. The oil in the petroleum field is covered with a gaseous mixture known as natural gas. The main constituents of the natural gas are methane, ethane, propane and butane.

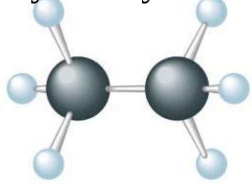
CLASSIFICATION OF HYDROCARBONS:



Alkanes:-

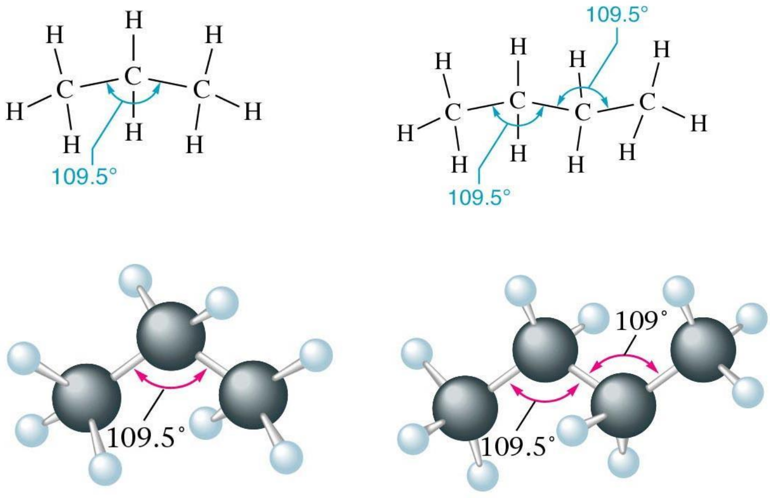
- Paraffins
- General formula C_nH_{2n+2}
- sp^3 hybridisation
- C–C bond length1.54A^0
- Chemically unreactive
- Show chain, position and optical isomerism.
- Heptane has 9 isomers, Octane18 and Decane 75.





(c)

Nomenclature:



(a) Propane (b) Butane

Preparation:-

❶Wurtz reaction:-

$$2CH_3CH_2Br + 2Na \xrightarrow[\text{ether}]{\text{Dry}} CH_3CH_2CH_2CH_3 + 2NaBr$$

- ➢Follow mainly free radical mechanism
- ➢ Useful in preparing an alkane containing even number of carbon atoms
- ➢ Stepping upreaction

Frankland reaction

$$RX + Zn + Rx \longrightarrow \quad + ZnX_2$$

❷FromGrignardreagent (RMgX)

$$RMgX + HOH \rightarrow RH + Mg(OH)X$$
$$RMgX + R'OH \rightarrow \quad Mg(OR')X$$
$$RMgX + R'NH_2 \rightarrow \quad Mg(NHR')X$$

❸Fromunsaturatedhydrocarbons:-

Sabatier-Sendersen’s reduction

$$R-CH=CH_2 + H_2 \xrightarrow{Ni/\Delta} R-CH_2-CH_3$$

$$R-C\equiv CH + H_2 \xrightarrow{Ni/\Delta} R-CH_2-CH_3$$

4.Fromcarboxylicacids-

Decarboxylation.-

$$CH_3COO^-Na^+ + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

Sodium ethanoate

Kolbe’selectrolyticmethod-

$$2CH_3COO^-Na^+ + 2H_2O$$

Sodium acetate

$$\downarrow \text{Electrolysis}$$

$$CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH$$

❖**PhysicalProperties:-**

(1) Nature:-Non-Polar due to covalent nature of C—C bond and C—H bond. C—C bond energy=83 kJ/mole and C—H bond energy=99 kJ/mole.
C_1—C_4=gases, C_5—C_{17}=colourless odourless liquid and >C_{17}=Solid.

(2) Solubility:-Like dissolves like

Viz, Polar compounds dissolve in polar solvent and Non-Polar compound dissolve in non polar solvent.

(3) Boiling point:-Low boiling point due to non polar in nature.

The molecules are held together only by weak Vander Waals’ forces.

Since we know that the magnitude of Van der Waals’ forces is directly proportional to the molecular size. Therefore, the boiling point increases with increase in the molecular size i.e. with increase in number of carbon atoms.

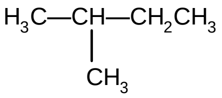
Note:- *T*he boiling points of the branched chain alkanes are less than the straight chain isomers.

This is due to the fact that branching of the chain makes the molecule more compact and thereby decreases the surface area and consequently, the magnitudes of Vander Waals’forces also decrease.

$CH_3CH_2CH_2CH_2CH_3$

n-pentane

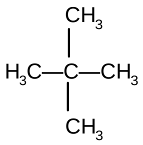
boilingpoint=309K



$H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2CH_3$

iso-pentane

boilingpoint=301K



$H_3C-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$

neo-pentane

boilingpoint=282.5 K

Chemical Properties

1. Combustion:-

$$CH_4(g)+2O_2(g) \rightarrow CO_2(g)+2H_2O(l); \quad \Delta_c H^\ominus = -890\,kJ\,mol^{-1}$$

Alkanes on heating with air undergoes complete oxidation to give carbon dioxide and water along with a large amount of heat energy.

2. Substitution reaction:-
   Halogenation reaction

$$CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$$

$$CH_3Cl \xrightarrow{UV} CH_2Cl_2 \xrightarrow{UV} CHCl_3 \xrightarrow{UV} CCl_4$$

Note:-Iodination is a reversible reaction. So it is carried out by heating alkane in The presence of some oxidizing agent like iodic acid (HIO_3) or nitric acid (HNO_3) or mercuric oxide (HgO) which oxidizes HI formed during the reaction.

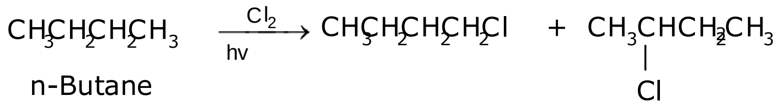
$$CH_4 + I_2 \xrightarrow{Heat} CH_3I + HI$$

$$5HI + HIO_3 \longrightarrow 3H_2O + 3I_2$$

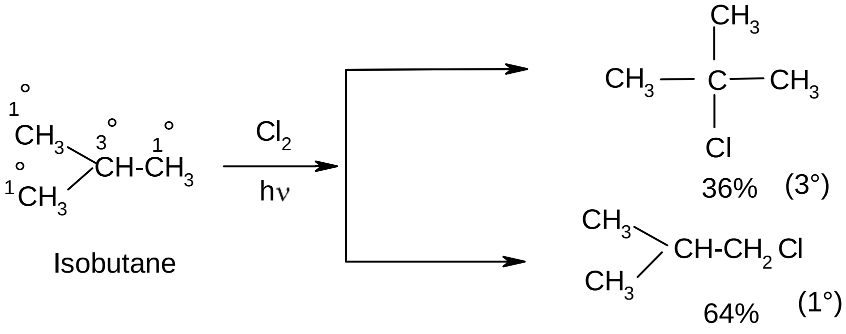
$$2HI + 2HNO_3 \longrightarrow 2H_2O + I_2 + 2NO_2$$

Noted:-Fluorination of alkane takes place explosively resulting even in the rupture of C—C bond in higher alkanes.

- Features of Halogenations:-
  (i) The reactivity of Halogens:- $F_2 > Cl_2 > Br_2 > I_2$.
  (ii) The rate of replacement of Hydrogen atoms of alkanes is:
  3° > 2° > 1°



$$CH_3CH_2CH_2CH_3 \xrightarrow[hv]{Cl_2} CH_3CH_2CH_2CH_2Cl + CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_3$$



Mechanism:-halogenation reactions take place by free radical mechanism. The reaction proceeds in the following steps:

Initiation

(i) Chain initiation step:-

$$Cl—Cl \xrightarrow{h\nu} 2\overset{\bullet}{Cl}$$

(ii) Chain Propagation step:-

$$CH_4 + Cl^{\bullet} \longrightarrow \overset{\bullet}{C}H_3 + HCl$$

$$\overset{\bullet}{C}H_3 + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$$

(iii) Chain Termination step:-

$$Cl^{\bullet} + \overset{\bullet}{Cl} \longrightarrow Cl_2$$

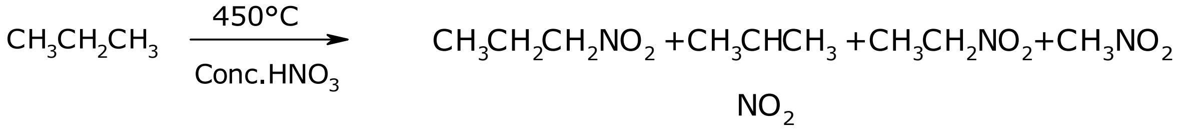
$$\overset{\bullet}{C}H_3 + \overset{\bullet}{C}H_3 \longrightarrow CH_3\ CH_3$$

$$\overset{\bullet}{C}H_3 + Cl^{\bullet} \longrightarrow CH_3Cl$$

②Nitration:-

☞The reaction takes place by free radical mechanism at high temp (450^0C).

☞At high temp C—C bond is also broken so that mixture of nitro alkanes is obtained.



$$CH_3CH_2CH_3 \xrightarrow[\text{Conc.}HNO_3]{450°C} CH_3CH_2CH_2NO_2 + \underset{NO_2}{CH_3CHCH_3} + CH_3CH_2NO_2 + CH_3NO_2$$

25% **40%** **10%** **25%**

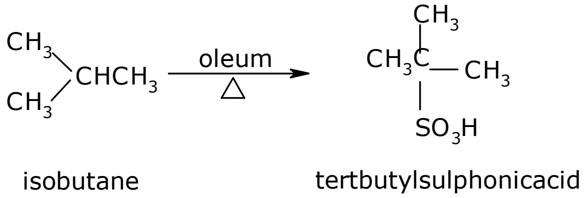
Thereactionoccurs as:

$$HO\text{-}NO_2 \xrightarrow[\text{Homolytic fission}]{450^{0}C} HO^{\circ} + {}^{\circ}NO_2$$

$$RH + {}^{0}OH \longrightarrow R^{o} + HOH$$

$$R^{o} + {}^{\circ}NO_2 \longrightarrow RNO_2$$

③Sulphonation:- replacement of hydrogen atom of alkane by–SO_3H group.



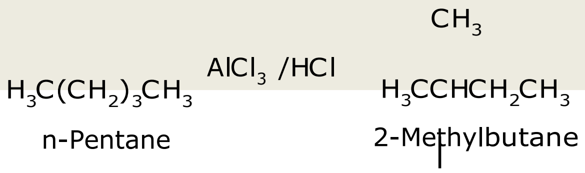
The reaction occurs as:

$$HO\text{-}SO_3 \xrightarrow[\text{Homolytic fission}]{450^{0}C} HO^{\circ} + {}^{\circ}SO_3H$$

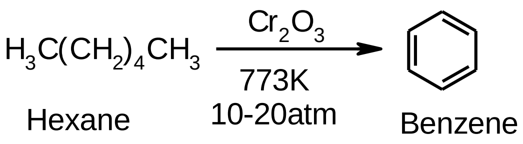
$$RH + {}^{0}OH \longrightarrow R^{o} + HOH$$

$$R^{o} + {}^{\circ}SO_3H \longrightarrow RSO_3H$$

❹Isomerization:-



❺Aromatization:-



This method is also called dehydrogenation or reforming

Similarly, heptanes gives toluene, n-Octane give o-Xylene and 2-Methylheptane give m-Xylene.

❻Thermal decomposition or Pyrolysis or cracking or Fragmentation:- When higher alkanes are heated at high temp (about700-800K) in the presence of alumina or silica catalysts, the alkanes break down to lower alkanes and alkenes.

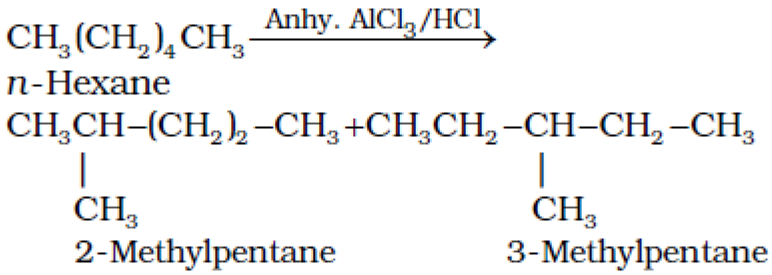
$$CH_3\text{-}CH_2\text{-}CH_3 \longrightarrow CH_3\text{-}CH\text{-}CH_2 + CH_3\text{-}CH_3 \quad + \quad C_2H_4 \quad + \quad CH_4$$

❼Actionofsteam:- catalyst: nickel, aluminaAl_2O_3

$$CH_4 + H_2O(\text{Steam}) \xrightarrow{1000^{0}C} CO + 3H_2$$

This reaction is used for the industrial preparation of hydrogen from natural gas.

8.Isomerisation:-



$$CH_3(CH_2)_4CH_3 \xrightarrow{\text{Anhy. }AlCl_3/HCl} \underset{\substack{|\\CH_3}}{CH_3CH}-(CH_2)_2-CH_3 + CH_3CH_2-\underset{\substack{|\\CH_3}}{CH}-CH_2-CH_3$$

n-Hexane

2-Methylpentane

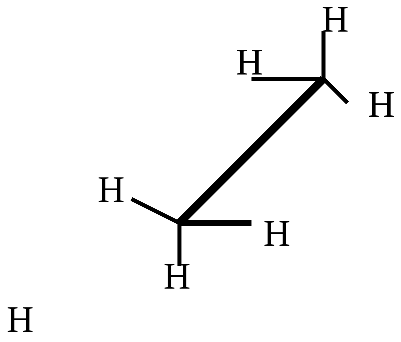
3-Methylpentane

❖CONFORMATIONAL ISOMERISM:

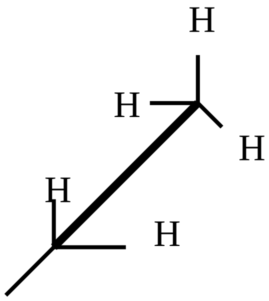
The different molecular arrangements arising as a result of rotation around carbon carbon single bonds are called conformational isomers or rotational isomers and the phenomenon is called conformational isomerism.

Numerous possible arrangements of ethane are possible.Two extreme conformations are known. These are eclipsed conformation and staggered conformation.

SAWHORSE REPRESENTATION

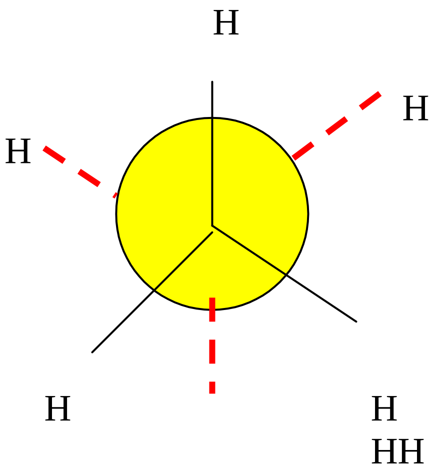


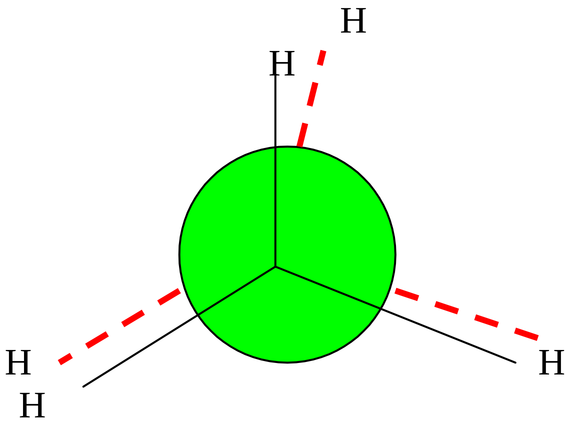
STAGGERED



ECLIPSED

NEWMAN PROJECTION





STAGGERED → SKEW ← ECLIPSED

Alkenes

☞Unsaturated hydrocarbons which have double bond.

☞General molecular formula C_nH_{2n}

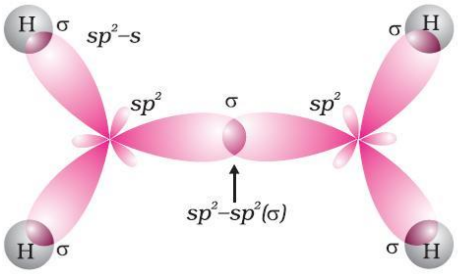
☞C–C bond hybridization1.34A^0

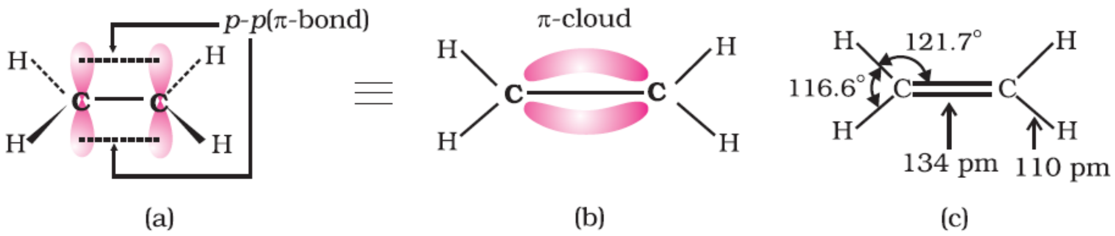
☞sp^{2}hybridization

☞When we treated Alkene with chlorine, oily products are obtained. So Alkenes are also known as Olefins. (Greek olefiant meaning oil forming).

☞Show chain, positional and geometrical isomerism

❖Structure of double bond:-





(a) (b) (c)

❖Preparation:-

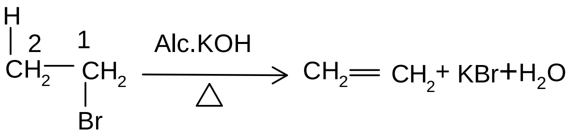
1. From Alkynes:-Alkynes on partial reduction with Partially deactivated Palladised charcoal known as *Lindlar's catalyst* give alkynes.

$$\underset{\text{Ethyne}}{CH{\equiv}CH+H_2} \xrightarrow{Pd/C} \underset{\text{Ethene}}{CH_2{=}CH_2}$$

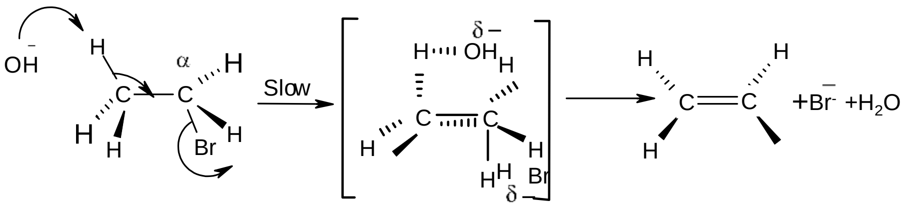
2.From Haloalkanes:- dehydrohalogenation

(E$_2$or1,2-elimination or β-elimination)

Mech

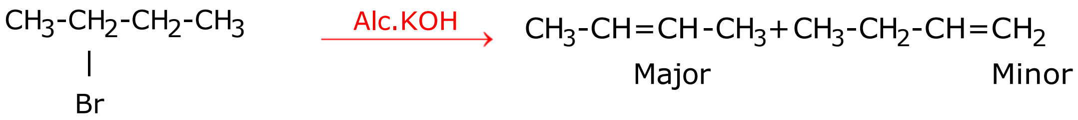


$$\overset{H}{\overset{|}{\underset{2}{CH_2}}}\!-\!\underset{\underset{Br}{|}}{\overset{1}{CH_2}} \xrightarrow[\triangle]{\text{Alc.KOH}} CH_2{=}CH_2 + KBr + H_2O$$



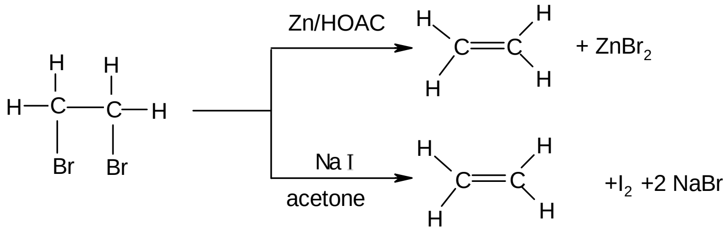
Transitionstate

➢predominant formation of a substituted alkene occurs According to Saytzeff's rule.



$$CH_3-\underset{\underset{Br}{|}}{CH_2}-CH_2-CH_3 \xrightarrow{\text{Alc.KOH}} \underset{\text{Major}}{CH_3-CH=CH-CH_3} + \underset{\text{Minor}}{CH_3-CH_2-CH=CH_2}$$

3.From Dihaloalkanes:-dehalogenation



4.From Alcohols:-Dehydration

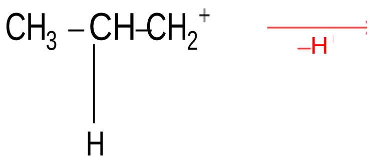
(E1-elimination)

$$CH_3CH_2CH_2OH \xrightarrow[160°]{Conc.H_2SO_4} CH_3CH{=}CH_2{+}H_2O$$

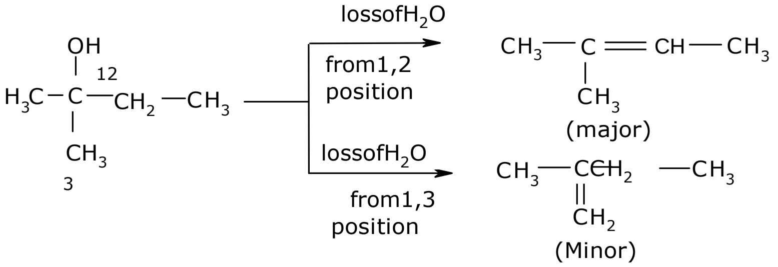
$$CH_3CH_2CH_2CH_2OH \xrightarrow[300°C]{Al_2O_3} CH_3CH_2CH{=}CH_2$$

Mechanism

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}OH \overset{H^+}{\rightleftharpoons} CH_3\text{-}CH_2\text{-}CH_2\text{-}O_2\ {}_2\,H^+ \xrightarrow{-H_2O} CH_3 - \quad - \quad +$$



$CH_3-\underset{H}{CH}\text{-}CH_2^+ \xrightarrow[-H]{} CH_3 - \quad =$ 1– e



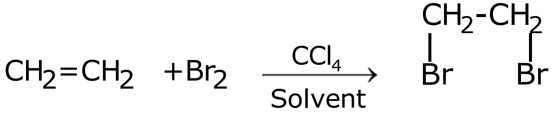
❖<u>Chemical Properties:-</u>

❶Addition Reaction:- Alkenes show electrophilic addition reactions.

1.Additionof Hydrogen:-

$$RCH{=}CH_2 \xrightarrow{H_2/Ni} RCH_2CH_3$$

2.AdditionofHalogens:-



$$CH_2{=}CH_2 \ +Br_2 \xrightarrow[Solvent]{CCl_4} \underset{Br}{CH_2}\text{-}\underset{Br}{CH_2}$$

$$CH_2 = CH_2 + Br_2 \xrightarrow[Solvent]{H_2O} Br—CH_2—CH_2—OH \quad +$$

(Browncolour) (Colourless)

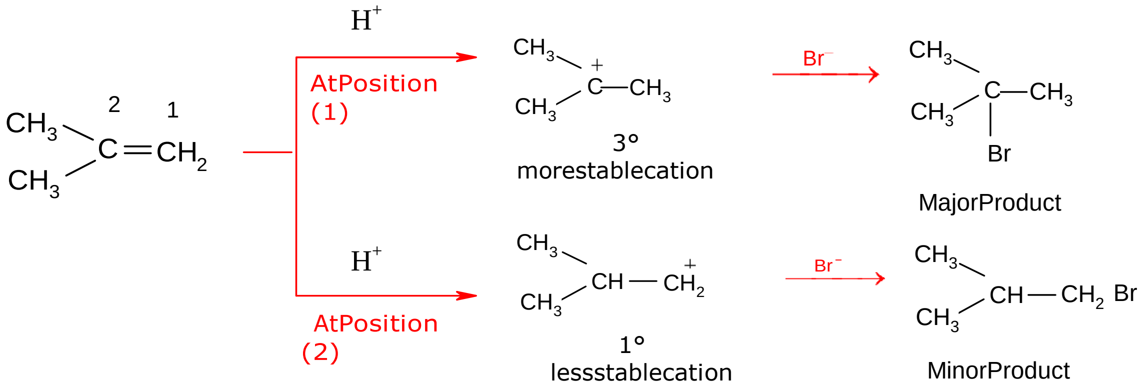
3.Addition of hydrogen halides-

Addition reaction of HBr to symmetrical alkenes

$$CH_2=CH_2+H-Br \longrightarrow CH_3-CH_2-Br$$

Addition reaction of HBr to unsymmetrical alkenes takes place according to Markovnikov's Rule

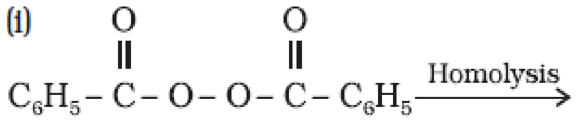
Markownikov's rule:-negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses less number of hydrogen atoms.eg



Peroxide effect or Kharasch (AntiMarkownikoff's addition):-In1933 Kharasch and Mayo observed that when HBr is added to an unsymmetrical double bond in the presence of organic peroxide, the reaction takes place opposite to the Markovnikov's rule.

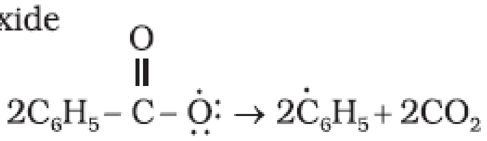
$$CH_3-CH=CH_2 \xrightarrow[\text{Peroxide}]{\text{HBr}} CH_3-CH_2-CH_2Br$$

(i)



$$C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_6H_5 \xrightarrow{\text{Homolysis}}$$

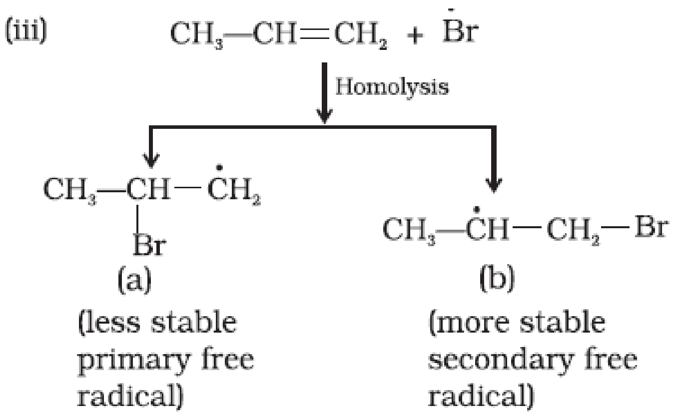
Benzoyl peroxide

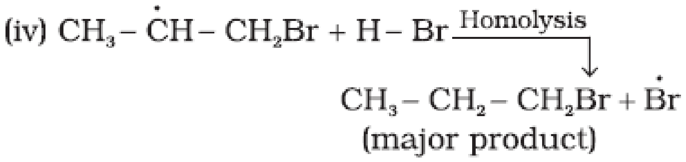


$$2C_6H_5-\overset{\overset{O}{\|}}{C}-\dot{O}: \rightarrow 2\dot{C}_6H_5+2CO_2$$

i) $\dot{C}_6H_5+H-Br \xrightarrow{\text{Homolysis}} C_6H_6+\dot{B}r$

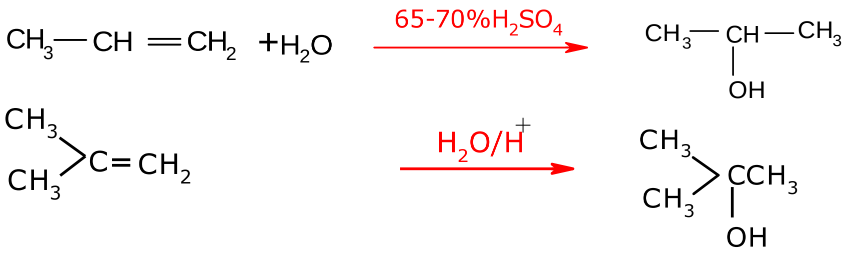
Propylbromide





Noted:-peroxide effect is applicable onlyto HBr and not to HF, HCl and HI. Addition of HF,HCl and HI takes place according to Markovnikov's rule even in the presence of peroxide.

4.Addition of water (Hydration):-Acid catalyzed addition of water



❷ Oxidation:-

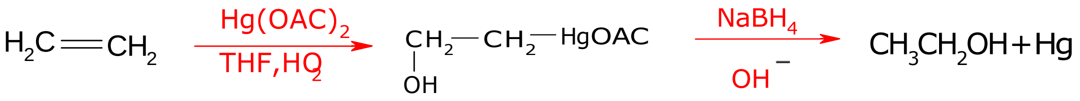
①Combustion:- CO_2 +H_2O

②Hydroboration–oxidation:-Alkanesreactwithdiboranetoformtrialkylboranes which on oxidation with alkaline H_2O_2 give alcohols.

$$3CH_2{=}CH_2 \xrightarrow{BH_3} (CH_3CH_2)_3B \xrightarrow{H_2O_2/OH^-} 3CH_3CH_2OH$$

Triethylborane　Ethylalcohol

③ Oxymercuration–demercuration:-

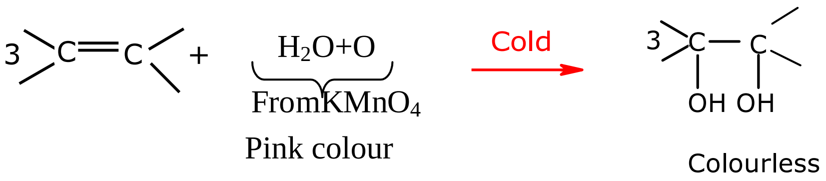


$$H_2C{=}CH_2 \xrightarrow[THF,H_2O]{Hg(OAC)_2} \underset{OH}{CH_2}{-}CH_2{-}HgOAC \xrightarrow[OH^-]{NaBH_4} CH_3CH_2OH+Hg$$

④ Oxidation with potassiumpermanganate:-

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 \quad +3[O]$$

+2MnO$_2$ +2KOH


3
C
C
+
H2O+O
From KMnO4
Pink colour
Cold
3
C
C
OH OH
Colourless

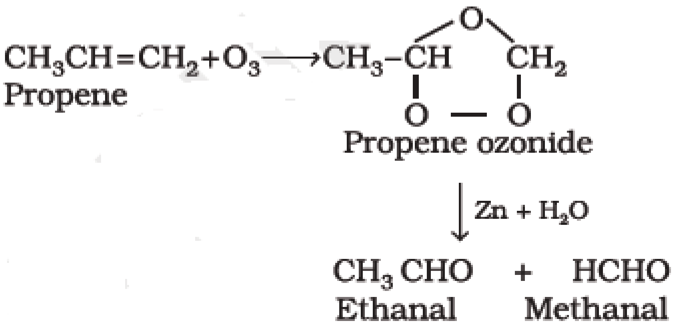
- This reaction is also called *Hydroxylation*
- *Cis product i.e.cis*-diol is obtained.

Noted:-The alkaline potassiumpermanganate solution is known a sBaeyer’sreagent. It has bright pink colour. It oxidizes alkenes to glycols which is colourless. This reaction is used as a test for the presence of double bond in a molecule. This is also known as Baeyer test.

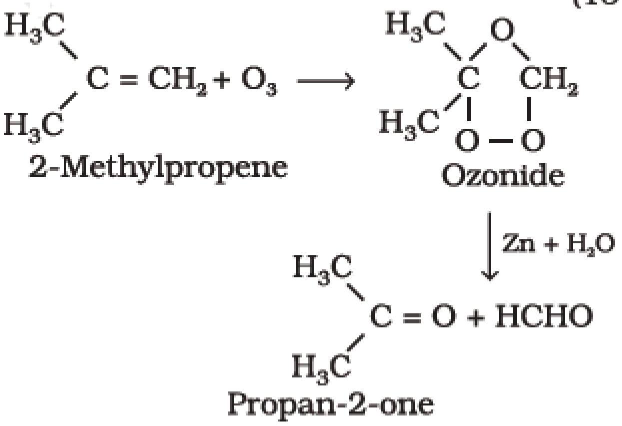
$$CH_3-CH=CH_2 \xrightarrow[\text{(ii)}H^+\ \Delta]{\text{(i)Alk.KMnO}_4} CH_3\ COOH+CO_2 + H_2O$$

Oxidation with Ozone:-

Ozonolysis–give carbonyl compounds



(13.51)



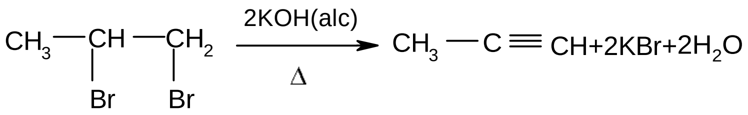
Noted:-Bromine water test and Baeyer’stest are used to detect the presence of double bond while ozonolysis is used to detect the position of double bond.

Alkynes

- Unsaturated hydrocarbon which have triple bond.
- General molecular formula C_nH_{2n-2}
- sp hybridization
- Shows chain, positional and functional isomerism

❖Preparation:-

From vicinal dihalides:-dehalogenation



$CH_3-\underset{Br}{CH}-\underset{Br}{CH_2} \xrightarrow[\Delta]{2KOH(alc)} CH_3-C\equiv CH+2KBr+2H_2O$

By the action of water on calcium carbide:-

$CaC_2 + H_2O \rightarrow HC \equiv CH + Ca(OH)_2$

❖Chemical Properties:-

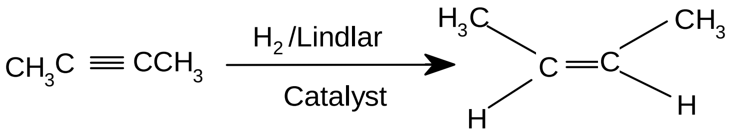
➊Addition Reaction:-Alkynes show electrophilic addition reaction.

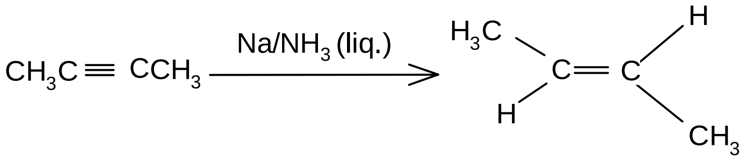
①Addition of Hydrogen:- Hydrogenation.

$$\underset{\text{Propyne}}{CH_3C\equiv CH} + 2H_2 \xrightarrow{Ni} CH_3CH_2CH_3$$

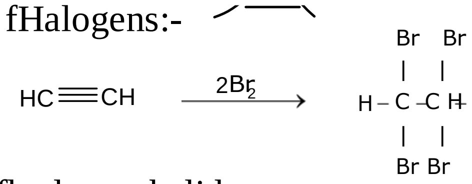
Note:-It may be noted that the hydrogenation can be controlled at the alkene stage only. This is possible by using a *Lindlar's catalysts* or *sodium in liquid* NH_3 at 200 K temp.

Noted:-It may be again noted that the catalytic reduction of alkynes in the presence of Lindlar's catalyst gives cis-alkenes while in the presence of sodium in liquid NH_3 (Birch reduction) gives trans-alkenes.





②Additiono fHalogens:-



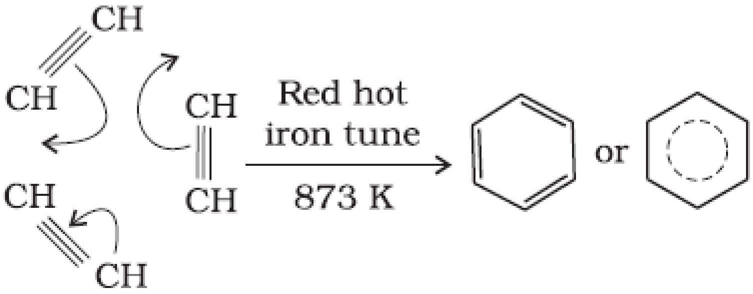
③Additionofhydrogenhalides:-

$$HC \equiv CH + 2HBr \longrightarrow CH_3CHBr_2$$

Polymerisation-

a. ***Linear polymerisation*:**of ethyne gives polyacetylene or poly ethyne which is a high molecular weight polyene containing repeating units of (CH=CH– CH=CH) and can be represented as—(CH=CH–CH=CH)n—

b. Cyclic polymerization- results in the formation of aromatic compound.



Acidity of Alkynes-Terminal Hydrogen atoms in alkynes are acidic in nature.

$$HC \equiv CH + Na \rightarrow HC \equiv C^{-}Na^{+} + \frac{1}{2}H_2$$

Monosodium
ethynide

$$CH_3 - C \equiv C - H \quad + \quad Na^{+}NH_2^{-}$$
$$\downarrow$$
$$CH_3 - C \equiv C^{-}Na^{+} \quad + \quad NH_3$$

Sodium propynide

Alkanes, alkenes and alkynesfollow the following trend in their acidic behaviour:

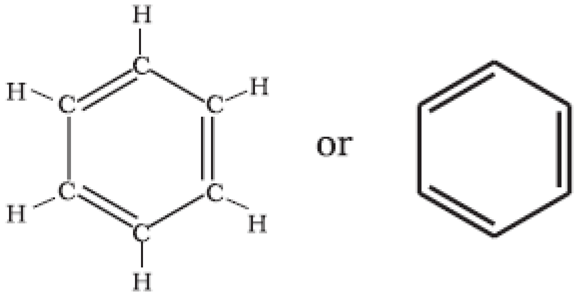
i) $HC \equiv CH > H_2C = CH_2 > CH_3 - CH_3$

ii) $HC \equiv CH > CH_3 - C \equiv CH >> CH_3 - C \equiv C - CH_3$

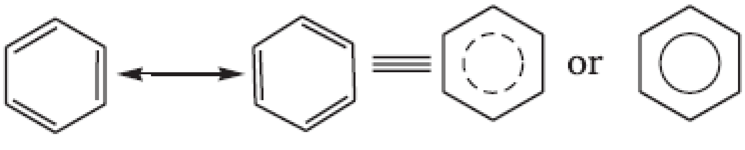
AROMATIC HYDROCARBON

Aromatic compounds containing benzene ring are known as **benzenoids** and those not containing a benzene ring are known as **non-benzenoids**.

Structure of Benzene- Kekulé structure

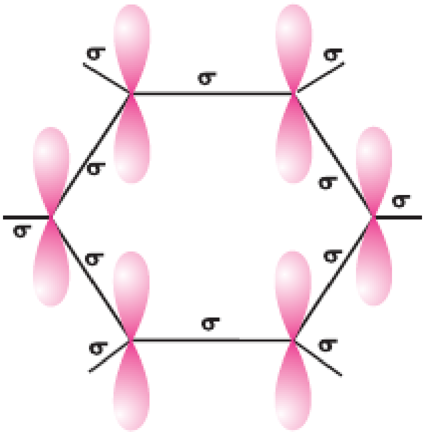


Resonanceand stabilityof benzene-Benzene is a hybrid of various resonating structures.

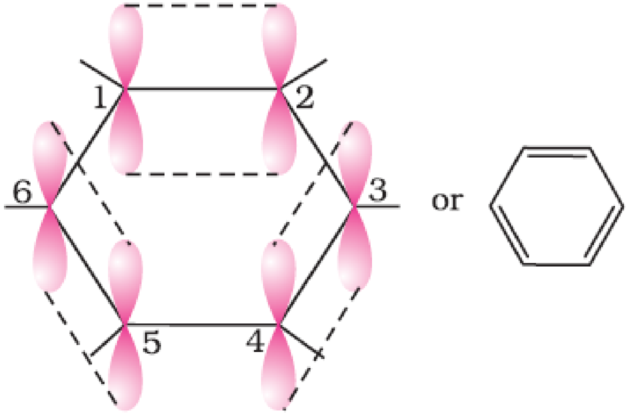


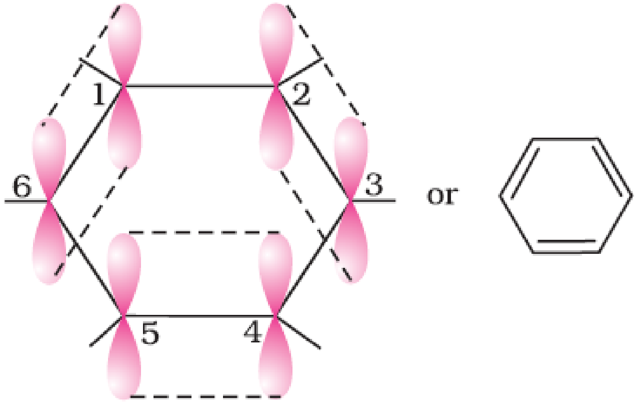
(A) (B) (C)

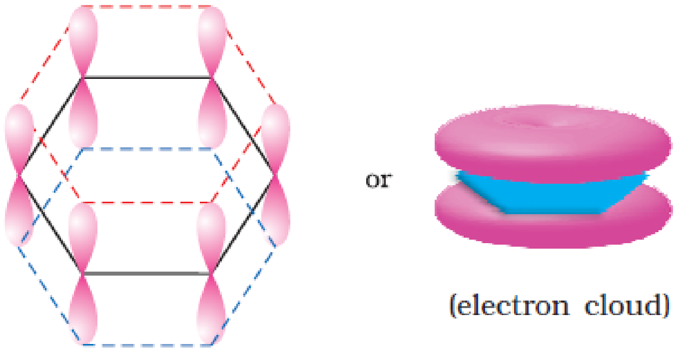
The orbital overlapping picture of benzene-All the six carbon atoms in benzene are sp^2 hybridized and these hybrid orbitals form sigma bonds.



The unhybridised *p* orbital of carbon atoms are close enough to form a π bond by lateral overlap.







The six π electrons are thus delocalized and can move freely about the six carbon nuclei. The delocalized π electron cloud is attracted more strongly by the nuclei of the carbon atoms than the electron cloud localized between two carbon atoms. Therefore, presence of delocalized π electrons in benzene makes it more stable.

Aromaticity:- The compounds that follow the following features are to be considered aromatic.

(i)Planarity

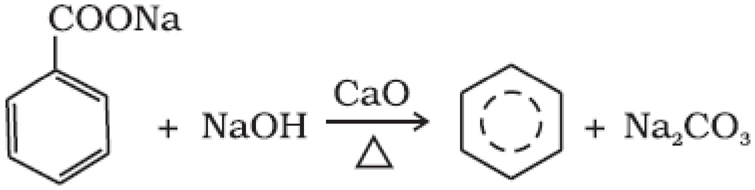
(ii)Complete delocalization of the π electrons in the ring

(iii)Presence of ($4n+2$) π electrons in the ring where n is an integer (n=0,1, 2,) This is often referred to as **Hückel Rule**.

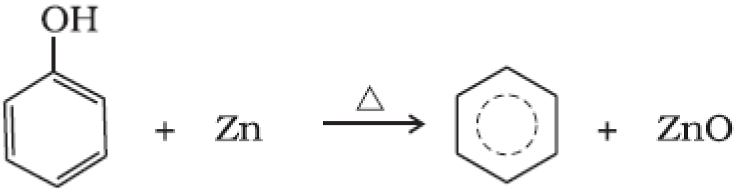
Preparation of Benzene:

(i)Cyclic polymerization of ethyne:

(ii)Decarboxylation of aromatic acids*:*



(iii)*Reduction of phenol:* Phenol is reduced to benzene by passing its vapours over heated zinc dust



Physical properties:

1. Aromatic hydrocarbons are non-polar molecules and are usually colourless liquids or solids with a characteristic aroma.
2. Aromatic hydrocarbons are immiscible with water but are readily miscible with organic solvents.
3. They burn with sooty flame.

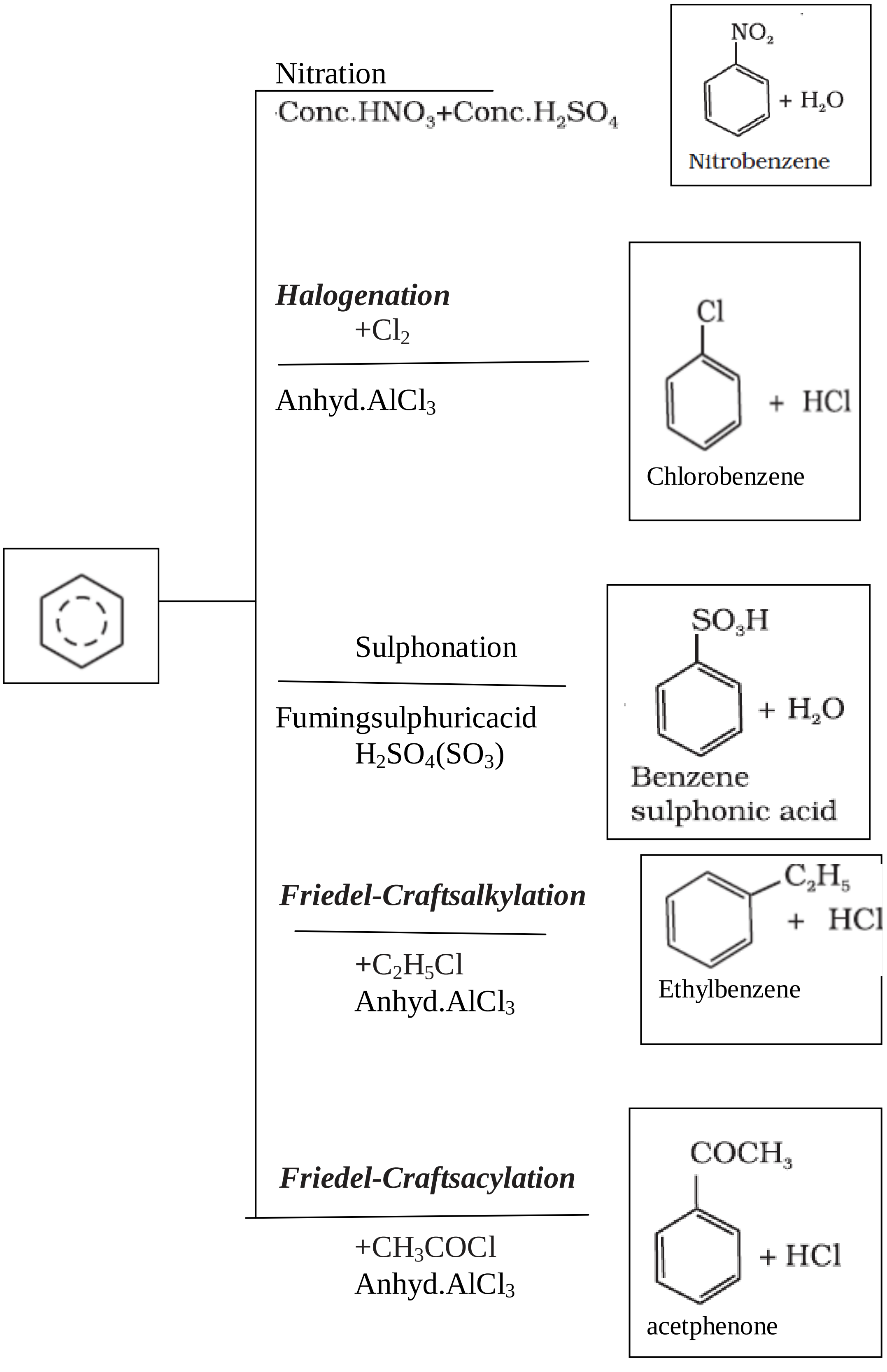
Chemical properties

Arenes are characterized by electrophilic substitution reactions that proceed via the following three steps:

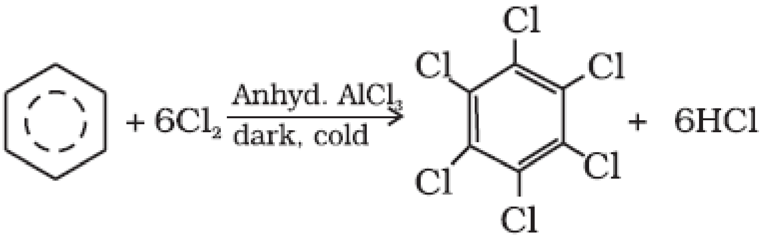
(a)Generation of the eletrophile

(b)Formation of carbocation intermediate

(c)Removal of proton from the carbocation intermediate

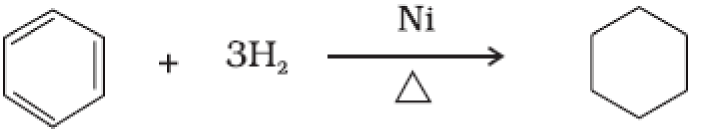


benzene on treatment with excess of chlorine in the presence of anhydrous $AlCl_3$ in dark yields hexa chlorobenzene (C_6Cl_6)

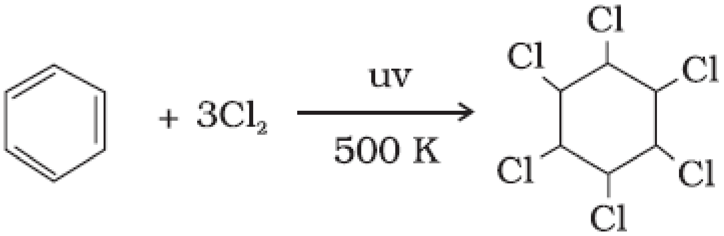


Hexachlorobenzene (C_6Cl_6)

Addition reactions of benzene-



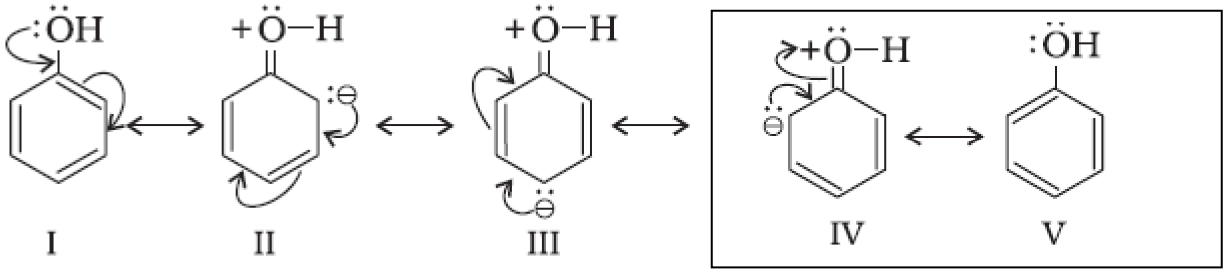
Cyclohexane



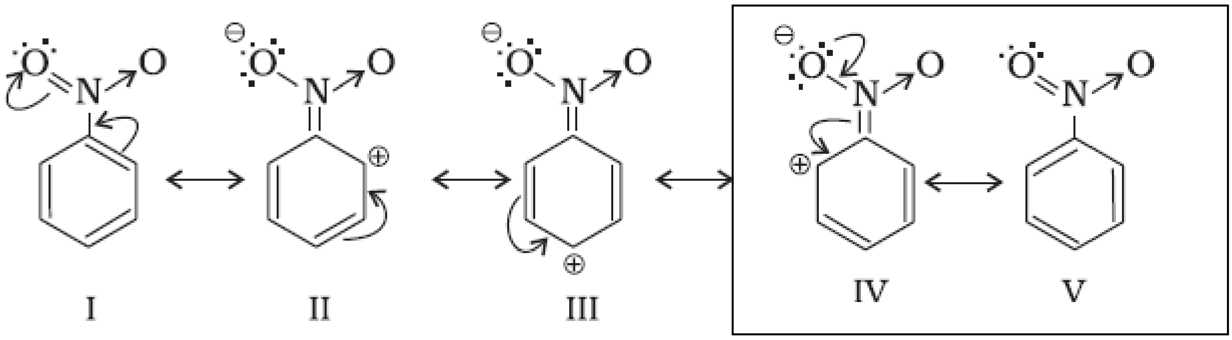
Benzene hexachloride, (BHC)

Directive influence of a functional group in mono substituted benzene:-

1.Ortho and para directing groups and activating-–OH,–NH_2,–NHR,–$NHCOCH_3$, –OCH_3,–CH_3,–C_2H_5,etc.



2. *Meta directing group and deactivating:*–NO_2,–CN,–CHO,–COR,–COOH,–COOR,–SO_3H,etc.



3.Ortho and para directing groups and deactivating-Halogens because of their strong–I effect, overall electron density on benzene ring decreases. However, due to resonance the electron density on *o*–and *p*–positions is greater than that at the *m*-position. Hence, they are also *o*–and *p*–directing groups.

CARCINOGENICITY AND TOXICITY-Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and are said to possess cancer producing (carcinogenic) property.

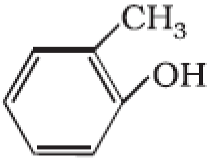
ONE MARK QUESTIONS

1.What are hydrocarbons?
Ans.Compounds of hydrogen and carbon.
2.What is the general formula of alkanes?
Ans. C_nH_{2n+2}
3.Write the general formula of alkenes.
Ans.C_nH_{2n}
4.What is the general formula of alkynes?
Ans. C_nH_{2n-2}
5.Give the IUPAC name of lowest molecularweight alkane that contains a Quaternary carbon.
Ans. 2,2-Dimethylpropane.
6.Arrange the following in the increasing order of C-C bond length -C_2H_6 C_2H_4 C_2H_2
Ans. $C_2H_2 < C_2H_4 < C_2H_6$
7.Out of ethylene and acetylene which is more acidic and why?
Ans.Acetylene, due to greater electonegativity of the sp hybrid carbon.
8.Nametwo reagents which can be used to distinguish between ethane and ethyne.
Ans.Tollen’s reagent and ammonical CuCl solution.
9.Arrange thefollowing in order of decreasing reactivity towards alkanes.
HCl,HBr,HI,HF
Ans.HI>HBr>HCl>HF
10.How will you detect the presence of unsaturation in an organic compound?
Ans.Generally Unsaturated organic compounds decolourise Baeyer’s reagent
and Bromine water.
11.What is Grignard reagent?
Ans.Alkylmagnesiumhalides

TWO MARKS QUESTIONS

1.Write the IUPAC names of the following-

a. $CH_2=CH-C\equiv C-CH_3$

b. 

Ans.a .Pent-en-3-yne b.2-methylphenol

2.Write chemical equations for combustion reaction of(i)Butane(ii)Toluene

Ans.

(i) $$\underset{\text{Butane}}{2C_4H_{10(g)}} + 13O_{2(g)} \longrightarrow 8CO_{2(g)} + 10H_2O_{(g)} + \text{Heat}$$

.

(ii) 

Toluene

3.What are the necessary conditions for any system to be aromatic?

Ans.A compound is said to be aromatic if it satisfies the following three conditions: **(i)**It should have a planar structure.

(ii) The π–electrons of the compound are completely delocalized in the ring.

(iii)The total number of π–electrons present in the ring should be equal to ($4n+2$), where $n=0,1,2\ldots$ etc.This is known asHuckel'srule.

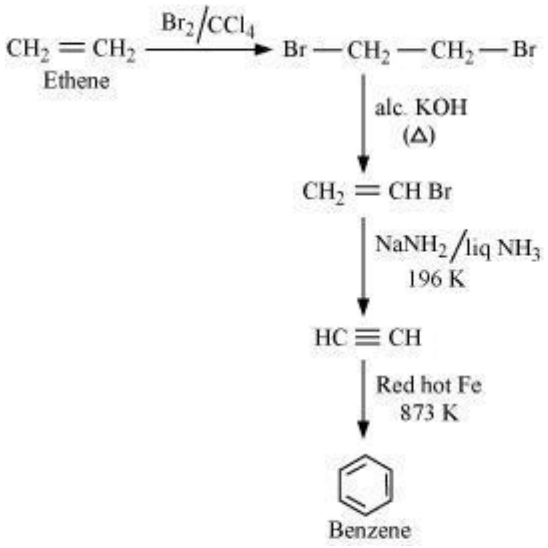
4.What effect does branching of an alkane chain has on its boiling point?

Ans. As branching increases, the surface area of the molecule decreases which results in a small area of contact. As a result, the Vander Waals force also decreases which can be over come at a relatively lower temperature. Hence, the boiling point of an alkane chain decreases with an increase in branching.

5.How would you convert the following compounds into benzene?(i) Ethyne(ii)Ethene

Ans.**(i)**Benzene from Ethyne: 

(ii)Benzene from Ethene:



6.Suggest the name of Lewis acids other than anhydrous aluminium chloride which can be used during ethylation of benzene.

Ans. Anhydrous $FeCl_3$,$SnCl_4$,BF_3etc.

7.Write the name of all the possible isomers of $C_2H_2Cl_2$ and indicate which of them is non-polar.

Ans.(i)cis-1,2-dichloroethene (ii)trans-1,2-dichloroethene (iii)1,1-dichloroethene.trans-1,2-dichloroethene is non-polar.

8.Although benzene is highly unsaturated, it does not undergo addition reactions, why?

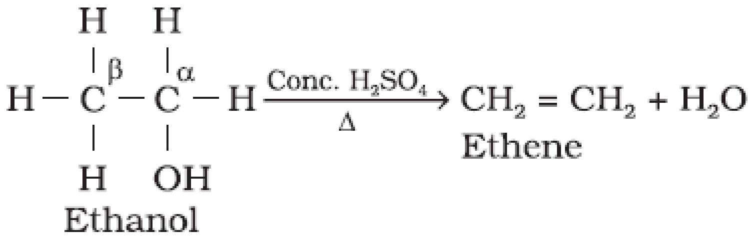
Ans.Because of extra stability due to delocalization of π-electrons.

9.What are alkanes? Why are they called paraffins?

Ans. Those hydrocarbons which contain single bond between carbon-carbon are called alkanes. They are called paraffins because they are very less reactive (Latin-Parum=little,affins=affinity)

10.How can ethane be prepared from (i) ethanol (ii) ethylbromide?

Ans.(i)Ethene from ethanol- by acidic dehydration of alcohols



$$H-\overset{H}{\underset{H}{\overset{|\beta}{\underset{|}{C}}}}-\overset{H}{\underset{OH}{\overset{|\alpha}{\underset{|}{C}}}}-H\xrightarrow[\Delta]{Conc.\ H_2SO_4}CH_2=CH_2+H_2O$$

Ethanol Ethene

(ii) Ethene from ethyl bromide- by dehydrohalogenation of ethylbromide

$$CH_3CH_2Br+KOH(alc)\rightarrow H_2C=CH_2+KBr+H_2O$$

THREE MARKS QUESTIONS

1.What is Wurtz reaction?How can it be used to prepare butane?

Ans-When alkyl halide is treated with metallic Na in presence of dry ether, alkanes are formed. This reaction is called Wurtz reaction.

Butane is prepared by the reaction of bromo ethane with metallic Na in presence of dry ether

$$\underset{\text{Bromoethane}}{C_2H_5Br} + 2Na + BrC_2H_5 \xrightarrow{\text{dry ether}} \underset{\text{n-Butane}}{C_2H_5-C_2H_5}$$

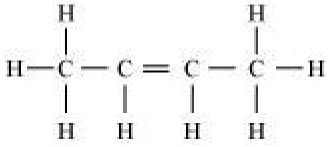
2.An alkene‘A’contains three C– C, eight C–H σ bonds and one C–C π bond.‘A’on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Deduce IUPAC name of‘A’.

Ans..The formation of two moles of an aldehyde indicates the presence of identical structural units on both sides of the double bond containing carbon atoms.Hence, the structure of‘A’can be represented as:

XC=CX

There are eight C–H σ bonds.Hence, there are 8 hydrogen atoms in ‘A’. Also, there are three C–C bonds. Hence, there are four carbon atoms present in the structure of ‘A’.

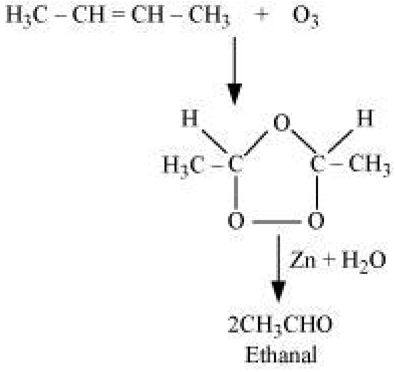
Combining the inferences, the structure of‘A’can be represented as:



(A)

the IUPAC name of ‘A’ is But-2-ene.

Ozonolysis of ‘A’takes place as:

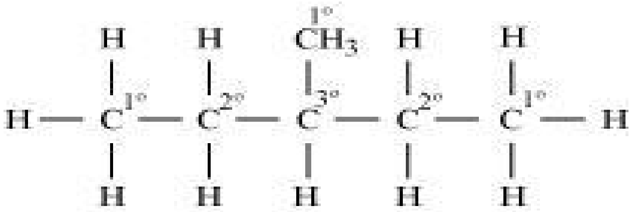


The final product is ethanal with molecular mass

$$= [(2\times12)+(4\times1)+(1\times16)]$$
$$= 44\ u$$

3.In the alkane $H_3C–CH_2–CH(CH3)–CH_2–CH_2\text{-}(CH_3)_2$, identify 1°,2°,3° carbon atoms and give the number of H atoms bonded to each one of these.

Ans.



The given structure has three 1°carbon atoms and each such carbon atom is attached with three H – atoms.

The given structure has two 2° carbon atoms and two hydrogen atoms remain attached to such a carbon atom.

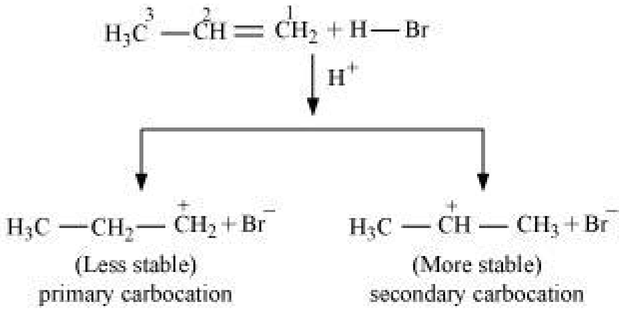
The given structure has one 3°carbon atom and only one hydrogen atom is attached to it

FIVE MARKSQUESTIONS

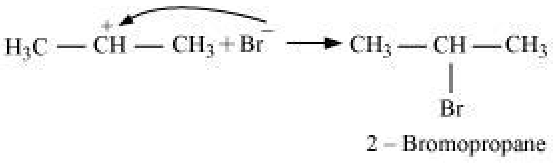
4.Addition of HBr to propene yields 2-bromopropane, while in the presence of benzoyl peroxide, the same reaction yields1-bromopropane. Explain and give mechanism

Ans.Addition of HBr to propene is an example of an electrophilic substitution reaction.

Hydrogen bromide provides an electrophile, H^+. This electrophile attacks the double bond to form1°and 2°carbocations as shown:



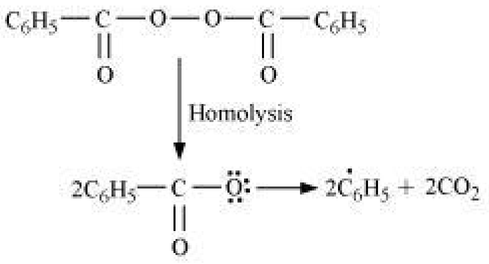
Secondary carbocations are more stable than primary carbocations. Hence, the former predominates since it will form at a faster rate.Thus, in the next step, Br^-attacks the carbocation to form 2–bromopropane as the major product.



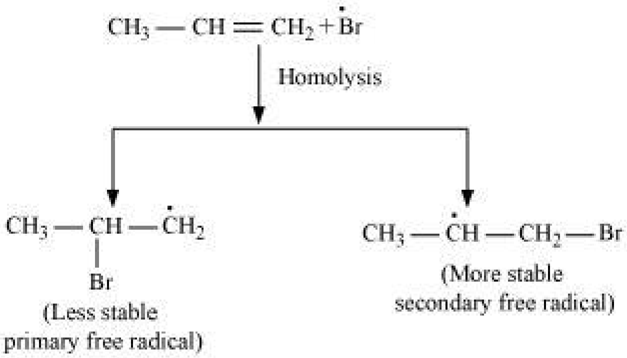
This reaction follows Markovnikov’srule

In the presence of benzoyl peroxide, an addition reaction takes place according to anti

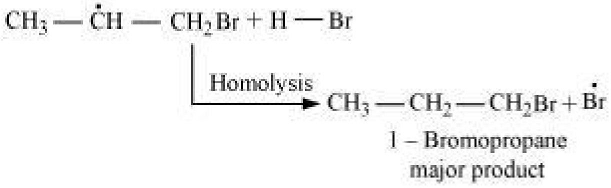
Markovnikov’s rule. The reaction follows a free radical chain mechanism as:



$$\dot{C}_6H_5 + H - Br \xrightarrow{\text{Homolysis}} C_6H_5 + \dot{Br}$$



Secondary free radicals are more stable than primary radicals. Hence, the former predominates since it forms at a faster rate.Thus, 1–bromopropane is obtained as the major product.



HOTS QUESTIONS

1.How will you demonstrate that double bonds of benzene are some what different from that of olefins?

Ans.The double bonds of olefins decolourize bromine water and discharge the Pink colour of Bayer’s reagent while those of benzene do not.

2.How will you separate propene from propyne?

Ans. By passing the mixture through ammonical silvernitrate solution when propyne reacts while propene passes over.

3.Write the structure of the alkene which on reductive ozonolysis gives butanone and ethanal,

Ans.-$CH_3CH_2C(CH_3)=CHCH_3$

CHAPTER14

ENVIRONMENTALCHEMISTRY

- Environmental chemistry deals with the study of the origin,transport,reactions,effects,fates ofchemicalspeciesintheenvironment.

- ENVIRONMENTALPOLLUTION:-Environmentalpollutionistheeffectof undesirablechangesinour surroundingsthathaveharmfuleffectsonplants, animalsandhumanbeings.Asubstancewhichcauses pollutioniscalledapollutant.theycanbesolid,liquidorinthegaseousstate.

- ATMOSPHERICPOLLUTION:-Theatmospherethatsurroundstheearthis not of the same thickness at different heights.Atmospheric pollution isgenerallystudiedastroposphericandstratosphericpollution.Theozonelayerpreventsabout 99.5%ofthesun'sUV rays.

- TROPOSPHERICPOLLUTION:-Troposphericpollution occursduetothe presenceofundesirablesolid or gaseousparticlesintheair.Thefollowingarethemajor gaseousandparticulatepollutantspresentinthetroposphere;

  - Gaseousairpollutants:Theseareoxidesofsulphur,nitrogenandcarbon,hydrogen sulphide, hydrocarbons, ozone and otheroxidants.
  - Particulate pollutants;thesearedust,mist,fumes,smoke,smogetc

- GLOBALWARMINGANDGREENHOUSEEFFECT:-About75%ofthesolar energy reaching theearthis absorbed by the earth's surface,whichincreases it's temperature.The rest of the heat radiates back to theatmosphere.Some of the heat is trapped by the gases such as carbondioxide,methane,ozone,CFCSandWatervapour.theyaddtotheheatingoftheatmospherecausingGlobalwarming

  Inagreenhouse,visiblelightpassesthroughthetransparentglassandheatsupthesoilandtheplants.The warmsoilandplantsemitinfraredrays,itpartly reflectsandpartly absorbstheseradiations,thismechanismkeepstheenergyofthesuntrappedinthegreenhouse.

- ACIDRAIN:WhenthepHoftherainwaterdropsbelow5.6,itiscalledacid rain.Acidrainisharmfulforagriculture,treesandplantsasitdissolvesand washesawaynutrientsneededfortheirgrowth.Itcausesrespiratoryailments

  In human beings and animals.When acid rain falls and flows as ground water to reach rivers, lakes etc. it affects plants and animal life in aquatic ecosystem

- SMOG:The word smog is derived from smoke and fog. There are two types of smog: classical and photochemical smog. Classical smog occurs in cool humid climate. It is a mixture of smoke, fog and sulphurdioxide. It is also called reducing smog. Where as photochemical smog occurs in warm and dry sunny climate. It has high concentration of oxidizing agents and therefore, it is also called oxidizing smog.

- OZONEHOLE: Depletion of ozone layer is known as ozone hole.

- EFFECTS OF DEPLETION OF THE OZONE LAYER: With the depletion of ozone layer, more UV radiation filters into troposphere. UV radiations lead to ageing of skin, cataract, sunburn, skincancer, killing of many phytoplanktons, damage to fish productivity etc
- WATER POLLUTION:-contamination of water by foreign substances which make it harmful for health of animals or plants or aquatic life and make it unfit for domestic,industrial and agriculture use.

- SOURCES/CAUSES OFWATERPOLLUTION-
    - Sewage and domestic wastes
    - Industrial effluents
    - Agriculture effluents
    - Siltation-mixing of soil or rock into water
    - Thermal pollutants
    - Radioactive discharge
- EUTROPHICATION: The process in which nutrient enriched water bodies support a dense plant population, which kills animal life by depriving it of oxygenand results in subsequent loss of biodiversity is known as Eutrophication

- BOD:The amount of oxygen required bybacteria to break down the organic matter present in a certain volume of a sample of water, is called Biochemical Oxygen Demand(BOD).

- SOIL POLLUTION: Insecticides, pesticides and herbicides cause soil pollution.

- GREENCHEMISTRY: Greenchemistry is a way of thinking and is about utilizing the existing knowledge and principles of chemistry and other sciences to reduce the adverse impact on environment. Green chemistry is a production process that would bring out minimum pollution or deterioration to the environment.Utilization of existing knowledge base for reducing the chemicalhazardsalongwiththedevelopmentofactivitiesisthefoundationof greenchemistry.

ONEMARKQUESTION

1.What is the name of the compound formed when CO combines with blood?
Ans:-Carboxyhaemoglobin.
2.Whichzoneisknownasozonosphere?
Ans:-Stratosphere.
3.Name the main gases responsible for damage to ozone layer?
Ans:-NO and CFCs(freons).
4.What is the nature of classical smog?
Ans:-Reducing
5.Name the acids which are responsible for acid rain?
Ans:-H_2SO_4,HNO_3 and HCl.
6.List out the gases which are considered as major source of air pollution?
Ans:-Carbonmonoxide (CO),sulphur dioxide(SO_2)and oxides of nitrogen(NO_2).
7.What does PAN stand for?
Ans:-It is peroxyacetylnitrate.
8.Give the examples of insecticides?
Ans:-DDT,BHC.
9.Which gas was mainly responsible for BHOPAL gas tragedy?
Ans:-Methylisocyanate.
10.What should be the tolerable limit of F^- ions in drinking water?
Ans:-1ppmor1mgdm^{-3}.

TWO MARKsQUESTION

1.What is ‘acidrain’?How is it harmful to the environment?
Ans:-Acid rain is the rain water mixed with small amount of sulphuric acid, nitric acid along with hydrochloric acid which are formed from the oxides of sulphur and nitrogen present in air as pollutants. It has a pH of 4-5.
Harmful effects of acid rain:-
It is toxic to vegetation and aquatic life. It
damages buildings and statues.

2.Whatdoyou mean by Green house effect? What is the role of CO_2 in the green house effect.
Ans:-It is the phenomenon in which earth’s atmosphere traps the heat from the sun and prevents it from escaping in outer space. Gases such as CO_2

, methane, ozone, CFCs are believed to be responsible for this effect.
Heat from the sun after being absorbed by the earth gets radiated by the earth in the atmosphere. This heat is absorbed by CO_2 of air thus making the environment of the earth warm.

3.Which gases are responsible for greenhouse effect?List some of them.
Ans:-CO_2 is mainly responsible for greenhouse effect. Other green house gases are methane, nitrous oxide, water vapours and CFCs.

4.What is smog? How is classical smog different from photo chemical smog?
Ans:-The word smog is a combination of smoke and fog. It is a type of air pollution that occurs in many cities through out the world. Classical smog occurs in cool humid climate. It is also called reducing smog.
Whereas photochemical smog occurs in warm and dry sunny climate. It has high concentration of oxidizing agents and therefore ,it is also called as oxidizingsmog.

5.What are the reactions involved for ozone layer depletion in the stratosphere?
Ans:-$CF_2Cl_2(g)UV \longrightarrow Cl^*(g)+CF_2Cl^*(g)$
$Cl^*(g) +O_3(g) \longrightarrow ClO^*(g)+O_2(g)$
$ClO^*(g)+O(g) \longrightarrow Cl^*+O_2(g)$

6.What is the full form of BOD and COD?
Ans:-BOD stands for Biochemical Oxygen Demand whereas COD stands for Chemical Oxygen Demand.

7.What are viable and non-viable particulates?
Ans:-Viable particulates:-They are minute living organisms that are dispersed in the atmosphere including bacteria,fungi,moulds,algae etc.
Non-viable particulates:-They are formed by the breakdown of larger materials or by the condensation of minute particles and droplets.

8.What is B.H.C? Give its IUPAC name?
Ans:-B.H.C is BENZENE HEXA CHLORIDE Its IUPAC name is 1,2,3,4,5,6-hexachlorocyclohexane.

9.What is meant by PCBs?
Ans:-PCBs are polychlorinated biphenyls.They are contaminates of water.They are used as fluids in transformers and capacitors.

10.What is the compound formed when CO combines with blood?
Ans:-When CO combines with blood, the following reaction occurs forming carboxyhaemoglobin:-

$$HB+CO \longrightarrow (HBCO)\ \text{Carboxyhaemoglobin}$$

THREE MARKS QUESTIONS

1. What do you understand by- (i)Mist (ii)Smoke (iii)Fumes

Ans(i) Mists:-Mists are produced by particles of spray liquids and the condensation of vapours in air.

(ii)Smoke:-They are very small soot particles produced by burning of organic matter.

(iii)Fumes:-These are condensed vapours; fumes of metals are well known particulates of this type.

2. Define the term pesticides? What are three categories of pesticides?

Ans:-Pesticides are substances which are used to kill or block the reproductive process of unwanted organisms.

The three main categories of pesticides are:-

(i)Insecticides:-These are used to control insects and curb diseases and protect crops.

(ii)Herbicides:-These are used to kill weeds. Example- sodiumchlorate ($NaClO_3$), sodiumarsenite(Na_3AsO_3)

(iii)Fungicides:- These are used to check the growth of fungi. Example-methylmercury.

3.What do you mean by ozone hole? What are its consequences?

Ans:-Depletion of ozone hole creates some sort of holes in the blanket of ozone which surrounds us.This is known as ozone hole.

(i)With the depletion of the ozone layer UV radiation filters into the troposphere which leads to ageing of skin, cataract, sunburn etc.

(ii)By killing many of the phytoplanktons it can damage the fish productivity.

4.What are harmful effects of photochemical smog and how can they be controlled?

Ans:-(i)Photochemical smog causes eye irritation.

(ii)It damages plants (the leaves develop a metallic sheet)

(iii)Rubber on exposure to photochemical smog loses its elasticity and becomes inflexible and brittle.

Usually catalytic converters are used in the automobiles. The catalytic converters prevent the release of nitrogen oxide and hydrocarbons to the atmosphere. Certain plants e.g.,Pinus, Juniparus, Quercus, Pyrus and Vitis can metabolise nitrogenoxide and therefore, their plantation could help in this matter.

5.Give three examples in which greenchemistryhasbeenapplied.

Ans:-

(i) In dry cleaning ,use of liquefied CO_2 in place of tetrachloroethene($Cl_2C=CCl_2$)

(ii)In bleaching of paper using H_2O_2 in place of chlorine.

(iii)In the manufacture of chemicals like ethanol using environment-friendly chemicals and conditions.