केन्द्रीय विद्यालय संगठन
Kendriya Vidyalaya Sangathan

रसायन विज्ञान
CHEMISTRY

कक्षा/**Class: XI**
2024-25

विद्यार्थी अध्ययन सामग्री
Student Support Material

KENDRIYA VIDYALAYA SANGATHAN
ZONAL INSTITUTE OF EDUCATION & TRAINING, MUMBAI
CHEMISTRY STUDY MATERIAL
CLASS - XI

संदेश

विद्यालयी शिक्षा में शैक्षिक उत्कृष्टता प्राप्त करना केन्द्रीय विद्यालय संगठन की सर्वोच्च वरीयता है। हमारे विद्यार्थी, शिक्षक एवं शैक्षिक नेतृत्व कर्ता निरंतर उन्नति हेतु प्रयासरत रहते हैं। राष्ट्रीय शिक्षा नीति 2020 के संदर्भ में योग्यता आधारित अधिगम एवं मूल्यांकन संबन्धित उद्देश्यों को प्राप्त करना तथा सीबीएसई के दिशा निर्देशों का पालन, वर्तमान में इस प्रयास को और भी चुनौतीपूर्ण बनाता है।

केन्द्रीय विद्यालय संगठन के पांचों **आंचलिक शिक्षा एवं प्रशिक्षण संस्थान** द्वारा संकलित यह 'विद्यार्थी सहायक सामाग्री' इसी दिशा में एक आवश्यक कदम है । यह सहायक सामग्री कक्षा 9 से 12 के विद्यार्थियों के लिए सभी महत्वपूर्ण विषयों पर तैयार की गयी है । केन्द्रीय विद्यालय संगठन की 'विद्यार्थी सहायक सामग्री' अपनी गुणवत्ता एवं परीक्षा संबंधी सामाग्री-संकलन की विशेषज्ञता के लिए जानी जाती है और अन्य शिक्षण संस्थान भी इसका उपयोग परीक्षा संबंधी पठन सामग्री की तरह करते रहे हैं । शुभ-आशा एवं विश्वास है कि यह सहायक सामग्री विद्यार्थियों की सहयोगी बनकर सतत मार्गदर्शन करते हुए उन्हें सफलता के लक्ष्य तक पहुंचाएगी ।

शुभाकांक्षा सहित ।

निधि पांडे

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CHEMISTRY THEORY (043) SYLLABUS FOR SESSION-2024-25

TIME: 3 HRS. MAX. MARKS: 70

S. No.	UNIT	No. OF PERIODS	MARKS
1	Some Basic Concepts of Chemistry	12	7
2	Structure of Atom	14	9
3	Classification of Elements and Periodicity in Properties	8	6
4	Chemical Bonding and Molecular Structure	14	7
5	Chemical Thermodynamics	16	9
6	Equilibrium	14	7
7	Redox Reactions	6	4
8	Organic Chemistry: Some basic Principles and Techniques	14	11
9	Hydrocarbons	12	10
		TOTAL	70

Unit I: Some Basic Concepts of Chemistry 12 Periods

General Introduction: Importance and scope of Chemistry.

Nature of matter, laws of chemical combination, Dalton's atomic theory: concept of elements, atoms and molecules.

Atomic and molecular masses, mole concept and molar mass, percentage composition, empirical and molecular formula, chemical reactions, stoichiometry and calculations based on stoichiometry.

Unit II: Structure of Atom 14 Periods

Discovery of Electron, Proton and Neutron, atomic number, isotopes and isobars. Thomson's model and its limitations. Rutherford's model and its limitations, Bohr's model and its limitations, concept of shells and subshells, dual nature of matter and light, de Broglie's relationship, Heisenberg uncertainty principle, concept of orbitals, quantum numbers, shapes of s, p and d orbitals, rules for filling electrons in orbitals - Aufbau principle, Pauli's exclusion principle and Hund's rule, electronic configuration of atoms, stability of half-filled and completely filled orbitals.

Unit III: Classification of Elements and Periodicity in Properties 08 Periods

Significance of classification, brief history of the development of periodic table, modern periodic law and the present form of periodic table, periodic trends in properties of elements - atomic radii, ionic radii, inert gas radii, Ionization enthalpy, electron gain enthalpy, electronegativity, valency. Nomenclature of elements with atomic number greater than 100.

Unit IV: Chemical Bonding and Molecular Structure 14 Periods

Valence electrons, ionic bond, covalent bond, bond parameters, Lewis structure, polar character of covalent bond, covalent character of ionic bond, valence bond theory, resonance, geometry of covalent molecules, VSEPR theory, concept of hybridization, involving s, p and d orbitals and shapes of some simple molecules, molecular orbital theory of homonuclear diatomic molecules(qualitative idea only), Hydrogen bond.

Unit V: Chemical Thermodynamics 16 Periods

Concepts of System and types of systems, surroundings, work, heat, energy, extensive and intensive properties, state functions.
First law of thermodynamics -internal energy and enthalpy, heat capacity and specific heat, measurement of U and H, Hess's law of constant heat summation, enthalpy of bond dissociation, combustion, formation, atomization, sublimation, phase transition, ionization, solution and dilution. Second law of Thermodynamics (brief introduction)
Introduction of entropy as a state function, Gibb's energy change for spontaneous and non-spontaneous processes, criteria for equilibrium.
Third law of thermodynamics (brief introduction).

Unit VI: Equilibrium 14 Periods

Equilibrium in physical and chemical processes, dynamic nature of equilibrium, law of mass action, equilibrium constant, factors affecting equilibrium - Le Chatelier's principle, ionic equilibrium- ionization of acids and bases, strong and weak electrolytes, degree of ionization, ionization of poly basic acids, acid strength, concept of pH, hydrolysis of salts (elementary idea), buffer solution, Henderson Equation, solubility product, common ion effect (with illustrative examples).

Unit VII: Redox Reactions 06 Periods

Concept of oxidation and reduction, redox reactions, oxidation number, balancing redox reactions, in terms of loss and gain of electrons and change in oxidation number, applications of redox reactions.

Unit VIII: Organic Chemistry -Some Basic Principles and Techniques 14 Periods

General introduction, methods of purification, qualitative and quantitative analysis, classification and IUPAC nomenclature of organic compounds. Electronic displacements in a covalent bond: inductive effect, electromeric effect, resonance and hyper conjugation.
Homolytic and heterolytic fission of a covalent bond: free radicals, carbocations, carbanions, electrophiles and nucleophiles, types of organic reactions.

Unit IX: Hydrocarbons 12 Periods

Classification of Hydrocarbons

Aliphatic Hydrocarbons:
Alkanes - Nomenclature, isomerism, conformation (ethane only), physical properties, chemical reactions including free radical mechanism of halogenation, combustion and pyrolysis.
Alkenes - Nomenclature, structure of double bond (ethene), geometrical isomerism, physical properties, methods of preparation, chemical reactions: addition of hydrogen, halogen, water, hydrogen halides (Markovnikov's addition and peroxide effect), ozonolysis, oxidation, mechanism of electrophilic addition.
Alkynes - Nomenclature, structure of triple bond (ethyne), physical properties, methods of preparation, chemical reactions: acidic character of alkynes, addition reaction of - hydrogen, halogens, hydrogen halides and water.

Aromatic Hydrocarbons:

Introduction, IUPAC nomenclature, benzene: resonance, aromaticity, chemical properties: mechanism of electrophilic substitution. Nitration, sulphonation, halogenation, Friedel Craft's alkylation and acylation, directive influence of functional group in monosubstituted benzene. Carcinogenicity and toxicity.

CHEMISTRY (Code No. 043)
QUESTION PAPER DESIGN
CLASSES –XI and XII (2024-25)

S. No.	Domains	Total Marks	%
1	Remembering and Understanding: Exhibit memory of previously learned material by recalling facts, terms, basic concepts and answers. Demonstrate understanding of facts and ideas by organizing, comparing, translating, interpreting, giving descriptions and stating main ideas.	28	40
2	Applying: Solve problems to new situations by applying acquired knowledge, facts, techniques and rules in a different way.	21	30
3	Analysing, Evaluating and Creating: Examine and break information into parts by identifying motives or causes. Make inferences and find evidence to support generalizations. Present and defend opinions by making judgments about information, validity of ideas or quality of work based on a set of criteria. Compile information together in a different way by combining elements in a new pattern or proposing alternative solutions.	21	30

1. No chapter wise weightage. Care to be taken to cover all the chapters.
2. Suitable internal variations may be made for generating various templates. Choice(s):
    a. There will be no overall choice in the question paper.
    b. However, 33% internal choices will be given in all the sections.

CHAPTER-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 substance has 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.

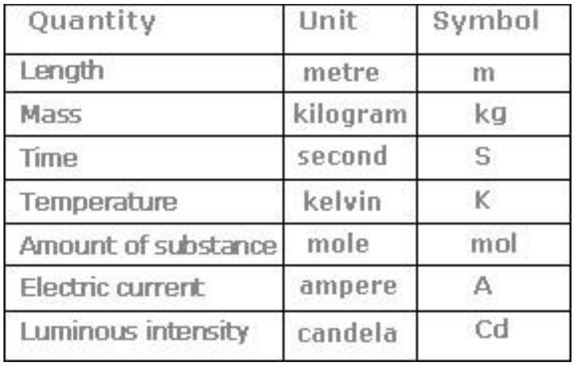
The measurement or observation of **chemical properties** requires a chemical change to occur. e.g. Burning of Mg-ribbon in air

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 *ConferenceGenerale 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 (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 accuratelywe express it with digits that are known with certainty. These 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

All non-zero digits are significant. For example, 6.9 has two significant figures, while 2.16 has three significantfigures. The decimal place does not determine the number of significant figures.

- A zero becomes significant in case it comes in between non zero numbers. For example, 2.003 has four significantfigures, 4.02 has three significant figures.
- Zeros at the beginning of a number are not significant. For example, 0.002 has one significant figure while 0.0045has two significant figures.
- 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.

- In exponential notations, the numerical portion represents the number of significant figures. For example, 0.00045 isexpressed as 4.5×10^{-4} in terms of scientific notations. The number of significant figures in this number is 2, while inAvogadro's number (6.023×10^{23}) it is four.
- The decimal point does not count towards the number of significant figures. For example, the number 345601 has sixsignificant figures but can be written in different ways, as 345.601 or 0.345601 or 3.45601 all having same number ofsignificant 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 precedingsignificant 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 isrounded 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 ithappens to be odd. In case of even figure, the preceding digit remains unchanged. 8.375 is rounded off to 8.38 while8.365 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

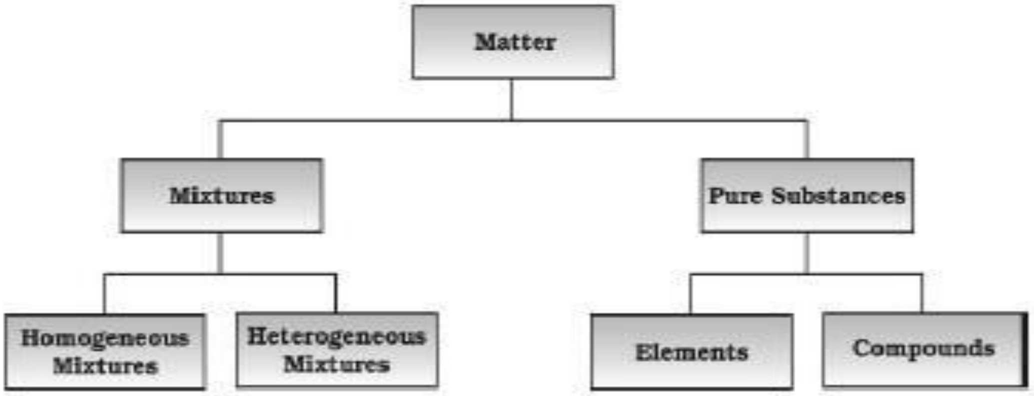
$$= 62\ \text{inch} \times \frac{2.54 \times 10^{-2}\ \text{m}}{1\ \text{inch}} = 1.58\ \text{m}$$

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 areobtained from non-living sources such as minerals. For example, common salt, marble and limestone. Organiccompounds are those, which occur in living sources such as plants and animals. They all contain carbon. Commonorganic 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.

e.g.$H_2(g) + Cl_2(g)$ ---→$2HCl(g)$

1V 1V 2V

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 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.

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

Gram Atomic Mass

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

For example, the atomic mass of oxygen = 16 amu

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-

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

Mole Concept.

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

A mole represents a collection of 6.022×10^{23}(Avogadro's number) chemical units.. **The mass of one mole of a substance in grams is called its molar mass.**

Molar Volume

The volume occupied by one mole of any substance is called its molar volume. It is denoted by 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.

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

Relationship between empirical and molecular formulae

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

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

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 of the following ways.

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

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

   A 5 % solution of sodium chloride means that 5 g of NaCl is present in 100g of the solution.
2. **Volume percent** is the number of units of volume of the solute per 100 units of the volume of solution.

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

   A 5 % (v/v) solution of ethyl alcohol contains 5 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 isdenoted by the symbol M. Measurements in Molarity can change with the change in temperature because solutionsexpand or contract accordingly.

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

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

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

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

Molarity equation

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

M1V1 = M2V2, where M1= initial molarity, M2= molarity of the new solution, V1= initial volume and V2= volume of the new solution.

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

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

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

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

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

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

CHAPTER -1

SOME BASIC CONCEPTS OF CHEMISTRY

SECTION –A (MCQs)

Q.No.	QUESTIONS	Marks
1.	Which one of the following will have the largest number of atoms? (a) 1 g Au(s) (b) 1 g Na(s) (c) 1 g Li(s) (d) 1 g of Cl_2(g	1
2.	A hydrocarbon was found to contain 75% by mass of carbon and 25% by mass of hydrogen. What is empirical formula of the compound? (a) C_2H_4 (b) C_2H_6 (c) CH_4 (d) C_6H_6	1
3.	Which of the following is used for treatment of cancer? (a) Cis-Platin (b) Taxol (c) A ZT (Azidothymidine) (d)Both (a) and (b)	1
4.	Which of the following is used for treatment of AIDS? (a) A ZT (Azidothymidine) (b) Azithromycin	1

(c) Streptomycin

(d) Chloromycin

5. Which of the following are homogeneous mixtures? 1

(a) Salt solution

(b) Sugar solution

(c) Air

(d)All of these

6. The number of significant figures in 0.001620 are 1

(a) 4

(b) 3

(c) 6

(d) 2

7. Accuracy means 1

(a) agreement of a particular value to true value

(b) The closeness of various measurements for the same quantity.

(c) Both (a) and (b)

(d)None of these

8. Which of the following measurement is more precise? 1

(a) 4.0

(b) 4.00

(c) 4.000

(d) 4.0000

9. A solution is prepared by adding 2 g of a substance A to 18 g of water. The mass percentage of the solute is- 1

(a) 90 %

(b) 10 %

(c) 20 %

(d) 50 %

10. What is mass percent silicon in 100 g of sodium silicate, Na_2SiO_3? 1

[Given : Atomic masses of Na = 23u, Si = 28u, O = 16u]

(a) 16.7%

(b) 23.0%

(c) 28.0%

(d) 82.0 %

11. Which of the following terms are unit less? 1

(a) Molality

(b) Molarity

(c) Mole fraction

(d)Density

12. The scientific notation for 0.00016 is - 1

(a) 1.6 X 10^{-2}

(b) 16 X 10^{-4}

(c) 1.6 X 10^{4}

(d) 1.6 X 10^{-4}

Assertion- Reason type Questions (Q. No.13 to 16)

In the following question, a statement of assertion followed by statement of a reason is given. Choose the correct answer out of the following choices.

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

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

(c) A is true but R is false.

(d) A is false but R is true.

13 **Assertion (A):** 2.000 has four significant figures. 1

Reason (R): All zeros after decimal are significant.

14. **Assertion (A):** Equal masses of He, O_2 and SO_2 contain equal number of molecules. 1

Reason (R): Equal volume of He, O_2 and SO_2 contain equal number of molecules at same temperature and pressure.

15. **Assertion (A):** Molarity does have unit, i.e. mol L^{-1} 1

Reason (R): Molarity does not change with temperature.

16. **Assertion (A):** The closeness of various measurements for the same quantity is called precision. 1

Reason (R): The agreement of a particular value to the true value of the result is called accuracy.

SECTION –B Short Answer Type Questions (2 marks each)

17. An organometallic compound on analysis was found to contain, C = 64.4%, H = 5.5% and Fe = 29.9%. Determine its empirical formula. 2
(At. mass of Fe = 56 u).

18. 1 M solution of $NaNO_3$ has density 1.25 g cm^{-3}. Calculate its molality. (Molecular weight of $NaNO_3$ = 85 g mol^{-1}) 2

19. The density of 3 molal solution of NaOH is 1.110 g ml^{-1}. Calculate the molarity of the solution. 2

20. If 4 g of NaOH dissolves in 36 g of H_2O, calculate the mole fraction of each component in the solution. Also, determine the molarity of solution. 2
(specificgravity of solution is 1g mL^{-1}).

21. What is the symbol for SI unit of mole? How is the mole defined? 2

SECTION -C Short Answer Type Questions (3 Marks each)

22. Calculate the amount of carbon dioxide that could be produced when- 3
(i) 1 mole of carbon is burnt in air.
(ii) 1 mole of carbon is burnt in 16 g of dioxygen.
(iii) 2 moles of carbon are burnt in 16 g of dioxygen.

23. (i) What is limiting reagent? 3
(ii) Oxygen is prepared by catalytic decomposition of potassium chlorate ($KClO_3$).
If 2.4 mol of oxygen is needed for an experiment, how many grams of potassium chlorate must be decomposed? (Atomic mass of K = 39, Cl=35.5, O = 16)

24. 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 formulae? 3

25. The reactant which is entirely consumed in reaction is known as limitingreagent. In the reaction $2A + 4B \rightarrow 3C + 4D$, when 5 moles of A react with 6 moles of B, then- 3
(i) which is the limiting reagent?
(ii)Calculate the amount of C formed.

26. Calculate the average atomic mass of hydrogen using the following data : 3

Isotope % Natural abundance

$^{1}H_{1}$ - 99.985 %

$^{1}H_{2}$ - 0.015 %

27. Which of the following solutions have the same concentration? 3

(a) 20 g of NaOH in 200 mL of solution

(b) 0.5 mol of KC1 in 200 mL of solution

(c) 40 g of NaOH in 100 mL of solution

(d) 20 g of KOH in 200 mL of solution

28. Write difference between – 3

(a)-Molarity and Molality

(b)-Mass and Weight.

SECTION –D Long Answer Type Questions (5 Marks each)

29. A vessel contains 1.6 g of dioxygen at STP (273.15 K, 1 atm pressure). The gas isnow transferred to another vessel at constant temperature where pressure becomes half of the original pressure. Calculate 5

(i) volume of the new vessel.

(ii) number of molecules of dioxygen.

30. Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction given below: 5

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

What mass of $CaCl_2$ will be formed when 250 ml of 0.76 M HCl reacts with 1000 g of $CaCO_3$? Name the limiting reagent. Calculate the number of moles of $CaCl_2$ formed in the reaction.

31. A box contains some identical red coloured balls, labelled as A, each weighing 2grams. Another box contains identical blue coloured balls, labelled as B, each weighing 5 grams. Consider the combinations AB, AB_2, A_2B and A_2B_3 and show that the law of multiple proportion is applicable. 5

SECTION -E **CASE BASED QUESTIONS** ***(4 Marks each)***

32. **Read the passage and answer the Questions-** 4

The uncertainty in the experimental or the calculated values is indicated by mentioning the number of significant figures. Significant figures are meaningful digits which are known with certainty plus one which is estimated or uncertain. The uncertainty is indicated by writing the certain digits and the last uncertain digit. There are certain rules for determining the Number of significant figures. These are Stated below:

All non-zero digits are significant. For Example in 285 cm, there are three Significant figures and in 0.25 mL, there are two significant figures.

Zeros preceding to first non-zero digit are not significant, such zero indicates the position of decimal point. Thus, 0.03 has one significant figure and 0.0052 has two significant figures.

Zeros between two non-zero digits are significant. Thus, 2.005 has four Significant figures.

Zeros at the end or right of a number are significant, provided they are on theright side of the decimal point. For example, 0.200 g has three significant figures. But, if otherwise, the terminal zeros are not significant if there is no decimal point.

Write the answer of following questions –

1. What are significant figures? 1
2. How many significant figures in 2.30002 ? 1
3. **3.** What is difference between precision and accuracy ? 2

33. **Read the passage and answer the Questions-** 4

Chemistry is the science of molecules and their transformations. It is the science not so much of the one hundred elements but of the infinite variety of molecules that may be built from them. Chemistry plays a central role in science and is often intertwined with other branches ofscience.to understand the basic concepts of chemistry, which begin with the concept of matter. Let us start with the nature of matter. Matter can exist in three physical states viz. solid, liquid and gas. Particles are held very close to each other in solids in an orderly fashion and there is not much freedom of movement. In liquids, the particles are close to each other but they can move around. However, in gases, the particles are far apart as compared to those present in solid or liquid states and their movement is easy and fast. different states of matter exhibit the following characteristics:

(i) Solids have definite volume and definite shape.

(ii) Liquids have definite volume but do not have definite shape. They take the shape of the container in which they are placed.

(iii) Gases have neither definite volume nor definite shape. They completely occupy the space in the container in which they are placed.

Matter can be classified as mixture or pure substance. A mixture may be homogeneous or heterogeneous. Pure substances can further be classified into elements and compounds. Particles of an element consist of only one type of atoms. These particles may exist as atoms or molecules. When two or more atoms of different elements combine together in a definite ratio, the molecule of a compound is obtained.

Every substance has unique or characteristic properties. These properties can be classified into two categories — physical properties, such as colour, odour, melting point, boiling point, density, etc., and chemical properties, like composition, combustibility, reactivity with acids and bases, etc. Physical properties can be measured or observed without changing the identity or the composition of the substance. The measurement or observation of chemical properties requires a chemical change to occur. Measurement of physical properties does not require occurance of a chemical change.

Write the answer of following questions –

1.What is difference between homogenous and heterogenous mixture ? 1

2.What is density ? Write its unit. 1

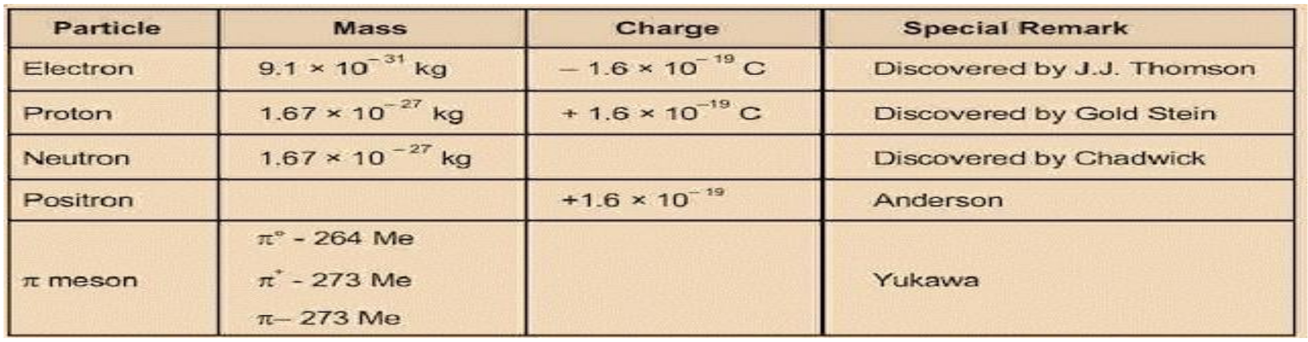
3.What are the different physical properties of matter ? Why these properties are called physical properties?

OR

What Are the Characteristics of The different States of Matter? 2

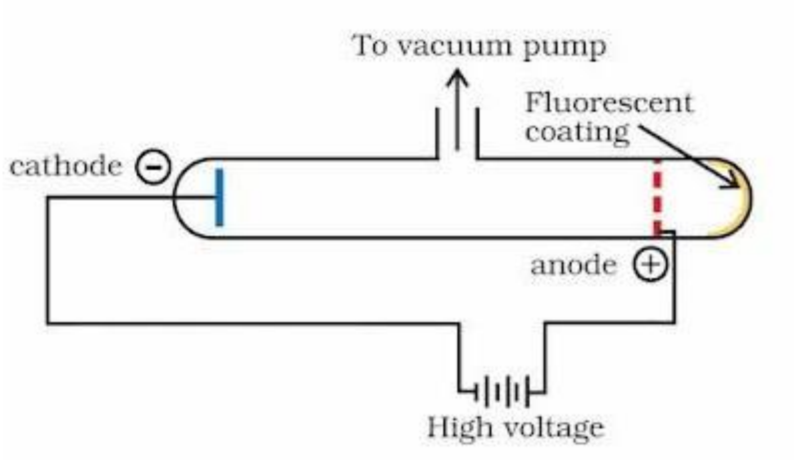
CHAPTER 2 -STRUCTURE OF ATOM

Atom is made up of smaller units like proton, neutron and electron.



Particle	Mass	Charge	Special Remark
Electron	9.1×10^{-31} kg	-1.6×10^{-19} C	Discovered by J.J. Thomson
Proton	1.67×10^{-27} kg	$+1.6 \times 10^{-19}$ C	Discovered by Gold Stein
Neutron	1.67×10^{-27} kg		Discovered by Chadwick
Positron		$+1.6 \times 10^{-19}$	Anderson
π meson	π^{0} - 264 Me π^{+} - 273 Me π^{-} 273 Me		Yukawa

Discovery of Electron



J.J. Thomson took a discharge tube and applied a voltage of a 10000 volt potential difference across it at a pressure of 10–2 mm of Hg. He found some glowing behind anode. It means some invisible rays produced at cathode strike behind anode and produce fluorescence. He named them cathode rays.

Properties of Cathode Rays

i. These rays have mechanical energy and travel in straight line.

ii. These rays are deflected towards positive plate of electric field. It means these are made up of negatively charged particle called **electron**.

iii. Colour observed is independent from nature of gas.

iv. Mulliken determined the charge on electron which is 1.602×10^{-19} C.

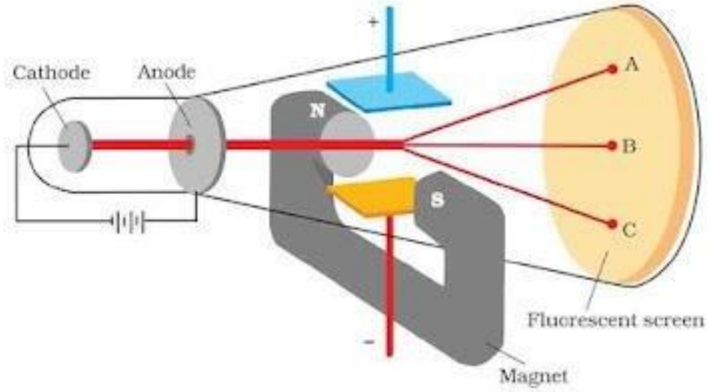
v. Specific charge on electron is calculated by J.J. Thomson.

Charge to mass ratio

J.J. Thomson for the first time experimentally determined charge/mass ratio called e/m ratio for the electrons. For this, he subjected the beam of electrons released in the

discharge tube as cathode rays to influence the electric and magnetic fields. These were acting perpendicular to one another as well as to the path followed by **electrons**. According to Thomson, the amount of deviation of the particles from their path in presence of electrical and magnetic field depends on,

1. Magnitude of the negative charge on particle
2. Mass of particle
3. Strength of magnetic field



When electric field is applied, deviation from path takes place. If only electric field is applied, cathode rays strike at A. If only magnetic field is applied, cathode rays strike at
C. In absence of any field, cathode rays strike at B.

By carrying out accurate measurements on the amount of deflections observed by the electrons on the electric field strength or magnetic field strength, Thomson was able to determine the value of $e/m_e = 1.758820 \times 10^{11}$ C kg^{-1}

where me = Mass of the electron in kg

e = magnitude of charge on the electron in coulomb (C).

Discovery of anode rays

In 1886, Goldstein modified the discharge tube by using a perforated cathode. On reducing the pressure, he observed a new type of luminous rays passing through the holes or perforations of the cathode and moving in a direction opposite to the cathode rays. These rays were named as positive rays or anode rays or as canal rays. Anode rays are not emitted from the anode but from a space between anode and cathode.

Properties of anode rays

1. These rays deflect towards negative plate of applied electric field. It means these are made up of positively charged particle.
2. Property of anode rays depends on nature of gas.
3. These rays travel in straight line and have mechanical energy.

Discovery of Neutron

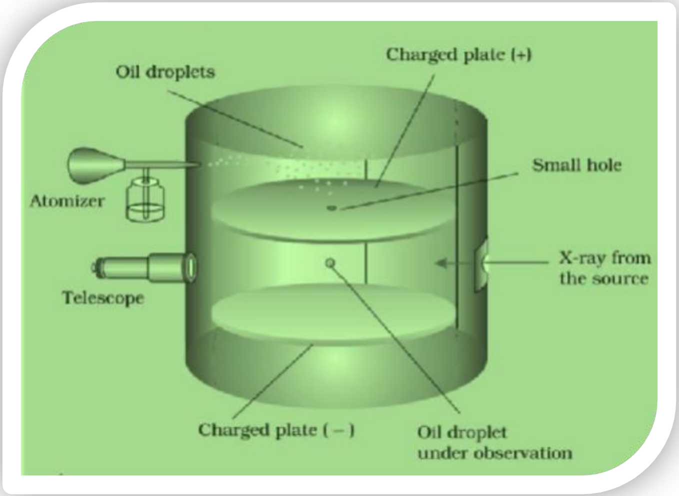
Chadwick in 1932 found the evidence for the production of neutron in given reaction.

$$_4Be^9 + _2He^4 \longrightarrow _6C^{12} + _0n^1$$

Neutron is chargeless particle and have mass equal to proton.

Millikan's Oil Drop Experiment

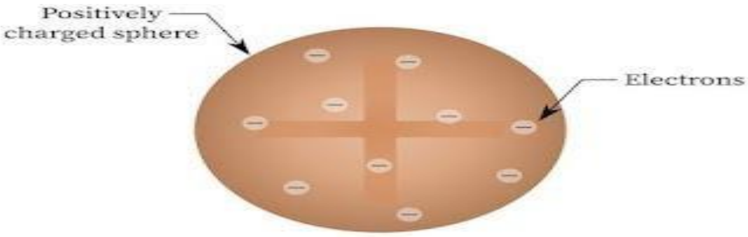
In this experiment, some fine oil droplets were allowed to enter through a tiny hole into the upper plate of electrical condenser. These oil droplets were produced by atomiser. The air in the chamber was subjected to the ionization by X-rays. The electrons produced by the ionization of air attach themselves to the oil drops.



Thus oil droplets acquire negative charge. When sufficient amount of electric field is applied, the motion of the droplets can be accelerated, retarded or made stationary. Millikan observed that the smallest charge found on them was –1.6 × 10–19 coulomb and the magnitude of electrical charge, q on the droplets is always an integral multiple of the electrical charge ‘e’ i.e., q = ne

Thomson’s Model of Atom

J.J. Thomson in 1898, proposed a model of atom which looked more or less like plum pudding or raisin pudding. He assumed atom to be a spherical body in which electrons are unevenly distributed in a sphere having positive charge which balance the electron’s charge. It is called Plum pudding model.

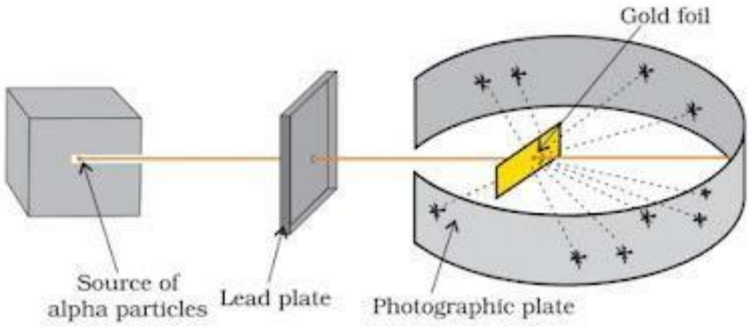


Important Feature of This Model: The mass of the atom is assumed to be uniformly distributed over whole atom.

Failure: This model was able to explain the overall neutrality of the atom, it could not satisfactorily, explain the results of scattering experiments carried out by Rutherford in 1911.

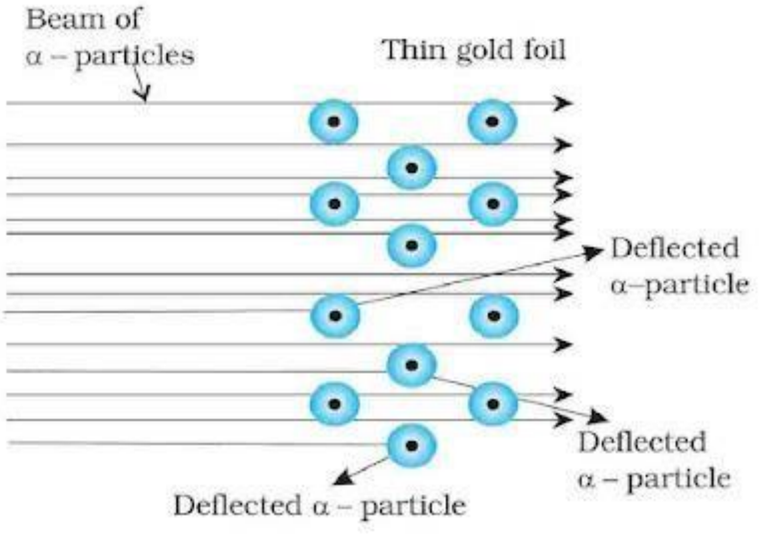
Rutherford's Model

Rutherford in 1911, performed some scattering experiments in which he bombarded thin foils of metals like gold, silver, platinum or copper with a beam of fast moving a- particles. The thin gold foil had a circular fluorescent zinc sulphide screen around it. Whenever a-particles struck the screen, a tiny flash of light was produced at that point.



From these experiments, he made the following observations: **6**

1. Most of the α - particles pass without any deviation.
2. Few particles deviate with small angle.
3. Rare particles retrace its path or show deflection greater than 90°.



On the basis of these observation, he proposed a model.

1. Atom is of spherical shape having size of order 10–10 meters.
2. Whole mass is concentrated in centre called nucleus having size of order 10–15 meters.
3. Electron revolves around the nucleus in circular path like planets revolve around sun.

Limitation: This model could not explain stability of atom. According to Maxwell's classic theory, an accelerated charged particle liberates energy. So, during revolution, it must radiate energy and by following the spiral path it should comes on nucleus.

Atomic number

It is equal to the number of protons present in the nucleus of an atom. Atomic number is designated by the letter ‘Z’. In case of neutral atom atomic number is equal to the number of protons and even equal to the number of electrons in atom.

Z = Number of protons (p) = Number of electrons (e)

Mass number

It is equal to the sum of the positively charged protons (p) and electrically neutral neutrons (n). Mass number of an atom is designated by the letter 'A'.

Mass number (A) = Number of protons (p or Z) + Number of neutrons (n)

Note: The atom of an element X having mass number (A) and atomic number (Z) may be represented by a symbol ${}_{Z}X^{A}$.

Isotopes

Atoms with identical atomic number but different atomic mass number are known as Isotopes. Isotopes of Hydrogen ${}_{1}H^{1}$, ${}_{1}H^{2}$ and ${}_{1}H^{3}$

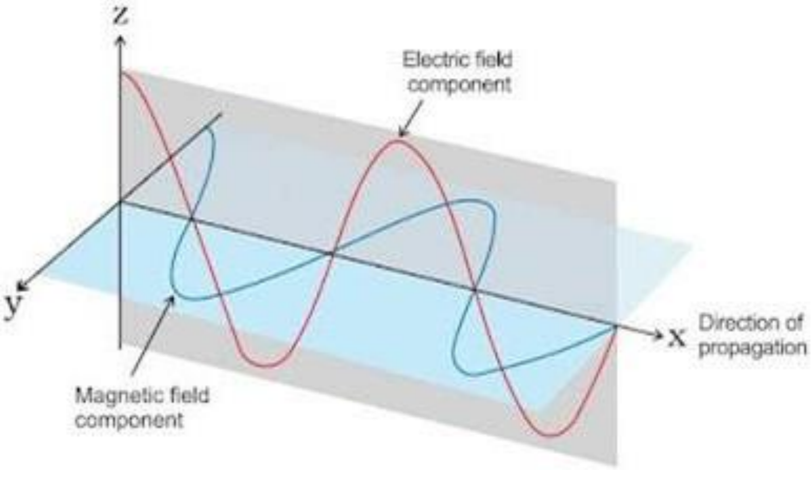
Isobars

Isobars are the atom with the same mass number but different atomic number, for example ${}_{6}C^{14}$ and ${}_{7}N^{14}$

Electromagnetic Waves Theory

This theory was put forward by James Clark Maxwell in 1864.

Electromagnetic Waves are the waves which are produced by varying electric field and magnetic field which are perpendicular to each other in the direction perpendicular to both of them.



The main points of this theory are as follows:

1. The energy is emitted from any source continuously in the form of

radiations and is called the radiant energy.

2. The radiations consist of electric and magnetic fields oscillating perpendicular to each other and both perpendicular to the direction of propagation of the radiation.
3. The radiations possess wave character and travel with the velocity of light 3 × 10^8 m/sec.
4. These waves do not require any material medium for propagation. For example, rays from the sun reach us through space which is a non-material medium.

Characteristics of a Wave

Wavelength (λ): It is the distance between two consecutive crests or troughs and is denoted by λ.

Frequency (v): It is the number of waves passing through a given point in one second. The unit frequency is hertz or cycle per second.

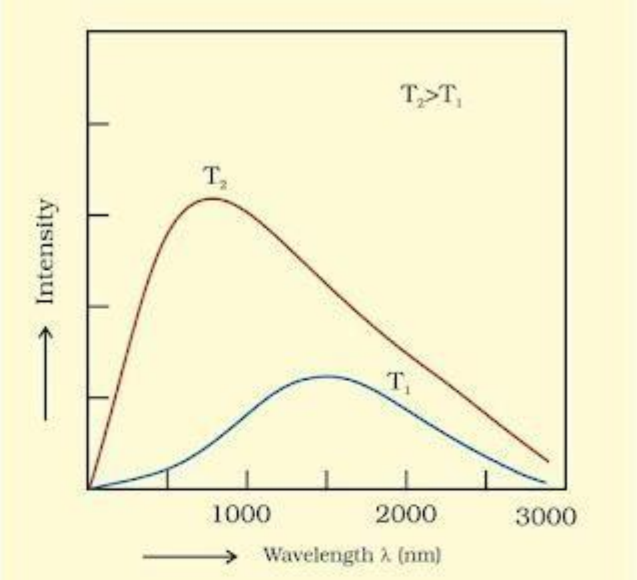
Wave number: It is the number of waves in a unit cycle. wave number =1λ=1λ

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

Amplitude: Amplitude of a wave is the height of the crest or the depth of the through. It is represented by V and is expressed in the units of length.

Black Body Radiations

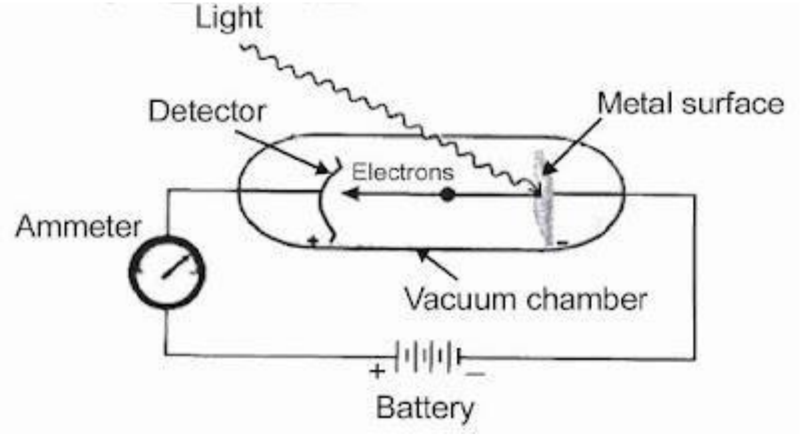
Black-body is an ideal body which emits and absorbs radiations of all frequencies. The radiation emitted by these bodies is called **black-body radiation**.



At a given temperature, the intensity and frequency of the emitted radiation depends is temperature. At a given temperature, the intensity of radiation emitted increases with decrease of wavelength.

Photoelectric Effect

When light of a suitable frequency is allowed to incident on a metal, ejection of electrons take place. This phenomenon is known as photo electric effect.



Observations in Photoelectric Effect

1. Only photons of light of certain minimum frequency called threshold frequency (v0) can cause the photoelectric effect. The value of v0 is different for different metals.
2. The kinetic energy of the electrons which are emitted is directly

proportional to the frequency of the striking photons and is quite independent of their intensity.

3. The number of electrons that are ejected per second from the metal surface depends upon the intensity of the striking photons or radiations and not upon their frequency.

Explanation of Photoelectric Effect

Einstein in (1905) was able to give an explanation of the different points of the photoelectric effect using Planck's quantum theory as under:

1. Photoelectrons are ejected only when the incident light has a certain minimum frequency (threshold frequency v0).
2. If the frequency of the incident light (v) is more than the threshold frequency (v0), the excess energy (hv–hv0) is imparted to the electron as kinetic energy.
3. On increasing the intensity of light, more electrons are ejected but the energies of the electrons are not altered.

   K.E. of the ejected electron.

   $\frac{1}{2} mv^2 = hv - hv_0$

Planck's Theory

According to this theory, energy cannot be absorbed or released continuously but it is emitted or released in the form of small packets called quanta. In case of light this quanta is known as photon. This photon travels with speed of light. Energy of the photon is directly proportional to frequency.

$E \propto \nu$ $E = h\nu$

h is ***Planck's constant***, value is 6.62×10^{-34} Js

Bohr's Model

1. Niels Bohr in 1913, proposed a new model of atom on the basis of Planck's Quantum Theory. The main points of this model are as follows:

2. Atom is of spherical shape having size (of order 10^{-10} metre).
3. Whole mass is concentrated in centre called nucleus (having order of size 10^{-15} metre).
4. Electron revolves around nucleus only in limited circular path and he assumed that electron does not radiate energy during its revolution in permitted paths.
5. Only those orbits are allowed whose orbit angular momentum is integral multiple of h2πh2π.
6. mvr = nh/2π, where n = 1, 2, 3, 4...
7. When electron absorbs energy, it jumps to higher orbit and when it comes back, it radiates energy. This postulate explains spectra.

Achievements of Bohr's Theory

1. Bohr's theory has explained the stability of an atom.
2. Bohr's theory has helped in calculating the energy of electron in hydrogen atom and one electron species.
3. Bohr's theory has explained the atomic spectrum of hydrogen atom.

Limitations of Bohr's Model

1. The theory could not explain the atomic spectra of the atoms containing more than one electron or multielectron atoms.
2. Bohr's theory failed to explain the fine structure of the spectral lines.
3. Bohr's theory could not offer any satisfactory explanation of Zeeman effect and Stark effect.
4. Bohr's theory failed to explain the ability of atoms to form molecule formed by chemical bonds.
5. It was not in accordance with the Heisenberg's uncertainty principle.

Spectra

The most compelling evidence for the quantization of energy comes from spectroscopy. Spectrum word is taken from Latin word which means appearance.

The record of the intensity transmitted or scattered by a molecule as a function of frequency or wavelength is called its spectrum.

Cosmic rays < gamma rays < x rays < ultraviolet rays < visible rays < infra red < micro waves < radio waves.

Line Spectrum of Hydrogen Atom

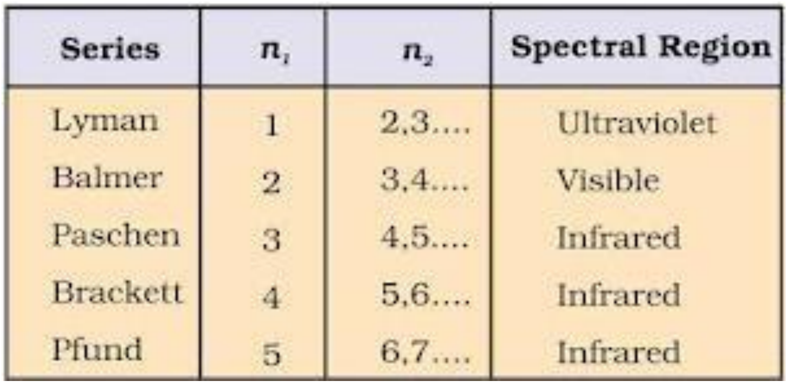
When electric discharge is passed through hydrogen gas enclosed in discharge tube under low pressure and the emitted light is analysed by a spectroscope, the spectrum consists of a large number of lines which are grouped into different series. The complete spectrum is known as hydrogen spectrum.

On the basis of experimental observations, Johannes Rydberg noted that all series of lines in the hydrogen spectrum could be described by the following expression:

wave number = 1λ = R(1n21 − 1n22)1λ =

R(1n12 - 1n22) R = Rydberg constant

R = 109678 cm^{-1}



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

Zeeman Effect

When spectral line (source) is placed in magnetic field, spectral lines split up into sublines. This is known as zeeman effect.

Stark Effect

If splitting of spectral lines take place in electric field, then it is known as stark effect.

Dual Behaviour of Matter (de Broglie Equation)

De Broglie in 1924, proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle like and wave like properties. This means that like photons, electrons also have momentum as well as wavelength.

Assume light have wave nature, then its energy should be given by Planck's theory

$$E = h\nu E = h\nu \ \ldots(i)$$

If it have particle nature, then its energy should be given by Einstein relation,

$$E = mc^2 \ \ldots(ii)$$

On comparing equation (i) and (ii),

$$h\nu = mc^2$$

$$\lambda = hmc \text{ (for light) } \ldots(iii)$$

$$\lambda = hmc \text{ (for matter) } \ldots(iv)$$

$$\lambda = hp \ \ldots(v) \text{ (p= momentum}$$

This equation is called de Broglie equation.

Heisenberg’s Uncertainty Principle

It states that, "It is impossible to measure simultaneously the exact position and exact momentum of a microscopic particle".

If uncertainty in position = Δx and

Uncertainty in momentum = ΔP

When both are measured simultaneously, According to this principle,

$$\Delta x \,.\Delta P \geq h4\pi$$

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.

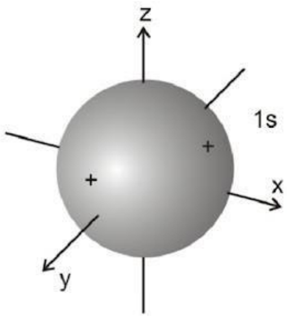
1. **Principal quantum number (n)**: It identifies shell, determines sizes and energy of orbitals. It is indicated by ‘n’ and its values are 1, 2, 3, 4...
2. **Azimuthal quantum number (l)**: Azimuthal quantum number. ‘l’ is

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., The number of orbitals in a sub shell = $2l + 1$. For a given value of n, it can have n values ranging from 0 to n-1.

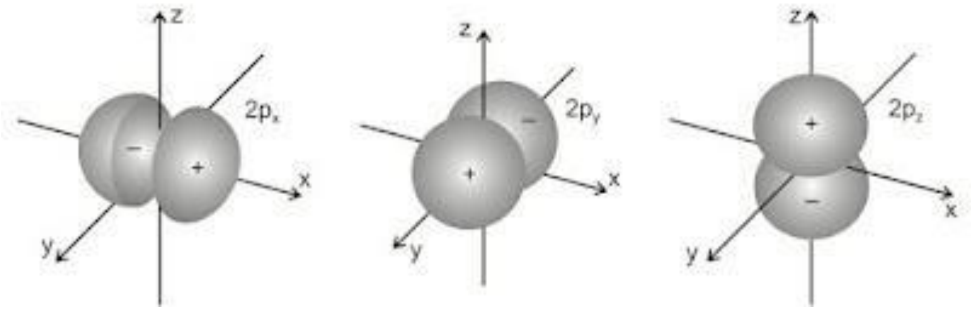
3. **Magnetic quantum number (ml)**: It gives information about the spatial orientation of the orbital with respect to standard set of co-ordinate axis.For any sub-shell (defined by ‘l’ value) 2l+1 values of ml are possible. For each value of l, ml = – l, – (l–1), – (l– 2)... 0,1...(l–2), (l–1), l
4. **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.

Shape of Atomic Orbitals

Shapes of s-orbitals: s-orbital is present in the s-sub shell. For this sub shell, l = 0 and ml = 0. Thus, s-orbital with only one orientation has a spherical shape with uniform electron density along all the three axes. The probability of Is electron is found to be maximum near the nucleus and decreases with the increase in the distance from the nucleus.



Shapes of p-orbitals: p-orbitals are present in the p-subshell for which l = 1 and ml can have three possible orientations –1, 0, +1. Thus, there are three orbitals in the p-subshell which are designated as px, py and pz orbitals depending upon the axis along which they are directed. The general shape of a p-orbital is dumb-bell consisting of two portions known as lobes.



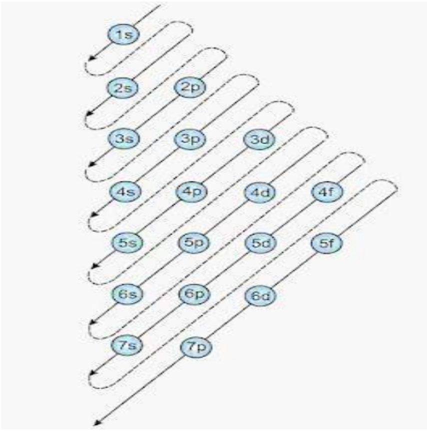
Shapes of d-orbitals: d-orbitals are present in d-subshell for which l = 2 and ml = -2, -1, 0, +1 and +2. This means that there are five orientations leading to five different orbitals. d orbitals are of five types: dxy, dyz, dzx, dx^2-y^2, dz^2

Electronic Configuration

Distribution of electron in various orbitals is known as electronic configuration. The electrons filled in orbitals must obey the following rules-

- Aufbau's principle
- Pauli's exclusion principle
- Hund's rule of maximum multiplicity

1. **Aufbau's principle:** According to this principle, orbitals with lowest energy are filled before the orbitals having higher energy.

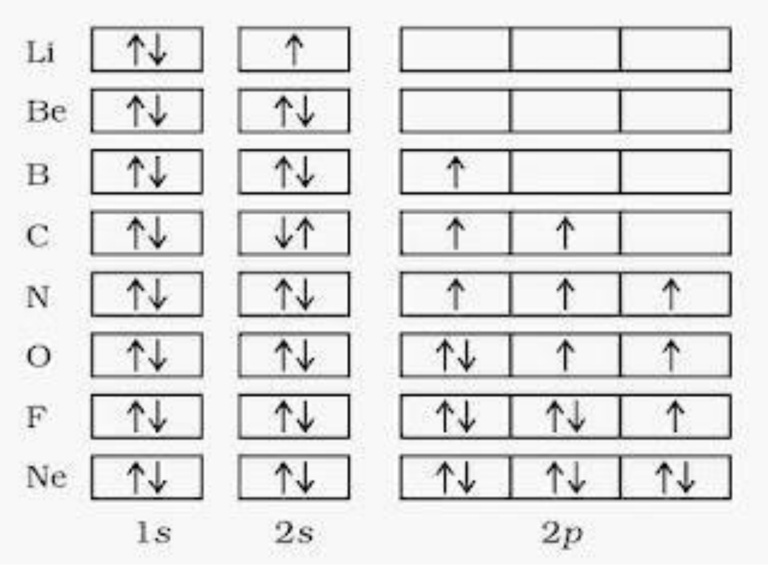


1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d< 7p

(n + l) rule (Bohr Bury’s Rule)

According to this, The orbital which has lower value of (n + l) is lower in energy.

2. **Pauli’s exclusion principle:** According to this principle, in an atom, no two electrons have same value of all the four quantum numbers. In the same orbital, electron always accommodate in opposite spins. An orbital can have a maximum of two electrons, with opposite spin.
3. **Hund’s rule of maximum multiplicity:** According to this rule, electrons are distributed among the orbital of a subshell in such a way so as to give the maximum number of unpaired electrons with a parallel spin.



CHAPTER –STRUCTURE OF ATOM
MCQ

Select and write one most appropriate option out of the four options given for each of the questions 1 – 16.

1. The total no. of orbitals associated with third shell will be

a.2
b.4
c.9
d.3

2. Which of the following options represent ground state electronic configuration of a copper atom?

a. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$
b. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9\ 4s^2$
c. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
d. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

3. Calculate the wavelength associated with a proton moving at $1.0\text{x}10^3$m/sec.(Mass of proton=$1.67\text{x}10^{-27}$kg and h=$6.63\text{x}10^{-34}$Js)

a. 0.032nm
b. 0.40nm
c. 2.5nm
d. 14.0nm

4. Which of the following statements about the electron is incorrect?

a. It is a negatively charged particle.
b. The mass of electron is equal to the mass of neutron.
c. It is a basic constituent of all atoms.
d. It is a constituent of cathode rays.

5. Which of the following atom is isoelectronic with Cr^{3+} ion?

a. Mn^{2+}
b. V^{2+}
c. Fe^{2+}
d. Co^{2+}

6. Which of the following statements is not correct regarding orbits and orbitals?

a. Except s-orbitals, all orbitals have directional characteristics.
b. Maximum number of electron occupied by an orbital is always 4.
c. An orbital is well defined circular path around nucleus in which electron revolves.
d. Orbits do not have directional characteristics.

7. The number of radial nodes for 3*p* orbital is __________.

a. 3

- b. 4
- c. 2
- d. 1

8. Which of the following orbitals will have lowest energy?
   - a. 6s
   - b. 4p
   - c. 5d
   - d. 4f

9. The shape of an orbital is determined by
   - a. Principal quantum number
   - b. Azimuthal quantum number
   - c. Magnetic quantum number
   - d. Spin quantum number

10 .The atomic number of two elements X and Y are 6 and 7 respectively while their mass number are 14 and 15 respectively. The relationship between X and Y is
   - a. Isotopes
   - b. Isobars
   - c. Isotones
   - d. Isoelectronic

11. The mass number of NH_4^+ion will be
   - a.20
   - b.22
   - c.18
   - d.9

12. The total possible values for magnetic quantum number for the value of l=3 is
   - a. 3
   - b. 1
   - c. 5
   - d. 7

ASSERTION-REASONING QUESTIONS

These consist of two statements – Assertion (A) and Reason (R). Answer these questions selecting the appropriate option given below:

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

1. Assertion- All isotopes of a given element show the same type of chemical behavior.
   Reason- The chemical properties of an atom are controlled by the number of electrons in the atom.

2. Assertion-Rutherford postulated that electrons revolves around nucleus in fixed circular paths.
Reason- As long as electron moves in its orbit,it does not loose or gain energy.

3. Assertion- It is impossible to determine the exact position and exact momentum of an electron simultaneously.
Reason -The path of an electron in an atom is clearly defined.

4. Assertion- No two electrons in an atom can have same values of all four Quantum numbers.
Reason- An orbital cannot hold more than two electrons which should have opposite spin.

COMPETENCY BASED QUESTIONS (2M)

1. An atom of an element has 19 electrons .Find out its atomic number, total number of neutrons, valency and no. of unpaired electrons.

2. Write the electronic configurations of the following ions- Na^+, $O_2{}^-$.

3. Arrange the following orbitals in the increasing order of energy 3d, 2s, 3s, 2p. State the rule which determines energy sequence of orbitals.

4. State main postulate of Planck's quantum Theory. Write expression for it.

5. Write any one property of electromagnetic radiations. Arrange the following electromagnetic waves in the order of increasing wavelength -visible radiations, infrared radiations, X-rays, ultraviolet rays, Micro waves.

6. How are the following terms related?
   a. Wave number and Wavelength.
   b. Frequency and Time period.

COMPETENCY BASED QUESTIONS (3M)

1. Calculate the wavelength, frequency and wave number of a light wave whose period is 2×10^{-10} second.

2. State photoelectric effect. Find energy of each of the photons which corresponds to the light of
   a. frequency of 3×10^{15} hertz .
   b. have wavelength of 0.50 Angstrom.

3. State Heisenberg Uncertainity principle. Write its mathematical expression. Calculate the uncertainity in momentum of an electron, if uncertainity in position is 10^{-10}m.

4. Consider a 4f subshell, (attempt any three)

   a. What is the maximum no. of electrons having spin in the same direction if it contains 10 electrons.

b. What are the value for Principal and Azimuthal quantum No. for 4f subshell.
c. How many orbitals are associated with f subshell?
d. What are the maximum no. of electrons that can be accommodated in f subshell?

5. Draw the shapes of s, p, d-orbitals.

6. What is the significance of Principal, Azimuthal and Magnetic quantum number in electronic configuration of an atom?

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

CASE BASED QUESTIONS (4M)

1. Nature of matter was proposed by the de Broglie in 1923. It was experimentally verified by Davisson in Germer by diffraction experiment .Wave character of matter has significance only for microscopic particles de Broglie hypothesis suggested that electron waves were being diffracted by target, much as X rays are diffracted by planes of atoms.
(1+1+2)

A. Write the expression to calculate the de Broglie wavelength.
B. According to de Broglie formula, calculate mass of a microscopic particle of wavelength 3.6 x10^{-6}m and moving at a velocity of 100 cm per second.
C. According to de Broglie, matters exhibits dual behaviour that is both particle like and wave like properties. How a cricket ball of mass 100 gram does not move like a way when it is thrown by a bowler at is speed of 100 km per hour. Calculate the wavelength of the ball and explain why it do not show wave nature.

OR

C. Calculate the momentum of a particle having de Broglie wavelength of 0.1nm. (Given h=6.62x10^{-34}Js)
a. 6.62x10-24kgm/s
b. 6.62x10-14kgm/s
c. 6.62x10-34kgm/s
d. None of the above.

2. According to quantum mechanical model of the atom, the electron distribution of an atom containing a number of electrons is divided into shells .The shells in turn are thought to consist of one almost subshells and subshells are assumed to be composed of one or more orbitals which the electrons occupy. While for hydrogen and hydrogen like systems all the orbitals within a given shell have same energy and that of energy of the orbitals in a multi electron atom are not same. (1+1+2)

1. Among the following pair of orbitals, which orbital will experience the largest effective nuclear charge : 4d or 4f?

2. Which of the following sets of quantum number are not possible (give reason)
   a. n = 0 ,l = 0, m =0,m_s =+ 1/2 .
   b. n=1, l =0,m =0,m_s =-1/ 2 .

3. State Pauli Exclusion Principle.

OR

Using s, p d f notation, describe the orbital with the following quantum number.

a. n=2,l=1
b. n=4,l=0

COMPETENCY BASED QUESTIONS (5M)

1. **Answer the following questions (attempt any five parts)**
   a. Why do we observe large number of spectral lines in hydrogen sample?
   b. Which series of hydrogen spectrum lies in the visible region?
   c. Differentiate Absorption and Emission Spectra?
   d. State first five series of lines in hydrogen spectrum.
   e. Write Rydberg formula for line spectrum of hydrogen atom.

2. Write Major postulates of Rutherford Atomic model. What was its major drawback?
(3+2)

3.Write the electronic configuration of – Cr, Zn and Mn. Account for Stability of half filled and completely filled subshells.
(3+2)

4.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? 3

4a.A monochromatic yellow light has a wavelength of 580nm. Calculate the frequency and wave number associated with it. 2

CHAPTER 3

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

NEED FOR CLASSIFICATION-

It is difficult to study individually the chemistry of more than hundred elements and their innumerable compounds. The periodic table provides a systematic framework for organizing the large available information on the chemical behaviour of the elements into simple logical patterns.

Genesis of Periodic Classification Dobereiner's Triads

In 1829, Dobereiner arranged certain elements with similar properties in groups of three in such a way that the atomic mass of the middle element was nearly the same as the average atomic masses of the first and the third elements. A few triads proposed by him are listed.

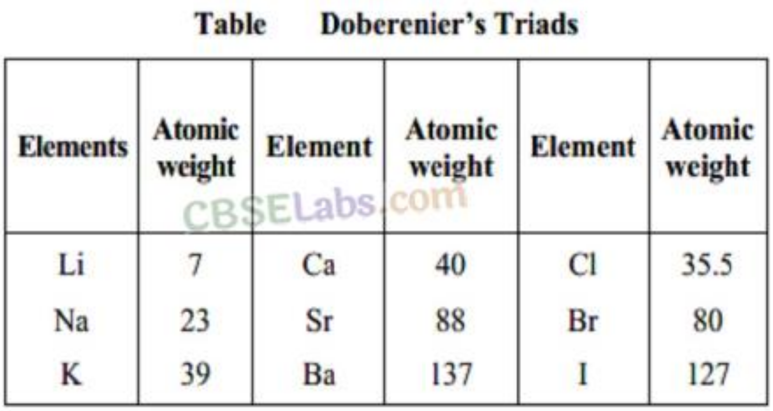


Table Doberenier's Triads

Elements	Atomic weight	Element	Atomic weight	Element	Atomic weight
Li	7	Ca	40	Cl	35.5
Na	23	Sr	88	Br	80
K	39	Ba	137	I	127

Limitations of Dobereiner's Trids

The triads given by Dobereiner were helpful in grouping some elements with similar characteristics together, but he could not arrange all the elements known at that time into triads.

- **Newlands' Law of Octaves**

John Newlands proposed the law of octaves by stating that when elements are arranged in order of increasing atomic masses, every eighth element has properties similar to the first. Newlands called it law of octaves because similar relationship exists in the musical notes also.

Newland's octaves

sa (do)	re (re)	ga (mi)	ma (fa)	pa (so)	da (la)	ni (ti)
H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe
Co and Ni	Cu	Zn	Y	In	As	Se
Br	Rb	Sr	Ce and La	Zr	—	—

Limitations of Newlands' Law of Octaves

(i) This classification was successful only up to the element calcium. After that, every eighth element did not possess the same properties as the element lying above it in the same group.

(ii) When noble gas elements were discovered at a later stage, their inclusion in the table disturbed the entire arrangement.

Mendeleev's Periodic Table

Mendeleev's Periodic Law: ' The physical and chemical properties of the elements are a periodic function of their atomic masses'.

Mendeleev arranged the elements known at that time in order of increasing atomic masses and this arrangement was called periodic table.

Elements with similar characteristics were present in vertical rows called groups. The horizontal rows were known as periods.

Importance of Mendeleev's Periodic Table

(i) This made the study of the elements quite systematic in the sense that if the properties of one element in a particular group are known, those of others can be predicted.

(ii) This helped to a great extent in the discovery of these elements at a later stage.

(iii) Mendeleev corrected the atomic masses of certain elements with the help of their expected positions and properties

There are some defects in **Mendeleev's Periodic Table**

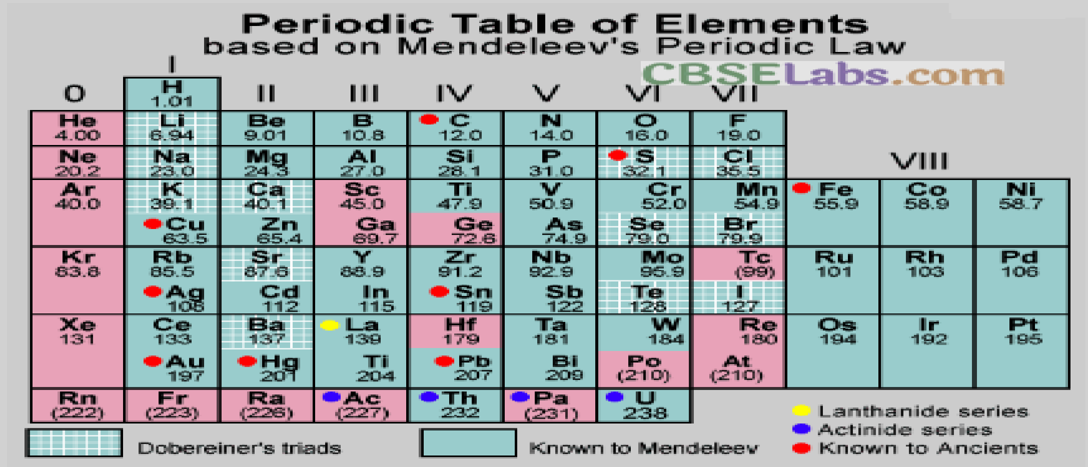
(i) Hydrogen has been placed in group IA along with alkali metals. But it also resembles halogens of group VII A in many properties.

ii) Although the elements in the Mendeleev's periodic table have been arranged in order of their atomic masses, but in some cases the element with higher atomic mass precedes the element with lower atomic mass.

iii) The isotopes of an element have different atomic masses but same atomic number. Since, periodic table has been framed on the basis of increasing atomic masses of the elements, different positions must have been allotted to all the isotopes of a particular element.

iv) According to Mendeleev, the elements placed in the same group must resemble in their properties. But there is no similarity among the elements in the two sub-groups of a particular group.

In some cases, elements with similar properties have been placed in different groups.
v) Lanthanoids and actinoids were placed in two separate rows at the bottom of the periodic table without assigning a proper reason.
(vi) No proper explanation has been offered for the fact that why the elements placed in group show resemblance in their properties.



Periodic Table of Elements
based on Mendeleev's Periodic Law

O	I	II	III	IV	V	VI	VII	VIII		
	H 1.01									
He 4.00	Li 6.94	Be 9.01	B 10.8	🔴 C 12.0	N 14.0	O 16.0	F 19.0			
Ne 20.2	Na 23.0	Mg 24.3	Al 27.0	Si 28.1	P 31.0	🔴 S 32.1	Cl 35.5			
Ar 40.0	K 39.1	Ca 40.1	Sc 45.0	Ti 47.9	V 50.9	Cr 52.0	Mn 54.9	🔴 Fe 55.9	Co 58.9	Ni 58.7
	🔴 Cu 63.5	Zn 65.4	Ga 69.7	Ge 72.6	As 74.9	Se 79.0	Br 79.9			
Kr 83.8	Rb 85.5	Sr 87.6	Y 88.9	Zr 91.2	Nb 92.9	Mo 95.9	Tc (99)	Ru 101	Rh 103	Pd 106
	🔴 Ag 108	Cd 112	In 115	🔴 Sn 119	Sb 122	Te 128	I 127			
Xe 131	Ce 133	Ba 137	🟡 La 139	Hf 179	Ta 181	W 184	Re 180	Os 194	Ir 192	Pt 195
	🔴 Au 197	🔴 Hg 201	Ti 204	🔴 Pb 207	Bi 209	Po (210)	At (210)			
Rn (222)	Fr (223)	Ra (226)	🔵 Ac (227)	🔵 Th 232	🔵 Pa (231)	🔵 U 238				

▦ Dobereiner's triads
🟦 Known to Mendeleev
🟡 Lanthanide series
🔵 Actinide series
🔴 Known to Ancients

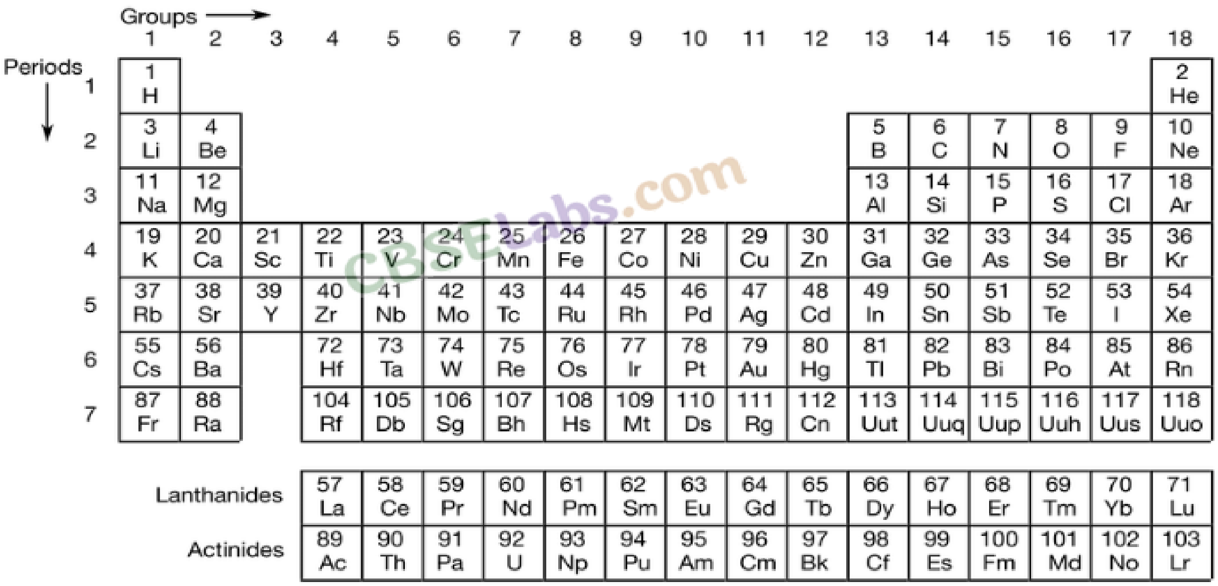
Modern Periodic Law

Physical and chemical properties of the elements are the periodic function of their atomic numbers.

- Present Form of the Periodic Table (Long form of Periodic Table)

The long form of periodic table, also called Modem Periodic Table, is based on Modern periodic law. In this table, the elements have been arranged in order of increasing atomic numbers.

- Nomenclature of Elements with Atomic No. more than 100.



Periods ↓ / Groups →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

The modern periodic table.

Groups

The long form of periodic table also consists of the vertical rows called groups. There are in all 18 groups in the periodic table. Unlike Mendeleev periodic table, each group is an independent group.

On the basis of the electronic configuration elements can be recognised as s-block ,p-block, d-block and f-block elements.

Characteristics of s-block elements:

1) Except H all elements of s-Block elements are active metals.
2) They have +1/ +2 oxidation state.
3) They form basic oxides
4) They impart characteristic colour to the flame
5) Generally they form ionic salts with nonmetals.
6) They have low ionization potentials.
7) They have very small electron gain enthalpies.
8) They are solids at room temperature (Cs is liquid at about at 35 degree C)
9) Their hydroxides are basic in nature.

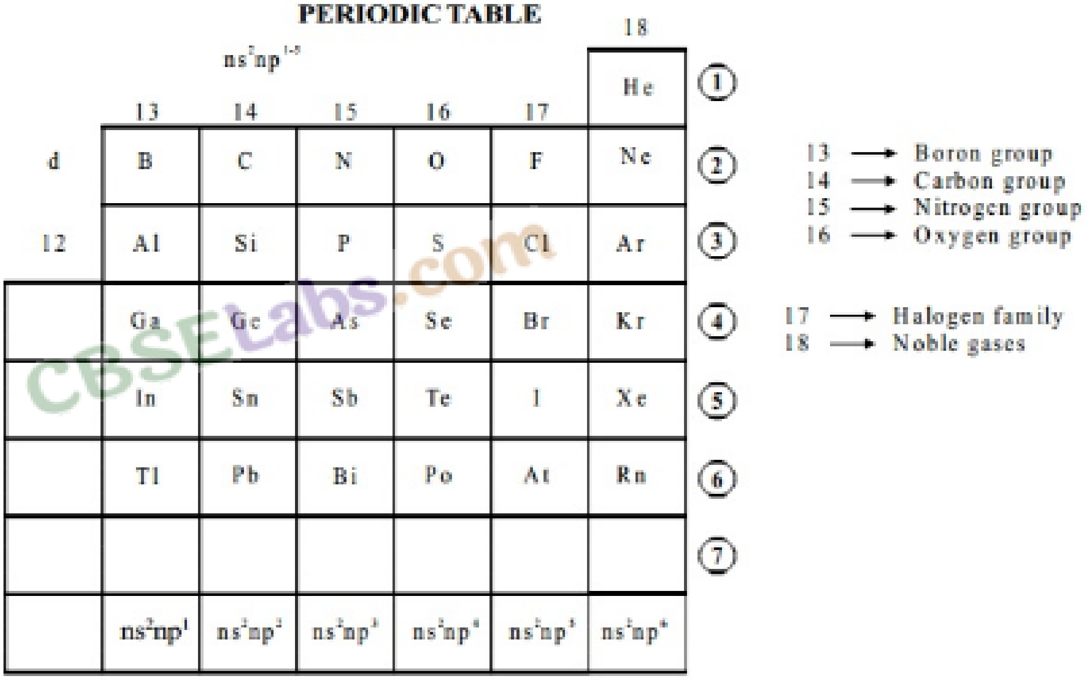
Characteristics of p-block elements:

(i) The compounds of these elements are mostly covalent in nature.
(ii) They show variable oxidation states.
(iii) In moving from left to right in a period, the non-metallic character of the elements increases.
(iv) The reactivity of elements in a group generally decreases downwards.

(v) At the end of each period is a noble gas element with a closed valence shell ns^2 np^6 configuration.
(vi) Metallic character increases as we go down the group.

Characteristics of d -block elements:

General electronic configuration: (n -1) d^{1-10} ns^{0-2}
The d-block elements are known as transition elements because they have incompletely filled d-orbitals in their ground state or in any of the oxidation states.



PERIODIC TABLE

ns^2np^{1-6}

	13	14	15	16	17	18	
						He	①
d	B	C	N	O	F	Ne	②
12	Al	Si	P	S	Cl	Ar	③
	Ga	Ge	As	Se	Br	Kr	④
	In	Sn	Sb	Te	I	Xe	⑤
	Tl	Pb	Bi	Po	At	Rn	⑥
							⑦
	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6	

13 → Boron group
14 → Carbon group
15 → Nitrogen group
16 → Oxygen group

17 → Halogen family
18 → Noble gases

Characteristics of d-block elements:
(i) They are all metals with high melting and boiling points.
(ii) The compounds of the elements are generally paramagnetic in nature.
(iii) They mostly form coloured ions, exhibit variable valence (oxidation states).
(iv) They are of tenly used as catalysts.

Elements are classified as

Metals
(i) Metals comprise more than 78% of all known elements and appear on the left side of the Periodic Table.
(ii) Metals are solids at room temperature.
(iii) Metal usually have high melting and boiling points.
(iv) They are good conductors of heat and electricity.

(u) They are malleable and ductile.

• Non-metals

(i) Non-metals are located at the top right hand side of the Periodic Table.

(ii) Non-metals are usually solids or gases at low temperature with low melting and boiling points.

(iii) They are poor conductors of heat and electricity.

(iv) The non-metallic character increases as one goes from left to right across the Periodic Table.

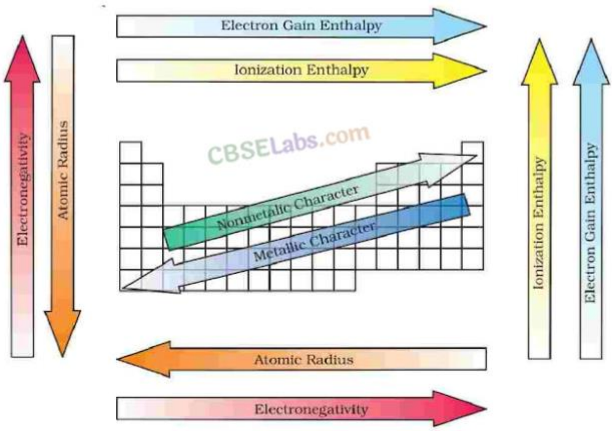
(v) Most non-metallic solids are brittle and are neither malleable nor ductile.

• Metalloids

The elements (e.g., silicon, germanium, arsenic, antimony and tellurium) show the characteristic, of both

Periodic Trends in Properties of Elements-

a) Atomic sizes- atomic radii decreases while going from left to right in a period and increases with atomic number in a group.
b) Ionisation enthalpies – increases across the periods and decreases down the group.
c) Electronegativity- increases across the periods and decreases down the group.
d) Electron gain enthalpy – becomes more negative across a period and less negative down a group.
e) Valency- the valence is either equal to the number of electron in the outermost orbit or eight minus this number.
f) Chemical reactivity – is highest at two extremes of a period and is lowest in the centre. Reactivity on the left extreme of a period is because of the ease of electron loss or low ionisation enthalpy.
g) Highly reactive elements do not exist in free state in nature, they usually exist in combined form.
h) Oxides – oxides form of the element on the left are basic and of the element on the right are acidic in nature. Oxides of elements in the centre are amphoteric or neutral.



SOME MORE POINTS TO REMEMBER-

- **Groups.** There are 18 groups. These are vertical rows.
- **Periods**. There are 7 periods. These are horizontal rows.
- **Representative Elements.** The S and P block of elements are known as representative elements.
- **Transition Elements.** They are also called d-block elements. They have general electronic configuration (n – 1) d^{1-10} ns^{0-2}.
- **Inner Transition Elements.** Lanthanoids (the fourteen elements after Lanthanum) and actinides (the fourteen elements after actinium) are called inner transition elements. General electronic configuration is (n – 2) f^{1-14}(n – 1) d^{0-1} ns^2.
They are also called f-block elements.

Periodic Classification of Elements

Multiple Choice Questions (1 Marks each)

1	The Vander Waal's radii of O, N, Cl, F and Ne increase in the order (a) F, O, N, Ne, Cl (b) N, O, F, Ne, Cl (c) Ne, F, O, N, Cl (d) F, Cl, O, N, Ne	1
2	Which of the following correctly represents the increasing order of effective nuclear charge in Na, Al, Mg and Si atoms? (a) Na < Mg < Si <Al (b) Na < Mg <Al < Si (c)Mg < Na <Al< Si (d)Na = Mg =Al = Si	1
3	The correct order of increasing values of second ionisation potential of C_6, N_7, O_8 and F_9 is: (a) C > N > F > O (b) C < F < N < O (c) C < F < N < O (d) C < N < F< O	1
4	Which oxide of N is isoelectronic with CO_2? (a) NO_2 (b) NO (c) N_2O (d) N_2O_3	1
5	For reaction, $O(g) + 2e^- \rightarrow O^{-2}(g)$ $-E = +744.7$ value of E is positive because (a) It is an endothermic reaction (b) It is an exothermic reaction (c) Both 1 and 2 (d) None of the above is correct	1
6	Which of the following has lowest electron affinity? (a) Kr (b) O (c) N (d) S	1
7	The increasing order of electron affinity values of O, S and Se is (a) O < S < Se (b) S < O < Se (c) O < Se < S (d) Se < O > S	1
8	Which electronic configuration among the following will have the highest electron affinity? (a) $1s^2\ 2s^2\ 2p^3$ (b) $1s^2\ 2s^2\ 2p^5$ (c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ (d) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$	1
9	The screening effect of d-electrons is - (a) equal to the p-electrons (b) much more than p-electron (c) same as f-electrons (d) less than p-electrons	1
10	Which one of the following is correct order of the size of iodine species? (a) $I > I^- > I^+$ (b) $I > I+ > I^-$ (c) $I^+ > I^- > I$ (d) $I^- > I > I^+$	1
11	___________ gave the idea for the first time to classify elements as per their properties. (a) Mendeleev (b) Dobereiner (c) Newland (d) John	1
12	Eka Aluminium is __________ (a) Germanium (b) Gallium (c) Silicon (d) Copper	1
Reason-Assertion based Questions		
	Question 13-16 contain two statements, Assertion and Reason. Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a),	

	(b), (c) and (d) given below. (a) Assertion is correct, reason is correct; reason is a correct explanation for assertion. (b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion (c) Assertion is correct, reason is incorrect (d) Assertion is incorrect, reason is correct.	
13	**Assertion :** Second period consists of 8 elements. **Reason :** Number of elements in each period is four times the number of atomic orbitals available in the energy level that is being filled.	1
14	**Assertion :** In a triad, the three elements present have same gaps of atomic masses. **Reason :** Elements in a triad have similar properties.	1
15	**Assertion :** Second ionization enthalpy will be higher the first ionization enthalpy. **Reason :** Ionization enthalpy is a quantitative measure of the tendency of an element to lose electron.	1
16	**Assertion :** Atomic size increases along a period. **Reason :** Effective nuclear charge increases as the atomic number increases resulting in the increased attraction of electrons to the nucleus.	1
Short Answer Type Questions (2 Marks each)		
17	Why the electron gain enthalpy of the elemental fluorine is less negative than the elemental chlorine?	2
18	All the transition elements are d-block elements, but all the d-block elements are not the transition elements. Explain.	2
19	Among the given elements B, Al, C and Si, (i) which of the following elements has the highest first ionisation enthalpy? (ii) which element contains the most metallic character? Explain your answer in each case.	2
20	Identify the group and valency of the following element having atomic number 119. Also, predict the outermost electronic configuration for it and write the general formula of the oxide.	2
21	Nitrogen possesses the positive electron gain enthalpy, whereas the oxygen possesses the negative. But oxygen has lower ionisation enthalpy than nitrogen. Explain.	2
Short Answer Type Questions (3 Marks each)		
22	What is the atomic number of elements keeping in mind both the cases given below; 1. Element is in the 3rd period of the periodic table. 2. Element is in the 17th group of the periodic table.	3
23	Define the ionisation enthalpy. Discuss the factors affecting ionisation enthalpy of elements and their trends in the periodic table.	3
24	How would you explain the fact that first ionisation enthalpy of sodium is lower than that of magnesium but its second ionisation enthalpy is higher than that of magnesium?	3
25	**Among the second period elements, the actual ionization enthalpies are in the order: Li <B< Be <C<0<KI<F< Ne** **Explain why** **(i) Be has higher $\Delta_i H_1$ than B ?** **(ii) O has lower $\Delta_i H_1$ than N and F?**	3
26	**What do you understand by isoelectronic species? Name a species that tvill be iso electronic with each of the following atoms or ions.**	3

(i) F^-(ii) Ar (iii) Mg^{2+}(iv) Rb^+

27 **Consider the following species:** 3

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

(a) What is common in them?

(b) Arrange them in order of increasing ionic radii?

28 **On the basis of quantum numbers, justify that the sixth period of the periodic table should have 32 elements.** 3

Case Based Questions

29 Modern periodic table arranges the elements in the increasing order of atomic number. It has 18 groups and 7 periods. Atomic numbers are consecutive in a period and increases in group in a pattern. Elements are divided into four blocks, s-block,p-block, d-block andf-block based on their electronic configuration. 78% of elements are metals, about 20 elements are non-metals and few elements like B, Si, Ge, As are metalloids. Metallic character increases down the group but decreases along the period from left to right. The physical and chemical properties vary periodically with their atomic numbers. Periodic trends are observed in atomic size, ionisation enthalpies, electron gain enthalpies, electronegativity and valence. Oxides of metals are basic, some are amphoteric. Non-metals form acidic oxides, some form neutral oxides. s-block elements are soft, highly reactive, do not show variable oxidation states. p-block elements are metals, non-metals as well as metalloids, show variable oxidation states, exist as solids, liquids and gases. d-block elements are metals, form coloured ions, show variable oxidation states, have high melting and boiling points. Lanthanoids and actinoids are f-block elements, form coloured ions. All actinoids are radioactive. 4

(a) Name the elements which belong to d-block but are not transition metals.

(b) What is difference between oxidation states of p-block and d-block elements?

(c) Which group elements are most electropositive and why?

30 Study the table 1 and 2 related to electronegativity values along the period 2 and 3 Group 1 and 17 and answer the questions that follow based on these. 4

Electronegativity Values (on Pauling scale) Across the Periods

Atom (Period II)	Li	Be	B	C	N	O	F
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	3.0
Atom (period III)	Na	Mg	AI	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

Electronegativity Values (on Pauling scale) Down a Family

Atom (Group I)	**Electronegativity Value**	**Atom (Group XVII)**	**Eledronegativity Value**
Li	1.0	F	4.0
Na	0.9	CI	3.0
K	0.8	Br	2.8
Rb	0.8	I	2.5
Cs	0.7	At	2.2

(a) How does electronegativity varies along a period and why?

(b) Why does K and Rb have same electronegativity although Rb is bigger than K?

(c) Why is CI_2 O_7 more acidic than Cl_2O_5?

Long Answer Type Questions

31 **a. Assign the position of the element having outer electronic configuration,** 5

	(i) $ns^2\ np^4$ for n = 3 (ii) $(n – 1)\ d^2\ ns^2$ for n = 4 and (iii) $(n – 2)\ f^7\ (n – 1)\ d^1\ ns^2$ for n = 6 in the periodic table? **b. Write the general electronic configuration of $s^{–}$ $p^{–}$ $d^{–}$, and f-block elements?**	
32	First member of each group of representative elements (i.e., s and p-block elements) shows anomalous behaviour. Illustrate with two examples.	5
33	p-Block elements form acidic, basic and amphoteric oxides. Explain each property by giving two examples and also write the reactions of these oxides with water	5

Answers / Hints

1	(c) Ne, F, O, N, Cl	1
2	(b) Na < Mg <Al < Si	1
3	(d) C < N < F< O	1
4	(c) N_2O	1
5	(a) It is an endothermic reaction	1
6	(c) N	1
7	(c) O < Se < S	1
8	(c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$	1
9	(d) less than p-electrons	1
10	(d) $I^- > I > I^+$	1
11	(b) Dobereiner	1
12	(b) Gallium	1

13	C	1
14	D	1
15	B	1
16	C	1
17	Fluorine has a smaller size as compared to chlorine. As a result, the attraction outside the shell to gain the electrons is less. Moreover, they possess inter-electronic repulsions in the 2p orbitals, resulting in less negative electron gain enthalpy.	2
18	The elements having their outermost shell filled with the d electrons are called the d block elements. All the d blocks are not the transition elements as it is important to have an incompletely filled d orbital of the given element like calcium and zinc etc.	2
19	(i) Carbon possesses the highest ionisation enthalpy. It increases from left to right along the period and also decreases as we go down the group. (ii) Aluminium possesses the most metallic character. On moving down, the metallic character increases and decreases across the period from left to right.	2
20	There are 118 elements found in the seven periods of the modern periodic table. Thus, the element with the atomic number 119 will lie in the 8th period of the first group and have the outermost electronic configuration of 8**s1**. It belongs to group 1 and has the valency one. The formula of the oxide would be M_2O.	2
21	The ionisation enthalpy of oxygen is lower than that of nitrogen as when we remove one electron from the oxygen then it easily donates it to attain half-filled stability; however, in the case of nitrogen, it is difficult to remove one electron because it already has half-filled stability and it will become unstable after that.	2
22	In the third period, we provided that element. The element's highest principal quantum number (n) into which the last electron enters is called the period number. As a result, n=3 for the 3rd period. In addition, the element could be found in the seventeenth group. The elements for the seventeenth group have the following general configuration: n**s2**n**p5**. As a result, the needed element's overall electronics configuration is 3**s2**3**p5** (because n=3). The element's complete electrical configuration will now be: 1**s2**2**s2**2**p6**3**s2**3**p5**. then add up the total number of electrons in the element's ground state: 1+2+6+2+5=17 electrons. The element's atomic number equals its ground state's total number of electrons. As determined above, the element has 17 electrons in its ground state; its atomic number is 17. Chlorine is an atomic number 17 element (Cl).	3
23	Ionisation enthalpy is the energy required by the isolated and gaseous atom in its ground state to remove an electron. The effective nuclear charge is due to the screening effect; inner core electrons shield the valence electrons. eThe effective nuclear charge is less than the actual charge on the atom. Penetrated orbital: It is difficult to remove an electron from the orbitals closer to the nucleus and penetrate towards the nucleus. The order of the penetration has been given by s>p>d>f Stability of the orbitals: Half-filled and filled orbital have a high ionisation enthalpy as well as they don't want to lose their stability. Across a period,	3

	ionisation enthalpy increases along with the period. Down the group, the ionisation enthalpy decreases.	
24	The electronic configuration of both the atoms are as follows: Na: [Ne]$3s^1$ Mg: [Ne]$3s^2$ The ion formed after removing one electron from the sodium atom takes on the configuration of an inert gas, neon, whereas Mg retains one electron. As a result, the first ionisation energy of Na is lower than that of Mg. High energy is required to remove an electron from a noble gas configuration. As a result, the second ionisation enthalpy of calcium is greater than that of magnesium.	3
25	(i) In case of Be ($1s^2\ 2s^2$) the outermost electron is present in 2s-orbital while in B ($1s^2\ 2s^2\ 2p^1$) it is present in 2p-orbital. Since 2s – electrons are more strongly attracted by the nucleus than 2p-electrons, therefore, lesser amount of energy is required to knock out a 2p-electron than a 2s – electron. Consequently, At of Be is higher than that Δ_iH_1 of B. (ii) The electronic configuration of $N_7 = 1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$ $O_8 = 1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$ We can see that in case of nitrogen 2p-orbitals are exactly half filled. Therefore, it is difficult to remove an electron from N than from O. As a result Δ_iH_1 of N is higher than that of O.	3
26	Isoelectronic species are those species (atoms/ions) which have same number of electrons. The isoelectronic species are: (i)Na^+ (iii) Na^+ (ii)K^+ (iv) Sr^{2+}	3
27	(a) All of them are isoelectronic in nature and have 10 electrons each. (b) In isoelectronic species, greater the nuclear charge, lesser will be the atomic or ionic radius. $Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$	3
28	The sixth period corresponds to sixth shell. The orbitals present in this shell are 6s, 4f, 5p, and 6d. The maximum number of electrons which can be present in these sub¬shell is 2 + 14 + 6 + 10 = 32. Since the number of elements in a period corresponds to the number of electrons in the shells, therefore, sixth period should have a maximum of 32 elements.	3
29	(a)Zn (b) The oxidation state of p -block elements varies by 1 unit while the oxidation state of p -block elements differs by 2 units. (c) The atomic radii of group 1 elements are large, hence the nuclear attraction will be less on the electrons. As a result, the elements can easily lose electrons. Hence, elements of group 1 of the periodic table are the most electropositive as compared to the rest of the elements.	4
30	(a)Electronegativity increases as we move left to the right in the period because as we move across the period, the effective nuclear charge increases and the atomic size decreases.	4

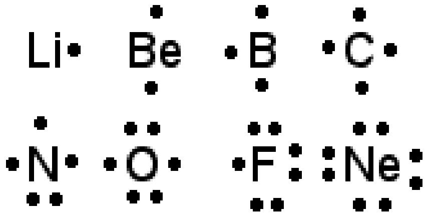
	Therefore, the tendency to attract shared pairs of electrons increases, thereby increasing electronegativity. (b) the electronegativity of potassium and rubidium is similar because they have the same number of inner-shell electrons, resulting in a comparable effective nuclear charge experienced by their valence electrons. (c) Because it reacts with water, it gives the strongest acid perchloric acid. In Dichlorine heptoxide, chlorine is the highest oxidation state of chlorine is +7.	
31	a. (i) n = 3 Thus element belong to 3rd period, p-block element. Since the valence shell contains = 6 electrons, group No = 10 + 6 = 16 configuration =$1s^2 2s^2 2p^6 3s^2 3p^4$ element name is sulphur. (ii) n = 4 Means element belongs to 4th period belongs to group 4 as in the valence shell (2 + 2) = 4 electrons. Electronic configuration.=$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$, and the element name is Titanium (T_i). (iii) n = 6 ” Means the element belongs to 6th period. Last electron goes to the f-orbital, element is from f-block. group = 3 The element is gadolinium (z = 64) Complete electronic configuration =$[X_e]\ 4f^7 5d^1 6s^2$. b. (i) s-Block elements: ns^{1-2} where n = 2 – 7. (ii) p-Block elements: $ns^2 np^{1-6}$ where n = 2-6. (iii) d-Block elements:$(n-1)d^{1-10} ns^{0-2}$ where n = 4-7. (iv) f-Block elements: $(n-2)f^{0-14} (n-1)d^{0-1} ns^2$where n = 6 – 7.	5
32	The first member of each group of representative elements (i.e., the s- and p- block elements) exhibits anomalous behaviour due to: (i) small size (ii) higher ionisation enthalpy (iii) higher electronegativity	5

	(iv) the absence of d- orbitals. For example, in s – block elements, lithium behaves differently than the other alkali metals. (a) Lithium compounds have a high covalent character. Alkali metal compounds are predominantly ionic. (b) Lithium nitride is formed when lithium reacts with nitrogen, whereas other alkali metals do not form nitrides. In p- block elements, the first member of each group has four orbitals in their valence shell, one 2s orbital and three 2 p orbitals. As a result, these elements have a maximum covalency of four, whereas other members of the same or different group have a maximum covalency that is greater than four due to the availability of vacant d – orbitals.	
33	Due to their various properties, p – block elements produce acidic, basic, and amphoteric oxides: • The higher an element's electronegativity, the more acidic its oxide. For example- Boron has an electronegativity of -2, carbon has an electronegativity of 2.5, and nitrogen has an electronegativity of 3. As a result, the order of acidic character of B, C, and N oxides is $B_2O_3 < CO_2 < N_2O_3$ • If the ionisation enthalpy of an element is high, it will form acidic oxide; if it is intermediate, it will form amphoteric oxide; and if it is low, it will form basic oxides. For example, the ionisation enthalpy of boron is 800 while that of carbon is 1086.5, implying that carbon oxide is more acidic than boron oxide. • The oxides of the first element in each group in the p – block are more acidic than the oxides of other elements. As we move down the group, the acidic character decreases, followed by elements that form amphoteric oxides and then basic oxides. For example- In the Boron family, B forms a weak acidic oxide, while Al, Ga, and In form amphoteric oxides, and Tl forms a strong basic oxide. Reactions of some of the oxides with water: • Acidic Oxides: $B_2O_3 + 3H_2O \rightarrow 2H_3BO_3$ • Basic Oxides: $Tl_2O + H_2O \rightarrow 2TlOH$ • Amphoteric Oxides are insoluble in water and thus reacts with acid and base: $Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$ $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$	5

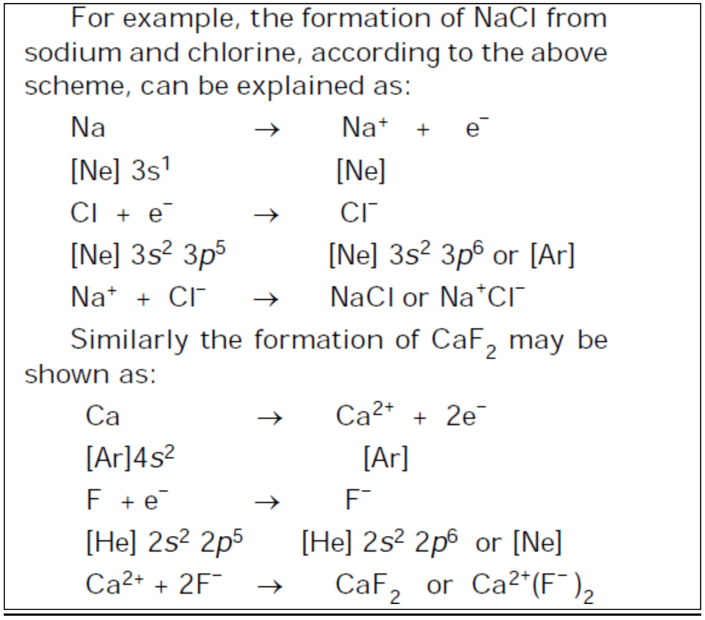
CHAPTER-4: CHEMICAL BONDING AND MOLECULAR STRUCTURE

GISTS OF THE LESSON-

1. **CHEMICAL BOND-** The chemical force which keeps the atoms in any molecule together is calleda chemical bond.
2. **Lewis dot structures** are a shorthand to represent the valence electrons of an atom. The structures are written as the element symbol surrounded by dots that represent the valenceelectrons.



3. **Electrovalent bond or Ionic Bond**: The chemical bond as result of transfer of electron from one atom(electropositive) to another atom (electronegative). Ionic bonds will be formed more easily between elements with comparatively low ionization enthalpies and elements with comparatively high negative value of electron gain enthalpy. Most ionic compounds have cations derived from metallic elements and anions from non-metallic elements.



For example, the formation of NaCl from sodium and chlorine, according to the above scheme, can be explained as:

$Na \rightarrow Na^+ + e^-$

$[Ne]\ 3s^1 \qquad [Ne]$

$Cl + e^- \rightarrow Cl^-$

$[Ne]\ 3s^2\ 3p^5 \qquad [Ne]\ 3s^2\ 3p^6$ or $[Ar]$

$Na^+ + Cl^- \rightarrow NaCl$ or Na^+Cl^-

Similarly the formation of CaF_2 may be shown as:

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

$[Ar]4s^2 \qquad [Ar]$

$F + e^- \rightarrow F^-$

$[He]\ 2s^2\ 2p^5 \qquad [He]\ 2s^2\ 2p^6$ or $[Ne]$

$Ca^{2+} + 2F^- \rightarrow CaF_2$ or $Ca^{2+}(F^-)_2$

4. **Electrovalency:** The number of electrons lost or gain by an atom of an element is called as electrovalency. The element 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 tohave negative valency.

5. **Formation of Ionic Bond:** It is favoured by, (i) the low ionisation enthalpy of a metallic elementwhich 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

$$M(g) \rightarrow M^+(g) + e^- ;$$

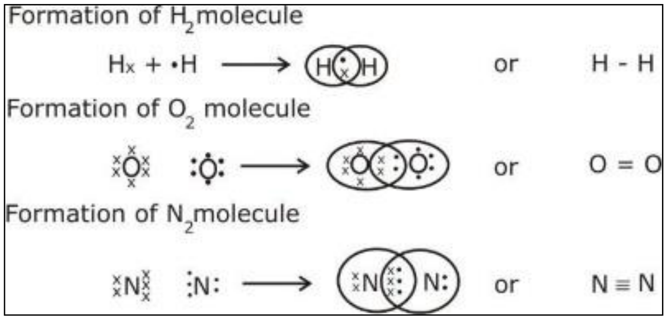
Ionization enthalpy

$$X(g) + e^- \rightarrow X^-(g) ;$$

Electron gain enthalpy

$$M^+(g) + X^-(g) \rightarrow MX(s)$$

6. **Covalent Bonds**- The bond formed between two atoms by mutual sharing of electrons betweenthem so as to complete their octets or duplets.
7. **COVALENCY:**The number of electrons which an atom contributes towards mutual sharing duringthe formation of a chemical bond called its covalency in that compound.
8. **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. H_2
9. **DOUBLE COVALENT BOND:** A covalent bond formed by the mutual sharing of two pair of electrons is called a double covalent bond, or simply a double bond. A double covalent bond isrepresented by two small horizontal lines (=) between the two atoms. E.g. O=O, O=C=O etc.
10. **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.



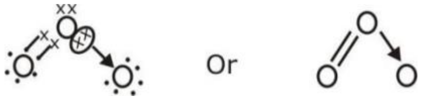
11. **FORMATION OF A COVALENT BOND:** Formation of a covalent bond is favoured by (i) High ionisation enthalpy of the combining elements. (ii) Nearly equal electron gain enthalpy and equal electro-negativities of combining elements. (iii) High nuclear charge and small atomic sizeof the combining elements.
12. **Octet Rule-** Kossel and Lewis in 1916 developed an important theory of

chemical combinationbetween atoms known as electronic theory of chemical bonding. According to this, atoms cancombine either by transfer of valence electrons from one atom to another or by sharing of valence electrons in order to attain their octet. This is known as octet rule.

13. **Limitations of octet rule-**

a) Incomplete octet of the central atom: In some compounds the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than fourvalence electrons. Examples- LiCl ,$BeCl_2$, BCl_3
b) Odd-electron molecules: In molecules with an odd number of electrons like nitric oxide, NO andnitrogen dioxide, the octet rule is not satisfied for all the atoms.
c) The expanded octet : Elements in and beyond the third period of the periodic table have, apartfrom 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Some of examples of such compounds are :PF_5, SF_6.
d) This theory does not account for the shape of molecules.

14. **POLAR COVALENT BOND:** The bond between two unlike atoms which differ in their affinities forelectrons is said to be polar covalent bond. E.g. H-Cl
15. **COORDINATE BOND:** The bond formed when one sided sharing of electrons take place is called acoordinate bond. Such a bond is also known as dative bond. It is represented by an arrow (→) pointing towards the acceptor atom. Example :O_3 (ozone)



16. **Bond length** is defined as the equilibrium distance between the nuclei of two bonded atoms in amolecule.
17. **Bond Angle:**It is defined as the angle between the orbital containing bonding electron pairs around the central atom in a molecule/complex ion. It gives some idea regarding the distributionof orbital around the central atom in a molecule/complex ion and hence it helps us in determining its shape
18. **Bond enthalpy**: It is defined as the amount of energy required to break one mole of bonds of aparticular type between two atoms in a gaseous state. The unit of bond enthalpy is kJ mol^{-1}
19. **Bond Order :**The Bond Order is given by the number of bonds between the two atoms in a molecule. E.g.: Bond Order Of O_2= 2. With increase in bond order, bond enthalpy increases andbond length decreases.
20. **Covalent character in ionic compounds (Fajan's rule) :**

- There is no compound which is 100% ionic.
- Covalent character in ionic compound can be explained with the help of Fajan's rule.
- **Small size of cation**
- **polarisation :**

e.g. $BeCl_2$ $MgCl_2$ $CaCl_2$ $SrCl_2$ $BaCl_2$

$\xrightarrow[\text{Size of cation}]{\hspace{8cm}}$

□ Polarisation □Covalent character

□Large size of anion □ Polarisation

$LiF \quad LiCl \quad LiBr \quad LiI$

$\xrightarrow{\hspace{3cm}}$

- size of anion □

e.g.

- polarisation □
- covalent character □

□ **Charge on cation or anion □ polarisation.**

(a) charge on cation :

$NaCl,\ MgCl_2,\ AlCl_3$

$\xrightarrow{\hspace{3cm}}$

$Na^+ \quad Mg^{+2} \quad Al^{+3}$

- Charge of cation □
- Polarisation □
- Covalent character □

(a) Charge on anion :

$AlF_3,\ Al_2O_3 \quad AlN$

$\xrightarrow{\hspace{3cm}}$

$F^-, \quad O^{-2}, \quad N^{-3}$

- Charge on anion □
- Polarisation □
- Covalent character □

□ Cation which has pseudo inert gas configuration, shows more polarizing power incomparison of cation that has inert gas configuration. CuCl > NaCl (Covalent character)

$Cu^+ = [Ne]\ 3s^2p^6d^{10}$ $\qquad$ $Na^+ = 1s^2, 2s^2p^6$ $18e^-$ $\qquad$ $8e^-$

Pseudo inert inert gas configurationgas configuration

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

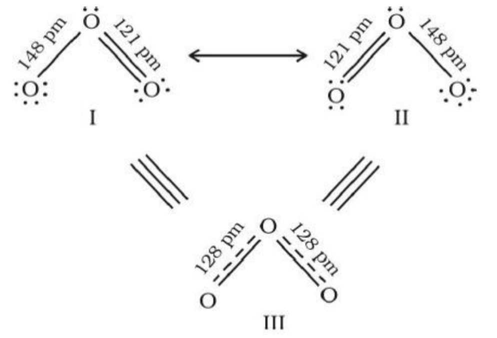
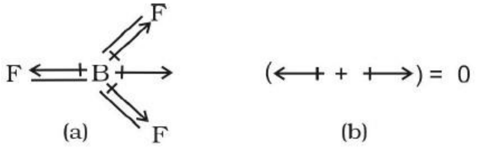


Fig. 4.3 Resonance in the O_3 molecule

(structures I and II represent the two canonical forms while the structure III is the resonance hybrid)

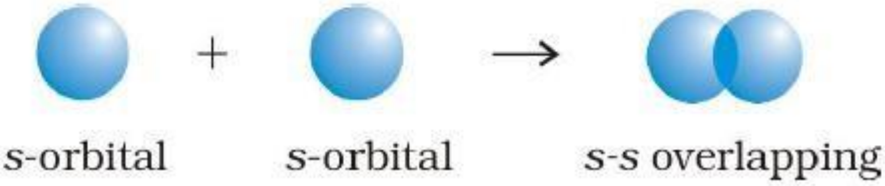
22. **Polarity of bonds:**In case of heteronuclear molecules like HCl, the shared pair of electron between the two atoms gets displaced more towards chlorine since the electronegativity ofchlorine is far greater than that of hydrogen. The resultant covalent bond is called a polar covalent bond.
23. **Dipole moment** : As a result of polarization, the molecule possesses the dipole moment whichcan be defined as the product of charge and the distance between the centers of positive and negative charge. It is usually designated by a Greek letter ‘μ’. Mathematically, it is expressed asfollows:

Dipole moment (μ) = charge (Q) X distance of separation (r)

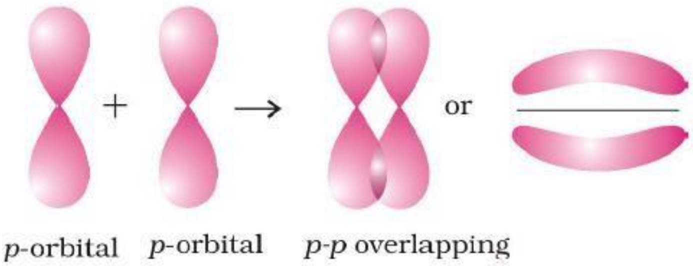


BF_3 molecule; representation of (a) bond dipoles and (b) total dipole moment

24. **Sigma(σ) bond :** This type of covalent bond is formed by the end to end (hand-on) overlap ofbonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap.



25. **pi(π) bond :** In the formation of π bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane ofthe participating atoms.

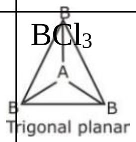


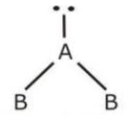
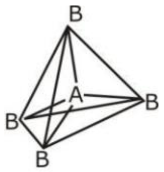
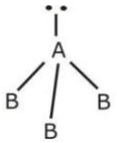
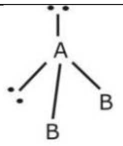
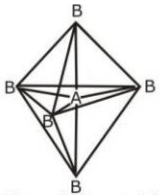
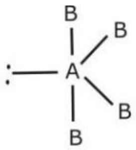
26. In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent.

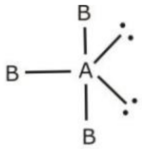
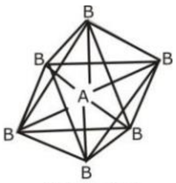
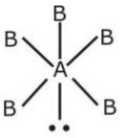
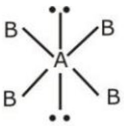
27. VSEPR theory

- The shape of a molecule depends upon the number of valence shell electron pairs(bonded or nonbonded) around the central atom.
- Pairs of electrons in the valence shell repel one another since their electron clouds arenegatively charged.
- These pairs of electrons tend to occupy such positions in space that minimize repulsionand thus maximise distance between them.
- The valence shell is taken as a sphere with the electron pairs localising on the sphericalsurface at maximum distance from one another.
- A multiple bond is treated as if it is a single electron pair and the two or three electronpairs of a multiple bond are treated as a single super pair.
- Where two or more resonance structures can represent a molecule, the VSEPR model isapplicable to any such structure.
- The repulsive interaction of electron pairs decrease in the order: Lone pair (lp) – Lone pair(lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) –Bond pair (bp)

☐ **Geometry of Molecules** on the basis of VSEPR Theory

Bond pair	**Lone pair**	**Shape**	**Examples**
2	0	Linear	$BeCl_2$
3	0	Trigonal Planar	BCl_3 

2	1	Bent  Trigonal planar	SO_2
4	0	Tetrahedral  Tetrahedral	CH_4
3	1	Pyramidal  Tetrahedral	NH_3, ,PH_3,
2	2	V-shape  Tetrahedral	H_2O
5	0	Trigonal bipyramidal  Trigonal bipyramidal	PCl_5
4	1	See saw  Trigonal bi-pyramidal	SF_4

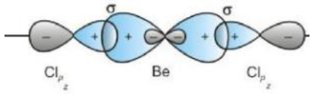
3	2	T-shaped  Trigonal bi-pyramidal	ClF_3,
2	3	Linear	XeF_2
6	0	Octahedral  Octahedral	SF_6
5	1	Square pyramidal  Octahedral	ClF_5, IF_5
4	2	Square planar  Octahedral	XeF_4,
6	1	Distorted Octahedral	XeF_6

28. **Hybridization:** It can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formations of new set of orbitals ofequivalent energies and shape.

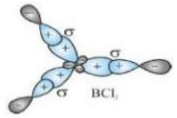
- **Salient Features of hybridization :**
- The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
- The hybridised orbitals are always equivalent in energy and shape.
- The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
- These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement.

29. **Types of Hybridisation**

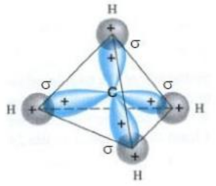
(a) **sp hybridisation**: This type of hybridisation involves the mixing of one s and one p orbital resulting in the formation of two equivalent sp hybrid orbitals. Each sp hybrid orbitals has 50% s-character and 50% p-character. Such a molecule inwhich the central atom is sp-hybridised and linked directly to two other central atoms possesses linear geometry. Example $BeCl_2$ molecule



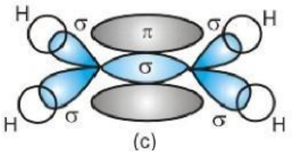
(b) sp^2 hybridisation : In this hybridization there is involvement of one s and two p-orbitals in order to form three equivalent sp^2 hybridised orbitals. Each sp^2 hybrid orbitals has 33.33% s- character and 66.66 % p-character. Such a molecule in which the central atom is sp^2 hybridisedand linked directly to three other central atoms possesses trigonal planar geometry. Example BCl_3 molecule**.**



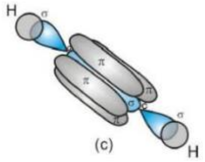
(c) **sp^3 hybridisation**: In this type of hybridisation there is mixing of one s-orbital and three p-orbitals of the valence shell to form four sp^3 hybrid orbital of equivalent energies and shape. There is 25% s-character and 75% pcharacter in each Sp^3 hybrid orbital. The four Sp^3 hybrid orbitals so formed are directed towards the four corners of the tetrahedron Example CH_4 molecule



30. sp^2 hybridisation in C_2H_4 molecule

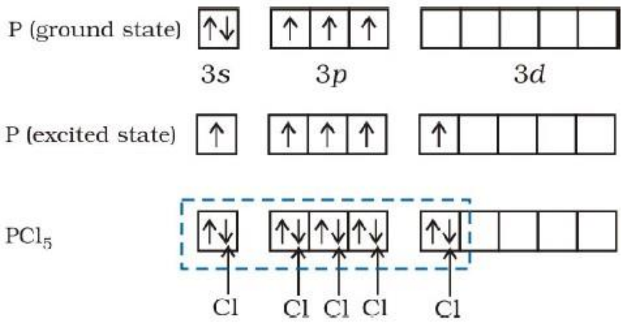


31. sp hybridisation in C_2H_2 molecule



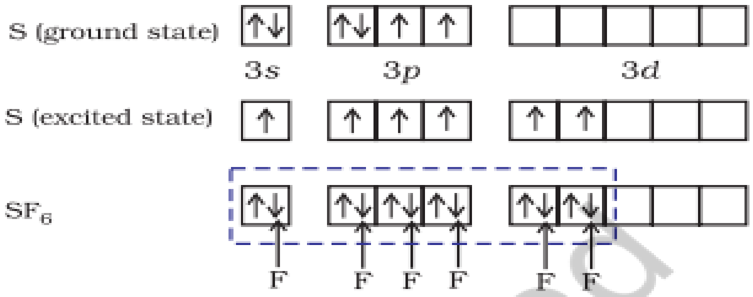
32. Formation of PCl_5

(i) Formation of PCl_5 (sp^3d hybridisation): The ground state and the excited state outer electronic configurations of phosphorus (Z=15) are represented below.



sp^3d hybrid orbitals filled by electron pairs donated by five Cl atoms.

33. Formation of SF_6



sp^3d^2 hybridisation

34. **Molecular orbital.** It gives electron probability distribution around a group of nuclei in a molecule. They are filled in the same way as atomic orbitals. Molecular orbitals are formed bylinear combination of atomic orbitals.

35. **Conditions for the Combination of Atomic Orbitals.** The linear combination of atomic orbitalstakes place only if the following conditions are satisfied :

(i) The combining atomic orbitals must have same or nearly same energy.

(ii) The combining atomic orbitals must have the same symmetry about the molecular axis. Byconvention, z-axis is taken as the molecular axis.

(iii) The combining atomic orbitals must overlap to the maximum extent. Greater the extent ofoverlapping, the greater will be electron density between the nuclei of a molecular orbital.

36. **Sigma (σ) molecular orbitals.** A molecular orbital which is formed from the overlap of two s atomic orbitlas or head to head overlap of one s and p-atomic orbitals or head to head overlap oftwo p-atomic orbitals, is known as sigma molecular orbital.

37. **pi (π) molecular orbitals.** A molecular orbital which is formed by lateral overlap

of two parallelp-orbitals is known as pi(□) molecular orbital.

38. **Bonding molecular orbital.** A molecular orbital that is formed by addition overlap (i.e., whenthe lobes of atomic orbitals overlap with the same sign) of two atomic orbitals is known as bonding molecular orbital.
Its energy is lower than the atomic orbitals from which it is formed.

$$\Psi MO = \Psi A + \Psi B$$

39. **Anti-bonding molecular orbital.** A molecular orbital that is obtained by the subtraction overlap(i.e., when the lobes of atomic orbitals overlap with the opposite sign) of two atomic orbitals is known as anti-bonding molecular orbital. It is represented as

$$\Psi MO = \Psi A - \Psi B$$

Its energy is higher than the atomic orbitals from which it is formed

40. **Bond order.** It is defined as half of the difference between number of electrons in bonding andanti-bonding orbitals, i.e., B.O. = ½ (N_b – N_a) ‘where N_b are number of electrons in bonding orbitals’ and N_a are number of electrons in anti-bonding orbitals. Bond order helps in estimatingstability of atom.

41. **Significance of Bond Order**

☐ **If bond order = 0, it means species does not exist.**
☐ **Bond order of 1, 2 & 3 corresponds to a single bond, double & triple bond respectively →Bond order increases → stability of molecule increases → Bond length decreases →If the molecule has one or more unpaired electron, it will be paramagnetic, while ifall the electrons are paired it will be diamagnetic.**

42. **Energy level Diagrams for Molecular Orbitals.** The increasing order of energies of variousmolecular orbitals for O_2 and F_2 is given below.

$$\sigma 1s \; {*\sigma 1s} \; \sigma 2s \; {*\sigma 2s} \; \sigma 2p_z \; (\pi 2p_x = \pi 2p_y) \; ({*\pi 2p_x} = {*\pi 2p_y}) \; {*\sigma 2p_z}$$

However, this sequence of energy levels of molecular orbitals is not correct for remaining molecules Li_2, Be_2, B_2, C_2, N_2. For instance, it has been observed experimentally that for molecules such as B_2, C_2,N_2 etc., the increasing order of energies of various molecular orbitals is

$$\sigma 1s \; {*\sigma 1s}, \; \sigma 2s \; {*\sigma 2s}, \; (\pi 2p_x = \pi 2p_y) \; \sigma 2p_z, \; ({*\pi 2p_x} = {*\pi 2p_y}) \; {*\sigma 2p_z}$$

The important characteristic feature of this order is that the energy of $\sigma 2p_z$ molecular orbital is **higher than that of** $\pi 2p_x$ **and** $\pi 2p_y$

43. **Examples :**
molecular orbitals in these molecules.

a) **H2** $\sigma 1s^{2}$ B.O. = ½ (Nb – Na) B.O. = ½ (2 – 0)=1 , This means that the two hydrogen atoms are bonded together by a single covalent bond.

b) **He2** $\sigma 1s^{2}$, $*\sigma\ 1s^{2}$ B.O. = ½ (Nb – Na) B.O. = ½ (2 – 2)=0 He_2 *molecule is therefore unstable and does not exist.*

c) **Be2**: Bond order =1/2[4-4] =0,

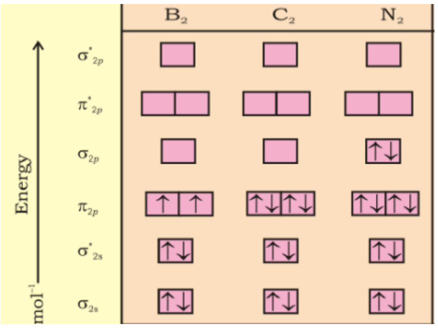
$(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2$

Therefore Be_2 molecule is unstable and does not exist

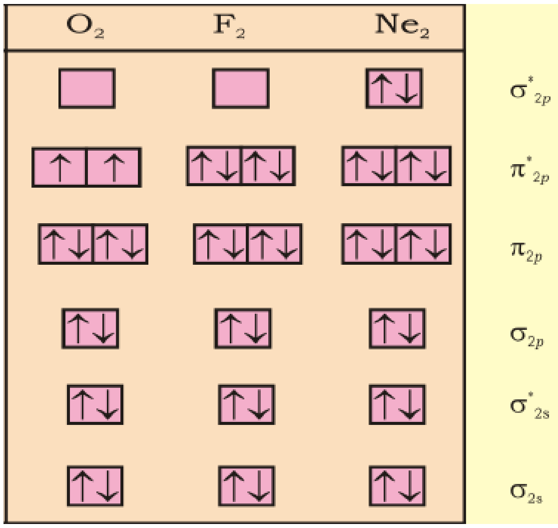
d) **Li2** $\sigma\ 1s^{2}\ \sigma\ 1s^{2}\ \sigma\ 2s^{2}$ B.O. = ½ (Nb – Na) B.O. = ½ (4 – 2)=1

The above configuration is also written as KK(s2s)^2 where KK represents the closed K shellstructure $(\sigma 1s)^2$ $(\sigma^* 1s)^2$. It means that Li_2 molecule is stable and since it has no unpaired electrons it should be diamagnetic.

44. **Energy level Diagrams for Molecular Orbitals.** B_2, C_2, N_2 is given below



45. **Energy level Diagrams for Molecular Orbitals.** O_2 F_2 and Ne_2 is given below



46. **Hydrogen bond** can be defined as the attractive force which binds hydrogen atom

of one molecule with the electronegative atom (F, O or N) of another molecule. **For example**, in HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom

of another molecule as depicted below :

$$---H^{\delta+}-F^{\delta-}---H^{\delta+}-F^{\delta-}---H^{\delta+}-F^{\delta-}$$

47. Conditions required for H-bond.

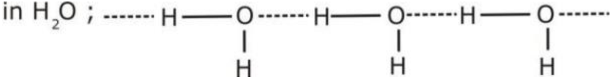
- Molecule should have more electronegative atom (F, O, N) linked to the H-atom
- Size of electronegative atom should be smaller.
- A lone pair should be present on electronegative atom.

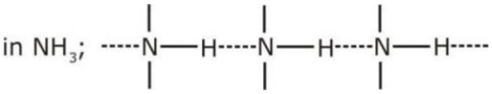
48. **Types of H-Bonds** There are two types of H-bonds

(i) Intermolecular hydrogen bond

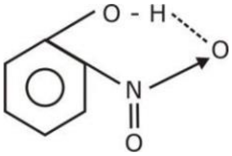
(ii)Intramolecular hydrogen bond

49. **Intermolecular hydrogen bond :** It is formed between two different molecules of the same or different compounds. For example, H-bond in case of HF molecule, alcohol or water molecules,etc.





50. **Intramolecular hydrogen bond :** It is formed when hydrogen atom is in between the two highlyelectronegative (F, O, N) atoms present within the same molecule. For example, in o- nitrophenol the hydrogen is in between the two oxygen atoms.



CHEMICAL BONDING

MCQ

Q.1Which of the following have identical bond order ?

a) NO^+, O_2^+

b) CN^- , NO^+

c) O_2^+, O_2^-

d) O_2^- , CN^-

Q.2 The type of hybrid orbitals of nitrogen in NO_2^+ and NH_4^+ respectively are expected to be

a) sp and sp2

b) sp and sp3

c) sp2 and sp3

d) sp2 and sp

Q.3.The angle corresponds to sp2 hybridisation is ?

(a) 90^0

(b) 120^0

(c) 180^0

(d) 109^0

Q.4In NO3- ion , the number of bond pairs and lone pairs of electrons on nitrogen atom are ?

a) 2,2

b) 3,1

c) 1,3

d) 4,0

Q.5 The electronic configuration of the outermost shell of the most electronegative element is.
a) $5s^25p^5$
b) $4s^24p^5$
c) $3s^23p^5$
d) $2s^22p^5$

Q.6 The number of sigma and pi bonds in C_2H_2 are?

a) 2,3

b) 3,1

c) 3,2

d) 4,0

Q.7 The species showing tetrahedral geometry is

a) NH_2^-

b) BH_4^-

c) CO_3^{2-}

d) H_3O^+

Q.8 Which of the following doesn't follow octet rule?
a) CH_4
b) CCl_4
c) HCl
d) NO_2

Q.9 More than one sort of hybridization can occur in a complex with geometry.
a) tetrahedral

b) octahedral

c) trigonal bipyramidal

d) square planar

Q.10 Highly electropositive Alkali metals are separated from highly electronegative halogens by __________

a) noble gases
b) oxygen family
c) f-block elements
d) 7th period

Q.11 Find the molecule with the maximum dipole moment

(a) CH_4

(b) NH_3

(c) CO_2

(d) NF_3

Q.12 **Which one has a pyramidal shape?**

(a) PCl_3

(b) SO_3

(c) CO_3^{2-}

(d) NO_3^-

ASSERTION AND REASONING QUESTIONS

Q . 1 Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion (A) Sodium chloride formed by the action of chlorine gas on sodium metal is a stable compound.

Reason (R) This is because sodium and chloride ions acquire octet in sodium chloride formation.

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

b) Both A and R are true and R is not the correct explanation of A

c) A is true but R is false

d) A is false but R is true.

Q.2 Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion : Though the central atom of both NH_3 and H_2O molecules are sp3 hybridised , yet H-N-H bond angle is greater then that of H-O-H .

Reason : This is because nitrogen atom has one lone pair and oxygen atom has two lone pairs.

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

b) Both A and R are true and R is not the correct explanation of A

c) A is true but R is false

d) A is false but R is true.

Q.3 Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion: Among two O-H bonds in H_2O molecule, the energy required to break the first O-H bond and the other 0-H bond is the same .

Reason: This is because the electronic environment around oxygen is the same even after breakage of one O-H bond.

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

b) Both A and R are true and R is not the correct explanation of A

c) A is true but R is false

d) A is false but R is true.

Q.4 Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion: The dipole moment helps to predict whether a molecule is polar or non polar.

Reason: The dipole moment helps to predict the geometry of molecules .

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

b) Both A and R are true and R is not the correct explanation of A

c) A is true but R is false

d) A is false but R is true.

COMPETENCY BASED QUESTIONS (2M)

Q.1 Calculate formal charge (a) FC on nitrogen atom in nitrite ion .

b)FC on carbon atom in carbonate ion.

Q.2 Give the reason

(a) Melting point of NaCl is higher then $AlCl_3$.

(b) Formic acid exists as dimer.

Q.3 Draw resonating structures of nitrous oxide (N_2O)?

Q.4 Each carbon-oxygen bond in CO_2 molecule is polar but the molecule as a whole is nonpolar. Explain.

Q.5 Compare relative stability of the following species and indicate their magnetic properties:

O_2, O_2^+ , O_2^- (superoxide), O_2^{2-}(peroxide)

Q.6 Which hybrid orbitals are used by carbon atoms attached to functional group in the following molecules.

a) CH_3-CH=CH_2 B) CH_3-CHO

COMPETENCY BASED QUESTIONS (3M)

Q.1 Explain the non linear shape of H_2S and non planar shape of PCl_3 using valence shell electron pair repulsion theory.

Q . 2 What is meant by the term bond order ? calculate bond order of N_2 and O_2

Q.3 How does molecular orbital theory account for the following

a) Bond order of N_2 is greater than $N_2{}^+$ But the bond order of O_2 is less than that of $O_2{}^+$

b) Be_2 does not exist

Q.4 Explain the following

a) O_2^- is paramagnetic but O_2^{2-} is not
b) B_2 molecule is paramagnetic

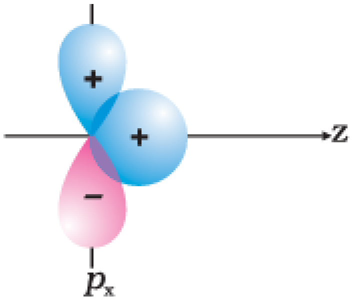
Q.5 (a) Which of the following has higher dipole moment and why ?

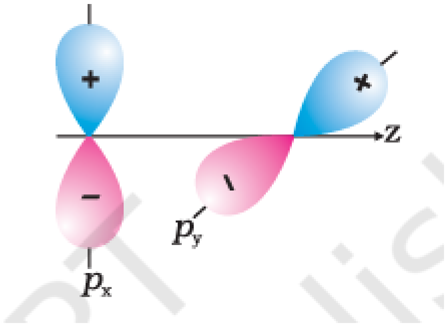
But-1-ene or But-1-yne

(b) Which is expected to have the highest melting point PH_3 or $(CH_3)_3N$

Q.6 Giving one example explain the shapes of following molecules
a) Molecule containing one lone pair and four bond pair
b) Molecule containing two lone pairs and three bond pairs
c) Molecule containing two lone pairs and two bond pairs

Q.7 a) Why does type of overlap given in the following figure not result in bond formation ?





b) With the help of suitable example explain polar covalent bond.

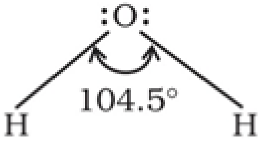
Q.8 a) Explain the shape of BrF_5 .

b) Write significance of dipole moment .

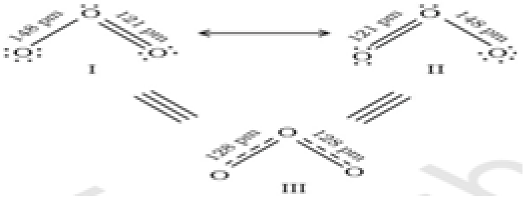
CASE BASED QUESTIONS (4M)

Q.1 Read the passage given below and answer the following questions:

The bond Angle is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion. Bond angle is expressed in degree which can be experimentally determined by spectroscopic methods. It gives some idea regarding the distribution of orbitals around the central atom in a molecule/complex ion and hence it helps us in determining its shape. For example H–O–H bond angle in water can be represented as under :



Bond Enthalpy It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. The unit of bond enthalpy is kJ mol^{-1}. For example, the H–H bond enthalpy in hydrogen molecules is 435.8 kJ mol–1. H2 (g) → H(g) + H(g); ΔaH = 435.8 kJ mol–1.In the Lewis description of a covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule. The bond order, for example in H2(with a single shared electron pair), in O2(with two shared electron pairs), and in N2(with three shared electron pairs) is 1,2,3respectively. A general correlation is useful for understanding the stabilities of molecules that: with an increase in bond order, bond enthalpy increases and bond length decreases. The concept of resonance was introduced to deal with the type of difficulty experienced in the depiction of accurate structures of molecules like O3. According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding, and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately.



Thus for O_3, the two structures shown above constitute the canonical structures or resonance structures, and their hybrid i.e., the structure represents the structure of O3 more accurately. This is also called a resonance hybrid.

i) Which of the following techniques is used to measure bond length?
- (a) spectroscopic techniques
- (b) X-ray diffraction

- (c) electron-diffraction techniques
- (d) All the above

ii) The unit of bond enthalpy is …
- (a) kJ mol^{-1}
- (b) Cal mol^{-1}
- (c) Cal mol
- (d) kJ mol

iii) With the increase in bond order, bond enthalpy … and bond length ….
- (a) decreases, decreases
- (b) increases decreases
- (c) increases, increases
- (d) decreases , increases

iv) The …………………….. is measured approximately as the radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation.
- (a) ionic radius
- (b) Metallic radius
- (c) covalent radius
- (d) None of above

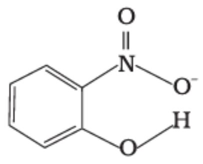
Q.2 Read the passage given below and answer the following questions:

- Hybridisation helps us to understand the geometry of molecules. This is because hybridized orbitals are directed in space in some preferred direction to have stable arrangement , which determine the geometry. The presence of lone pairs in addition to bond pairs distort the geometry due to repulsion.

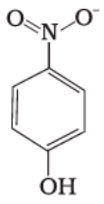
a) What is the hybridisation of sulphur in SF_4
b) give example of molecule having square planer geometry.
c) Give shape of the molecule having four bond pairs and one lone pair .
d) Distinguish sigma and pi bond .

COMPETENCY BASED QUESTIONS (5M)

Q.1 Structures of molecules of two compounds are given below :



(I)



(II)

(a) Which of the two compounds will have intermolecular hydrogen bonding and which compound is expected to show intramolecular hydrogen bonding.

(b) Which of the above two compounds will show higher melting point.

(c) Solubility of compounds in water depends on power to form hydrogen bonds with water. Which of the above compounds will form hydrogen bond with water easily and be more soluble in it

Q.2 Give reasons for the following :

i) Covalent bonds are directional bonds while ionic bonds are non directional.

(ii) Water molecule has bent structure whereas carbon dioxide molecule is linear.

(iii)Ethyne molecule is linear.

Q.3 complete any five

i) Give one example of tetra atomic polar molecule.

ii) Give one example of tetra atomic non polar molecule.

iii) molecule having six bond pairs .

iv) shape of sp^3d hybrid orbitals

v) shape of sp^3d^2 hybrid orbitals

vi) Draw Lewis dot structure of O_2^-

MARKING SCHEME

S.NO	ANSWER SECTION -A	Mark's
1	B	1
2	B	1
3	B	1
4	D	1
5	D	1

6	C	1
7	B	1
8	D	1
9	B	1
10	A	1
11	B	1
12	A	1
1	A	1
2	A	1
3	D	1
4	A	1
	SECTION B	1
1	FC on N Atom = V-L-1/2S 5-2-1/2.6 = 0 FC 0n C atom = 4-0-1/2.2 = -1	1 1
2	a) NaCl is more ionic due to bigger size of Na+ then Al^{3+} b) Due to intermolecular hydrogen bonding	1 1
3	Correct explanation	2
4	Correct explanation.	2
5	(i)sp2 (ii)sp2	1 1
	SECTION C	
1	S Atom in H_2S Is surrounded by 4 electron pairs Two bonded and two lone	$1^{1/2}$X2

	pairs .These four electron pairs adopt tetrahedral arrangement. the presence of two lone pairs brings distortion in the molecule on account of repulsion with bonded pairs of Electrons .Thus the shape of H_2S molecule is V shaped and not linear. P Atom in PCl_3 is surrounded by 4 electron pairs (Three bonded and one lone pair) These four pairs Adopt a tetrahedral geometry due to presence of lone pair PCl_3 has a distorted tetrahedral geometry thus it is pyramidal in shape and not non planar shape	
2	Number of covalent bond in covalent molecules. - N_2 - 3 - O_2 - 2	1 1 1
3	a) When N_2 changes to N_2^+ the electron is removed from the bonding Molecular orbital while when O2 changes to O_2^+ the electron is removed from anti bonding molecular orbital This is the reason why the bond order of N_2 is greater than N_2^+ but the bond order of O2 is less than that of O_2^+ b) A negative or zero bond order makes the molecule unstable hence Be_2 molecule does not exist OR a) O_2^- has unbaired electron in its anti bonding molecular orbital Thus it is paramagnetic b) The presence of 2 unpaired electrons in π bonding orbitals makes B_2 paramagnetic	$1^{1/2}$ 1 ½ $1^{1/2}$ $1^{1/2}$
4	a) In but-1-ene doubly bonded carbon atom is sp^2 hybridised and in but-1-yne triply bonded carbon atom is sp hybridised since sp-C is more electronegative but-1-yne has higher dipole moment . (b) NH_3 Has strongest intermolecular forces due to hydrogen bonding so it’s melting point is higher then $(CH_3)_3$ N	$1^{1/2}$ $1^{1/2}$

5	a. sp3d, SF_4 , SEA SAW b. sp^3d , ClF_3 , T SHAPE c. sp^3 H_20 , BENT	1 1 1
6	A) In first figure + + overlap is equal to + - overlap so due to cancellation net overlap is zero . In second figure no overlap is possible as two orbitals are perpendicular to each other . B) polar due to greater difference in electronegativity , H-F , H-O	2 1
7	a) sp3d2 hybridised, square pyramidal shape due to one lone pair of electron . b)used to differentiate polar and non polar bonds , help in calculating percentage ionic character.	1 1 1
	SECTION D	
1	i) d ii) a iii) b iv) c	1 1 1 1
2	a) sp3d b) XeF_4 c) See-saw d) Sigma is formed by co axial overlapping but pi is formed by lateral overlapping .	1 1 1 1

	SECTION E	
1	a) Compound I will form intramolecular hydrogen bonding because NO2 and OH groups are close to each other while compound II will form intermolecular hydrogen bonding b) Compound II will have higher melting pointdue to hydrogen bond . c) Due to intramolecular hydrogen bonding compound I will not form hydrogen bonds with water therefore it will be less soluble in water	2 1½ 1½
2	a) Covalent bonds are formed by one side only hence are directional but ionic bonds are non directional because charge is uniform in all direction . b) Water is bent structure because it has two lone pairs carbon dioxide is linear due to no lone pair of electron . c) Due to sp hybridised carbon ethyne is linear .	2 2 1
3	i) ammonia ii) BF_3 iii) Methane . iv) trigonal bipyramidal v) octahedral vi) correct structure	1 1 1 1 1 1

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CHAPTER -5: THERMODYNAMICS

Thermodynamics deals with the relationship between various forms of energy in a process. Thermodynamics deals with macroscopic properties. This chapter introduces a major subsidiary thermodynamic property, the Gibbs free energy which lets us express the spontaneity of a process in terms of the properties of the system. This chapter helps to explain why gases expand or diffuse.

System and Surrounding

1. **System**: A system can be defined as where the observations were made, it is the part of the universe.
2. **Surroundings**: Surrounding can be defined as the part other than the system is, surrounding. The system and surroundings can be differentiated by a wall called a boundary.

Types of System:

1. **Open system**: System can be open if it can exchange both energy and matter with surroundings.

2. **Closed system**: System can be closed if it can exchange energy but not matter with surroundings.

3. **Isolated system**: System can be isolated if it can neither exchange energy nor matter with surroundings.

Extensive Properties

The properties which depend upon mass of the substance is known as extensive properties i.e., mass, volume, internal energy, enthalpy etc.

Intensive Properties

The properties which are independent of mass of the substance is known as intensive Properties i.e., temperature, pressure, density, refractive index.

Thermodynamic State of a System

A state is the condition of a system as specified by its physical properties. We can describe

the state of a gas by quoting its pressure (p), volume (V), temperature (T), amount (n) etc. Variables like p, V, T are called state variables or state functions because their values depend only on the state of the system and not on how it is reached.

State Functions

The thermodynamic parameters which depends only on initial and final states of system is known as state function. i.e., internal energy(E), Enthalpy (H), entropy (S), Gibb's free energy (G).

Path Functions

The thermodynamic parameters where value does not depend merely on initial and final state but depends upon the path followed is known as path function. i.e., heat (q), work done (W).

Thermodynamic Process

The sequence followed to change one thermodynamic state of a system into another is called thermodynamic process. The types of thermodynamic processes are:

1**. Isothermal process**: It is the process in which temperature is kept constant means temperature of initial and final state of system along with entire path of process is same.

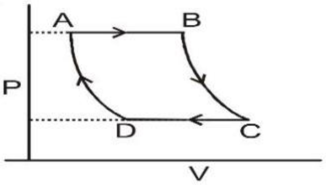
2. **Isobaric process**: It is the process in which pressure is kept constant for entire process.

3. **Isochoric process**: It is the process in which volume is kept constant.

4. **Adiabatic process**: The process in which heat transaction across boundary is not allowed.

5. **Reversible process and Irreversible process**: In thermodynamics, a process is said to be reversible when energy change in each step of the process can be reversed by changing the variables such as pressure, volume or temperature acting on them. In such a process, the driving and opposing forces differ infinitesimally and the process can be reversed completely by increasing the opposing force by an infinitesimally small amount.

Any process which does not take place in the above mentioned manner is said to be an irreversible process. In an irreversible process the driving and opposing force differ by a large amount.



6**. Cyclic process**: It is the process which runs in close loop, means process in which initial and final states are identical.

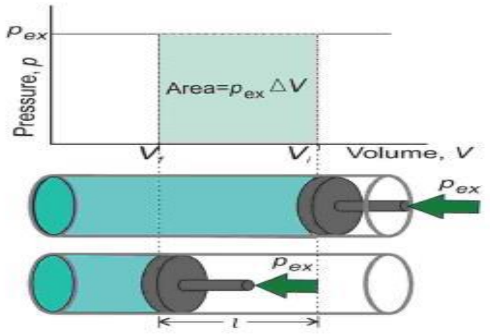
Internal Energy :

Every substance is associated with definite amount of energy that is called internal energy. It is an extensive property and a state function. Internal energy of ideal gases is a function of temperature only.

Pressure-Volume Work :

It is the work done when the gas expands or contracts against the external pressure. Consider a cylinder containing one mole of an ideal gas fitted with a frictionless and

Weightless piston having an area of cross-section A. The total volume of the gas is Vi and the initial pressure of the gas inside P.



Let the external pressure acting on the piston is Pex. If the external pressure Pex is slightly greater than P piston moves downward till the pressure inside the cylinder becomes equal to Pex. Let this change be achieved in a single step and the final volume be Vf. During this compression, suppose the piston moves a very small distance Δl. Thus, the work done on the gas is given by,

$\omega=-\int Pexdv$

$dv= Vf-Vi$

Heat

The change in internal energy of a system can be brought about by the transfer of heat from the surroundings to the system or vice-versa. This exchange of energy between the system and surroundings is possible as a result of the temperature difference between them. This energy called heat is represented by Q.

First Law of Thermodynamics

The first law of thermodynamics states that energy can neither be created nor destroyed. According to first law of thermodynamics,

$\Delta U = q + W$

Where, Q = Heat change

W = Work done

ΔU = Change in internal energy.

The sign conventions are given as;

Work done by the system = – W

Work done on the system = + W

Heat flows into the system = + Q

Heat flows out of the system = – Q

Enthalpy (H)

The total heat content of a system at constant pressure is known as its enthalpy. Mathematically it is the sum of internal energy and pressure-volume energy

$\Delta H = \Delta U + P\Delta V$

It is an extensive property and a state function. Increase in enthalpy H is equal to heat absorbed at constant pressure.

Heat Capacity

Heat capacity is amount of heat require to raise the temperature of a system by unity. It is represented as "C". It is an extensive property and temperature dependent

Types of heat capacity

1**. Specific heat**: For 1 gram system the heat loose or gained by system to bring one unit change in temperature is called specific heat denoted by 's'. specific heat is the intensive property.
S= C/ m

2. **Molar heat capacity**: It is heat capacity for a system having 1 mole of material. It is represented as Cm. It is an intensive property.
Cm= C/m

3. **Heat capacity at constant volume**: Heat capacity of a system in isochoric condition is called heat capacity at constant volume, it is represented as Cv means molar heat capacity at constant volume.
Cv= dU/dT

4. **Heat capacity at constant pressure**: Heat capacity of a system in isobaric condition. It is represented by Cp means molar heat capacity at constant pressure.
Cp= dH/dT

Relation between Cp and Cv

We know that,
$\Delta H = \Delta U + P\Delta V$ .....(i)
As per ideal gas equation
$P\Delta V = R\Delta T$ .....(ii)
From (i) and (ii)
$\Delta H = \Delta U + R\Delta T$
$\Delta H/\Delta T= \Delta U/\Delta T+R$
$Cp = Cv + R$
$Cp – Cv = R$

Hess's Law

According to Hess's law, If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature.

1st method: $C(s)+O2(g)\rightarrow CO2(g)=\Delta H$

2nd method: $C(s)+1/2O2(g)\rightarrow CO(g)=\Delta H1$
$CO(s)+1/ 2O2(g)\rightarrow CO2(g)=\Delta H2$

According to Hess's law,
$\Delta H=\Delta H1+\Delta H2$

Application of Hess's Law

1. Calculation of enthalpy of formation.
2. Determination of standard enthalpies of reactions.

Bond Dissociation Energy

The energy required to break one mole bond of a particular type in gaseous molecule is known as bond dissociation energy. For example, we consider the dissociation of water,
$H{-}OH(g) \rightarrow H(g)+OH(g)$ ΔH =498 kJ/mol

Second Law of Thermodynamics

This states that the entropy of the universe always increases in every spontaneous (natural) change.

Enthalpy Changes During Phase Transformation Enthalpy of fusion: Enthalpy of fusion is the heat energy or change in enthalpy when one mole of a solid at its melting point is converted into liquid state.

Enthalpy of vaporisation: It is defined as the heat energy or change in enthalpy when one mole of a liquid at its boiling point changes to gaseous state.

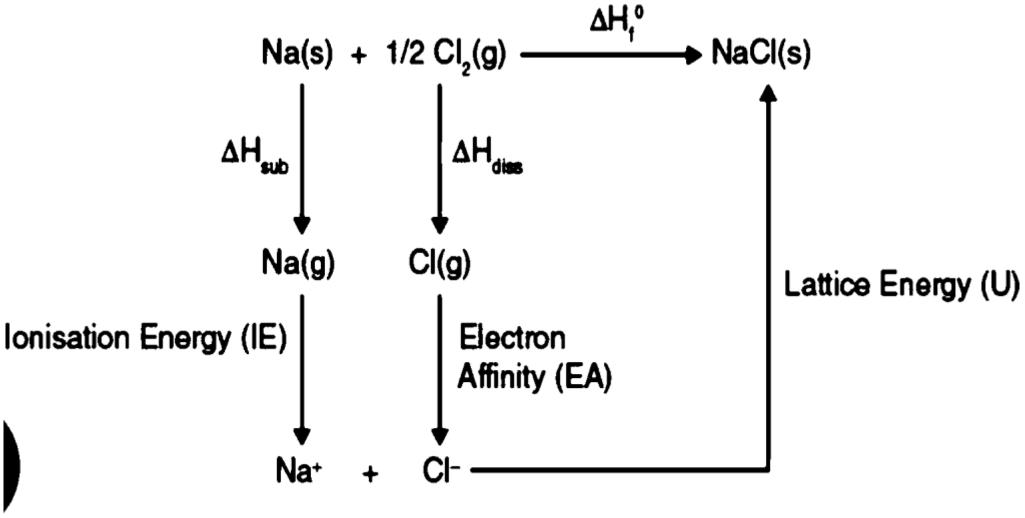
Enthalpy of Sublimation: Enthalpy of sublimation is defined as the change in heat energy or change in enthalpy when one mole of solid directly changes into gaseous state at a temperature below its melting point.

Standard Enthalpy of Formation Enthalpy of formation is defined as the change in enthalpy in the formation of 1 mole of a substance from its constituting elements under standard conditions of temperature at 298K and 1 atm pressure.

Enthalpy of Combustion: It is defined as the heat energy or change in enthalpy that accompanies the combustion of 1 mole of a substance in excess of air or oxygen. CO (g) + ½ $O2$ (g) $CO2$(g) $\Delta H\mathbf{O} = -283$ KJ

Hess’s Law of Constant Heat Summation The total amount of heat evolved or absorbed in a reaction is same whether the reaction takes place in one step or in number of steps

Born-Haber Cycle It is not possible to determine the Lattice enthalpy of ionic compound by direct experiment. Thus, it can be calculated by following steps. The diagrams which show these steps is known as Born-Haber Cycle.



Born Harber Cycle for Sodium Chloride

• **Spontaneity Spontaneous Process:** A process which can take place by itself or has a tendency to take place is called spontaneous process. Spontaneous process need not be instantaneous. Its actual speed can vary from very slow to quite fast.

A few examples of spontaneous process are: (i) Common salt dissolves in water of its own. (ii) Carbon monoxide is oxidised to carbon dioxide of its own.

• **Entropy (S)** The entropy is a measure of degree of randomness or disorder of a system. It is an extensive property and a state function.. Its value depends upon the amount of substance present in the system.

Entropy of a substance is minimum in solid state while it is maximum in gaseous state. The change in entropy in a spontaneous process is expressed as ΔS

$$\Delta S = \Delta S_{system} + \Delta S_{surroundings}$$
$$\Delta S = \text{Overall Change in Entropy}$$
$$\Delta S_{system} = \text{Change in Entropy of the System}$$
$$\Delta S_{surroundings} = \text{Change in Entropy of the Surroundings}$$

$$\Delta S > 0, + \text{ entropy change, reaction is spontaneous}$$
$$\Delta S < 0, - \text{ entropy change, reaction is nonspontaneous}$$

Equation for the Total Change in Entropy

• Gibbs Energy and Spontaneity

A new thermodynamic function, the Gibbs energy or Gibbs function G, can be defined as

$G = H - TS$ $\Delta G = \Delta H - T\Delta S$ Gibbs energy change = enthalpy change – temperature x entropy change ΔG gives a criteria for spontaneity at constant pressure and temperature,

(i) If ΔG is negative (< 0) the process is spontaneous.
(ii) (ii) If ΔG is positive (> 0) the process is non-spontaneous.

THERMODYNAMICS

MULTIPLE CHOICE QUESTIONS (1 MARK EACH)

Q1. Thermodynamics is not concerned about -
(a) energy changes involved in a chemical reaction.
(b) the extent to which a chemical reaction proceeds.
(c) the rate at which a reaction proceeds.
(d) the feasibility of chemical reaction.

Q2. Which of the following statements is correct?
(a) The presence of reacting species in a covered beaker is an example of open system.
(b) There is an exchange of energy as well as matter between the system and the surroundings in a closed system.
(c) The presence of reactants in a closed vessel made up of copper is an example of a closed system.
(d) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.

Q3. The state of gas can be described by quoting the relationship between
(a) pressure, volume, temperature
(b) temperature, amount, pressure
(c) amount, volume, temperature
(d) pressure, volume, temperature, amount

Q4. The volume of gas is reduced to half from its original volume. The specific heat will
(a) reduce to half
(b) be doubled
(c) remain constant

(d) increase four times

Q5.Third law of thermodynamics provides a method to evaluate which property?
(a) Absolute Energy
(b) Absolute Enthalpy
(c) Absolute Entropy
(d) Absolute Free Energy

Q6. The species which by definition has ZERO standard molar enthalpy of formation at 298 K is
(a) $Br_2(g)$
(b) $Cl_2(g)$
(c) $H_2O(g)$
(d) $CH_4(g)$

Q 7. In which of the following process, a maximum increase in entropy is observed?
(a) Dissolution of Salt in Water
(b) Condensation of Water
(c) Sublimation of Naphthalene
(d) Melting of Ice

Q 8. The enthalpies of combustion of carbon and carbon monoxide are -393.5 and -283.0 kJ mol^{-1} respectively. The enthalpy of formation of carbon monoxide is:
(a) -676 kJ
(b) 110.5 kJ
(c) -110.5 kJ
(d) 676.5 kJ

Q9. Based on the first law of thermodynamics, which one of the following is correct?
(a) For an isothermal process, $q = +w$
(b) For an isochoric process, $\Delta U = -q$
(c) For an adiabatic process, $\Delta U = -w$
(d) For a cyclic process, $q = -w$

Q10. A system absorb 10 kJ of heat at constant volume and its temperature rises from 270°C to 370°C. The value of ΔU is -
(a) 100 kJ
(b) 10 kJ
(c) 0 kJ
(d) 1 kJ

Q11. The temperature of the system decreases in an ______.
(a) Adiabatic Compression
(b) Isothermal Expansion

(c) Isothermal Compression
d) Adiabatic Expansion

Q12. One mole of which of the following has the highest entropy?
(a) Liquid Nitrogen
(b) Hydrogen Gas
(c) Mercury
(d) Diamond

Q13. For the reaction $C(s) + O_2(g) \rightarrow CO_2(g)$
(a) $\triangle H > \triangle U$
(b) $\triangle H < \triangle U$
(c) $\triangle H = \triangle U$
(d) None of these

Q14. For an ideal gas, CV and CP are related as :
(a) $C_V - C_P = R$
(b) $C_V + C_P = R$
(c) $C_P - C_v = RT$
(d) $C_P - C_v = R$

Q15. Considering entropy(S) thermodynamic parameters the criteria for the spontaneity of any process is:
(a) $\triangle S$ system + $\triangle S$ surroundings > 0
(b) $\triangle S$ system – $\triangle S$ surroundings < 0
(c) $\triangle S$ system > 0
(d) $\triangle S$ surroundings > 0

Answers of MCQs with Explanation

Q1 (c) Thermodynamics is not concerned with rate at which a reaction proceeds. The rate of reaction is dealt by kinetics.

Q2 (c) For a closed vessel made up of copper, no matter can be exchanged between the system and the surroundings but energy exchange can occur through its walls.

Q3 (d) State of a system can be described by state functions or state variables which are pressure, volume, temperature and amount of the gas ($PV= nRT$).

Q4 (c) The specific heat of a substance is the heat required to raise the temperature of 1 gram of a substance by one degree (1 K or 1 °C). It is an intensive property and is independent of the volume of the substance.

Q5 (c) Absolute entropy, third law of thermodynamics states that the absolute entropy of a perfectly crystalline substance at 0 kelvin (absolute zero) is zero.

Q6 (b) $Cl_2(g)$, This is possible only for elements, chlorine is a gas at this temperature, but bromine is a liquid, so it is possible only for chlorine.

Q7 (c) Sublimation of Naphthalene
The order of entropy in solid, liquid and gas is gas > liquid > solid. Hence, in sublimation of naphthalene, maximum increase in entropy is observed.

Q8 (c) -110.5 kJ
$C(s) + O_2 \rightarrow CO_2\ \Delta H_1 = -393.5$
$CO + (1/2)\ O_2 \rightarrow CO_2\ \Delta H_2 = -283.0$
$C(s) + (1/2)\ O_2 \rightarrow CO\ \Delta H = \Delta H_1 - \Delta H_2$
$= -393.5 + 283 = -110.5$ KJ

Q9 (d) For a cyclic process, $q = -w$

(1) $\Delta U = q + w$. For an isochoric process, $w = -P\Delta V = 0$. Hence, $\Delta U = qv$
(2) For an adiabatic process, $q = 0$. Hence, $\Delta U = w$
(3) For an isothermal process, $\Delta U = 0$ Hence, $q = -w$
(4) For a cyclic process , $\Delta U = 0$. Hence, $q = -w$

Q10 (b) $\Delta V=0$ --> $w=0$
$\Delta U=q = 10$kJ
Q11. (d) Adiabatic Expansion
In adiabatic process heat is neither added nor removed from system. So the work done by the system (expansion) in adiabatic process will result in decrease of internal energy of that system (from first law).
As internal energy is directly proportional to the change in temperature there will be temperature drop in an adiabatic process.

Q12. (b) Hydrogen Gas
Q13. (c) $\triangle H = \triangle U$
Q14. (d) $C_P - C_v = R$
Q15. (a) $\triangle S$ system + $\triangle S$ surroundings > 0

REASON ASSERTION TYPE QUESTIONS

These questions consist of two statements, Assertion and Reason. While answering these questions, choose any one of the following four responses.

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

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

(c) Assertion is correct but Reason is incorrect.

(d) Assertion is Incorrect but Reason is correct.

Q1. Assertion : Enthalpy of formation of graphite is zero but of diamond it is not zero.

Reason : Enthalpy of formation of the most stable allotrope is taken as zero.

Ans: (a)

2. Assertion : Heat of neutralisation for both H_2SO_4 and HCl with NaOH is 53.7 kJ mol^{-1}.

Reason : Both HCl and H_2SO_4 are strong acids.

Ans:(a)

3. Assertion : Some salts are sparingly soluble in water at room temperature.

Reason : The entropy increases on dissolving the salts.

Ans:(b)

4. Assertion : Spontaneous process is an irreversible process and may be reversed by some external agency.

Reason : Decrease in enthalpy is a contributory factor for spontaneity.

Ans:(b)

5. Assertion : Decrease in free energy causes spontaneous reaction.

Reason : Spontaneous reactions are invariable exothermic reactions.

Ans:(c)

6. Assertion : The heat absorbed during the isothermal expansion of an ideal gas against vaccum is zero.

Reason : The volume occupied by the molecules of an ideal gas is zero.

Ans:(b)

7. Assertion : U is a state function.

Reason : T is an intensive property.

Ans:(b)

8. Assertion : Entropy of system increases for a spontaneous reaction.

Reason : Enthalpy of reaction always decreases for spontaneous reaction.

Ans:(a)

9. Assertion : Sublimation of the solid is nonspontaneous.

Reason : Sublimation is endothermic process.

Ans:(d)

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

Reason : Work and heat are state functions.

Ans:(c)

COMPETENCY BASED QUESTIONS

1) State First Law of thermodynamics.

Ans -Energy can neither be created nor destroyed. The energy of an isolated system is constant. U = q + w.

2) Define a system

Ans: A system in thermodynamics is a part of the universe within a specified boundary.

3) Name the different types of the system.

Ans: There are three types of system

Open system

Closed system

Isolated system

4) What is a thermodynamic state function?

Ans : A function whose value is independent of path. eg. P, V, E, H.

5) Define extensive properties.

Properties which depend upon amount of substance called extensive properties. Volume, enthalpy, entropy.

6) Give relationship between H, U for a reaction in gaseous state.

H = U + ng. RT.

7. What do you understand by state function? Neither q nor w is a state function but q + w is a state function? Explain.

Ans) The property whose value depends upon state of system and is independent of path. q + w = U, which is a state function as value of U does not depends upon path.

8. Give the mathematical expression of enthalpy.

Ans: Mathematically H=U+PV where U is internal energy.

9. In a process, 701J heat is absorbed and 394J work is done by system. What is change in Internal energy for process?
Ans - q = 701J, w = 394J,
so U = q + w
= 701 – 394 = 307J.

10. What is bond energy? Why is it called enthalpy of atomization?
Ans - 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.

11. Define Heat capacity

Ans: Specific heat /specific heat capacity is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree Celsius (or one Kelvin).

12. Define specific heat.

Ans: Specific heat /specific heat capacity is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree Celsius (or one Kelvin).

13. Give the mathematical expression of heat capacity.

Ans: The mathematical expression of heat capacity is as follows

$q=mc\Delta T$

If, $m=1$

$q=C\Delta T$

14. Define standard enthalpy.

Ans: The standard enthalpy of reaction is defined as the enthalpy change for a reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.

15. Define spontaneous process.

Ans: A process which occurs without use of an external agent is termed as spontaneous process.

16. Define non-spontaneous processes.

Ans: A process which occurs with the use of an external agent is termed as spontaneous process.

17. 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.

18. 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.

19. What are extensive property and intensive properties?

Ans. 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.

20. With the help of first law of thermodynamics and $H = U + pVH = U + pV$ prove $\Delta H=q_p$

Ans: Enthalpy is defined as follows

$H=U+pV$

$\Delta H=\Delta(U+pV)$

$\Delta H=\Delta U+\Delta(pV)$

$\Delta H=\Delta U+p\Delta V+V\Delta p$……(i)

From first law of thermodynamics,

$\Delta U=q+w$

$=q-p\Delta V$

From equation (i) and (ii), we get

$\Delta H=q-p\Delta V+p\Delta V+V\Delta p$

$\Delta H=q+V\Delta p$

At constant pressure,

$\Delta p=0$

$V\Delta p=0$

$\Delta H=qp$ at constant pressure

Therefore, $\Delta H=qp$

21.What is an extensive and intensive property?

Ans: Extensive property is defined as the property which depends on the quantity or size of the matter present in the system.

Intensive property is defined as the property which depends on the quantity or size of matter present in the system.

22. Show that for an ideal gas $CP-CV=R$

Ans: At constant pressure, when gas is heated, heat is required for increase in the temperature of gas and for doing mechanical work against expansion

At constant volume, heat capacity is written as CV and at constant pressure it is written as CP

At constant volume $qv=CV\Delta T$ which is equal to ΔU

At constant pressure $qP=CP\Delta T$ which is equal to ΔH

For one mole ideal gas $\Delta H=\Delta U+\Delta(PV)$

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

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

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

On substituting values of $\Delta H,\Delta U$, we have

$CP\Delta T=CV\Delta T+R\Delta T$

$CP=CV+R$

$CP-CV=R$

23. Give the relationship between ΔH and ΔU for gases.

Ans: For an appreciable volume change,

Let VA represent the volume of gaseous reactants

Let VB represent the volume of gaseous products

Let nA be the moles of reactant

Let nB be the moles of product

At constant pressure and temperature

$pVA = nART$

$pVB = nBRT$

$pVB - pVA = (nB - nA)RT$

$p\Delta V = \Delta ngRT$

$\Delta ng = nB - nA$

Now substituting the value of $p\Delta V$, we get

$\Delta H = \Delta U + \Delta ngRT$

Heat change at constant pressure, $\Delta H = qp$

Heat change at constant temperature, $\Delta H = qV$

For gaseous system

$qP = qV + \Delta ngRT$

24. The equilibrium constant for a reaction is 10. What will be the value of ΔG^o ? R = 8.314J.K-1mol-1 T = 300K.

Ans $\Delta rG^o = -2.303\ RT\ \log K$

$= -2.303 \times 8.314 \times 300 \times \log 10$

$= -19.147 \times 300 \times 1 = -5744.1J$

$\Delta rG^o = -5.7441KJ.mol-1$

25. What is entropy? Why is the entropy of a substance taken as zero at 0 K?

Calculate the ΔrG for the reaction?

$N2(g) + 3H2(g) \rightarrow 2NH3(g)$ at 298K

The value of equilibrium constant (K) is 6.6x105 , R = 8.314JK-1mol-1.

Ans: It is measure of randomness or disorder of system.

Because at O K there is complete order in the system.

$\Delta G^o = -2.303\ RT\ \log K = -2.303 \times 8.314 \times 298 \times \log 6.6 \times 105$

$= -5705.8[\log 6.6 + \log 105]$

$= -5705.8[0.8195 + 5.0] = -5705.8 + 5.8195J$

$= -33204.903J$

$\Delta G^o = -33.205$ KJ mol-1.

Q. 26 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.

Ans . (a) It is false, exothermic reaction is not always spontaneous. If $\Delta S = +ve$ and $T.\ \Delta S > \Delta H$. 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.

Q.27 Why is the difference between $\Delta H \Delta$ and ΔU not significant for solids or liquids?

Ans: The difference between ΔH and ΔU is not significant for solids or liquids because systems made up entirely of solids and/or liquids do not experience significant volume changes when heated, the difference between and is usually insignificant.

Q.28 . Will the heat released in the following two reactions be equal? Give reasons in support of your answer

.$H2_{(g)} +_{1/2} O2_{(g)} \rightarrow H2O_{(g)}$
I.$H2_{(g)} +_{1/2} O2_{(g)} \rightarrow H2O(l)$

Ans: The heats released in the two reactions are not equal. The heat released in a reaction depends on the reactants, products and the physical states.

In reaction:

.Water is produced in the gaseous state whereas in

.It is in liquid state.

Also, when water vapours condensed to form water latent heat of vaporization is released. Therefore, more heat is released in reaction (ii).

Q.29 The reaction C(graphite)+O2(g)→CO2(g)+393.5kJmol –
1 represents the formation of CO2 and also combustion of carbon. Write the ΔH° values of the two processes.

Ans: The standard enthalpy of formation of CO2CO2 is −393.5kJmol $^{-1}$
ΔH° f (CO2$_{(g)}$=−393.5kJmol – 1

The standard enthalpy of formation of combustion of carbon is
- 393.5kJmol - 1

ΔH comb (CO2$_{(g)}$)=−393.5kJmol - 1

30. Explain how is enthalpy related to spontaneity of a reaction?

Ans: Most of the exothermic reactions are spontaneous due to an increase in energy.

Burning a substance is a spontaneous process.

$C_{(s)}+O2_{(g)}\rightarrow CO2_{(g)}$ ΔH=−394kJmol – 1

Many spontaneous reactions start with the absorption of heat. Conversion of water into water vapour is an endothermic spontaneous reaction. Hence the change in enthalpy is not the only criteria for deciding the spontaneity of the reaction.

31. The molar enthalpy of vaporization of acetone is less than that of water. Why?

Answer. Acetone lacks a hydrogen bond, so intermolecular forces are weaker, causing it to boil/evaporate quickly, lowering the molar enthalpy of vaporisation. Furthermore, because acetone lacks a polar O-H bond, it has a low enthalpy. Water has both a non-polar region and a strong hydrogen bond.

32. Heat capacity (C_p) is an extensive property but specific heat (c) is an intensive property. What will be the relation between C_p and c for 1 mol of water?

Answer

For water, heat capacity = 18 × specific heat

or $C_p = 18 \times c$

Specific heat, c = 4.18 Jg^{-1} K^{-1}

Heat capacity, C_p = 18 × 4.18 JK^{-1} = 75.3 J K^{-1}.

33. Predict the change in internal energy for an isolated system at constant volume.

Answer. There is no energy transfer as heat or work in an isolated system,

so w=0 and q=0.

According to the first law of thermodynamics-

Δ U = q + w = 0 + 0 = 0

$\Delta U = 0$.

CHAPTER-6: CHEMICAL EQUILIBRIUM

Equilibrium Constant:

When the number of molecules leaving the liquid to vapour equals the number of molecules returning to the liquid from vapour equilibrium is said to be attend and is dynamic in nature equilibrium can be established for both physical and chemical processes and at this stage rate of forward and reverse reactions are equal equilibrium constant K_C is expressed as the concentration of products divided by reactants and each term raised to the stoichiometric coefficient.

For reaction aA +bB = cC + dD

K_c is equal to $[C]^c [D]^d/[A]^a[B]^b$

Law Of Mass Action

Proposed by Guldberg and Waage so also known as Guldberg - Waage Law

Rate of a chemical reaction is directly proportional to the product of the concentrations of the reactants

$aA+bB \rightleftharpoons cC+dD$

Units of equilibrium constant are based on molarity or pressure.

For Kc the concentration terms in mol/L and for Kp partial pressure is substituted in Pa, kPa, bar or atm.

If the exponents of both the numerator and denominator are same, equilibrium constant has no units.

For example,

$H2(g)+I2(g) \rightleftharpoons 2HI(g)$, Kc and Kp have no unit.

$N2O4(g) \rightleftharpoons 2NO2(g)$, Kc has unit mol/L and Kp has unit bar

Equilibrium constants can also be expressed as dimensionless quantities if the standard state of reactants and products are specified.

For a pure gas, the standard state is 1bar.

Therefore a pressure of 4 bar in standard state can be expressed as 4 bar/1 bar = 4, which is a dimensionless number.

Standard state for a solute is 1 molar solution and all concentrations can be measured with respect to it.

Thus, in this system both Kc and Kp are dimensionless quantities

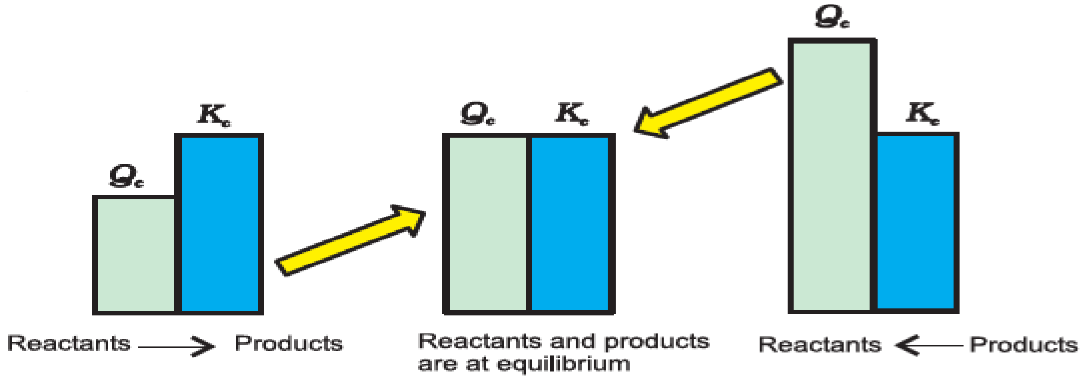


Fig. *Predicting the direction of the reaction*

$\Delta G = \Delta G^{\ominus} + RT \ln Q$ where, $G^{\ominus}$ is standard Gibbs energy.

At equilibrium, when $\Delta G = 0$ and $Q = K_c$,

$\Delta G = \Delta G^{\ominus} + RT \ln K = 0$

$\Delta G^{\ominus} = -RT \ln K$ $\quad\Delta G^{\ominus} = -2.303\, RT \log K$

$\ln K = -\Delta G^{\ominus} / RT$ Taking antilog of both sides, we get,

$K = e^{-\Delta G^{\ominus}/RT}$

If $\Delta G^{\Theta}<0$, then $-\Delta G^{\Theta}/RT$ is positive and $e-\Delta G^{\Theta}/RT>1$, making $K>1$ Reaction is spontaneous in forward direction and products are present predominantly.

If $\Delta G^{\Theta}>0$, then $-\Delta G^{\Theta}/RT$ is negative and $e^\wedge-\Delta G^{\Theta}/RT<1$, making $K<1$ Reaction is non-spontaneous in forward direction and only a very minute quantity of product is formed.

Factors Affecting Equilibria

- Concentration
- Temperature
- Pressure
- Catalyst

Le Chatlier’s Principle:

Equilibrium constant has constant value at a fixed temperature and at this stage all the microscopic properties such as concentration pressure etc become constant for a gaseous reaction equilibrium constant is expressed as K_P and is written by replacing concentration term by partial pressures in K_C expressions the direction of reaction can be predicted by reaction question Q_C which is equal to K_C at equilibrium. Le Chatlier’s principle states that the change in any factor such as temperature pressure concentration etc will cause the equilibrium to shift in such a direction so as to reduce or counter act the effect of the change. It can be used to study the effect of various factors such as temperature, concentration, pressure, catalyst and inert gases on the direction of equilibrium and to control the yield of products by controlling these factors. Catalyst does not affect the equilibrium composition of a reaction mixture but increases the rate of chemical reaction by making available a new lower energy pathway for conversion of reactants to products and vice versa.

Michael Faraday classified the substances into two categories based on their ability to conduct electricity.

(1) Electrolytes:-substances that conduct electricity in their aqueous solutions

(2) Non-electrolytes :- substances that do not conduct electricity in their aqueous solutions

Faraday further classified electrolytes into strong and weak electrolytes.

Strong electrolytes on dissolution in water dissociate almost completely into ions for example sodium chloride , while the weak electrolytes only partially ionize into ions for example acetic acid.

Electolytes:

All substances that conduct electricity in aqueous solutions are called electrolyte.

Ionization of electrolytes:

Acids, bases and salts are electrolytes and the conduction of electricity by the aqueous solutions is due to anions and cation produced by the dissociation or ionization of electrolytes in aqueous solution. The strong electrolytes are completely dissociated in electrolytes. There is equilibrium between the ions and the unionized electrolyte molecules.

Arrhenius Concept of Acids and Bases:

According to Arrhenius acids give hydrogen ions while bases produce hydroxyl ion in their aqueous solutions.

Bronsted Lowry Theory:

According to Brönsted-Lowry theory,

Acid is a substance that is capable of donating a hydrogen ion H+ and

Bases are substances capable of accepting a hydrogen ion, Bronsted Lowry defined an acid as a proton donor and a base as a proton acceptor when a bronsted lorry acid reacts with the base it produces its conjugate base and a conjugate acid or responding to the base with which it reacts does a conjugate pair of acid base differs only by one proton.

Lewis Theory:

Lewis further generalized the definition of an acid as an electron pair accepted and a base as an electron pair donor. The expressions for ionization constants of weak acids (Ka) and weak bases (Kb) are developed using Arrhenius definition. The degree of ionization and its dependence on concentration and common ion is important.

Acid is a species which accepts electron pair .

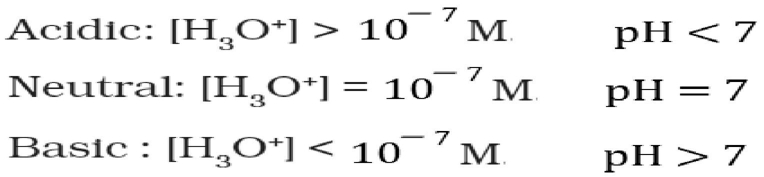
Base is a species which donates an electron pair.

For example , BF_3 is an acid and reacts with NH_3 by accepting its lone pair of electrons.

pH scale:

Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the pH scale. The pH of the solution is defined as the negative logarithm to base 10 of the activity of hydrogen ion.

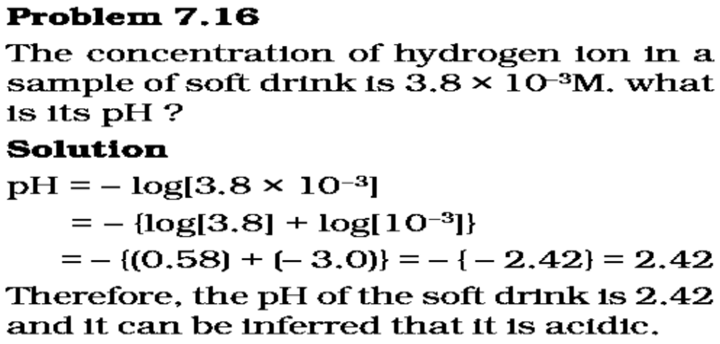
$pH= -\log [H]^+$



Acidic: $[H_3O^+] > 10^{-7}$ M $\quad$ $pH < 7$

Neutral: $[H_3O^+] = 10^{-7}$ M $\quad$ $pH = 7$

Basic : $[H_3O^+] < 10^{-7}$ M $\quad$ $pH > 7$



Problem 7.16

The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3}M. what is its pH ?

Solution

$$\begin{aligned} pH &= -\log[3.8 \times 10^{-3}] \\ &= -\{\log[3.8] + \log[10^{-3}]\} \\ &= -\{(0.58) + (-3.0)\} = -\{-2.42\} = 2.42 \end{aligned}$$

Therefore, the pH of the soft drink is 2.42 and it can be inferred that it is acidic.

This has been extended to other quantities;

pOH= -log $[OH]^-$

pKa= -log [Ka]

pKb= -log [Kb]

pKw= -log [Kw]

Ionization of water:

For the ionization of water **pH + pOH = pKw** equation is always satisfied. The salts of strong acid and weak base, and weak acid and strong base and weak acid and weak base under hydrolysis in aqueous solution. Water is acting both as an acid and a base.

Self ionization of water:-In pure water, one H2O molecule donates proton and acts as an acid and another water molecules accepts a proton and acts as a base at the same time.

Buffer solution:

The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.

Two types-Acidic buffer solution and Basic buffer solution

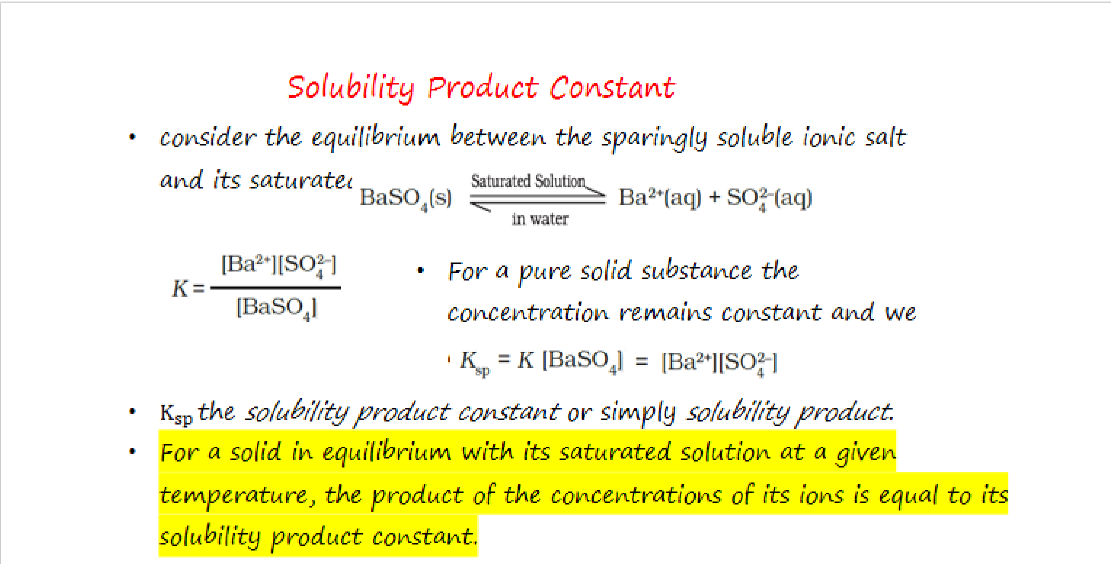
Acidic buffer solution:- weak acid and its salt formed with strong base.

For example solution formed by acetic acid and sodium acetate(pH=4.75)

Basic buffer solution:- weak base and its salt formed with strong acid.

For example solution formed by ammonium hydroxide and ammonium chloride (pH=9.25)

Solubility product Constant: Ksp



Solubility Product Constant

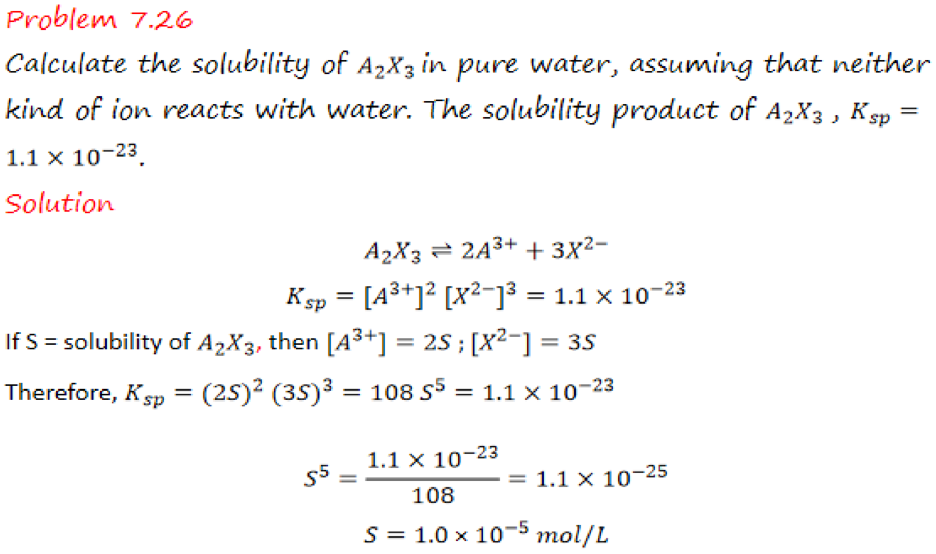
- consider the equilibrium between the sparingly soluble ionic salt and its saturate $BaSO_4(s) \underset{\text{in water}}{\overset{\text{Saturated Solution}}{\rightleftharpoons}} Ba^{2+}(aq) + SO_4^{2-}(aq)$

$$K = \frac{[Ba^{2+}][SO_4^{2-}]}{[BaSO_4]}$$

- For a pure solid substance the concentration remains constant and we

$K_{sp} = K\,[BaSO_4] = [Ba^{2+}][SO_4^{2-}]$

- K_{sp} the solubility product constant or simply solubility product.
- For a solid in equilibrium with its saturated solution at a given temperature, the product of the concentrations of its ions is equal to its solubility product constant.



Problem 7.26

Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. The solubility product of A_2X_3 , $K_{sp} = 1.1 \times 10^{-23}$.

Solution

$$A_2X_3 \rightleftharpoons 2A^{3+} + 3X^{2-}$$

$$K_{sp} = [A^{3+}]^2\,[X^{2-}]^3 = 1.1 \times 10^{-23}$$

If S = solubility of A_2X_3, then $[A^{3+}] = 2S$; $[X^{2-}] = 3S$

Therefore, $K_{sp} = (2S)^2\,(3S)^3 = 108\,S^5 = 1.1 \times 10^{-23}$

$$S^5 = \frac{1.1 \times 10^{-23}}{108} = 1.1 \times 10^{-25}$$

$$S = 1.0 \times 10^{-5}\ mol/L$$

EQUILIBRIUM

MULTIPLE CHOICE QUESTIONS (1 MARK EACH)

1- Le Chatelier’s principle is applicable to:
(a) only homogeneous chemical reversible reactions
(b) only heterogeneous chemical reversible reactions
(c) only physical equilibria
(d) all systems, chemical or physical in equilibrium.

2-When NH_4Cl is added to NH_4OH solution the dissociation of ammonium hydroxide is reduced. It is due to:
(a) common ion effect
(b) hydrolysis no
(c) oxidation
(d) reduction

3- The pH of a solution of hydrochloric acid is 4. The molarity of the solution is:
(a) 4.0
(b) 0.4
(c) 0.0001
(d) 0.04

4- What does it indicate having a higher equilibrium constant?
(a) reaction occurs faster
(b) rate of backward reaction is faster
(c) both the backward and forward reactions are equal
(d) reaction may be slower than usual

5- The equilibrium constant of a reaction is 20 units and the equilibrium constant of other reaction is 30 units when both the reactions are added up together then the equilibrium constant of the resultant reaction is given by _____________
(a) 20 units
(b) 600 units
(c) 50 units
(d) 10 units

6- What is the equilibrium constant of the following reaction: $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$?
(a) $[NO][H_2O]/[NH_3][O_2]$
(b) $[C]^c[D]^d/[A]^a[B]^b$
(c) $[NO_4[H_2]^6/NH_3]^4[O_2]^5$
(d) $[NO]^4[H_2O]^6/[NH_3]^4[O_2]^5$

7- If the chemical reaction is:

$aA + bB \rightarrow cC + dD$ and K is the equilibrium constant. Then what is the equilibrium constant of the reaction $naA + nbB \rightarrow ncC + ndD$?

(a) K
(b) nK
(c) K^n
(d) K/n

8- Consider the following equilibrium in a closed container $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$.
At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements hold true regarding the equilibrium constant (K_p) and degree of dissociation (α)?
(a) Neither K_p nor α changes
(b) Both K_p and α change
(c) K_p changes but α does not change
(d) K_p does not change but α changes.

9- We know that the relationship between K_c and K_p is
$K_p = K_c\ (RT)^{\Delta n}$
What would be the value of Δn for the reaction
$NH_4Cl\ (s) \Leftrightarrow NH_3\ (g) + HCl\ (g)$
(a) 1
(b) 0.5
(c) 1.5
(d) 2

10- K_{a1}, K_{a2} and K_{a3} are the respective ionisation constants for the following reactions.
$H_2S \Leftrightarrow H^+ + HS^-$
$HS^- \Leftrightarrow H^+ + S^{2-}$
$H_2S \Leftrightarrow 2H^+ + S^{2-}$

The correct relationship between K_{a1}, K_{a2} and K_{a3} is
(a) $K_{a3} = K_{a1} \times K_{a2}$
(b) $K_{a3} = K_{a1} + K_{a2}$
(c) $K_{a3} = K_{a1} - K_{a2}$
(d) $K_{a3} = K_{a1} / K_{a2}$

11- Acidity of BF_3 can be explained on the basis of which of the following concepts?
(a) Arrhenius concept
(b) Bronsted Lowry concept

(c) Lewis concept

(d) Bronsted Lowry as well as Lewis concept.

12- A reversible reaction, two substances are in equilibrium. If the concentration of each one is doubled the equilibrium constant will be

(a) Reduce to half its original value.
(b) Reduced to one fourth of its original value.
(c) Doubled.
(d) Constant.

ASSERTION- REASON TYPE QUESTIONS

In the following questions (13-16)a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

a) Both A and R are true and R is correct explanation of A.
b) Both A and R are true but R is not correct explanation of A.
c) A is true but R is false.
d) Both A and R are false

13-**Assertion (A):** For any chemical reaction at a particular temperature, the equilibrium constant is fixed and is a characteristic property.
Reason (R) : Equilibrium constant is independent of temperature.

14- **Assertion :** K_p can be less than, greater than or equal to K_c.

Reason: Relation between K_p and K_c depends on the change in number of moles of gaseous reactants and products (Δn).

15- **Assertion:** The endothermic reactions are favoured at lower temperatures and the exothermic reactions are favoured at a higher temperature.

Reason: when a system in equilibrium is disturbed by changing the temperature, it will tend to adjust itself so as to overcome the effect of change.

16- **Assertion:** If water is heated to 59°C, the pH will increase.

Reason: K_w increases with an increase in temperature.

SECTION –B SHORT ANSWER TYPE QUESTIONS (2 M)

17 - The equilibrium constant expression for a gas reaction is,

$$K_c = \frac{[NH_3]^4[O_2]^5}{[NO]^4[H_2O]^6}$$

Write the balanced chemical equation corresponding to this expression.

18- Arrange the following compounds in increasing order for pH
KNO_3(aq), CH_3COONa (aq), NH_4Cl (aq), $C_6H_5COONH_4$ (aq)

OR

Conjugate acid of the weak base is always stronger. The decreasing order of the basic strength for the following conjugate bases will be?

OH^-, RO^-, CH_3COO^-, CI^-

19- What will be the effect on equilibrium when Δn is negative and pressure is decreased?

20- (i) Calculate the pH of 0.001 N HCl.
(ii) What will be the effect of presence of HCl on dis sociation of H_2S?

21 - For the following equilibrium, Kc = 6.3×10^{14} at 1000K

$$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$$

Both the forward and backward reactions in the equilibrium are elementary bimolecular reactions. What is Kc, for the backward reaction?

SECTION –C SHORT ANSWER TYPE QUESTIONS (3 M)

22- (i) State Le chatelier’s principle?
(ii) Can a catalyst change the position of equilibrium in a reaction?

23 - The aqueous solution of sugar does not conduct electricity. However, when sodium chloride is added to water, it conducts electricity. How will you explain this statement on the basis of ionisation and how is it affected by the concentration of sodium chloride?

24-How can you predict the following stages of a reaction by comparing the value of Kc and Qc?
(i) Net reaction proceeds in the forward direction.
(ii) Net reaction proceeds in the backward direction.

(iii)No net reaction occurs.

25- Following data is given for the reaction: $CaCO_3(s) \rightarrow CaO\ (s) + CO_2\ (g)$

$\Delta_f H^- [CaO\ (s)] = -635.1$ kJ / mol

$\Delta f\ H^- [CO_2\ (g)] = -393.5$ kJ / mol

$\Delta f\ H^- [CaCO_3\ (s)] = -1206.9$ kJ / mol

Predict the effect of temperature on the equilibrium constant of the above reaction.

26- Explain the following:
(i) Common ion effect
(ii) solubility products
(iii) pH

27- Hydrogen gas is obtained from the natural gas by partial oxidation with steam as per the following endothermic reaction:

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

Write the expression for Kp for the above reaction
How will the value of K_p and composition of equilibrium mixture be affected by:
(i) increasing the pressure, (ii) increasing the temperature,

28-The vapour pressures of water, acetone and ethanol at 293 K are 2.34 kPa, 12.36 kPa and 5.85 kPa respectively. Which of the following has the lowest boiling point and why?

SECTION –D CASE/PASSAGE BASED QUESTIONS (4 M)

From question no (29-30) read the passage and answer the questions

29- Reactants and products coexist at equilibrium, so that the conversion of reactant to products is always less than 100%. Equilibrium reaction may involve the decomposition of a covalent (nonpolar) reactant or ionization of ionic compound into their ions in polar solvents. Ostwald dilution law is the application of the law of mass action to the weak electrolytes in solution. A binary electrolyte AB which dissociates into A^+ and B^- ions i.e.

$$AB \rightleftharpoons A^+ + B^-$$

for every weak electrolyte, Since $\alpha << 1$ $(1 - \alpha) = 1$

$$K = C\,\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K}{C}} \Rightarrow \alpha = \sqrt{KV}\,.$$

(i)A monobasic weak acid solution has a molarity of 0.005 M and pH of 5. What is its percentage ionization in this solution?

(a) 2.0

(b) 0.2

(c) 0.5

(d) 0.25

(ii)Calculate ionisation constant for pyridinium hydrogen chloride. (Given that H+ ion concentration is 3.6×10^{-4} M and its concentration is 0.02 M.)

(a)6.48×10^{-2}
(b) 6×10^{-6}
(c) 1.5×10^{-9}
(d) $12 \times 10^{-}$

(iii)What is Ostwald dilution Law and on what type of electrolytes is it applicable?

30 - According to Arrhenius theory, acids are substances that dissociate in water to give hydrogen ions H^+ (aq) and bases are substances that produce hydroxyl ions OH^- (aq). The ionization of an acid HX (aq) can be represented by the following equations:

$HX (aq) \rightarrow H^+ (aq) + X^- (aq)$ or $HX(aq) + H2O(l) \rightarrow H3O^+ (aq) + X^- (aq)$

Similarly, a base molecule like MOH ionizes in aqueous solution according to the equation:

$MOH(aq) \rightarrow M+ (aq) + OH–(aq)$

Bronsted acids are proton donors whereas Bronsted bases are proton acceptors. Acids on donating proton form conjugate bases whereas bases form conjugate acids after accepting proton. Buffer solution is a solution whose pH does not change. By adding small amount of H^+ or OH^- .The decrease in concentration of the ion by adding other ion as common ion is called common ion effect. Ksp (solubility product) is product of molar concentrations of ions raised to power no. of ions per formula of ions per formula of the compound in sparingly soluble salt.

Precipitation occurs only if ionic product exceeds solubility product. Solubility of salt decreases in presence of common ion. Kw the ionic product of water is $1x10^{-14}$ at 298 k. Kw increases with increase in temperature.

pH is $–\log[H_3O^+]$

where $[H_3O^+]$=cα in monoprotic acid, is molar conc., α is degree of ionisation.

(a) What will be the conjugate base of

(i)H_2SO_4 (ii) HCO_3-?

(b) What will be the conjugate acid of

(i)NH_2^-

(ii)NH_3

(c) The conc. of H_3O^+ is $4x\ 10^{-4}$. Find its pH.

(d) Kb forNH_3 is$1.80\ x\ 10^{-5}$, what will be Ka? [Kw is $1\ x10^{-14}$]

SECTION-E Long Answer Type Questions (5 Marks each)

31- (i)State Henry's law.

(ii)A solution of NH_4Cl in water shows pH less than 7.why?

(iii)What is the effect of increasing pressure in the given reactions? Give reasons.

(a)$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(b)$N_2(g)+O_2(g) \rightleftharpoons 2NO(g)$

(iv) Which of the following are lewis acids?

H_2O, BF_3, H^+, NH_4^+

32- The solubility product of the given compound $Al(OH)_3$ is given as $2.7\ x\ 10^{-11}$. Calculate the solubility in g / L and also find out the pH of the given solution. (Atomic mass of Al = 27 u).

33. (i)The pH of a solution of a strong acid is 5.0. What will be the pH of the solution obtained after diluting the given solution 100 times?

(ii) The pH of 0.08 mol dm^{-3} HOCI solution is 2.85. Calculate its ionisation constant.

34- Calculate the pH of a solution formed by mixing equal volumes of two solutions A and B of a strong acid having pH = 6 and pH = 4 respectively.

ANSWERS/HINTS

1-(d)
2- (a)
3- (c)
4- (a)
5- (b)
6- (d)
7- (c)
8- (b)
9- (d)
10-(a)
11- (a)
12-(c)
13-(a)
14-(a)
15-(d)
16-(d)

SECTION-B

17- The balanced chemical equation corresponding to the given expression can be written as:

$$4NO_{(g)} + 6H_2O_{(g)} \rightleftharpoons 4NH_{3(g)} + 5O_{2(g)}$$

18- The increasing order of the pH would be;

$CH_3COONa < KNO_3 < C_6H_5COONH_4 < NH_4Cl$

OR

Conjugate acid of the weak base is always stronger. The decreasing order of the basic strength for the following conjugate bases will be?

$OH^-, RO^-, CH_3COO^-, CI^-$

19- When Δn is negative and pressure is decreased then the equilibrium will be shifted to left and the yield of product will decrease.

20- (i) $pH = -\log10\,[H^+] = -\log10\,[10^{-3}]$

$= 3\log10 = 3 \times 1 = 3$

(ii) The dissociation of H_2S is suppressed by the presence of HCl due to common ion effect.

21- $NO(g) + O_3 (g) \rightarrow NO_2 (g) + O_2 (g)$
$K_c = 6.3 \times 10^{14}$ for forward reaction
For backward reaction,

$K_c(reverse)=1/K_c$

$=1/6.4\times10^{-14}$

$=1.59\times10^{-15}$

SECTION -C

22-(i) 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.
(ii) No, a catalyst cannot change the position of equilibrium in a chemical reaction. A catalyst affects the rate of reaction.

23- Sugar is a non-electrolyte, and when it dissolves in water, there will be no ionisation. If there are no free ions, it will not conduct electricity. In contrast, When sodium chloride is added to water, it is wholly ionised to give Na^+ ions and Cl^- ions. Due to the presence of ions, there will be electrical conductance as ions are carriers of electric current.

24- The values of Kc and Qc are self-explanatory and less than or greater than one another decides the direction in which reaction will proceed as follows-
(i) As $Q_c < K_c$, the reaction will proceed in the direction of products (forward direction).
(ii) If $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse direction).
(iii) If $Q_c = K_c$, no net reaction will occur.

25- $\Delta f\ H– = \Delta f\ H– [CaO (s)] + \Delta f\ H– [CO_2 (g)] - \Delta f\ H– [CaCO_3 (s)]$
$\therefore \Delta f\ H– = 178.3$ kJ / mol.
The reaction is endothermic.
Hence, according to Le Chatelier’s principle, the reaction will proceed in the forward direction on increasing temperature.

26 - (i) Suppression of ionization of weak electrolytes 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.
(iii) Negative logarithm of hydrogen ion concentration.

27- The expression for Kp for the reaction is
(i) By increasing the pressure, the number of moles per unit volume will increase. In order to decrease the same, the equilibrium gets shifted to the left or in the backward direction. As a result, more of reactants will be formed and the value of Kp will decrease.
(ii) If the temperature is increased, according to Le Chatelier's principle, the forward reaction will be favoured as it is endothermic. Therefore, the equilibrium gets shifted to the right and the value of Kp will increase.
The vapour pressures of water, acetone and ethanol at 293 K are 2.34 kPa, 12.36 kPa and 5.85 kPa respectively. Which of the following has the lowest boiling point?

28- The substance with the lowest boiling point will be the one with the highest vapor pressure at 293 K.
Comparing the vapor pressures:
The vapor pressure of water at 293 K: 2.34 kPa
The vapor pressure of acetone at 293 K: 12.36 kPa
The vapor pressure of ethanol at 293 K: 5.85 kPa
The substance with the highest vapor pressure at 293 K is acetone. Therefore, according to the relationship between the boiling point and vapor pressure, acetone has the lowest boiling point among the substances.

SECTION -D

29- (i) b
(ii) c
(iii) The degree of dissociation of a weak electrolyte is inversely proportional to the square root of molar concentration or directly proportional to the square root of volume holding one mole of the solute for a weak electrolyte. This is applicable for weak electrolytes only.
30 - (a) (i)HSO4 – (ii) CO_3^{2-}
(b) (i)NH_3 ii) NH^{4+}
(c) 3.398
d)$5.5x10^{-10}$
31- (i) The mass of Gas dissolved in given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.

(ii) NH4Cl is salt of weak base NH4OH and strong acid HCl, therefore H+

ions are more than OH-ions thus,
pH is less than 7.

(iii) (a)The equilibrium will shift in backward reaction because number of moles of products are more than reactants $\Delta n>0$.

(b)No effect because number of moles of reactants and products are equal, i.e.,
$\Delta n=0$.
(iv) H_2O, BF_3, H+
32- Assume S be the solubility of Al(OH)3

$Ksp = [Al^{3+}]\ [O\mathbf{H}^{-}]^3$

$Ksp = (S)\ (3S)^3$

Ksp = 27S4

S4 = Ksp / 27

S4 = 27×10^{-11} / 27 x 10

S4 = 1 x 10^{-12} mol / L.

S = 1 x 10^{-3} mol / L.

(i) Solubility for $Al(OH)_3$: The molar mass of the given compound $Al(OH)_3$ is 78g.

Hence, the solubility of the given compound $Al(OH)_3$ in g / L = $1\times\mathbf{10^3} \times 78$ g / L

Solubility of the given compound $Al(OH)_3$ in g / L = 78×10^{-3} g / L

Solubility of the given compound Al(OH)3 in g / L = 7.8×10^{-2} g / L

(ii) pH of the given solution: S = 1×10^{-3} mol / L

[OH] = 3S = $3 \times 1 \times 10^{-3} = 3 \times 10^{-3}$

pOH =3 − log 3

pH = 14 − pOH = 11 + log 3 = 11.4771.

33. (i) pH = 5 means [H+] = 10^{-5}

On diluting 100 times ,

[H+] = 10^{-5} / 100 = 10^{-7}

On calculating the pH using the equation pH = − log [H+], the pH value comes out to be 7, which is impossible.

Hence, Total H+ ion concentration = H+ ions from acid + H^+ ion from water

[H+] = 10^{-7} +10^{-7} M

[H+] = 2 X 10^{-7}

pH = 7 – 0.3010

pH = 6.699

(ii) pH of HOCl = 2.85

But, – pH = log [H+]

∴ -2.85 = log [H+]

-3.15 = log [H+] [H+] = 1.413 × 10^{-3}

For the weak monobasic acid [H+] = (Ka X C) 1 / 2

Ka = $[H^+]^{2}$ / C

$K_a = (1.413 \times 10–3\ )^2 / 0.08$

$K_a = 24.957 \times 10^{-6}$

$K_a = 2.4957 \times 10^{-5}$

34- The pH of solution A = 6,

Therefore, the concentration of $[H^+]$ ion in solution A=10^{-6} mol / L

The pH of solution B = 4

Therefore, the concentration of $[H^+]$ ion in solution B=10^{-4}mol / L.

On mixing one litre of each solution, total volume = 1L + 1L = 2L.

Amount of H^+ ions in 1L of solution A = concentration × Volume (V) =

Amount of H^+ ions in 1L of solution A = 10^{-6} X 1 = 10^{-6}

Amount of H^+ ions in 1L of solution B =10^{-4} X 1 = 10^{-4}

∴ The total amount of H+ ions in the solution formed by mixing solutions A and B is (10^{-5} mol + 10^{-4} mol)

This amount is present in 2L solution,

∴ Total $[H^+] = 10^{-4} (1 + 1.01) / 2$ mol / L

Total $[H^+] = 1.01 \text{ X } 10^{-4} / 2$ mol / L

Total $[H^+] = 0.5 \text{ X } 10^{-4}$ mol / L

Total $[H^+] = 5 \text{ X } 10^{-5}$ mol / L

$pH = – \log [H^+]$

$pH = – \log [5 X 10^{–5}]$

$pH = – [\log 5 – 5 \log 10]$

$pH = – \log 5 + 5$

$pH = 5 – \log 5$

$pH = 5 – 0.6990$

$pH = 4.3010$

$pH = 4.3$

Thus, the pH will be 4.3.

CHAPTER-7: REDOX REACTIONS (GIST)

Redox is a term used for the oxidation-reduction reaction. A redox reaction is a chemical reaction where a change in the oxidation state of atoms occurs. It involves electron transfer, i.e. if one chemical species gains electrons, then another chemical species gives or loses electrons. The species from which the electron is lost is said to be oxidized, whereas the species to which the electron is added is said to be reduced. For example, zinc displaces copper in an aqueous solution called copper sulphate.

Oxidizing And Reducing Agents

- The role of an oxidizing agent (Oxidant) in a chemical reaction is to gain electrons. They are highly electronegative. Once they gain electrons, these substances are reduced. An oxidant is also known as an electron acceptor. For example, nitric acid and halogen.
- The role of a reducing agent (Reductant) in a chemical reaction is to lose electrons. Once they lose electrons, these substances are oxidized. A reductant is also known as an electron donor. Examples include sulphite compounds and earth metals.

OXIDATION NUMBER

Rules for assigning oxidation number to an atom

- Oxidation number of Hydrogen is always +1 (except in hydrides, it is -1).
- Oxidation number of oxygen in most of compounds is -2. In peroxides it is (-1). In superoxides, it is (-1/2). In OF_2 oxidation number of oxygen is +2. In O_2F_2 oxidation number of oxygen is +1
- Oxidation number of Fluorine is -1 in all its compounds
- For neutral molecules sum of oxidation number of all atoms is equal to zero
- In the free or elementary state, the oxidation number of an atom is always zero. This is irrespective of its allotropic form
- For ions composed of only one atom, the oxidation number is equal to the charge on the ion
- The algebraic sum of the oxidation number of all the atoms in a compound must be zero
- For ions the sum of oxidation number is equal to the charge on the ion
- In a polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion must be equal to the charge on the ion

Oxidation state and oxidation number are often used interchangeably

According to 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

Types of Redox Reactions

- **Combination Reactions:** Chemical reactions in which two or more substances (elements or compounds) combine to form a single substance

- **Decomposition Reactions:** Chemical reactions in which a compound break up into two or more simple substances
- **Displacement Reactions:** Reaction in which one ion(or atom)in a compound is replaced by an ion(or atom) of other element

Metal Displacement Reactions: Reactions in which a metal in a compound is displaced by another metal in the uncombined state

Non-metal Displacement Reactions: Such reactions are mainly hydrogen displacement or oxygen displacement reactions

- **Disproportionation Reactions:** Reactions in which an element in one oxidation state is simultaneously oxidized and reduced

Steps involved in balancing a Redox reaction by oxidation number method

- Write the skeletal redox reaction for all reactants and products of the reaction
- Indicate the oxidation number of all the atoms in each compound above the symbol of element
- Identify the element/elements which undergo change in oxidation numbers
- Calculate the increase or decrease in oxidation number per atom
- Equate the increase in oxidation number with decrease in oxidation number on the reactant side by multiplying formula of oxidizing agent and reducing agents with suitable coefficients
- Balance the equation with respect to all other atoms except hydrogen and oxygen
- Finally balance hydrogen and oxygen. For balancing oxygen atoms add water molecules to the side deficient in it. Balancing of hydrogen atoms depend upon the medium

For reactions taking place in acidic solutions add H+ ions to the side deficient in hydrogen atoms

For reactions taking place in basic solutions add H2O molecules to the side deficient in hydrogen atoms and simultaneously add equal number of OH^- ions on the other side of the equation

- Finally balance the equation by cancelling common species present on both sides of the equation

Steps involved in balancing a Redox by Ion-Electron Method (Half reaction method)

- Find the elements whose oxidation numbers are changed. Identify the substance that acts as an oxidizing agent and reducing agent
- Separate the complete equation into oxidation half reaction and reduction half reaction
- Balance the half equations by following steps

Balance all atoms other than H and O

Calculate the oxidation number on both sides of equation. Add electrons to whichever side is necessary to make up the difference

Balance the half equation so that both sides get the same charge

Add water molecules to complete the balancing of the equation

- Add the two balanced equations. Multiply one or both half equations by suitable numbers so that on adding two equations the electrons are balanced

Application of Redox reactions: Redox Titrations

- Potassium permanganate in redox reactions: Potassium permanganate ($KMnO_4$) is very strong oxidizing agent and is used in determination of many reducing agents like Fe^{2+}, oxalate ions etc. It acts as self indicator in redox reactions.

Equation showing $KMnO_4$ as an oxidising agent in acidic medium is:

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

- Acidified Potassium dichromate ($K_2Cr_2O_7$) in redox reactions: $K_2Cr_2O_7$ is used as an oxidizing agent in redox reactions. Titrations involving $K_2Cr_2O_7$ uses diphenylamine and potassium ferricyanide (external indicator).

Equation showing $K_2Cr_2O_7$ as an oxidising agent in acidic medium is:

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

- Iodine (I_2) in redox reactions: I_2 acts as mild oxidising agent in solution according to equation

$I_2 + 2e^- \rightarrow 2I^-$

Direct redox reaction: Redox reactions in which reduction and oxidation occurs in same solution (i.e. same reaction vessel). In these reactions transference of electrons is limited to very small distance.

Indirect redox reactions: Redox reactions in which oxidation and reduction reactions take place in different reactions vessels and thus transfer of electrons from one species to another does not take place directly

- Electrochemical cell is a device that converts chemical energy produced in a redox reaction into electrical energy. These cells are also called Galvanic cells or Voltaic cells
- The electrode at which oxidation occurs is called anode and is negatively charged
- The electrode at which reduction takes place is called cathode and is positively charged

In an electrochemical cell the transfer of electrons takes place from anode to cathode

In an electrochemical cell the flow of current is from cathode to anode

In the electrochemical cell, the electrical circuit is completed with a salt bridge. Salt bridge also maintains the electrical neutrality of the two half cells

A salt bridge is a U shaped tube filled with solution of inert electrolyte like sodium chloride or sodium sulphate which will not interfere in the redox reaction. The ions are set in a gel or agar agar so that only ions flow when inverted

Electrical potential difference developed between the metal and its solution is called electrode potential. It can also be defined as tendency of an electrode in a half cell to gain or lose electrons

Oxidation potential is the tendency of an electrode to lose electrons or to get oxidized

Reduction potential is the tendency of an electrode to gain electrons or get reduced

In an electrochemical cell, by the present convention, the electrode potentials are represented as reduction potential

The electrode having a higher reduction potential will have a higher tendency to gain electrons

By convention, the standard electrode potential of hydrogen electrode is 0.00 volts

A redox couple is defined as having together oxidized and reduced forms of a substance taking part in an oxidation or reduction half reaction

The difference between the electrode potentials of eth two electrodes constituting the electrochemical cell is called EMF (Electromotive force) or the cell potential

EMF = $E^\ominus$ cathode – $E^\ominus$ anode

A negative $E^\ominus$ means that the redox couple is a stronger reducing agent than the H^+/H_2 couple

A positive $E^\ominus$ means that the redox couple is a weaker reducing agent than the H^+/H_2 couple

REDOX REACTIONS

MCQ

Q.1 The oxidation number of an atom in the elemental state is:

(a) –1

(b) 0

(c) 1

(d) 2

Q.2 The oxidation number of iron in Fe_3O_4 is

(a) +2

(b) +3

(c) 8/3

(d) 2/3

Q.3.A standard hydrogen electrode has zero electrode potential because

(a) hydrogen is easiest to oxidize

(b) the electrode potential is assumed to be zero

(c) hydrogen atom has only one electron

(d) hydrogen is the lightest element

Q.4 Values of standard electrode potential of three metals X, Y and Z are -1.2V, +0.5V and -3.0V respectively. The reducing power of these metals will be in order

(a) X>Y>Z

(b) Y>Z>X

(c) Y>X>Z

(d) Z>X>Y

Q.5 In the reaction $3Br_2 + 6CO_3^{2-} + 3H_2O \rightarrow 5Br^- + BrO^{3-} + 6HCO_3^-$

(a) bromine is oxidised and carbonate is reduced

(b) bromine is reduced and water is oxidised

(c) bromine is neither reduced nor oxidised

(d) bromine is both reduced and oxidised

Q.6 In which of the following compounds, ‘Mn’ exhibits the highest oxidation state?

(a) $KMnO_4$

(b) K_2MnO_4

(c) MnO_2

(d) MnO

Q.7 In this reaction $Cu^{+2} + Zn \rightarrow Cu + Zn^{+2}$, what is an oxidizing agent?

a) copper

b) zinc

c) hydrogen

d) oxygen

Q.8 Which of the following is true as per metal activity series?

a) $Zn<Ag<Cu$

b) $Zn<Cu<Ag$

c) $Zn>Ag>Cu$

d) $Zn>Cu>Ag$

Q.9 Which of the following is not a redox reaction?

(a) Burning of candle

(b) Rusting of iron

(c) Dissolving salt in water

(d) Dissolving Zinc in dil. H_2SO_4

Q.10 Oxidation number of P in PO_4^{3-}, of S in SO_4^{2-} and that of Cr in $Cr_2O_7^{2-}$ are respectively:

(a) +3, +6 and +5

(b) +5, +3 and +6

(c) +3, +6 and +6

(d) +5, +6 and +6

Q.11 Reduction never involves:

(a) gain of electrons

(b) decrease in oxidation number

(c) loss of electrons

(d) decrease in valency of electropositive component

Q.12 One mole of ferrous oxalate requires____ moles of MnO_4^- to get oxidised completely in an acidic medium

(a) 0.6 moles

(b) 0.4 moles

(c) 0.2 moles

(d) 7.5 moles

ASSERTION-REASON TYPE QUESTIONS

Q.1 Given below are two statements labeled as Assertion (A) and Reason (R)

Assertion (A) - In a reaction

$Zn(s) + CuSO4 (aq) \rightarrow ZnSO_4(aq) + Cu(s)$

Zn is a reductant but itself get oxidized.

Reason(R): In a redox reaction, oxidant is reduced by accepting electrons and reductant is oxidized by losing electrons.

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

b) Both A and R are true and R is not the correct explanation of A

c) A is true but R is false

d) A is false but R is true.

Q.2 Given below are two statements labeled as Assertion (A) and Reason (R)

Assertion: The reaction:

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ is an example of decomposition reaction.

Reason: Above reaction is not a redox reaction.

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

b) Both A and R are true and R is not the correct explanation of A

c) A is true but R is false

d) A is false but R is true.

Q.3 Given below are two statements labeled as Assertion (A) and Reason ®

Assertion (A): Elements with greater electron affinities are better oxidizing agents.

Reason (R): Oxidation is the gaining of electrons.

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

b) Both A and R are true and R is not the correct explanation of A

c) A is true but R is false

d) A is false but R is true.

Q.4 Given below are two statements labeled as Assertion (A) and Reason (R

Assertion :Decomposition of potassium chlorate is an example of redox reaction.

Reason: There is no change in the oxidation number of potassium in decomposition of potassium chlorate.

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

b) Both A and R are true and R is not the correct explanation of A

c) A is true but R is false

d) A is false but R is true.

COMPETENCY BASED QUESTIONS (2 M)

Q.1 MnO_4^{2-} undergoes a disproportionation reaction in an acidic medium but MnO_4^{-} does not. Give a reason.

Q.2 Write a balanced chemical equation for the following reaction:

(i) Permanganate ion (MnO_4^{-}) reacts with sulphur dioxide gas in an acidic medium to produce Mn^{2+} and hydrogen sulphate ion.

(Balance by ion electron method)

Q.3 Reaction of liquid hydrazine (N_2H_4) with chlorate ion (ClO_3^{-}) in basic medium produces nitric oxide gas and chloride ion in a gaseous state.

(Balance by oxidation number method)

Q.4 (a) Why F^{-} ions Cannot be converted to F_2 by chemical means?

(b)All decomposition reactions are not redox reactions. Give a reason.

Q.5 (a)Set up an electrochemical cell for the redox reaction

$Ni^{2+}_{(aq)} + Fe(s) \rightarrow Ni(s) + Fe^{2+}_{(aq)}(aq)$

(b) Define half-cell.

Q.6 An electrochemical cell is constituted by combining Al electrode (E0=−1.66V) and Cu electrode (E0=+0.34V). Which of these electrodes will work as a cathode and why?

COMPETENCY BASED QUESTIONS (3M)

Q.1 (a) What is the role of a salt bridge in an electrochemical cell?

(b) Calculate the oxidation numbers of each sulphur atom in the following compounds:

1. $Na_2S_2O_3$
2. $Na_2S_4O_6$

Q.2 Which method can be used to find the strength of an oxidant/reductant in a reaction? Explain with an example.

Q.3 Write the balanced half-reaction and overall equations for the following equations.

- $NO^{3-} + Bi(S) \rightarrow Bi^{3+} + NO_2$ (in acid solution)
- $Fe(OH)_2(S) + H_2O_2 \rightarrow Fe(OH)_3(S) + H_2O$ (in basic medium)

Q.4 How would you come to know that a redox reaction is taking place in an acidic/alkaline or neutral medium?

Q.5 (a) Can we store copper sulphate solution in a gold vessel?

Given $E°_{Cu2+|\,Cu} = +0.34$ V and $E°_{Au3+|\,Au} = +1.50$V

(b) What are the highest and lowest oxidation numbers of N?

Q.6 Consider the following galvanic cell.

$Cd \mid Cd^{2+}$ (1M) $\|$ H^+(1M) $\mid H_2$ (g/atm)

(i) Write the overall cell reaction

(ii) What do the double vertical lines denote?

Q.7 HNO_3 acts only as an oxidant whereas HNO_2 acts both as an oxidant and reductant. Why?

Q.8 Identify the species being oxidized and reduced in each of the following reactions:

1. $Cr^+ + Sn^{4+} \rightarrow Cr^{3+} + Sn^{2+}$
2. $3Hg^{2+} + Fe(s) \rightarrow 3Hg_2 + 2Fe^{3+}$
3. $2As(s) + 3Cl_2(g) \rightarrow 2AsCl_3$

CASE BASED QUESTION (4M)

Q.1 Read the passage given below and answer the following questions:

Redox reactions are an important class of reactions which are taking place in our daily life. Metals are good reducing agents because they can lose electrons easily whereas non-metals are good oxidizing agents which can gain electrons easily. In electrolytic cells, electricity is passed to bring about a redox reaction. All rechargeable batteries act as electrolytic cells while recharging. Electrochemical cells produce electricity as a result of redox reaction. Salt bridge is used in electrochemical cells to complete internal circuits and prevent accumulation of charges.

1. In an Electrochemical Cell ,Oxidation takes place at _____ and Reduction takes place at _____

2.What is the direction of flow of current and electrons?

3. Electrochemical cell is

a) The cell in which electrical energy is converted into chemical energy

b) The cell in which chemical energy is converted into electrical energy

c) The cell in which chemical energy is converted into mechanical energy

d) The cell in which mechanical energy is converted into chemical energy

4.E°Zn2+/Zn= –0.76V, What is the meaning of –ve value of reduction potential?

a) Zn is stronger oxidizing agent than H2

b) Zn is a weaker reducing agent than H2 .

c) Zn is stronger reducing agent than H2

d) None of the above

OR

What is the meaning of standard electrode potential?

Q.2 Read the passage given below and answer the following questions:

Redox reactions are reactions in which oxidation and reduction takes place simultaneously. Oxidation numbers are assigned in accordance with the set of rules. Oxidation number and ion electron methods both are used in balancing ionic equations. Redox reactions are classified as combination, decomposition, displacement and disproportionation reactions. The concept of redox couple and electrode processes is the basis of electrolysis and electrochemical cells.

(a) What is the oxidation number of each individual Br in Br_3O_8 ?

(b) If electrolysis of $CuSO_4$ solution is carried out using Cu electrodes, what reaction will be reaction taking place at anode.

(c) What is the oxidation number of Cr in CrO_5?

(d) Give one example of a disproportionation reaction.

OR

Define disproportionation reaction.

COMPETENCY BASED QUESTION (5 M)

Q.1 Write the formula for the following compounds:

(a)Mercury(II) chloride

(b)Nickel(II) sulphate

(c)Tin(IV) oxide

(d)Thallium(I) sulphate

(e)Iron(III) sulphate

Q.2 (a) PbO and PbO_2 react with HCl according to the following chemical equations:

$2PbO + 4HCl \rightarrow 2PbCl_2 + 2H_2O$

$PbO_2 + 4HCI \rightarrow PbCl_2 + Cl_2 + 2H_2O$

Why do these compounds differ in their reactivity?

(b) Why does fluorine not show a disproportionation reaction?

Q.3 (a) The compound AgF_2 is an unstable compound. However, if formed, the compound acts as a very strong oxidising agent. Why?

(b) Calculate the oxidation number of phosphorus in the following species.

(a) HPO_3^{2-} and

(b) PO_4^{3-}

Q.4 Identify the redox reactions out of the following reactions and identify the oxidising and reducing agents in them.

(i) $3\ HCl(aq) + HNO_3(aq) \rightarrow Cl2(g) + NOCl\ (g) + 2H_2O(l)$

(ii) $HgCl_2(aq) + 2KI\ (aq) \rightarrow HgI_2(s) + 2KCl\ (aq)$

(iii) $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

(iv) $PCl_3(l) + 3H_2O(l) \rightarrow 3HCl(aq) + H_3PO_4\ (aq)$

(v) $4NH_3 + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(g)$

Q.5 Consider the elements:

Cs, Ne, I and F

(a) Identify the element that exhibits only negative oxidation state.

(b) Identify the element that exhibits only positive oxidation state.

(c) Identify the element that exhibits both positive and negative oxidation states.

(d) Identify the element which exhibits neither the negative nor does the positive oxidation state.

(e) Arrange the given metals in the order in which they displace each other from the solution of their salts.

(i) Al

(ii) Fe

(iii) Cu

(iv) Zn

(v) Mg

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MARKING SCHEME

1 (b)

2 (c)

3 (d)

4 (d)

5 (d)

6 (a)

7 (a)

8 (d)

9 (c)

10 (d)

11 (c)

12 (b)

13 (a)

14 (b)

15 (c)

16 (b)

17 Disproportionation is a redox reaction in which one intermediate oxidation state component transforms into two higher and lower oxidation state compounds.

Oxidation states of manganese ranges from +2 to +7 in its various compounds. MnO_4^- has the maximum oxidation state of +7 hence disproportionation is impossible, but MnO_4^{2-} has a +6 oxidation state, which can be oxidised as well as reduced.

18 $MnO_4^- + SO_2 \rightarrow Mn^{2+} + HSO_4^-$ (acidic medium)

Balancing by ion-electron method we get:

$2 \times \{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$5 \times \{SO_2 + 2H_2O \rightarrow HSO_4^- + 3H^+ + 2e^-$

$$\begin{array}{rcl} 2MnO_4^- + 16H^+ + \cancel{10}e^- & \longrightarrow & 2Mn^{2+} + 8H_2O \\ 5SO_2 + 10H_2O & \longrightarrow & 5HSO_4^- + 15H^+ + \cancel{10}e^- \\ \hline 2MnO_4^- + H^+ + 5SO_2 + 2H_2O & \longrightarrow & 2Mn^{2+} + 5HSO_4^- \end{array}$$

OR

$N_2H^4 + ClO_3^- \rightarrow NO + Cl^-$ (basic medium)

To make the gain and loss of electrons equal, balancing by oxidation number method we get:

$3N_2H_4 + 4ClO_3^- \rightarrow 6NO + 4Cl^- + 6H_2O$

$$\begin{array}{rcl} 2Cl_2O_7 + 12H^+ + \cancel{16}e^- & \longrightarrow & 4ClO_2^- + 6H_2O \\ 8H_2O_2 & \longrightarrow & 8O_2 + 12H^+ + \cancel{16}e^- \\ \hline 2Cl_2O_7 + 8H_2O_2 & \longrightarrow & 4ClO_2^- + 6H_2O + 8O_2 + 4H^+ \end{array}$$

19 (a) It is chemically impossible as fluorine is an oxidizing agent, it does not lose electrons.

(b)It is because in a decomposition reaction both the products or one of the two products should be in elemental form, so all decomposition reactions are not redox reactions. Example-Decomposition of calcium carbonate.

20 (a)Fe(s)|Fe2+||Ni2+(aq)|Ni(s)

(b)A half cell consists of conducting electrolyte and electrode structure, separated by a Helmholtz double layer.

21 Since the electrode potential of Al is lower than that of Cu, therefore, Cu has a higher tendency to get reduced and hence Cu electrode acts as a cathode, as reduction occurs in the cathode.

22.(a) The role of a salt bridge in an electrochemical cell is that it provides electrical neutrality and prevents the mixing of the electrolytes.

(b)Sodium thiosulfate has the formula $Na_2S_2O_3xH_2O$. In the chemical compound, one Sulphur molecule possesses +6 oxidation state., whereas the other has -2.

(2) Let the oxidation number of sulphur in $Na_2S_4O_6$ be x

$2 + 4x – 12 = 0$

$\Rightarrow 4x = +10$

$\Rightarrow x = 10/4$

$\Rightarrow x = +2.5$

Hence, the oxidation number of sulphur in $Na_2S_4O_6$ is given as +2.5.

23. The relative electrode potential can be measured when a reducing agent or an oxidizing agent is linked to a solution using an electrode cell.

Let us take an example. We can consider Fe3+/Fe with a standard hydrogen electrode. For Fe and H, the half-life reaction is given below.

$H^+ + e^- \rightarrow H_2E^o = 0.0V$

$Fe_3^+ + e– \rightarrow Fe_2+E^o= 0.77$

Any element that needs to be calculated properly using SHE can be used as an electrode. Electric potential is the quantity of an emf that an element produces in the cell. The reaction is given below.

E^ocell = Eocathode – Eoanode

E^ocell= 0 – Eoanode

E^ocell = 0 – 0.77

E^ocell= -0.77

Fe3+ has a higher chance to undergo reduction when compared to hydrogen.

24 In the first reaction, H+ ions can be seen.

Therefore, oxidation half-reaction is: Bi (S) Bi_3^++ $3e^-$

Reduction half-reaction is: [NO_3^- + $2H^+$ + e- NO_2 + H_2O] x^3

Balanced equation is: Bi (S) + $3NO_3^-$ + 6H+ $Bi3^+$+ $3NO_2$ + $3H_2O$

In the second reaction, Fe $(OH)^2$ (S) + H_2O_2

→ Fe $(OH)_3$(S) + H_2O.

The solution is basic, which means that OH- ions are involved in the reaction. Therefore,

Oxidation half reduction reaction is: [Fe $(OH)_2$ + OH^- Fe $(OH)_3$ + e^-] x^2

Reduction half-reaction is: H_2O_2+ $2e\rightarrow^-$ 2OH-

Balanced equation is: 2Fe $(OH)_2$ + $H_2O_2 \rightarrow 2Fe(OH)_3$.

OR

If H+ or any acid appears on either side of the chemical equation, then the reaction has taken place in the acidic solution. If OH- or in fact any base appears on either side of the equation, the solution is basic. If neither of them (H^+, OH^-, acids or alkali) appear on any side of the equation, the solution is neutral.

25. (a)If the following redox reactions occur, we can store CuSO4 solution in a gold vessel.

$2Au + 3Cu^{2+} \rightarrow 2Au^{3+} + 3Cu$

The cell corresponding to the preceding redox reaction can be represented as follows:

$Au \mid Au^{3+} \parallel Cu^{2+} \mid Cu$

Since the reduction potential of $Au^{3+}|Au$ is higher than $Cu^{2+}|Cu$. So, the copper ion will not be reduced. Therefore, copper sulphate solution can be stored in a gold vessel. Thus, the $CuSO_4$ solution can be stored in a gold vessel.

(b)N has a maximum oxidation number of +5 because it has five electrons in the valence shell ($2s^2 2p^3$) and a minimum oxidation number of -3 because it can accept three more electrons to achieve the nearest inert gas (Ne) configuration.

26. (i) The anodic reaction is

$Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-$

The Cathodic reaction is

$2H^+(aq) + 2e^- \rightarrow H_2(g)$

The overall reaction is

$Cd(s) + 2H^+(aq) \rightarrow Cd^{2+}(aq) + H_2(g)$

(ii) The salt bridge that connects the oxidation and reduction half cells is represented by the double vertical lines.

27. The oxidation number of N in HNO_3 = +5

The oxidation number of N in HNO_2 = +3

The maximum oxidation number that N can show is = + 5

($\therefore$ It has only 5 valence electrons $2s^2 2p^3$)

The Oxidation number of N in HNO_3 is maximum and it can only decrease. Therefore HNO_3 can act only as an oxidant. The minimum Oxidation number of N is -3.

Thus HNO_2 in which the oxidation number of N is +3 can decrease as well as increase. Thus HNO_2 can act as an oxidant as well as a reductant.

28. 1.$Cr^+ + Sn^{4+} \rightarrow Cr^{3+} + Sn^{2+}$
Cr^+: oxidized, Sn^{4+}: reduced

2. $3Hg^{2+} + Fe(s) \rightarrow 3Hg_2 + 2Fe^{3+}$
Hg^{2+}: reduced, Fe: oxidized

3. $2As(s) + 3Cl_2(g) \rightarrow 2AsCl_3$
As: oxidized, Cl_2: reduced

SECTION D

29. i) Anode , Cathode

(ii) Electrons flow from anode to cathode whereas current flows from cathode to anode

(iii)(b)

(iv)(c)

OR

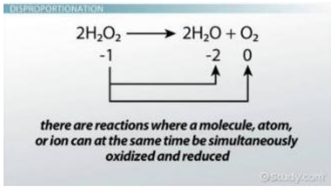
(iv) The standard electrode potential, abbreviated as E, is the measure of potential of a reaction that occurs at the electrode when all the substances involved in the reaction are in their standard states

30. (a) The two Br at the terminal, have 3 oxygen atoms attached, hence its oxidation number is +6. The Br atom in the center has 2 oxygen atoms attached ,so its oxidation state is +4. Hence, +6, 4+ 6 is the sequence.

(b) Cu(s)→Cu2+(aq)+2e−

(c) +6

(d)



there are reactions where a molecule, atom, or ion can at the same time be simultaneously oxidized and reduced

OR

A disproportionation reaction is a reaction in which, the same element is simultaneously oxidized and reduced.

31 (a)Mercury (II) chloride: $HgCl_2$

(b)Nickel (II) sulphate: $NiSO_4$

(c)Tin (IV) oxide: SnO_2

(d)Thallium (I) sulphate: TI_2SO_4

(e)Iron (III) sulphate: $Fe_2(SO_4)_3$

OR

(a)None of the atoms' O.N. changes in the first reaction. As a result, it cannot be classified as a redox reaction. Because PbO is a basic oxide that combines with HCl acid, it is an acid-base reaction.PbO_2 is reduced and functions as an oxidising agent in the second process, a redox reaction.

(b)Disproportionation is a redox reaction in which one intermediate oxidation state component transforms into two higher and lower oxidation state compounds.The element must be in at least three oxidation states for such a redox reaction to occur. As a result, that element is in the intermediate state during the disproportionation reaction and can transition to both higher and lower oxidation states.Fluorine is the most electronegative and oxidising element of all the halogens, and it is also the smallest.It doesn't have a positive oxidation state (only one) and doesn't go through the disproportionation reaction.

32. (a)Ag in AgF2 has an oxidation state of +2, which is an unstable oxidation state of Ag. Silver hence readily accepts an electron to generate Ag+ whenever AgF2 is formed. This brings the oxidation state of Ag from +2 to +1, which is more stable. Hence, AgF2 acts as a very strong oxidising agent.

(b) (a). Let the oxidation number of phosphorus in HPO32- be x.

H + P + 3O2-⇒ +1 + x + (-2)×3 = -2

⇒ +1 + x – 6 = -2

⇒ x – 5 = -2

⇒ x = – 2 + 5

⇒ x = +3

Thus, the oxidation number of phosphorus in HPO32- is +3.

(b). Let the oxidation number of phosphorus in PO43-

be x.

PO43-⇒ x + 4 ×(-2) = -3

⇒ x = -3 + 8 = +5

⇒ x = +5

Thus, the oxidation number of phosphorus in PO43- is +5.

OR

(i) Putting the oxidation number of each atom, we get:

3HCl + HNO3 → Cl2 + NOCl + 2H2O

The oxidation number of Cl goes from -1 (in HCl) to 0 (in Cl2). HCl is used as a reducing agent because of the oxidation of Cl–.

HNO3 functions as an oxidising agent because the oxidation number of N reduces from +5 (in HNO3) to +3 (in NOCl).

Thus, reaction (i) is a redox reaction.

(ii) HgCl2 + 2Kl → Hgl + 2KCl

There is no change in the oxidation number. Hence this reaction doesn’t qualify as a redox reaction.

(iii) Fe2O3 + 3CO → 2Fe +3CO2

Fe2O3 works as an oxidising agent because the oxidation number of Fe changes from +3 (in Fe2O3) to 0 (in Fe).

CO works as a reducing agent as the oxidation number of C increases from +2 (in CO) to +4 (in CO2). As a result, it is a redox reaction.

(iv) PCl3 + 3H2O → 3HCl + H2PO3

There is no change in the oxidation number of any of the atoms. Hence it is not a redox reaction.

(v) 4NH3 + 3O2 → 2N2 + 6H2O

Because the oxidation number of N in N2 grows from -3 to 0, NH3 functions as a reducing agent.

Furthermore, O2 functions as an oxidising agent because the oxidation number of O drops from 0 in O2 to -2 in H2O.

Hence, this is a redox reaction.

33. (a) F exhibits only a negative oxidation state of –1.

(b) Cs exhibit a positive oxidation state of +1.

(c) I exhibit both positive and negative oxidation states. It exhibits oxidation states of – 1, + 1, + 3, + 5, and + 7.

(d) The oxidation state of Ne is zero. It exhibits neither negative nor positive oxidation states.

(e) A metal with stronger reducing power displaces another metal with weaker reducing power from its solution of salt.

The order of the increasing reducing power of the given metals is as given below:

Cu < Fe < Zn < Al < Mg

Therefore, Mg can displace Al from its salt solution, but Al cannot displace Mg. Thus, the order in which the given metals displace each other from the solution of their salts is as given below:
Mg >Al>Zn> Fe >Cu

CHAPTER-8: ORGANIC CHEMISTRY: SOME BASIC PRINCIPLES AND TECHNIQUES

Organic Chemistry

Organic chemistry is the study of hydrocarbons and their derivatives, and it is a branch of chemistry.

Carbon Compounds and Their Shapes:

- The s and p orbitals are important in the hybridization of organic or carbon molecules.
- This results in three forms of hybridization: sp3, sp4, and sp5 (in alkanes) – sp2 is a tetrahedral form (in alkenes) – Spherical structure spherical structure spherical structure spherical (in alkynes) – Molecule with a linear shape.
- The chemical characteristics of an organic molecule are determined by the functional group, which is an atom or group of atoms linked in a certain way.
- The hydroxyl group (—OH), aldehyde group (—CHO), and carboxylic acid group (—COOH) are only a few examples.

Why Are There So Many Organic Compounds?

(a) Catenation It is a self-combination propensity that is strongest in carbon. A carbon atom can form single, double, or triple bonds with other carbon atoms. As a result, it produces a greater number of compounds than the others.

(b) Small size and Tetravalency Carbon, being a tetravalent element, may form bonds with four additional C atoms or monovalent atoms. Carbon may react with oxygen, hydrogen, chlorine, sulphur, nitrogen, and phosphorus to produce compounds. The type of the element or group linked to the carbon determines the characteristics of these compounds.

General Characteristics of Organic Compounds

1. Carbon compounds including H, 0, N, S, P, F, CI, Br, and I.
2. These can be present in most living species. carbs, proteins, and so forth.
3. These can be liquids, gases, or solids.
4. Because they are covalent, they have a low boiling and melting point and are soluble in organic solvents.
5. They’re usually combustible and volatile.
6. They do not conduct electricity because of the absence of free ions.
7. They have a unique appearance and smell.

CLASSIFICATION OF CARBON COMPOUNDS

Based on the number of Cs attached

(i) The first carbon atom A primary or 1° carbon atom is one that has only one other carbon atom bonded to it.

(ii) Carbon atoms with a secondary carbon atom Secondary or 2°carbon atoms are formed when a carbon atom is joined to two additional carbon atoms.

iii) Carbon atom in the tertiary state the tertiary or 3° carbon atom is formed when a carbon atom is joined to three additional carbon atoms.

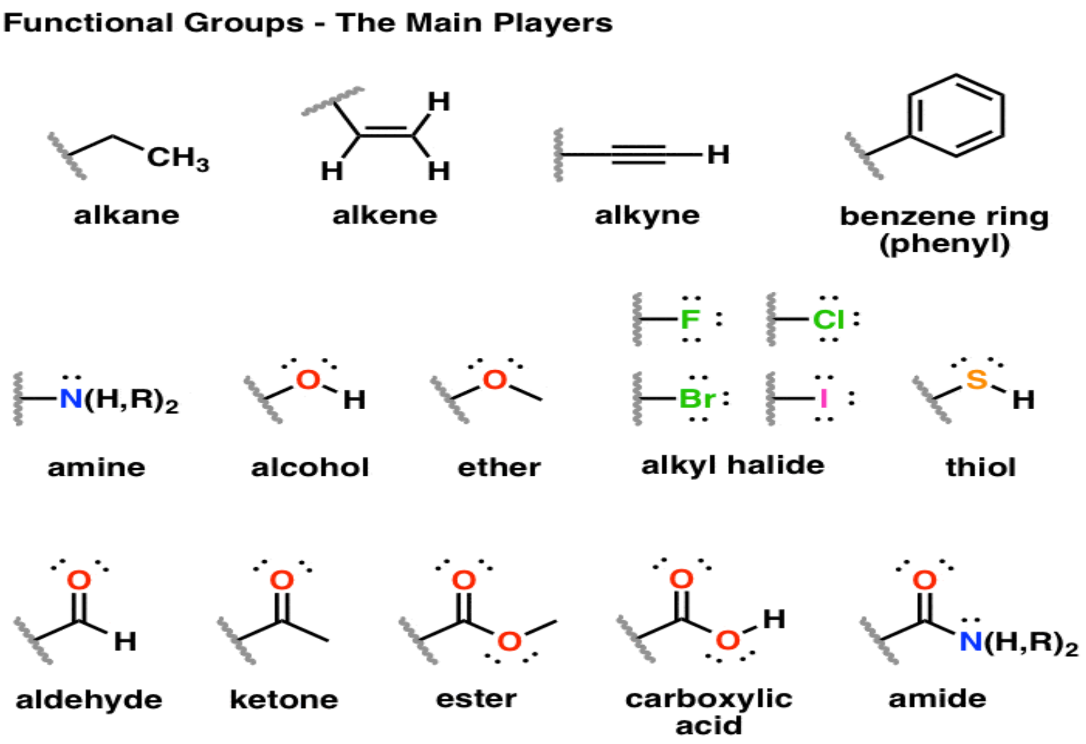
(iv) Carbon atom from the Quaternary Period The quaternary or 40 carbon atom is formed when a carbon atom is joined to four additional carbon atoms.

The following is the reactivity order of carbon atoms: 3° vs. 2° vs. 1°.

On the Basis of Position of Functional Group

(i) carbon dioxide: The functional group is directly connected to carbon.

(ii) Carbon that is bonded to the n-carbon directly.



Hydrogen Atom Classification

1°-hydrogen (primary) is connected to a ten-carbon molecule.

2°-hydrogen linked to 2°-carbon (secondary).

3°-hydrogen linked to 3°-carbon (tertiary).

- the element hydrogen (s) Hydrogens linked to the n-carbon atom.
- the element hydrogen (s) Hydrogens with a carbon atom bonded to them.

Functional Group

- A functional group is an atom (-CI, -Br, etc.) or a group of atoms (-COOH, – CHO) that is responsible for the chemical characteristics of a molecule.
- Functional groupings include double and triple bonds.
- The R–F functional group is a subset of the R–F functional group.
- R stands for alkyl group, which has just one bond: alkenyl stands for double bond, and alkenyl stands for triple bond.

Homologous Series

- Homologous series are those in which the molecular formulas of adjacent members differ by a – CH2 unit, and homologous members are those in which the molecular formulas of adjacent members differ by a – CH2 unit.
- The following are some of the series' general characteristics:
    1. The functional groups of all homologues are the same. As a result, their chemical characteristics are almost identical.
    2. A series members all have the same general formula.
    3. Almost identical approaches may be used to prepare all the members.
    4. The physical characteristics of a series gradually change as the molecular weight of the series increases.

Different Formulae Representation

The following are some examples of how an organic compound might be represented:

1. Formula in its entirety

It vividly depicts all the bonds that exist between any two atoms.

2. Formula in Condensed Form

All the bonds aren't depicted clearly in it.

3. Formula for Bond Lines

In such formulas, it is assumed that the requisite number of H-atoms are present where they are required (to meet carbon's Tetravalency)

Nomenclature of Organic Compounds

Trivial System

- It is the earliest approach for deriving names from a source or an attribute.
- Most of them are taken from Latin or Greek names, such as, acetic acid (acetum = vinegar), oxalic acid (oxalic), malic acid (pyrus malus), citric acid (citric), formic acid (obtained from red ants), oxalic acid (oxalic), malic acid (pyrus malus), citric acid (citric), formic acid (obtained from red ants)

The International Union of Pure and Applied Chemistry (IUPAC)

- The improved and widely used IUPAC (International Union of Pure and Applied Chemistry) approach was established in 1957.
- These regulations are updated by IUPAC on a regular basis. We are using the IUPAC nomenclature standards from 1993.
- The name of an organic compound has three elements, according to the IUPAC system: (i) word root, (ii) suffix, and (iii) prefix.

  (i) Word root: The number of carbon atoms in the primary chain, which is the longest conceivable chain of carbon atoms, is represented by the word root.

  (ii) Suffix: There are two sorts of suffix: main and secondary.

  (a) Primary Suffix: It denotes the kind of carbon atom link.

  (iii) Prefix: A prefix occurs before the word root in an IUPAC name. There are two sorts of prefixes:

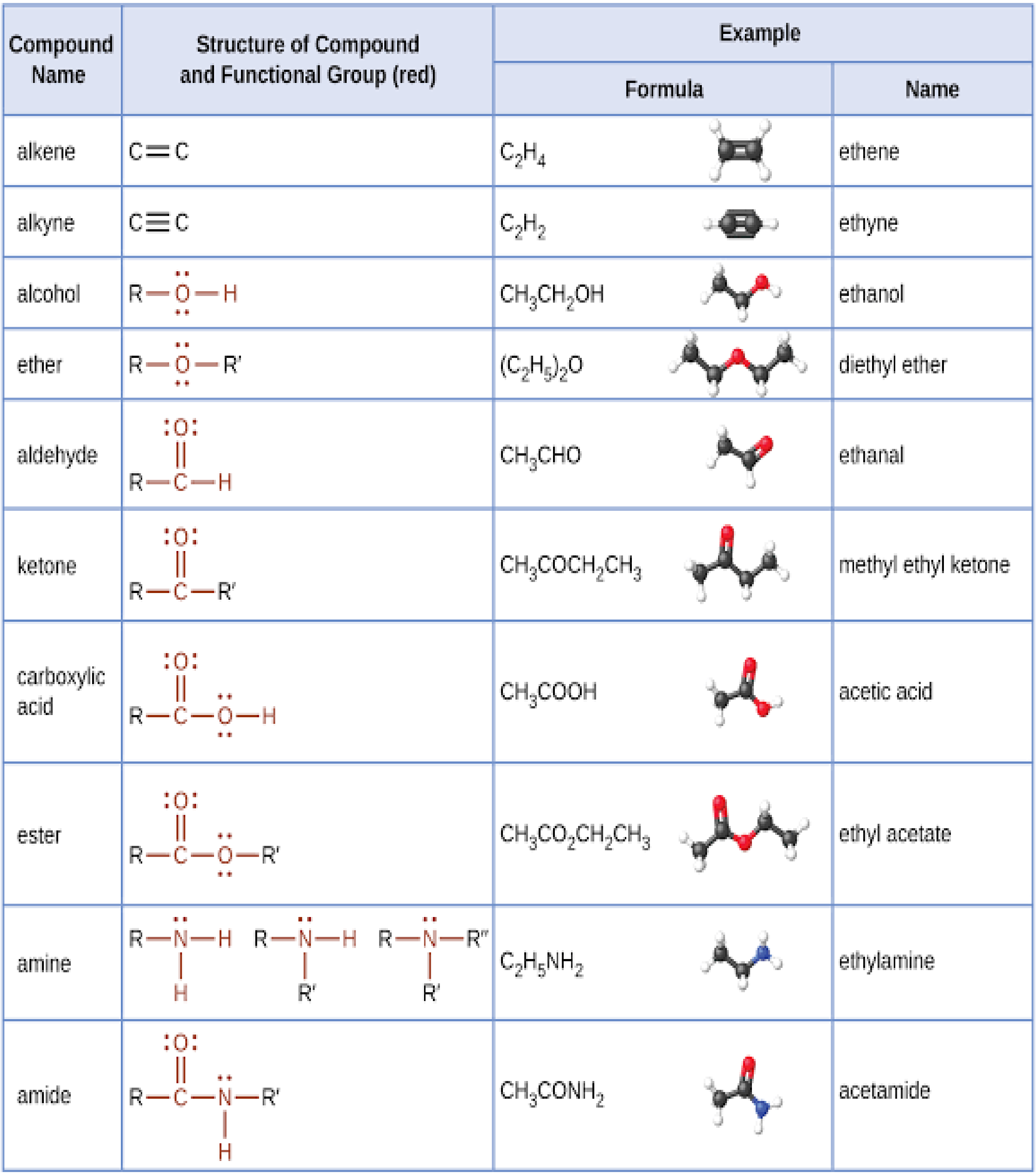
  (a) Main prefix: The primary prefix cyclo, for example, is used to distinguish cyclic compounds.

(b) Secondary prefix: Some functional groups are termed substituents and are designated by secondary prefixes.

Naming of Functional Group-Containing Compounds

- The functional group is connected to the carbon atoms with the lowest possible number in the longest chain of carbon atoms carrying the functional group.
- When it comes to polyfunctional compounds, one of the functional groups is chosen as the primary functional group, and the molecule is called after it.

- The order of preference is used to determine the primary functional group.



Compound Name	Structure of Compound and Functional Group (red)	Example	
		Formula	Name
alkene	$C{=}C$	C_2H_4	ethene
alkyne	$C{\equiv}C$	C_2H_2	ethyne
alcohol	$R-\ddot{\underset{\cdot\cdot}{O}}-H$	CH_3CH_2OH	ethanol
ether	$R-\ddot{\underset{\cdot\cdot}{O}}-R'$	$(C_2H_5)_2O$	diethyl ether
aldehyde	$R-\overset{\overset{:O:}{\Vert}}{C}-H$	CH_3CHO	ethanal
ketone	$R-\overset{\overset{:O:}{\Vert}}{C}-R'$	$CH_3COCH_2CH_3$	methyl ethyl ketone
carboxylic acid	$R-\overset{\overset{:O:}{\Vert}}{C}-\ddot{\underset{\cdot\cdot}{O}}-H$	CH_3COOH	acetic acid
ester	$R-\overset{\overset{:O:}{\Vert}}{C}-\ddot{\underset{\cdot\cdot}{O}}-R'$	$CH_3CO_2CH_2CH_3$	ethyl acetate
amine	$R-\underset{\underset{H}{\vert}}{\ddot{N}}-H$ $\quad R-\underset{\underset{R'}{\vert}}{\ddot{N}}-H$ $\quad R-\underset{\underset{R'}{\vert}}{\ddot{N}}-R''$	$C_2H_5NH_2$	ethylamine
amide	$R-\overset{\overset{:O:}{\Vert}}{C}-\underset{\underset{H}{\vert}}{\ddot{N}}-R'$	CH_3CONH_2	acetamide

Isomerism

- Isomerism occurs when two or more compounds have the same molecular formula but distinct structural formulas, as well as differing physical and chemical characteristics.
- Isomers are the name for such compounds.

  There are two types:

  (1) Isomerism in Structure

  (2) Stigmatization

(1) Structural Isomerism: Compounds with the same molecular formula but different structural formulas differ in the arrangement of atoms demonstrate structural isomerism.

(2) Stereoisomerism: Stereoisomerism is a phenomenon that occurs when isomerism is generated by various configurations of atoms or groups in space.

The steroeoisomers contain the same structural formula, but their atoms are arranged differently in space. There are two forms of stereoisomerism:

(i) Cis-Trans Isomerism or Geometrical Isomerism

(ii) Optical Isomerism

Organic Reaction Mechanisms: Basic Concepts

A covalent bond's fission: Fission can occur in two ways in a covalent bond:

(i) By Homolytic Fission or Homolysis
(ii) By Heterotypic Fission or Heterolysis

Resonance Structure

- A single structure cannot accurately describe a large number of chemical molecules.
- The length of a carbon-carbon double bond is 1.34 A.
- The length of a single carbon-carbon bond is 1.54A. However, experimental evidence has shown that all carbon-carbon bonds in benzene are similar and have the same bond length (1.39A).

- As a result, benzene's structure cannot be described by a single structure. 'He energetically comparable structures I and II can both be used to describe it. Resonance structures are the names given to the two structures.
- When a double or triple bond is attacked by an electrophile E+ (a reagent), the two electrons from the bond are totally transferred to one atom or the other, resulting in the electromeric effect (E Effect).

Orbital Concept of Hyperconjugation

- It entails the delocalization of o electrons in an alkyl group's C—H bond when it is connected directly to an unsaturated system atom or an atom with an unshared p-orbital.
- Consider CH3CH2 (ethyl cation), which possesses an empty p-orbital due to the positively charged carbon atom.

Organic Compounds Qualitative Analysis

Carbon and hydrogen detection: Put Copper Oxide Test: About three times the weight of dry copper oxide is mixed in with the organic component. After that, the mixture is transferred to a hard glass test tube with a bent delivery tube. The other end is dipped in lime water in a separate test tube.

Sodium Test for Halogens

- The halogens in the organic component are transformed to sodium halides when they fuse with sodium.
- Add silver nitrate solution to a portion of the 'sodium extract' that has been acidified with dilute nitric acid. Chlorine is shown by a white ppt. soluble in ammonia.
- Bromine is indicated by a yellow ppt. that is sparingly soluble in ammonia.
- Iodine is indicated by a yellow ppt. that is insoluble in ammonia.
- When the molecule also contains nitrogen or sulphur, the sodium extract is heated with strong nitric acid before being tested for halogens to destroy the cyanide and sulphite generated during the sodium fusion.
- When silver nitrate is added, these radicals will create a white and black precipitate if they are not eliminated.

QUANTITATIVE EVALUTION

Carbon and hydrogen estimation

- In one process, both carbon and hydrogen are calculated. In the presence of abundant oxygen and copper (II) oxide, a known weight of an organic molecule is burned. Carbon is oxidized to carbon dioxide while hydrogen is oxidized to water.

- The weight of carbon dioxide and water generated is computed, as well as the carbon and hydrogen content of the original material.

Nitrogen estimation

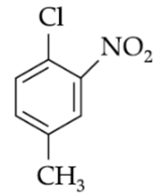
(i) Dumas method: This approach is based on the fact that when nitrogenous chemicals are burned with copper oxide in a carbon dioxide environment, free nitrogen is produced.

By passing through a heated copper spiral, traces of nitrogen oxides, which may occur in some situations, are converted to elemental nitrogen.

(ii) Kjeldahl's Methods: Kjeldahl's technique is based on the fact that an organic molecule containing nitrogen is transformed to ammonium sulphate when heated with con. H2S04. The resulting liquid is subsequently treated with too much alkali, and the released ammonia gas is absorbed with too much acid. Finding the quantity of acid neutralized by back filtration with a standard alkali yields the amount of ammonia.

MCQ

1. The IUPAC name for



(A) 1 -Chloro-2-nitro-4-methylbenzene (B) l-Chloro-4-methyl-2-nitrobenzene

(C) 2-Chloro-1 -nitro-5-methylbenzene (D) m-Nitro-p-chlorotoluene

Ans. Option (B) is correct.

2. In which of the following, functional group isomerism is not possible?

(A) Alcohols (B) Aldehydes

(C) Alkyl halides (D) Cyanides

Ans. Option (C) is correct.

3. The principle involved in paper chromatography is

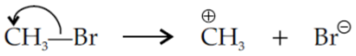
(A) adsorption (B) partition

(C) solubility (D) volatility

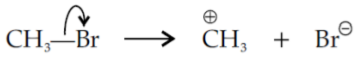
Ans. Option (B) is correct.

4. Covalent bonds can undergo fission in two differentways. The correct representation involving theheterolytic fission of CH_3 – Br is:

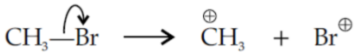
(A)



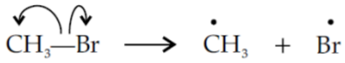
(B)



(C)

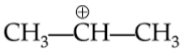


(D)



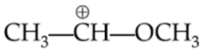
Ans. Option (B) is correct.

5. What is the correct order of decreasing stability of the following cations?



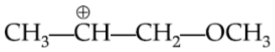
$CH_3—\overset{\oplus}{C}H—CH_3$

I



$CH_3—\overset{\oplus}{C}H—OCH_3$

II



$CH_3—\overset{\oplus}{C}H—CH_2—OCH_3$

III

(A) II > I > III (B) II > III > I

(C) III > I > II (D) I > II > III

Ans. Option (A) is correct.

6.The displacement of electrons in a multiple bond in the presence of attacking reagent is called

(a) Inductive effect

(b) Electromeric effect

(c) Resonance

(d) Hyperconjugation

Answer: (b) Electromeric effect

7.Which of the following behaves both as a nucleophile and as an electrophile?

(a) $CH_3C \equiv N$

(b) CH_3OH

(c) $CH_2 = CHCH_3$

(d) CH_3NH_2

Answer: (a) $CH_3C \equiv N$

8. Which of the following cannot be represented by resonance structures?

(a) Dimethyl ether

(b) Nitrate anion

(c) Carboxylate anion

(d) Toluene

Answer: (a) Dimethyl ether

9. Which one is the strongest acid among the following options?

(a) CH_2FCOOH

(b) $CH_2ClCOOH$

(c) $CHCl_2COOH$

(d) CHF_2COOH

Answer: (d) CHF_2COOH

10. Homolytic fission leads to the formation of

(a) nucleophile

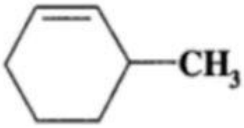
(b) carboanion

(c) free radical

(d) carbocation

Answer: (c) free radical

11. The I.U.P.A.C. name of



(a) 3–Methyl cyclohexene

(b) 1–methyl cylohex–2–ene.

(c) 6–methyl cyclohexene

(d) 1–methyl cyclohex5–ene

Answer: (a) 3–Methyl cyclohexene

12.Which of the ion is the most resonance stabilized?

(a) C_2H_5O-

(b) C_6H_5O-

(c) (CH_3)3CO-

(d) (CH3)2CHO-

Answer: (b) C6H5O-

Given below are two statements labelled as Assertion (A) and Reason (R) Select the most appropriate answer from the options given below:

- **(a)** Assertion and reason both are correct statements and reason is correct explanation for assertion.
- **(b)** Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- **(c)** Assertion is correct statement but reason is wrong statement.
- **(d)** Assertion is wrong statement but reason is correct statement.

13. Assertion: Olefins have the general formula C_nH_{2n+1}.

Reason: There is one double bond between 2-C-atoms in their molecules.

Ans. Option (d) is correct.

14. Assertion : Sulphur present in an organiccompound can be estimated quantitatively byCarious method. **Reason** : Sulphur is separated easily from otheratoms in the molecule and gets precipitated as light yellow solid.

Ans. Option (c) is correct

15. Assertion : SO_3 act as an electrophile.

Reason : Electronegative oxygen atoms attached to sulphur atom makes it electron deficient.

Ans. Option (a) is correct.

16. Assertion : Pent-1-ene and pent-2-ene are position isomers.

Reason : Position isomers differ in the position of functional group or substituent.

Ans. Option (a) is correct.

SECTION B

17. State the hybridisation in ethyne. Explain why Ethyne is stronger acid than propyne.

Ans Sp hybridisation. Terminal alkynes are weakly acidic in nature because of sp-hybridized state of the triple bonded carbon atom. Due to substantial s-character (50%), the triple bonded carbon is electronegative in nature and this enables the release of H^+ ion from $\equiv C - H$ bond. However, ethyne is stronger acid than propyne. This is attributed to +I effect of the methyl group which tends to increase the electron density on the triple bond carbon atom in propyne. The release of H^+ ion from propyne is more difficult than from ethyne or it weaker acid than ethyne.

$C-H \equiv C-H$ $CH_3-C \equiv C-H$

18. For testing halogen in an organic compound with $AgNO_3$ solution, sodium extract (Lasssaigne’s test) is acidified with dilute HNO_3 . What will happen if a student acidifies the extract with dilute H_2SO_4 in place of dilute HNO_3?

Ans. $AgNO_3$ reacts with dilute H_2SO_4 to form a white precipitate of silver sulphate. $2AgNO_3(aq) + H_2SO_4(aq) \text{-------}> Ag_2SO_4(s) + 2HNO_3(aq)$

This precipitate interferes with the precipitate of silver halide (AgX)

Q19 Arrange the following in the increasing order of stability. Give reason $CH_3CH_2CH_2CH_2^+$, $(CH_3)_3C^+$, $CH_3CH_2CH^+$, $CH_3CH_2CH^+CH_3$, CH_3CH^+

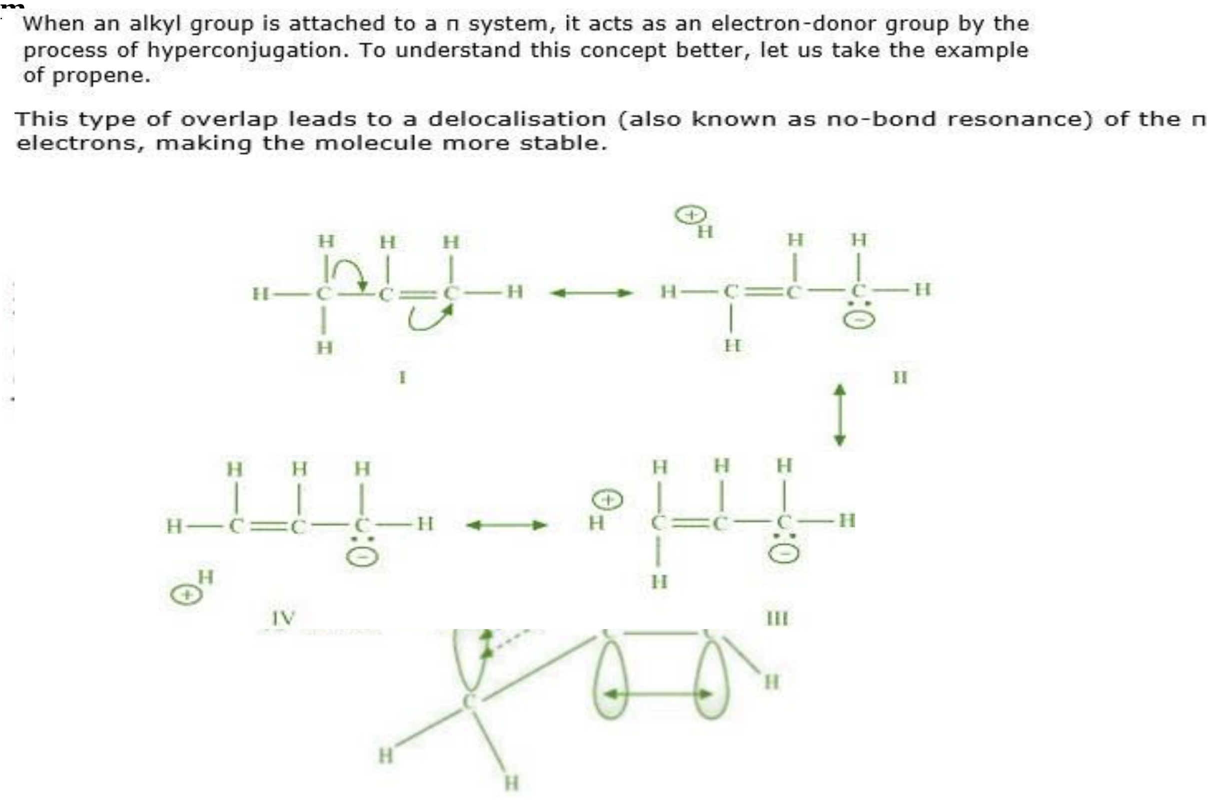
Ans The increasing order of stability is :

$CH_3CH_2^+ < CH_3CH_2CH_2^+ < CH_3CH_2CH_2CH_2^+ < CH_3CH_2CH^+CH_3 < (CH_3)_3C^+$

Reason: Tertiary carbocation is more stable than secondary than primary carbocation due to more Hyperconjugation and +I effect of more alkyl groups

Q20 Explain why an alkyl group acts as an electron donor when attached to a π electron system

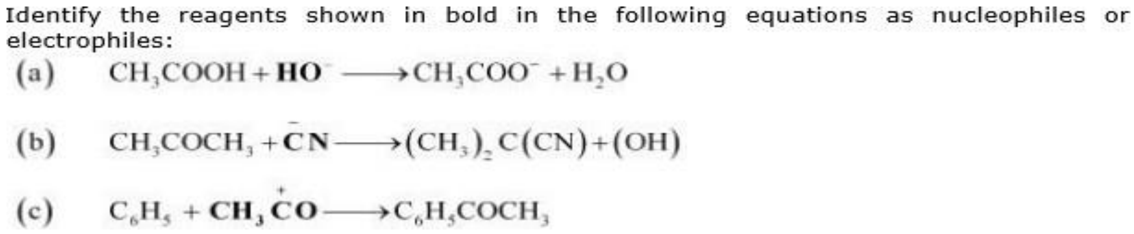
Ans



When an alkyl group is attached to a π system, it acts as an electron-donor group by the process of hyperconjugation. To understand this concept better, let us take the example of propene.

This type of overlap leads to a delocalisation (also known as no-bond resonance) of the π electrons, making the molecule more stable.

Q21



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

(a) $CH_3COOH + \mathbf{HO^-} \longrightarrow CH_3COO^- + H_2O$

(b) $CH_3COCH_3 + \mathbf{\bar{C}N} \longrightarrow (CH_3)_2C(CN) + (OH)$

(c) $C_6H_5 + \mathbf{CH_3\overset{+}{C}O} \longrightarrow C_6H_5COCH_3$

Ans (a) OH^{-}(nucleophile) (b) NC^{-}(nucleophile) (c) $CH3CO^{+}$ (electrophile)

SECTION C

Q. 22. 0.395 g of an organic compound by Carius method for the estimation of sulphur gave 0.582 g of BaSO4. Calculate the percentage of sulphur in the compound.

Ans Mass of

BaSO4 = 0.582g

BaSO4 = S

233g 32g

233g of BaSO4 contain sulphur = 32g

0.582g of BaSO4 contains Sulphur

$$weight\ of\ Sulphur\ = \frac{32\ \times 0.582}{233}\ = 0.07993g$$

$$Percenatre\ of\ Sulphur\ = \frac{Sulphur\ in\ O.C. \times 100}{Mass\ of\ O.C. taken}$$

$$Percenatre\ of\ Sulphur\ = \frac{0.07993\ \times 100}{0.395}\ = 20.24\%$$

Q. 23. Ammonia produced when 0.75g of a substance was kjeldahlized, neutralized 30cm^3 of 0.25 N H2SO4. Calculate the percentage of nitrogen in the compound.

Ans Mass of organic

compound = 0.75g

Volume of H_2SO_4

used us = $30cm^3$

Normality of H_2SO_4 =

0.25N

$30cm^3$ of H_2SO_4 of normality 0.25N ≡ 30ml of NH_3 solution

of normality 0.25N But $1000cm^2$ of NH_3 of normality 1

contains 14g of nitrogen $\frac{=14}{1000}x30x0.25$

∴ $30cm^3$ of 0.25N NH_3 contains nitrogen

% of nitrogen = $\frac{Mass\text{ of nitrogen}}{Mass\text{ of substance}}x1000$

= $\frac{14}{1000}x\frac{30x0.25}{0.75}x100$ $\underline{\underline{=14.00}}$

Q 24. (a)Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound?

(b) Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test?

(c) Explain, why an organic liquid vaporizes at a temperature below its boiling point in its steam distillation?

Ans (a) Carbon dioxide is acidic in nature and potassium hydroxide is a strong base.

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

Hence, carbon dioxide reacts with potassium hydroxide to form potassium carbonate and water as

(b) Although the addition of sulphuric acid will precipitate lead sulphate, the addition of acetic acid will ensure a complete precipitation of sulphur in the form of lead sulphate due to common ion effect. Hence, it is necessary to use acetic acid for acidification of sodium extract for testing sulphur by lead acetate test.

(c) In steam distillation, the organic liquid starts to boil when the sum of vapour pressure due to the organic liquid (p1) and the vapour pressure due to water (p2) becomes equal to atmospheric pressure (p), that is, p = p1 + p2 Since p1 < p2, organic liquid will vapourise at a lower temperature than its boiling point.

Q. 25. What is the shape of the following molecules:

(a) H_2 C=O (b) CH_3F (c) HC≡N.

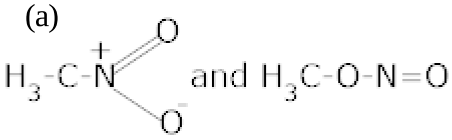
Ans (a) sp^2 hybridized carbon, trigonal planar

(b) sp^3 hybridized carbon, tetrahedral

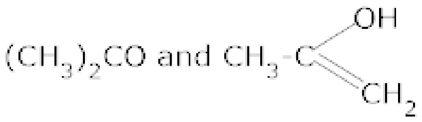
(c) sp hybridized carbon, linear.

Q. 26. Which of the following pairs of structures do not constitute resonance structures?

(a)



(b)



(c) $CH_3CH=CHCH_3$ and $CH_3CH_2CH = CH_2$.

Ans (a) $H_3C\text{-}O\text{-}N=O$

(b) $(CH_3)_2$ CO

(c) $CH_3CH_2CH=CH_2$.

Q27 Write the Line formula structure of compounds whose Names are given below :

(i) 3-ethyl-4-methylhept-5-en-2-one.

(ii) 3-nitrocyclohex-1-en

Q 28 Identify the most stable species in the following set of ions giving reasons

i. CH_3^+ , $^+CH_2Br$, $^+CHBr_2$, $^+CBr_3$

ii. CH_3^- , $^-CH_2Cl$, $^-CHCl_2$, $^-CCl3$

Answer:

(i) CH_3^+ is the most stable species because replacing H atom by Br (-Inductive effect) increases +ve charge on carbon atom and destabilised the species.

(ii) $^-CCl_3$ is most stable because the -ve charge on the carbon atom is dispersed due to the -I effect of Cl. More Cl atoms correspond to more dispersal of-ve charge and thus more stabilisation.

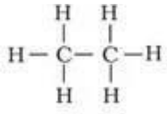
SECTION D

CASE STUDY BASED - 1 (4 MARKS)

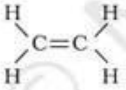
Q29 Read the passage carefully and answer the questions that follow.

The knowledge of fundamental concepts of molecular structure helps in understanding and predicting the properties of organic compounds. You have already learnt theories of valency and molecular structure. Also, you already know that tetravalence of carbon and the formation of covalent bonds by it are explained in terms of its electronic configuration and the hybridisation of s and p orbitals. It may be recalled that formation and the shapes of molecules like methane (CH_4), ethene (C_2H_4), ethyne (C_2H_2) are explained in terms of the use of sp3, sp2 and sp hybrid orbitals by carbon atoms in the respective molecules. Hybridisation influences the bond length and bond enthalpy (strength) in compounds. The sp hybrid orbital contains more s character and hence it is closer to its nucleus and forms shorter and stronger bonds than the sp3 hybrid orbital. The sp2 hybrid orbital is intermediate in s character between sp and sp3 and, hence, the length and enthalpy of the bonds it forms, are also intermediate between them. The change in hybridisation affects the electronegativity of carbon. The greater the s character of the hybrid orbitals, the greater is the electronegativity. Thus, a carbon atom having ansp hybrid orbital with 50% s character is more electronegative than that possessing sp2 or sp3 hybridised orbitals. This relative electronegativity is reflected in several physical and chemical properties of the molecules concerned, about which you will learn in later units.

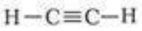
Characteristic Features of π Bonds In a π (pi) bond formation, parallel orientation of the two p orbitals on adjacent atoms is necessary for a proper sideways overlap. Thus, in $H_2C=CH_2$ molecule all the atoms must be in the same plane. The p orbitals are mutually parallel and both the p orbitals are perpendicular to the plane of the molecule. Rotation of one CH_2 fragment with respect to other interferes with maximum overlap of p orbitals and, therefore, such rotation about carbon-carbon double bond (C=C) is restricted. The electron charge cloud of the π bond is located above and below the plane of bonding atoms. This results in the electrons being easily available to the attacking reagents. In general, π bonds provide the most reactive centres in the molecules containing multiple bonds.



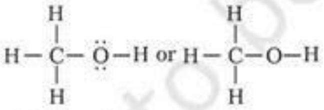
Ethane



Ethene



Ethyne



Methanol

(1) … synthesised an organic compound, urea from an inorganic compound, ammonium cyanate.

(a) Wohler (b) Adams

(c) Roger (d) William Evans

Ans- (a) F. Wolher

(2) Dot structure is also known as …

(a) Zigzag structure (b) Lewis structure

(c) Line structure (d) Bond line structure

Ans-(b) Lewis Structure

(3) Terminals in zigzig structure denotes … Group.

(a) Bromyl (b) Propyl

(c) Methyl (d) Pentyl

Ans- (c) Methyl

(4) Triple dash represents …

(a) Single bond (b) Double bond

(c) Triple bond (d) Equivalent bond

Ans- (c) Triple bond

CASE STUDY BASED - 2 (4 MARKS)

Q 30 Read the passage carefully and answer the questions that follow.

Aromatic hydrocarbon, are hydrocarbons containing sigma bonds and delocalized pi electrons between carbon atoms in a ring. For example, benzene. They are known as aromatic due to their pleasant smell. Aromatic compounds are broadly divided into two categories: benzenoids (one containing benzene ring) and non- benzenoids (those not containing a benzene ring), Arenes are mostly nonpolar and non-miscible in water. These compounds are usually unreactive and are used as solvents for various other nonpolar compounds. Their carbon to hydrogen ratio is high therefore, they are characterized by sooty yellow flame.

(i) Give one example of non-benzenoid aromatic compound.

Ans: Tropolone

(ii) What is Huckel's rule of aromaticity?

Ans. Huckel's rule of aromaticity states that for a ring to be aromatic, it should be planar and have fully conjugated (4n + 2) pi electrons, where n is an integer.

(iii) What are heterocyclic aromatic compounds? Give on example:

Ans. A heterocyclic compound is an organic compound where an atom other than carbon has substituted one or more of the carbon atoms in the molecule's backbone. Example: Furan

(iv) What is the difference between aliphatic and aromatic?

Ans. The carbon compounds are related in a straight chain way in aliphatic compounds. In aromatic compounds, the carbon compounds are associated with conjugated pi electrons in the manner of a ring structure.

SECTION E

Q31. (a) 0.45g of an organic compound when analysed by combustion gave 1.1g carbon dioxide and 0.30 g of water. Calculate the percentage of Carbon and Hydrogen in it.

(b) Can we use potassium in place of Sodium for preparing Lassaigne extract?

Ans (a) mass of organic

compound = 0.45g

mass of CO_2 = 1.1g

mass of H_2O = 0.30g

Percentage of Carbon = $\frac{12 \times mass\ of\ Carbon\ dioxide}{44 \times mass\ of\ Org.Compound} \times 100$

Percentage of Carbon = $\frac{12 \times 1.1g}{44 \times 0.45g} \times 100 = 66.67\ \%$

Percentage of Hydrogen = $\frac{2 \times mass\ of\ Water}{18 \times mass\ of\ Org.Compound} \times 100$

Percentage of Carbon = $\frac{2 \times 0.30g}{18 \times\ 0.45g} \times 100 = 7.41\%$

(b) No, Potasium is normally not used because it is more reactive than sodium and will therefore react violently upon heating.The handling of the tube will become difficult.

Q32 (a) 0.4g of an organic compound gave 0.30 g of AgBr by Carius method. Determine the percentage of Bromine in the compound.

(b)Explain how electronegativity of carbon atom is related to their state of hybridization in an organic compound?

Ans a) Mass of compound = 0.40 Mass of AgBr = 0.30g

188 g AgBr contain Bromine = 80g

Percentage of Carbon = $\frac{80\ \times 0.30g}{188\ \times\ 0.40g} \times 100 = 31.92\%$

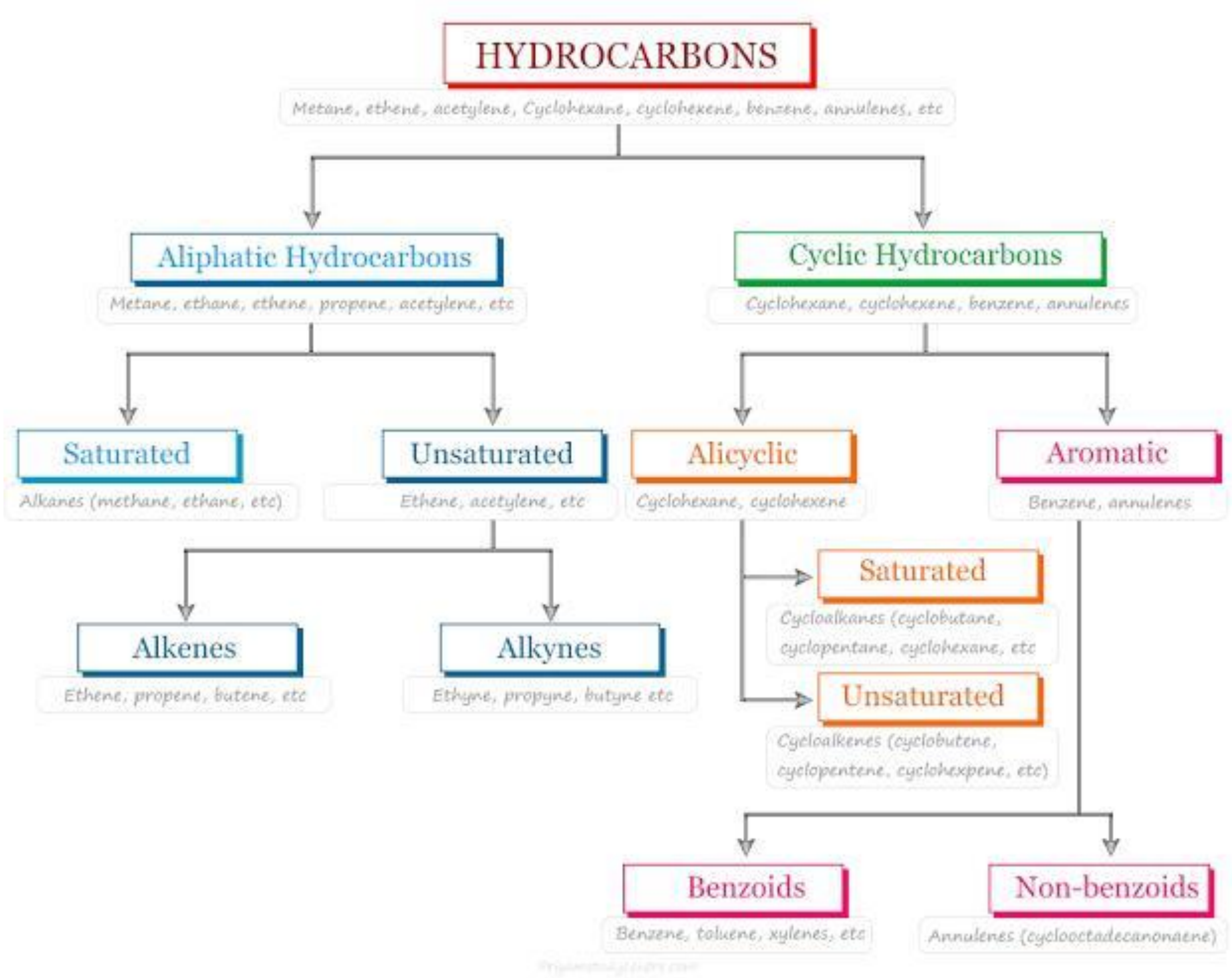
b) Electronegativity is related to the % of s character.Greater the s character ,more is the electronegativity of carbon.Therefore the electronegativity of carbon increases in the order

$sp^3 < sp^2 < sp$

CHAPTER-9: HYDROCARBON

Hydrocarbons are the chemical compounds composed of Carbon and Hydrogen.:

Classifications of Hvdrocarbons



Alkanes are saturated, open chain hydrocarbons containing carbon-carbon single bonds. e.g.. methane (CH_4), ethane (C_2H_6) propane (C_3H_8), etc. Common formula for alkanes is C_nH_{2n+2}.

Preparation of Alkanes

From unsaturated hydrocarbons:

$$CH_3-CH=CH_2+H_2 \xrightarrow{Pt/Pd/Ni} CH_3-CH_2-CH_3$$

Propene Propane

$$CH_3-C\equiv C-H + 2H_2 \xrightarrow{Pt/Pd/Ni} CH_3-CH_2-CH_3$$

Propyne Propane

<u>From alkyl halides:</u> Alkyl halide on reduction with zinc and dil. HCl give alkanes.

$$CH_3-Cl + H_2 \xrightarrow{Zn,\ H^+} CH_4 + HCl$$

Chloromethane Methane

$$C_2H_5-Cl + H_2 \xrightarrow{Zn.H^+} C_2H_6 + HCl$$

Chloroethane Ethane

<u>Wurtz reaction :</u> This reaction is used for preparation of higher alkanes.

$$CH_3Br+2Na+BrCH_3 \xrightarrow{dry\ ether} CH_3-CH_3+2NaBr$$

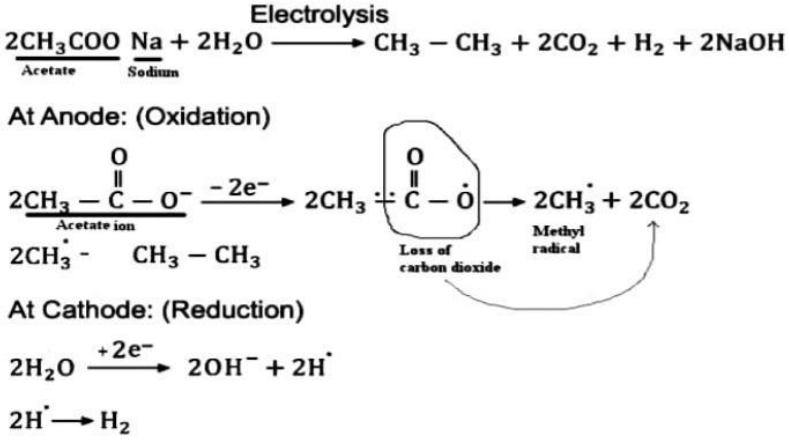
Bromomethane Ethane

<u>From carboxylic acids:</u> Degradation reactions/ decarboxylation reaction.

$$CH_3\boxed{COONa \quad + \quad NaO}H \xrightarrow[Heat]{CaO} CH_4 \quad + \quad Na_2CO_3$$

Sodium ethanoate Sodium hydroxide Methane Sodium carbonate

Kolbe's electrolytic method: An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms at the anode.



$$\underset{\text{Acetate}}{\underline{2CH_3COO}}\ \underset{\text{Sodium}}{\underline{Na}} + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH$$

At Anode: (Oxidation)

$$\underset{\text{Acetate ion}}{\underline{2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^-}} \xrightarrow{-2e^-} 2CH_3 \mathbin{\vdots} \boxed{\overset{\overset{\displaystyle O}{\|}}{C}-\dot{O}} \longrightarrow \underset{\text{Methyl radical}}{2\dot{C}H_3} + 2CO_2$$

Loss of carbon dioxide

$$2\dot{C}H_3 - \quad CH_3-CH_3$$

At Cathode: (Reduction)

$$2H_2O \xrightarrow{+2e^-} 2OH^- + 2H^{\cdot}$$

$$2H^{\cdot} \longrightarrow H_2$$

Chemical Properties –

Alkanes being saturated compounds can undergo only substitution reactions.

Halogenation:

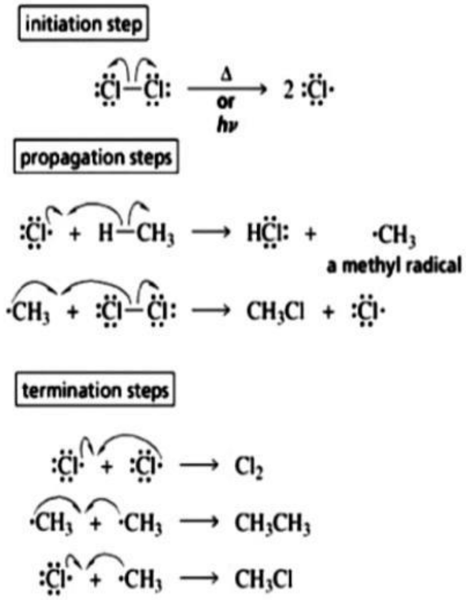
$$CH_3Cl + Cl_2 \xrightarrow[\text{light}]{\text{Heat or}} CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow[\text{light}]{\text{Heat or}} CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow[\text{light}]{\text{Heat or}} CCl_4 + HCl$$

The rate of reaction of alkanes with halogens is $F_2 > Cl_2 > Br_2 > I_2$,. Rate of replacement of hydrogens of alkanes is: 3° > 2° > 1°.

Mechanism halogenation of alkanes: it can be explained with free radical mechanism as below:



Combustion:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l); \quad \Delta_c H^\ominus = -890\ \mathrm{kJ\ mol^{-1}}$$

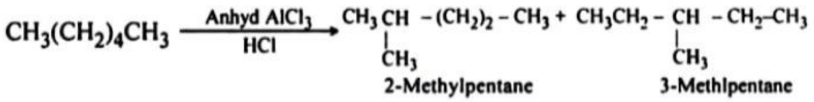
Controlled oxidation:

$$2CH_4 + O_2 \xrightarrow{Cu/523K/100atm} \underset{\text{Methanol}}{2CH_3OH}$$

$$CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} \underset{\text{Methanal}}{HCHO} + H_2O$$

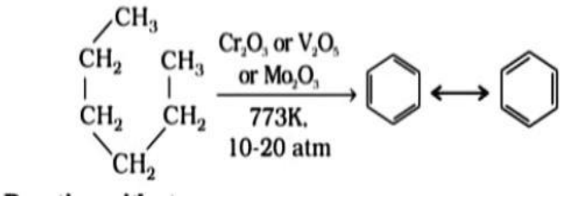
$$2CH_3CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} \underset{\text{Ethanoic acid}}{2CH_3COOH} + H_2O$$

Isomerisation:



$CH_3(CH_2)_4CH_3 \xrightarrow[HCl]{Anhyd\ AlCl_3} CH_3\underset{CH_3}{\underset{|}{CH}}-(CH_2)_2-CH_3 + CH_3CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$

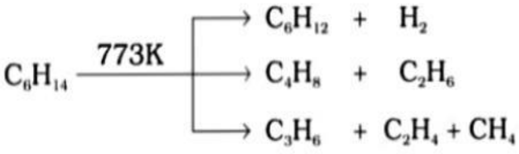
Aromatization (Reforming): The process of converting aliphatic compounds into aromatic compounds is called aromatisation.



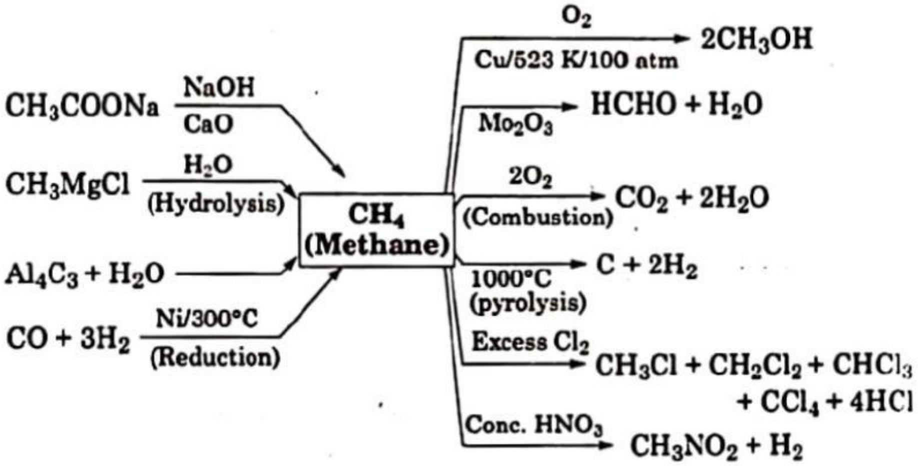
Reaction with steam:

$$CH_4 + H_2O \xrightarrow{Ni,\ 1273\ K} CO + 3H_2$$

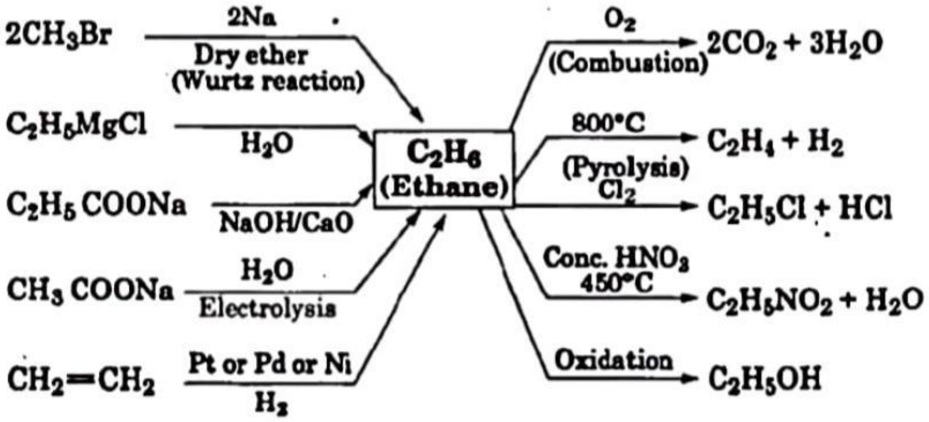
Pyrolysis or cracking: It is process of decomposing higher hydrocarbons into lower hydrocarbons with low boiling point by strong heating. Products depend on reaction situations.



General reactions or methane:



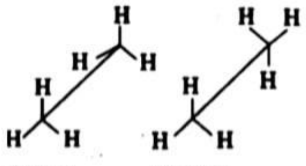
General reactions for Ethane:



CONFORMATIONS:

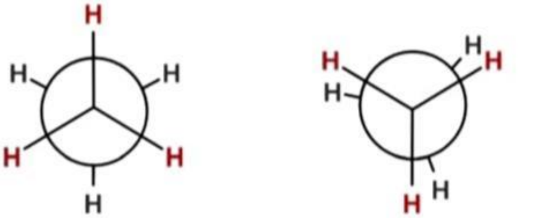
Spatial arrangements which are obtained by rotation around sigma bons are called conformation or conformational isomers and this phenomenon is called conformational isomerism

Sawhorse projections of ethane: In this projection, the molecule is viewed along the molecular axis.



Eclipsed Staggered

Newman projections of ethane:

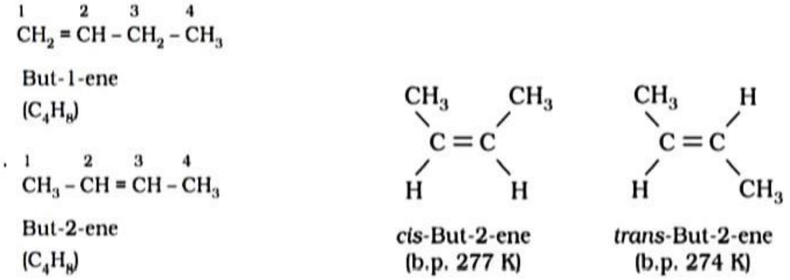


Staggered conformation Eclipsed conformation

ALKENES:-

Alkenes are unsaturated hydrocarbons containing at least one double bond. General formula for alkenes is C_nH_{2n}.

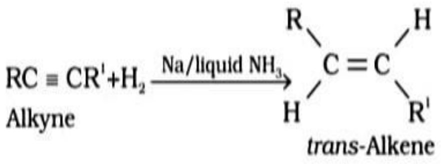
Isomerism: Alkenes show both structural isomerism and geometrical isomerism.

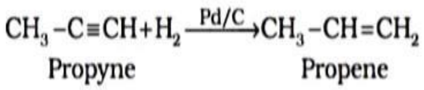


Structural isomer **Geometrical isomer**

Preparation

From alkynes:

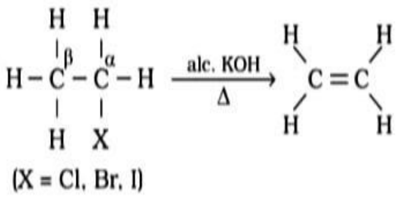




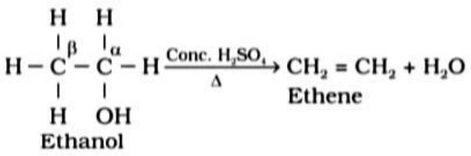
$$CH_3-C\equiv CH+H_2 \xrightarrow{Pd/C} CH_3-CH=CH_2$$

Propyne Propene

From alkyl halides:

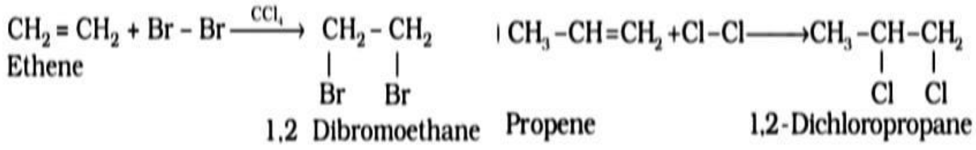


From alcohols by acidic dehydration:



CHEMICAL PROPERTIES –

Addition of halogens:

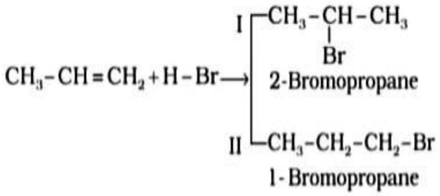


$$\underset{\text{Ethene}}{CH_2=CH_2} + Br-Br \xrightarrow{CCl_4} \underset{\text{1,2 Dibromoethane}}{\underset{Br\quad\ Br}{CH_2-CH_2}}$$

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + Cl-Cl \longrightarrow \underset{\text{1,2-Dichloropropane}}{CH_3-\underset{Cl}{CH}-\underset{Cl}{CH_2}}$$

Addition of hydrogen halides:

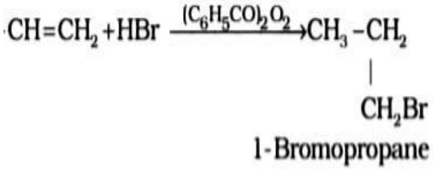
Addition of hydrogen halides:



$$CH_3-CH=CH_2+H-Br \longrightarrow \begin{cases} \text{I} \quad \underset{\text{2-Bromopropane}}{CH_3-\underset{Br}{CH}-CH_3} \\ \text{II} \quad \underset{\text{1-Bromopropane}}{CH_3-CH_2-CH_2-Br} \end{cases}$$

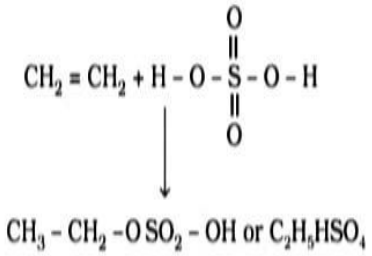
Markovnikov rule: The rule states that negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms.

Anti Markovnikov addition or peroxide effect or Kharash effect: In the presence of peroxide, addition of HBr to unsymmetrical alkenes like propene takes place contrary to the Markovnikov rule.

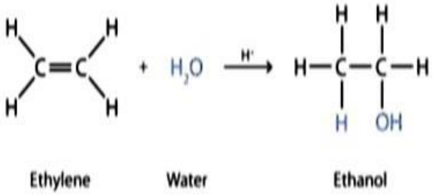


$$CH=CH_2+HBr \xrightarrow{(C_6H_5CO)_2O_2} \underset{\text{1-Bromopropane}}{CH_3-\underset{CH_2Br}{CH_2}}$$

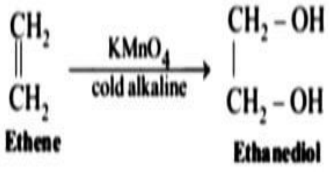
Addition of sulphuric acid:



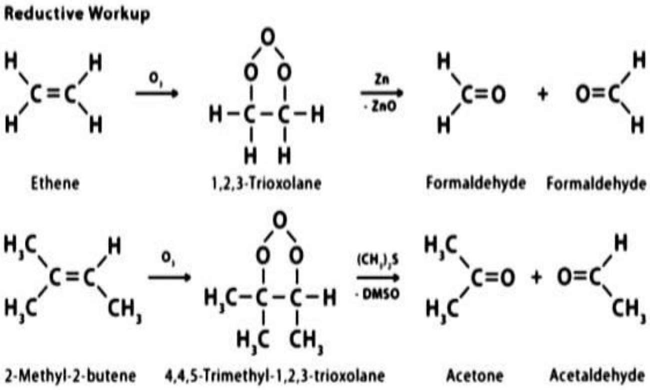
Addition of water:



Oxidation: In alkaline solution of KMnO4 (Baeyer's Reagent).



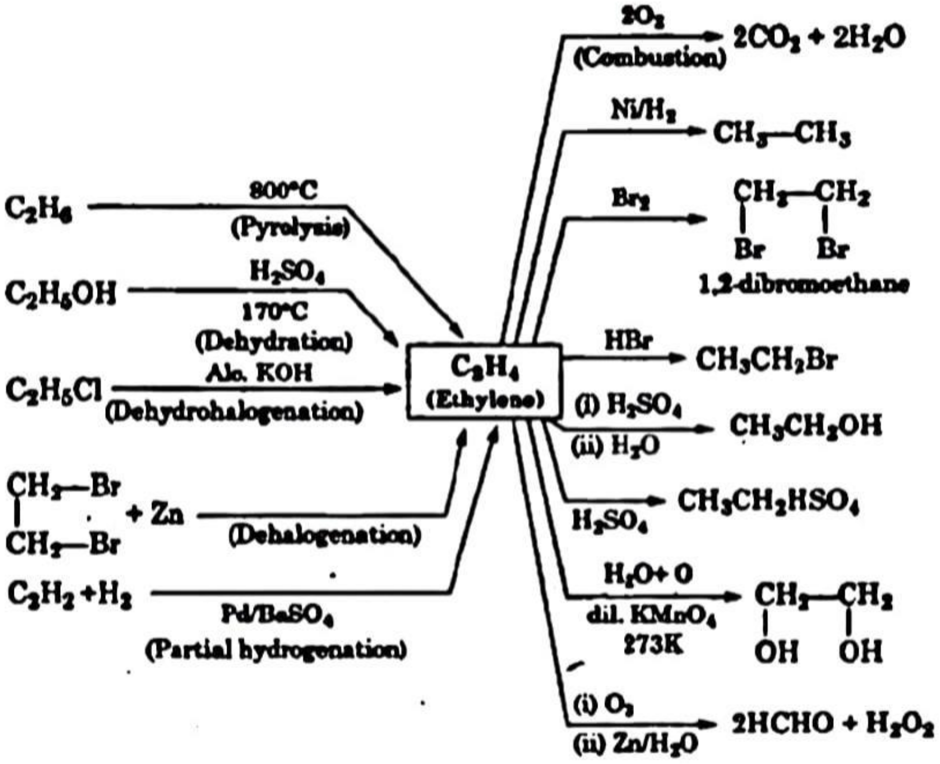
Ozonolysis:



Polymerisation –

$$n(\mathrm{CH_2=CH_2}) \xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} \underset{\text{Polythene}}{-\!\left(\mathrm{CH_2-CH_2}\right)\!-_{n}}$$

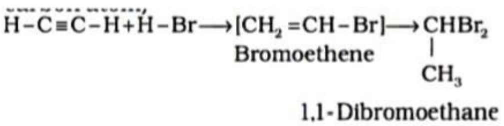
General *reactions* for Ethene:



ALKYNES:-

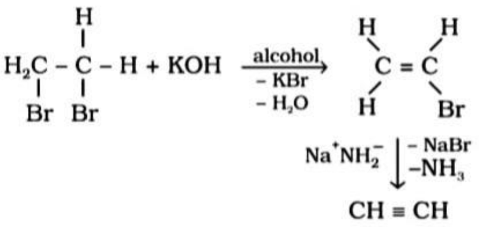
Alkynes are also unsaturated hydrocarbons. They contain at least one triple bond between two carbon atoms. Their general formula is C_nH_{2n-2}.

Preparation - From calcium carbide:



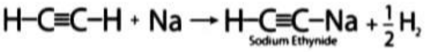
$$H-C\equiv C-H + H-Br \longrightarrow \underset{\text{Bromoethene}}{[CH_2=CH-Br]} \longrightarrow \underset{\substack{CH_3 \\ \text{1,1-Dibromoethane}}}{CHBr_2}$$

From vicinal dihalides:



Chemical properties

Acidic character of alkyne:

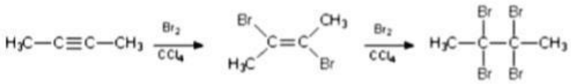


$$H-C\equiv C-H + Na \rightarrow \underset{\text{Sodium Ethynide}}{H-C\equiv C-Na} + \frac{1}{2}H_2$$

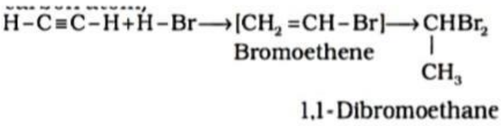
Addition of dihydrogen:

$$HC\equiv CH + H_2 \xrightarrow{Pt/Pd/Ni} [H_2C=CH_2] \xrightarrow{H_2} CH_3-CH_3$$

Addition of halogens:

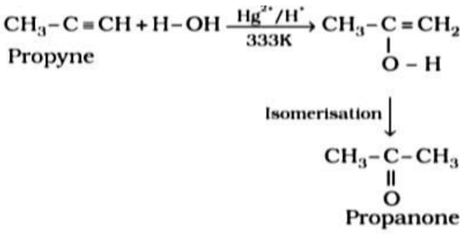


Addition of hydrogen halides:

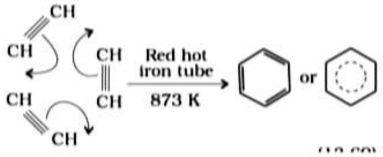


$$H-C\equiv C-H + H-Br \longrightarrow \underset{\text{Bromoethene}}{[CH_2=CH-Br]} \longrightarrow \underset{\text{1,1-Dibromoethane}}{\begin{matrix} CHBr_2 \\ | \\ CH_3 \end{matrix}}$$

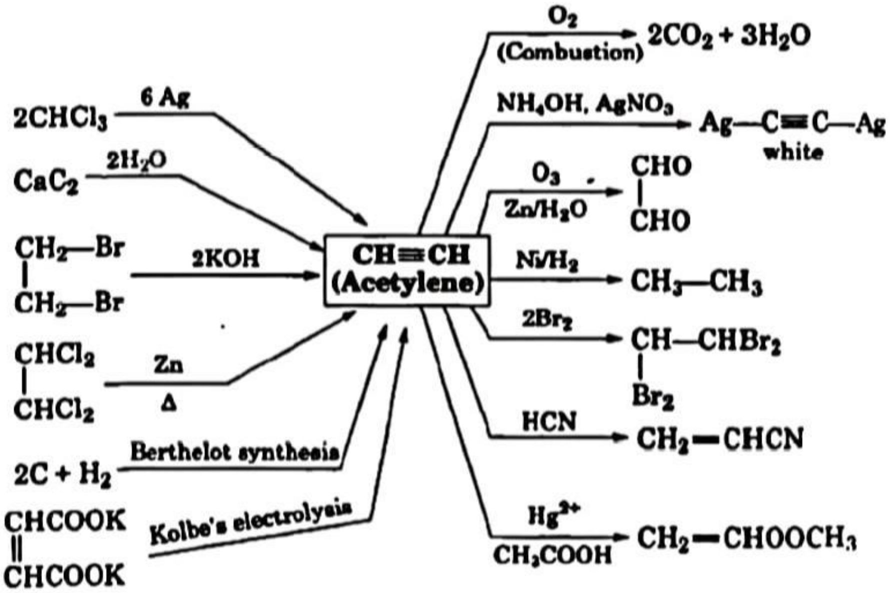
Addition of water:



Cyclic polymerisation:



General reactions for Ethyne:



AROMATIC HYDROCARBONS –

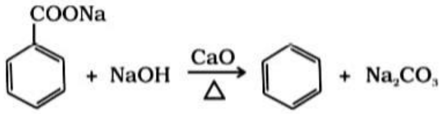
These hydrocarbons are also known as ‘arenes’.

Aromaticity : Aromaticity compounds possessing following characteristics –

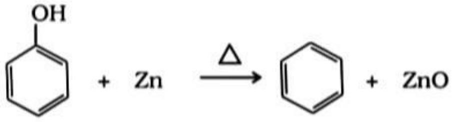
(I) Planarity
(II) Complete delocalisation of the z electrons in the ring
(III) Presence of (4n+ 2) n electrons in the ring where n is an integer (n =0, 1, 2,…). This is often referred to a huckel rule .

Preparation of Benzene

Decarboxylation of aromatic acids:

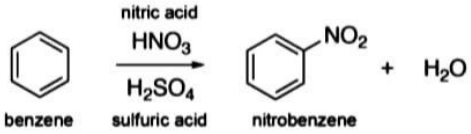


Reduction of phenol:

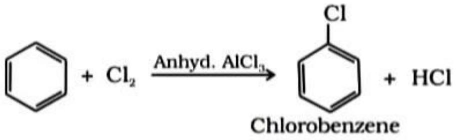


CHEMICAL PROPERTIES –

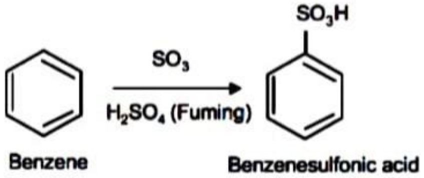
Nitration-



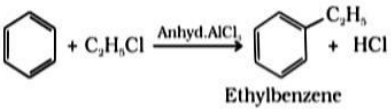
Halogenation-



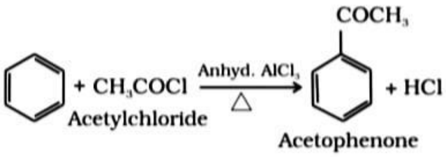
Sulphonation-



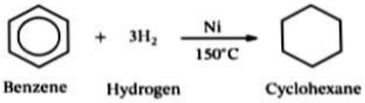
Friedel-crafts alkylation-



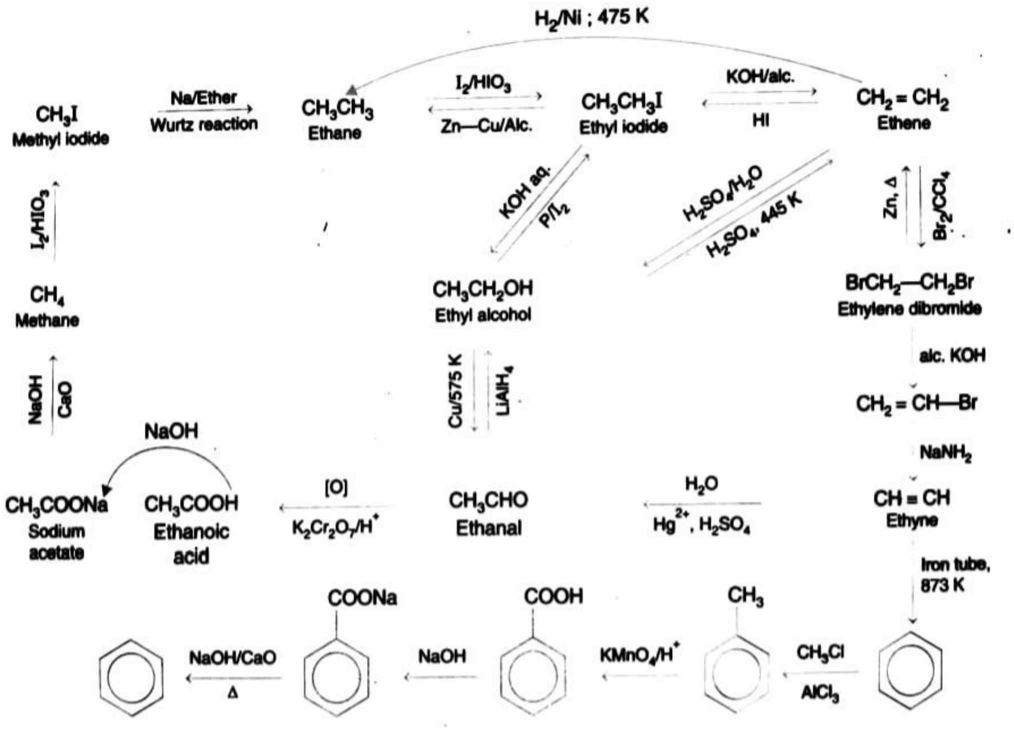
Friedel- crafts acylation-



Addition reactions:



Interconversion of Hydrocarbons



General reactions for Benzene –

CARCINOGENICITY AND TOXICITY: Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer producing (carcinogenic) property.

SOME IMPORTANT QUESTIONS

01. Write IUPAC name: $CH_3CH - C(CH_3)_2$

Ans. 2-methylbutane

02. How would you convert ethene to ethane molecule?

Ans. Unsaturated alkene (ethene) is get converted into saturated alkane (ethane) by the process of reduction in the presence of reducing agents like Pt/Pd//Ni etc.

$$CH_2 = CH_2 \text{ (ethene)} + H_2 \xrightarrow{Pt/Pd/Ni} CH_3 - CH_3 \text{ (ethane)}$$

03.How is alkene produced by vicinal dihalide?

Ans. Alkene are produced from Vicinal dihalide by the process of dehalogenations. Vicinal dihalide on treatment with Zn metal lose a molecule of ZnX_2 to form an alkene.

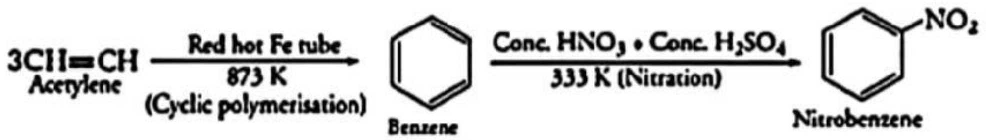
$$CH_2Br\text{-}CH_2Br + Zn \rightarrow CH_2{=}CH_2 + ZnBr_2.$$

04.How will you distinguish between propene and propane?

Ans. Pass them through dilute cold $KMnO_4$ solution (purple) or Br_2in CCl_4 solution (rud).proopene will decolourise both the solutions but propane does not react.

05. Suggest a route for the preparation of nitrobenzene starting from acetylene?

Ans.



MULTIPLE CHOICE QUESTIONS

01) Benzene reacts with chlorine in the presence of an iron catalyst to produce-

a. Benzene hexachloride
b. Benzyl chloride
c. Chlorobenzene
d. More than one of the above

02) How many Isomers does C_6 H_{14} have?

a. 3. b .6 c .4 d . 5

ASSERTION AND REASON QUESTIONS

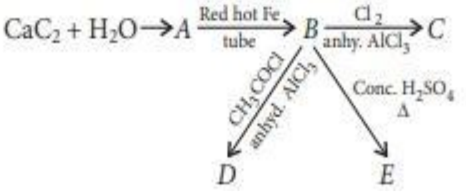
Directions: (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(C) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

01) Assertion : Sodium acetate on Kolbe's electrolysis gives methane.
Reason : Methyl free radical is formed at anode.

02)Assertion : All the hydrogen atoms in CH2 =C= CH2 are attached to sp2 hybridised carbon atom.
Reason : All the carbon atoms in its are sp2 hybridized.

CASE STUDY BASED QUESTIONS

Compound (A) is an important industrial feed stock, but its largest use is as the fuel for the oxyacetylene torch. It is a colorless, foul-smelling gas that burns in the air with a yellow, sooty flame.



01)Identify the product A.
(a) ethane. (b) ethyne. (c) ethene. (d) methane
02)The product E is
(a) nitrobenzene
(b) benzene sulphonic acid
(c) both (a) and b (d) none of these.

03)Identify the product ‘D’.
(a) Chlorobenzene (b) Bromobenzene
(c) Toluene (d) Acetophenonone

COMPETENCY BASED QUESTIONS

1. 896 ml of a hydrocarbon (A) having 87.809% C and 12.19% H weights 3.28 g at STP. Hydrogenation of (A) gives 2-methylpentane. Also compound (A) on hydration in presence of H2SO4 and HgS04 gives Ketone (B) having Molecular formula C6H120. The ketone (B) gives a positive iodoform test. Find the structure of (A) give all reactions.

[Hint: (i) l mole of a compound at STP contains 22400 mL volume (iü) Ketones having structures gives positive iodoform test]

2. Explain why the central carbon-carbon bond in 1,3-Butadiene is shorter than that of butane.
3. How do you explain that dehydration of 3,3-Dimethyl, butan-2-ol yield 2,3 dimethyl but-2-ene as the major product.[Hint: Rearrangement of 1,2 methyl shift]
4. In alkyl halide X of molecular formula C6H13Cl on treatment with potassium tertiary butoxide gives two isomeric alkenes, Y and Z.(C 6H12).Both alkene on hydrogenation give 2,3 dimethyl butane. Predict the structures of X,Y and Z.

5. Two cyclic dienes, A and B have M.FC6Hs. The mixture of the two on reductive ozonolysis gave the following products: Succinaldehyde, Propan 1,3 dial, and glyoxal. The mixture of A and B on hydrogenation produces only cyclohexane. Suggest the structures of A and B.
6. Arrange the following compounds in the order of their decreasing relative reactivity with an electrophile.

    a) Toluene, 4-nitro toluene. 1,4-DinitroBenzene
    b) Chlorobenzene, p-Nitro chlorobenzene, 2,4-Dinitro chlorobenzene
7. What effect does branching of an alkane chain has on its melting point than that of its long chain isomers? Explain.
8. In the presence of peroxide addition of HBr to propene takes place according to anti Markonikov’s rule, but peroxide effect is not seen in the case of HCI and HI. Explain.
9. An alkane C&HI8 is obtained as the only product on subjecting a primary alkyl halide to Wurtz reaction. On monobromination this alkane yields a single isomer of a tertiary bromide. Write the structure alkane and the tertiary bromide.
10. Write down a method of preparation of Nitrobenzene from Acetylene.

KVS ZIET MUMBAI

BLUE PRINT (SAMPLE PAPER-1)

SESSION -2024-25

CHEMISTRY THEORY (043)

CLASS:XI

S. NO.	Chapter Name	MCQ (1)	MCQ Assertion Reason (1)	VSA (2)	SA (3)	Case based question (4)	LONG ANSWER (5)	Total Marks
1	Some Basic Concepts of Chemistry	2(2)		1(2)	1(3)			7 Marks
2	Structure of Atom	1(1)			1(3)		1(5)	9 Marks
3	Classification of Elements and Periodicity in properties	1(1)	1(1)			1(4)		6 Marks
4	Chemical Bonding and Molecular Structure	1(1)	1(1)				1(5)	7 Marks
5	Chemical Thermodynamics	2(2)		2(4)	1(3)			9 Marks
6	Equilibrium	2(2)		1(2)	1(3)			7 Marks
7	Redox Reactions		1(1)		1(3)			4 Marks
8	Organic chemistry some basic principles and Techniques	1(1)		1(2)	1(3)		1(5)	11 Marks
9	Hydrocarbons (Aliphatic and Aromatic)	2(2)	1(1)		1(3)	1(4)		10 Marks
	Total	12(12)	4(4)	5(10)	7(21)	2(8)	3(15)	33(70)

KENDRIYA VIDYALAYA SANGATHAN (ZIET MUMBAI)

SAMPLE PAPER-1

CLASS-XI

Time: 3 hours CHEMISTRY (043) MM:-70

General Instructions:

Read the following instructions carefully.

(a) There are 33 questions in this question paper with internal choice.

(b) SECTION A consists of 16 multiple -choice questions carrying 1 mark each.

(c) SECTION B consists of 5 short answer questions carrying 2 marks each.

(d) SECTION C consists of 7 short answer questions carrying 3 marks each.

(e) SECTION D consists of 2 case - based questions carrying 4 marks each

(f) SECTION E consists of 3 long answer questions carrying 5 marks each.

(g) All questions are compulsory.

(h) Use of log tables and calculators is not allowed.

SECTION- A

Q.1 Whatwillbethemolarityofasolution,whichcontains5.85gofNaCl(s)per500mL?

(A) 4 mol L^{-1}

(B) 20 mol L^{-1}

(C) 0.2 mol L^{-1}

(D) 2 mol L^{-1}

Q.2 The empirical formula and molecular mass of a compound are CH_2O and 180 g respectively. What will be the molecular formula of the compound?
(A) $C_9H_{18}O_9$

(B) CH_2O

(C) $C_6H_{12}O_6$

(D) $C_2H_4O_2$

Q.3. WhichofthefollowingconclusionscouldnotbederivedfromRutherford'salpha-particlescatteringexperiment?

(A) Most of the space in the atom is empty.
(B) The radius of the atom is about 10^{-1O} m while that of nucleus is 10^{-15} m.
(C) Electrons move in a circular path of fixed energy called orbits.
(D) Electrons and the nucleus are held together by electrostatic forces of attraction.

Q.4 What electronic arrangement of an atom has the lowest ionization enthalpy among the following?

(A) $1s^2\ 2s^2\ 2p^3$

(B) $1s^2\ 2s^2\ 2p^6 3s^1$

(C) $1s^2\ 2s^2\ 2p^6$

(D) $1s^2\ 2s^2\ 2p^5$

Q.5 The correct bond order in the following species is ——————.

(A) $O_2^+ < O_2^- < O_2^{2+}$

(B) $O_2^- < O_2^+ < O_2^{2+}$

(C) $O_2^{2+} < O_2^+ < O_2^-$

(D) $O_2^{2+} < O_2^- < O_2^+$

Q.6 The enthalpy change in a reaction does not depend upon

(A) the state of reactions and products

(B) the nature of the reactants and products

(C) different intermediate steps in the reaction

(D) initial and final enthalpy of the reaction

Q.7 If liquids A and B form an ideal solution

(A) the entropy of mixing is zero

(B) the free energy of mixing is zero

(C) the free energy as well as the entropy of mixing are zero

(D) the enthalpy of mixing is zero

Q.8 When NH_4Cl is added to NH_4OH solution the dissociation of ammonium hydroxide is reduced. It is due to:
(A) common ion effect
(B) hydrolysis
(C) oxidation
(D) reduction

Q.9 The addition of carbonyl compound to HCN is an example of

(A) Nucleophilic substitution

(B) Electrophilic addition

(C) Nucleophilic addition

(D) Electrophilic substitution

Q10.A base according to Bronsted concept is a substance which can:

(A) lose pair of electron

(B) donate protons

(C) gain a pair of electrons

(D) accept protons

Q.11 In Chlorination of benzene, which of the following acts as an electrophile?

(a) Cl^+

(b) Cl^-

(c) Cl

(d) $FeCl_3$

Q.12 Which of the following will not undergo Friedel-Craft's reaction readily?

(a) Toluene

(b) Xylene

(c) Cumene

(d) Nitrobenzene

Q.13 Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion : Smaller the size of an atom greater is the electronegativity.
Reason : Electronegativity refers to the tendency of atom so share electrons with other atom.

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

b) Both A and R are true and R is not the correct explanation of A

c) A is true but R is false

d) A is false but R is true.

Q.14 **Assertion :** BF_3 molecule has zero dipole moment.
Reason : F is electronegative and B–F bonds are polar in nature.

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

b) Both A and R are true and R is not the correct explanation of A

c) A is true but R is false

d) A is false but R is true.

Q.15 **Assertion:** In the reaction $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$ sodium is oxidised.
Reason: Sodium acts as an oxidising agent in given reaction.

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

b) Both A and R are true and R is not the correct explanation of A

c) A is true but R is false

d) A is false but R is true.

Q.16 Assertion: 1-butene on reaction with HBr in presence of peroxide produces 1-bromo-butane.

Reason: It involves the free radical mechanism.

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

b) Both A and R are true and R is not the correct explanation of A

c) A is true but R is false

d) A is false but R is true.

SECTION- B

Q.17 (a)Give the balanced chemical equation for combustion of Methane gas.

(b) Calculate the amount of water (g) produced by the combustion of 16 g of methane.

Q.18 The enthalpy of atomisation for the reaction $CH_4(g) \rightarrow C(g) + 4H(g)$ is 1665 kJ mol^{-1}. What is the bond energy of C–H bond?

OR

The molar enthalpy of vaporization of acetone is less than that of water. Why?

Q.19 Expansion of a gas in vacuum is called free expansion. Calculate the work done and the change in internal energy when 1.5 litre of ideal gas expands isothermally into vacuum until is total volume is 6litre?

Q.20 The solubility product of $Al(OH)_3$ is 2.7×10^{-11}. Calculate its solubility in g / L and also find out the pH of this solution. (Atomic mass of Al = 27 u).

Q.21 Write structures of various carbocations that can be obtained from 2-methylbutane.

Arrange these carbocations in order of increasing stability.

SECTION- C

Q.22 Calculate:

(i) Mass in gramn of 5.8 mol N_2O
(ii) Number of moles in 8.0 g of O_2
(iüü) Molar mass if 11.2 L at STP weigh 8.5 g

Q.23 According to de Broglie, the matter should exhibit dual behaviour, that is, both particle and wave like properties. However, a cricket ball of mass 100 g does not move like a wave when it is thrown by a bowler at a speed of 100 km/h. Calculate the wavelength of the ball and explain why it does not show wave nature.

Q.24 Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.

Q.25 How can you predict the following stages of a reaction by comparing the value of Kc and

Qc? Answer any two of the following-

(i) Net reaction proceeds in the forward direction.

(Ii) Net reaction proceeds in the backward direction.

(iii) No net reaction occurs.

Q.26 Find out the oxidation number of chlorine in the following compounds and arrange them in increasing order of oxidation number of chlorine.

$NaClO_4$, $NaClO_3$, NaCIO, $KCIO_2$, ClO_3

Q.27 What are electrophiles and nucleophiles? Explain with examples.

Q.28 How will you convert benzene into

(i) p – nitrobromobenzene

(ii) m – nitrochlorobenzene

SECTION- D

Q.29 Read the passage given below and answer the following questions:

The energy needed to remove the neutral atom's most loosely bonded electron is known as the first ionization enthalpy (IE1). The second ionisation enthalpy (IE2) is the energy needed to remove the second electron from theresultant cation, and so on. The energy needed to remove an s-electron from the same shell would require more ionisation enthalpy than it would to remove a p-electron, which in turn would take more energy than it wouldto remove a d-electron, and so on. Due to a rise in the number of inner electrons that balance off the increase in nuclear charge, there is an increase in the shielding effect on the outermost electron, and the removal of the outermost electron takes less energy down a group.

(A) Which element in periodic table has highest ionization energy (lE)?
(B) How size of an atom affects its ionization enthalpy?
(C) How does screening effect work? In what ways does it affect the ionisation enthalpy?

OR

Although B is larger than Be, it has a lower first ionisation energy than Be. Why?

Q.30 Read the passage given below and answer the following questions:

Arenes are the aromatic hydrocarbons which contain one or more Benzene rings. Benzene is a Six- membered Carbon ring with alternate single and double bonds. Arenes contain high proportion of Carbon compared to aliphatic hydrocarbons. Aromatic hydrocarbons are less reactive than Alkenes and Alkynes because their π bonds are involved in delocalisation and are not available for addition reactions. But Benzene being electron rich the electrophiles replace the Hydrogen atom of Benzene and undergoes electrophilic substitution reactions.

(i) Explain why Benzene is extraordinarily stable even though it contains three double bonds.

(ii) Name an ortho and para directing deactivating group.

(iii) OH group attached to Benzene is ortho, para directing and activating group. Explain with the help of resonating structures.

OR

(iv) What are meta directing groups? Give example.

SECTION-E

Q.31 Attempt any five of the following

(a) Dipole moment of hydrogen halides decreases from HF to HI. Why?
(b) What is the covalency of NH_3, NH^{4+} and BF^{4-}?
(c) Which of the following compounds does not show resonance -CO_3^{2-}, BO_3^{3-}, SO_4^{2-}?
(d) Discuss the shape of following molecules based on VSEPR theory BCl_3, $SiCl_4$
(e) Indicate the number of Sigma and π ones in $HCONHCH_3$
(f) Which hybrid orbitals are used by underlined carbon in the following molecules
    (i)CH_3CHO (ii) CH_3CHCH_2
(g) Explain on the basis of molecular orbital diagram why O_2 should be paramagnetic?

Q32.Why was a change in the Bohr Model of atom required? Due to which important development (s), the concept of movement of an electron in an orbit was replaced by, the concept of probability of finding an electron in an orbital? What is the name given to the changed model of the atom?

OR

(a) The electronic energy in Bohr's orbit is negative. How will you account for it?

(b) The ionization energy of hydrogen atom is 13.6 eV. What will be the energy of the first orbit of He^+ and Li^{2+} ions?

Q.33 (i) Give a brief description of the principles of the following techniques taking an

example in each case.

(a) Crystallisation (b) Distillation (c) Chromatography

(ii) Why does SO_3 act as an electrophile?

OR

$C_5H_{11}Br$ (A) is a given alkyl halide that reacts with ethanolic KOH to give an alkene 'B', this then reacts with Br2 and gives a compound 'C', which on dehydrobromination gives an alkyne 'D'. When this is treated with sodium metal in liquid ammonia, 1 mole of 'D' give us 1 mole of the sodium salt of 'D' and 1/2 mole of the hydrogen gas. Complete the hydrogenation of 'D' which yields a straight-chain alkane. Identify A, B, C and D. Write the reactions involved.

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SESSION -2024-25

CHEMISTRY THEORY (043) Sample Paper-1

CLASS:XI

MARKING SCHEME

1 (C)
2 (C)

3 (C)

4 (B)

5 (B)

6 (C)

7 (D)

8 (A)

9 (C)

10 (D)

11 (D)

12 (D)

13 (A)

14 (B)

15 (C)

16 (A)

17.For Every Part Correct Answer-1+1
18. 2 Marks for Correct answer
19. For Every Part Correct Answer-1+1
20. Solubility and pH Correct Answer-1+1
21. For Every Part Correct Answer-1+1
22. For Every Part Correct Answer-1+1+1
23. calculation 2 marks Reason 1 mark
24 For correct answer 1.5 +1.5
25 For correct answer 1.5 +1.5
26. For oxidation states ½ x 5 and for correct order ½ mark.
27.Correct definitions-1+1 andexamples-1/2+1/2
28. For correct answer 1.5 +1.5

29. For correct answer 1+1+2
30 For correct answer 1+1+2
31. For each part correct answer-01 Mark x 5
32.For correct answer 3+1+1
32 (OR) For correct answer- 2 +1.5+1.5
33.For correct explanation-1+1+1 and 2 marks for part (b)
33(OR) For correct answer -3+2 marks

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