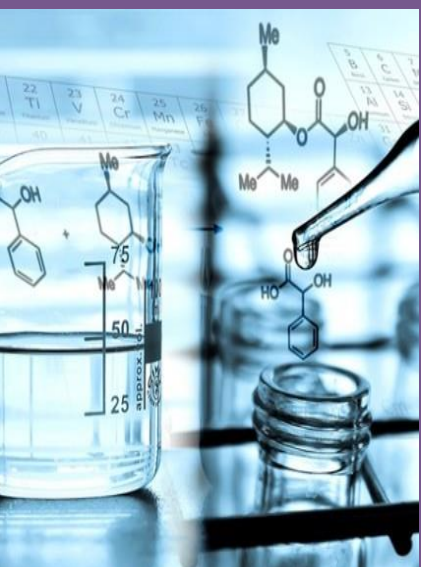तत् त्वं पूषन् अपावृणु
केन्द्रीय विद्यालय संगठन

Session :2022-23

Class-XI

CHEMISTRY

KENDRIYA VIDYALAYA SANGATHAN

CHENNAI REGION

OUR PATRONS

Smt. T RUKMANI

Offg. DEPUTY COMMISIONER

KVS RO CHENNAI

Sh. P.I.T. RAJA

ASSISTANT COMMISSIONER

KVS RO CHENNAI

MEMBERS AND DETAILS OF TOPICS ALLOTTED

S.No.	Name of the co-ordinator	Name of the Teacher	Name of the KV	Name of the Chapter allotted
1	Shri.L.Natarajan	Smt.Anisha T.M	KV Vijayanarayanam	Some Basic Concepts of Chemistry
2		Ms.Nekki	KV No.1, Pondicherry, Shift - I	Structure of Atom
3		Smt N Vijayachandrika	KV AFS Avadi	Classification of Elements and Periodicity in Properties
4		Shri.L.Natarajan	KV Karaikudi	Sample question paper 1 along with scoring key
5	Shri T.Velu	Shri.G.Ravi	KV IIT Chennai	Chemical Bonding and Molecular Structure
6		Ms.Sameena J	KV Island Grounds	Chemical Thermodynamics
7		Mrs.Roshni Samuel	KV No.1, Port Blair	Equilibrium
8		Shri T.Velu	KV NO.1 Narimedu, Madurai	Sample question paper 2 along with scoring key
9	Smt..Meera.G	Mr. V.Ramesh pandian	KV Sivaganga	Redox Reactions
10		G.Uma	No.2 Madurai	Organic Chemistry: Some basic Principles and Techniques
11		Shri.Mohan Lal	KV Mandapam	Hydrocarbons
12		Smt..Meera.G	KV Nagercoil	Sample question paper 3 along with scoring key
13		Smt.B.Bindu	KV Coimbatore	Sample question paper 4 along with scoring key

SUBJECT CO-ORDINATOR

Sh. S. VALLABHAN
PRINCIPAL
KV ANNA NAGAR, CHENNAI

REVIEW COMMITTEE

S NO	NAME OF THE TEACHER	NAME OF KV
1	Dr.S VASUDHEVAN,PGT (CHEMISTRY)	KV NO 2 AFS TAMBARAM
2	Smt.B MUTHULAKSHMI, PGT(CHEMISTRY)	KV ANNA NAGAR
3	Shri R SEKAR, PGT(CHEMISTRY)	KV ANNA NAGAR

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COURSE STRUCTURE
CLASS–XI (THEORY) (2022-23)

Time:3Hours   Total Marks70

S.NO	UNIT	PERIODS	MARKS
1	Some Basic Concepts of Chemistry	18	7
2	Structure of Atom	20	9
3	Classification of Elements and Periodicity in Properties	12	6
4	Chemical Bonding and Molecular Structure	20	7
5	Chemical Thermodynamics	23	9
6	Equilibrium	20	7
7	Redox Reactions	9	4
8	Organic Chemistry: Some basic Principles and Techniques	20	11
9	Hydrocarbons	18	10
	TOTAL	**160**	**70**

Unit I: Some Basic Concepts of Chemistry   18 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   20 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   12 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   **20 Periods**

Valence electrons, ionic bond, covalent bond, bond parameters, Lewis's 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 theoryof homonuclear diatomic molecules (qualitative idea only), Hydrogen bond.

Unit VI: Chemical Thermodynamics   **23 Periods**

Concepts of System and types of systems, surroundings, work, heat, energy, extensive and intensive properties, state functions. First law of thermodynamics -internal energy andenthalpy, heat capacity and specific heat, measurement of ΔU and ΔH, Hess's law of constant heat summation, enthalpy of bond dissociation, combustion, formation, atomization, sublimation, phase transition, ionization, solution and dilution. Second law ofThermodynamics (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 VII: Equilibrium   **20 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 VIII: Redox Reactions   **09 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 XII: Organic Chemistry -Some Basic Principles and Techniques 20 Periods General introduction, methods of purification, qualitative and quantitative analysis, classification and IUPAC nomenclature of organic compounds. Electronic displacementsin 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 XIII: Hydrocarbons   **18 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, the 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, the structure of triple bond (ethyne), physical properties, methodsof 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 the functional group in monosubstituted benzene. Carcinogenicity and toxicity

1.SOME BASIC CONCEPTS OF CHEMISTRY

Chemistry is the branch of Science that deals with the properties, structure and composition of matter. There are a large number of branches for Chemistry. Some of them are: The International System of Units (SI)

Base Physical Quantity	Symbol for Quantity	Name of SI Unit	Symbol for SI Unit
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Thermodynamic temperature	T	kelvin	K
Amount of substance	n	mole	mol
Luminous intensity	I_v	candela	cd

Matter: Matter is anything that occupies space, has a definite mass and can be perceived by any of our sense organs.

Chemical Classification of matter---
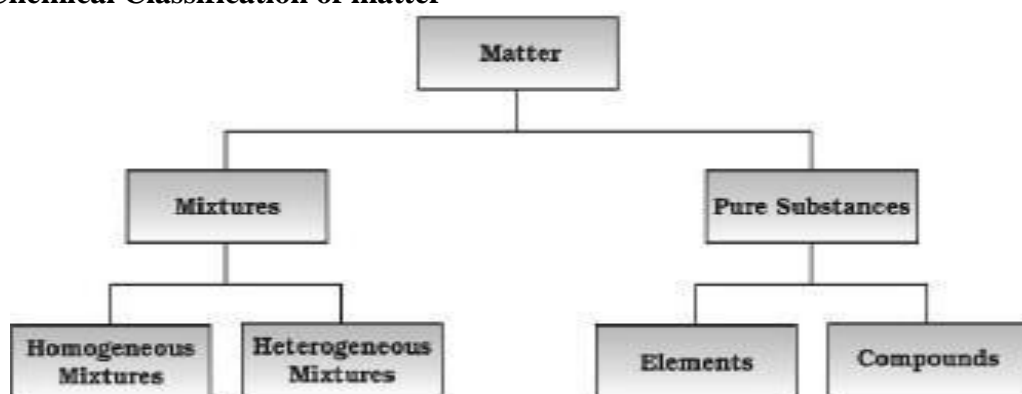
Classification of matter

Matter can be divided into two categories – pure substances and mixtures.

Pure substances contain only one type of particles. These are further divided into two – **elements and compounds**.

Elements are pure substances which contain only one type of particles. These particles may be atoms or molecules. E.g. Hydrogen, Nitrogen, Oxygen (diatomic), Sodium, Potassium, Lithium, Calcium (monoatomic), Phosphorus, Sulphur (polyatomic) etc.

Compounds are pure substances which contain more than one type of atoms in a fixed ratio by mass. E.g. CO_2, H_2O, NH_3, H_2SO_4 etc.

Mixtures contain more than one type of particles. There are two types of mixtures –**Mixtures having uniform composition throughout are called homogeneous mixtures.** E.g. all type of solutions, air etc. Mixtures having different compositions at different parts are called **heterogeneous mixtures**. E.g. sea water, soil etc.

Mass and Weight : Mass is the amount of matter present in a body. It is a constant quantity. Its SI unit is kilogram (kg). Weight is the gravitational force acting on a body. It is a variable quantity. i.e. it changes with place. Its SI unit is newton (N).

Temperature (T)

It is the degree of hotness or coldness of a body. It is commonly expressed in degree Celsius (^{0}C). Other units are degree Fahrenheit (^{0}F), Kelvin (K) etc. its SI unit is Kelvin (K).

Degree Celsius and degree Fahrenheit are related as:

^{0}F = 9/5(^{0}C) + 32

Degree celsius and Kelvin are related as:

$$K = {}^{0}C + 273.15$$

Precision and Accuracy

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

Scientific Notation: In which any number can be represented in the form $N \times 10^n$

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

Significant Figures

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**.

There are certain rules for determining the number of significant figures. These are:

1. All non-zero digits are significant.
2. Zeros preceding to first non-zero digit are not significant. Such zero indicates the position of decimal point.
3. Zeros between two non-zero digits are significant.
4. Zeros at the end or right of a number are significant if they are on the right side of the decimal point; otherwise, they are not significant.
5. Exact numbers have an infinite number of significant figures.
6. When numbers are written in scientific notation, the number of digits between 1 and 10 gives the number of significant figures.

LAWS OF CHEMICAL COMBINATIONS

The combination of elements to form compounds is governed by the following five basic laws:

1. Law of Conservation of Mass : This law was proposed by **Antoine Lavoisier**. **It states that matter can neither be created nor destroyed. We can only convert one form of matter into another form. Or, in a chemical reaction, the total mass of reactants is equal to the total mass of products**.

Consider the reaction $2H_2 + O_2 \rightarrow 2H_2O$

Total mass of reactants = 4 + 32 = 36g

Total mass of products = 36 g

2. **Law of Definite Proportions (Law of definite composition):** This law was proposed by **Joseph Proust**. **It states that a given compound always contains exactly the same proportion of elements by weight. Or, the same compound always contains the same elements combined in a fixed ratio by mass.**

Illustration: Carbon dioxide contains only two elements Carbon and Oxygen combined in a mass ratio 3:8.

3. **Law of Multiple Proportions**: This law was proposed by **John Dalton. It states that if two elements can combine to form more than one compound, the different masses of one of the elements that combine with a fixed mass of the other element, are in small whole number ratio.**

Illustration: Hydrogen combines with oxygen to form two compounds – water and hydrogen peroxide.

Hydrogen + Oxygen → Water

   2g   16g   18g

Hydrogen + Oxygen → Hydrogen Peroxide

   2g   32g   34g
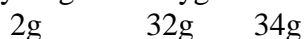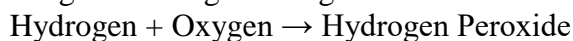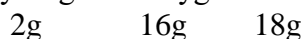
Here, the masses of oxygen (i.e. 16 g and 32 g) which combine with a fixed mass of hydrogen (2g) bear a simple ratio, i.e. 16:32 or 1: 2.

4. **Gay Lussac's Law of Gaseous Volumes**: This law was proposed by **Gay Lussac**. **It states that when gases combine to form gaseous products, their volumes are in simple whole number ratio at constant temperature and pressure.**

Illustration:

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$. the volumes of hydrogen and oxygen which combine together bear a simple ratio of 2:1.

5. **Avogadro's Law**: **It states that equal volumes of all gases at the same temperature and pressure should contain equal number of moles or molecules**.

DALTON'S ATOMIC THEORY

The important postulates of this theory are:

1. Matter is made up of minute and indivisible particles called atoms.
2. Atoms can neither be created nor be destroyed.
3. Atoms of same element are identical in their properties and mass. While atoms of different elements have different properties and mass.
4. Atoms combined to form compound atoms called molecules.
5. When atoms combine, they do so in a fixed ratio by mass.

Atomic mass

Atomic mass of an element is a number that expresses how many times the mass of an atom of the element is greater than $1/12^{th}$ the mass of a C^{12} atom.

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

For e.g. atomic mass of Nitrogen is 14, which means that mass of one N atom is 14 times greater than $1/12^{th}$ the mass of a C^{12} atom. $1/12^{th}$ the mass of a C^{12} atom is called atomic mass unit (amu). Today, 'amu' has been replaced by 'u' which is known as unified mass.

Average atomic mass: All most all the elements have isotopes. So we can calculate an average atomic mass of an element by considering the atomic mass of the isotopes and their relative abundance. For e.g. chlorine has two isotopes Cl^{35} and Cl^{37} in the ratio 3:1. So the average atomic mass Cl = (3x35 + 1x37)/4 =35.5

Molecular mass: Molecular mass is the sum of atomic masses of the elements present in a molecule. For e.g. molecular mass of H_2SO_4 is calculated as: 2 x 1 + 32 + 4 x 16 = 98 u.

Formula mass:

In the case of ionic compounds (like NaCl), there is no discrete (separate) molecules. Here the positive ions and the negative ions are arranged in a three-dimensional structure. So we can calculate only formula mass by taking molecular formula of the compound.

Mole concept

Mole is the unit of amount of substance. It is defined as the amount of substance that contains as many particles as there are atoms in exactly 12 g C^{12} isotope. **1 mole of any substance contains 6.022 x 10^{23} atoms**. This number is known as **Avogadro number or Avogadro constant** (N_A or N_0).

1 mol of hydrogen atoms = 6.022×10^{23} atoms
1 mol of water molecules = 6.022×10^{23} water molecules
1 mol of sodium chloride = 6.022×10^{23} formula units of sodium chloride

Molar mass: The mass of one mole of a substance in gram is called its molar mass (gram molecular mass).
Molar volume: It is the volume of 1 mole of any substance at STP. molar volume of any gas = 22.4
For e.g. 22.4 L of hydrogen gas = 1 mole of H_2 = 6.022×10^{23} molecules of hydrogen = 2 g of H_2

Percentage composition

It is the percentage of each element present in 100g of a substance.

$$\text{percentage of an element} = \frac{Mass \ of \ the \ element \ in \ the \ compound}{molar \ mass \ of \ the \ compound} \ x100$$

Empirical Formula and Molecular Formula—

An **empirical formula** represents the simplest whole number ratio of various atoms present in a compound. Eg. 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. Eg. 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

$$n = \frac{molar\ mass}{empirical\ formula\ mass}$$

Stoichiometry and Stoichiometric calculations

The study about the quantitative relationship between the masses or the volumes of reactants and the products.

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

Reactions in solutions

Solutions are homogeneous mixture containing 2 or more components. **The component which is present in larger quantity is called solvent and the other components are called solutes.** For e.g. in NaCl solution, NaCl is the solute and water is the solvent.

Concentration of solution

It is defined as the amount of solute present in a given volume of solution. Concentration can be expressed in the following ways:

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

$$\textbf{Mass \%} = \frac{mass\ of\ the\ solute}{mass\ of\ the\ solution}\ x100$$

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

$$\textbf{Volume\%} = \frac{volume\ of\ the\ solute}{volume\ of\ the\ solution}\ x100$$

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

$$Molarity\ (M) = \frac{No.of\ moles\ of\ solute}{volume\ of\ solution\ in\ litre} = \frac{n}{V}$$

Molarity equation

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

$$M_1V_1 = M_2V_2,$$

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

$$Molality = \frac{no,of\ moles\ of\ solute}{mass\ 0f\ solvent\ in\ kilogram} = \frac{n}{WA}$$

6. **Mole Fraction**. It 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'. If n_A and n_B are the number of moles of solute and solvent. then

Mole fraction of the solute = $X_B = \frac{nB}{nA+nB}$

Mole fraction of the solvent = $X_A = \frac{nA}{nA+nB}$

for a binary solution $X_A + X_B = 1$

Questions	Answer
1. Which of the following is dependent on temperature? (a) Molarity (b) Molality (c) Mole fraction (d) Mass percentage	**(a)**
2. If the concentration of glucose ($C_6H_{12}O_6$) in blood is 0.9 g L molarity of glucose in blood? a) 5M b) 50M c) 0.005 M d) 0.5 M	(c)
3. What is the mass percent of carbon in carbon dioxide? a) 0.034% b) 27.27% c) 3.4% d) 28.7%	(b)
4. The empirical formula and molecular mass of a compound are CH_2O and 180 g respectively. What will be the molecular formula of the compound? a) $C_9H_{18}O_9$ b) CH_2O c) $C_6H_{12}O_6$ d) $C_2H_4O_2$	(c)
5. the total number of ions present in 111 g of $CaCl_2$ is (a) One Mole (b) Two Mole (c) Three Mole (d) Four Mole	(c)

6. Which one will have maximum numbers of water molecules?
   (a) 18 molecules of water   (b) 1.8 grams of water
   (c) 18 grams of water   (d) 18 moles of water
	(d)

7. There are two chlorides of sulphur S_2Cl_2 and SCl_2. What is the equivalent mass of Sin SCl_2 (a) 64.8 g/mole (b) 32 g/mole (c) 16 g/mole (d) 8 g/mole	(c)
8. Which is not a unit of pressure: (a) Bar (b) N/m² (c) Kg/m² (d) Torr	(c)
9. What is the normality of a 1 M solution of H_3PO_4 (a) 0.5 N (b) 1.0 N (c) 2.0 N (d) 3.0 N	(d)
10. The significant figures in 3400 are (a) 2 (b) 5 (c) 6 (d) 4	(d)
11. Which of the following contains the same number of carbon atoms as are in 6.0 g of carbon (C – 12)? (a) 6.0 g Ethane (b) 8.0g Methane (c) 21.0g Propane (d) 28.0 g CO	(b)

ASSERTION AND REASON QUESTIONS

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.
 a) If both Assertion & Reason are true and the reason is the correct explanation of the assertion.
 b) If both Assertion & Reason are true but the reason is not the correct explanation of the assertion.
 c) If Assertion is a true statement but Reason is false.
 d) If both Assertion and Reason are false statements.
 1. Assertion (A): The empirical mass of ethene is half of its molecular mass.
 Reason (R): The empirical formula represents the simplest whole number ratio of various atoms present in a compound.   **Answer : (b)**
 2.Assertion (A) : One atomic mass unit is defined as one twelfth of the mass of one carbon-12 atom.
 Reason (R) : Carbon-12 isotope is the most abundant isotope of carbon and has been chosen as standard.

Answer : (b)

3.Assertion (A) : Significant figures for 0.200 is 3 whereas for 200 it is 1.
Reason (R) : Zero at the end or right of a number are significant provided they are not on the right side of the decimal point. **Answer: (c)**

4. Assertion (A): Combustion of 16 g of methane gives 28 g of water.
Reason (R): In the combustion of methane, hydrogen is one of the products. **Answer: (d)**

5. Assertion: Molarity is number of moles of solute in 1 lit of solution
Reason: Molality does not change with temperature. **Answer: (b)**

One Mark questions with answers

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

Ans: Molar mass of H_2SO_4= 2+32+4*16=98 amu
     Molar mass of NaOH = 23+16+1=40amu

2. What do mean by Mole fraction?

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

3.What is the limiting reagent?

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

4.What is the relation between temperature in degrees Celsius and degree Fahrenheit?
   Ans.

$$°F = \frac{9}{5}(°C) + 32$$

5.Define one mole?

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

6.Write the empirical formula of the following:

   (a)N_2O_4 (b)$_6H_{12}O_6$ (c) H_2O (d) H_2O_2
   Ans. (a)NO_2 (b) CH_2O (c) H_2O (d) HO

7.Briefly explain the difference between precision and accuracy.

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

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

Compound	CO	CO_2
Mass of C	12	12
Mass of O	16	32

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

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

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

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

Ans. Molar mass of Na_2CO_3= 2 x 23 +12 + 3 x 16 = 106 g / mol
     0.50 mol Na_2CO_3 and 0.50 x 106 = 53 g

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

Three Marks questions with answers-

1.How many molecules approximately do you expect to be present in a small crystal of sugar which weighs 10 mg?

Answer:

10 mg sugar $(C_{12}H_{22}O_{11})$ = 0.01 g = 0.01/342 mol

= 2.92×10^{-5} mole

= $2.92 \times 10^{-5} \times 6.02 \times 10^{23}$ molecules

= 1.76×10^{19} molecules.

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

And. The number of moles of solute dissolved per litre (dm^3) of the solution is called molarity
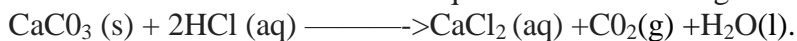
$$\text{Since molarity (M)} = \frac{n}{V \text{ in lit}} = \frac{w}{M.V \text{ in lit}} = \frac{4}{40*0.25 \text{ lit}} = 0.4M$$

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

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

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

4.Calcium carbonate reacts with aqueous HCl according to the reaction

$CaCO_3$ (s) + 2HCl (aq) ———->$CaCl_2$ (aq) +CO_2(g) +H_2O(l).
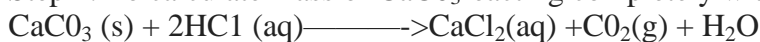
What mass of $CaCO_3$ is required to react completely with 25 mL of 0.75 M

Step 1. To calculate mass of HCl in 25 mL of 0.75 m HCl

1000 mL of 0.75 M HCl contain HCl = 0.75 mol = 0.75 x 36.5 g = 24.375 g

$\therefore$ 25 mL of 0.75 HCl will contain HCl = $\frac{24.375}{1000} \times 25$ g = 0.6844 g.

Step 2. To calculate mass of $CaCO_3$ reacting completely with 0.9125 g of HCl

$CaCO_3$ (s) + 2HCl (aq)———->$CaCl_2$(aq) +CO_2(g) + H_2O

2 mol of HCl, i.e., 2 x 36.5 g = 73 g HCl react completely with $CaCO_3$ = 1 mol = 100 g

$\therefore$ 0.6844 g HCl will react completely with $CaCO_3$ = $\frac{100}{73} \times 0.6844$ g = 0.938 g.

5.Chlorine is prepared in the laboratory by treating manganese dioxide (MnO_2) with aqueous hydrochloric acid according to the reaction.

4 HCl (aq) + MnO_2 (s) ———> 2 H_2O (l) + $MnCl_2$(aq) +Cl_2(g)
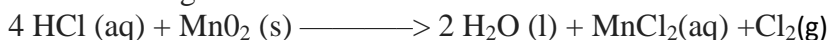
How many grams of HCl react with 5.0 g of manganese dioxide? (Atomic mass of Mn = 55 u)

Answer: 1 mole of MnO_2, i.e., 55 + 32 = 87 g MnO_2 react with 4 moles of HCl, i.e., 4 x 36.5 g = 146 g of HCl.

$\therefore$ 5.0 g of MnO_2 will react with HCl = $\frac{146}{87} \times 5.0$ g = 8.40 g

Case based questions with answers

1.The mass of one mole of a substance in grams is called its molar mass. the molar mass in grams is numerically equal to atomic molecular/formula mass in u. An empirical formula represents the simplest whole number ratio of various atoms present in a compound, whereas, the molecular formula shows the exact number of different types of atoms present in a molecule of a compound. If the mass per cent of various elements present in a compound is known, its empirical formula can be determined. Molecular formula can further be obtained if the molar mass is known. Many a time, reactions are carried out with the Amounts of reactants that are different than The amounts as required by a balanced chemical reaction. In such situations, one Reactant is in more amount than the amount required by balanced chemical reaction. The reactant which is present in the least amount Many a time, reactions are carried out with the amounts of reactants that are different than the amounts as required by a balanced chemical reaction. In such situations, one reactant is in more amount than the amount required by balanced chemical reaction. The reactant which is present in the least amount gets consumed after sometime and after that further reaction

does not take place whatever be the amount of the other reactant. Hence, the reactant, which gets consumed first, limits the amount of product formed and is, therefore, called the limiting reagent.

1) One atomic mass unit (amu) is defined as a mass exactly equal to one-twelfth of the mass of one …atom.

(a) Hydrogen – 1   (b) carbon – 12   (c) Oxygen -12   (d) Chlorine – 35

Ans – b) carbon – 12

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

(a) Atomic mass   (b) Molecular Weight   (c) Molecular mass   (d) molar mass.

Ans – d) molar mass

3) … is the sum of atomic masses of the elements present in a molecule.

(a) Atomic mass   (b) Molecular Weight (c) Molecular mass   (d) molar mass.

Ans – c) Molecular mass

4) One mole contains exactly …elementary entities.

(a) 02214076×10^{21} (b) 02214076×10^{22} (c) 02214076×10^{23} (d) 02214076×10^{24}

Ans – c) $6.02214076 \times 10^{23}$

Five Marks questions with answers-

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

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

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

The empirical formula of the above compound is CH_2Cl. empirical formula mass is 12 + (1x2) + 35.5 = 49.5

n= molecular mass/ empirical formula mass =98.96/49.5 = 2 Hence molecular formula is $C_2H_4Cl_2$

2. . Dinitrogen and dihydrogen react with each other to produce ammonia according to the following chemical equation:(i) N_2 (g) + $3H_2$(g) ——> $2NH_3$ (g)
(ii) Will any of the two reactants remain unreacted?
(iii) If yes, which one and what would be its mass?
Answer:

(i) 1 mol of N_2 i.e., 28 g react with 3 mol of H_2, i.e., 6 g of H_2

∴ 2000 g of N_2 will react with $H_2 = \dfrac{6}{28} \times 200\ g = 428.6\ g$. Thus, N_2 is the limiting reagent while H_2 is the excess reagent.

2 mol of N_2, i.e., 28 g of N_2 produce $NH_3 = 2\ mol = 34\ g$

∴ 2000 g of N_2 will produce $NH_3 = \dfrac{34}{28} \times 2000\ g = \mathbf{2428.57\ g}$

(ii) H_2 will remain unreacted.

(iii) Mass left unreacted = 1000 g – 428.6 g = 571.4 g

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

We know that

44g of CO2 contains 12 g of carbon.

3.38 g of CO_2 will contain carbon $= \dfrac{12\ X\ 3.38}{44} = 0.9217g$

18 g of water contains 2 g of hydrogen.

0.690 g of water will contain hydrogen $= \dfrac{2\ x\ 0.690}{18} = 0.0767g$

Since carbon and hydrogen are the only constituents of the compound, the total mass of

the compound is:= 0.9217 g + 0.0767 g= 0.9984 g

Percent of C in the compound $= \dfrac{0.9217\ x100}{0.9984} = 92.32\%$

Percent of H in the compound $= \dfrac{0.0767\ x100}{0.9984} = 7.68$

Moles of carbon in the compound $= \dfrac{92.32}{12} = 7.69$

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

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

(ii) Given,

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

Weight of 22.4 L of gas at STP $= \dfrac{11.6g\ x22.4\ L}{10L} = 25.984\ g = 26g$

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

Empirical formula mass of CH = 12 + 1 = 13 g

$n = \dfrac{molar\ mass\ of\ gas}{empirical\ formula\ mass\ of\ gas} = \dfrac{26g}{13g} = 2$

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

HOTS (Higher Order Thinking Skills

1. A compound made up of two elements A and B has A= 70 %, B = 30 %. Their relative number of moles in the compound are 1.25 and 1.88. calculate
   a. Atomic masses of the elements A and B

b. Molecular formula of the compound , if its molecular mass is found to be 160

Ans: No. of moles $= \frac{\% \text{ of element}}{\text{atomic mass}}$, Atomic mass $= \frac{\% \text{ of element}}{\text{no, of moles}}$

Atomic mass of A $= \frac{\% \text{ of element}}{\text{no, of moles}} = \frac{70}{1.25} = 56$

Atomic mass of B $= \frac{\% \text{ of element}}{\text{no, of moles}} = \frac{30}{1.88} = 16$

Empirical formula

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

Empirical formula $= A_2B_3$

Calculation of molecular formula-

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

N$= \frac{\text{molecular mass}}{\text{empirical formula mass}} = \frac{160}{160} = 1$

Molecular formula $= A_2B_3$

2.STRUCTUREOF ATOM

1. Discovery of Electron by cathode ray discharge tubes

In 1879, William Crooks studied the conduction of electricity through gases at low pressure. A cathode ray tube is made of glass containing two thin pieces of metal, called electrodes, sealed in it. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages. When sufficiently high voltage is applied across the electrodes, current starts flowing through a stream of particles moving in the tube from the negative electrode (cathode) to the positive electrode (anode). These were called **cathode rays or cathode ray particles**.
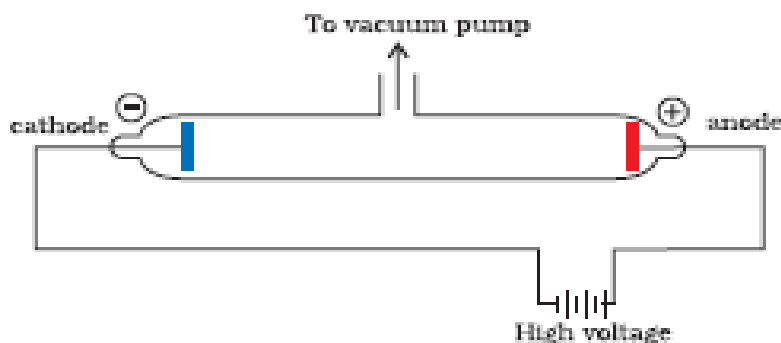
Properties of cathode rays:
(i) The cathode rays start from cathode and move towards the anode.
(ii) These rays themselves are not visible but they produce fluorescence on ZnS screen.
(iii) In the absence of electrical or magnetic field, these rays travel in straight lines
(iv) In the presence of electrical or magnetic field, the behavior of cathode rays are similar to that expected from negatively charged particles, suggesting that the cathode rays consist of negatively charged particles, called **electrons.**
(v) The characteristics of cathode rays(electrons) do not depend upon the material of electrodes and the nature of the gas present in the cathode ray tube.

Charge to Mass Ratio of Electron
J.J. Thomson measured the ratio of electrical charge (e) to the mass of electron (m_e) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons .
$e/m_e = 1.758820 \times 10^{11}$ C kg^{-1}
where me = Mass of the electron in kg
e = magnitude of charge on the electron in coulomb (C).

Discovery of proton anode ray
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
(i) The value of positive charge on the particles constituting anode rays depends upon the nature of the gas in the discharge tube.
(ii) The charge to mass ratio of the particles is found to depend on the gas from which these originate.
(iii) Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge.
(iv)The behavior of these particles in the magnetic or electric field is opposite to that observed for electron or cathode rays.

Proton: The smallest and lightest positive ion was obtained from hydrogen and was called proton. Mass of proton = 1.676×10^{-27} kg
Charge on a proton = (+) 1.602×10^{-19} C

Neutron: It is a neutral particle. It was discovered by Chadwick (1932).
By the bombardment of thin sheets of beryllium with fast moving a-particles he observed • that highly penetrating rays consist of neutral particles which were named neutrons.

Thomson Model of Atom: An atom possesses a spherical shape (radius approximately 10–10 m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement
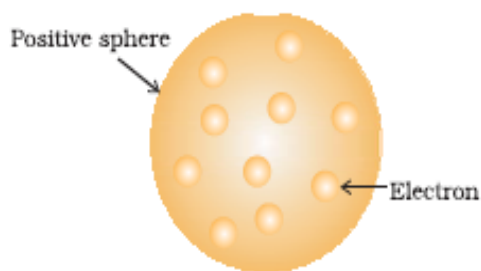

An important feature of this model is that the mass of the atom is assumed to be uniformly distributed over the atom.

Drawback of Thomson Model of Atom
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 Nuclear Model of Atom
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.
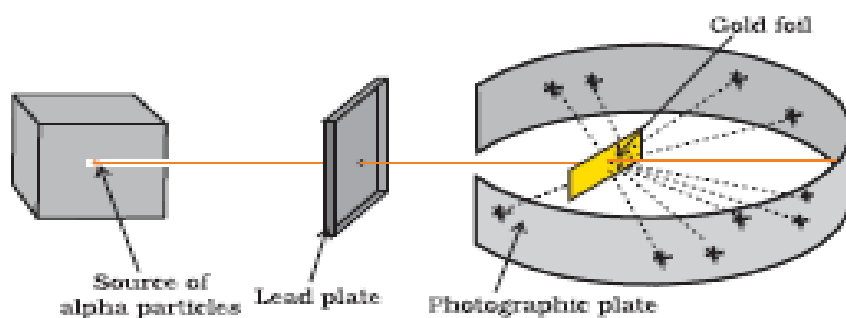
A. Rutherford's scattering experiment

The important observations are:
(i) Most of the a-particles passed through the foil without undergoing any deflection,
(ii) A few a-particles underwent deflection through small angles.
(iii) Very few mere deflected back i.e., through an angle of nearly 180°.

Conclusions:
(i) Since most of the a-particles passed through the foil without undergoing any deflection, there must be sufficient empty space within the atom.
(ii) A small fraction of a-particles was deflected by small angles. The positive charge has to be concentrated in a very small volume that repelled and deflected a few positively charged a-particles. This very small portion of the atom was called nucleus.
(iii) The volume of nucleus is very small as compared to total volume of atom..

Rutherford's Nuclear Model of an Atom
(i) The positive charge and most of the mass of the atom was densely concentrated in an extremely small region. This very small portion of the atom was called nucleus by Rutherford.
(ii) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits.
(iii) Electrons and nucleus are held together by electrostatic forces of attraction

Drawbacks of Rutherford Model

(i) Rutherford's model cannot explain the stability of atom if the motion of electrons is described on the basis of classical mechanics and electromagnetic theory.

(ii) Rutherford's model does not give any idea about distribution of electrons around the nucleus and about their energies.

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

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

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

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

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

Isobars : Isobars are the atoms with same mass number but different atomic number for Example $^{14}_{8}C$ and $^{14}_{7}N$.
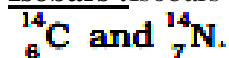
Developments Leading to the Bohr's Model of Atom -Two developments played a major role in the formulation of Bohr's model of atom. These were:

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

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

Nature of Electromagnetic Radiation (Electromagnetic Wave Theory)

This theory was put forward by James Clark Maxwell in 1864. The main points of this theory are as follows:

(i) The energy is emitted from any source (like the heated rod or the filament of a bulb through which electric current is passed) continuously in the form of radiations and is called the radiant energy.

(ii) The radiations consist of electric and magnetic fields oscillating perpendicular to each other and both perpendicular to the direction of propagation of the radiation.

(iii) The radiations possess wave character and travel with the velocity of light 3×10^{8} m/sec.

(iv) 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 –

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

(ii)Frequency: Frequency of a wave is defined as the number of waves passing through a point in one second. It is represented by v (nu) and is expressed in Hertz (Hz).

1 Hz = 1 cycle/sec. Velocity:

(iii) Velocity of a wave is defined as the linear distance travelled by the wave in one second.

It is represented by c and is expressed in cm/sec or m/sec.

(iv)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.

(v)Wave Number: It is defined as the number of waves present in 1 metre length. Evidently it will be

$$\overline{\nu} = \frac{1}{\lambda}$$

equal to the reciprocal of the wavelength. It is represented by bar v (read as nu bar).

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

Limitations of Electromagnetic Wave Theory

Electromagnetic wave theory was successful in explaining properties of light such as interference,

diffraction etc; but it could not explain the following:

(i) The phenomenon of black body radiation.

(ii) The photoelectric effect.

(iii) The variation of heat capacity of solids as a function of temperature.

(iv) The line spectra of atoms with reference to hydrogen.

Black Body Radiation

The ideal body, which emits and absorbs all frequencies is called a black body and the radiation emitted by such a body is called black body radiation. The exact frequency distribution of the emitted radiation from a black body depends only on its temperature.

At a given temperature, intensity of radiation emitted increases with decrease of wavelength, reaches a maximum value at a given wavelength and then starts decreasing with further decrease of wavelength as shown in Fig
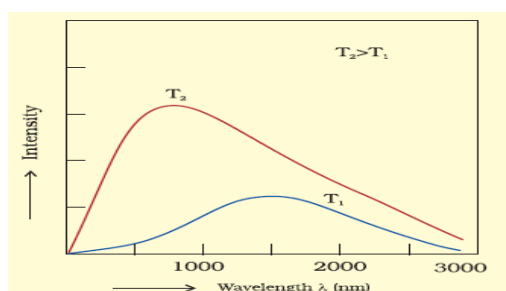
Planck's Quantum Theory

The main points of this theory was as follows:

i. Atoms and molecules could emit (or absorb) energy only in discrete quantities and not in a continuous manner.

ii. The smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation is called **quantum**.

The energy (E) of a quantum of radiation is proportional to its frequency (v) and is expressed by equation (2.6).

$$E = nhv \text{ , '}h\text{' is known as Planck's constant} = 6.626 \times 10^{-34} \text{ J s.}$$

Photoelectric effect

It is the phenomenon of ejection of electrons by certain metals (like potassium, rubidium, caesium etc.) when light of suitable frequency incident on them. The electrons ejected are called photoelectrons. This phenomenon was first observed by **H.Hertz**.

The important characteristics of photoelectric effect are:

1. Only photons of light of certain minimum frequency called threshold frequency (v_0) can cause the photoelectric effect. The value of v_0 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.
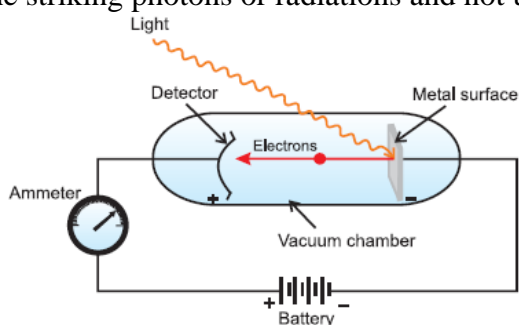
Explanation of Photoelectric Effect

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

(i) Photoelectrons are ejected only when the incident light has a certain minimum frequency (threshold frequency v_0)

(ii) If the frequency of the incident light (v) is more than the threshold frequency (v_0), the excess energy ($hv - hv_0$) is imparted to the electron as kinetic energy.

(iii) On increasing the intensity of light, more electrons are ejected but the energies of the electrons are not altered.

Following the law of conservation of energy principle, the kinetic energy of the ejected electron is given by

K.E = hv - hv$_0$

hv = hv$_0$ + 1/2m$_e$v^2

Dual Behaviors of Electromagnetic Radiation

Light possesses both particle and wave-like properties, i.e., light has dual behaviour.

The particle nature of light could be explained the black body radiation and photoelectric effect. The wave behavior of light could be explained by the phenomena of interference and diffraction.

Atomic spectrum

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

Emission and Absorption Spectra

Emission Spectra   Emission Spectra is noticed when the radiations emitted from a source are passed through a prism and then received on the photographic plate. Radiations can be emitted in a number of ways such as:

(i) from sun or glowing electric bulb.

(ii) by passing electric discharge through a gas at low pressure.

(iii) by heating a substance to high temperature.

The emission spectra of atoms in the gas phase do not form a continuous spectrum.

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

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

Line Spectrum of Hydrogen

When electric discharge is passed through hydrogen gas enclosed in discharge tube under low pressure and the emitted light is 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.

$$\bar{v} = 109,677 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] cm^{-1}$$

where

$n_1 = 1, 2 \ldots\ldots\ldots$

$n_2 = n_1 + 1, n_1 + 2 \ldots\ldots\ldots$

The value 109, 677 cm^{-1} is called the Rydberg constant for hydrogen.
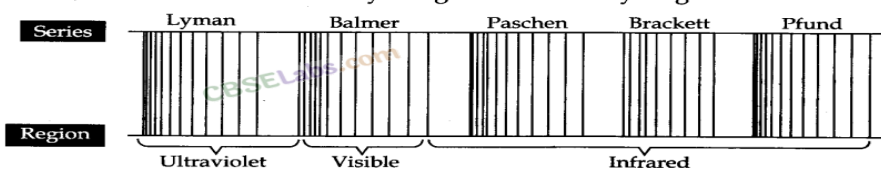

Fig. 2.8 Atomic spectrum of hydrogen.

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

Here R_H = constant, called Rydberg constant for hydrogen and n_1 , n_2 are integers (n2 > n1)

For any particular series, the value of n1 is constant while that of n2 changes. For example,

For Lyman series, n_1= 1, n_2= 2, 3, 4, 5………..

For Balmer series, n_1 = 2, n_2 = 3, 4, 5, 6………..

For Paschen series, n_1= 3, n_2 = 4, 5, 6, 7………..

For Brackett series,n_1 = 4, n_2 = 5, 6, 7, 8………..

For Pfund series, n_1 =5, n_2 = 6, 7, 8, 9………..

Thus, by substituting the values of n_1 and n_2 in the above equation, wavelengths and wave number of different spectral lines can be calculated. When n_1 = 2, the expression given above is called Balmer's formula.

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

(i) In an atom, the electrons revolve around the nucleus in certain definite circular paths called orbits.

(ii) Each orbit is associated with definite energy and therefore these are known as energy levels or energy shells. These are numbered as 1, 2, 3, 4……….. or K, L, M, N………..

(iii) Only those energy orbits are permitted for the electron in which angular momentum of the electron is a whole number multiple of $h/2\pi$

Angular momentum of electron (mvr) $= \frac{nh}{2\pi}$ (n = 1, 2, 3, 4 etc).

m = mass of the electron   v = tangential velocity of the revolving electron.

    r = radius of the orbit.   h = Planck's constant.   n is an integer.

(iv) As long as electron is present in a particular orbit, it neither absorbs nor loses energy and its energy, therefore, remains constant.

(v) When energy is supplied to an electron, it absorbs energy only in fixed amounts as quanta and jumps to higher energy state away from the nucleus known as excited state. The excited state is unstable, the electron may jump back to the lower energy state and in doing so, it emits the same amount of energy. ($\Delta E = E_2 - E_1$).

vi. The radius of orbits can be given by the equation: $r_n = a_0 n^2$ where $a_0 = 52.9$ pm. Thus the radius of the first stationary state is 52.9 pm (called the Bohr radius). As n increases, the value of r will increase.

vii. It is also possible to calculate the velocities of electrons moving in these orbits. Qualitatively the magnitude of velocity of electron increases with increase of positive charge on the nucleus and decreases with increase of principal quantum number

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.

Limitations of Bohr Atom Model

Bohr atom model could explain the stability and line spectra of hydrogen atom and hydrogen like ions (e.g. He^+, Li^{2+}, Be^{3+} etc). But it has the following limitations:

1. It could not explain the fine spectrum of hydrogen atom.

2. It could not explain the spectrum of atoms other than hydrogen.

3. It was unable to explain the splitting of spectral lines in the presence of electric field (**Stark effect**) and in magnetic field (**Zeeman effect**).

4. It could not explain the ability of atoms to form molecules by chemical bonds.

5. It did not consider the wave character of matter and Heisenberg's uncertainty principle.

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.

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

Heisenberg's Uncertainty Principle

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

$$\Delta x.\Delta p \geq \frac{h}{4\pi} \ , \qquad \Delta x.m\Delta v \geq \frac{h}{4\pi} \ , \qquad \Delta x.\Delta v \geq \frac{h}{4\pi m}$$

Significance of Uncertainty Principle

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

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

Reasons for the Failure of Bohr Model

(i) The wave character of the electron is not considered in Bohr Model.

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

Quantum Mechanical Model of Atom

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

Important Features of Quantum Mechanical Model of Atom:

(i) The energy of electrons in atom is quantized i.e., can only have certain values.

(ii) The existence of quantized electronic energy level is a direct result of the wave like properties of electrons.

(iii) Both the exact position and exact velocity of an electron in an atom cannot be determined simultaneously.

(iv) An atomic orbital has wave function φ. There are many orbitals in an atom. Electron occupy an atomic orbital which has definite energy. An orbital cannot have more than two electrons. The orbitals are filled in increasing order of energy. All the information about the electron in an atom is stored in orbital wave function φ.

(v) The probability of finding electron at a point within an atom is proportional to square of orbital wave function i.e., $|\varphi^2|$ at that point. It is known as probability density and is always positive.

From the value of φ^2 at different points within atom, it is possible to predict the region around the nucleus where electron most probably will be found.

Quantum Numbers

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

The principal quantum number gives us the following information:

The following information's are obtained from n.

1. It gives the size the orbit.

2. It gives the energy of electron in an orbit.

3. It gives the shell in which the electron is found.

4. It also gives the average distance between the electron and the nucleus. As the value of n increases, the distance between the electron and the nucleus also increases.

The possible values of n are 1, 2, 3, 4, 5 etc.

If n = 1 the electron is in K shell

n = 2 the electron is in L shell

n = 3 the electron is in M shell and so on.

5. The maximum number of electrons in the shell with principal quantum number n is equal to **$2n^2$.**

Azimuthal or Subsidiary or Orbital Angular Quantum Number (l)

The following information's are obtained from l.

1. It gives the shape of the orbital.

2. It gives the sub shell or sub level in which the electron is located.

3. It also gives the orbital angular momentum of the electron.

4. the values of l = 0 to (n-1)

The number of sub shells in a principal shell is equal to the value of n. For example,

When n = 1, l = 0. i.e. K shell contains only one sub shell - s sub shell

when n = 2, l = 0 and 1. i.e. L shell contains two sub shells - s and p sub shells

when n = 3, l = 0, 1 and 2. i.e. M shell contains three sub shells – s, p and d sub shells

when n = 4, l = 0, 1, 2 and 3. i.e. N shell contains four sub shells – s, p,d and f sub shells

4. the number of electrons that can be accommodated in sub-energy level is equal to **2(2l+1).**

If l = 0 for   s orbital then= 2(2*1+1)=2 electrons

If l =1 for   p orbital then= 2(2*2+1)=6 electrons

If l = 2 for   d orbital then= 2(2*3+1)=10 electrons

if l = 3 for   f orbital then= 2(2*3+1)=14 electrons

Magnetic Orbital Quantum Number (m or m1)

1. The magnetic orbital quantum number determines the number of preferred orientations of the electrons present in a sub-shell.

2. The magnetic quantum number is denoted by letter m and for a given value of l, it can have all the values ranging from $-l$ to $+l$ including zero.

Thus, for energy value of l, m has $2l + 1$ values.

For example,

For l = 0 (s-sub-shell), m can have only one value i.e., m = 0.

This means that s-sub-shell has only one orientation in space. In other words, s-subshell has only one orbital called s-orbital.

## Spin Quantum Number (S or ms)

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

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

The plots of probability density (ψ^2) against distance from the nucleus (r) for 1s and 2s atomic orbitals are as follows:
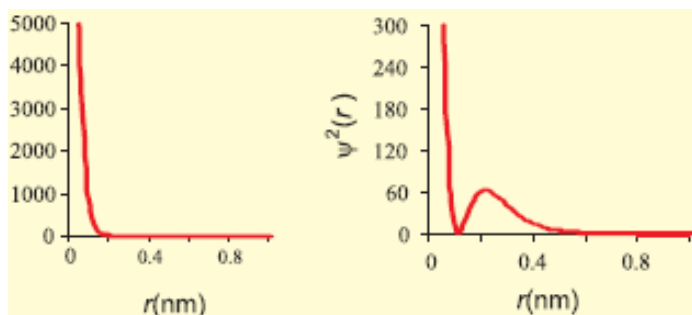
The probability of 1s electron is found to be maximum near the nucleus and decreases with the increase in the distance from the nucleus. In 2s electron, the probability is also maximum near the nucleus and decreases to zero probability. The spherical empty shell for 2s electron is called nodal surface or simply node.
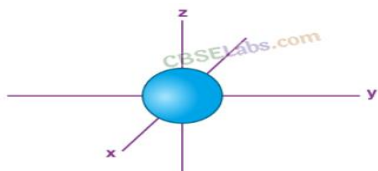
Shapes of p-orbitals

p-orbitals are present in the p-subshell for which l = 1 and m_l can have three possible orientations – 1, 0, + 1.

Thus, there are three orbitals in the p-subshell which are designated as p_x, p_y and p_z orbitals depending upon the axis along which they are directed. The general shape of a p-orbital is dumb-bell consisting of two portions known as lobes. Moreover, there is a plane passing through the nucleus along which finding of the electron density is almost nil. This is known as nodal plane as shown in the fig.
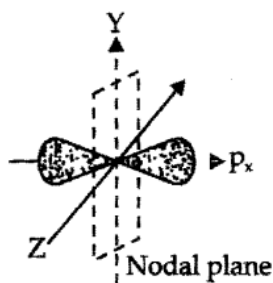
General shape of p-orbital
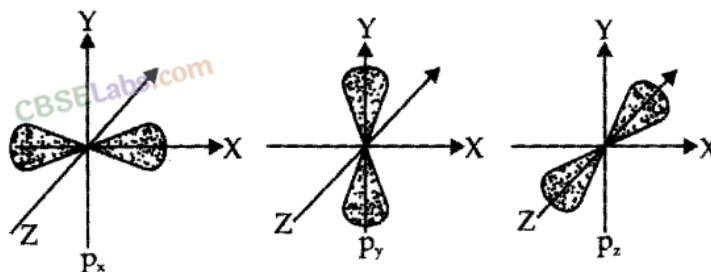
Shapes of $2p_x$, $2p_y$ and $2p_z$ orbitals.

Fig. 2.10

From the dumb-bell pictures, it is quite obvious that unlike s-orbital, a p-orbital is directional in nature and hence it influences the shapes of the molecules in the formation of which it participates.

Number of radial nodes = n - l – 1

Number of angular nodes = l

Total number of nodes = n-1

• Shapes of d-orbitals

For d-orbitals, l = 2 and ml = -2, -1, 0, +1 and +2. i.e., there are five possible orientations for d orbitals. So there are 5 types of d-orbitals. They are dxy, dxz, dyz, dx^2-y^2 and dz^2. . The shapes of the first four d-orbitals are double dumb-bell and that of the fifth one, dz^2, is dumb-bell having a circular collar in the XY-plane. The five d-orbitals have equivalent energies. For d orbitals the number of radial nodes is 2 and the total number of nodes is n-2. Boundary surface diagrams for d-orbitals are as follows.
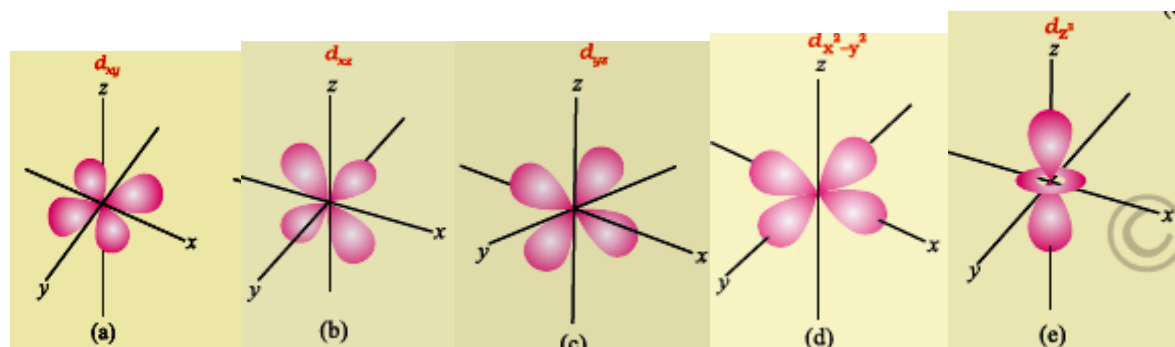

f-orbitals:

For f-orbitals, l = 3 and m_l = -3, -2,-1.0.+1,+2 and +3. i.e., there are seven possible orientations for f orbitals.so there are 7 types of f-orbitals. They have diffused shapes.

Electronic Configuration of Atoms

The distribution of electrons into orbitals of an atom is called its electronic configuration. The electronic configuration is explained based on **Aufbau principle,** Hund's rule, Pauli's exclusion principle and stability concept.

1. **Aufbau principle**:

The principle states: **In the ground state of the atoms, the orbitals are filled in order of their increasing energies.**

In other words, electrons first occupy the lowest energy orbital available to them and enter into higher energy orbitals only after the lower energy orbitals are filled.

This rule has two sub rules:

a) The various orbitals are filled in the increasing order of their (n+l) value.

b) If two orbitals have the same (n+l) values, the orbital with the lower n value is filled first. The increasing order of orbitals is as follows.
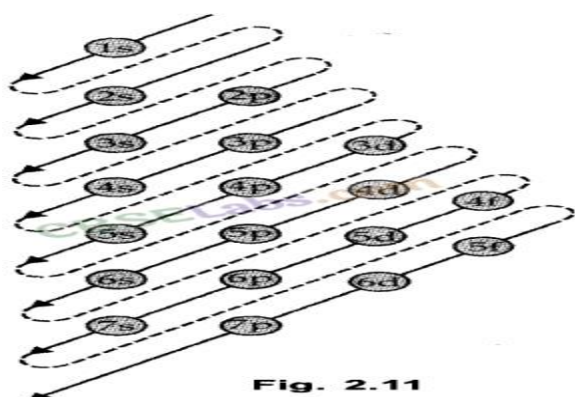

Fig. 2.11

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Pauli Exclusion Principle

According to this principle, no two electrons in an atom can have the same set of four quantum numbers. Only two electrons may exist in the same orbital and these electrons must have opposite spins.If 2 electrons have same values for n, l and m, they should have different values for s. i.e. if s = +1/2. for the first electron, it should be -1/2. for the second electron.

3. Hund's rule of maximum multiplicity

It states that: pairing of electrons in the orbitals belonging to the same sub-shell (p, d or f) does not take place until each orbital belonging to that sub-shell has got one electron each with parallelspin. For example the electronic configuration of N is $1s^2 2s^2 2p_x^1 p_y^1 p_z^1$ and not $1s^2 2s^2 2p_x^2 p_y^1$.
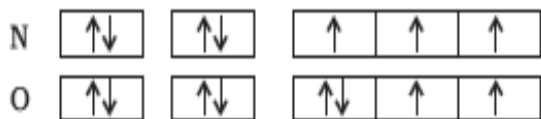
Stability of Completely Filled and Half Filled Subshells

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

$Cr(24) = [Ar] 3d^5 4s^1$ not $[Ar] 3d^4 4s^2$
Similarly
$Cu(29) = [Ar] 3d^{10} 4s^1$ not $[Ar] 3d^9 4s^2$
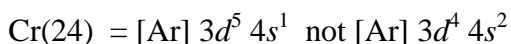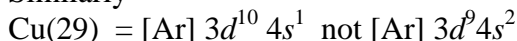
MCQ

1.Which of the following options does not represent ground state electronic configuration of an 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) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
 Ans .(b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$

2.Number of angular nodes for 4d orbital is _____.
(a) 4   (b) 3   (c) 2   (d) 1
Ans: (c) 2 Angular nodes = 'l' = 2 for d-orit.
3. The number of radial nodes for 3p orbital is _____.
(a) 3   (b) 4   (c) 2   (d) 1
Ans: d) 1. Number of radial nods = n – l – 1 = 3 – 1 – 1 = 1
4. g subshell is characterised by:
(a)n = 5   (b) m = 3   (c) l = 4   (d)l = 5
Ans: (c)
5. Which expression represents de Brogile relationship?
(a) h/mu = p   (b) λ = h/mv   (c)λ = h/mp   (d)λ = u/p
Ans: (b)
6.Which of the following is responsible to rule out the existence of definite paths or trajectories of electrons? (a) Pauli's exclusion principle. (b) Heisenberg's uncertainty principle. (c) Hund's rule of maximum multiplicity. (d) Aufbau principle
Ans: (b) Heisenberg's uncertainty principle.
7. For which of the following sets of quantum numbers, an electron will have the highest energy?
(a) 3, 2, +1, +1/2 (b) 4, 2,-1,+1/2 (c) 4,1,0,-1/2 (d) 5,0,0,+1/2
Ans: (b)
8.Which of the following atoms or atom/ion have identical ground state configuration ?
(a) Li+ and He$^+$ (b) Cl$^-$ and Ar   (c)Na and K   9d)F$^+$ and Ne
Ans: (b)

9.The number of spherical nodes for 4d orbital is

(a) zero   (b) one   (c)two   (d)three

Ans: (b)

10. The configuration $1s^2 2s^2 2p^5 3s^1$ shows:

(a)ground state of fluorine   (b)exited state of fluorine

(c)exited state of neon   (d)exite state of O^{2-} ion

Ans: (c)

11.Which of the following orbitals has dumb-bell shape?

(a)s   (b)p   (c)d   (d) f

Ans: (b)

12.The total number of orbitals in a shell having principal quantu number n is

(a) 2n   (b)n^2 (c)$2n^2$ (d)n+1

Ans: (b)

13..What is the wavelength of light.Given energy $=3.03 \times 10^{-19}$ J, $h=6.6 \times 10^{-34}$ JS, $c=3 \times 10^8$ m/s

(a) 6.54 nm   (b)654nm   (c)0.654nm   (d)65.4nm

Ans: (b)

14.Azimuthal quantum number defines:

(a) e/m ratio of electron   (b)spin of electron

(c) angular momentum of electron   (d)magnetic momentum of electron

Ans: (c)

15..The correct order of increasing energy energy of atomic orbital is:

(a)5p<4f<6s<5d   (b)5p<6s<4f<5d

(c)4f<5p<5d<6s   (d)5p<5d<4f<6s

Ans: (b)

16.Iso-electronic species are:

(a)F^-,O^{-2} (b)F^-,O   (c)F^-,O^+ (d)F^-,O^{+2}

Ans: (a)

17.Quantum numbers n=2,l=1 represent:

(a)1s orbital   (b)2s orbital   (c) 2p orbital   (d)3d orbital

Ans: ©

18. The quantum number m of a free gaseous atom is associated with:

(a)The effective volume of the orbital

(b) The shape of the orbital

(c)The spatial orientation of the orbital

(d)The energy of the orbital in the absence of the magnetic field.

Ans: (c)

19. The energy of second Bohr orbit of hydrogen atom is -328 KJ/mol. Hence the energy of forth orbit would be:

(a)-41 KJ/mol   (b)-82 KJ/mol (c)-164 K/mol   (d)-1312 KJ/mol

Ans: (b)

20.The orientation of an atomic orbital is governed by:

(a) Principal quantum number   b) Azimuthal quantum number

C) Spin quantum number   d) Magnetic quantum number

Ans : (d)

Assertion –Reason type question

The questions given below consist of assertion (A)and reason (R).Use the following key to select the correct answer.

(a)If both assertion and reason are correct and reason is correct explanation for assertion.

(b) If both assertion and reason are correct and reason is not correct explanation for assertion.

(c) If assertion is correct and reason is in correct

(d) If both assertion and reason are incorrect.

1.A: Photoelectric effect is most readily shown by cesium.

  R: Photon have easiest access to the surface of cesium metal. **Answer: (c)**

2. A: An orbital cannot have more than 2 electrons and their spin must be opposite.

R: No two electrons in an atom can have same set of all four quantum numbers. **Answer:(a)**

3.A: Both position and momentum of an electron can not be determined simultaneously with maximum accuracy.

R: This is because of microscopic nature of electron. **Answer: (a)**

4 .A: The energy of an electron is mainly determined by principal quantum number.

R: The principal quantum number is the measure of the most probable distance of finding the electron around the nucleus. **Answer: (a)**

5.A: Fe^{3+} ion is more stable than Fe^{2+} ion in ground state.

R: Fe^{3+} ion has more number of unpaired electrons than Fe^{2+} ion. **Answer:(b)**

6.A: An orbital cannot have more than two electrons.

R: The two electrons in an orbital create opposite magnetic field **Answer: (c)**

7.A: The 19th electron in potassium atom enters 4s-orbital and not 3d orbital'

R: The energies of the orbitals can be compared with the help of(n+l) rules. **Answer:(a)**

Short answer questions   - (2 marks)

1. We don't see a car moving as a wave on the road why?

According to de Broglie's relation, $\lambda=h/mv$ i.e. $\lambda\alpha 1/m$ $\lambda=h/mv$ i.e. $\lambda\alpha 1m$ the mass of the car is very large and its wavelength (λ) or wave character is negligible. Therefore, we do not see a car moving like a wave.

2.What is the physical significance of Ψ^2?

Ans: Ψ^2 represents the probability of finding an electron. It is the probability of finding a particle specified by a particular wave function.

3.Which orbital is non directional?

Ans: S- orbital is spherically symmetrical i.e. it is non-directional. It has a spherical shape, like a hollow ball.

4.What is quantisation of energy?

Ans: Quantization of energy means the energy is distributed and transmitted in the form of packets. These packets are called photons.

5.Why spectral lines are considered as finger print?

Ans: identification of the elements can be done from these lines. Just like fingerprints, the spectral lines of no two elements resemble each other.

6. The two electrons in the 1s orbital of He have anti-parallel spin. Why do not they have parallel spin ?

Ans Two electrons present in same orbital cannot have parallel spin since they tend to repel each other. The inter-electronic repulsion will be high leading to increase in energy of the atom and decrease instability.

7.Why are 2d and 3f orbitals not possible?

Ans For n=2 ,the permitted value of l are 0 and 1.this means that 2nd shell has only s and p orbitals and not d .Similarly for n=3 ,the permissible values are 0,1and2 .thus only s,p and d orbitals are permitted not f.

8. Heinsberg uncertainity principle has no significance in our every day life. Explain.

Ans; In our daily life we can see only the moving macro and semi-micro-obejcts. The mass of the striking photons of light is too small to cause any shift in their position by the time the reflected photons form the image of the object. For such particles, there is no problem in measuring the exact momentum simultaneously. Thus, the principle has no relevance for such objects.

9.Out of 3d and 4s orbitals which is filled first?

Ans: 4s orbital is filled first because it has lower energy. The energies of the orbitals can be compared by their n+l values. For 4s orbital n+l(4+0) value is 4 while for 3d orbital, n+l (3+2) value is 5,Therefore 4s

orbital is filled before3d orbital.

10. A certain element A undergoes photoelectric emission when bombarded by one photon of indigo light. When the material containing the same element was bombarded by two photons of red light with a total of same energy as that of indigo photon , no electron was emitted. Explain.

Ans: It may be noted that an electron can absorb only one photon at a time and not two photons. Since the energy of the incident red light is less than the threshold energy, photoelectric effect will not take place or no electron will be emitted.

11. How many electrons can be filled in all the orbitals with n+l=5?

Ans: (n+l)=5 has 5s,4p and 3d orbitals with two, six and ten electrons respectively. Therefore, the total number of electrons=18.

Short answer questions   (3marks)

1Which of the followings are iso-electronic species, i.e. those having the same number of electrons?

Na^+, K^+, Mg^{2+}, Ca^{2+}, S^{2-}, Ar.

ANS: Na^+ $(11 - 1 = 10)$, Mg^{2+} $(12 - 2 = 10)$ have same number of electrons.

K^+ $(19 - 1 = 18)$, Ca^{2+} $(20 - 2 = 18)$,

S^{2-} $(16 + 2 = 18)$, Ar (18) are iso-electronic, i.e. they have same number of electrons.

2.What is the uncertainty in locating its position? [Given, $m_e = 9.11 \times 10^{-31}$ kg] An electron speed   of 40 m s^{-1} accurate upto 99.9 percent

Uncertainty in speed $= 100 - 99.99 = 0.01\%$

$$\Delta V = 40 \text{ m s}^{-1} \times \frac{0.01}{100} = 40 \times 10^{-4}$$
$$= 4 \times 10^{-3} \text{ m s}^{-1}$$

$$\Delta x. \, \Delta V = \frac{h}{4\pi m}$$

$$\Delta x = \frac{h}{4\pi m \Delta V}$$

$$\Delta x = \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 4 \times 10^{-3} \text{ m s}^{-1} \times 9.11 \times 10^{-31} \text{ kg} \times 3.142}$$

$$\Delta x = 1.447 \times 10^{-2} \text{ m}$$

3. An atom of an element contains 29 electrons and 35 neutrons. Deduce

(i) number of protons.

(ii) electronic configuration of the element.

(iii) number of paired electrons.

(iv) number of unpaired electrons.

ANS: (i) Electrons = 29, Neutrons = 35, Protons = Electrons = 29

(ii) Electronic configuration is

$1s^2 \, 2s^2 \, 2p^6 \, 3s^2 \, 3p^6 \, 4s^1 \, 3d^{10}$.

(iii) There are 28 paired electrons

(iv) There is one unpaired electron.

4.Yellow light emitted from a sodium lamp has a wavelength (2) of 580 nm. Calculate the frequency (v) and wave number (v) of yellow light.

Answer:

Step I. *Calculation of frequency of yellow light*

We know that

$$\nu = \frac{c}{\lambda}$$

$$c = 3 \times 10^8 \text{ m s}^{-1} ; \lambda = 580 \text{ nm} = 580 \times 10^{-9} \text{ m}$$

$$\therefore \quad \nu = \frac{(3 \times 10^8 \text{ m s}^{-1})}{(580 \times 10^{-9} \text{ m})} = \mathbf{5 \cdot 17 \times 10^{14} \text{ s}^{-1}}$$

Step II. *Calculation of wave number of yellow light*

$$\text{Wave number } (\bar{\nu}) = \frac{1}{\lambda} = \frac{1}{(580 \times 10^{-9} \text{ m})} = \mathbf{1 \cdot 724 \times 10^6 \text{ m}^{-1}}.$$

5. What is the number of photons of light with wavelength 4000 pm which provide 1 Joule of energy ?

Answer:

Energy of photon $(E) = \dfrac{hc}{\lambda}$

$h = 6.626 \times 10^{-34}$ Js, $c = 3 \times 10^8$ m s^{-1}, $\lambda = 4000$ pm $= 4000 \times 10^{-12} = 4 \times 10^{-9}$ m

$$\therefore \quad \text{Energy of photon } (E) = \frac{(6 \cdot 626 \times 10^{-34} \text{Js}) \times (3 \times 10^8 \text{m s}^{-1})}{(4 \times 10^{-9} \text{m})} = 4 \cdot 969 \times 10^{-17} \text{ J}$$

Now, $4 \cdot 965 \times 10^{-17}$ J is the energy of photon $= 1$

$$\therefore \quad 1 \text{ J is the energy of photons} = \frac{1}{4 \cdot 969 \times 10^{-17}} = \mathbf{2 \cdot 012 \times 10^{16} \text{ photons}}.$$

6.Calculate the wave number for the longest wavelength transition in the Balmer series of atomic hydrogen.

Answer:

According to Balmer formula, $\bar{\nu} = \dfrac{1}{\lambda} = R_H \left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2} \right]$

In order that the wavelength (λ) may be the maximum, wave number ($\bar{\nu}$) must be the least. This is possible in case $n_2 - n_1$ is minimum. Now, for Balmer series, $n_1 = 2$ and n_2 must be 3. Substituting these values in the Balmer formula,

$$\bar{\nu} = (1 \cdot 097 \times 10^7 \text{ m}^{-1}) \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = 1 \cdot 097 \times 10^7 \text{m}^{-1} \left(\frac{5}{36} \right) = \mathbf{1 \cdot 523 \times 10^6 \text{ m}^{-1}}$$

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

Answer:

According to Bohr's theory,

$$m\upsilon r = \frac{nh}{2\pi}$$

or $\quad 2\pi r = \dfrac{nh}{m\upsilon} \qquad$ or $\qquad m\upsilon = \dfrac{nh}{2\pi r}$

According to de Broglie equation,

$$\lambda = \frac{h}{m\upsilon} \qquad \text{or} \qquad m\upsilon = \frac{h}{\lambda}$$

Comparing (*i*) and (*ii*),

$$\frac{nh}{2\pi r} = \frac{h}{\lambda} \quad \text{or} \quad 2\pi r = n\lambda$$

Thus, the circumference ($2\pi r$) of the Bohr orbit for hydrogen atom is an integral multiple of the de Broglie wavelength.

8. Calculate the energy required for the process :
He$^+$fe) $\rightarrow$ He^{2+}(g) + e$^-$
The ionisation energy' for the H atom in the ground state is 2.18 × 10-18 J atom-1
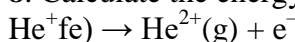
Answer:

The expression for the ionisation energy atom :

$$E_n = \frac{2.18 \times 10^{-18} \times Z^2}{n^2} \text{ J atom}^{-1}$$

For H atom (Z = 1), En =2.18 × 10⁻¹⁸ × (1)² J atom-1 (given)
For He+ ion (Z = 2), En =2.18 × 10⁻¹⁸ × (2)² = 8.72 × 10⁻¹⁸ J atom-1 (one electron species)

9.Red light has wavelength 750 nm, whereas violet light has wavelength 400 nm. Calculate their frequency

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ m s}^{-1}}{750 \times 10^{-9} \text{ m}} = 4 \times 10^{14} \text{ Hz};$$
$$E = h\nu = 6.63 \times 10^{-34} \times 4 \times 10^{14}$$
$$= 2.652 \times 10^{-19} \text{ J}$$

$$\nu = \frac{3 \times 10^8 \text{ m s}^{-1}}{400 \times 10^{-9} \text{ m}} = 7.5 \times 10^{14} \text{ Hz};$$

and energy (c = 3 × 108 m s⁻¹, h = 6.63 × 10⁻³⁴ J s). $E = 6.63 \times 10^{-34} \times 7.5 \times 10^{14} = 4.972 \times 10^{-19}$ J Th

10.The threshold frequency ν_0 for a metal is 7.0×10^{14} s⁻¹. Calculate the kinetic energy of an electron

$$\text{K.E.} = \frac{1}{2}mV^2 \Rightarrow \frac{1}{2}m_e V^2 = h(\nu - \nu_o)$$

$$= (6.626 \times 10^{-34} \text{ J s})(1.0 \times 10^{15} \text{ s}^{-1} - 7.0 \times 10^{14} \text{ s}^{-1})$$
$$= (6.626 \times 10^{-34} \text{ J s})(10 \times 10^{14} \text{ s}^{-1} - 7.0 \times 10^{14} \text{ s}^{-1})$$
$$= (6.626 \times 10^{-34} \text{ J s})(3.0 \times 10^{14} \text{ s}^{-1})$$

emitted when radiation of v = 1.0×10^{15} s⁻¹ hits the metal $= 1.988 \times 10^{-19}$ J

11.The mass of an electron is 9.1 × 10-31 kg. If its kinetic energy is 3.0 × 10-25 J, calculate its wavelength.
Answer:

Step I. *Calculation of velocity of the electron*
 Kinetic energy $= 1/2\, mv^2 = 3.0 \times 10^{-25}$ J $= 3.0 \times 10^{-25}$ kg m² s⁻²

$$v^2 = \frac{2 \times \text{K.E.}}{m} = \frac{2 \times (3.0 \times 10^{-25} \text{ kg m}^2 \text{ s}^{-2})}{(9.1 \times 10^{-31} \text{ kg})} = 65.9 \times 10^4 \text{ m}^2 \text{ s}^{-2}$$
$$v = (65.9 \times 10^4 \text{ m}^2 \text{ s}^{-2})^{1/2} = 8.12 \times 10^2 \text{ m s}^{-1}$$

Step II. *Calculation of wavelength of the electron*
According to de Broglie's equation,

$$\lambda = \frac{h}{mv} = \frac{(6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1})}{(9.1 \times 10^{-31} \text{ kg}) \times (8.12 \times 10^2 \text{ m s}^{-1})}$$
$$= 0.08967 \times 10^{-5} \text{ m} = 8967 \times 10^{-10} \text{ m} = \textbf{8967 Å.} \qquad (\because 1 \text{ Å} = 10^{-10} \text{ m})$$

12.Calculate the wavelength of an electron moving with a velocity of 2.05×10^7 m s-1
Answer:

According to de Broglie's equation, $\lambda = \dfrac{h}{mv}$

 Mass of electron (m) $= 9.1 \times 10^{-31}$ kg
 Velocity of electron (v) $= 2.05 \times 10^7$ m s⁻¹
 Planck's constant (h) $= 6.626 \times 10^{-34}$ kg m² s⁻¹

$$\therefore \qquad \lambda = \frac{(6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1})}{(9.1 \times 10^{-31} \text{ kg}) \times (2.05 \times 10^7 \text{ m s}^{-1})} = \textbf{3.55} \times \textbf{10}^{-11} \textbf{ m.}$$

13.Table-tennis ball has a mass 10 g and a speed of 90 m/s. If speed can be measured within an accuracy of

$$m = 10 \text{ g} = \frac{10}{1000} = 0.01 \text{ kg} , c = 90 \text{ m s}^{-1}$$

$$\text{Uncertainty in speed of ball} = \frac{90 \times 4}{100} = 3.6 \text{ m s}^{-1}$$

$$\Delta x = \frac{h}{4\pi m \Delta V} = \frac{6.626 \times 10^{-34} \text{ J s}}{4 \times 3.14 \times 0.01 \text{ kg} \times 3.6 \text{ m s}^{-1}}$$

4%, what will be the uncertainty in speed and position?

$$= 1.46 \times 10^{-33} \text{ m}$$

Case study based question

The presence of positive charge on the nucleus is due to the protons in the nucleus. As established earlier, the charge on the proton is equal but opposite to that of electron .Atomic number (Z) = number of protons in the nucleus of an atom = number of electrons in a nuetral atom. protons and neutrons present in the nucleus are collectively known as nucleons.The total number of nucleons is termed as mass number (A) of the atom.

mass number (A) = number of protons (Z) + number of neutrons (n).

Isobars are the atoms with same mass number but different atomic number for example, $_6^{14}C$ and $_7^{14}N$. On the other hand, atoms with identical atomic number but different atomic mass number are known as Isotopes. For example, considering of hydrogen atom again, 99.985%of hydrogen atoms contain only one proton. This isotope is called protium ($_1^1H$). Rest of the percentage of hydrogen atom contains two other isotopes, the one containing 1 proton and 1neutron is called deuterium ($_1^2D$, 0.015%) and the other one possessing 1 proton and 2neutrons is called tritium ($_1^3T$).The studies of interactions of radiations with matter have provided immense information regarding the structure of atoms and molecules. Neils Bohr utilized these results to improve upon the model proposed by Rutherford. Two developments played a major role in the formulation of Bohr's model of atom.

1. The pair of ions having same electronic configuration is _____.
(a) Cr^{3+}, Fe^{3+} (b) Fe^{3+}, Mn^{2+} (c) Fe^{3+}, Co^{3+} (d) Sc^{3+}, Cr^{3+}

Ans: (b) Fe^{3+}, Mn^{2+}

2.They have same mass number, different atomic number. These are isobars.
.In which of the following pairs, the ions are isoelectronic?
(a) Na^+, Mg^{2+} (b) Al^{3+}, O^- (c) Na^+, O^{2-} (d) N^{3-}, Cl^-
Ans: (a) and (c).
3.Two atoms are said to be isobars if.
(a) they have same atomic number but different mass number.
(b) they have same number of electrons but different number of neutrons.
(c)they have same number of neutrons but different number of electrons.
(d)sum of the number of protons and neutrons is same but the number of protons is different.
Ans (d) sum of number of protons and neutrons is same but the number of protons is different.

Long answer question   (5 marks)

1. (i) List two main differences between orbit and orbital.
(ii) If an electron is moving with a velocity 600 m/s which is accurate upto 0.005%, then calculate the uncertainty in its position.
($h = 6.626 \times 10^{-34}$ J s and mass of electron = 9.11×10^{-31} kg)

ANS: (i) Differences between orbit and orbitals:

Orbit	Orbital
Orbit is a well defined 2-D circular path around the nucleus in which the electron revolve.	Orbital is a3-D space around the atom where the probability of finding electron is maximum.
It is not in accordance of wave character	It is in accordance with wave character.
Orbits do not have direction	Except s orbital ,all orbitals are direction.

(ii) Uncertainity in speed, $\Delta v = 0.005 \times 600/100 = 0.03$

According to Heisenberg uncertainity principal

$$\Delta x . m\Delta v \geq \frac{h}{4\pi}$$

$$\Delta x = \frac{h}{4\pi m\, \Delta v} = \frac{6.626 \times 10^{-34} \text{Js}}{4 x 3.14 x 9.1 x 10-31 x .03} = 1.93 \times 10^{-3} \text{m}$$

2.The electronic energy in hydrogen atom is given by En (-2.18 × 10-18 s) / n2J. Calculate the energy required to remove an electron completely from the n = 2 orbit. What is the longest wavelength of light in cm that can be used to cause this transition?

Answer:

Step I. *Calculation of energy required*

The energy required is the difference in the energy when the electron jumps from orbit with $n = \infty$ to orbit with $n = 2$

The energy required, $(\Delta E) = E_\infty - E_2$

$$= 0 - \left(-\frac{2 \cdot 18 \times 10^{-18}}{4} \text{J} \right) = \textbf{5·45} \times \textbf{10}^{\textbf{-19}} \textbf{ J}$$

Step II. *Calculation of the longest wavelength of light in cm used to cause the transition*

$$\Delta E = h\nu = hc/\lambda$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6 \cdot 626 \times 10^{-34} \text{Js}) \times (3 \times 10^8 \text{ms}^{-1})}{(5 \cdot 45 \times 10^{-19} \text{J})}$$

$$= 3 \cdot 644 \times 10^{-7} \text{ m} = 3 \cdot 644 \times 10^{-7} \times 10^2 = \textbf{3·645} \times \textbf{10}^{\textbf{-5}} \textbf{ cm}$$

3.What is the energy in joules required to shift the electron of the hydrogen atom from the first Bohr orbit to the fifth Bohr orbit and what is the wavelength of light emitted when the electron returns to the ground state ? The ground state electronic energy is – 2.18 × 11-11 ergs.

Answer:

Step I. *Calculation of energy required*

The energy of electron $(E_n) = \dfrac{-2 \cdot 18 \times 10^{-11}}{n^2}$ ergs $= \dfrac{-2 \cdot 18 \times 10^{-18} \text{J}}{n^2}$ $(\because 1 \text{J} = 10^7 \text{ ergs})$

The energy in Bohr's first orbit $(E_1) = \dfrac{-2 \cdot 18 \times 10^{-18} \text{J}}{(1)^2} = \dfrac{-2 \cdot 18 \times 10^{-18} \text{J}}{1}$

The energy in Bohr's fifth orbit $(E_5) = \dfrac{-2 \cdot 18 \times 10^{-18} \text{J}}{(5)^2} = \dfrac{-2 \cdot 18 \times 10^{-18} \text{ J}}{25}$

$\therefore$ Energy required $(\Delta E) = E_5 - E_1 = \left(\dfrac{-2 \cdot 18}{25} \times 10^{-18} \text{J} \right) - \left(-\dfrac{2 \cdot 18}{1} \times 10^{-18} \text{J} \right)$

$$= 2 \cdot 18 \times 10^{-18} \left(1 - \frac{1}{25} \right) \text{J}$$

$$= 2 \cdot 18 \times 10^{-18} \times 24/25 = \textbf{2·09} \times \textbf{10}^{\textbf{-18}} \textbf{ J}$$

Step II. *Calculation of wavelength of light emitted*

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

$\therefore$ $\lambda = \dfrac{hc}{\Delta E} = \dfrac{(6 \cdot 626 \times 10^{-34} \text{J} - \text{s}) \times (3 \times 10^8 \text{ms}^{-1})}{(2 \cdot 09 \times 10^{-18} \text{J})}$

$$= \textbf{9·50} \times \textbf{10}^{\textbf{-8}} \textbf{m} = 950 \text{ Å}.$$ $(\because 1 \text{ Å} = 10^{-10} \text{m})$

4.How much energy is required to ionise a hydrogen atom if an electron occupies n = 5 orbit ? Compare your answe r with the ionisation energy of H atom (energy required to remove the electron from n = 1 orbit)

Answer:

Energy for a hydrogen electron present in a particular energy shell,

$$E_n = -\frac{13 \cdot 12}{n^2} \times 10^5 \, J \, mol^{-1} = -\frac{13 \cdot 12 \times 10^5}{n^2 \times 6 \cdot 022 \times 10^{23}} \, J \, atom^{-1}$$

$$= \frac{-2 \cdot 18 \times 10^{-18}}{n^2} \, J \, atom^{-1}$$

Step I. *Ionisation energy for hydrogen electron present in orbit n = 5*

$$IE_5 = E_\infty - E_5 = 0 - \left(\frac{-2 \cdot 18 \times 10^{-18}}{25}\right) J \, atom^{-1} = 8 \cdot 72 \times 10^{-20} \, J \, atom^{-1}$$

Step II. *Ionisation energy for hydrogen electron present in orbit n = 1.*

$$IE_1 = E_\infty - E_1 = 0 - \left(\frac{-2 \cdot 18 \times 10^{-18}}{1}\right) = 2 \cdot 18 \times 10^{-18} \, J \, atom^{-1}$$

On comparing : $\quad \dfrac{IE_1}{IE_5} = \dfrac{(2 \cdot 18 \times 10^{-18} \, J \, atom^{-1})}{(8 \cdot 72 \times 10^{-20} \, J \, atom^{-1})} = 25$

The energy required to remove an electron from first orbit in a hydrogen atom is 25 times the energy needed to remove an electron from fifth orbit.

5(i) Write outer electronic configuration of Cr atom. Why are half filled orbitals more stable?

Ans: *(i)* Cr(24): $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

(ii)A 25 watt bulb emits monochromatic yellow light of wavelength 0.57 μm. Calculate the rate of emission of quanta per second.

Answer:

Energy of one photon (E) = $h\nu = hc/\lambda$

$$h = 6 \cdot 626 \times 10^{-34} \, J \, s \, ; \, c = 3 \times 10^8 \, m \, s^{-1} \, ; \, \lambda = 0 \cdot 57 \times 10^{-6} \, m$$

$$E = \frac{(6 \cdot 626 \times 10^{-34} \, Js) \times (3 \times 10^8 \, m \, s^{-1})}{(0 \cdot 57 \times 10^{-6} \, m)} = 3 \cdot 48 \times 10^{-19} \, J$$

Rate of emission of quanta per second = $\dfrac{Power}{Energy}$

Power (P) = 25 watt = 25 Js^{-1} ; E = $3 \cdot 48 \times 10^{-19}$ J

$$= \frac{(25 \, watt)}{(3 \cdot 48 \times 10^{-19} \, J)} = \frac{(25 \, Js^{-1})}{(3 \cdot 48 \times 10^{-19} \, J)} = 7 \cdot 18 \times 10^{19} \, s^{-1}.$$

HOTS

1.The work function for cesium atom is 1.9 eV. Calculate (a) the threshold wavelength and (b) the threshold frequency of the radiation. If the cesium element is irradiated with a wavelength 500 nm, calculate the kinetic energy and the velocity of the ejected photoelectron

Answer:

$$E_0 = 1 \cdot 9 \, eV = 1 \cdot 9 \times 1 \cdot 602 \times 10^{-19} \, J$$

Threshold frequency $(\nu_0) = \dfrac{E_0}{h} = \dfrac{1 \cdot 9 \times 1 \cdot 602 \times 10^{-19} \, J}{6 \cdot 626 \times 10^{-34} \, Js} = 0 \cdot 459 \times 10^{15} \, s^{-1} = 4 \cdot 59 \times 10^{14} \, s^{-1}$

Threshold wavelength $(\lambda_0) = \dfrac{c}{\nu_0} = \dfrac{3 \times 10^8 \, m \, s^{-1}}{4 \cdot 59 \times 10^{14} \, s^{-1}} = 0 \cdot 6536 \times 10^{-6} \, m = 653 \cdot 6 \, nm \approx 654 \, nm$

$$E = E_0 + \frac{1}{2} m\upsilon^2$$

Kinetic energy $\left(\dfrac{1}{2} m\upsilon^2\right) = E - E_0 = hc \left[\dfrac{1}{\lambda} - \dfrac{1}{\lambda_0}\right]$

$$= \frac{(6 \cdot 626 \times 10^{-34} \, Js) \times (3 \times 10^8 \, m \, s^{-1})}{10^{-9} \, m} \times \left[\frac{1}{500} - \frac{1}{654}\right]$$

$$= \frac{6 \cdot 626 \times 3 \times 154}{500 \times 654} \times 10^{-34+8+9} = 9 \cdot 36 \times 10^{-20} \, J$$

Velocity $(\upsilon) = \sqrt{\dfrac{2 \times 9 \cdot 36 \times 10^{-20}}{m} \, J} = \sqrt{\dfrac{2 \times 9 \cdot 36 \times 10^{-20} \, kg \, m^2 s^{-2}}{9 \cdot 1 \times 10^{-31} \, kg}}$

$$= \sqrt{2 \cdot 057 \times 10^{11} \, m^2 \, s^{-2}} = \sqrt{20 \cdot 57 \times 10^{10} \, m^2 \, s^{-2}} = 4 \cdot 5356 \times 10^5 \, m \, s^{-1}$$

3.CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES OF ELEMENTS

Earlier classifications

1) **Dobereiner's classification**:

Johann Dobereiner classified elements into small groups each containing three elements. These small groups were called *triads*.

E.g. for triads are: i) ^{7}Li ^{23}Na ^{39}K

ii) ^{40}Ca ^{88}Sr ^{137}Ba

In triads, the atomic mass of the middle element is approximately the average of the other two elements. This is known as Law of Triads. This classification was applicable to very few elements and so it was rejected.

2) **Newlands classification:**

Newland arranged elements in the increasing order of their atomic masses. The properties of every eighth element are similar to that of the first element. The relationship is just like the resemblance of first and eighth musical notes. He named this **as law of octaves**.

It was rejected since the law of octaves was applicable to elements upto calcium.

Mandeleev's Periodic Law:-

The periodic law states that "**The properties of elements are the periodic functions of their atomic weights.**" That is, when elements are arranged in the increasing order of their atomic weights, their properties repeat after a regular interval.

Merits of Mendeleev's periodic table

1It was the first comprehensive classification of elements.

2.He corrected the wrong atomic weights of some elements and placed them in correct position in the periodic table.

3.He left vacant places for undiscovered elements and predicted some of their properties. 4)Elements with similar properties are placed in the same group.

Demerits of Mendeleev's periodic table

1.Elements with dissimilar properties are found in same group.

2.He could not give an exact position for hydrogen.

3.He could not give exact position for Lanthanoids and Actinoids and also for isotopes.

4.Mendeleev's periodic table did not strictly obey the increasing order of atomic weights.

Modern Periodic table (Henry Moseley)

Modern Periodic lawstates that"*the physical and chemical properties of elements are the periodic functions of their atomic numbers*".

In this periodic table, the elements are arranged in the increasing order of their atomic number. It contains **7** horizontal rows called **periods** and **18** vertical columns called **groups**. Elements having similar outer electronic configurations are arranged in same group or family and have similar properties.

The blocks in the Modern periodic table

The Modern periodic table is divided into 4 blocks based on the subshell in which the last electron enters. They are s block, p block, d block and f block.

1. The s block elements

These are elements in which the last electron enters in the outer most s sub shell. They include elements of the groups 1 and 2. Their general outer electronic configuration is ns^{1} or ns^{2}.

They are all reactive metals with low ionization enthalpies.

They lose their outer most electrons readily to form +1 and +2 ions.

Their metallic character and reactivity increases down the group.

They mainly form ionic compounds (except Li and Be).

2. The p block elements

These are elements in which the last electron enters in the outer most p sub shell. They include elements

of the groups 13 to 18. They are also called **Representative elements.**

Their general outer electronic configuration is $ns^2 np^{1\,to\,6}$. The 18th group elements are called Noble gases.

The d block elements

These are elements in which the last electron enters in the penultimate d sub shell. They include elements of the groups 3 to 12. They are also called **Transition elements**, since they show a transition (change) from the most electropositive s block elements to the least electropositive p block elements. Their general outer electronic configuration is $(n-1)d^{1\,to\,10} ns^{0\,to\,2}$.

They are all metals, form-coloured compounds or ions,

They show variable oxidation states and valencies,

They show paramagnetism and catalytic properties.

The f block elements

These are elements in which the last electron enters in the anti-penultimate f sub shell. They include *lanthanides of 6th period and actinides of 7th period*. They are also called **Inner transition elements**. Their general outer electronic configuration is $(n-2)f^{1\,to\,14}(n-1)d^{0\,to\,1} ns^2$. They are all metals.

Periodic properties of Elements

The properties which repeat after a regular interval are called periodic properties. Some of the important periodic properties of elements are atomic and ionic radii, ionization enthalpy, electron gain enthalpy, electro positivity, electronegativity etc.

1. **Atomic Radius**

It is defined as the distance from the centre of the nucleus to the outermost shell having electrons. Atomic radius of individual atoms cannot be determined. So it is expressed in any of the following methods:

Covalent radius: It is half of the inter nuclear distance between two covalently bonded (single bonded)atoms. It is used to express the atomic radius of non-metal atoms. For e.g. the bond distance of C^{l2} molecule is 198 pm. So the covalent radius is 99 pm.

Metallic radius: It is the half of the inter nuclear distance between two metallic ions in a metal crystal.

van der Waal's radius: It is defined as the half of the inter nuclear distance between two non bonded atoms of separate molecules in the solid state.

Atomic radius is commonly expressed in picometre (pm) or angstrom (A^0).it is measured by x-ray diffraction method or by spectroscopic methods.

Variation of atomic radius along a group and period

The atomic size decreases from left to right in a period. This is because in a period, the electrons are added to the same valence shell. Thus the number of shells remains same, but the effective nuclear charge increases. So the atomic radius decreases.

Down a group, the atomic radius increases from top to bottom. This is because of the increase in no. of shells and shielding effect.
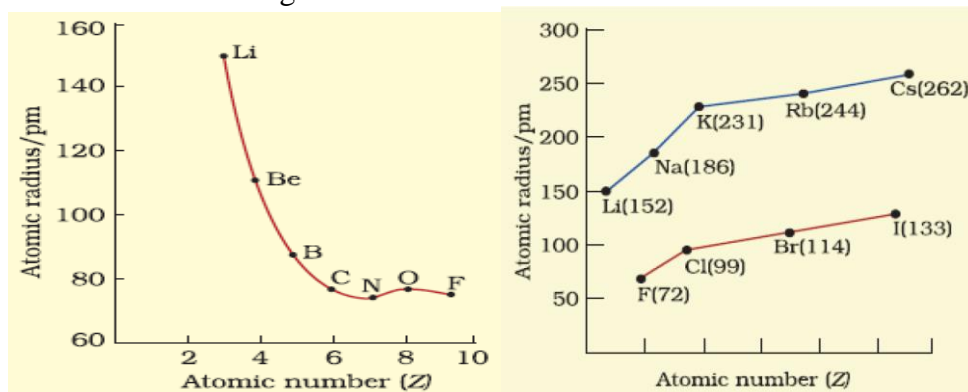
Atomic radius of noble gases is larger than that of halogens. This is because noble gases are monoatomic . So van der Waal's radius is used to express the atomic radius which is greater than covalent radius or metallic radius.

2. Ionic radius

It is defined as the half of the inter nuclear distance between cations and anions of an ionic crystal. The variation of ionic radius is same as that of atomic radius.

Generally a cation is smaller than its parent atom (e.g. Na^+ is smaller than Na atom). This is because a cation has fewer electrons, but its nuclear charge remains the same as that of the parent atom.

An anion is larger than its parent atom (e.g. Cl^- is larger than Cl atom). This is because the addition of one or more electrons would result in an increased electronic repulsion and a decrease in effective nuclear charge.

Isoelectronic species:

Atoms and ions having the same number of electrons are called isoelectronic species. E.g. O^{2-}, F^-, Ne, Na^+, Mg^{2+} etc. (All these contain 10 electrons)

Among isoelectronic species, *the cation with greater positive charge will have the smaller radius*. This is because of the greater attraction of electrons to the nucleus. *The anion with greater negative charge will have the larger radius*. Here the repulsion between electrons is greater than the attraction of the nucleus. So the ion will expand in size.

3. Ionisation enthalpy ($\Delta_i H$)

It is defined as the energy required to remove an electron from the outer most shell of an isolated gaseous atom in its ground state. It may be represented as: $X_{(g)} + \Delta_i H \rightarrow X^+_{(g)} + e^-$
Its unit is kJ/mol or J/mol.

The energy required to remove the first electron from the outer most shell of a neutral atom is called first ionisation enthalpy ($\Delta_i H_1$)
$$X_{(g)} + \Delta_i H_1 \rightarrow X^+_{(g)} + e^-$$
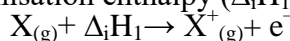
Second ionization enthalpy ($\Delta_i H_2$) is the amount of energy required to remove an electron from a unipositive ion. $X^+(g) + \Delta_i H_2 \rightarrow X^{2+}(g) + e^-$

The second ionisation enthalpy is always higher than first ionization enthalpy. This is because it is more difficult to remove an electron from a positive charged ion than from a neutral atom.

Similarly third ionisation enthalpy is higher than second ionisation enthalpy and so on. i.e. $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3 \ldots\ldots\ldots$
As the ease of removal of electron increases, the ionisation enthalpy decreases.

Factors affecting ionisation enthalpy

The important factors which affect ionisation enthalpy are:

Atomic size: Greater the atomic size (atomic radius), smaller will be the ionisation enthalpy.

Nuclear charge: The value of ionisation enthalpy increases with nuclear charge.

Shielding effect: As the shielding effect increases, the electrons can easily be removed and so the ionisation enthalpy decreases.

Presence of half filled or completely filled orbitals increases ionisation enthalpy.

Variation of $\Delta_i H$ along a period and a group

Along a *period*, ionisation enthalpy *increases* from left to right. This is because of the *decrease in atomic radius and increase in nuclear charge*. Thus alkali metals have the least $\Delta_i H$ and noble gases have the most.

Down a *group*, $\Delta_i H$ *decreases due to increase in atomic radius and shielding effect*. Thus among alkali metals, lithium has the least $\Delta_i H$ and francium has the most.
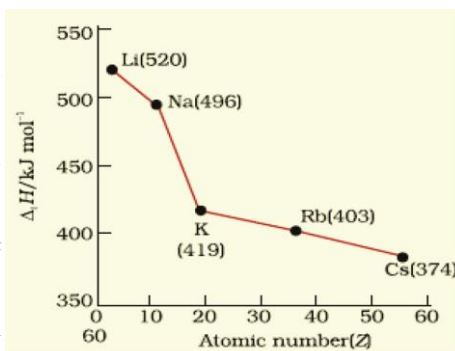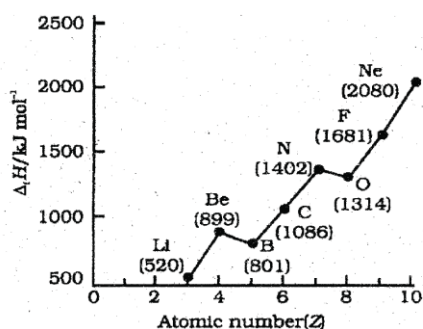
In the second period of modern periodic table, *the first ionisation enthalpy of Boron is slightly less than that of Beryllium*. This is because of the completely filled orbitals in Be ($1s^2 2s^2$).

Similarly *the first ionisation enthalpy of N is greater than that of Oxygen*. This is because N has half filled electronic configuration ($1s^2 2s^2 2p^3$), which is more stable and so more energy is required to remove an electron.
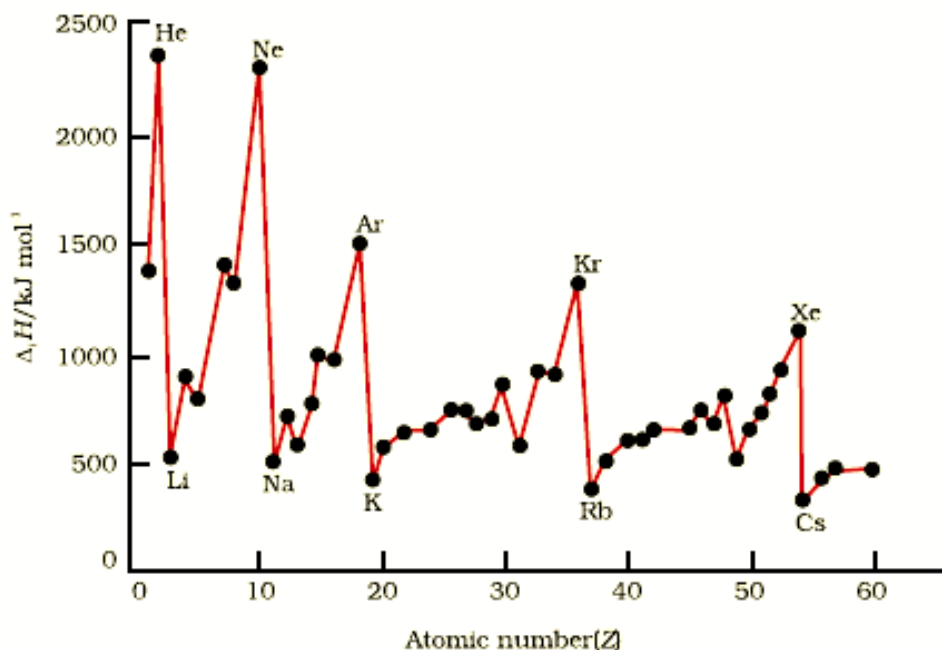
4. Electron gain enthalpy ($\Delta_{eg}H$)

It is the heat change (enthalpy change) when an electron is added to the outer most shell of an isolated gaseous atom. It can be represented as $X_{(g)} + e^- \rightarrow X^-_{(g)}$

For most of the elements, energy is released when electron is added to their atoms. So $\Delta_{eg}H$ is negative. Noble gases have large positive electron gain enthalpy because of their completely filled (stable) electronic configuration.

Electron gain enthalpy also depends on atomic size, nuclear charge, shielding effect etc. As the atomic size increases $\Delta_{eg}H$ decreases.

1. When nuclear charge increases, electron gain enthalpy increases and become more negative.
2. Shielding effect decreases $\Delta_{eg}H$.
3. Presence of half filled or completely filled orbitals makes $\Delta_{eg}H$ less negative.

Periodic variation of $\Delta_{eg}H$

1. From left to right across a *period*, $\Delta_{eg}H$ become *more negative*. This is *because of decrease in atomic radius and increase in nuclear charge*. So the ease of addition of electron increases and hence the $\Delta_{eg}H$.

2. Down a *group*, $\Delta_{eg}H$ becomes less negative. This is *due to increase in atomic radius and shielding effect*.

3. *Electron gain enthalpy of fluorine is less negative than chlorine*. This is because, when an electron is added to F, it enters into the smaller 2nd shell. Due to the smaller size, the electron suffers more repulsion from the other electrons. But for Cl, the incoming electron goes to the larger 3rd shell. So the electronic repulsion is low and hence Cl adds electron more easily than F. Due to the same reason $\Delta_{eg}H$ of Oxygen is less negative than S.

4. Thus in modern periodic table, alkali metals have the least –ve $\Delta_{eg}H$ and halogens have the most –ve $\Delta_{eg}H$. Among halogens, the negative $\Delta_{eg}H$ decreases as follows.

Cl> F > Br > I
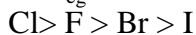
The negative electron gain enthalpy is also called electron affinity.

5. Electronegativity

Electronegativity of an atom in a compound is the ability of the atom to attract shared pair of electron of electrons.

Electronegativity depends on atomic size and nuclear charge. As the atomic radius increases, electronegativity decreases. Greater the nuclear charge, greater will be the electronegativity.

Periodicity:
(i) In period- The electro-negativity increases from left to right in a period.
(ii) In group- The electro-negativity decreases from top to bottom in a group.

6. Electropositivity

It is the tendency of an atom to lose the most loosely bound electron (valence electron). It is directly related to the metallic character of elements. It depends on atomic size and nuclear charge. As the atomic radius increases, electropositivity increases.

Along a period, electro positivity decreases from left to right. But down a group, it increases. So francium is the most electropositive element and fluorine is the least electropositive element.

7. Valency

It is the combining capacity of an element. Or, it is the number of electrons lost or gained by an atom during a chemical reaction.

Along a period, valency first increases upto the middle and then decreases (for s and p block elements only). **In a group**, valency remains constant. Transition elements can show variable valency.

REACTIVITY OF METALS:

Periodicity:
(i) In period- The tendency of an element to lose electrons decreases in a period. So the reactivity of metals decreases from left to right in a period.
(ii) In group- The tendency of an element to lose electrons increases in a period. So the reactivity of metals increases from top to bottom in a group.

REACTIVITY OF NON- METALS:

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

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

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

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

$$Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$$
Basic strength increases
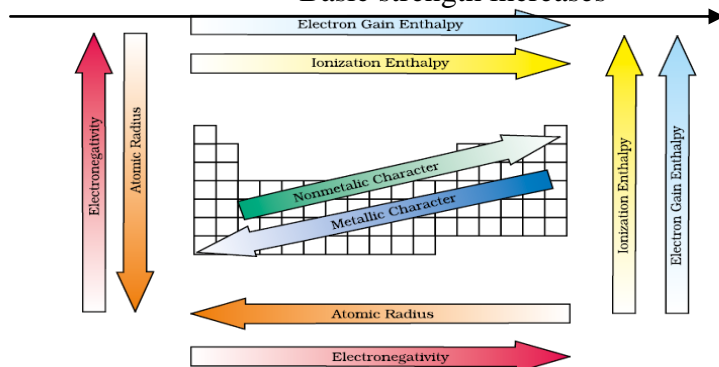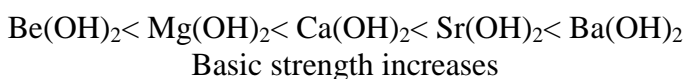
The periodic trends of elements in the periodic table

MULTIPLE CHOICE QUESTIONS (MCQ)

1. 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   **ANSWER- D**

2. 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   **ANSWER- B**

3. 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   **ANSWER- C**

4. Whenever a list of radii is given, we find that the size of the noble gases is larger than the size of their adjacent halogens. The reason is
(A) Noble gases have a complete octet
(B) They have a higher inter electronic repulsion
(C) In halogens it is covalent radii and in noble gases it is Vander walls radii (D)Noble gases cannot be liquefied   **ANSWER- B**

5. Which of the following has the largest size
(A) N^{-3} (B) O^{-2} (C) K^{+1} (D) Ca^{+2} **ANSWER- A**

6. 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+ **ANSWER- D**

7. Which of the following should be the order of increasing values of second ionisation potential of C_6, N_7, O_8 and F_9.
(A) C > N > F > O (B) C < F < N < O (C) C < F < N < O (D) C < N < F< O **ANSWER- D**

8. One mole of magnesium in the vapour state absorbed 1200 kJ of energy. If the first and second ionization enthalpies of magnesium are 750 and 1450 kJ mole–1 respectively, the final composition of the mixture is
(A) 69% Mg^+, 31% Mg^{2+} (B) 59% Mg^+, 41% Mg^{2+}
(C) 49% Mg^+, 51% Mg^{2+} (D) 29% Mg+, 71% Mg^{2+} **ANSWER- A**

9. The incorrect statement in the following is
(A) The third ionisation potential of Mg is greater than the third ionisation potential of Al
(B) The first ionisation potential of Na is less than first I.P of Mg
(C) The first I.P. of Al is less than the first I.P. of Mg
(D) The second I.P. of Mg is greater than the second I.P. of Na   **ANSWER- D**

10. O(g) + 2e– O–2(g) –E = + 744.7
The reason for the positive value of E is
(A) endothermic reaction   (B) exothermic reaction
(C) both 1 and 2   (D) All of the above are wrong   **ANSWER- A**

11. 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   **ANSWER- C**

12. The least electron affinity is found in
(A) Kr   (B) O   (C) N   (D) B   **ANSWER- C**

13.Of the following element of which electronic configuration will have the highest electron affinity
(A) 1s2 2s2 2p3 (B) 1s2 2s2 2p5 (C) 1s2 2s2 2p6 3s2 3p5 (D) 1s2 2s2 2p6 3s2 3p3 ANSWER- C

14. Which oxide of N is isoelectronic with CO2 -
(A) NO_2 (B) NO   (C) N_2O (D) N_2O_3 **ANSWER**- A

15.The correct order of ionic radius is -
(A) Ce > Sm > Tb > Lu (B) Lu > Tb > Sm > Ce
(C) Tb > Lu > Sm > Ce (D) Sm > Tb > Lu > Ce   **ANSWER**- A

16. According to the Modern Periodic Law of elements, the Variation in properties of elements is related to them?
(A)Nuclear masses (B)Atomic numbers
(C)Nuclear neutron-proton number ratio (D)Atomic masses   **ANSWER**- B

17. Atomic radius decreases in a period, but after halogens, the atomic radius suddenly increases. Thus, inert gases have almost highest radius in a period. The explanation for such an increase is-
(A) Inert gases have most stable configuration.
(B) Inert gases do not take part in bonding.
(C) Vander Wall's radius is reported in case of inert gases.
(D)None of these.   **ANSWER**- C

18. Which one of the following groups represent a collection of isoelectronic species?
(At. no. Cs = 55, Br = 35)
(A) N^{3-}, F^-, Na^+ (B) Be, Al^{3+}, Cl^- (C) Ca^{2+}, Cs^+, Br   (D) Na^+, Ca^{2+}, Mg^{2+} **ANSWER**- A

19. Consider the following statements:
I. The radius of an anion is larger than that of parent atom
II. The I.E. increases from left to right in a period generally
III. The electronegativity of an element is the tendency of an isolated atom to attract an electron
The correct statements are -
(A)I alone (B) II alone (C) I and II (D) II and III   **ANSWER**- C

20. For the same value of n, the penetration power of orbital follows the order
(a) s = p = d = f (b) p > s > d > f (c) f < d < p < s (d) s < p < d < f   **ANSWER**- C

REASONING AND ASSERTION TYPE QUESTIONS
The following questions consist of two statements, one labelled as Assertion A and the other labelled as Reason R. Examine both the statements and mark the correct choice according to the instructions given below:
(a)   if both A and R are correct and R is the correct reason of A
(b)   if both A and R are correct but R is not the correct reason of A
(c)   if A is correct and R is wrong
(d)   if A is wrong and R is correct.
1. Assertion A: Noble gases have highest ionization energies in their respective periods.
   Reason R.: Noble gases have stable electronic configurations. **ANSWER: (a)**
2.Assertion A: Nitrogen has higher I.E. than that of oxygen.
 Reason R: Nitrogen atom has smaller atomic size than that of oxygen. **ANSWER: (c)**
3.Assertion A: Chlorine has higher greater negative electron gain enthalpy than that of fluorine.
Reason R: Fluorine is stronger oxidizing agent than chlorine. **ANSWER: (b)**
4.Assertion A: Helium has the highest value of ionization enthalpy among all the elements.
Reason R: Helium has the highest value of electron affinity among all the elements. **ANSWER: (c)**
5.Assertion A: Sixth period is the longest period of the periodic table.
 Reason R: Sixth period involves the filling of all the orbitals of sixth energy level.
ANSWER: (c)

6.Assertion A: F atom has a less negative electron affinity than Cl atom.
Reason R: Additional electrons are repelled more effectively by 3p electron in Cl atom than by 2p electrons in F atom. **ANSWER: (c)**

7.Assertion A: Alkali metals impart characteristic flame colourations to the flame.
Reason R: Alkali metals have low ionization enthalpies and hence their electrons can be excited to higher levels easily. **ANSWER: (a)**

8.Assertion A: Noble gases have highest first ionization enthalpies in their respective periods.
Reason R: Noble gases have stable electronic configurations. **ANSWER: (a)**

TWO MARKS QUESTIONS

Q.1. Describe the two merits of long form periodic table over the Mendeleev's periodic table?
Ans- 1. It removed the anomalies about the position of isotopes which existed in the Mendeleev's table. 2. It relates the position of an element in the periodic table with its electronic configuration.

Q.2. What is meant by periodicity in properties of elements? What is the reason behind this?
Ans- The repetition of similar properties after regular intervals is called as periodicity. It is due to the similarity in the outer electronic configurations which gives rise to the periodic properties of the elements.

Q.3. How do atomic radii vary in a group and a period?
Ans- In group- Atomic size increases on moving from top to bottom. In period- Atomic size decreases on moving left to right in a period.

Q.4. Name the factors which affect the ionisation enthalpy of an element.
Ans- (i) Size of atom or ion (ii) Nuclear charge (iii) Electronic configuration (iv) Screening effect (v) Penetration effect of the electrons

Q.5. Noble gases have zero electron gain enthalpy values. Explain.
Ans- Because the outer most shell of noble gases is completely filled and no more electrons can be added.

THREE MARKS QUESTIONS

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

Q.2. Among the elements of the second period Li to Ne pick out the element:
(i) with the highest first ionisation energy
(ii) with the highest electronegativity
(iii) with the largest atomic radius Give the reason for your choice.
Ans- (i) Ne .due to higher nuclear charge.
(ii) F. due to small size
(iii) Li .due to less nuclear charge.

Q.3. Arrange the following as stated:
(i) N_2, O_2, F_2, Cl_2 (Increasing order of bond dissociation energy)
(ii) F, Cl, Br, I (Increasing order of electron gain enthalpy)
(iii) F_2, N_2, Cl_2, O_2 (Increasing order of bond length)

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

Q.4. Explain why are cations smaller and anions larger in size than their parent atoms?
Ans- (a) The cations are smaller than their parent atoms due to the following reasons:
(i) Disappearance of the valence shell.
(ii) Increase of effective nuclear charge

(b) The anions are larger than their parent atoms due to the following reason: An increase in the number of electrons in the valence shell reduces the effective nuclear charge due to greater mutual shielding by the electrons. As a result, electron cloud expands, i.e., the ionic radius increases.

Q.5. Consider the following species: N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+} and Al^{3+}
(a) What is common in them?
(b) Arrange them in the order of increasing ionic radii.
Ans- (a) the same number of electrons (10 electrons). Hence, the given species are isoelectronic.
(b) $Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$

CASE BASED QUESTIONS
PASSAGE II
Read the passage given below and answer the following questions:
In the periodic table electronegativity increases from left to right in a period and decreases from top to bottom in a group. The non-metallic character of an element is directly related to the electronegativity while the metallic character is inversely related to it.
1.   The element with maximum electronegativity belongs to
(a) Period-1, Group-18   (b) Period-2, Group-17
(c) Period-3, Group-17   (d) Period-2, Group-1.
ANSWER: (b)
2.   Which of the following groups contains metals, non-metals as well as metalloids?
(a) Group-1   (b) Group-17   (c) Group-14   (d) Group-2.
ANSWER: (c)
3.   The least, metallic element of group-13 is
(a) Aluminium(b) Boron   (c) Gallium   (d) Indium.
ANSWER: (b)
4.   The electronegativity increases with
(a) decrease in nuclear charge   (b) increase in atomic mass
(c) decrease in atomic size   (d) increase in atomic number.
ANSWER: (c)

FIVE MARKS QUESTIONS

Q.1. What is the cause of the periodicity in the properties of the elements? How do the following properties vary in (a) a group and (b)in a period
(i) electronegativity
(ii) ionisation enthalpy
(iii) Atomic size
Ans- It is due to the similarity in the outer electronic configurations which gives rise to the periodic properties of the elements.
(a) In a group:
(i) Electronegativity- It decreases down the group.
(ii) Ionisation enthalpy- It decreases down the group.
(iii) Atomic size- It increases down the group.

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

4.CHEMICAL BONDING AND MOLECULAR STRUCTURE

CHEMICAL BOND

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

KÖSSEL-LEWIS APPROACH TO CHEMICAL BONDING

Kossel and Lewis developed the **electronic theory of valence** to explain the formation of chemical bonds between the two atoms. According to this theory, every atom tries to attain octet configuration (presence of eight electrons) in its valence shell by losing or gaining or by sharing of electrons.

Lewis Symbols:

A Lewis Symbol is **constructed by placing dots representing electrons in the outer energy around the symbol for the element**.
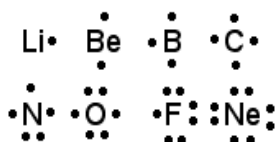
Octet Rule

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

Formal Charge

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

$$FC = V - N - \frac{B}{2}$$

FC = formal charge
V = number of valence electrons
N = number of nonbonding valence electrons
B = total number of electrons shared in bonds

For example,

Lewis structure of O_3 is ½

Formal charge on O(1) = $6 - 4 - \frac{1}{2}(4) = 0$

Formal charge on O(2) = $6 - 2 - \frac{1}{2}(6) = +1$

Formal charge on O(3) = $6 - 6 - \frac{1}{2}(2) = -1$. ½

Hence we represent O_3 along with formal charges as follows. **1**
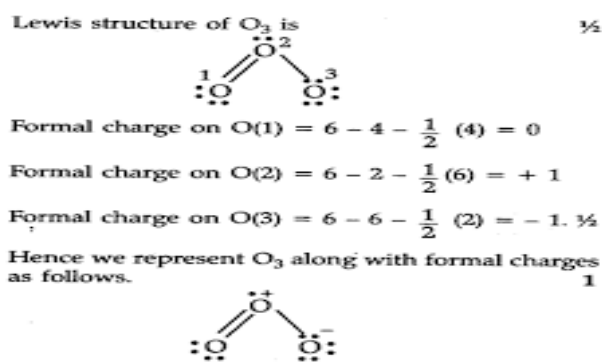
Limitations of the Octet Rule

The incomplete octet of the central atom

For example: In some polyatomic molecules like LiCl, BeH_2 and BCl_3, the number of electrons surrounding the central atom is less than eight. Li, Be and B have 1,2 and 3 valence electrons only.

Odd-electron molecules

Molecules having an odd number of electrons like nitric oxide, NO and nitrogen dioxide, NO_2, do not satisfy the octet rule for all the atoms.

The expanded atom

Ten valence electrons
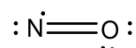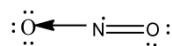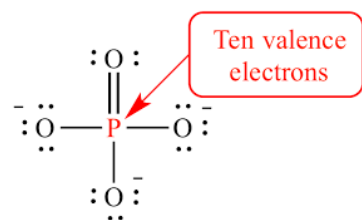
Born Haber cycle

Born Haber cycle is a cycle of enthalpy change of process that leads to the formation of a solid crystalline ionic compound from the elemental atoms in their standard state and of the enthalpy of formation of the solid compound such that the net enthalpy becomes zero.

Born Haber Cycle for Sodium Chloride
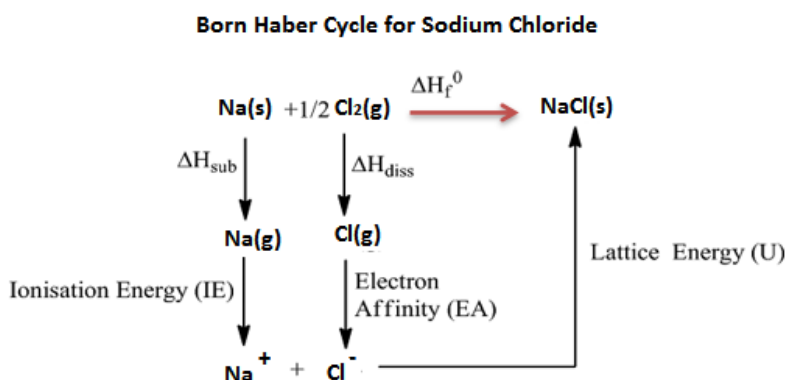
BOND PARAMETERS

Bond Length

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

Bond Angle

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

Bond Enthalpy

It is defined as the amount of energy required to break one 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 molecule is 435.8 kJ mol^{-1}. $H_2(g) \rightarrow H(g) + H(g)$; $\Delta H = 435.8$ kJ mol^{-1}

Bond Order

Bond Order is given by the number of bonds between the two atoms in a molecule. The bond order, for example in H_2 (with a single shared electron pair), in O_2 (with two shared electron pairs) and in N_2 (with three shared electron pairs) is 1,2,3 respectively.

Resonance

According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-

bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately.

Figure 1

Figure 2
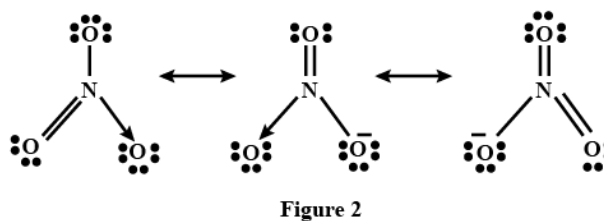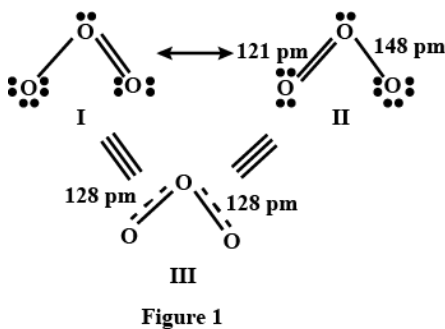
Dipole moment

Dipole moment (μ) = charge (Q) $\times$ distance of separation ®

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

Fagan's rule:

☐ The smaller the size of the cation and the larger the size of the anion, the greater the covalent character of an ionic bond.

☐ The greater the charge on the cation, the greater the covalent character of the ionic bond.

THE VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

The main postulates of VSEPR theory are as follows:

☐ 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 are negatively charged.

☐ These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.

☐ The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another

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)

# of Atoms	# of electron pairs	Formula Type	Geometry	Bond Angle	Examples	Hybridization	Structure
3	0	AB_2	Linear	180	CO_2, CS_2, BeH_2		
3	1	AB_2	Bent	117.5	$GeCl_2$, SO_2, NO_2	sp^2	
3	2	AB_2	Bent	105	H_2O, H_2S	sp^3	
4	0	AB_3	Trigonal planar	120	BCl_3, $AlBr_3$,	sp^2	
4	1	AB_3	Pyramidal	107	NH_3, PCl_3, $AsBr_3$	sp^3	
4	2	AB_3 (Inter halogen)	T-shaped	90, 180	ICl_3, BrF_3,	sp^3d	
5	0	AB_4	Tetrahedron	109.5	CCl_4, CH_4, $SiBr_4$	sp^3	
5	1	AB_4	Distorted tetrahedron (Seesaw)		SF_4, SBr_4, $SeCl_4$	sp^3d	
5	2	AB_4	Square planar	90, 180	XeF_4,	sp^3d^2	
6	0	AB_5	Trigonal bipyramidal	90, 180, 120	PCl_5,	sp^3d	
6	1	AB_5 (Inter halogen)	Square pyramid		ClF_5, ICl_5, IBr_5	sp^3d^2	
7	0	AB_6	Octahedron	90, 180	SF_6	sp^3d^2	

Hybridisation

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

Hybridisation of Elements involving d Orbitals

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

Shape of molecules/ ions	Hybridisation type	Atomic orbitals	Examples
Square planar	dsp^2	$d+s+p(2)$	$[Ni(CN)_4]^{2-}$, $[Pt(Cl)_4]^{2-}$
Trigonal bipyramidal	sp^3d	$s+p(3)+d$	PF_5, PCl_5
Square pyramidal	sp^3d^2	$s+p(3)+d(2)$	BrF_5
Octahedral	sp^3d^2 d^2sp^3	$s+p(3)+d(2)$ $d(2)+s+p(3)$	SF_6, $[CrF_6]^{3-}$ $[Co(NH_3)_6]^{3+}$

(i) Formation of PCl$_5$ (sp^{3}d hybridisation):

The ground state and the excited state outer electronic configurations of phosphorus (Z=15) are represented below.

sp^{3}d hybrid orbitals filled by electron pairs donated by five Cl atoms.
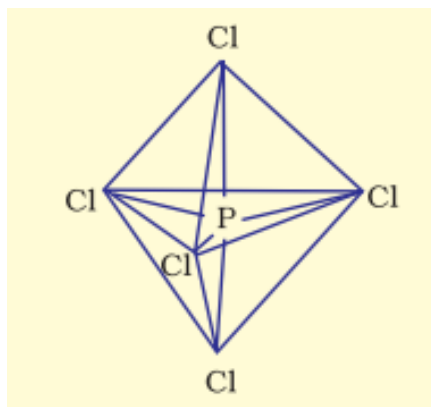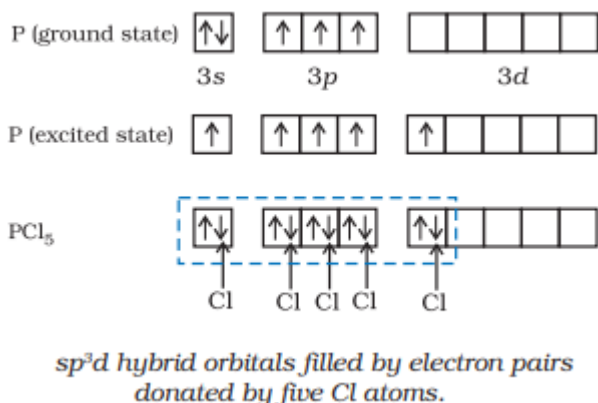
Now the five orbitals (i.e., one s, three p and one d orbitals) are available for hybridisation to yield a set of five sp^{3}d hybrid orbitals which are directed towards the five corners of a trigonal bipyramidal as depicted in the above fig.

Molecular Orbital Theory

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

1. The molecular orbitals are formed by LCAO (Linear combination of atomic orbitals) method, i.e., by addition or subtraction of wave functions of individual atoms, thus

Ψ MO = ΨA ± Ψ B

Ψ b = Ψ A + Ψ B

Ψ a = Ψ A – Ψ B

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

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

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

   (i) Combination between s-atomic orbitals
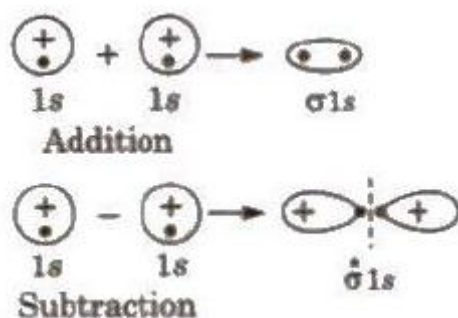
   (ii) Combination between 2s and 2s orbitals gives σ2s and σ 2s orbitals.

   (iii) Combination between p-atomic orbitals
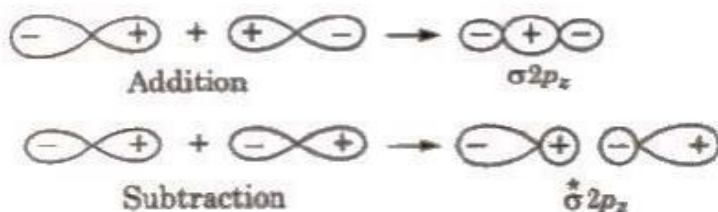
   (iv) Combination between $2p_x$ and $2p_y$ atomic orbitals
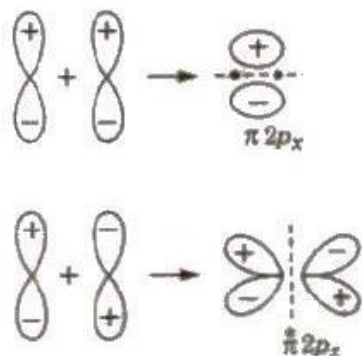
2py atomic orbitals will also overlap in the same way and thus, resulting molecular orbitals are π2p y and π2py .

If molecular orbital has symmetry with respect to centre, it is called gerade (g) otherwise ungerade (u). All σ bonding and π anti-bonding MO are g while all π bonding and σ anti-bonding MO are u.

Electronic Configuration and Bond Order (BO) Of Molecular

The order of energy of molecular orbitals has been determined experimentally by spectroscopy for the elements of the second period. The increasing order of energies of the molecular orbitals in homonuclear diatomic molecules is

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$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \left(\pi 2p_x \approx \pi 2p_y\right) < \left(\pi^* 2p_x \approx \pi^* 2p_y\right) < \sigma^* 2p_z \left[\text{For } O_2, F_2\right]$$
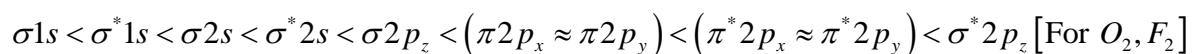
Hydrogen Bond

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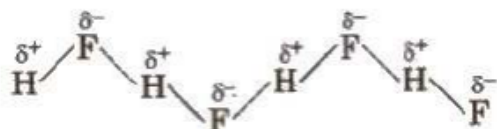
(Hydrogen bond is purely electrostatic and a weak bond.
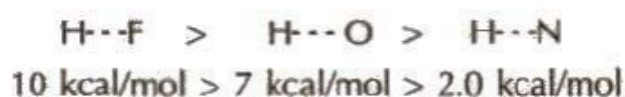
Types of hydrogen bonds are

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

Applications of Intermolecular H-bonding

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

Applications of Intramolecular H-bonding

Volatile character of nitrophenols o-nitrophenol is more volatile (b.p. 214°C) as compared to meta (b.p. 290°C) and para (b.p. 279°C). It is due to chelation.
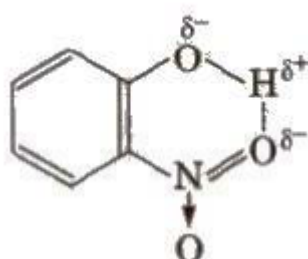
Metallic Bond

Metallic bond is the force of attraction between a metal ion to a number of electrons within its sphere of influence. Electron-sea theory of metallic bond explains number of the properties of the metal

Strength of bonds

Ionic bond > covalent bond > metallic bond > H-bond

Multiple Choice Questions

1.   Molecules are held together in a crystal by
      (a) hydrogen bond
      (b) electrostatic attraction
      (c) Van der Waal's attraction
      (d) dipole-dipole attraction
      Answer: (c) Van der Waal's attraction

2.   Find the molecule with the maximum dipole moment
      (a) CH_4
      (b) NH_3
      (c) CO_2
      (d) NF_3
      Answer: (c) CO_2

3. MX_6 is a molecule with octahedral geometry. How many $X - M - X$ bonds are at 180°?
      (a) four
      (b) two
      (c) three
      (d) six
      Answer: (c) three

4.   The formal charge and P-O bond order in PO_4^{3-} respectively are
      (a) 0.6, -0.75
      (b) -0.75, 1.25
      (c) 1.0, -0.75
      (d) 1.25, -3
      Answer: (b) -0.75, 1.25

5. Which of the molecules does not have a permanent dipole moment?

(a) SO_3

(b) SO_2

(c) H_2S

(d) CS_2

Answer: (d) CS_2

6. Which one has a pyramidal shape?

(a) SO_3

(b) PCl_3

(c) CO_3^{2-}

(d) NO_3^-

Answer: (b) PCl_3

7. Polarity in a molecule and hence the dipole moment depends primarily on electronegativity of the constituent atoms and shape of a molecule. Which of the following has the highest dipole moment?

(i) CO_2

(ii) HI

(iii) H_2O

(iv) SO_2

Answer: (iii) H_2O

8. Hydrogen bonds are formed in many compounds e.g., H_2O, HF, NH_3. The boiling point of such compounds depends to a large extent on the strength of hydrogen bond and the number of hydrogen bonds. The correct decreasing order of the boiling points of above compounds is

(i) $HF > H_2O > NH_3$

(ii) $H_2O > HF > NH_3$

(iii) $NH_3 > HF > H_2O$

(iv) $NH_3 > H_2O > HF$

Answer: (ii) $H_2O > HF > NH_3$

9. Which of the following attain the linear structure:

(i) $BeCl_2$

(ii) NCO^+

(iii) NO_2

(iv) CS_2

Answer: (i) $BeCl_2$

10. Which of the following statements are not correct?

(i) NaCl being an ionic compound is a good conductor of electricity in the solid state.

(ii) In canonical structures there is a difference in the arrangement of atoms.

(iii) Hybrid orbitals form stronger bonds than pure orbitals.

(iv) VSEPR Theory can explain the square planar geometry of XeF_4.

Answer: (i) NaCl being an ionic compound is a good conductor of electricity in the solid state.

11. The bond length between hybridised carbon atom and other carbon atom is minimum in

(a) Propane

(b) Butane

(c) Propene

(d) Propyne

Answer: (d) Propyne

12. The number of nodal planes present in s × s antibonding orbitals is

(a) 1

(b) 2

(c) 0

(d) 3

Answer: (a)1

13. Which one of the following does not have sp² hybridised carbon?

(a) Acetone

(b) Acetic acid

(c) Acetonitrile

(d) Acetamide

Answer: (c) Acetonitrile

14. Which of the following will have the lowest boiling point?

(a) 2-MethylButane

(b) 2-MethylPropane

(c) 2,2-Dimethylpropane

(d) n-Pentane

Answer: (b) 2-MethylPropane

15. Among the following mixtures, dipole-dipole as the major interaction, is present in

(a) benzene and ethanol

(b) acetonitrile and acetone

(c) KCl and water

(d) benzene and carbon tetrachloride

Answer: (c) KCl and water

16. Which of the following types of hybridisation leads to three dimensional geometry of bonds around the carbon atom?

(a) sp

(b) sp^2

(c) sp^3

(d) None of these

Answer: (c) sp^3

17. The maximum number of hydrogen bonds that a molecule of water can have is

(a) 1

(b) 2

(c) 3

(d) 4

Answer: (d) 4

18. The number of types of bonds between two carbon atoms in calcium carbide is

(a) Two sigma, two pi

(b) One sigma, two pi

(c) One sigma, one pi

(d) Two sigma, one pi

Answer: (b) One sigma, two pi

19. Dipole-induced dipole interactions are present in which of the following pairs?

(a) H_2O and alcohol

(b) Cl_2 and CCl_4

(c) HCl and He atoms

(d) SiF_4 and He atoms

Answer: (c) HCl and He atoms

20. The structure of IF_7 is

(a) Pentagonal bipyramid

(b) Square pyramid

(c) Trigonal bipyramid

(d) Octahedral

Answer: (a) Pentagonal bipyramid

Assertion and Reason Questions

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

(a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.

(b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion

(c) Assertion is correct, reason is incorrect

(d) Assertion is incorrect, reason is correct.

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

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

  Answer: (a)

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

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

  Answer: (d) Assertion is false but reason is true.

  The greater the lattice enthalpy, more stable is the ionic compound.

3 **Assertion :** BF_3 molecule has zero dipole moment.

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

  Answer: (b)

4 **Assertion :** Lone pair-lone pair repulsive interactions are greater than lone pair-bond pair and bond pair-bond pair interactions.

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

  Answer: (a) While the lone pairs are localised on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons. This results in greater repulsion between lone pairs of electrons as compared to the lone pair - bond pair and bond pair – bond pair repulsions.

5 **Assertion :** pi bonds are weaker than σ bonds.

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

  Answer: (a) Both assertion and reason are true and reason is the correct explanation of assertion. pi bonds are formed by the overlapping of p-p orbitals perpendicular to their axis i.e., sidewise overlap.

VERY SHORT ANSWER QUESTIONS

1(a)	What change in energy takes place when a molecule is formed from its atoms?
	Answer: There is a fall in energy.
1(b)	Name the shapes of the following molecules: CH_4, C_2H_2, CO_2.
	Answer: CH_4: Tetrahedral; C_2H_2: Cylindrical; CO_2: linear
2(a)	Arrange the following in order of increasing strengths of hydrogen bonding O, F, S, Cl, N.
	Answer: $Cl < S < N < O < F$
2(b)	Which orbitals can overlap to form a cr-bond and which orbitals can do so to form a π bond?
	Answer: s-s, s-p, p-p form a bond, and only p-p form π bond
3 (a)	Which electrons take part in bond formation?
	Answer: Valence electrons present in the outermost shell.
b)	How is bond length is related to bond order ?
	Answer: Greater the bond order ,lesser the bond length.
4 (a)	Name the method generally used for the calculation of lattice energy or electron affinity.
	Answer: Borh-Haber cycle.
(b)	Which type of forces holds the atoms together in an ionic compound?
	Answer: Electrostatic forces of attraction.
5 (a)	Write the Lewis structure of the polyatomic ions CN^-, SO_4^{2-}.
	Answer:
(b)	Arrange the following in order of decreasing C-C bond length: C_2H_6, C_2H_2, C_2H_4
	Answer: $H_3C - CH_3 > H_2C = CH_2 > HC \equiv CH$.
6 (a)	Write down the resonance structures of nitrous oxide.
	Answer:
(b)	What kind of bond exists between two non-metallic elements?

	Answer: Covalent bonds because the difference of electronegativity between two non-metals is usually very small.
7(a)	Define valency
	Answer: The number of electrons that an atom gains or loses or shares with other atoms to attain noble gas configuration is termed its valency.
(b)	Though chlorine has nearly the same electronegativity as nitrogen, yet there is no hydrogen bonding in HCl. Why?
	Answer: The size of the chlorine atom (3 orbits) is bigger than N (2 orbits).
8 (a)	On what factors the polarity of the bond depends?
	Answer: Difference of electronegativity of the two atoms.
(b)	What type of orbitals can overlap to form a covalent molecule?
	Answer: Half-filled atomic orbitals containing electrons with opposite spins.

Short Answer Questions-II

1 (a)	Which out of CH_3F and CH_3Cl has a higher dipole moment and why?
	Answer: The dipole moment of CH_3Cl is greater than that of CH_3F. The C-F bond length in CH_3F is smaller than the C-Cl bond length in CH_3Cl. The charge separation in the C-F bond is more than in the Cl-C bond- fluoride being more electronegative than chlorine. The bond length has a greater effect than the charge separation. Hence the dipole moment of CH_3Cl is greater than that of CH_3F.
(b)	Why covalent bonds are called directional bonds whereas ionic bonds are called non-directional?
	Answer: A covalent bond is formed by the overlap of half-filled atomic orbitals which have definite directions. Hence covalent bond is directional. In ionic compounds, each ion is surrounded by a number of oppositely charged ions and hence there is no definite direction.
(c)	Account for the following: The experimentally determined N-F bond length in NF_3 is greater than the sum of the single covalent radii of N and F.
	Answer: This is because both N and F are small and hence have high-electron density. So they repel the bond pairs thereby making the N-F bond length larger.
2(a)	Why HCl is polar whereas the Cl_2 molecule is non-polar?
	Answer: In Cl_2 both atoms have the same electronegativity. Hence the shared pair of electrons is attracted equally by both and remains exactly in the center. NO end acquires a negative or positive charge. In HCl, chlorine is more electronegative than H. Hence shared pair of electrons is more attracted towards chlorine, which, therefore acquires a negative charge while H acquires a positive charge.
(b)	Out of sigma and pi bonds, which one is stronger and why?

	Answer: Sigma (a) bond is stronger This is because a bond is formed by head-on overlapping of atomic orbitals and such overlapping being on the internuclear axis is large, n bond is formed by sidewise overlapping which is small and so a Pi bond is weaker.
(c)	Out of p-orbital and sp-hybrid orbital which has greater directional character and why?
	Answer: sp orbital has a greater directional character than p-orbital. This is because the p-orbital has equal-sized lobes with equal electron density in both the lobes whereas the sp-hybrid orbital has greater electron density on one side.
3 (a)	Explain giving reasons whether BH_4 and H_3O^+ will have the same/different geometry?
	Answer: The central atom in both the ions is surrounded by the same number of pairs of electrons, that is, 4. Hence they have the same tetrahedral geometry.
(b)	Out of peroxide ion (O_2^{2-}) and superoxide ion (O_2^{-}) which has larger bond length and why?
9 (c)	**Answer:** The bond order of O_2^- is 1.5 while that of O_2^{2-} is 1.0. The lesser the bond order, the greater is the bond length as the bond order is inversely proportional to bond length. (Hence O_2^{2-} has a larger bond length than O_2^{2-}.

Long Answer

1   **Discuss the shape of the following molecules using the VSEPR model:**
    $BeCl_2$, BCl_3 , $SiCl_4$, AsF_5,

Answer:
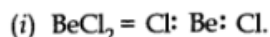
(i) $BeCl_2$ = Cl: Be: Cl.
The central atom has only two bond pairs and there is no lone pair, *i.e.*, it is of the type AB_2. Hence, shape is **linear**.
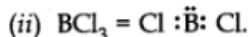
(ii) BCl_3 = Cl :B̈: Cl.
The central atom has only 3 bond pairs and no lone pair, *i.e.*, it is of the type AB_3. Hence, shape is **triangular planar**.
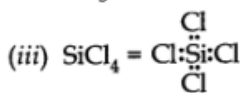
(iii) $SiCl_4$ = Cl:S̈i:Cl
The central atom has
Bond pairs = 4, lone pairs = 0, *i.e.*, it is of the type AB_4.
Hence, shape is **Tetrahedral**.
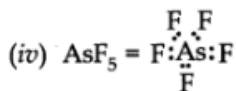
(iv) AsF_5 = F:Äs:F
Bond pairs = 5, lone pairs = 0, *i.e.*, it is of the type AB_5.
Hence, shape is **Trigonal bipyramidal**.
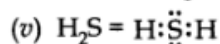
(v) H_2S = H:S̈:H
Bond pairs = 2, lone pairs = 2, *i.e.*, it is of the type AB_2L_2.
Hence, shape is **Bent/V-shaped**.
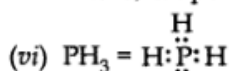
(vi) PH_3 = H:P̈:H
Bond pairs = 3, lone pair = 1, *i.e.*, it is of the type AB_3L.
Hence, shape is **Trigonal**.

H_2S, PH_3

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

Answer: Hybridisation: It is defined as the process of intermixing of atomic oribitals of slightly different energies to give rise to new hybridized orbitals having equivalent energy and identical shapes.

Shapes of Orbitals:

sp hybridisation: When one s-and one p-orbital, intermix then it is called sp-hybridisation. For example, in BeF_2, Be atom undergoes sp-hybridisation. It has linear shape. Bond angle is 180°.

sp^2 hybridisation: One s-and two p-orbitals get hybridised to form three equivalent hybrid orbitals. The three hybrid orbitals directed towards three corners of an equilateral triangle. It is, therefore, known as trigonal hybridisation.

sp^3 hybridisation: One s-and three p-orbitals get hybridised to form four equivalent hybrid orbitals. These orbitals are directed towards the four corners of a regular tetrahedron.

3 **Which hybrid orbitals are used by carbon atoms in the following molecules?**

(a) CH_3-CH_3 (b) CH_3-$CH = CH_2$ (c) CH_3-CH_2-OH (d) CH_3-CHO (e) CH_3COOH.

Answer:
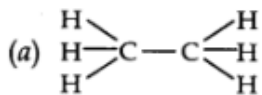
(a) Both C—atoms use sp^3 hybrid orbitals.
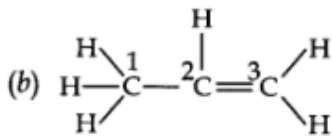
(b) $C_1 = sp^3$, $C_2 = sp^2$, $C_3 = sp^2$
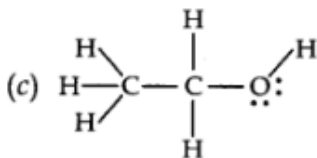
(c) Both C—atoms use sp^3 hybrid orbitals.
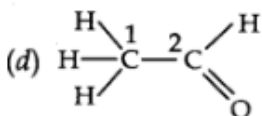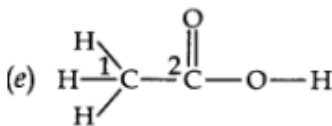
(d) $C_1 = sp^3$, $C_2 = sp^2$

(e) $C_1 = sp^3$, $C_2 = sp^2$

4 **What is meant by the term bond order? Calculate the bond order of N_2, O_2, O_2^+, O_2^-**

Answer: Bond order is defined as the half of the difference between the number of electrons present in bonding and antibonding molecular orbitals.

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

$$\text{E.C of } N_2 = 1s^2\, 2s^2\, 2p_x{}^1 2p_y{}^1 2p_z{}^1$$

(i) M.O. configuration of $N_2 = [\sigma 1s]^2 [\sigma * 1s]^2 [\sigma 2s]^2 [\sigma * 2s]^2 [\pi 2p_x]^2 [\pi 2p_y]^2 [\sigma 2p_z]^2$

$$\text{Bond order (B.O.)} = \frac{1}{2}(N_b - N_a)$$

$$= \frac{1}{2}[8-2] = 3$$

(ii) M.O. configuration of $O_2 = [\sigma 1s]^2 [\sigma * 1s]^2 [\sigma 2s]^2 [\sigma * 2s]^2 [\sigma 2p_z]^2$

$$\text{B.O} = \frac{1}{2}[N_b - N_a]$$

$$= \frac{1}{2}[8-4] = 2$$

(iii) M.O. configuration of $O_2{}^+ = KK[\sigma 2s]^2 [\sigma * 2s]^2 [\sigma 2p_z]^2 [\pi 2p_x]^2 [\pi 2p_y]^2 [\pi * 2p_x]^1$

$$\text{B.O.} = \frac{1}{2}[8-3] = 2.5$$

(iv) M.O. configuration of $O_2{}^-$

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

$$\text{B.O.} = \frac{1}{2}[8-5] = 1.5$$

Case study

1. Read the passage and answer the questions that follow:

The attractive force which holds the two atoms together is called a chemical bond. A covalent bond is formed by an equal sharing of electrons. A coordinate bond is formed by unequal sharing of electrons. An ionic bond is formed by the transfer of electrons from one atom to another. Octet rule, although very useful but is not universally applicable. According to valence bond theory, a covalent bond is formed by overlapping of half-filled atomic orbitals resulting in a lowering of energy and more stability. Bond order is the number of bonds between atoms in a molecule. The higher the bond order more will be stability and bond dissociation enthalpy but the smaller the bond length. The polarity of a covalent bond depends upon the difference in electronegativity. The covalent character of a bond depends upon polarising power, smaller cation and bigger anions have higher polarising power. VSEPR theory helps to predict the shapes of molecules.

(a) Write the electron dot structure of N_2O.

Ans (a). $N \equiv N^+ - O^-$

(b) What are the ions present in CsI$_3$?

Ans (b). Cs^+ and I_3^-.

(c) Out of CN$^+$, CN$^-$, NO, which has the highest bond order?

Ans (c). CN$^-$ (14): $\sigma(1s)^2, \sigma^*(1s)^2, \sigma(2s)^2, \sigma^*(2s)^2, \pi(2p_x)^2= \pi(2p_y)^2, \sigma(2pz)^2$.

(d) What is the correct order of repulsion bp – bp, lp – lp, and lp – bp?

Ans (d). lp – lp > lp – bp > bp – bp (bp is bond pair, lp is lone pair).

(e) Draw the structure of XeOF$_4$ on the basis of VSEPR theory.

Ans (e).

Square pyramidal
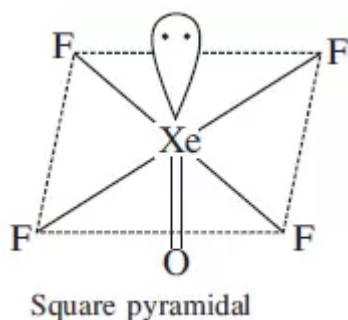
f) Which out of B$_2$, CO, O$_2{}^{2-}$ and NO$^+$ are paramagnetic and why?

Ans (f). B$_2$(10): $\sigma(1s)^2, \sigma^*(1s)^2, \sigma(2s)^2, \sigma^*(2s)^2, \pi(2p_x)^1= \pi(2p_y)^1$

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

This theory provides a simple procedure to predict the shapes of covalent molecules. Based on the repulsive interactions of the electron pairs in the valence shell of the atoms. The shape of a molecule depends upon the number of valence shell electron pairs (bonded or non–bonded) around the central atom. Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged. These pairs of electrons tend to occupy such positions in space that minimize repulsion and thus maximize distance between them. The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another. A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair. Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure. The repulsive interaction of electron pairs decrease in the order:

lp – lp>lp –bp>bp – bp

lone pairs are localised on the central atom and each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons. These results in greater repulsion between lone pairs of electrons as compared to the lone pair – bond pair and bond pair – bond pair repulsions.

1. Percentage of s–character in sp^2 hybrid orbital is
   a) 25
   b) 50
   c) 33
   d) 75

   Answer: c) 33

2. Shape of XeF_4 molecule is
   a) Linear
   b) Pyramidal
   c) Tetrahedral
   d) Square planar

   Answer: d) Square planar

3. Shape of methane molecule is
   a) Pyramidal
   b) Tetrahedral
   c) Octahedral
   d) Square planer

   Answer: b) Tetrahedral

4. Hybridisation involves
   a) Mixing up of atomic orbitals
   b) Addition of an electron pair
   c) Removal of an electron pair
   d) Separation of orbitals

   Answer: a)Mixing up of atomic orbitals

5. Number of lone pair (s) in $XeOF_4$ is/are
   a) 0
   b) 1
   c) 2
   d) 3
   Answer: b)1

5. CHEMICAL THERMODYNAMICS

THERMODYNAMIC TERMS

- System It refers to the part of universe in which observations are carried out.

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

- Boundary The wall that separates the system from the surroundings is called boundary.

- Thermodynamic equilibrium A system in which the macroscopic properties do not undergo any change with time is called thermodynamic equilibrium.

- Thermal equilibrium If there is no flow of heat from one portion of the system to another, the system is said to be in thermal equilibrium.

Types of Systems

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

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

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

Intensive Properties

Properties of the system which depend only on the nature of matter but not on the quantity of matter are called Intensive properties, e.g., pressure, temperature, specific heat, etc

Extensive Properties

Properties of the system which are dependent on the quantity of matter are called extensive properties, e.g., internal energy, volume, enthalpy, etc.

State of System:

When microscopic properties have definite value, the conditions of existence of the system is known as state of system.

State functions: When values of a system is independent of path followed and depend only on initial and final state, it is known as state function, e.g., ΔU, ΔH, ΔG etc.

Path functions: These depend upon the path followed only, e.g., work, heat, etc.

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

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

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

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

Adiabatic process: In which heat is not exchanged by system with the surroundings$(\Delta q = 0)$.

Cyclic process: It is a process in which system returns to its original state after undergoing a series of change.

Reversible process: A process that follows the reversible path, i.e., the process which occurs in infinite number of steps in this Way that the equilibrium conditions are maintained at each step, and the process can be reversed by infinitesimal change in the state of functions.

Irreversible process: The process which cannot be reversed and amount of energy increases. All natural processes are Irreversible.

Internal Energy (E or U) :

It is the total energy within the substance. It is the sum of many types of energies like vibrational energy, translational energy. etc. It is a extensive property and state function.

Its absolute value cannot be determined but experimentally change in internal energy (Δ) can be determined by $\Delta U = U2 - U1$ or $\Sigma U_P - \Sigma U_R$

First Law of Thermodynamics:

Energy can neither be created nor destroyed although it can be converted from one form to the other.

Mathematically, $\Delta U = q + W$

where, ΔU = internal energy change q = heat added to system

W = work added to system

Sign convention:

(i) q is + ve = heat is supplied to the system

(ii) q is – ve = heat is lost by the system

(iii) W is + ve = work done on the system

(iv) W is – ve =work done by the system

Enthalpy (H): At constant volume $\Delta V = 0$, $q_v = \Delta U$
So $H = U + p\Delta V$, $q_p = H_2 - H_1 = \Delta H$
$\Delta H = \Delta U + P.\Delta V$.

Exothermic and Endothermic reactions: $\Delta H = -Ve$ for exothermic and ΔH = +Ve for endothermic reaction i.e. evolution and absorption of heat respectively

HEAT CAPACITY

- Heat Capacity of a System

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

The enthalpy change accompanying a reaction is called the **reaction enthalpy**

Measurement of ΔH and ΔU The process is carried out in a vessel called calorimeter, immersed in a known volume of a liquid.
(a) ΔU measurements: The energy changes are measured a t c o n s t a n t v o l u m e. No work is d o n e .A bomb calorimeter is used.
(b) ΔH measurements: In exothermic reaction, heat is evolved, so q and H will be negative. In endothermic p reaction, heat is absorbed, so q and H will be positive

Standard Enthalpy of Reactions
The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.

The standard state of a substance at a specified temperature is its pure form at 1 bar

Enthalpy changes during phase transformations:

- **Standard enthalpy of fusion / molar enthalpy of fusion**, H is the enthalpy _fus_ change that accompanies melting of one mole of a solid substance in standard state.
- **Standard enthalpy of vaporization or molar enthalpy of vaporization**. ΔH vap is the amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure.
- **Standard molar enthalpy of formation** $\Delta H_{r\_}$ is the standard enthalpy change for the formation of one mole of a compound from its elements in their most stable state of aggregation
- **Standard enthalpy of sublimation,** $\Delta_{sub}H^0$ is the change in enthalpy when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1bar.

Hess's Law of constant heat summation: The total amount of heat change is same whether the reaction

takes place in one step or in several steps.

i.e. H = H1 + H2 + H3 + --------

Bond enthalpy: It is amount of energy released when gaseous atoms combines to form one mole of bonds

between them or heat absorbed when one mole of bonds between them are broken to give free gaseous

atoms. Further ΔH r = B.E. (Reactants) - B.E. (Products)

Lattice Enthalpy
The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

Spontaneous & Non Spontaneous Processes: A process which can take place by itself is called

spontaneous process. A process which can neither take place by itself or by initiation is called non

Spontaneous.

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

Enthalpy of Dilution It is known that enthalpy of solution is the enthalpy change associated with the addition of a specified amount of solute to the specified amount of solvent at a constant temperature and pressure

Driving forces for spontaneous process: (i) Tendency for minimum energy

state. (ii) Tendency for maximum randomness.

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

i.e. Gas>Liquid>Solid.

Entropy change (ΔS) = $\underline{q(rev.)}$J.K^{-1} .mol $^{-1}$

T

Spontaneity in term of (ΔS)

- ΔS(total) = ΔS(universe) = ΔS(system) + ΔS(surrounding)
- If ΔS(total) is +ve, the process is spontaneous.
- If ΔS(total) is –ve, the process is non spontaneous.

Second Law of thermodynamics: In any spontaneous process, the entropy of

the universe always increases. A spontaneous process cannot be reversed.

Gibb's free energy (ΔG): defined as G = H – T.S & ΔG = H – TΔS (Gibb's

Helmholts equation) it is equal useful work i.e. - ΔG = W(useful) = W(max.)

If $\Delta G = -ve$ the process is spontaneous. If it is positive the process is non spontaneous. For reversible process $\Delta G = 0$

SOME IMPORTANT FORMULAE

$\Delta U = q + w$
$\Delta H = \Delta U + P\Delta V$
$\Delta H = \Delta U + \Delta n_g RT$
$C_P - C_V = R$
$\Delta H_r = \Sigma a_i H_{products} - \Sigma b_i H_{reactants}$
$\Delta_r H^0 = \Delta_{r1} H_1 + \Delta_{r2} H_2 + \Delta_{r3} H_{3......}$
$\Delta S_{fusion} = \dfrac{\Delta H_{fusion}}{T}$
$\Delta S = \dfrac{q_{rev}}{T}$
$\Delta G = H - T\Delta S$
$\Delta G_r = -RT \ln K$

MCQ

1. Thermodynamics is not concerned about_____.
(i) energy changes involved in a chemical reaction.
(ii) the extent to which a chemical reaction proceeds.
(iii) the rate at which a reaction proceeds.
(iv) the feasibility of a chemical reaction.

(Answer) (iii) the rate at which a reaction proceeds

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

 (Answer) (iii) The presence of reactants in a closed vessel made up of copper is an example of a closed system.

3. The state of a gas can be described by quoting the relationship between____.
(i) pressure, volume, temperature   (ii) temperature, amount, pressure
(iii) amount, volume, temperature   (iv) pressure, volume, temperature, amount

(Answer) (iv) pressure, volume, temperature, amount

4. The volume of gas is reduced to half from its original volume. The specific
heat will be _____.
(i) reduce to half   (ii) be doubled   (iii) remain constant (iv) increase four times

(Answer) (**iv**) **pressure, volume, temperature, amount**

5. The enthalpies of elements in their standard states are taken as zero. The
enthalpy of formation of a compound
(i) is always negative   (ii) is always positive
(iii) may be positive or negative   (iv) is never negative

(Answer) (iii) may be positive or negative

6. Enthalpy of sublimation of a substance is equal to
(i) enthalpy of fusion + enthalpy of vapourisation   (ii) enthalpy of fusion
(iii) enthalpy of vapourisation   (iv) twice the enthalpy of vapourisation
(Answer) (i) enthalpy of fusion + enthalpy of vapourisation

7. Which of the following is not correct?
(i) ΔG is zero for a reversible reaction
(ii) ΔG is positive for a spontaneous reaction
(iii) ΔG is negative for a spontaneous reaction   (iv)
ΔG is positive for a non-spontaneous reaction
(Answer) (ii) ΔG is positive for a spontaneous reaction

8. A thermodynamic state function is a quantity
(i) used to determine heat changes
(ii) whose value is independent of path
(iii) used to determine pressure volume work
(iv) whose value depends on temperature only.
(Answer) (ii) whose value is independent of path

9.The work done in case of isothermal free expansion is
a)maximum   b)minimum   c)zero   d)positive
(Answer) c)zero

10. The enthalpies of all elements in their standard states are:
(i) unity   (ii) zero   (iii) < 0 (iv) different for each element
(Answer) (ii) zero

11. ΔU^0 of combustion of methane is $-$ X kJ mol^{-1}. The value of ΔH^0 is
(i) $= \Delta U^0$ (ii) $> \Delta U^0$ (iii) $< \Delta U^0$ (iv) $= 0$
(Answer) (iii) $< \Delta U^0$

12. The enthalpy of combustion of methane, graphite and dihydrogen at 298 K
are, -890.3 kJ mol^{-1} -393.5 kJ mol^{-1}, and -285.8 kJ mol^{-1} respectively. Enthalpy
of formation of CH$_4$(g) will be
(i) -74.8 kJ mol^{-1} (ii) -52.27 kJ mol^{-1} (iii) $+74.8$ kJ mol^{-1} (iv) $+52.26$ kJ mol$^{-1.}$
(Answer) (i) -74.8 kJ mol^{-1}

13. A reaction, A + B $\rightarrow$ C + D + q is found to have a positive entropy change. The
reaction will be
(i) possible at high temperature
(ii) possible only at low temperature
(iii) not possible at any temperature
(iv) possible at any temperature
(Answer) (iv) possible at any temperature

14. Which of the following is an extensive property

a) Molar heat capacity   b) Temperature   c) Enthalpy   d) All of these

(Answer) c) Enthalpy

15. In an open system, for maximum work, the process must be entirely

a) irreversible b) reversible c) adiabatic d) none of the mentioned

(Answer) b) reversible

**(II) In the following questions a statement of Assertion (A) followed by a statement
of Reason (R) is given. Choose the correct option out of the choices given below each question**
(i) Both A and R are true and R is the correct explanation of A.
(ii) Both A and R are true but R is not the correct explanation of A.
(iii) A is true but R is false.
(iv) A is false but R is true.

1.*Assertion (A):* Combustion of all organic compounds is an exothermic reaction.
Reason (R) : The enthalpies of all elements in their standard state are zero

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

2.*Assertion (A) :*Spontaneous process is an irreversible process and may be reversed by some external
agency.
Reason (R) : Decrease in enthalpy is a contributory factor for spontaneity

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

3 *Assertion (A) :* A liquid crystallises into a solid and is accompanied by decrease in entropy.
Reason (R) : In crystals, molecules organise in an ordered manner

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

SA(I) 2 MARK QUESTIONS

1. Given: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, $\Delta H_0 = -92.4 KJ.mol^{-1}$ What is the standard enthalpy of formation of $NH_3(g)$.

   (**Answer**)

   The reaction for formation of one mole of ammonia is

   $\frac{1}{2} N_2(g) + 3/2 H_2(g) \rightarrow NH_3(g)$
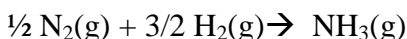
   The standard enthalpy of formation of ammonia is

   $\Delta_f H^0 NH_3(g) = \dfrac{-92.4}{2} = 46.2 KJmol^{-1}$

2. Predict the entropy change in- (i) A liquid crystallizes into solid

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

   (**Answer**)

   (i) Entropy decreases because molecules attain an ordered state.

   (ii)Entropy increase because from OK to 115K particles begin to move.

3. Identify the state functions and path functions out of the following :
   enthalpy, entropy, heat, temperature, work, free energy

   (**Answer**)

   State Functions : Enthalpy, Entropy, Temperature, Free energy

   Path Functions : Heat, Work

4. For the reaction, $2 Cl(g) \rightarrow Cl_2(g)$, what are the signs of ΔH and ΔS ?
   (**Answer**)
   ΔH and ΔS are negative

5. Predict the change in internal energy for an isolated system at constant volume.
   (**Answer**)

   For isolated system, there is no transfer of energy as heat or as work i.e.,
   w=0 and q=0. According to the first law of thermodynamics.
   $\Delta U = q + w$
   $= 0 + 0 = 0$
   $\Delta U = 0$

SA(II) 3 Marks

1. Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24 J mol^{-1} K^{-1}..
   (**Answer**)
   Given: T1=35°C=(35+273)K=308 K
   T2=55°C=(55+273)K=328 K

$C_p = 24 \text{ J mol}^{-1} \text{ K}^{-1}$

Number of mole of Aluminium $= \dfrac{60 \text{ g/mol}}{27 \text{ g}} = 2.23$ mole

$\triangle H = nCp\triangle T$

$\triangle H = 2.23 \text{ mole} \times 24 \text{ Jmol}^{-1}\text{K}^{-1} \times 20 \text{ K}$

$\triangle H = 1.07 \text{KJ}$

2.For the reaction at 298 K, $2A + B \rightarrow C$ $\Delta H = 400$ kJ mol–1 and $\Delta S = 0.2$ kJ K–1 mol–1
At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range.

(**Answer**)

$\Delta G = \Delta H - T\Delta S$

Assume that the equation is at equilibrium then

$\Delta G = 0$

$\Delta G = \Delta H - T\Delta S = 0$
Therefore $T = \dfrac{\Delta S}{\Delta H} = \dfrac{400}{0.2} = 2000K$
                                                              For the
reaction to be spontaneous ΔG must be negative.

Therefore temperature should be greater than 2000 K.

3.For the reaction $2 A(g) + B(g) \rightarrow 2D(g)$ $\Delta U^{0} = -10.5$ kJ and $\Delta S^{0} = -44.1$ JK^{-1}. Calculate ΔG^{0} for the reaction, and predict whether the reaction may occur spontaneously.

$\Delta n_g = 2 - (3) = -1$ mole
$\Delta H^{o} = \Delta U^{o} + \Delta n_g RT$
$= (-10.5 \text{ kJ}) - (-1)(8.314 \times 10{-3} \text{ kJ K–1 mol–1})(298 \text{ K}) = -10.5 \text{ kJ} - 2.48 \text{ kJ}$
$\Delta H^{o} = -12.98$ kJ
Substituting the values of ΔH^{o} and ΔS^{o} in the expression of ΔG^{o}
$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} = -12.98 \text{ kJ} - (298 \text{ K})(-44.1 \text{ J K}^{-1}) = -12.98 \text{ kJ} + 13.14 \text{ kJ}$
$\Delta G^{o} = + 0.16$ kJ
Since ΔG^{o} for the reaction is positive, the reaction will not occur spontaneously.

CASE BASES STUDY

We can measure energy changes associated with chemical or physical processes by an experimental technique called calorimetry. In calorimetry, the process is carried out in a vessel called calorimeter, which is immersed in a known volume of a liquid. Knowing the heat capacity of the liquid in which calorimeter is immersed and the heat capacity of calorimeter, it is possible to determine the heat evolved in the process by measuring temperature changes. Measurements are made under two different conditions
i) at constant volume, qV
ii) at constant pressure, qp
1. The quantity of of heat required to raise the temperature of one unit mass of a substance by one degree Celsius is called a)Heat capacity b)Specific heat capacity c)Molar heat capacity d)Heat content
(**Answer**) **b)Specific heat capacity**

2.For adiabatic change a)q=0,w ad =0 b) q=0, w ad =ΔU c) q=0, w ad =ΔH d) q=-w=ΔU
(**Answer**) **a)q=0** w ad =0

3. In bomb calorimeter which quantity is kept constant to calculate ΔU?
a)volume   b)pressure   c)temperature   d) all of these
(**Answer**) **a)volume**

4. What is the relation between heat capacity and temperature
a)$q=C\Delta T$ b) $q=mc\Delta T$ c)$q=C/n\ \Delta T$ (d) $q=mc/\Delta T$
(**Answer**) **a)$q=C\Delta T$**

LONG ANSWER (5 MARKS)

1.(a) Define standard molar enthalpy of formation.
(b) Calculate the enthalpy change for the process
$CCl_4(g) \rightarrow C(g) + 4\ Cl(g)$ and calculate bond enthalpy of C – Cl in $CCl_4(g)$.
$\Delta_{vap}H^0(CCl_4) = 30.5$ kJ mol^{-1}. Δ_fH^0 (CCl_4) $= –135.5$ kJ mol^{-1}. Δ_aH^0 (C) $= 715.0$ kJ mol^{-1} , where Δ_aH^0 is
enthalpy of atomisation Δ_aH^0 (Cl_2) $= 242$ kJ mol^{-1}

   (**Answer**)

(a) The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states)is called Standard Molar Enthalpy of Formation

(b) $CCl_{4(l)}$ $\rightarrow$ $CCl_{4(g)}$ $\Delta_{vap}H^0 = 30.5$ kJ mol^{-1}→eqn I
$C_{(s)}$ $\rightarrow$ $C_{(g)}$ $\Delta_aH^0 = 715.0$ kJ mol^{-1}→eqn II
$Cl_{2(g)}$ $\rightarrow$ $2Cl_{(g)}$ $\Delta_aH^0 = 242$ kJ mol^{-1}→eqn III
$C_{(g)} + 4Cl_{(g)}$ $\rightarrow$ $CCl_{4(g)}$ $\Delta_fH^0 = -135.5$ kJ mol^{-1}→eqn IV
Enthalpy change for the given process $C_{(g)} + 4Cl_{(g)} \rightarrow CCl_{4(g)}$ can be calculated as given below
ΔH =Equation (II) + 2 × Equation (III) - Equation (I) - Equation (IV)
$\Delta H = \Delta_aH^0$ (C) + $2\Delta_aH^0$ (Cl_2) - $\Delta_{vap}H^0$ - Δ_fH^0
$= (715.0$ kJ $mol^{-1}) + 2(242$ kJ $mol^{-1}) - (30.5$ kJ $mol^{-1}) - (-135.5$ kJ $mol^{-1})$
$\therefore \Delta H = 1304$ kJ mol^{-1}
Bond enthalpy of C-Cl bond in $CCl_{4(g)} = \dfrac{1304 \text{ kJ mol}^{-1}}{4} = 326$ kJ mol^{-1}

2. (a) What are extensive property and intensive properties?
    (b) Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the following data:
       CH_3OH (l) $+3/2\ O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$; $\Delta rH^0 = –726$ kJ mol^{-1}

       $C(graphite) + O_2(g) \rightarrow CO_2(g)$; $\Delta cH^0 = –393$ kJ mol^{-1}
       $H_2(g) +1/2\ O_2(g) \rightarrow H_2O(l)$; $\Delta f\ H^0 = –286$ kJ mol^{-}
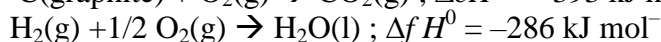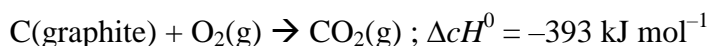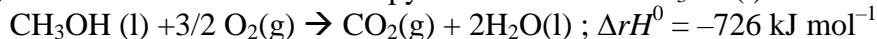
(**Answer**)

 a) Intensive Properties

Properties of the system which depend only on the nature of matter but not on the quantity of matter are

called Intensive properties, e.g., pressure, temperature, specific heat, etc

<u>Extensive Properties</u> Properties of the system which are dependent on the quantity of matter are called extensive properties, e.g., internal energy, volume, enthalpy, etc.

(b)CH_3OH (l) +3/2 O_2(g) → CO_2(g) + 2H_2O(l) ; ΔrH^0 = –726 kJ mol^{-1}
On reversing the eqn 1
$CO2$(g)+2H_2O(l)→CH_3OH(l)+ 3/2O_2(g); ΔrH^o=+726kJmol^{-1} →eqn 1

C(graphite)+O_2(g)→CO_2(g);$\Delta_c H^0$=−393kJmol^{-1} →eqn 2
H_2(g) +1/2 O_2(g) → H_2O(l) ; $\Delta f H^0$ = –286 kJ mol^{-1}. -→eqn 3

Multiply eqn 3 by 2

$2H_2$(g)+O_2(g)→$2H_2O$(l);$2\Delta_f H^0$=2×−286kJmol^{-1}=−572kJmol^{-1} → eqn 4
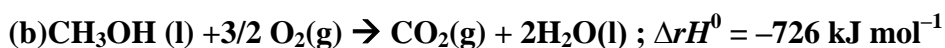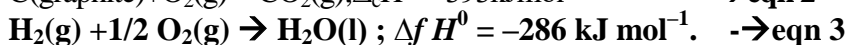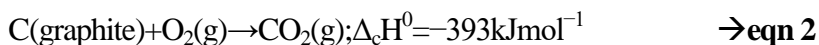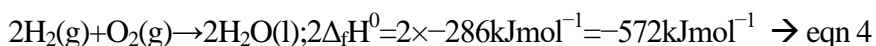
On adding eqn 1,eqn 2 and eqn 4,

C(graphite)+$2H_2$(g)+1/2 O_2(g)→CH_3OH(l)
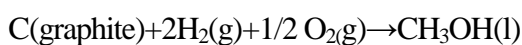
Enthalpy of formation of CH_3OH
$\Delta_f H^0$=+726−393−572kJmol−1=−239kJmol^{-1}

HOTS

1. The difference between C_P and C_V can be derived using the empirical relation $H = U + pV$. Calculate the difference between C_P and CV for 10 moles of an ideal gas.

   (**Answer**)

   $C_P - C_V = nR$
   $= 10 \times 4.184$ J

2. The enthalpy of atomisation for the reaction CH_4(g)→ C(g) + 4H (g) is 1665 kJ mol–1. What is the bond energy of C–H bond?

   (**Answer**)
   $\underline{1665}$ kJ mol^{-1} = 416.2 kJ mol^{-1}
     4

3. Given that ΔH= 0 for mixing of two gases. Explain whether the diffusion of these gases into each other in a closed container is a spontaneous process or not?

   (**Answer**)

   It is spontaneous process. Although enthalpy change is zero but randomness or disorder (i.e., ΔS) increases. Therefore, in equation $\Delta G = \Delta H - T\Delta S$, the term T$\Delta$S will be negative. Hence, ΔG will be negative

4. Enthalpy diagram for a particular reaction is given in the figure below. Is it possible to decide spontaneity of a reaction from the given diagram. Explain
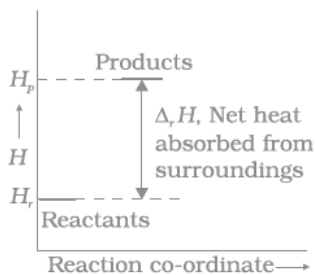
(**Answer**)

No.

Enthalpy is one of the contributory factors in deciding spontaneity but it is not the only factor. One must look for contribution of another factor i.e., entropy also, for getting the correct result

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6.EQUILIBRIUM

KEY POINTS

- Equilibrium in physical processes:
- Solid-liquid equilibrium
- Liquid-vapour equilibrium
- Solid-vapour equilibrium
- Dynamic equilibrium
- law of chemical equilibrium and equilibrium constant
- homogeneous equilibrium
- Equilibrium constant in gaseous systems
- Factors affecting equilibrium-Le Chatteliers principle
- Ionic equilibrium-ionisation of acids and bases
- Strong and weak electrolytes
- Degree of ionisation
- Ionisation of polybasic acids
- Acid strength –pH
- Hydrolysis of salt, buffer solution
- Henderson equation
- Solubility product
- Common ion effect

Chemical Equilibrium: In a chemical reaction chemical equilibrium is defined as the state at which there is no further change in concentration of reactants and products.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
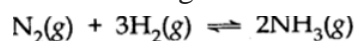
Characteristics of equilibrium:

i) equilibrium can be achieved only in a closed vessel

ii)   equilibrium is reversible in nature

iii)   equilibrium is dynamic in nature. ie., the system is always in motion in both directions at the microscopic level

iv)at equilibrium the rate of forward reaction = rate of backward reaction.

v) Equilibrium state can be recognised by the constancy of measurable properties like colour ,concentration, pressure, density etc.

Types:
- Physical equilibrium
- Chemical equilibrium

Physical equilibrium

It is the equilibrium between same chemical species in different physical states

- ➢ Solid-liquid equilibrium

  $H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$
- ➢ Liquid-vapour equilibrium

  $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$
- ➢ Solid-vapour equilibrium

  $H_2O_{(s)} \rightleftharpoons H_2O_{(g)}$

  Camphor (solid) $\rightleftharpoons$ Camphor (vapour)
- ➢ Solid –solution equilibrium

  Sugar in its saturated solution
- ➢ Gas-solution equilibrium

  CO2 dissolved in H_2O

Some features of physical equilibrium

Process	Conclusion
Liquid $\rightleftharpoons$ Vapour H_2O (l) $\rightleftharpoons$ H_2O (g)	p_{H_2O} constant at given temperature
Solid $\rightleftharpoons$ Liquid H_2O (s) $\rightleftharpoons$ H_2O (l)	Melting point is fixed at constant pressure
Solute(s) $\rightleftharpoons$ Solute (solution) Sugar(s) $\rightleftharpoons$ Sugar (solution)	Concentration of solute in solution is constant at a given temperature
Gas(g) $\rightleftharpoons$ Gas (aq) CO$_2$(g) $\rightleftharpoons$ CO$_2$(aq)	[gas(aq)]/[gas(g)] is constant at a given temperature [CO$_2$(aq)]/[CO$_2$(g)] is constant at a given temperature

Chemical equilibrium: Equilibrium between reactants and products in a chemical reaction.

Characteristics:

a) It's a dynamic equilibrium i.e. at this stage , the reaction take place in both the direction with same speed

b) At equilibrium the reaction proceed both side ,equally

c) At equilibrium ,both reactant and products are present and their concentration do not change with respect to time

d) The state of equilibrium is not effected by the presence of catalyst :it only helps to attain the equilibrium state faster

e) Change in pressure, temperature and concentration favours one of the reactions and thus shift the equilibrium point in one direction

Types:

Homogeneous equilibrium:

the equilibrium between reactants and products in the same physical state is called homogeneous equilibrium

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
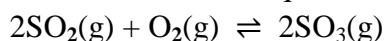
Heterogeneous equilibrium:

The equilibrium between reactants and products in different physical states is called heterogeneous equilibrium

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Law of Chemical Equilibrium.

At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the Equilibrium Law or Law of Chemical Equilibrium.

For a reaction $A+B \rightleftharpoons C+D$, rate of forward reaction, $R_f = k_f[A][B]$, rate of backward reaction

$R_b = k_b [C][D]$

At equilibrium $= R_b,$

ie: $k_f[A][B] = k_b[C][D]$

Or, $k_c = \dfrac{k_b}{k_f} = \dfrac{[C][D]}{[A][B]}$

for a reaction with non-unitary stoichiometric coefficient: $aA + bB \rightleftharpoons c\,C + dD$,

$k_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

Eg: K_c for the reaction, $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

is written as $Kc = [NO]^4 [H_2O]^6 / [NH_3]^4 [O_2]^5$

Equilibrium constant for reverse reaction is the inverse of the equilibrium constant for the reaction in the forward reaction.

Equilibrium Constant in Gaseous Systems

If an equilibrium involves gaseous species then the concentration terms are replaced by partial pressures

$Kp = \dfrac{pC^c\, pD^d}{pA^a\, pB^b}$

Relation between Kp and Kc: $Kp = Kc(RT)^{\Delta n}$

Units: For K_p: P_a, kP_a, bar or atm

For K_c: mol L^{-1}

Reaction Quotient Q_c : It is the ratio of product of molar concentration of products to the ratio of product of molar concentration of the reactants at any stage of reaction.

For a reaction $aA + bB \rightleftharpoons cC + dD$, $Qc = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

Application of K_c:

i) Higher the value of K_c, higher will be the extent of reaction. , smaller value of K indicates, reactant concentration is predominant.

ii) If $Q_c > K_c$, the reaction proceeds in the backward reaction

iii) If $Q_c < K_c$, the reaction proceeds in the forward reaction

iv) If $Q_c = K_c$, the reaction is at equilibrium.

- Factors affecting equilibrium-Le Chateliers principle

If a system in equilibrium is subjected to a change of concentration, pressure or temperature ,the equilibrium shifts in the direction to minimise the the effect the change.

Factors:

1.Concentration	Reactant concn increased	Forward direction
	Product concn. increased	Backward direction
2.Pressure	For reactions involving gases	P∞1/v ,so to the direction where there is decrease in no.of moles
3.Temperature	Exothermic Rn. Endothermic Rn.	Backward Forward
4. Catalyst		No effect
5.Addition of inert gas	a)at constant volume b)at constant volume	No effect Towards larger no. of gaseous molecules

- Ionic equilibrium-ionisation of acids and bases
- Strong and weak electrolytes
- Degree of ionisation
- Ionisation of polybasic acids
- Acid strength –pH
- Hydrolysis of salt, buffer solution
- Henderson equation
- Solubility product
- Common ion effect
- Factors affecting equilibrium-Le Chateliers principle

IMPORTANT FORMULAE

1. $aA + bB \rightleftharpoons c\,C + d\,D$, $K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$
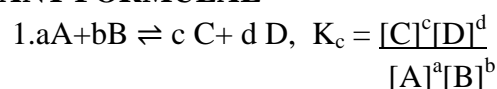
2. $K_p = K_c(RT)^{\Delta n}$

3. $\Delta G^0 = -RT \ln K = -2.303RT \log K$

4. $K_a \times K_b = K_w$

5. $pH = -\log[H^+]$, $pOH = -\log[OH^-]$

6. $pK_w = pH + pOH = 14$

7. $x^- + H_2O \rightleftharpoons OH^- + HX$
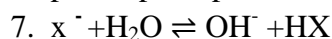
Degree of hydrolysis $h = \sqrt{kw/ka \times c}$ (for salts of strong acid and weak base)

$pH = \frac{1}{2}(pK_w + pK_a + \log c)$

$pH = \frac{1}{2}(pK_w - pK_b - \log c)$

Degree of hydrolysis $h = \sqrt{K_w/K_a \times K_b}$ (for salts of weak acid and weak base)

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

pH of buffer solution of salt of weak acid and and its salt:

$pH = pK_a + \log \dfrac{[salt]}{[Base]}$

$pOH = pK_b + \log \dfrac{[salt]}{[Base]}$ (for basic buffers)

Solubility:

Salt type	Relation between K_{sp} and S	Example
AB AB_2 A_2B AB_3	$K_{sp}=s \times s=s^2$ $K_{sp}=s \times(2s)^2= 4s^3$ $K_{sp}=(2s)^2 \times(s)= 4s^3$ $K_{sp}=(s)\times(3s)^3= 27s^3$	$AgCl,ZnS$ $PbCl_2,HgCl_2$ Ag_2SO_4 $Fe(OH)_3$

Multiple Choice Questions:

1.At equilibrium,rate of forward reaction will be ……rate of backward reaction.
    a) less than   b) greater than c) equal to   d) none of these

2. For a pure substance ,at atmospheric pressure the temperature at which the solid and liquid phases are at equilibrium at is called:
    a) freezing point b)boiling point   c) kraft temperature d) absolute temperature

3) Henry's Law is applicable for
    a) solid-liquid equilibrium   b) solid-gas equilibrium   c) gas –liquid equilibrium d) gas – solution of gas equilibrium

4. $K_p=K_c$ when :
    a)$\Delta n=1$ b) $\Delta n>1$ c)$\Delta n=0$ d) $\Delta n<1$

5. If $Q_c > K_c$,the reaction proceeds in the
    a) forward reaction b) backward reaction c) at equilibrium d) none of these .

6. For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$: $\Delta H = -92.38 kJmol^{-1}$, raising the temperature ……the equilibrium   concentration of ammonia
    a) increases b) decreases c) doesnot change d) all of these

7. The acid –base pair that differs by one …is called a conjugate acid –base pair
    a)electron b)proton c) hydronium ion   d) hydroxyl ion

8. Which of the following is amphoteric in nature:
    a)H_3O+ b)HCl c) SO_4^{2-} d) HSO_4^{-}

9. Which of the following salts will give the highest pH in water.
    a) KCl b)   NaCl   **c)** Na_2CO_3 d) $CuSO_4$

10. 0.10 M CH_3COOH is 1.34% ionised, calculate its Ka.
    a) 1.8×10^{-5} b) 5×10^{-4} c) 1.8×10^{-4} d)4×10^{-5}

11. In which of the following equilibrium, K_c and K_p are not equal?
a. $2C (s) + O_2 (g)$ $\rightleftharpoons$ $2CO_2 (g)$
b. $2NO (g)$ $\rightleftharpoons$ $N_2 (g) + O_2 (g)$
c. $SO_2 (g) + NO_2 (g)$ $\rightleftharpoons$ $SO_3(g) + NO(g)$
d. $H_2(g) + I_2 (g)$ $\rightleftharpoons$ $2 HI(g)$

12. For the reversible reaction, $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3 (g)$ at 500^0C, the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_c, with concentration in mole litre^{-1}, is :
    (a)$1.44 \times 10^{-5} / (0.082 \times 500)^{-2}$ (b) $1.44 \times 10^{-5}/(8.314 \times 773)^{-2}$
    (c) $1.44 \times 10^{-5} / (0.082 \times 773)^{2}$ (d) $1.44 \times 10^{-5} / (0.082 \times 773)^{-2}$

13. K_p/K_c for the reaction, $CO(g) + ½ O_2 (g) \rightleftharpoons CO_2(g)$ is :

(a) 1   (b) RT   (c) $1/\sqrt{RT}$ (d) $(RT)^{1/2}$

14. For the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, the production of NO will be favoured by

    (a) High pressure.   (b) Low pressure.

    (c) Presence of catalyst   (d) High concentration of N_2.

15.In 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.

16. The solubility product of $CaSO_4$ is 6.4 x 10^{-5}.The solubility of salt in mol/Lis

    (a)$8x10^{-16}$ (b) $8x10^{-2}$ (c) $8x10^{-3}$ (d)$16x\ 10^{-3}$

17. Among the following ,the weakest Bronsted acid is

        (a)F-(b)Cl- (c)Br- (d)I-

18. For a buffer solution which of the following is true?

    (a) pH does not change at all on addition of acid or base

    (b) pH change is very little on addition of acid or base

    (c) It is a mixture of strong acid with its salt.

    (d) It is a mixture of strong base with its salt.

19. For $Zr_3(PO4)_4$ the solubility product is Ksp and solubility product is S. Find the correct relation.

    (a) $S=[Ksp/6912]^{1/7}$ (b) $S=[Ksp/216]^{1/7}$

     (c) $S= [Ksp/216]^{1/8}$ (d) $S=[Ksp/912]^{1/3}$

20. The pKa of acetic acid and pKb of ammonium hydroxide are 4.76 and 4.75 respectively. The pH of ammonium acetate solution will be

    (a)6.0   (b) 6.05   (c)7.05   (d)7.005.

ANSWERS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
c	a	d	c	b	b	b	d	c	a	a	a	c	d	d	c	d	b	a	d

ASSERTION –REASONING QUESTIONS

In each of the following questions, a statement of Assertion (A) is given followed by a corresponding statement of Reason (R) just below it. Of the statements, mark the correct answer as –

a.   If both assertion and reason are true, and reason is the true explanation of the assertion.

b.   If both assertion and reason are true, but reason is not the true explanation of the assertion.

c.   If assertion is true, but reason is false.

d.   If both assertion and reason are false.

1. Assertion (A). The equilibrium constant is fixed and characteristic for any given chemical reaction at a specified temperature

Reason (R). The composition of the final equilibrium mixture at a particular temperature depends upon the starting amount of reactants.

2. Assertion (A). When a catalyst is added to a reaction mixture in equilibrium, the amount of the products increases.

Reason (R). The forward reaction becomes faster on adding the catalyst.

3. Assertion (A). If standard free energy change of a reaction is zero, this implies that equilibrium constant of the reaction is unity.

Reason (R). For a reaction in equilibrium, equilibrium constant is always unity.

4. Assertion (A). If to the equilibrium $PCl_5 (g) \rightarrow$ $PCl_3(g) + Cl_2 (g)$, in a closed vessel, an inert gas is added, total pressure will increase and hence, equilibrium will shift backward.

Reason (R). Addition of an inert gas to an equilibrium mixture at constant volume shifts the equilibrium in the backward direction

5. Assertion (A). If reaction quotient (Q_c) is less than the equilibrium constant (K_c), the equilibrium tends to shift in the direction of products.

  Reason (R). The expression for equilibrium constant is different than the expression for reaction quotient.

6. Assertion (A). K_p can be equal to or less than or even greater than the value of K_c.

  Reason (R). $K_p = K_c (RT)^{\Delta n}$.

Relation between K_p and K_c depends on the change in the number of moles of gaseous reactants and products.

7. Assertion (A). For N_2 (g) + $3H_2$ (g) $\rightarrow$ $2NH_3$ (g), the equilibrium constant is 'K', then for

$1/2\ N_2(g) + 3/2\ H_2(g) \rightarrow NH_3$ (g) the equilibrium constant will be $\sqrt{K}$.

Reason (R). If concentrations are changed to half the equilibrium, equilibrium constant will be halved.

8. Assertion (A). A catalyst does not influence the values of equilibrium constant.

Reason (R). Catalysts influence the rate of both forward and backward reactions equally.

9. Assertion (A). The active mass of pure solid and pure liquid is taken unity.

Reason (R). The active mass of pure solids and liquids depends on density and molecular mass. The density and molecular mass of pure liquids and solids are constant.

10. Assertion (A). For $PCl_5(g) \rightarrow PCl_3(g) + Cl_2$ (g). If more Cl_2 is added, the equilibrium will shift in backward direction, hence equilibrium constant will decrease.

Reason (R). Addition of inert gas to be equilibrium mixture at constant volume, does not alter the equilibrium.

.
ANSWERS

1	2	3	4	5	6	7	8	9	10
a	d	c	d	c	a	c	a	a	c

2 marks questions:

1. For the following equilibrium, K =6.3 x 10^{14} at 1000 K. $NO(g)+O_3 \rightleftharpoons NO_2(g) + O_2(g)$ Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is reaction? Kc for the reverse reaction?
Answer: For the reverse reaction

$\qquad$ $K'_c=1/K_c =1/6.3$ x $10^{14}=1.59$ x 10^{-15}

2. What is K_c for the following equilibrium when the equilibrium concentration of each substance is: [SO2]=0.60M
[O2]=0.82 M and [SO$_3$] =1.90M?
$\qquad$ $2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)$
$K_c= \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$ $\qquad$ =(1.9X1.9)/0.60x0.6.x0.82 =12.23 L/mol
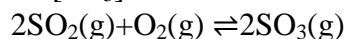
3. Find out the value of Kc for each of the following equilibria from the value of K_p:
(a) $2NOCl(g) \rightleftharpoons 2NO+Cl2$, $K_p=1.8$ x 10^{-2} at 500k
(b) $CaCO_3(s) \rightleftharpoons CaO$ (s) + CO_2. $K_p=167$ at 1073k

4. The value of K_c for the reaction, $2A \rightleftharpoons B +C$ is 2 x 10^{-3}.At a given time, the composition of reaction mixture
is[A]=[B]=[C]=3 x 10^{-4} M. In which direction the reaction will proceed?
$\qquad$ $Q_c=(3$ x $10^{-4})$ x $(3$ x $10^{-4})/(3$ x $10^{-4})2=1$
$\qquad$ Given, $K_c=2$ x 10^{-3}
$\qquad$ $Q_c > K_c$, so the reaction will proceed in the reverse direction.

5.What is Le Chatelier's principle?
   Le Chatelier's principle states that if a reaction at equilibrium is subjected to change in parameters like temperature, pressure or concentration of reactants and products, then the reaction equilibrium shifts in a direction in which the change is counteracted upon.

6. Classify the following species into Lewis acids and bases.
(a) OH-   (b) F- (c) H+ (d) BCl_3

7. Explain common ion effect?
  The common ion effect is an effect that suppresses the ionization of an electrolyte when another electrolyte (which contains an ion which is also present in the first electrolyte, i.e. a common ion) is added. It is considered to be a consequence of Le Chatelier's principle.

8. Why is NH4Cl added in excess before addition of NH4OH in qualitative analysis of group III?
  Due to common ion effect (NH_4^+ ions), NH_4Cl supresses the ionisation of NH_4OH. Then hydroxides of III group only (but   not of those of IV group) are precipitated.

9. The solubility product of A_2B is 32 x 10^{-9} mol^3/L. Calculate its solubility.
$$\underset{s}{A_2B} \rightleftharpoons \underset{2s}{2A^+} + \underset{s}{B^{2-}}$$

$$K_{sp} = [A^+]^2 \text{ x } [B^{2-}]/[A_2B]$$
$$32 \text{ x } 10^{-9} = (2s)^2 (s)$$
$$4S^3 = 32 \text{ x } 10^{-9}$$
$$S = 2 \text{ x } 10^{-3}$$

10. Arrange in the increasing order of pH.
        $KNO_{3(aq)}$, $NH_4Cl_{(aq)}$, $C_6H_5COONH_{4(aq),}$, $CH_3COONa_{(aq),}$
  Ans. $NH_4Cl_{(aq),}$ < $C_6H_5COONH_{4(aq),}$ < $KNO_{3(aq),}$ < $CH_3COONa_{(aq)}$

3 MARKS QUESTIONS

1. A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was reached, the concentration of PCl_5 was found to be 0.5 x 10^{-1} mol L^{-1}. If K_c is 8.3 x 10^{-3} what are the concentrations of PCl_3 and Cl_2 at equilibrium?

Answer:
Let the initial molar concentration of PCl_5 per litre = x mol
Molar concentration of PCl_5 at equilibrium = 0.05 mol
∴ Moles of PCl_5 decomposed = (x – 0.05) mol
Moles of PCl_3 formed = (x – 0.05) mol
Moles of Cl_2 formed = (x – 0.05) mol
The molar conc./litre of reactants and products before the reaction and at the equilibrium point are:
      PCl_5 PCl_3 + Cl_2
      Applying Law of equilibrium, K_c=[PCl_3][Cl_2]/PCl_5
                      8.3 x 10^{-3} = $(x-0.05)^2$/.05
                   Solving ,X = 0.07 mol
            At equilibrium,[PCl_5] = [Cl_2]=0.07-0.05 =0.02 mol/L

2. It has been found that the pH of a 0.01 M solution of an organic acid is 4.15. Calculate the concentration of the
  anion, the ionization constant of the acid and its PK_a.
  Answer: HA $\rightleftharpoons$ H^+
           pH= - log[H^+]
           4.15 = - log[H^+]
           Log [H^+]= - 4.15
           [H^+]   = antilog (-4.15)
                =7.08 x 10^{-5} M
            K_a =(7.08 x 10^{-5} x 7.08 x 10^{-5})/0.01= 5 x 10^{-7}
           pK_a = -log K_a = -log 5 x 10^{-7}=6.301

3. The values of K_{sp} of two sparingly soluble salts $Ni(OH)_2$ and AgCN are 2.0 x 10^{-15} and

6×10^{-17} respectively.

Which salt is more soluble? Explain.

Answer:

$AgCN \rightleftharpoons Ag^+ + CN-$
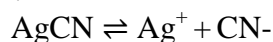
$K_{sp} = [Ag+][CN-] = 6 \times 10^{-17}$

let $[Ag+] = [CN-] = x$

$Ni(OH)_2 \rightleftharpoons [Ni^{2+}] + 2[OH-]$

Let $[Ni^{2+}] = y$, $[OH^-] = 2y$

$x^2 = 6 \times 10^{-17,}$ $x = 7.8 \times 10^{-9}$

$(y) \times (2y)^2 = 2 \times 10^{-15,}$ $y = 0.58 \times 10^{-4}$

$y > x$, $Ni(OH)_2$ is more soluble.

4. The ionization constant at 298K is 1.8×10^{-4} . Calculate the ionization constant of the corresponding conjugate base.

$K_a \times K_b = K_w$

$K_b = K_w/K_a$

$= (1 \times 10^{-14}) / 1.8 \times 10^{-8}$

$= 5.55 \times 10^{-7}$

5. Ionic product of water at 363K is 10^{-12} . What will be the pH? Will it be the acidic?

$[H+] [OH-] = 10^{-12}$

$[H+] = 10^{-12}/10^{-7} = 10^{-5}$

$pH = - \log(H+)$

$= - \log(10^{-5})$

pH = 5   Acidic

6. A solution is found to contain 0.63 g of nitric acid per 100ml of solution. What is the pH of solution if acid is completely dissociated?

No. of moles $n = w2/M2$

$= 0.63/63 = 0.01$

Molarity $= n/v$

$= 0.01 \times 1000/100$

$= 0.1 \text{ molL}^{-1}$

$[H^+]$ $= [HNO_3]$

$= 10^{-1}$

pH $= - \log(H^+)$

$= - \log(10^{-1})$

$= -(-1)\log 10$

pH $= 1$

7. For a water gas reaction at 1000k, the standard Gibb's free energy change is -8.1kJ/mol. Calculate the Value of equilibrium constant K_c, for the reaction.

ΔG^0 $=$ $-8.1 \times 1000 \text{J/mol}$

R $=$ 8.314J/mol/k,

 T $=$ 1000k

ΔG^0 $=$ $-2.303RT \log K_c$

$\text{Log } K_c = -\dfrac{\Delta G^0}{2.303RT}$

$= 0.4230$

Kc $=$ 2.65

8   Calculate the pH at the equivalence point when a solution of 0.10M acetic acid is titrated with a solution of 0.10M NaOH. Ka for acetic acid is $1.9 \times 10^{-5.}$

$pH = 1/2(pKw + pKa + \log C)$

$= 1/2(14 - \log(1.9 \times 10^{-5}) + \log(0.05)$

$= 8.71$

Case Based Questions:

1. 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) → H+ (aq) + X – (aq) or HX(aq) + H2O(l) → H3O + (aq) + X – (aq)
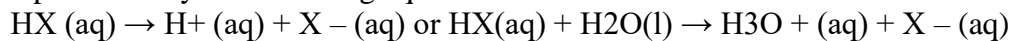
Similarly, a base molecule like MOH ionizes in aqueous solution according to the equation:

MOH(aq) → M+ (aq) + OH⁻ (aq)
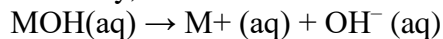
Bronsted acids are proton donors where as Bronsted bases are proton acceptors. Acids on donating proton form conjugate bases whereas bases form conjugate acids after accepting proton. Buffer solution is a solution whose pH does not change.

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 1×10^{-14} at 298 k. Kw increases with increase in temperature. pH is $-\log[H_3O^+]$where $[H_3O^+]=c\alpha$ 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 4×10^{-4} find its pH
      (d) Kb forNH_3 is1.80×10^{-5}, what will be K_a? [K_w is 1×10^{-14}]
        Answer:
        (a) (i)HSO_4 – (ii) CO_3^{2-}
        (b) (i)NH_3 ii) NH_4^+
        (c) 3.398
        d)5.5×10^{-10}

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

The Haber process for the synthesis ammonia from molecular hydrogen and nitrogen is represented by the following thermochemical equations.

N_2(g)+$3H_2$(g) ⇌ $2NH_3$(g): ΔH^0=-92.6kJ/mol the reaction is carried out in the presence of a heterogeneous catalyst containing iron the value of K_c for the reaction is 1.2 at 375^0c.

      1. Write the equilibrium constant expression for the reaction taking place during Haber process.
      2. How does the value of K_c for this reaction change with increase in temperature?
      3. Write the expression which represents the relationship between K_p and K_c for this reaction.
      4. starting with two mol each (N_2, H_2, NH_3) predict the direction of reaction?

Answer
      1. $K_c = [NH_3]^2/[N_2][H_2]^3$
      2. Decreases
      3. $K_p = K_p/(RT)^2$
      4. Backward direction

5mark Questions
1. (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) ⇌ PCl_3(g)+Cl_2(g)
      (b)N_2(g)+O_2(g) ⇌$2NO$(g)
  (iv) Which of the following are lewis acids?H_2O,BF_3,H^+,$NH_4^{+.}$
  Answers:
     (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) NH_4Cl is salt of weak base NH_4OH 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^+

2. (a)Define solubility product. Write solubility product expression for $Zr_3(PO_4)_4$.

(b) Calculate pH of 0.01 M CH_3COOH solution[k_a (CH_3COOH) = 1.74 x 10^{-5}]

(c) Explain why NaCl is precipitated when HCl (g) is passed through the saturated solution of NaCl.

Answers:

(a) It is defined as the product of molar concn. Of the ions (formed in the saturated solution at a given temperature). Raised to the power equal to the no.of times each ion occurs in the equation for solubility

equilibrium

$Zr_3(PO_4)_4 \rightleftharpoons 3Zr^{4+}$ $+ 4PO_4^{3-}$
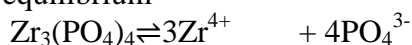
$Ksp = [Zr^{4+}][PO_4^{3-}]^4$

(b)   pH $= -\log[H_3O^+]$

$= -\log C\alpha$

$= -\log\sqrt{Ka \times C}$

$= -\log\sqrt{1.74 \times 10^{-5} \times 0.01}$

$= 3.3783$

(c) It is due to common ion ,Cl^- increase, rate of backward reaction increases, solubility of NaCl decreases.

3. The equilibrium constant at 298k for the reaction $Cu(s)+2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$ is 2.0 x 10^{15}. In a solution in which Cu has displaced some Ag ions from solution , the concentration of Ag^+ ions is 3.0 x 10^{-9}mol/L Is this system at equilibrium?

Answer:

$Cu(s)+2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq)+2Ag(s)$
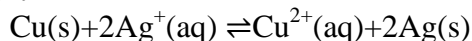
According to the Law of Chemical Equilibrium,

$K_c = \dfrac{[Cu^{2+}(aq)]}{[Ag^+(aq)]^2}$

$Q_c = \dfrac{1.8 \times 10^{-2}}{(3.0 \times 10^{-9})^2}$

$= 2 \times 10^{15}$

Since $Q_c = K_c$, the reaction is in equilibrium.

4. The ionization constant of propanoic acid is 1.32×10^{-5}. Calculate the degree of ionization of the acid in its 0.05 M solution and also its pH. What will be its degree of ionization if the solution is 0.01M in HCl ?

Answer:

Let x be the degree of dissociation.

$x = \sqrt{K_a/c} = \sqrt{1.32 \times 10^{-5}/0.05} = 0.0162$

$[H+] = cx = 0.05 \times 0.0162 = 8.12 \times 10^{-4}$

pH$= \log[H+] = -\log(8.12 \times 10^{-4}) = 3.09$

If the solution is 0.01M in HCl solution, then, $x = \sqrt{K_a/c} = \sqrt{1.32 \times 10^{-5}/0.01} = 0.00132$

5. The ionization constant of chloroacetic acid is 1.35×10^{-3}. What will be the pH of 0.1 M acid and its 0.1 M sodium salt solution?

Answer:

(i) For acid solution,$[H+] = \sqrt{Ka\ C} = \sqrt{1.35 \times 10^{-3} \times 0.1} = 0.0116$ m

pH = -log[H+] =-log[0.0116]= 1.936

(ii) For 0.1M sodium salt solution, the solution contains sodium salt of chloroacetic acid which is weak acid and strong base,

pKa = - logKa = -log(1.35×10^{-3}) =2.8697

pKw = 14, logC= log 0.1 = -1

pH   = 0.5(pKa+pKw+log C)

          =0.5(2.8697+14+-1)

          = 7.935

6. The pH of 0.1 M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

	HCNO	H_2O	H_3O^+	CNO^-
Initial conc.	1		0	0
	1- α		α	α
Final Conc.	c(1- α)		cα	cα
	c= 0.1 M		pH = 2.34	
			pH= -log[H_3O^+]	

Answer:

log[H_3O^+]= -2.34

[H_3O^+] =4.571 x 10^{-3} mol L^{-1}

[H_3O^+] = cα   a= $\frac{[H_3O^+]}{C}$ = $\frac{(4.57 \times 10^{-3})}{0.1}$ =4.57 x 10^{-2} =0.0457

Kα = $\frac{cα \times cα}{c(1- α)}$ = $\frac{cα^2}{1-a}$

Since a<<<1   1- α   =1

K_a = $cα^2$ = 0.1 x $(0.0457)^2$

Ka = 2.088x 10^{-4} = 2.09 x 10^{-4}

7.REDOX REACTIONS

KEY POINTS

The chemical changes that occur when electrons are transferred between reactants are called **oxidation – reduction reactions**.

OXIDATION	REDUCTION
1. Addition of oxygen	1. Removal of oxygen
2. Removal of hydrogen	2. Addition of hydrogen
3. Addition of an electronegative element	3. Removal of an electronegative element
4. Removal of an electropositive element	4. Addition of an electropositive element
5. Loss of electron	5. Gain of electron

Oxidation number denotes the charge assigned to an atom of a compound or an ion according to some arbitrary rules. It is equal to the number of electrons in the valence shell of an atom, that are gained or lost while forming a bond in a compound.

Calculation of oxidation number:

1.Oxidation state (O.S) of all the elements in their elemental form (in standard state) is taken as zero. Ex:

O. S. of elements in Cl_2, F_2, O_2, P_4, O_3, Fe(s), H_2, N_2, C(graphite) is zero.

2. Common O. S. of elements of group one (1st) is one. Common O. S. of elements of group two (2nd) is two.

3. For ions composed of only one atom, the oxidation number is equal to the charge on the ion.

4. The oxidation number of oxygen in most compounds is –2.While in peroxides (e.g., H_2O_2, Na_2O_2), each oxygen atom is assigned an oxidation number of –1, in superoxides (e.g., KO_2,RbO_2) each oxygen atom is assigned an oxidation number of –(½).

5. In oxygen difluoride (OF_2) and dioxygen difluoride (O_2F_2), the oxygen is assigned an oxidation number of +2 and +1,respectively.

6. The oxidation number of hydrogen is +1 but in metal hydride its oxidation no. is–1.

7. In all its compounds, fluorine has an oxidation number of –1.

8. The algebraic sum of the oxidation number of all the atoms in a compound must be zero.

9. In polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion must equal the charge on the ion.

Oxidation: An increase in the oxidation number

Reduction: A decrease in the oxidation number

Stock notation: The oxidation number is expressed by putting a Roman numeral representing the oxidation number in parenthesis after the symbol of the metal in the molecular formula. Thus aurous

chloride and auric chloride are written as Au(I)Cl and Au(III)Cl$_3$. Similarly, stannous chloride and stannic chloride are written as Sn(II)Cl$_2$ and Sn(IV)Cl$_4$.

Oxidising agent: A reagent which can increase the oxidation number of an element in a given substance. These reagents are also called as **oxidants** .

Reducing agent: A reagent which lowers the oxidation number of an element in a given substance. These reagents are also called as **reductants**.

Redox reactions: Reactions which involve change in oxidation number of the interacting species

Types of redox reactions

1. **Combination reactions**: A reaction in which two atoms or molecules combine together form

molecule or compound. For e.g. C (s) + O$_2$ (g) → CO$_2$ (g)

2. **Decomposition reactions**: They are the opposite reactions of combination reactions .or

breakdown of a compound into two or more components at least one of which must be in the

elemental state. For e.g. 2H$_2$O(l) → 2H$_2$(g) + O$_2$(g)

3. **Displacement reactions**: In a displacement reaction, an ion (or an atom) in a compound is

replaced by an ion (or an atom) of another element. For e.g.

(i) Metal displacement : CuSO$_4$(aq.) + Zn(s) → Cu(s) + ZnSO$_4$(aq.)

(ii) Non metal displacement : 2Na(s) + 2H$_2$O(l) → 2NaOH(aq.) + H$_2$(g)

4.**Disproportionation reactions** :In a disproportionation reaction an element in one oxidation

state is simultaneously oxidized and reduced.

For e.g. P$_4$(s) + 3OH$^-$ (aq.) +3H$_2$O(l) → PH$_3$(g) + 3H$_2$PO$_2^-$ (aq.)

Balancing of redox reactions:

Balance the following ionic equation

$$Cr_2O_7{}^{2-}(aq) + SO_3{}^{2-}(aq) \rightarrow Cr^{3+}(aq) + SO_4{}^{2-}(aq) \text{ (acidic medium)}$$
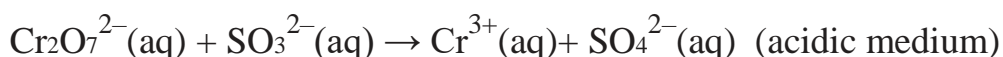
Method :1   Oxidation Number Method

Step 1: Write the correct formula for each reactant and product.

Step 2: Identify atoms which undergo change in oxidation number in the reaction by

assigning the oxidation number to all elements in the reaction.

Step 3: Calculate the increase or decrease in the oxidation number per atom and for the

entire molecule/ion in which it occurs. If these are not equal then multiply by suitable

number so that these become equal.

Step 4: Ascertain the involvement of ions if the reaction is taking place in water, add H$^+$ or

OH$^-$ ions to the expression on the appropriate side so that the total ionic charges of reactants

and products are equal. If the reaction is carried out in acidic solution, use H$^+$ ions in

the equation; if in basic solution, use OH^- ions.

Step 5 : Make the numbers of hydrogen atoms in the expression on the two sides equal by adding water (H_2O) molecules to the reactants or products. Now, also check the number of oxygen atoms. If there are the same number of oxygen atoms in the reactants and products, the equation then represents the balanced redox reaction.

Step 1: The skeletal ionic equation is:

$$Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$$
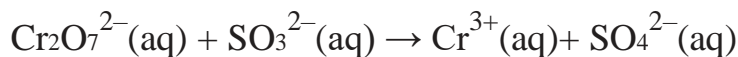
Step 2: Assign oxidation numbers for Cr and S

+6 –2   +4 –2   +3   +6-2

$$Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$$
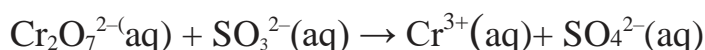
Step 3: Calculate the increase and decrease of oxidation number, and make them equal:

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq)$$
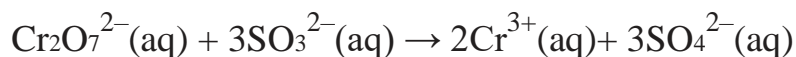
Step 4: Balance the charge by adding H^+ as the reaction occurs in the acidic medium,

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) + 8H^+ \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq)$$

Step 5: Balance the oxygen atom by adding water molecule.

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq)\, 8H^+ \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + 4H_2O(l)$$
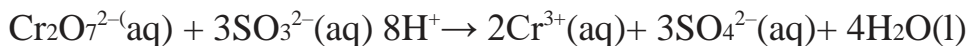
METHOD : 2 Half Reaction Method(or) **Ion Electron Method**

In this method, the two half equations are balanced separately and then added together to give balanced equation.

Ex :   Balance the following ionic equation

$$MnO_4^-(aq) + I^-(aq) \longrightarrow MnO_2(s) + I_2(s) \text{ (basic medium)}$$

Step 1: First we write the skeletal ionic equation, which is

$MnO_4^-(aq) + I^-(aq) \quad MnO_2(s) + I_2(s)$

Step 2: The two half-reactions are:

$$\qquad\qquad\qquad -1 \qquad\qquad\qquad 0$$

Oxidation half cell : $I^-_{(aq)} \longrightarrow I_2(s)$

$$\qquad\qquad +7 \qquad\qquad +4$$

Reduction half cell : $MnO_4^-(aq) \longrightarrow MnO_2(s)$
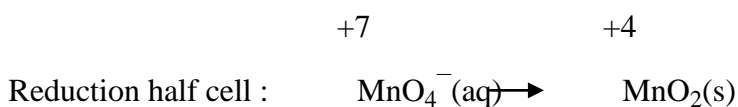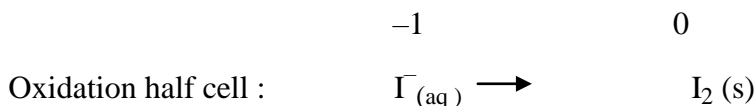
Step 3: To balance the I atoms in the oxidation half reaction, we rewrite it as:

$$2I^-_{(aq)} \longrightarrow I_2(s)$$

88
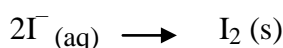
Step 4: To balance the O atoms in the reduction half reaction, we add two water molecules on the right:

MnO_4^- (aq) $\longrightarrow$ MnO_2 (s) + 2 H_2O (l)

To balance the H atoms, we add four H^+ ions on the left:

MnO_4^- (aq) + 4 H^+ (aq) $\longrightarrow$ MnO_2(s) + 2H_2O (l)
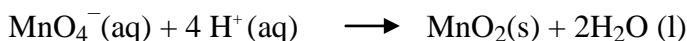
As the reaction takes place in a basic solution, therefore, for four H+ ions, we add four OH– ions to both sides of the equation:

MnO_4^- (aq) + 4H^+ (aq) + 4OH^-(aq) $\longrightarrow$ MnO_2 (s) + 2 H_2O(l) + 4OH^- (aq)
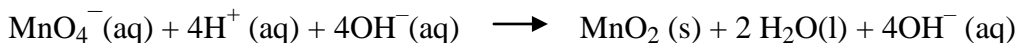
Replacing the H+ and OH– ions with water, the resultant equation is:

MnO_4^- (aq) + 2H_2O (l) $\longrightarrow$ MnO_2 (s) + 4 OH^- (aq)

Step 5 : In this step we balance the charges of the two half-reactions in the manner depicted as:

2I^-(aq) $\longrightarrow$ I_2(s) + 2e^-

MnO_4^- (aq) + 2H_2O(l) + 3e^- $\longrightarrow$ MnO_2(s)+ 4OH^-(aq)

Now to equalise the number of electrons, we multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2.

6I^- (aq) $\longrightarrow$ 3I_2 (s) + 6e^-

2 MnO_4^- (aq) + 4H_2O (l) +6e^- $\longrightarrow$ 2MnO_2(s)+ 8OH^-(aq)

Step 6: Add two half-reactions to obtain the net reactions after cancelling electrons on both sides.

6I^- (aq) + 2MnO_4^- (aq) + 4H_2O(l) $\longrightarrow$ 3I_2(s) +2MnO_2(s) +8 OH^-(aq)

Step 7: A final verification shows that the equation is balanced in respect of the number of atoms and charges on both sides.

A **redox couple** is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half reaction. Represented as Zn^{2+}/Zn // Cu^{2+}/Cu.

Electrochemical cells are the devices which are used to get electric current by using chemical reaction .

The potential associated with each electrode is known as **electrode potential**. If the concentration of each species taking part in the electrode reaction is unity (if any gas appears in the electrode reaction, it is confined to 1 atmospheric pressure) and further the reaction is carried out at 298K, then the potential of each electrode is said to be the **Standard Electrode Potential (SHE).**SHE is used to measure electrode potential and its standard electrode potential is taken as 0.00 V.

Redox titrations :In redox systems, the titration method can be adopted to determine the strength of a reductant/oxidant using a redox sensitive indicator.
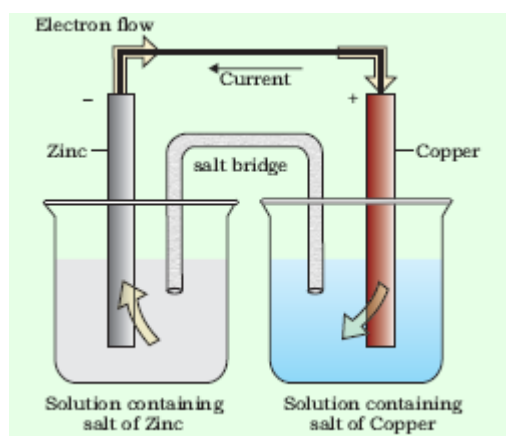
MULTIPLE CHOICE QUESTIONS :

1. The oxidation number of an atom in the elemental state is _____
   a) -1   b) 0   c) 1   d) 2

2. The oxidation number of an element in a compound is evaluated on the basis of certain rules. Which of the following rules is not correct in this respect?

(a) The oxidation number of hydrogen is always +1.

(b) The algebraic sum of all the oxidation numbers in a compound is zero.

(c) An element in the free or the un combined state bears oxidation number zero.

(d) In all its compounds, the oxidation number of fluorine is – 1.

3.In the reaction

$$3Br_2 + 6CO_3^{2-} + 3H_2O \rightarrow 5Br^- + BrO_3^- + 6HCO_3^-$$
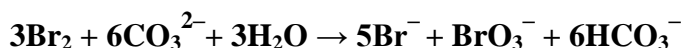
(a) bromine is oxidised and carbonate is reduced (b) bromine is reduced and water is oxidised

(c) bromine is neither reduced nor oxidised   (d) bromine is both reduced and oxidised

4.The oxidation number of iron in Fe_3O_4 is

     (a) +2   (b) +3   (c) 8/3   (d) 2/3

5.H_2SO_4 acts as a strong oxidising agent. In which of the reaction, is it not acting as an oxidising agent?

(a) $C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$ (b) $CaF_2 + 2H_2SO_4 \rightarrow CaSO_4 + 2HF$

(c) $S + 2H_2SO_4 \rightarrow 3SO_2 + H_2O$ (d) $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$

6.Find the oxidation state of I in $H_4IO_6^-$

(a) +7   (b) +5   (c) +1   (d) –1

7.In which of the following compounds, 'Mn' exhibits highest oxidation state?

(a) $KMnO_4$ (b) K_2MnO_4 (c) MnO_2 (d) MnO

8.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

(a) X>Y>Z   (b) Y>Z>X   (c) Y>X>Z   (d) Z>X>Y

9.The values of x and y in the following reaction,

x Cl_2 + 6OH⁻ (hot & conc.) → ClO_3^- + y Cl⁻ +3 H_2O are
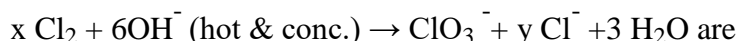
(a) x = 2, y = 4   (b) x = 5, y = 3   (c) x = 3, y = 5   (d) x = 4, y = 2

10.A standard hydrogen electrode has zero electrode potential because

(a) Hydrogen is easiest to oxidize(b) this electrode potential is assumed to be zero

(c) Hydrogen atom has only one electron (d) hydrogen is the lightest element

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

ASSERTION – REASONING TYPE QUESTIONS

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

(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

1.**Assertion (A)**: Among halogens fluorine is the best oxidant.

  Reason (R) : Fluorine is the most electronegative atom.

2.**Assertion (A)**: In the reaction between potassium permanganate and potassium iodide, permanganate ions act as oxidising agent.

  Reason (R) : Oxidation state of manganese changes from +2 to +7 during the reaction.

3. **Assertion (A)**: Lithium is a strong reducing agent

  Reason(R): Lithium has lowest value of the standard reduction potential

4.**Assertion(A)**: Zinc liberates hydrogen from a dilute solution of hydrochloric acid.

  Reason(R): E^0 of Zn is higher than that of H_2

5.**Assertion(A)**: The decomposition of hydrogen peroxide to form water and oxygen is an example of a disproportionation reactions.

  Reason(R): The oxygen of peroxide is in -1 oxidation state and it converted to zero oxidation state in O_2 and -2 oxidation in water

Answers   1 (b)   2(c)   3(a)   4(c)   5(a)

2 MARK QUESTIONS

1. **Show that F cannot undergo disproportionation reaction?**
F is most electronegative element and cannot possess three oxidation states. Hence it cannot undergo disproportionation reactions.

2.**What is a redox couple?**

Ans. A redox couple consists of oxidized and reduced form of the same substance taking part in an oxidation or reduction half reaction.

3.**Write formulas for the following compounds:**
(a) Mercury(II) chloride (b) Iron(II)sulphate

Ans a) $HgCl_2$ b) $FeSO_4$

4.**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.

Ans   a - F   b - Cs   c- I   d-Ne

5.**Given the standard electrode potentials,**

$K^+/K = -2.93V$, $Ag^+/Ag = 0.80V$, $Hg^{2+}/Hg = 0.79V$, $Mg^{2+/}Mg = -2.37V$, $Cr^{3+/}Cr = -0.74V$
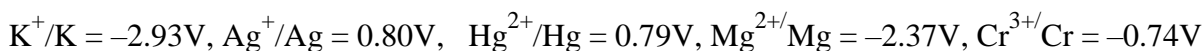
arrange these metals in their increasing order of reducing power.

Ans : Lower the electrode potential, better the reducing agent .Therefore increasing order of reducing

power is   Ag< Hg< Cr<Mg<K

6.**Define EMF of the cell.**

Ans. It is defined as the difference in the electrode potentials of the two half cells when the cell is not

sending current through the circuit.

7.**Arrange the following metals in which they displace each other from the solution of their salts: Al,**

Cu, Fe, Mg, Ag and Zn.

Ans. Metals which have lower electrode potentials can displace others which have higher

electrode potentials from the solutions of their salts. Thus the order is: Mg, Al, Zn, Fe, Cu, Ag.

8.**Using Stock notation, represent the following compounds: $HAuCl_4$, FeO, Fe_2O_3 and CuI.**

Ans. $HAu(III)Cl_4$, Fe(II)O, $Fe_2(III)O_3$, Cu(I)I   respectively.

9.**In the reaction given below, identify the species undergoing oxidation and reduction**

(i) H_2S (g) +Cl_2 (g) $\rightarrow$ 2HCl (g) +S (s)   (ii) 2Na(s) + H_2 (g) $\rightarrow$ 2NaH(s)
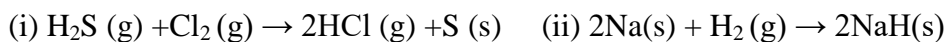
Ans (i) H_2S is oxidized to S while Cl_2 is reduced to HCl

(ii) Sodium is oxidized to sodium ion while hydrogen is reduced to hydride ion.

10.**Suggest a scheme of classification of the following redox reactions**

(i) $N_2(g) + O_2$ (g) $\rightarrow$ 2NO(g)

(ii) 2 $Pb(NO_3)_2$(s) $\rightarrow$ 2PbO(s) + $4NO_2$(g) + O_2(g)

(iii) NaH(s) +H_2O (l) $\rightarrow$ NaOH(aq.) +H_2(g)

(iv) $2NO_2$(g) + $2OH^-$(aq.) $\rightarrow$ NO_2^-(aq.) +NO_3^- (aq.) +H_2O(l)
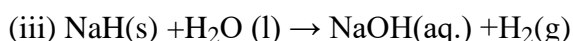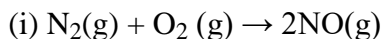
Ans. (i) Combination reaction(ii) Decomposition reaction

 (iii)   Displacement reaction(iv) Disproportionation reaction

11.**What is galvanization?**

Ans: Coating of a less reactive metal with a more reactive metal e.g.- coating of iron surface with Zn to prevent rusting of iron.

12.**Calculate the standard e.m.f. of the cell formed by the combination of Zn/Zn^{2+} ‖ Cu^{2+}/Cu.**

Solution : E^0cell = E^0cathode – E^0anode =0.34 – (-0.76) = 1.10V.

3 MARK QUESTIONS

1.**Depict the galvanic cell in which the reaction Zn(s) + 2Ag$^+$(aq) → Zn^{2+}(aq) +2Ag(s) takes place,**

Further show:

(i) which of the electrode is negatively charged,

(ii) the carriers of the current in the cell, and

(iii) individual reaction at each electrode

Ans :i) Oxidation occurs at Zinc electrode .Therefore Zinc electrode is negatively charged.

(ii) The ions carry current. The electrons flow from Zn to Ag while the current flows from Ag to Zn.

(iii) Zn → Zn^{2+} + 2 e$^-$ (Anode)   Ag$^+$ + e$^-$ →   Ag (Cathode)

2. **What is meant by 'Salt Bridge'? Give its function.**

Ans : Salt bridge is a U-shaped tube. It consists of Agar-agar and inert electrolyte like KCl or KNO$_3$.

Functions: (i) To complete the circuit

(ii) It helps to maintain the electrical neutrality of the solutions in the two half cells.

3.**Write short notes on :**

(a) Electrochemical series (b) redox reactions (c) oxidizing agents

Ans :(a) Electrochemical series :- arrangement of metals(non-metals also) in increasing order of their reducing power or vice versa.

(b) Reactions in which both Oxidation and reduction take place simultaneously are REDOX REACTIONS.

(c) Oxidizing agents : chemical specie which can oxidize the other one or can reduce itself.

4.**Account for the followings:**

(i) Sulphur exhibits variable oxidation states.

Ans. Due to the presence of vacant d - orbitals in S

(ii) Fluorine exhibits only -1 oxidation state..   Ans . It is most electronegative element

(iii) oxygen can't extend its valency from 2.

Ans. Small size and non-availability of vacant d-orbitals in Oxygen.

5.**Identify the oxidizing and reducing agents in the following equations:**

(i) Fe + H$_2$SO$_4$→FeSO$_4$ + H$_2$

 (ii)H$_2$ + Cl$_2$ →2HCl

(iii) MnO$_2$ + 4HCl→MnCl$_2$ + 2H$_2$O + Cl$_2$

Ans :(i) O.A. =H_2SO_4 ; R.A.= Fe (ii) O.A. = Cl_2; R.A.=H_2 (iii)O.A. = MnO_2; R.A. =HCl

6.**What is SHE? What is its use? Explain with the help of a diagram.**

Ans :Standard Hydrogen Electrode (SHE) has been selected to have zero standard potential at all temperatures. It consists of a platinum foil coated with platinum black (finely divided platinum) dipping partially into an aqueous solution in which the activity (approximate concentration 1M) of hydrogen ion is unity and hydrogen gas is bubbled through the solution at 1 bar pressure. The potential of the other half cell is measured by constructing a cell in which reference electrode is standard hydrogen electrode. The potential of the other half cell is equal to the potential of the cell.

the
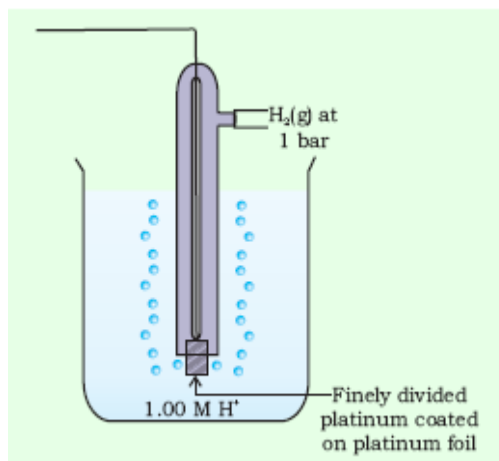
8. (i) Define electrochemical series .

(ii) Write down the reaction occurring in Daniel cell . **What is the direction of flow of current in it ?**

Ans. :- The arrangement of elements in the order of increasing standard reduction potential is known as electrochemical series .

(i)   At Anode :- $Zn \rightarrow Zn^{+2} + 2e^-$

(ii)   At Cathode :- $Cu^{+2} + 2e^- \rightarrow Cu$
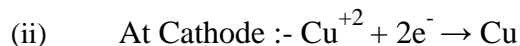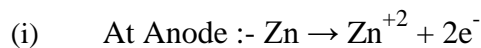
The current will flow from Cu electrode to Zn electrode

CASE BASED QUESTIONS -4 MARKS

Read the following passage and answer the questions that follow:

Redox reactions are 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 oxidising agents which can gain electrons easily. In electrolytic cells, electricity is passed to bring about 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 cell to complete internal circuit and prevents accumulation of charges.

1. **In an Electrochemical Cell ,Oxidation takes place at _____ and Reduction takes place at _____**
   a) Cathode , Anode   b) Anode , Cathode   c) Anode , Anode   d) Cathode, Cathode

2. **What is direction of flow of current and electrons?**
a)   Electrons flow from anode to cathode whereas current flows from cathode to anode
b)   Electrons flow from cathode to anode whereas current flows from anode to cathode
c)   Electrons flow from anode to cathode and current also flows from anode to cathode
d)   Electrons flow from cathode to anode and current also flows from anode to cathode

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 meaning of –ve value of reduction potential?

a) Zn is stronger oxidising agent than H_2

b) Zn is weaker reducing agent than H_2 .

c) Zn is stronger reducing agent than H_2

d) None of the above

Ans :   1(b)   2(a)   3(b)   4(c)

5 MARKS QUESTIONS

1.**Balance the equation**

$MnO_4^- + I^- \rightarrow Mn^{2+} + I_2 + H_2O$ by ion electron method in acidic medium.

Ans :

Step-I   Balancing of reduction half reaction by adding protons and electrons on LHS and more
water molecules on RHS: $8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Step-II   Balancing of oxidation half reaction by adding electrons on RHS: $2I^- \rightarrow I_2 + 2e^-$

Step-III   To multiply the Oxidation Half Reaction by 5; Reduction Half reaction by2 and to add both
to get overall redox reaction(cancellation of electrons of RH & OH reactions):

$[8H^+(aq) + MnO_4^-(aq) + 5e^- \rightarrow Mn2+(aq) + 4H_2O(l)]$ x 2

$[2I^- \rightarrow I_2 + 2e^-]$ x 5

OVERALL : $MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$
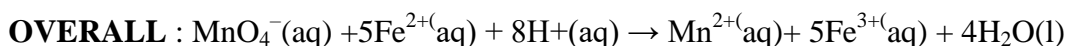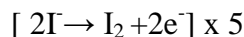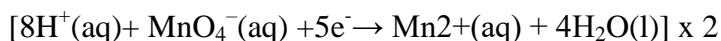
HOTS

1.**Justify that the reaction: $2Cu_2O(s) + Cu_2S(s) \rightarrow 6Cu(s) + SO_2(g)$ is a redox reaction. Identify the
species oxidised/ reduced, oxidant and /reductant.**

Ans. Cu_2O helps sulphur in Cu_2S to increase its oxidation number, therefore, Cu(I) is an oxidant; and

sulphur of Cu_2S helps copper both in Cu_2S itself and Cu_2O to decrease its oxidation number; therefore,

sulphur of Cu_2S is reductant.

2.**Match the items in Column I with relevant items in Column II**

Column I		Column II	
(i)	Ions having positive charge	(a)	+7
(ii)	The sum of oxidation number	(b)	–1
	of all atoms in a neutral molecule	(c)	+1
(iii)	Oxidation number of hydrogen ion (H⁺)	(d)	0
(iv)	Oxidation number of fluorine in NaF	(e)	Cation
(v)	Ions having negative charge	(f)	Anion

Ans .:- (i) - (e) , (ii) - (d) , (iii) - (c) , (iv) - (b) , (v) - (f)

2. Write short note on working of SHE .

Ans. (I)It can behave as anode and cathode depending upon another electrode taken.

(a) When it acts as anode, reaction will be :- $H_2 \rightarrow 2H^+ + 2e$-

Representation will be :-Pt, H_2 (1atm.) / H^+ (1M)

(b) When it acts as cathode, reaction will be

$2H^+ + 2e- \rightarrow H_2$ Representation will be :- / H^+ (1M) / H_2 (1atm.), Pt

3. In the following cell : - Cu / Cu⁺² (1M) // Ag+ (1M) / Ag Write down each half cell reaction and overall reaction .

Ans. :- At anode :- $Cu \rightarrow Cu^{+2} + 2e^-$

At Cathode :- $2 Ag^+ + 2e- \rightarrow 2Ag$

Overall reaction :- $Cu + 2 Ag^+ \rightarrow Cu^{+2} + 2Ag$

4. Using the given standard electrode potentials predict if the reaction between the following is feasible :

i) Fe^{3+} and Cu   ii) Ag and Fe^{3+}

Given : $E^o_{Cu+2 / Cu} = 0.34$ V, $E^o_{Fe+3 / Fe2+} = 0.77$ V , $E^o_{Ag+/Ag} = + 0.80V$

Ans. :- (i) $Fe^{3+} + Cu \rightarrow Fe^{2+} + Cu^{2+}$

$E^o_{Cell} = E^o_{Fe+3 / Fe2+} - E^o_{Cu2+/Cu}$

$E^o_{Cell} = 0.77 - 0.34 = 0.43$ V

As E^o **Cell** comes out to be **+ve** so reaction between Fe^{3+} and Cu is **feasible .**

(ii) $Fe^{3+} + Ag \rightarrow Fe^{2+} + Ag$

$E^o_{Cell} = E^o_{Fe^{+3} / Fe^{2+}} - E^o_{Ag+/Ag}$

$E^o_{Cell} = 0.77 – 0.80 = - 0.03$ V

As E^o_{Cell} comes out to be **- ve** so reaction between Fe^{3+} and Ag is **not feasible**

8. ORGANIC CHEMISTRY SOME BASIC PRINCIPLES AND TECHNIQUES

Organic compounds are the hydrocarbons and their derivatives and organic chemistry is that branch of chemistry that deals with the study of these compounds.

Synthesis of first Organic compounds: Wohler synthesized an organic compound, urea from an inorganic compound, ammonium cyanate.

$$NH_4CNO \xrightarrow{\text{Heat}} NH_2CONH_2$$
Ammonium cyanate   Urea
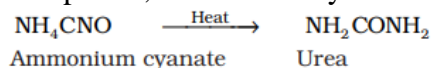
Tetravalency of Carbon :The atomic number of Carbon is 6 and its electronic configuration is 2,4 i.e. it has 4 valence electrons. It can share 4electrons with the other atoms to form 4 covalent bonds. It is called tetravalency of carbon.

Catenation- The self-linking property of carbon is known as catenation. This is the main reason of existence of such large number of compound

The Shapes of Carbon Compounds: CH_4 is sp^3 hybridized and has tetrahedral structure. In ethene, each carbon is sp^2hybridized and it has planar structure. In C_2H_2, carbon is sp hybridized and it is linear molecule.

Effect of hybridization on bond length and bond enthalpy: The bond length and bond strength depends upon hybridization.

sp hybridized: Carbon has 50% s character, and hence it is close to the nucleus and forms shorter and stronger bond. It is most electronegative

sp^2hybridized: Carbon has 33% s- character, and hence it is less close to the nucleus and forms slightly longer and less strong bonds than sp hybridized carbon. It is less electronegative than sp hybridized.

sp^3 hybridized: Carbon has 25% s-character and hence it is least close to the nucleus and forms longer and least strong bonds. It is bigger in size and is less electronegative than sp^2 and sp hybridized carbon.

Characteristic features of π –bonds:
   i)   Pi-bond is formed by sideways or lateral overlapping of parallel p-orbitals.
   ii) The p-orbitals should be parallel and perpendicular to the plane of the molecule.
   iii) Rotation of C=C is restricted.
   iv) The electron cloud of the pi-bond lies above and below the plane of the bonding atom.
        This results in the electrons being easily available to attacking agents.π bonds are more reactive than Sigma bond in unsaturated molecules.

STRUCTURAL REPRESENTATIONS OF ORGANIC COMPOUNDS:

Complete structural formula:

Ethane   Ethene

Ethyne   Methanol

Condensed structural formula:

CH_3CH_3 $H_2C=CH_2$ $HC\equiv CH$ CH_3OH
Ethane   Ethene   Ethyne   Methanol
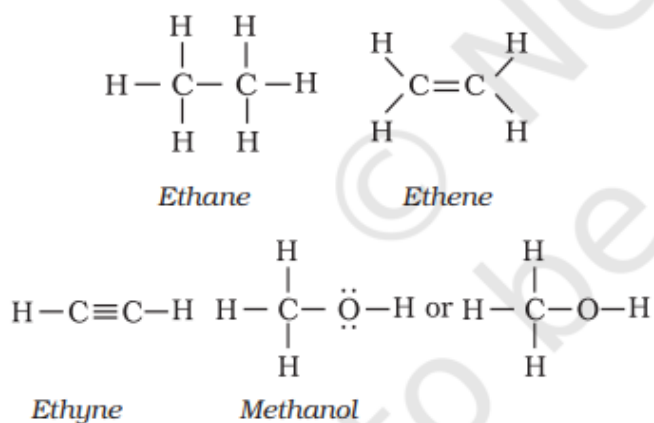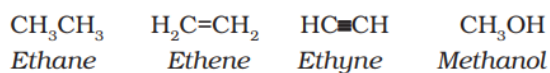
Bond-line structural formula:
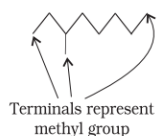
2-bromo butane   Terminals represent methyl group   3-methyl octane

Classification of organic compounds
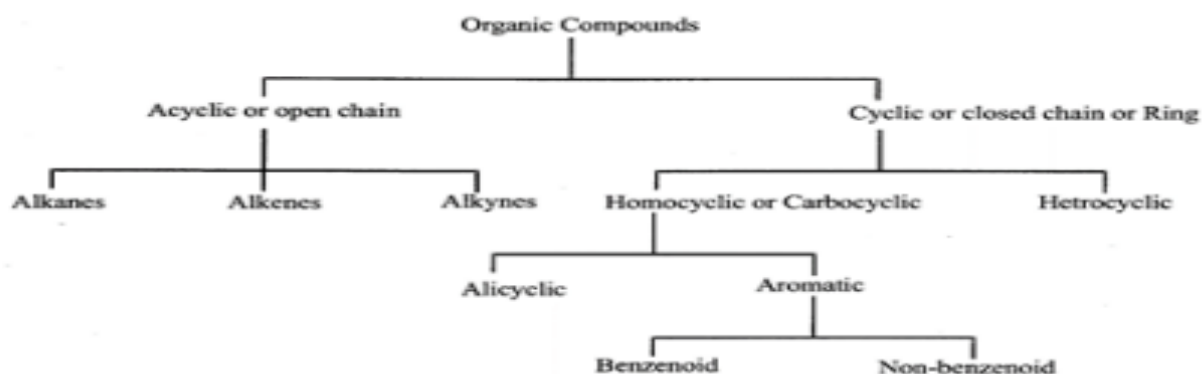
Functional group: Atom or group of atoms that largely decide the chemical properties.

Class of organic compounds	Name of functional group	Structure
Alkenes	double bond	$\diagup C=C \diagdown$
Alkynes	triple bond	$- C \equiv C -$
Halogens	halogen	$- X (F, Cl, Br, I)$
Alcohols	hydroxyl	$-OH$
Aldehydes	aldehydic(formyl)	$-CHO$
Carboxylic acids	carboxyl	$-COOH$
Acid amides	amides	$-CONH_2$
Primary amines	amino	$- NH_2$

Homologous Series:A group or a series of organic compounds each containing a characteristic functional group,show a gradation in physical and similarity in chemical properties.

The members of the series are called homologues. It can be represented by general molecular formula and the successive members differ from each other in molecular formula by a $-CH_2$ unit.

Eg : Alkanes, alkenes, alkynes.

NOMENCLATURE OF ORGANIC COMPOUNDS:

The IUPAC name consists of four parts:

Prefix   Word root   Suffix(primary, secondary)

Number of carbons	Word root	Number of carbons	Word root
One carbon	Meth	Six carbons	Hex
Two carbons	Eth	Seven carbons	Hept
Three carbons	Prop	Eight carbons	Oct
Four carbons	But	Nine carbons	Nona
Five carbons	Pent	Ten carbons	Dec

Primary suffix: Indicates saturation or unsaturation of the compound.

Saturation: All single bonds

Unsaturation: At least one carbon - carbon double bond or one carbon -carbon triple bond

Saturated / Unsaturated	Primary suffix
All single bond (alkanes)	ane
C =C (alkenes)	ene
C≡C (alkynes)	yne

Secondary suffix: Indicates functional group present in the organic compound(many functional groups are already mentioned in the previous topics)

Suffixing functional groups	Secondary suffix
-OH	**ol**
-CHO	**al**
>C=O	**one**
-COOH	**oic acid**

PREFIX: Some functional groups like halogens are prefixing functional groups

Prefixing functional groups	Prefix
-Cl	**Chloro**
-Br	**Bromo**
-I	**Iodo**
-OR	**Alkoxy**
-NO$_2$	**Nitro**

Order of writing the name of the organic compounds.

NOMENCLATURE OF ALKANES

Straight chain alkanes: The names of such compounds is based on their chain structure, and end with suffix '-ane' and carry a prefix indicating the number of carbon atoms present in the chain.

Branched chain hydrocarbons:

1) The longest carbon chain in the molecule is identified.

2) The numbering is done in such a way that the branched carbon atoms get the lowest possible value.

3) The names of the alkyl groups attached as a branch are then prefixed to the name of the parent alkane and its position is indicated by numbers.

4) The lower number is given to the first in alphabetical order.

5) The carbon atom of the branch that attaches to the root alkane is numbered

Organic compounds having Functional Groups: The longest chain of carbon atoms containing the functional groups is numbered in such a way that the functional group attached to the carbon atom gets the lowest possible number in the chain.

When there are more functional groups then a priority order is followed as:

-COOH, -SO₃H, -COOR,- COCl, -CONH₂, -CN, -HC=O, =C=O, -OH, -NH₂, -C=C, -CΞ C-.

Prefix, word root, primary suffix, secondary suffix

Formula	Prefix	Word root	Primary suffix	Secondary suffix (pri suffix e to be replaced by s. suffix)	Name
CH_4		Meth	Ane		Methane
CH_3-CH_3		Eth	Ane		Ethane
$CH_3-CH_2-CH_3$		Prop	Ane		Propane
CH_3-OH		Meth	Ane	ol	Methanol
CH_3-CH_2-OH		Eth	Ane	ol	Ethanol
HCOOH		Meth	Ane	oic acid	Methanoic acid
CH_3-COOH		Eth	Ane	oic acid	Ethanoic acid
HCHO		Meth	Ane	al	Methanal
CH_3-CHO		Eth	Ane	al	Ethanal
CH_3-Cl	Chloro	meth	Ane		Chloromethane
$CH_3-CO-CH_3$		Prop	Ane	one	Propanone
$CH_2=CH_2$		Eth	Ene		Ethene
$CH_3-CH=CH_2$		Prop	Ene		Propene
$CH\equiv CH$		Eth	Yne		Ethyne
$CH_3-C\equiv CH$		Prop	Yne		Propyne

Aromatic compounds:

Nomenclature of aromatic compounds: Benzene forms only one mono-substituted derivative. It can form three di-substituted derivatives ;ortho(1,2), meta(1,3) ,para(1,4).

Benzene   Naphthalene   Methylbenzene (Toluene)   Methoxybenzene (Anisole)   Aminobenzene (Aniline)   Nitrobenzene   Bromobenzene

| 1,2-Dibromo-benzene | 1,3-Dibromo-benzene | 1,4-Dibromo-benzene | 1-Chloro-2,4-dinitrobenzene | 2-Chloro-1-methyl-4-nitrobenzene |
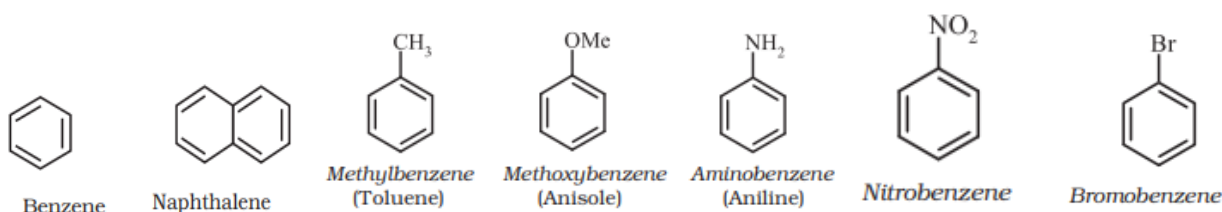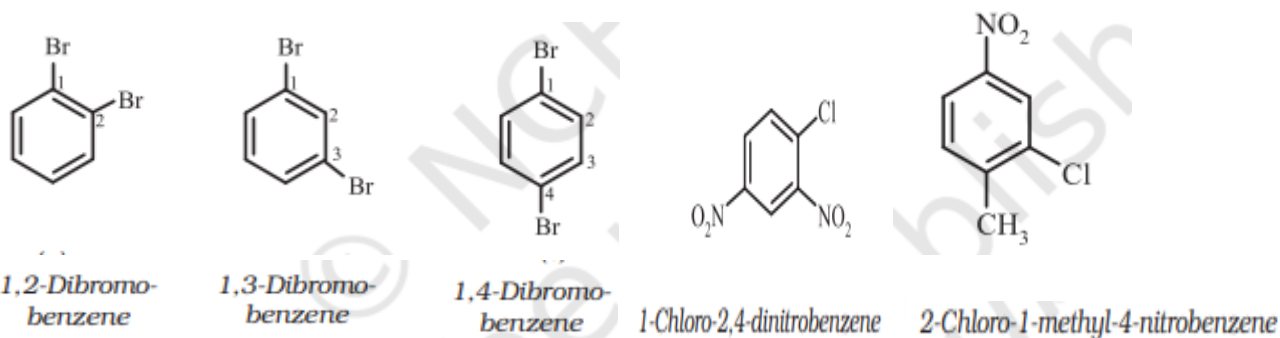
ISOMERISM

Two or more compounds having the same molecular formula but different physical and chemical properties are called isomers and this phenomenon is called isomerism.

Classification of isomerism: Isomerism is basically classified into 2 types i.e,

1) Structural isomerism
2) Stereo isomerism
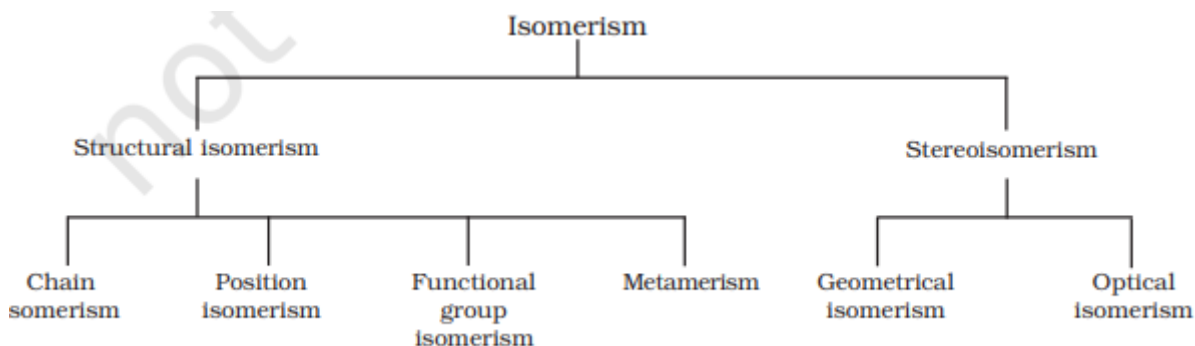
Structural isomerism: Compounds having same molecular formula but different structures are called Structural isomers..

Chain isomerism: When two or more compounds having same molecular formula but different carbon skeletons, these are referred to as chain isomers and this phenomenon is called chain isomerism.
Eg : Butane and isobutane.

Position Isomerism: Compounds which have the same structure of carbon chain but differ in position of double or triple bonds or functional group are called position isomers and this phenomenon is called Position Isomerism.

$$\text{eg} : CH_3\text{-}CH_2\text{-}CH=CH_2 \quad, CH_3\text{-}CH = CH - CH_3$$
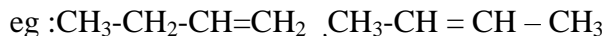
Functional Isomerism: Compounds which have the same molecular formula but different functional group are called functional isomers and this phenomenon is called functional Isomerism

eg : $CH_3 - CH_2 - OH$, $CH_3 - O - CH_3$

Metamerism: It is due to the presence of different alkyl groups on either side of functional group in the molecule. eg. $C_4H_{10}O$ represents $C_2H_5OC_2H_5$ and $CH_3OC_3H_7$.

FISSION OF COVALENT BOND

Heterolytic cleavage: In this cleavage the bond breaks in such a way that the shared pair of electron remains with one of the fragment.

$$H_3C - Br \longrightarrow H_3\overset{+}{C} + \overset{-}{Br}$$

A species having a carbon atom possessing sextet of electrons and a positive charge is called a carbocation (carbonium ion). The C^+H_3 ion is known as a methyl cation or methyl carbonium ion. Carbocations are classified as primary, secondary or tertiary depending on whether one, two or three carbons are directly attached to the positively charged carbon.

The observed order of carbocation stability is:

$$C^+H_3 < CH_3C^+H_2 < (CH_3)_2C^+H < (CH_3)_3C^+.$$

The heterolytic cleavage can also give a species in which carbon gets the shared pair of electrons. For example, when group Z attached to the carbon leaves without electron pair, the methyl anion is formed. Such a carbon species carrying a negative charge on carbon atom is called carbanion. Carbon in carbanion is generally sp^3 hybridised . Carbanions are also unstable and reactive species.
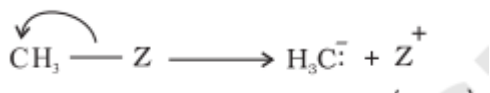
Homolytic Cleavage: This involves breaking of a covalent bond in such a way that each atom separates one electron of the shared pair.
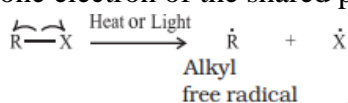
Alkyl radicals are classified as primary, secondary, or tertiary. Alkyl radical stability increases from primary to tertiary
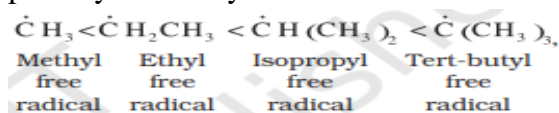
Attacking reagents:

Nucleophiles: A reagent that brings an electron pair is called nucleophile eg $-OH^-$,$-CN^-$

Electrophiles: A reagent that takes away an electron pair is called electrophile eg

Electrophiles: $BF_3, \overset{+}{C}l, CH_3 - \overset{+}{C} = O, \overset{+}{N}O_2.$
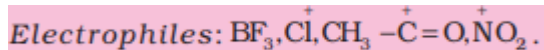
Electronic displacements:

Inductive Effect: The permanent electron displacement along a chain due to the presence of a polar covalent bond that is bond polarity is known as inductive effect. If an atom or group attracts electron more strongly than hydrogen, it is said to have –I Effect.
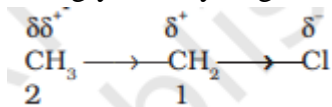
If an atom or group of atom attracts electron less strongly than hydrogen it is said to have +I Effect.

Resonance Effect: The polarity produced in the molecule by the interaction of two pi bonds or between a pi bond and lone pair of electron present on an adjacent atom.

There are two types of resonance effect:

1) **Positive resonance effect:** In this effect the transfer of electrons is away from an atom or substituent group attached to the conjugated system. The atoms or groups which shows +R effect are halogens, -OH , -OR,- NH_2.

2) **Negative resonance effect**: In this effect the transfer of electrons is towards the atom or substituent group attached to the conjugated system. The atoms or groups which shows -R effect are –COOH , -CHO , -CN.

Electrometric effect: It involves the complete transfer of shared pair of electrons to one of the atoms joined by a multiple bond at the requirement of the attacking reagent. It is temporary effect.

Hyperconjugation: Electron release by an alkyl group attached to unsaturated system. There should be at least one-H at alpha carbon with respect to sp2 hybrid carbon.

METHODS OF PURIFICATION OF ORGANIC COMPOUNDS:

Sublimation: This method is used to separate the sublimable compounds from non sublimable compounds.

Crystallisation: This method is based on the difference in the solubilities of compound and impurities in a suitable solvent.

Distillation: This method is used to separate volatile liquids from non-volatile liquids and liquids having sufficient difference in their boiling points.

Fractional distillation: If the boiling points of two liquids is not much, they are separated by this method.

Distillation under reduced pressure: This method is used to purify liquids having high boiling points and decomposes at or below their boiling points.

Steam distillation: This method is used to separate substances which are steam volatile and are immiscible with water

Differential Extraction: When an organic compound is present in an aqueous medium it is separated by shaking it with organic solvent in which it is more soluble than in water.

Chromatography:

Adsorption Chromatography: It is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Silica gel or alumina is used as adsorbents.

Partition Chromatography: It is based on the continuous differential partitioning of components of a mixture between stationary and mobile phase.

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Detection of carbon and hydrogen: The carbon and hydrogen present in the organic compound is deducted by heating the compound with copper (II) oxide in a hard glass tube when carbon present in the compound is oxidized to carbon dioxide which can be tested with lime water and hydrogen converted to water which can be tested with anhydrous copper sulphate which turns blue.

$$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$$
$$2H + CuO \xrightarrow{\Delta} Cu + H_2O$$
$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + H_2O$$
$$5H_2O + CuSO_4 \longrightarrow CuSO_4.5H_2O$$
$$\text{White} \qquad\qquad \text{Blue}$$

Detection of other elements:

Sodium fusion extract: A small piece of dry sodium metal is heated with an organic compound in a fusion tube for 2-3 minutes and the red hot tube is plunged into distilled water contained in a China dish the content of the China dish is boiled ,cooled and filtered. The filtrate is called as sodium fusion extract.

Test for Nitrogen: The sodium fusion extract is boiled with iron II sulphate and then acidified with Concsulphuric acid, the formation of Prussian blue colour confirms the presence of nitrogen.

$$6CN^- + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} Fe_4[Fe(CN)_6]_3.xH_2O$$
$$\text{Prussian blue}$$

Test for Sulphur: The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.

$$S^{2-} + Pb^{2+} \longrightarrow \underset{\text{Black}}{PbS}$$

Test for halogens: The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish ppt. sparingly soluble in ammonium hydroxide shows the presence of bromine, a yellowish ppt. insoluble in ammonium hydroxide shows the presence of iodine.

$$X^- + Ag^+ \longrightarrow AgX$$
X represents a halogen – Cl, Br or I.

QUANTITIVE ANALYSIS

1]Carbon and Hydrogen

Let the mass of organic compound be m g. Mass of water and carbon dioxide produced be m1 and m2 g respectively;

$$\text{Percentage of carbon} = \frac{12 \times m_2 \times 100}{44 \times m}$$

$$\text{Percentage of hydrogen} = \frac{2 \times m_1 \times 100}{18 \times m}$$

Dumass method: A known mass of organic compound is heated with excess of CuO in an atmosphere of carbon dioxide, when nitrogen of the organic compound is converted into N_2 gas .The volume of N_2 thus obtained is converted into STP and the percentage of nitrogen is determined by the following equation:

$$V \text{ mL } N_2 \text{ at STP weighs} = \frac{28 \times V}{22400} g$$

$$\text{Percentage of nitrogen} = \frac{28 \times V \times 100}{22400 \times m}$$

Kjeldahl's Method: A known mass of organic compound is heated with concentrated sulphuric acid in presence of potassium suplhate and little copper sulphate in a Kjeldahl flask when nitrogen is present in the organic compound is converted into ammonium sulphate. Ammonium sulphate thus obtained is boiled with excess of NaOH to liberate ammonia gas which is absorbed in an excess of standard acid such as sulphuric acid or HCl. The volume of the acid unused is found by titration against a standard alkali solution from the volume of the acid used the percentage of nitrogen is determined by applying the equation.

$$\text{Percentage of N} = \frac{14 \times M \times 2(V - V_1/2)}{1000} \times \frac{100}{m}$$

$$= \frac{1.4 \times M \times 2(V - V_1/2)}{m}$$

Estimation of Halogen:

Carius method: A known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as Carius tube, in a furnace. Carbon and hydrogen present in the compound are oxidised to carbon dioxide and water. The halogen present forms the corresponding silver halide (AgX). It is filtered, washed, dried and weighed.

Let the mass of organic compound taken = m g
Mass of AgX formed = m_1 g
1 mol of AgX contains 1 mol of X
Mass of halogen in m_1g of AgX

$$= \frac{\text{atomic mass of X} \times m_1 g}{\text{molecular mass of AgX}}$$

Percentage of halogen

$$= \frac{\text{atomic mass of } X \times m_1 \times 100}{\text{molecular mass of AgX} \times m}$$

Estimation of sulphur:

Let the mass of organic

compound taken = m g

and the mass of barium

sulphate formed = m_1g

1 mol of $BaSO_4$ = 233 g $BaSO_4$ = 32 g sulphur

m_1 g $BaSO_4$ contains $\dfrac{32 \times m_1}{233}$ g sulphur

Percentage of sulphur = $\dfrac{32 \times m_1 \times 100}{233 \times m}$

Estimation of phosphorous:

Let the mass of organic compound taken = m g and mass of ammonium phospho molydate = m_1g

Molar mass of $(NH_4)_3PO_4.12MoO_3$ = 1877g

Percentage of phosphorus = $\dfrac{31 \times m_1 \times 100}{1877 \times m}$ %

If phosphorus is estimated as $Mg_2P_2O_7$,

Percentage of phosphorus = $\dfrac{62 \times m_1 \times 100}{222 \times m}$ %

Estimation of oxygen:

Let the mass of organic compound taken be mg

Mass of carbon dioxide produced be m_1 g

∴ m_1 g carbon dioxide is obtained from

$\dfrac{32 \times m_1}{88}$ g O_2

∴Percentage of oxygen = $\dfrac{32 \times m_1 \times 100}{88 \times m}$ %

MULTIPLE CHOICE QUESTIONS

1) 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) Hyper conjugation

Answer: b) Electromeric effect

2) Homolytic fission leads to the formations of

a) nucleophile   b) carboanion   c) free radical   d) carbocation

Answer: c) free radical

3) 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

4) Which one is strongest acid among following options?

(A) CH_2FCOOH (B) $CH_2ClCOOH$ (C) $CHCl_2COOH$ (D) CHF_2COOH

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Answer:(D) CHF_2COOH

5)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) $CH_3C \equiv N$

6)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

7) The increasing order of electron donating inductive effect of alkyl group is:

(A) $-H<-CH_3<-C_2H_5<-C_3H_7$ (B) $-H>-CH_3>-C_2H_5>-C_3H_7$

(C) $-H<-C_2H_5<-CH_3<-C_3H_7$ (D)$-H>-C_2H_5>-CH_3>-C_3H_7$

Answer: (A) $-H<-CH_3<-C_2H_5<-C_3H_7$

8) Which one is the correct order of acidity?

(a) $CH_2=CH_2> CH_3-CH=CH_2> CH_3C\equiv CH > CH\equiv C$

(b) $CH\equiv CH > CH_3-C\equiv CH > CH_2=CH_2> CH_3CH_3$

(c) $CH\equiv CH > CH_2=CH_2 > CH_3-C\equiv CH > CH_3-CH_3$

(d) $CH_3-CH_3> CH_2=CH_2> CH_3-C\equiv CH > CH\equiv CH$

Answer: (b) $CH\equiv CH > CH_3-C\equiv CH > CH_2=CH_2> CH_3CH_3$

9)Which of the ion is the most resonance stabilized?

a) $C_2H_5O^-$ b) $C_6H_5O^-$

   c) $(CH_3)_3CO^-$ d) $(CH_3)_2CHO^-$

Answer: b) $C_6H_5O^-$

10) Which one of the following is least stable?

  a) $C^{\ominus}H_3$ b) $HC\equiv C^{\ominus}$ c) $(C_6H_5)_3C^{\ominus}$ d) $(CH_3)_3C^{\ominus}$

Answer: d) $(CH_3)_3C^{\ominus}$

ASSERTION AND REASON QUESTIONS

In the following questions the assertion and reason have been put forward read the statements carefully and choose the correct answer from the following choices

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

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

(C) Both A and R are not correct.

(D) A is not correct but R is correct.

1)   Assertion: IUPAC name of compound $CH_3CH = CH – CHO$ is But–2– enal.

Reason: Functional group gets preference over multiple in IUPAC name ofa compound.

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

2)   Assertion: pi– bond stronger than sigma bond.

    Reason: The extent of overlapping in sigma bond is greater than in pi– bond.

Answer:(D) A is not correct but R is correct.

3)   Assertion: Though the central atom of both NH_3 and H_2O molecule are sp3 hybridized, yet H−N−H bond angle is greater than that of H−O−H.

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

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

4)   Assertion: Tertiary carbonations are generally formed more easily than primary carbocations.

   Reason: Hyperconjugation as well as inductive effect due to additional Alkyl groups stabilize tertiary carbocations

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

5)   Assertion: Alkyl carbanions like ammonia have pyramidal shape.

   Reason: The carbon atom carrying negative charge has an octet of electrons.

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

6)   Assertion: The components of a mixture of red and blue ink can be separated by distributing the components between stationary and mobile phase in paper chromatography.

   Reason: The colored components of ink migrates at different rates because paper selectively retains different components according to the difference in the partition between the two phases.

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

7)   Assertion (A): Pent- 1- ene and pent- 2- ene are position isomers.

   Reason (R): Position isomers differ in the position of functional group or a substituent.

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

8)   Assertion: a mixture of ortho-nitrophenol and para- nitrophenol can be separated by steam distillation

   Reasons: para -nitrophenol is steam volatile while ortho -nitro phenol is not steam volatile.

Answer: (D) A is correct but R is not correct.

9)   **Assertion:** Heterolytic fission involves the breaking of a covalent bond in such a way that both the electrons of the shared pair are carried away by one of the atoms.

   Reason: Heterolytic fission occurs readily in polar covalent bonds. Heterolytic fission involves the breaking of a covalent bond in such a way that both the electrons of the shared pair are carried away by one of the atoms.

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

10)   **Assertion:**The order of stability of carbocation is 3>2>1.

   Reason: Carbon atom in carbocation is in sp3 state of hybridization.

Answer: (D) A is correct but R is not correct.

2mark question

   1) Draw the structure of the following compounds
   a) Hex-3enoic acid
   b) 2-chloro-2-methyl butan-1-ol
          a) $CH_3-CH_2-CH=CH-CH_2-COOH$ b)$CH_3-CH_2-CCl(CH_3)-CH_2-OH$

   2. Explain.Why $(CH_3)_3 -C^+$ is more stable than $CH_3-CH_2^+$ and CH_3^+ is the least stable cations.

Hyper conjugation interaction in $(CH_3)_3 -C^+$ is greater than in$CH_3-CH_2^+$ has$(CH_3)_3 -C^+$
9 CH bonds. In CH_3^+,vacant p-orbital is perpendicular to the plane in which C-H- lie; hence cannot
overlap with it thus C^+H_3 lacks hyper conjugative stability.

3) Give the number of sigma and pi bond in the following molecules
   a) CH_3-NO_2 b) $HCONHCH_3$
a) 6 sigma and 1πbond
b) 8 sigma and 1 πbond

4) It is not advisable to use sulphuric acid in place of acetic acid for acidification while testing sulphur by lead acetate test. Give reason.
   Lead acetate on reacting with sulphuric acid will give a white precipitate of lead sulphate which interfere in the detection of sulphur.

5) Under what condition can the process of steam distillation is used.
   Steam distillation is used to purify the liquids which has **steam volatile and immiscible in water.**

6) Suggest a method to purify
(i) Kerosene containing water
   (ii) A liquid that decomposes at its boiling point.

i) By solvent extraction using a separating funnel.
 ii)Distillation under reduced pressure.

7) 0.15g of an organic compound gave 0.12g of AgBr by carius method. Find the percentage of bromine in the compound.
   Mass of AgBr formed = 0.12g
   188 g of AgBr contains bromine = 80g.
Therefore, 0.12g of AgBr will contain bromine
$= 80\times0.12/188$
$= 0.051$ g
Percentage of bromine $= 0.051\times 100/0.15$
$= 34\%$

8.Define homologous series?
A group or a series of organic compounds each containing a characteristic functional group forms a homologous series and the members of the series are called homologues. The members of a homologous series can be represented by general molecular formula and the successive members differ from each other in molecular formula by a $-CH_2$ unit.

9. What is the cause of geometrical isomerism in alkenes?
In alkenes there is a double bond between two carbon atoms, due to presence of pi-electrons, the rotation between these C=C is not possible. Thus, geometrical isomerism in alkenes exists due to nonrotating double bond.

10.a. Define Sodium fusion extract.
    b.Why is sodium fusion extract made acidic with acetic acid before the addition of lead acetate in the detection of sulphur?

a. A small piece of dry sodium metal is heated with an organic compound in a fusion tube for 2-3 minutes and the red hot tube is plunged into distilled water contained in a China dish the content of the China dish is boiled ,cooled and filter this filtrate is called as sodium fusion extract.

b. Lead acetate is hydrolyzed by NaOH present in Sodium extract. It is neutralized first with acetic acid before the addition of lead acetate.

Three marks question

1. a. Name the type of isomerism exhibited by acetone and propanal.
   b. Distinguish between position and functional isomerism with example.
      a) Functional isomerism
      b) The isomers which differ in position of functional groups are called position isomers.

e.g But-1-ene and But-2-ene

The isomers which differ in functional group are called functional group isomers.

e.g C_2H_5OH and CH_3OCH_3

2. a. Which distillation method is used to separate a mixture of o-nitro phenol and p-nitro phenol?
   b. Distinguish between Steam distillation and distillation under reduced pressure.

a. Steam Distillation

   b. Steam distillation is used to separate substances which are steam volatile and are immiscible with water.

   Distillation under reduced pressure is used to purify those liquids which decompose at or below their normal boiling points.

3. Write IUPAC name of each of the following compound.

   a.   b.   c. $CH_2 = CHCH_2CH (OH)CH_3$.

$$CH_3CH_2\underset{\underset{\displaystyle CH_3}{\underset{\displaystyle |}{CHCH_2CH_2CH_3}}}{\overset{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{}}}{}}$$

$$CH_3 - \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}} - CH_2 - \underset{\underset{\displaystyle }{}}{\overset{\overset{\displaystyle Cl}{|}}{CH}} - CH_3$$
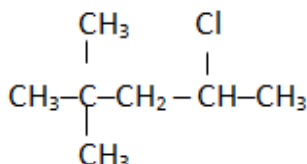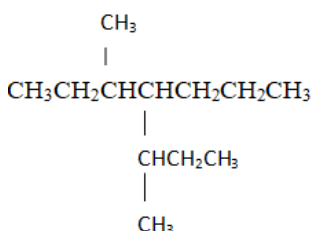
a.3,5-Dimethyl-4-propylheptane   b. 4-chloro-2,2-dimethylpentane   c.) Pent-4-en-2-ol.

4. a) 0.546 g of silver Bromide is obtained from 0.5372 g of an organic .compd. Calculate the percentage of Bromine. (At. mass Br=80g/mol Ag =108g/mol)

   b) How is the presence of chlorine detected in an organic .compound?

      a) Mass of org compound = 0.5372g Mass of AgBr = 108 +80=188g/mol

$$\frac{80 \, X \, mass \, of \, AgBr \, X \, 100}{188 \, X \, mass \, of \, org.compd} = \% \, of \, Bromine$$

$$\frac{80 \, X \, 0.546 \, X \, 100}{188 \, X \, 0.5372} = \% \, of \, Bromine$$

% of Br = 43.25 g

b) Sodium fusion extract of the given organic compd. is treated with dilute nitric acid and then Silver nitrate solution is added. Formation of white ppt indicates the presence of Chlorine in the given organic compound

.
5.Distinguish between inductive effect and resonance effect.

Inductive effect	Resonance effect
1.Involves displacement of sigma electrons and hence occurs only in saturated compound	1. Involves delocalization of pi electrons and lone pair and hence occurs in unsaturated compounds and conjugated systems.
2. Electronegativity difference induces this effect towards the more electronegative atom to give partial +ve or –ve charges.	2. It takes place due to interaction between two pi bonds or a pi bond and a lone pair of electron
3.Inductive effects are transmitted over short distances in saturated carbon chains and the magnitude of the effect decreases rapidly as the distance from the halogen atom increases	3. The resonance effects are transmitted all along the length in the conjugated system. The electron pair is completely transferred to form positive and negative charge centres.

6. In Dumas' method for estimation of nitrogen, 0.3g of an organic compound gave 50mL of nitrogen collected at 300K temperature and 715mm pressure. Calculate the percentage composition of nitrogen in the compound. (Aqueous tension at 300K=15 mm)

Volume of nitrogen collected at 300K and 715mm pressure is 50 mL

Actual pressure = 715-15 =700 mm

Volume of nitrogen at STP= $\dfrac{273 \times 700 \times 50}{300 \times 760}$

== 41.9 mL

22,400 mL of N2 at STP weighs = 28 g

41.9 mL of nitrogen weighs= $\dfrac{28 \times 41.9}{22400}$

Percentage of nitrogen = $\dfrac{28 \times 41.9 \times 100}{22,400 \times 0.3}$

=17.46%

7. a. Why is organic compound fused with Na metal during detection of nitrogen, sulphur halogens?

   B. Sometimes red colouration is obtained when Ferric Chloride is added during Lassaigne's test for detection of nitrogen. Why?

   Organic compound is fused with sodium metal to convert nitrogen, sulphur,halogens present it into ionisable form.

   When nitrogen and sulphur both are present in an organic compound, sodium thiocyanate is formed which gives red colouration with $FeCl_3$.

8.During estimation of nitrogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen, neutralized 10 mL of 1 M H2SO4 . Find out the percentage of nitrogen in the compound.

1 M of 10 mL H_2SO_4=1M of 20 mL NH_3
1000 mL of 1M ammonia contains 14 g nitrogen
20 mL of 1M ammonia contains

$$\frac{14 \times 20}{1000} \text{ g nitrogen}$$

$$\text{Percentage of nitrogen} = \frac{14 \times 20 \times 100}{1000 \times 0.5} = 56.0\%$$

9. On complete combustion, 0.246 g of an organic compound gave 0.198g of carbon dioxide and 0.1014g of water. Determine the percentage composition of carbon and hydrogen in the compound.

Percentage of carbon = $\dfrac{12 \times 0.198 \times 100}{44 \times 0.246}$

   = 21.95%

Percentage of hydrogen = $\dfrac{2 \times 0.1014 \times 100}{18 \times 0.246}$

   = 4.58%

10. a)Define the term functional group

   b) What is the functional group of an aldehyde and an nitro compound.

   c) What is the state of hybridization of carbon atom in CH3-CH=CH-CH3.

   a) The atom or group of atom attached to carbon chain which is responsible for specific chemical properties of organic compounds.

   b) $-CHO, -NO_2$

   c) Sp3 , sp2 ,sp2 ,sp3.

5 marks questions

Q.No 1

a) What are electrophiles? Give an example.

b) Explain the principle of paper chromatography

c) Write the chemistry of lassaigne's test for qualitative analysis of nitrogen

a. The species which are positively charged or electron deficient are called electrophiles(electron seeking agent).example: H^+, Cl^+, $AlCl_3$.

b. In paper chromatography, chromatographic paper dipped in solvents act as a stationary phase whereas mixture of compounds dissolved in suitable solvents forms the mobile phase. Different compounds have different adsorbing power, therefore they move with different speeds and gets separated.

c. Lassaigne's test for qualitative analysis of nitrogen: Fuse the organic compound with sodium metal. sodium reacts with C and N present in organic compound to form NaCN.

$$Na + C + N \xrightarrow{\Delta} NaCN$$

Add $FeSO_4$ to lassaigne's extract

$$6CN^- + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} Fe_4[Fe(CN)_6]_3 \cdot xH_2O$$
$$\text{Prussian blue}$$
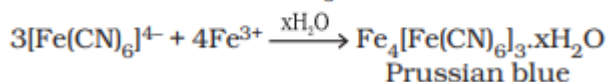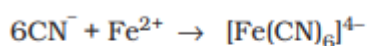
Dilute H_2SO_4 is added to convert Fe^{2+} to Fe^{3+} and blue color is formed due to the formation of ferric ferrocyanide.

Q.No 2

a) What are nucleophiles? Give one example of nucleophile.

b) Will CCl_4 give white ppt of AgCl on heating with silver Nitrate. Give reason for your answer.

c) Define hyper conjugation.

d) Draw the condensed formula and bond-line structural formula for

   a) 2,2,4-trimethylpentane

b) 2-hydroxy-1,2,3-propanetricarboxylic acid.

a.   Nucleophiles: Nucleophiles are negatively charged or neutral species with lone pair of electrons. example: Br⁻, H_2O

b.   No, it is because CCl_4 is non-polar compound, does not give Cl⁻ in aqueous solution, therefore it will not form any precipitate with silver nitrate (aq).

c.   Hyperconjugation is a general stabilising interaction. It involves delocalisation of σ electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared p orbital. The σ electrons of C—H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared p orbital. Hyperconjugation is a permanent effect.

d.

Condensed structures
$(CH_3)_2CHCH_2C(CH_3)_3$
$(HOOC)CH_2C(COOH)(OH)CH_2(COOH)$

Bond line structures
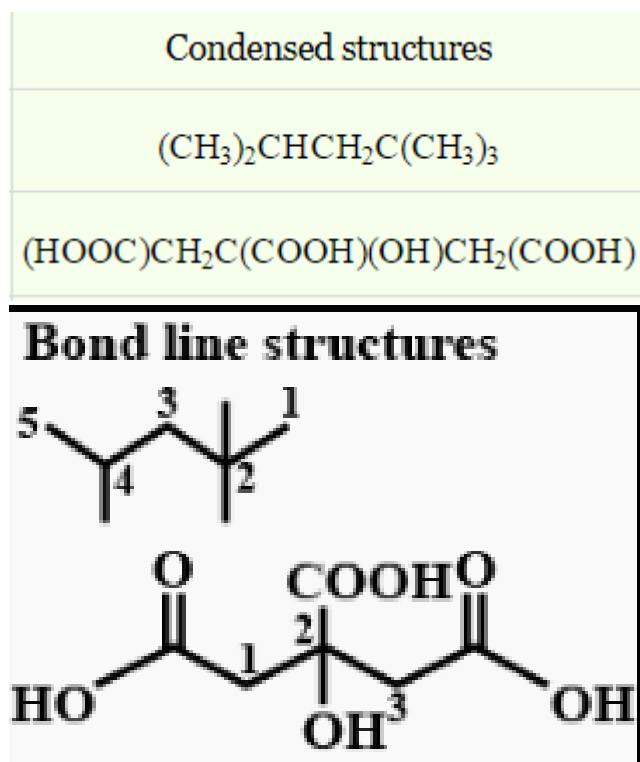
CASE BASED QUESTIONS

1)

Once an organic compound is extracted from a natural resource or synthesized in the laboratory,it is essential to purify it.Various methods used for the purification of organic compounds are based on the nature of the compound and the nature of the impurity present in it. Finally, the purity of a compound is ascertained by determining its boiling point and melting point. Most of the pure compounds have sharp melting and boiling points.New methods of checking the purity of an organic compound are based on different types of chromatographic and spectroscopic methods.

a) How will you separate mixture of camphor and benzoic acid?
b) Boiling point of Chloroform is 334K and that of aniline is 457K. Which method will be suitable to separate mixture of aniline and chloroform?
c) Which method is used to separate mixture of glycerol and spent-lye in soap industry is separated?
d) Name the method used to purify aniline.

a) As by the process of sublimation, both will get sublime. We can separate them by mixing them in hot water and then filtering the solution. Residue will be camphor and filtrate will be mixture of water & benzoic acid and we can get benzoic acid by crystallization method.
b) As the difference in their boiling point is sufficiently large, simple distillation method is used.
c) By distillation under reduced pressure.
d) Steam distillation method because it is steam volatile and immiscible with water.

2)

Carbon compounds show the phenomenon of isomerism. The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as isomerism. Such compounds are called as isomers. It shows mainly two types of isomerism structural and stereo isomerism. Compounds having same molecular formula and structure are classified as structural isomers. Compounds that have same composition and sequence of covalent compounds but differ in relative position of the atom in space are called stereo isomers.

i. Classify the following pairs as position, chain, functional isomers or metamers.
   a) Diethyl amine and methylpropylamine
   b) Ethanol and dimethyl ether

ii. Name the chain isomers of C_5H_{12} which has a tertiary hydrogen atom.
iii. In which of the following functional group isomerism is not possible.
   a) Alcohol   b)Aldehydes
   c) Alkyl halides   d) Cyanides

i. a)
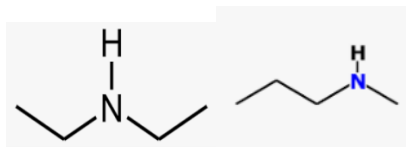
   They are Metamers

   b) C_2H_5OH , CH_3-O-CH_3
      They are Functional isomers

ii. The chain isomers of C_5H_{12} which has a tertiary hydrogen atom is 2-Methylbutane.
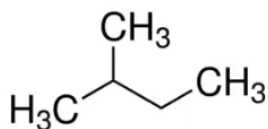
iii. c) alkyl halides

HOTS (higher order thinking skill)

1) In pyrrole
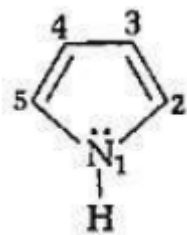
The electron density is maximum on
(1)2 and 3 (2) 3 and 3 (3) 2 and 4 (4) 2 and 5
Answer:(4)

2) A mixture contains two components A and B. The solubilities of A and B in water near its boiling point are 10 grams per 100 ml 2 g per 100 ml respectively How will you separate A and B from this mixture ?

Answer:A and B from the mixture can be separated by using fractional crystallization. When the saturated hot solution of this mixture is allowed to cool, the less soluble compound B crystallizes out first leaving the more soluble component A in the mother liquor.

3) With proper justification arrange the following in order of increasing stability
$CH_3-CH_2^-$, $CH\equiv C^-$, $CH_2=C^-$

Answer: In acetylide ,$CH\equiv C^-$,the carbon atom carrying the –ve charge is sp hybridized and has 50% s-character in $CH_2=C^-$, the carbon atom is sp2 hybridized and has 33% s-character while in $CH_3-CH_2^-$, the carbon atom bearing a –ve charge is sp3 and has 25% of s-character. Since s-electrons, on the average are close to the nucleus than p-electron, therefore a carbon atom with s-character can accommodate or stabilize the –ve charge better than a carbon atom with small s-character in other words the stability of the carbo-anion increases as the s-character of the carbon atom carrying the –ve charge increases. Since the s-character of the carbon decreases as we move from sp2 to sp2 to sp3 –carbon therefore the relative stability three carbo-anion follows the sequence $CH\equiv C^->CH_2=C^->CH_3-CH_2^-$.

9.HYDROCARBON

Hydrocarbons are the chemical compounds composed of Carbon and Hydrogen.:

Classifications of Hydrocarbons

Alkanes

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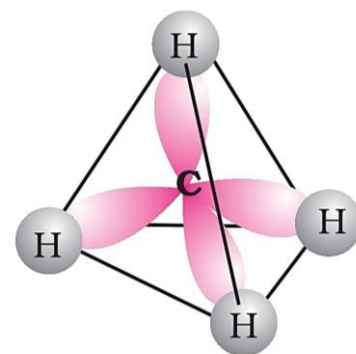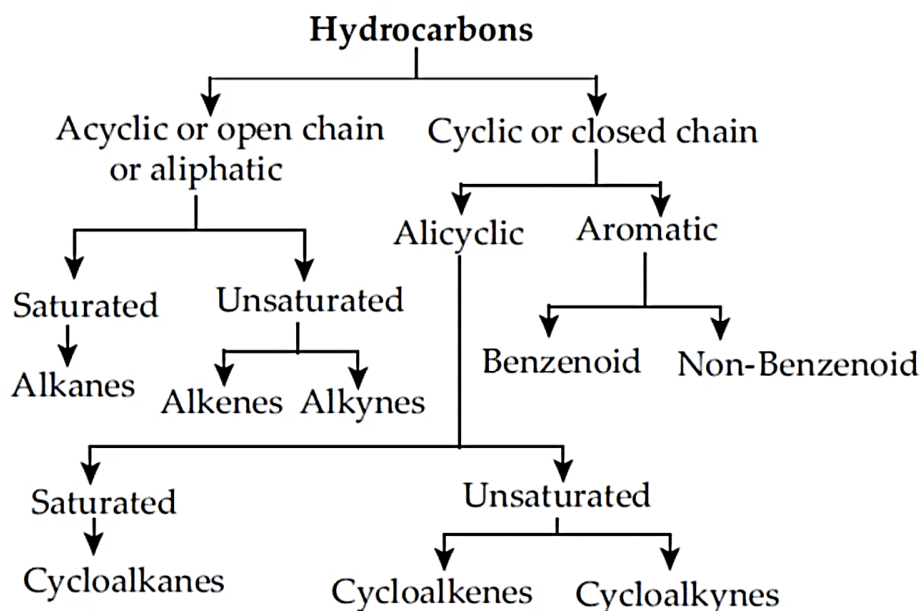
Alkanes are saturated, open chain hydrocarbons containing carbon-carbon single bonds. e.g., methane (CH_4), ethane (C_4H_6) propane (C_3H_8), etc. Common formula for alkanes is C_nH_{2n+2}.

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
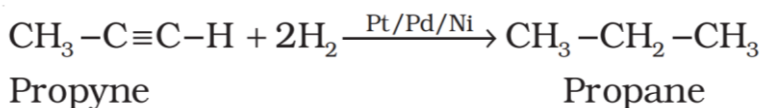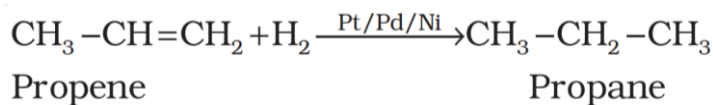
From alkyl halides: Alkyl halide on reduction with zinc and dil. HCl give alkanes.

$$CH_3-Cl + H_2 \xrightarrow{Zn,\ H^+} CH_4 + HCl$$
Chloromethane   Methane

$$C_2H_5-Cl + H_2 \xrightarrow{Zn,H^+} C_2H_6 + HCl$$
Chloroethane   Ethane
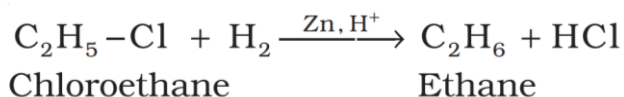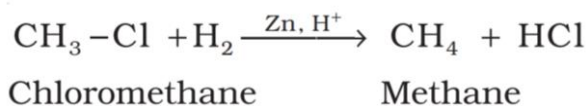
Wurtz reaction : This reaction is used for preparation of higher alkanes.

$$CH_3Br+2Na+BrCH_3 \xrightarrow{dry\ ether} CH_3-CH_3+2NaBr$$
Bromomethane   Ethane
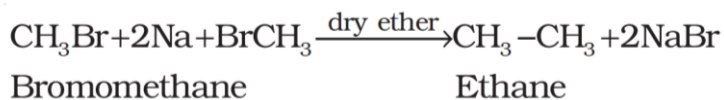
From carboxylic acids: Degradation reactions/ decarboxylation reaction.

$$CH_3COONa + NaOH \xrightarrow[\text{Heat}]{\text{CaO}} CH_4 + Na_2CO_3$$
Sodium ethanoate   Sodium hydroxide   Methane   Sodium carbonate
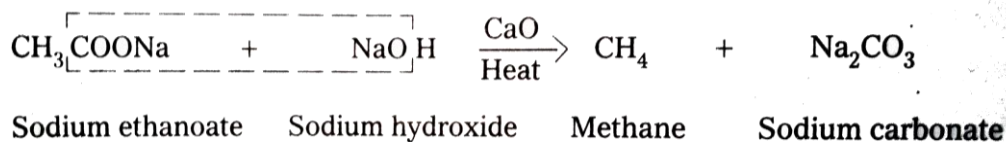
Kolbe's electrolytic method: An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms at the anode.

$$2CH_3COO \ Na + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3 - CH_3 + 2CO_2 + H_2 + 2NaOH$$

$\underline{CH_3COO}$ Acetate $\underline{Na}$ Sodium

At Anode: (Oxidation)

$$2\underline{CH_3 - \overset{O}{\overset{||}{C}} - O^-} \xrightarrow{-2e^-} 2CH_3 \overset{O}{\overset{||}{\vdots C - \dot{O}}} \longrightarrow 2C\dot{H}_3 + 2CO_2$$

Acetate ion

Loss of carbon dioxide

Methyl radical

$$2C\dot{H}_3 - \quad CH_3 - CH_3$$
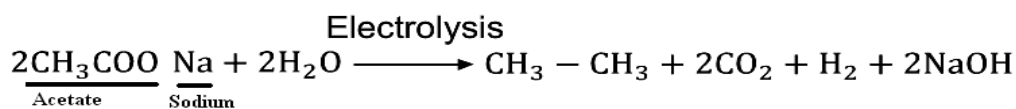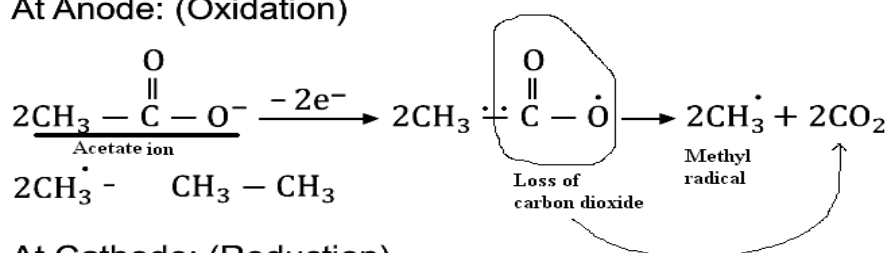
At Cathode: (Reduction)

$$2H_2O \xrightarrow{+2e^-} 2OH^- + 2\dot{H}$$

$$2\dot{H} \longrightarrow H_2$$
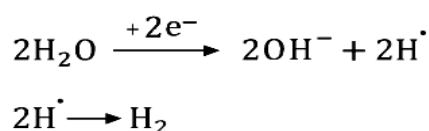
Chemical Properties

Alkanes being saturated compounds can undergo only **substitution reactions.**

Halogenation:

$$CH_3Cl + Cl_2 \xrightarrow[\text{light}]{\text{Heat or}} CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow[\text{light}]{\text{Heat or}} CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow[\text{light}]{\text{Heat or}} CCl_4 + HCl$$
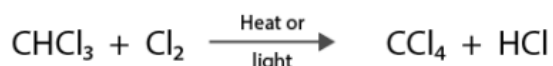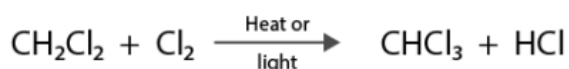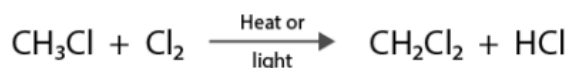
The rate of reaction of alkanes with halogens is $F_2 > Cl_2 > Br_2 > I_2$. Rate of replacement of hydrogens of alkanes is: $3° > 2° > 1°$.

Mechanism halogenation of alkanes: it can be explained with free radical mechanism as below:

initiation step
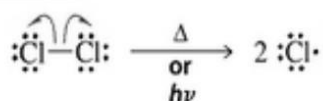
$$:\ddot{C}l - \ddot{C}l: \xrightarrow[\text{or } h\nu]{\Delta} 2 :\ddot{C}l\cdot$$

propagation steps

$$:\ddot{C}l\cdot + H - CH_3 \longrightarrow H\ddot{C}l: + \quad \cdot CH_3$$

a methyl radical

$$\cdot CH_3 + :\ddot{C}l - \ddot{C}l: \longrightarrow CH_3Cl + :\ddot{C}l\cdot$$

termination steps

$$:\ddot{C}l\cdot + :\ddot{C}l\cdot \longrightarrow Cl_2$$

$$\cdot CH_3 + \cdot CH_3 \longrightarrow CH_3CH_3$$

$$:\ddot{C}l\cdot + \cdot CH_3 \longrightarrow CH_3Cl$$

Combustion:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l);$$
$$\Delta_c H^\ominus = -890 \, kJ \, mol^{-1}$$

Controlled oxidation:

$$2CH_4 + O_2 \xrightarrow{\text{Cu/523K/100atm}} 2CH_3OH$$
$$\text{Methanol}$$

$$CH_4 + O_2 \xrightarrow[\Delta]{\text{Mo}_2\text{O}_3} HCHO + H_2O$$
$$\text{Methanal}$$

$$2CH_3CH_3 + 3O_2 \xrightarrow[\Delta]{\text{(CH}_3\text{COO)}_2\text{ Mn}} 2CH_3COOH + H_2O$$
$$\text{Ethanoic acid}$$

Isomerisation:

$$CH_3(CH_2)_4CH_3 \xrightarrow[\text{HCl}]{\text{Anhyd AlCl}_3} CH_3 CH - (CH_2)_2 - CH_3 + CH_3CH_2 - CH - CH_2\text{--}CH_3$$
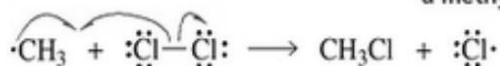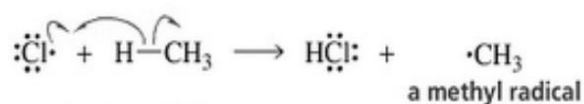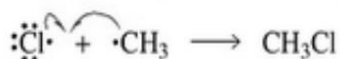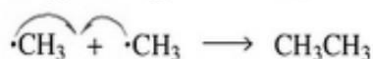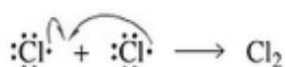
with:
- CH_3 branch — 2-Methylpentane
- CH_3 branch — 3-Methlpentane
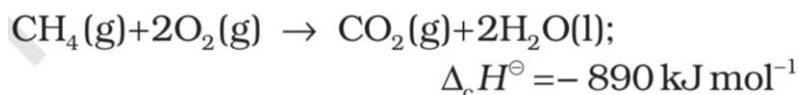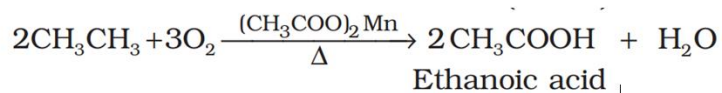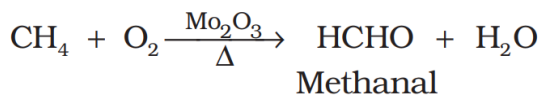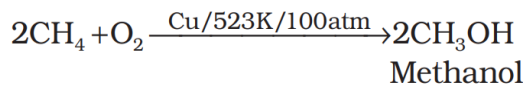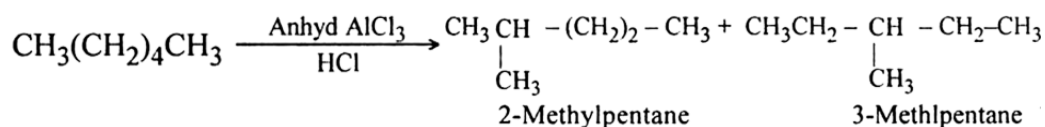
Aromatization (Reforming): The process of converting aliphatic compounds into aromatic compounds is called aromatisation.
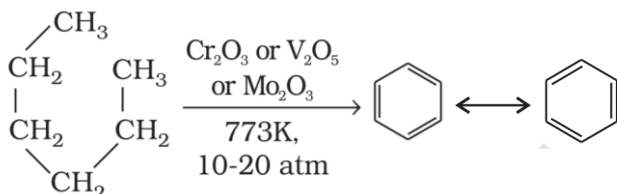
Reaction with steam:

$$CH_4 + H_2O \xrightarrow{Ni, \, 1273 \, K} CO + 3H_2$$
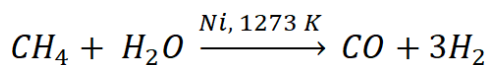
Pyrolysis or cracking: It is process of decomposing higher hydrocarbons into lower hydrocarbons with low boiling point by strong heating. Products depend on reaction situations.

$$C_6H_{14} \xrightarrow{773K} \begin{cases} C_6H_{12} + H_2 \\ C_4H_8 + C_2H_6 \\ C_3H_6 + C_2H_4 + CH_4 \end{cases}$$
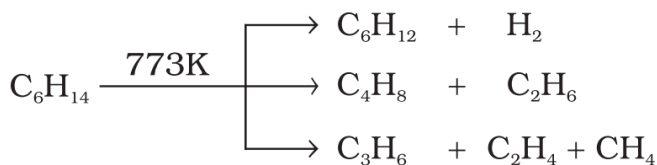
General reactions for methane:

$$CH_3COONa \xrightarrow[CaO]{NaOH}$$

$$CH_3MgCl \xrightarrow[\text{(Hydrolysis)}]{H_2O}$$

$$Al_4C_3 + H_2O \longrightarrow$$

$$CO + 3H_2 \xrightarrow[\text{(Reduction)}]{Ni/300°C}$$

CH₄ (Methane)

$$\xrightarrow[\text{Cu/523 K/100 atm}]{O_2} 2CH_3OH$$

$$\xrightarrow{Mo_2O_3} HCHO + H_2O$$

$$\xrightarrow[\text{(Combustion)}]{2O_2} CO_2 + 2H_2O$$

$$\xrightarrow[\text{(pyrolysis)}]{1000°C} C + 2H_2$$

$$\xrightarrow{\text{Excess } Cl_2} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 + 4HCl$$

$$\xrightarrow{\text{Conc. } HNO_3} CH_3NO_2 + H_2$$

General reactions for Ethane:

$$2CH_3Br \xrightarrow[\substack{\text{Dry ether} \\ \text{(Wurtz reaction)}}]{2Na}$$

$$C_2H_5MgCl \xrightarrow{H_2O}$$

$$C_2H_5COONa \xrightarrow{NaOH/CaO}$$

$$CH_3COONa \xrightarrow[\text{Electrolysis}]{H_2O}$$

$$CH_2{=}CH_2 \xrightarrow[H_2]{\text{Pt or Pd or Ni}}$$

C₂H₆ (Ethane)

$$\xrightarrow[\text{(Combustion)}]{O_2} 2CO_2 + 3H_2O$$

$$\xrightarrow[\text{(Pyrolysis)}]{800°C} C_2H_4 + H_2$$

$$\xrightarrow{Cl_2} C_2H_5Cl + HCl$$

$$\xrightarrow[450°C]{\text{Conc. } HNO_3} C_2H_5NO_2 + H_2O$$

$$\xrightarrow{\text{Oxidation}} C_2H_5OH$$

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
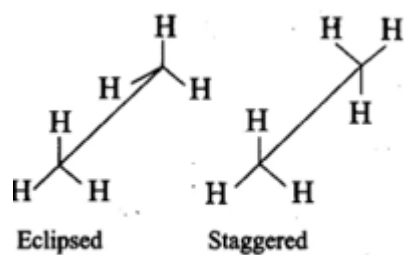
Newman projections of ethane:
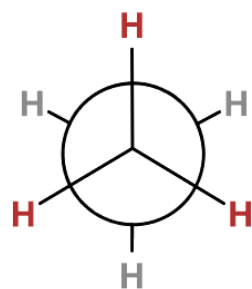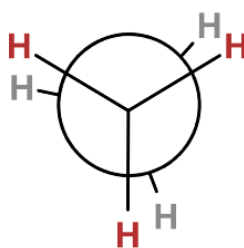
Staggered conformation   Eclipsed conformation

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.

$$\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H_2 - \overset{4}{C}H_3$$

But-1-ene
(C_4H_8)

$$\overset{1}{C}H_3 - \overset{2}{C}H = \overset{3}{C}H - \overset{4}{C}H_3$$
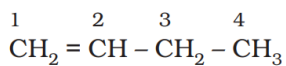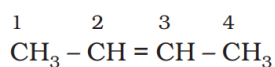
But-2-ene
(C_4H_8)
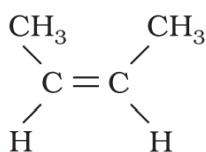
Structural isomer
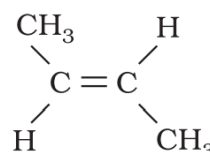
cis-But-2-ene
(b.p. 277 K)

trans-But-2-ene
(b.p. 274 K)

Geometrical isomer

Preparation

From alkynes:

$$RC \equiv CR^1 + H_2 \xrightarrow{Na/liquid\ NH_3}$$

R, H on one side; H, R¹ on other:

$$\underset{Alkyne}{RC \equiv CR^1 + H_2} \xrightarrow{Na/liquid\ NH_3} \underset{trans\text{-}Alkene}{\overset{R}{\underset{H}{>}} C = C \overset{H}{\underset{R^1}{<}}}$$

$$\underset{Propyne}{CH_3 - C \equiv CH + H_2} \xrightarrow{Pd/C} \underset{Propene}{CH_3 - CH = CH_2}$$

From alkyl halides:

$$\underset{(X\ =\ Cl,\ Br,\ I)}{H - \overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}} \overset{H}{\underset{X}{\overset{|}{\underset{|}{C}}}} - H} \xrightarrow[\Delta]{alc.\ KOH} \overset{H}{\underset{H}{>}} C = C \overset{H}{\underset{H}{<}}$$
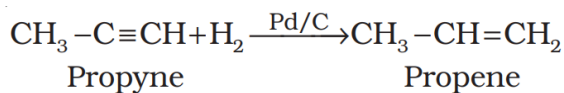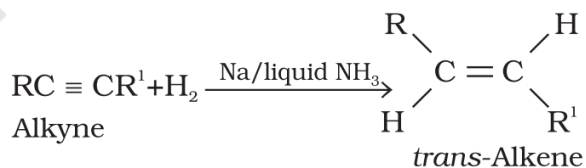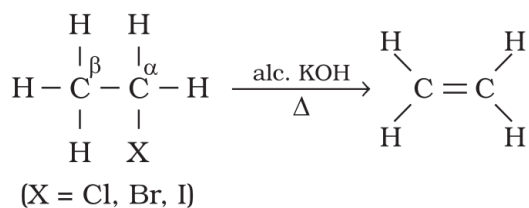
From alcohols by acidic dehydration:

$$\underset{Ethanol}{H - \overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}} \overset{H}{\underset{OH}{\overset{|}{\underset{|}{C}}}} - H} \xrightarrow[\Delta]{Conc.\ H_2SO_4} \underset{Ethene}{CH_2 = CH_2} + H_2O$$
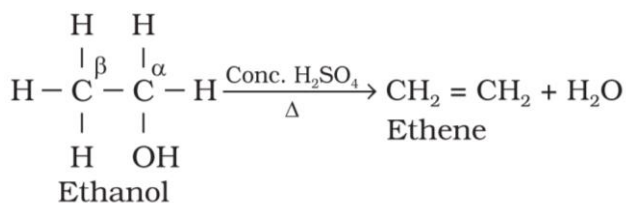
Chemical properties

Addition of halogens:

$$\underset{Ethene}{CH_2 = CH_2} + Br - Br \xrightarrow{CCl_4} \underset{\underset{1,2\ Dibromoethane}{Br\quad Br}}{CH_2 - CH_2}$$

$$\underset{Propene}{CH_3 - CH = CH_2} + Cl - Cl \longrightarrow \underset{\underset{1,2\text{-}Dichloropropane}{Cl\quad Cl}}{CH_3 - CH - CH_2}$$

Addition of hydrogen halides:

$$CH_3 - CH = CH_2 + H - Br \longrightarrow$$

I $\begin{array}{l} -CH_3 - CH - CH_3 \\ \quad\quad\quad | \\ \quad\quad\quad Br \\ \text{2-Bromopropane} \end{array}$

II $\begin{array}{l} -CH_3 - CH_2 - CH_2 - Br \\ \text{1-Bromopropane} \end{array}$
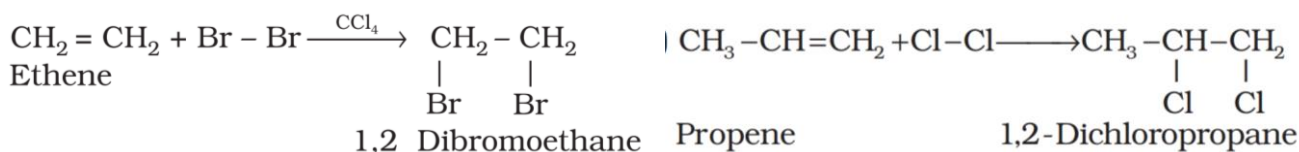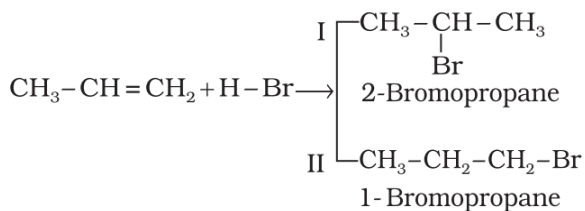
Markovnikov rule: The rule states that negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms.

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.

$$CH=CH_2 + HBr \xrightarrow{(C_6H_5CO)_2O_2} CH_3-CH_2$$

$$|$$
$$CH_2Br$$

1-Bromopropane
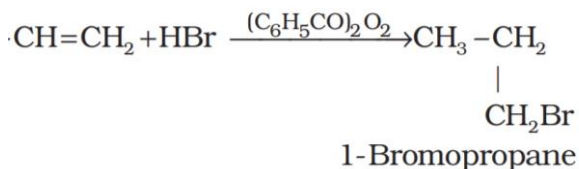
Addition of sulphuric acid:

$$CH_2 = CH_2 + H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-H$$

$$\downarrow$$

$$CH_3 - CH_2 - O\,SO_2 - OH \text{ or } C_2H_5HSO_4$$

Addition of water:

Ethylene   Water   Ethanol
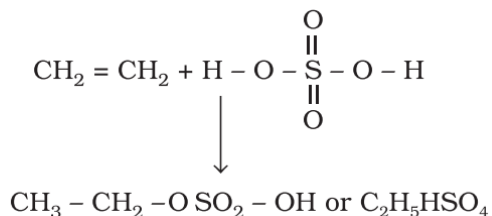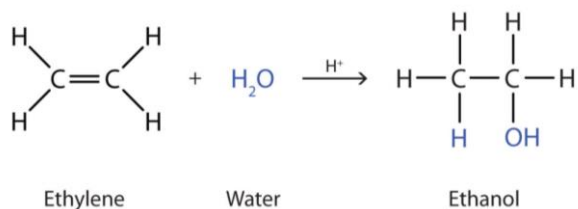
Oxidation: In alkaline solution of $KMnO_4$ (Baeyer's Reagent)

Ethene   **Ethanediol**

Ozonolysis:

Ethene   1,2,3-Trioxolane   Formaldehyde   Formaldehyde

2-Methyl-2-butene   4,4,5-Trimethyl-1,2,3-trioxolane   Acetone   Acetaldehyde

Polymerisation:

$$n(CH_2=CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} -(CH_2-CH_2)_n-$$
$$\text{Polythene}$$
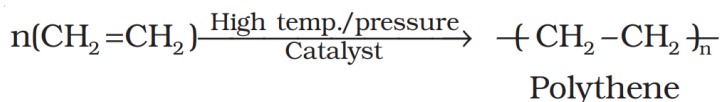
General reactions for Ethene:

ALKYNES :

Alkynes are also unsaturated hydrocarbons. They contain at least one triple bond between two carbon atoms. Their general formula is CnH_{2n-2}.

Preparation

From calcium carbide:

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$CaO + 3C \longrightarrow \underset{\substack{\text{Calcium} \\ \text{carbide}}}{CaC_2} + CO$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

From vicinal dihalides:

$$\underset{\substack{| \quad | \\ Br \quad Br}}{H_2C - \overset{\overset{\displaystyle H}{|}}{C} - H} + KOH \xrightarrow[\substack{- KBr \\ - H_2O}]{\text{alcohol}} \underset{\substack{H \quad\quad Br}}{\overset{\substack{H \quad\quad H}}{C = C}}$$

$$Na^+NH_2^- \Big\downarrow \substack{- NaBr \\ -NH_3}$$

$$CH \equiv CH$$
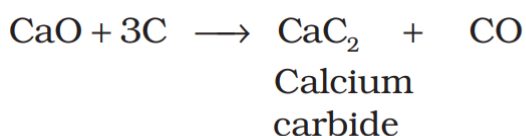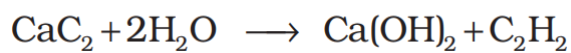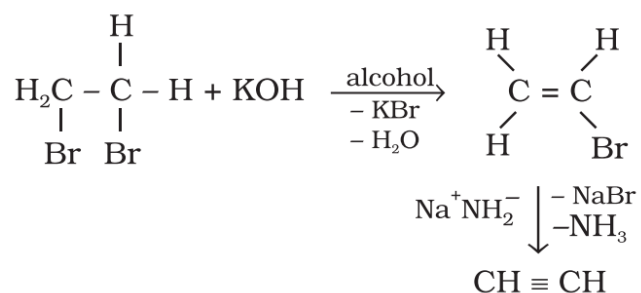
Chemical properties

Acidic character of alkyne:
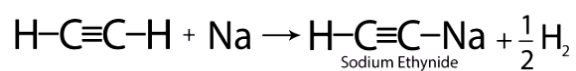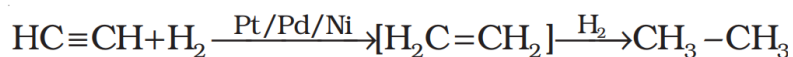
$$H-C\equiv C-H + Na \rightarrow H-\underset{\text{Sodium Ethynide}}{C\equiv C-Na} + \frac{1}{2}H_2$$

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:

$$H_3C-C\equiv C-CH_3 \xrightarrow[CCl_4]{Br_2} \underset{H_3C}{\overset{Br}{C}}=\underset{Br}{\overset{CH_3}{C}} \xrightarrow[CCl_4]{Br_2} H_3C-\underset{\substack{| \\ Br}}{\overset{\substack{Br \\ |}}{C}}-\underset{\substack{| \\ Br}}{\overset{\substack{Br \\ |}}{C}}-CH_3$$

Addition of hydrogen halides:

$$H-C\equiv C-H + H-Br \longrightarrow \underset{\text{Bromoethene}}{[CH_2 = CH - Br]} \longrightarrow \underset{\substack{| \\ CH_3}}{CHBr_2}$$

1,1-Dibromoethane

Addition of water:

$$CH_3-C\equiv CH + H-OH \xrightarrow[333K]{Hg^{2+}/H^+} CH_3-\underset{\underset{O-H}{|}}{C}=CH_2$$

Propyne

Isomerisation $\downarrow$

$$CH_3-\underset{\underset{O}{\parallel}}{C}-CH_3$$

Propanone
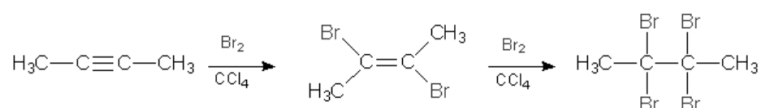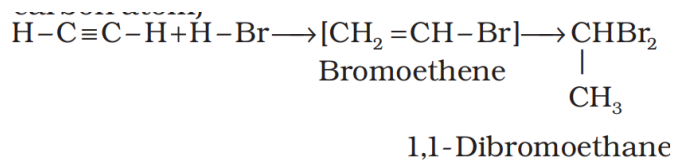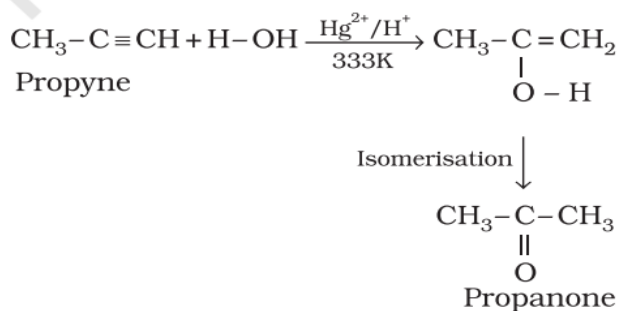
Cyclic polymerisation:
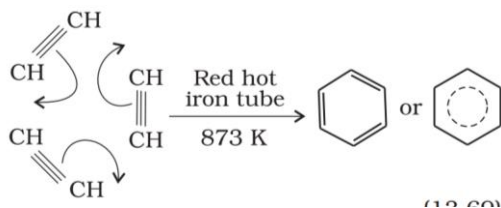
General reactions for Ethyne:
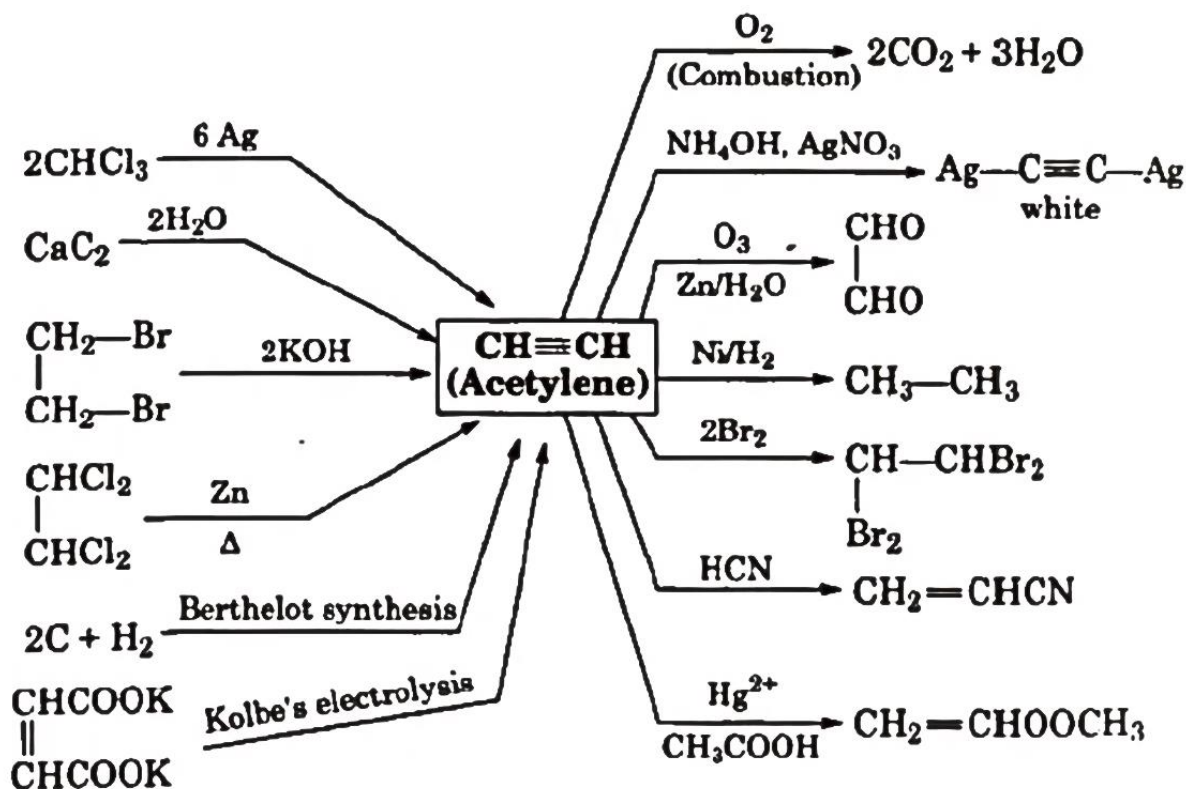
AROMATIC HYDROCARBON

These hydrocarbons are also known as 'arenes'.

Aromaticity : Aromaticity compounds possessing following characteristics –

(i) Planarity

(ii) Complete delocalisation of the π electrons in the ring

(iii) Presence of $(4n + 2)\,\pi$ electrons in the ring where n is an integer $(n = 0, 1, 2, \ldots)$. This is often referred to as Hückel Rule.

Preparation of Benzene

Decarboxylation of aromatic acids:
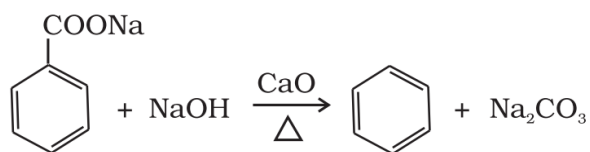
Reduction of phenol:
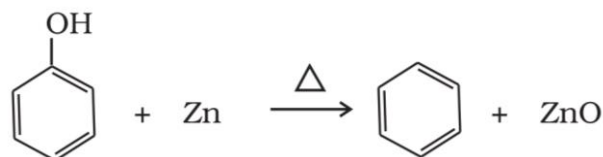
Chemical properties

Nitration:
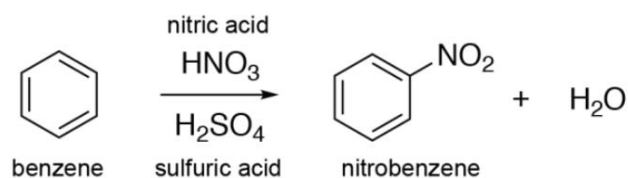
Halogenation:
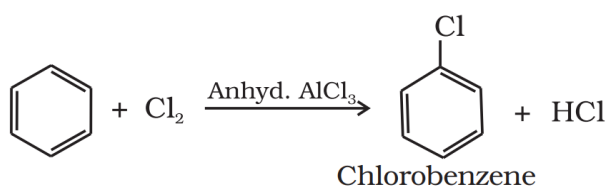
Sulphonation:
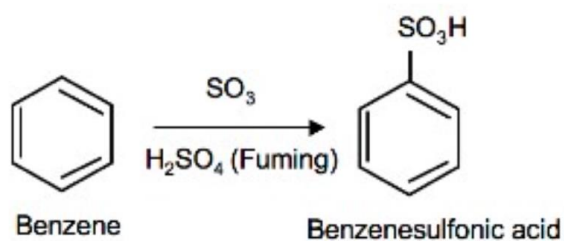
Friedel-Crafts alkylation reaction:

Benzene $+ C_2H_5Cl \xrightarrow{\text{Anhyd.AlCl}_3}$ Ethylbenzene (C_2H_5 substituted benzene) $+$ HCl

Friedel-Crafts acylation reaction:

Benzene $+ CH_3COCl$ (Acetylchloride) $\xrightarrow[\triangle]{\text{Anhyd. AlCl}_3}$ Acetophenone (COCH$_3$ substituted benzene) $+$ HCl

Addition reactions:

Benzene $+ 3H_2$ (Hydrogen) $\xrightarrow[150°C]{\text{Ni}}$ Cyclohexane

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.

Let's Practice:

1. Ozonolysis of acetylene gives-
    a) None of these   b) CHO-CHO
    c) CH3CHO   d) HCHO

2. Arrange the halogens F_2, Cl_2, Br_2, I_2, in order of their increasing reactivity with alkanes.
    a) $Br_2 < Cl_2 < F_2 < I_2$ b) $F_2 < Cl2 < Br_2 < I_2$ c) $Br_2 < I_2 < Cl_2 < F_2$
    d) $I_2 < Br_2 < Cl_2 < F_2$

3. Both ethane and methane can be obtained in a one-step reaction from_____.
    a) CH3OH   b) C2H5OH
    c) CH3Br   d) C2H5Br

4. Hydrocarbon which is liquid at room temperature is-
    a) butane   b) propane

c) ethane d) pentane

5. Phenol on heating with $NaNO_2$ and a few drops of conc. H_2SO_4 gives-

   a) p - Nitrosophenol b) m – Nitrosophenol

   c) o - Nitrophenol d) p – Nitrophenol

6. Which branched chain isomer of the hydrocarbon with molecular mass 72u gives only one isomer ofmonosubstituted alkyl halide?

   a) Tertiary butyl chloride b) Neohexane

   c) Neopentane d) Isohexane

7. An olefin on reductive ozonolysis gives only ethanal as the major product. Name the olefin.

   a) But-1-ene b) Propene

   c) Ethene d) But-2-ene

8. Photochemical fluorination is explosive while iodination is too slow to occur. The reason for this is:

   a) bond dissociation energy of I_2 is minimum.

   b) formation of CH_3 — F is most exothermic.

   c) formation of H — F is most exothermic while formation of HI is endothermic.

   d) F_2 has lower bond dissociation energy than Cl_2 and Br_2.

9. Isomerization of n-hexane on heating with anhydrous $AICI_3$ and HCl gas gives_.

   a) 2-methylpentane b) 3-methylpentane

   c) 2-methylhexane d) mixture of 2-methylpentane and 3-methylpentane

10. The IUPAC name of

is:CH_3
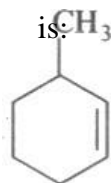
   a) 1-methylcyclohex-2-ene b) 1-methylcyclohex-5-ene

   c) 3-methylcyclohexene d) 6-methylcyclohexene

11. A dibromo derivative of an alkane reacts with sodium metal to form an alicyclic hydrocarbon. The derivative is _____.

   a) 2, 2-dibromobutane b) 1, 1-dibromopropane

   c) 1, 4-dibromobutane d) 1, 2-dibromoethane

12. The position of double bond in alkenes can be located by:

   a) Hydrogenation of oil **b) Ozonolysis**

   c) Photolysis d) Hydration

13. Some meta-directing substituents in aromatic substitution are given. Which one is most deactivating?

   a) $-C \equiv N$ b) $-SO_3H$

   c) -COOH **d) -NO$_2$**

14. The first fraction obtained during the fractionation of petroleum is:

   a) Gasoline b) Diesel Oil

   c) Hydrocarbon Gases d) Kerosene Oil

15. The catalyst used in Friedel – Crafts reaction is

   a) Aluminium Chloride **b) Anhydrous Aluminium Chloride**

   c) Ferric Chloride d) Copper

16. When acetylene is treated with HBr, the product is ————-

a) Methyl bromide

b) Ethylene bromide

c) Ethyl bromide

d) Ethylidene bromide

17. The dihedral angle in the staggered conformation of C_2H_6 is

a) 120^0

b) 60^0

c) 0^0

d) 90^0

18. Which one of the following is not an isomer of 3-Methylbut-1-yne?

a) Pent-1-yne

b) Buta-1,3-diene

c) Pent-2-yne

d) Penta-1,3-diene

19. Which of the following compounds will exhibit cis-trans isomerism?

a) Butanol

b) 2- Butyne

c) 2-Butenol

d) 2-Butene

20. The reaction, $CH_2= CH – CH_3 + HBr \rightarrow CH_3CHBr – CH_3$ is-

a) electrophilic substitution

b) free radical addition

c) nucleophilic addition

d) electrophilic addition.

21.Geometrical isomers differ in-

a) position of functional group

b) position of atoms

c) spatial arrangement of atoms

d) length of carbon chain

22. The compound that will react most readily with gaseous bromine has the formula

a) C_3H_6

b) C_2H_2

c) C_4H_{10}

d) C_2H_4

23. 2-Bromopentane is heated with potassium ethoxide in ethanol. The major product obtained is-

a) trans-2-pentene

b) 1-pentene

c) 2-ethoxy pentane

d) 2-cis-pentene.

24. Which is maximum stable?

a) 1-Butene

b) cis-2-Butene

c) trans-2-Butene

d) All have same stability.

25. A gas decolourised by KMno4 solution but gives no precipitate with ammoniacal cuprous chloride is-

a) Ethene

b) Propane

c) Propene

d) Methane

26. Addition reaction of hydrogen Bromide to the unsymmetrical alkene follows _____

a) anti markovnikov's rule

b) markovnikov's rule

c) kharish effect

d) peroxide effect

27. Which of the following is a Bayer's reagent?

a) The neutral solution of HCL

b) An alcoholic solution of sodium carbonate

c) An acidic solution of potassium hydroxide

d) An aqueous solution of potassium permanganate

28. What is the intermediate conformation between eclipsed and staggered?
    a) Staggered   **b) Skew**
    c) Eclipse   d) Newman
29. Which of the following statement is true regarding the reactivity order in order to form alkyl halides?
    a) Hydrogen iodide is less than that of hydrogen Bromide
    b) Hydrogen Bromide is less than that of HCL
    c) HCL is greater than that of hydrogen iodide
    d) Hydrogen Bromide is less than that of hydrogen iodide
30. Arrange the following in decreasing order of their boiling points.
    (A) n–butane (B) 2–methylbutane (C) n-pentane (D) 2,2–dimethylpropane
    a) A > B > C > D   b) B > C > D > A

    c) D > C > B > A   **d) C > B > D > A**

31. Which of the following conformation of n-butane is the most stable?
    a) eclipsed   b) gauche
    c) staggered   d) skew boat

32. The bond angle between H-C-C bonds in ethane is-
    a) 120°   b) 180°
    c) 109°   **d) 109.5°**

33. Alkanes undergo halogenation. It is an example of-
    a) nucleophilic substitution   b) elimination
    c) free-radical substitution   d) electrophilic substitution
34. Which of the following is the most volatile compound?
    a) n-pentane   b) Isobutane
    c) 2-methyl butane   **d) 2, 2-dimethyl propane**
35. Paraffin wax is-
    a) Saturated hydrocarbons   b) Unsaturated hydrocarbons
    c) Alcohol   d) Ester

Assertion-Reason type questions-
Note: select correct answer from the below options for question no 36 to 40.
    a) Both A and R are true and R is the correctexplanation of A
    b) Both A and R are true but R is not thecorrect explanation of A.
    c) A is true but R is false.
    d)   A is false but R is true.

36. **Assertion (A):** Alkylbenzene is not prepared by Friedel Crafts alkylation of benzene.

    Reason (R): Alkyl halides are less reactive than acyl halides.

37. **Assertion (A):** Addition of HBr on ⌇⌇ in presence of peroxide give ⌇Br as major

    product.

    Reason (R): Addition of HBr on alkene proceed by carbocation intermediate.

38. **Assertion (A):** Alkanes having more than three carbon atoms exhibit chain isomerism.

    Reason (R): All carbon atoms in alkanes are sp-hybridized.

39. **Assertion (A):** Addition of Br_2 to but-1-ene gives two optical isomers.

   Reason (R): The product contains one asymmetric carbon atom.

40. **Assertion (A):** The addition of one equivalent of HCl to 1,3-butadiene at 80°C gives

   3-chloro-1-butene as amajor product.
   Reason (R): 3-chloro-1-butene is a kinetically controlled product.

Some important questions

41. Write IUPAC name: $CH_3CH - C(CH_3)_2$.

Ans. 2-methylbutane

43. 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.

$$CH_2 = CH_2 \text{ (ethene)} + H_2 \xrightarrow{Pt/Pd/Ni} CH_3 - CH_3 \text{ (ethane)}$$
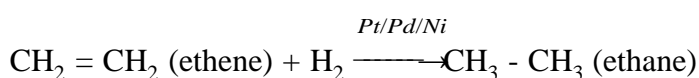
44. How is alkene produced by vicinal dihalide?

Ans. Alkene are produced from Vicinal dihalide by the process of dehalogenations. Vicinal dihalide on treatment with Zn metal lose amolecule of ZnX_2 to from an alkene.

$$CH_2Br-CH_2Br + Zn \rightarrow CH_2=CH_2 + ZnBr_2.$$
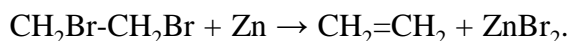
45. How will you distinguish between propene and propane?

Ans. Pass them through dilute cold $KMnO_4$ solution (purple) or Br_2 in CCl_4 solution (rud).

   Propene will decolourise both the solutions but propane does not react.

46. Suggest a route for the preparation of nitrobenzene starting from acetylene?

Ans.
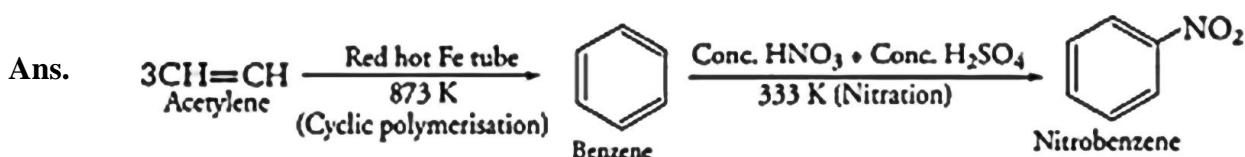
47. How will you distinguish between acetylene and ethylene?
Ans. Acetylene forms precipitate with ammoniacal silver nitrate solution, ethylene does not react with these reagents.

48. Arrange the following: HCl, HBr, Hl, HF in order of decreasing reactivity towards alkenes.

Ans. $HI > HBr > HCl > HF$

49. Which type of isomerism is exhibited by but-1-yne and but-2-yne?

Ans. Position isomerism.

50. How will you convert ethanoic acid into ethene?

Ans.
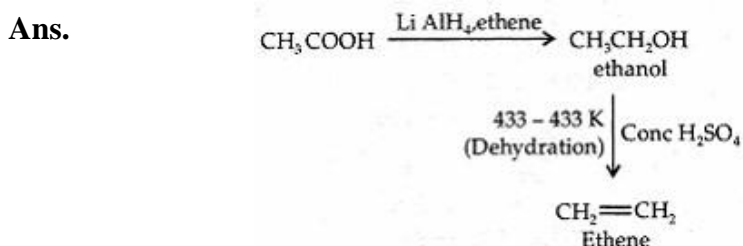
Two marks questions

51. State Kharasch effect.

Ans. Kharasch effect: In the presence of peroxides such as benzoyl peroxide, the addition of HBr to unsymmetrical alkenes occurs contrary to **Markovnikov's rule**. According to Kharasch effect, the negative part of the adding molecule gets attached to that carbon atom which possesses greater number of hydrogen atoms.

$$CH_3CH = CH_2 + HBr \xrightarrow[Peroxide]{} CH_3 - CH_2 - CH_2\text{-} Br$$
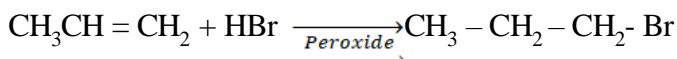
52. How will you convert benzene to iodobenzene? Give a chemical equation.

Ans.
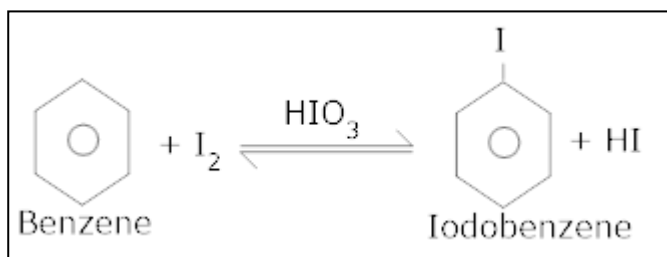
53. An unsaturated hydrocarbon **A** adds two molecules of H_2 and on reductive ozonolysis gives butane-1, 4-dial, ethanal, and propanone. Give the structure of **A**, write its IUPAC name, and explain the reactions involved.

Ans. Compound **A** on ozonolysis gives

$$CH_3 CHO + O = CH - CH_2 - CH_2 - CH=O + O = C (CH_3)_2$$
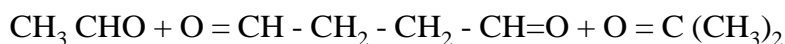
The structure of compound **A** is $CH_3 - CH = CH_2 - CH_2 - CH_2 - CH = C$ $(CH_3)_2$ IUPAC name: **2 -methyl octa 2,6 diene.**

54. The boiling point of hydrocarbons decreases with an increase in branching. Give reason.

Ans. The effective surface area of hydrocarbon reduces due to increase in branching and hence the strength of the Vander wall's forces decreases. Thus, less energy is required to separate the molecules of compound from its liquid surface and thereby leading to a decrease in the boiling point.

55. Which is more acidic: ethene or ethyne and why?

Ans. Ethyne is more acidic than ethene because it has 'sp' hybridised 'C' which is more electronegative.

57. What do you understated by Resonance energy?

Ans. The difference between the energy of the most stable contributing structure and the energy of the resonance hybrid is known as resonance energy. Example: The resonance energy of benzene is 147KJ/mole

58. Unsaturated compounds undergo addition reactions. Why?

Ans. Unsaturated hydrocarbon compounds undergo addition reactions because they contain carbon-carbon double or triple bonds. By addition reactions, these unstable π-bonds get broken and makes stable saturated hydrocarbons.

59. How will you distinguish between Ethene and benzene?

Ans. Ethene discharges bromine water colour and Baeyer's reagent colour. Benzene does not discharge bromine water colour and Baeyer's reagent colour.

60. What is Lindlar's catalyst? Give its use.

Ans. $Pb/BaSO_4$ is known as Lindlar's catalyst. It is used in the conversion of alkynes to alkenes with the help of H_2.

Three marks questions

61. Define substitution reactions. Why do benzene undergo substitution reactions even though they contain doublebonds?

Ans. Substitution reactions are those reactions in which an atom or groups of atoms directly attached to carbon in the substrate molecule is replaced by another atom or group of atoms, for example

Methylchloride
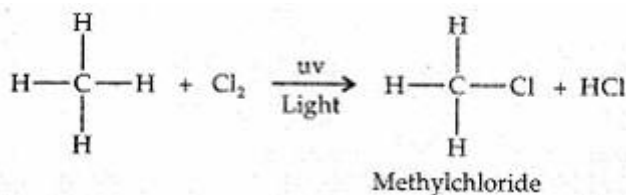
A hydrogen atom of the methane molecule is replaced by chlorine atom. Benzene undergoes electrophilic substitution reactions because benzene ring has delocalized electrons is an electron-rich system. It is attached by electrophiles giving substitution products.

62. N-pentane has a higher boiling point than neopentane but the melting point of neopentane is higher than that of n-pentane.

Ans. The boiling point of hydrocarbons depends upon extent of van der Waal's forces. Lesser the branching, greater the surface area and greater the van der Waal's forces. Because of the presence of branches in neo-pentane the surface area and van der Waal's forces of attraction are very weak in neopentane than in n-pentane. Therefore the b.p of neopentane is lower than that of n-pentane.

But, melting point depends upon the packing of the molecules in the crystal lattice. Since neopentane are more symmetrical than n-pentane therefore, it packs much more closely in the crystal lattice than n-pentane and hence neopentane has much higher m.p than n-pentane.

63. Write structures of different chain isomers of alkanes corresponding to the molecular formula C_6H_{14}. Also, write their IUPAC names.

Ans. The isomeric structure and IUPAC name is as follows:

i. $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$ (n-Hexane)

ii.
$$CH_3 - CH - CH_2 - CH_2 - CH_3 \quad (\text{2-Methylpentane})$$
$$| $$
$$CH_3$$

iii.
$$CH_3 - CH_2 - CH - CH_2 - CH_3 \quad (\text{3-Methylpentane})$$
$$|$$
$$CH_3$$

iv. $CH_3 - CH - CH - CH_3$ (2,3 - Dimethylbutane)
$$\qquad |\qquad |$$
$$\qquad CH_3 \quad CH_3$$

v.
$$CH_3 \text{--}$$
$$|$$
$$CH_3 - C - CH_2 - CH_3 \quad (\text{2,2 - Dimethylbutane})$$
$$|$$
$$CH_3$$
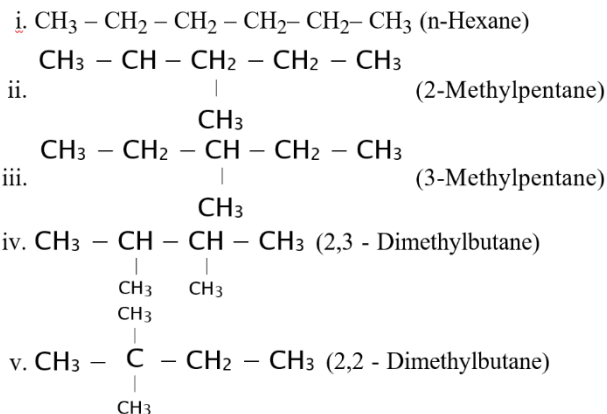
64. In the presence of peroxide, addition of HBr to propene takes place according to Anti-Markovnikov's rule butperoxide effect is not seen in the case of HCl and HI. Explain.

Ans. The mechanism of addition of HX in the presence of Peroxide is not observed in addition of HCl and HI. This is due to the fact that the H—Cl bond being stronger (430.5 kJ mol^{-1}) than H—Br bond (363.7 kJ mol^{-1}) is not cleaved symmetrically by the free radical and in case of H—I bond is weaker (296.8 kJ mol^{-1}) and iodine free radicals have greater tendency to combine to form iodine molecules instead of adding to the double bond.

65. Explain Wurtz reaction with an example.

Ans.

Wurtz reaction – The alkyl halides of lower alkanes are treated with sodium metal in the presence of dry ether. This reaction is used for the preparation of higher alkanes containing even number of carbon atoms.

$$RX + 2Na + XR^1 \xrightarrow{\text{ether}} R - R^1 + 2Na - X$$
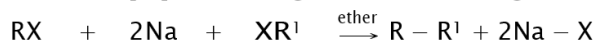
For example: Methyl iodide on treatment with sodium metal in the presence of dry ether gives ethane.

$$CH_3I + 2Na + CH_3I \xrightarrow{\text{ether}} CH_3 - CH_3 + 2NaI$$
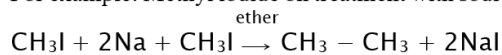
Note: Dry Ether is used as catalyst because Sodium reacts vigorously with moisture.

66. Why do alkenes prefer to undergo electrophilic addition reaction while arenes prefer electrophilic substitutionreactions? Explain.

Ans. Alkenes are rich source of loosely held pi(π) electrons, due to which they show electrophilic addition reaction. For example, HBrprovides an electrophile H$^+$ which attacks the double bond to form carbocation as shown below:

(a) less stable primary carbocation (b) more stable secondary carbocation
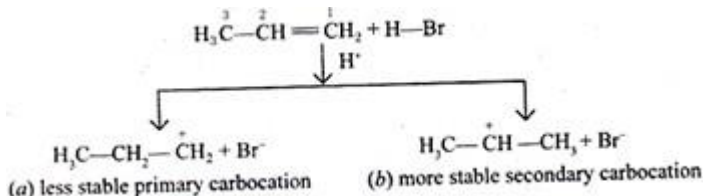
On the other hand, arenes have delocalized $(4n+2)\pi$ electrons which gives to the great stability of the ring systems by resonance. Therefore, electrophilic substitution take place.

The arenium ion gets stablished by resonance:

sigma complex (arenium ion)

134
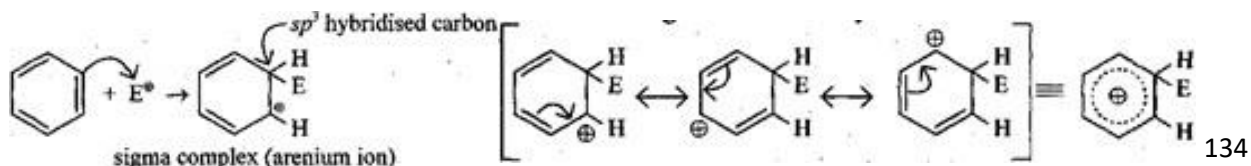
67. Account for the following: a. Gabriel phthalimide synthesis is not preferred for preparing aromatic primary amines. b. On reaction with benzene sulphonyl chloride, primary amine yields product soluble in alkali whereas secondary amine yields product insoluble in alkali.

Ans. CH_3, group is electron-donating while- NO_2 group is electron-withdrawing. Therefore, maximum electron density will be in toluene, followed by benzene and least in m-dinitrobenzene. Therefore, the ease of nitration decreases in the order: toluene > benzene > m-dinitrobenzene.

68. Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?
Ans. Due to the presence of an electron cloud containing 6 -electrons above and below the plane of the ring, benzene is a rich source of electrons. Consequently, it attracts the electrophiles (electron - deficient) reagents towards it and repels nucleophiles (electron rich) reagents. As a result, benzene undergoes electrophilic substitution reactions easily and nucleophilic substitutions with difficulty.

69. Draw the cis- and trans-structures for hex-2-ene. Which isomer will have higher b.p and why?

Ans. The structures of cis- and trans-isomer of hex-2-ene are:

cis–Hex–2–ene
(Higher dipole moment, higher b.p.)

trans–Hex–2–ene
(Lower dipole moment, lower b.p.)
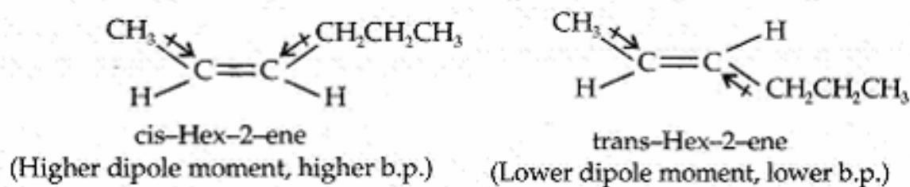
The boiling point of a molecule depends upon dipole dipole interactions. Since cis-isomer has higher dipole moment, therefore, it has higher boiling point.

70. Complete the following reactions:

Ans.

135
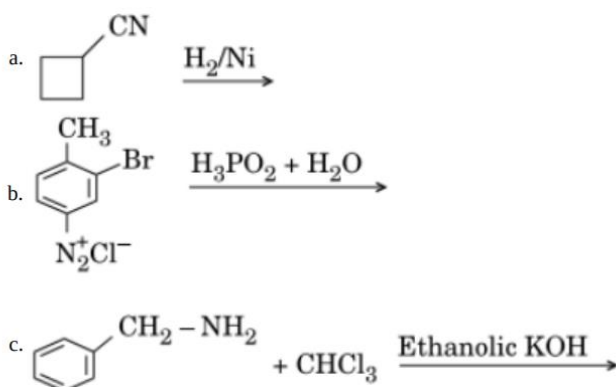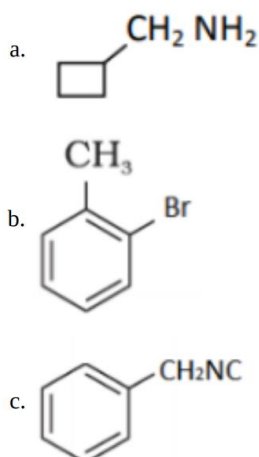
71. Read the text carefully and answer the questions:

In staggered conformation, since the electron clouds of carbon-hydrogen bonds are as far apart as possible, so ithas minimum repulsive forces, minimum energy and maximum stability.

On the other hand, eclipsed conformation has maximum repulsive forces, maximum energy and minimum stability because in it, the electron clouds of carbon hydrogen bonds are too close to each other.

The angle of rotation about C-C bond is called the **dihedral angle** or **torsional angle** and is maximum, i.e. 180° in staggered conformation and minimum (0°) in eclipsed conformation. Thus, torsional strain is minimum in staggered conformation and maximum in eclipsed form. The two forms differ in energy by $12.5kJ \, mol^{-1}$. This energy barrier is so small that small thermal or kineticenergy is sufficient to overcome it by intermolecular collisions.

(i) The most stable conformation of ethane.

  a) **staggered**   b) can't say

  c) eclipsed   d) Both are equally stable

(ii) The reason of more stability of chair form of cyclohexane than boat form is-

  a) free of angle strain

  b) Neither free of torsional train nor freeof angle strain

  c) Both free of torsional strain and free ofangle strain

  d) free of torsional strain

(iii) The most stable conformation of ethylene glycol is-

  a) eclipsed   b) all are equally stable

  c) **gauches**   d) staggered

(iv) Which is more stable among conformers butane?

  a) Fully eclipsed   b) Ecllipsed

  c) **Anti**   d) Skew

72. Read the text carefully and answer the questions:

Alkenes generally undergo electrophilic addition reactions because of the presence of a double bond (a strong σ and a weaker π-bond), π electrons of which being loosely held are easily polarisable. These reactions involvecleavage of a π-bond and formation of two new σ-bonds.

In polar solvents, addition proceed by ionic mechanism (at low temperature), whereas in the presence of light or non-polar solvents, the addition occurs by free radical mechanism (at high temperature). Apart from addition reactions alkenes also participate in the oxidation, ozonolysis and polymerisation reaction.

 (i) Assertion (A): 1-butene on reaction with HBr in the presence of a peroxide, produces bromobutane.

  Reason (R): It involves the formation of a primary radical.

  a) Both A and R are true and R is thecorrect explanation of A.

  b) Both A and R are true but R is not thecorrect explanation of A.

  c) A is true but R is false.

  d) A is false but R is true.

(ii) **Assertion (A):** Propene reacts with HI in the presence of peroxide to give 1-iodopropane.

Reason (R): 1^O free radical is less stable than 2^O free radical.

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

(iii) **Assertion (A):** Propene reacts with HBr to give isopropyl bromide.

Reason (A): Addition of hydrogen halide to alkenes follows Markownikoff's rule.

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

(iv) **Assertion (A):** Ethene on treating with Br_2 in presence of NaCl forms CH_2ClCH_2Br and CH_2BrCH_2Br.

Reason (R): This addition involves the formation of free radicals.

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

73. Read the text carefully and answer the questions:

Benzene (also called cyclohexatriene) is an organic chemical compound with the molecular formula C_6H_6. The benzene molecule is composed of six carbon atoms joined in a planar ring with one hydrogen atom attached to each. Because it contains only carbon and hydrogen atoms, benzene is classed as a hydrocarbon.

Benzene is a natural constituent of crude oil and is one of the elementary petrochemicals. Due to the cyclic continuous pi bonds between the carbon atoms, benzene is classed as an aromatic hydrocarbon. It is sometimes abbreviated PH. Benzene is a colorless and highly flammable liquid with a sweet smell and is partially responsible for the aroma around petrol (gasoline) stations. It is used primarily as a precursor to the manufacture of chemicals with more complex structures, such as ethylbenzene and cumene, of which billions of kilogramsare produced annually. Although a major industrial chemical, benzene finds limited use in consumer itemsbecause of its toxicity.
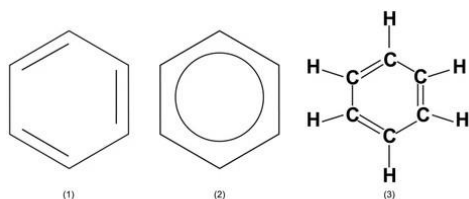
chemical structure of benzene

(i)   What happens when benzene is treated with acetyl chloride in the presence of $AlCl_3$?

Ans.   Acetophenone is formed.

(ii)   Benzene undergoes electrophilic substitution reactions easily and nucleophilic substitutions with difficulty. Why?

**Ans.** The orbital structure of benzene shows that the π-electrons cloud lying above and below the benzene ring is loosely held and is thus available to the π-electron seeking reagents i.e., electrophiles. Therefore, benzene undergoes electrophilic reactions readily and nucleophilic substitution reactions with difficulty.

(iii)   How would you convert Ethyne into benzene?

Ans. Ethyne is converted into benzene by passing its vapours through red hot tube at 873 K.

(iv)   How would you convert Ethene into benzene?
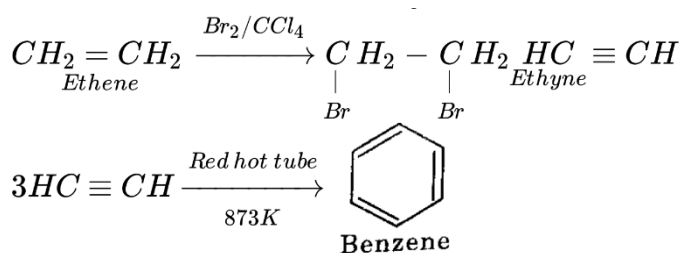
Ans.   Ethene is first converted into ethyne and then to benzene as:

$$CH_2 = CH_2 \xrightarrow{Br_2/CCl_4} \underset{Br}{C}H_2 - \underset{Br}{C}H_2 \underset{Ethyne}{HC} \equiv CH$$

$$3HC \equiv CH \xrightarrow[873K]{Red\ hot\ tube} \text{Benzene}$$

Five marks questions:

74. Assign structures for the following:

i. An alkyne (X) has a molecular formula C_5H_8. It reacts neither with sodamide nor with ammoniacal cuprous chloride.

ii. A hydrocarbon 'Y' decolourises bromine water. On ozonolysis it gives 3-methyl butanal and formaldehyde. Give the name of the compound.

iii. A hydrocarbon (Z) has molecular formula C_8H_{10}. It does not decolourise bromine water and is oxidised to benzoic acid on heating with $K_2Cr_2O_7$. It can also have three other isomers A, B and C. Write the structures of Z, A, B and C.

Ans. i. Since the given alkyne (X) does not react with sodamide or ammoniacal cuprous chloride, thus, in Alkyne C_5H_8, the triple bond cannot be terminal. Pent-2-yne

ii. Hydrocarbon 'Y' is alkene (unsaturated hydrocarbon) because it decolourises bromine water. From the products of ozonolysis, the structure of alkene can be predicted.
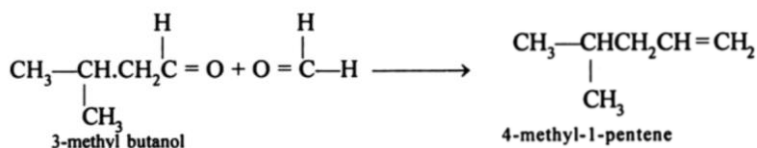
iii. The given compound (Z) is arene (Ethylbenzene) as it does not decolourise bromine water.
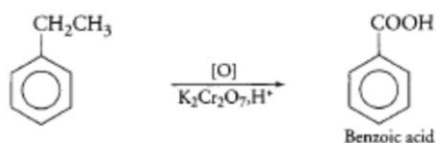
The other three isomers of Ethylbenzene are:
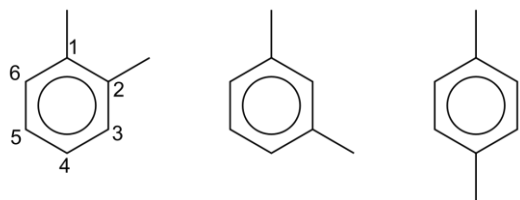
1,2-dimethylbenzene 1,3-dimethylbenzene 1,4-dimethylbenzene
  (*ortho*-xylene)   (*meta*-xylene)   (*para*-xylene)

75. i. Draw cis and trans isomers of hex-2-ene. Which isomer will have higher boiling point and why?

ii. Classify the following as Z or E   isomers:

a.

b.

c.

Ans.

i.

cis- Hex-2-ene   *trans*-Hex-2-ene
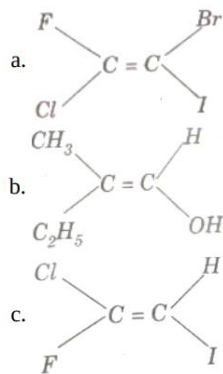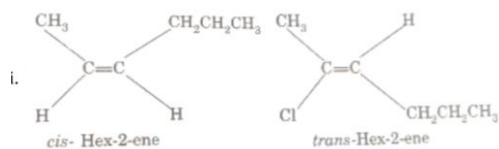
The cis form will have a higher boiling point due to the more polar nature of the molecular leading to strong intermolecular dipole-dipole interactions. As a result of stronger intermolecular interactions, it requires more energy to separate the molecules.

ii.

a. Z

b. Z

c. E

Interconversion of Hydrocarbons

$$H_2/Ni ; 475\ K$$

CH_3I
Methyl iodide

$\xrightarrow[\text{Wurtz reaction}]{Na/Ether}$

CH_3CH_3
Ethane

$\xrightleftharpoons[Zn—Cu/Alc.]{I_2/HIO_3}$

CH_3CH_3I
Ethyl iodide

$\xrightleftharpoons[HI]{KOH/alc.}$

$CH_2 = CH_2$
Ethene

I_2/HIO_3 ↑

CH_4
Methane

KOH aq. / P/I_2

H_2SO_4/H_2O / H_2SO_4, 445 K

Zn, Δ / Br_2/CCl_4

NaOH / CaO

CH_3CH_2OH
Ethyl alcohol

$BrCH_2—CH_2Br$
Ethylene dibromide

Cu/575 K / $LiAlH_4$

$\xrightarrow{\text{alc. KOH}}$

$CH_2 = CH—Br$

$\xrightarrow{NaNH_2}$

CH_3COONa
Sodium
acetate

CH_3COOH
Ethanoic
acid

$\xleftarrow[K_2Cr_2O_7/H^+]{[O]}$

CH_3CHO
Ethanal

$\xleftarrow[Hg^{2+}, H_2SO_4]{H_2O}$

$CH \equiv CH$
Ethyne

NaOH

$\xrightarrow{NaOH/CaO}{\Delta}$ ...

⬡ $\xleftarrow[\Delta]{NaOH/CaO}$ ⬡—COONa $\xleftarrow{NaOH}$ ⬡—COOH $\xleftarrow{KMnO_4/H^+}$ ⬡—CH_3 $\xleftarrow[AlCl_3]{CH_3Cl}$ ⬡

Iron tube,
873 K

Max.marks:70
                                                                 Max.time:3hrs

Read the following instructions carefully.

There are 35 questions in this question paper with internal choice.

SECTION A consists of 18 multiple choice questions carrying 1 mark each.

SECTION B consists of 7 very short answer questions carrying 2 marks each.

SECTION C consists of 5 short answer questions carrying 3 marks each.

SECTION D consists of 2 case based questions carrying 4 marks each.

SECTION E consists of 3 long answer questions carrying 5 marks each.

All questions are compulsory.

Use of log tables and calculators is not allowed.

SECTION A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark .There is no internal choice in this section.

1. The empirical formula and molecular mass of a compound are CH_2O and 180 g, respectively. The molecular formula of the compound is -

    A.$C_9H_{18}O_9$ **B**.CH_2O C. $C_6H_{12}O_6$ D. $C_2H_4O_2$

2. Which of the following parameters is temperature dependent?

   A. Molarity   B. Mole fraction. C. Weight percentage   D. Molality

3.Which of the following statements does not form a part of Bohr's model of hydrogen atom?

   A .Energy of the electrons in the orbit is quantized.

   B .The electron in the orbit nearest to the nucleus has the lowest energy.

   C. Electrons revolve in different orbits around the nucleus.

   D .The position and velocity of the electrons in the orbit cannot be determined simultaneously.

4. In photoelectric effect, the kinetic energy of photoelectrons increases linearly with the

   A. Wavelength of incident light   B. Frequency of incident light

   C. Velocity of incident light   D. Atomic mass of an element

5 . BCl_3 is a planar molecule whereas NCl_3 is pyramidal because:

   A. nitrogen atom is smaller than boron atom

   B. BCl_3 has no lone pair of electrons whereas NCl_3 has a lone pair of electrons

   C. N-Cl bond is more covalent than B-Cl bond

   D. B-Cl bond is more polar than N-Cl bond

6. For the following reaction,

 $H_2(g)+I_2(g)\rightleftharpoons 2HI(g)$ at 250°C,
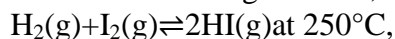
The effect on the state of equilibrium on doubling the volume of the system will be:

   A. Shift to the reactant side   B. Shift to the product side

   C. No effect on the state of equilibrium   D. Liquefaction of HI

7. When equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together (Ksp (cupric iodate) = 7.4×10^{-8}), from the following, the correct observation would be

   A. Precipitation will occur

   B. Precipitation will not occur

   C. There are 50 % chances of precipitation

D. Data is not sufficient to make any conclusive observation

8. When a buffer solution of CH_3COOH and CH_3COONa is diluted with water:
   A. CH_3COO^- ion concentration increases   B. $[H^+]$ ion concentration increases
   C. OH^- ion concentration increases   D. H^+ion concentration does not change

9. Select the compound in which chlorine shows oxidation state is: + 7:
   A. $HClO_4$ B. $HClO_3$ C. $HClO_2$ D. $HClO$

10. The pair of structures given below represents
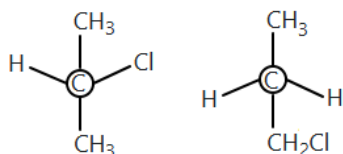
   A. Enantiomers   B. Conformers   C. Position isomers   D. None of the above

11. The most suitable reagent for the following conversion is-

cis-but-2-ene

   A. $Hg2+/H+,H_2O$ B. Na/lig NH_3 C. H_2,Pd/C,quinoline   D. Zn/HCl

12. The most suitable method used for the separation of 1:1 mixture of ortho and para-nitro phenol is:
   A. Chromatography   B. Crystallization   C. Steam distillation   D. Sublimation

13. The reactants used in Friedel-Craft`s alkylation are-
   A. $C_6H_6+NH_2$ B. $C_6H_6+CH_4$ C. $C_6H_6+CH_3Cl$ D. $C_6H_6+CH_3COCl$

14. The reaction of toluene with Cl2 in presence of FeCl3 gives 'X' and the reaction in presence of light gives 'Y'. 'X' and 'Y' are respectively-
   A. X= Benzal chloride, Y= o-chlorotoluene
   B. X= m-chlorotoluene, Y= p-chlorotoluene
   C. X= o and p-chlorotoluene, Y= trichloromethyl benzene
   D. X= Benzyl chloride, Y= m-chlorotoluene

The questions given below consist of an 'Assertion' (A) and the 'Reason' (R). Use the following keys for the appropriate answer:
   (A) .If both (A) and (R) are correct and (R) is the correct reason for (A).
   (B) .If both (A) and (R) are correct but (R) is not the correct explanation for (A).
   (C). If (A) is correct but (R) is incorrect.
   (D). If(A) is incorrect but (R) is correct.

15. **Assertion (A)** :In Rutherford's gold foil experiment, very few a-particles are deflected back.
   Reason (R) :Nucleus present inside the atom is heavy.   (A)
   (A) If both (A) and (R) are correct and (R) is the correct reason for (A).
   (B) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
   (C) If (A) is correct but (R) is incorrect.
   (D). If(A) is incorrect but (R) is correct.

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

Reason (R) The change in free energy is related to the change in enthalpy and change in entropy. The change in entropy for a process must always be positive if it is spontaneous.   (C)
  (A). If both (A) and (R) are correct and (R) is the correct reason for (A).
  (B). If both (A) and (R) are correct but (R) is not the correct explanation for (A).
  (C) .If (A) is correct but (R) is incorrect.
  (D). If (A) is incorrect but (R) is correct.

17. **Assertion (A)** : Energy of resonance hybrid is equal to the average of energies of all canonical forms.
Reason (R) : Resonance hybrid cannot be presented by a single structure.
  (A) Both A and R are correct and R is the correct explanation of A.
  (B) Both A and R are correct but R is not the correct explanation of A.
  (C) Both A and R are not correct.
  (D) A is not correct but R is correct.

18. **Assertion (A)** : Nitration of benzene with nitric acid requires the use of concentrated sulphuric acid.
Reason (R) : The mixture of concentrated sulphuric acid and concentrated nitric acid produces the electrophile, NO_2^+
  (A) Both A and R are correct and R is the correct explanation of A.
  (B Both A and R are correct but R is not the correct explanation of A.
  (C) Both A and R are not correct.
  (D) A is not correct but R is correct

SECTION B

19) What is the number of photons of light with a wavelength of 4000 pm that provide 1 J of energy?
20) Define the following terms: i. Molarity   ii. Limitng reagent
21) Ionization enthalpy and atomic radius are closely related properties. Analyze the following graph :
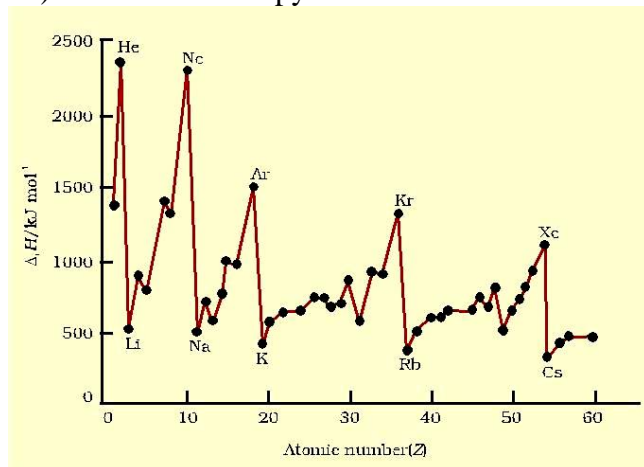
What conclusion can you derive from the graph regarding the first ionization enthalpies of alkali metals and noble gases? Justify your answer.
22. What is mean by bond order? Calculate the bond order of O_2 molecule
   OR
Discuss the shape of the following molecules using the VSEPR model:
 $SiCl_4$, AsF_5, ClF3, NH_3

23) Define entropy. predict whether entropy change in the following processes would be positive or negative.
i. $N_2O_3(g) \rightarrow N_2O(g) + O_2(g)$
ii. $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
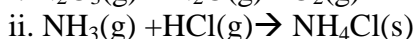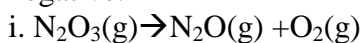
24) What is meant by the conjugate acid-base pair? Find the conjugate acid and base of NH_3

25) What is ozonolysis? Write the names of the products obtained when 2-Methyl propene undergoes ozonolysis?

   OR

a) Complete the following chemical equations:

   i) $CH_3CH_2Br + 2Na + BrCH_2CH_3 \xrightarrow{dry\ ether} ...$

   ii) $CH_3CH_2I \xrightarrow[\Delta]{alc.\ KOH} ......$
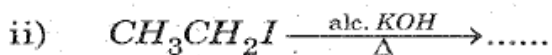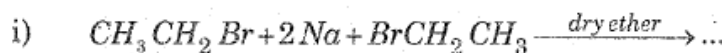
SECTION-C

26) An inorganic salt gave the following percentage composition-Na $=29.11$, S $= 40.51$ and O $=30.38$ .Calculate the empirical formula of the salt.(At .mass of Na=23,S=32 and O=16)

27) Explain the following with proper reasons:
i. Halogens have very high negative electron gain enthalpies.
ii. Mg^{2+} ion is smaller than O^{2-}ion although both have the same electronic configuration.
iii. Electron gain enthalpy of fluorine is less negative than that of chlorine.

28) i) Define the pH of the solution. The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.
ii)Write the expression for equilibrium constant, Kc for the reaction
   $4\ NH_3(g) + 5\ O_2(g) \rightleftharpoons 4\ NO(g) + 6\ H_2O(l)$
                  OR
a) State Le-Chatlier's principle.
b) What is the effect of:
(i) addition of H_2 (ii) addition of CH_3OH
(iii) removal of CO (iv) removal of CH_3OH
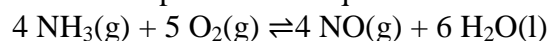
On the equilibrium $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$
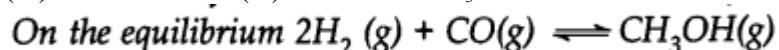
29. Balance the following redox reactions by ion – electron method :
   $Cr_2O_7^{2-}(aq) + SO_2(g) \longrightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$ **(in acidic solution)**
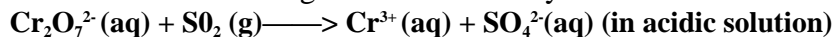
30. In the estimation of sulphur by carius method,0.468 gof an organic sulphur compound gave 0.668 g of barium sulphate.find the percentage of sulphur in the given compound.
                  OR
0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in carius estimation.calculate the percentage of chlorine present in the compound.

SECTION D

31) When anions and cations approach each other, the valence shell of anions are pulled towards cation nucleus and thus, shape of anion is deformed. The phenomenon of deformation of anion by a cation is known as polarization and the ability of the cation to polarize the anion is called as polarizing power of cation. Due to polarization, sharing of electrons occurs between two ions to some extent and the bond shows some covalent character. The magnitude of polarization depends upon a number of factors. These factors were suggested by Pajan and are known as Fajan's rules.
i. Greater is the polarization in a molecule, more is 0 covalent character.
ii. As the charge on cation increases, its tendency to polarize the anion increases.
iii. s the size of the cation decreases or size of the anion increases, the polarization increases.
iv.The cations with 18 electrons in the outermost shell bring greater polarization of the anion than those with inert gas configuration even both the cations have same size and same charge.

1. Considering $BeCl_2$, $MgCl_2$, $CaCl_2$ and $BaCl_2$, predict which of the following statements is true?
A. $BeCl_2$ is least ionic out' of the given chlorides
B. Covalent character increases as the atomic number of the metal atom increases

C. BeCl2 has the highest melting point among the given chlorides

D. All are highly ionic compounds

2. In which of the halides, there is maximum polarization?

A. AlF_3 B. $AlCl_3$ C. $AlBr_3$ D. AlI_3

3. Which is most covalent in nature?

A. NaCl   B. $AlCl_3$ C. $MgCl_2$ D. $CaCl_2$

4. Non-aqueous solvent like ether is added to the mixture of LiCl, NaCl and KCI. Which will be extracted into ether?

A. NaCI   B. LiCI   C. KCI   D. None

32. Dual nature of matter was proposed by de Broglie in 1923, it was experimentally verified by Davisson and Germer by diffraction experiment. Wave character of matter has significance only for microscopic particles. de Broglie wavelength or wavelength of matter wave can be calculated using the following relation:

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

where, 'm' and v' are the mass and velocity of the particle. de Broglie hypothesis suggested that electron. Waves were being diffracted by the target, much as X-rays are. Diffracted by planes of atoms in the crystals.

Answer the following questions:

1. Planck's constant has same dimension as that of:

A. work   B. energy   C. power   D. angular momentum

2. Wave nature of electrons is shown by:

A. photoelectric effect   B. Compton effect   C. diffraction experiment   D. Stark effect

3. de 'Broglie equation is obtained by combination of which of the following theories?

A. Planck's quantum theory   B. Einstein's theory of mass-energy equivalence

C. Theory of interference   D. Theory of diffraction'

4. Which among the following is not used to calculate the de Broglie wavelength?

(a) $\lambda = \frac{c}{v}$ (b) $\lambda = \frac{h}{mv}$

(c) $\lambda = \frac{h}{\sqrt{2Em}}$ (d) $\lambda = \frac{h}{\sqrt{2qVm}}$

SECTION –E

33)

i. Give the criteria for spontaneity of a process in terms of free energy change (ΔG).

ii. Exothermic reactions associated with a decrease in entropy are spontaneous at lower temperatures. Justify on the basis of Gibbs equation.

iii. For the reaction $2 A(g) + B(g) \rightarrow 2D(g)$ $\Delta U^0 = -10.5$ kJ and $\Delta S^0 = -44.1$ JK–1 . Calculate ΔG^0 for the reaction, and predict whether the reaction may occur spontaneously.

OR

a. For a reaction both ΔH and ΔS are negative. Under what conditions does the reaction occur spontaneously?

b. Define- Lattice enthalpy

c.

Calculate the enthalpy change for the process

$$CCl_4(g) \longrightarrow C(g) + 4\ Cl(g)$$
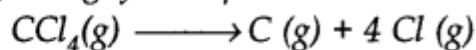
and calculate bond enthalpy of $C - Cl$ *in* $CCl_4(g)$

Given: $\Delta_{vap} H^{\ominus} (CCl_4) = 30.5\ kJ\ mol^{-1}; \quad \Delta_f H^{\ominus}(CCl_4) = -135.5\ kJ\ mol^{-1}$

                 $\Delta_a H^{\ominus} (C) = 715.0\ kJ\ mol^{-1}$ *where* $\Delta_a H^{\ominus}$ *is enthalpy of atomisation*

                 $\Delta_a H^{\ominus} (Cl_2) = 242\ kJ\ mol^{-1}$.

34. i. Explain the terms Inductive and Electromeric effects. Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids? $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

ii. Explain why alkyl groups act as electron donors when attached to a π system.

iii. Give condensed and bond line structural formula of 2-Hydroxy-1,2,3-propanetricarboxylic acid

35) Explain the following with suitable examples:

i. Decarboxylation   ii. Aromatization   iii. Kharash effect

 iv. Sulphonation   v. Friedel-Craft's Acylation reaction

OR

What happens when?
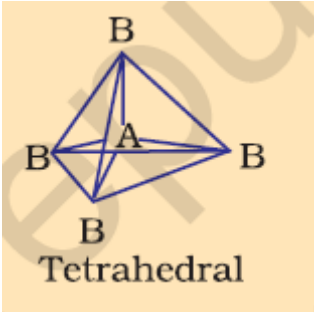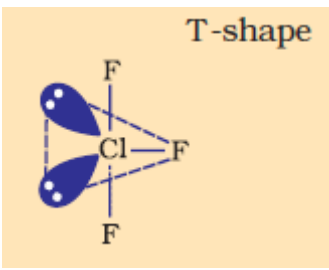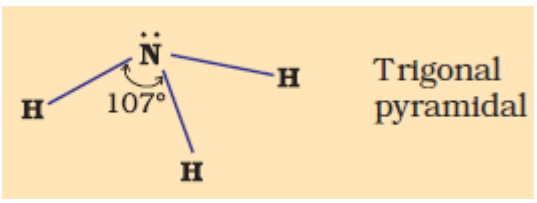
a. The vapours of Phenol are passed over heated zinc dust.

b. Ethyne (acetylene) on passing through red hot iron tube at 873K.

c. n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas

d. Benzene on treatment with excess of chlorine in the presence of anhydrous $AlCl_3$ in dark

e. Propene is treated with HBr

SECTION A

Q.No	Answer	Marks
1	A.$C_6H_{12}O_6$	1
2	A-Molarity	1
3	D-The position and velocity of the electrons in the orbitcannot be determined simultaneously.	1
4	A-Frequency of incident light	1
5	B-BCl_3 has no lone pair of electrons whereas NCl_3 has a lone pair of electrons	1
6	A-No effect on the state of equilibrium	1
7	A-Precipitation will occur	1
8	D- H^+ion concentration does not change	1
9	B- $HClO_3$	1
10	A-Position isomers	1
11	A-H2,Pd/C,quinoline	1
12	A-Steam distillation	1
13	A-$C_6H_6+CH_3Cl$	1
14	C-X= o and p-chlorotoluene, Y= trichloromethyl benzene	1
15	A-If both (A) and (R) are correct and (R) is the correct reason for (A).	1
16	C- If (A) is correct but (R) is incorrect.	1
17	D-A is not correct but R is correct.	1
18	A-Both A and R are correct and R is the correct explanation of A.	1
	SECTION B	
19	Energy (En) of 'n' photons = nhν $$n=\frac{E}{h\nu}=\frac{E\lambda}{hc}$$ λ = wavelength of light = 4000 pm = 4000 $\times 10^{-12}$ m c = velocity of light in vacuum = 3×10^8 m/s h = Planck's constant = 6.626×10^{-34}Js Substituting the values in the given expression of n: $$n =\frac{E\lambda}{hc} = \frac{1 J \ X \ 4000 \times 10^{-12} \ m}{6.626 \times 10^{-34} Js \ X \ 3 \times 10^8 \ m/s}$$ $$n =2.012 \times 10^{16}$$	1/5 1/5
20	i.M*olarity:*it can be defined as the number of moles of his solute present in one litre of solution . ii. Limitng reagent:The limiting reagent in a chemical reaction is a reactant that is totally consumed when the chemical reaction is completed. The amount of product formed is limited by this reagent, since the reaction cannot continue without it.	1 1
21	Alkali metals have very low ionization enthalpy because the outer electron if highly shielded from the nucleus by inner completely orbitals.	1

	Noble gases have very high ionization enthapies because of completely filled shell.	1
22	bond order: the number of bonds between two atoms in a molecule of an element or compound.	1
	Determining the electronic configuration of O2 $[\sigma(1s)]^2[\sigma*(1s)]^2[\sigma(2s)]^2[\sigma*(2s)]^2[\sigma(2pz)]^2[\pi(2px)]^2[\pi(2py)]^2[\pi*(2px)]^1[\pi*(2py)]^1$ The number of bonding electrons = 10 The number of anti-bonding electrons = 6	1/5
	Step 3: Calculating the bond order of O2 Bond order = $\dfrac{\text{Number of electrons in bonding} - \text{Number of electrons in antibonding}}{2}$ Bond order = $\dfrac{10-6}{2}$ Bond order = 2 Hence, the bond order for O2 is 2. OR Tetrahedral SiCl4 AsF5 triagonal bipyramidal T-shape ClF3 NH₃ Trigonal pyramidal	1/5
23	a) Entropy is a measure of the randomness or disorder of a system. b) $N_2O_3(g) \rightarrow N_2O(g) + O_2(g)$ -positive c) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$--negative	1, 1/5, 1/5
24	Conjugate acid base pairs differ by a proton.For example, HCl, Cl^- represents conjugate acid base pair.	1

	NH_4^+ is a conjugate acid of NH_3 and NH_2^- is a conjugate base of acid NH_3	1

25	Ozonolysis: Alkenes add ozone to form an ozonide which on hydrolysis in presence of Zn to form carbonyl compounds (Aldehydes or ketones).	1

2-Methylpropene + O_3 → Ozonide

1

↓ $Zn + H_2O$

$$\begin{array}{c} H_3C \\ \diagdown \\ C = O + HCHO \\ \diagup \\ H_3C \end{array}$$

Propan-2-one

OR

OR

i. $CH_3CH_2Br + 2Na + Br\ CH_2CH_3 \xrightarrow{\text{Dry ether}} CH_3CH_2\ CH_2CH_3\ +2NaBr$
                                 n-butane   1

ii. $CH_3CH_2I \xrightarrow[\Delta]{\text{alc KOH}} CH_2 = CH_2 + HI$
                     Ethene   1

SECTION C

26	elements	symbol	% of element	At.mass of elemets	No.of moles = $\frac{percentage}{at.mass}$	Simplest molar ratio	Simplest whole no.ratio	
	Sodium	Na	29.11	23	$\frac{29.11}{23} = 1.266$	$\frac{1.266}{1.266} = 1$	2	1
	Sulphur	S	40.51	32	$\frac{40.51}{32} = 1.266$	$\frac{1.266}{1.266} = 1$	2	1
	oxygen	O	30.38	16	$\frac{30.38}{16} = 1.897$	$\frac{1.897}{1.266} = 1.5$	3	1

Empirical formula of the salt= $Na_2S_2O_3$

27	i. Halogens have very high negative electron gain enthalpies because they can attain stable noble gas electronic configurations by picking up an electron.	1
		1
	ii. Mg^{2+} ion is smaller than O^{2-} ion although both have the same electronic configuration because of higher nuclear charge.	1
	iii. Electron gain enthalpy of fluorine is less negative than that of chlorine. This is because when an electron is added to F, the added electron goes to the smaller $n = 2$ quantum level and suffers significant repulsion from the other electrons present in this level.	

28	i. The pH of a solution is defined as the negative logarithm to base 10 of the concentration of hydrogen ion $[H^+]$. $p^H = -\log[H^+]$.	1

	$pH = -\log[H^+]$ or $\log[H^+] = -pH = -3.76 = \overline{4}.24$ $[H^+] = $ Antilog $\overline{4}.24 = 1.738 \times 10^{-4} = 1.74 \times 10^{-4}$ M	1
	ii. $$K_c = \frac{[NH_3]^4[O_2]^5}{[NO]^4[H_2O]^6}$$ OR	1 OR
	a. Le Chatelier's principle states that if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to reestablish an equilibrium.	1
	b. (i) Equilibrium will be shifted in the forward direction. (ii) Equilibrium will be shifted in the backward direction. (iii) Equilibrium will be shifted in the backward direction. (iv) Equilibrium will be shifted in the forward direction.	2
29	Oxidation half equation: $SO_2(g) + 2H_2O(l) \longrightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2 e^-$ …(i) Reduction half equation: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ …(ii) Multiply Eq. (i) by 3 and add it to Eq. (ii), we have, $Cr_2O_7^{2-}(aq) + 3SO_2(q) + 2H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + H_2O(l)$	1 1 1
30	Mass of the compound = 0.468 g Mass of barium sulphate= 0.668 g Percentage of sulphur $= \dfrac{32}{233} \times \dfrac{\text{Mass of barium sulphate}}{\text{Mass of compound}} \times 100$ $= \dfrac{32}{233} \times \dfrac{(0.668\ g)}{(0.468\ g)} \times 100 = \mathbf{19.60\%}$ Or Mass of the compound = 0.3780 g Mass of silver chloride = 0.5740 g Percentage of chlorine $= \dfrac{35.5}{143.5} \times \dfrac{\text{Mass of siliver chloride}}{\text{Mass of compound}} \times 100$ $= \dfrac{35.5}{143.5} \times \dfrac{(0.5740\ g)}{(0.3780\ g)} \times 100 = \mathbf{37.57\ g}$	1 2 OR 1 2
	SECTION D	
31	1. (a) $BeCl_2$ is least ionic out' of the given chlorides 2. (D) AlI_3 3. (B) $AlCl_3$ 4. (B) LiCI	1 1 1 1
32	1. (D) angular momentum 2. (C) diffraction experiment 3. (A) Planck's quantum theory (B) Einstein's theory of mass-energy equivalence 4. (A) $\lambda = \dfrac{C}{\gamma}$	1 1 1 1
	SECTION F	
33	i. For a reaction to be spontaneous ΔG should be negative. ii. if both ΔH and ΔS are negative, ΔG can be negative only if $T\Delta S < \Delta H$ in magnitude. $\Delta G = \Delta H - T\Delta S, \qquad \Delta G = (-) - T(-)$	1 1

This is possible only if either ΔH has a large negative value or T is so low that $T\Delta S < \Delta H$.

iii.

$$\Delta H^{\ominus} = \Delta U^{\ominus} + \Delta^{ng}RT$$

$\Delta U^{\ominus} = -10.5 \text{ kJ}; \quad \Delta^{ng} = 2 - 3 = -1 \text{ mol}$

$R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}; T = 298 \text{ K}$

$\therefore \quad \Delta H^{\ominus} = (-10.5 \text{ kJ}) + [(-1 \text{ mol}) \times (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298\text{K})]$

$= -10.5 \text{ kJ} - 2.478 \text{ kJ} = -12.978 \text{ kJ}$

According to Gibbs Helmholtz equation:

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

$\Delta G^{\ominus} = (-12.978 \text{ kJ}) - (298 \text{ K}) \times (-0.0441 \text{ kJ K}^{-1})$

$= -12.978 + 13.112 = -12.978 + 13.142 = \mathbf{0.164 \text{ kJ}}$

Since $\Delta G^{\ominus}$ is positive, the reaction is non-spontaneous in nature.

OR

a. Both ΔH and ΔS are positive so ΔG will be negative only if $T\Delta S > \Delta H$ in magnitude.

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = (+) - T(+)$$

Thus either ΔS should be very large so that even if T is low, $T\Delta S$ is greater than ΔH, or if ΔS is small, T should be high so that $T\Delta S > \Delta H$.

b. Lattice energy can be defined as the energy required to convert one mole of an ionic solid into gaseous ionic constituents.

c.
The available data is:

(i) $\quad CCl_4(l) \longrightarrow CCl_4(g), \quad \Delta_{vap}H^{\ominus} = 30.5 \text{ kJ mol}^{-1}$

(ii) $\quad C(s) + 2Cl_2(g) \longrightarrow CCl_4(l), \quad \Delta_f H^{\ominus} = -135.5 \text{ kJ mol}^{-1}$

(iii) $\quad C(s) \longrightarrow C(g), \quad \Delta_a H^{\ominus} = 715.0 \text{ kJ mol}^{-1}$

(iv) $\quad Cl_2(g) \longrightarrow 2 Cl(g), \quad \Delta_a H^{\ominus} = 242 \text{ kJ mol}^{-1}$

The equation we aim at is:

$$CCl_4(g) \longrightarrow C(g) + 4Cl(g); \Delta H = ?$$

Eqn. (iii) + 2 × Eqn. (iv) − Eqn. (i) − Eqn. (ii) gives the required equation with

$$\Delta H = 715.0 + 2(242) - 30.5 - (-135.5) \text{ kJ mol}^{-1}$$

$$= 1304 \text{ kJ mol}^{-1}$$

Bond enthalpy of C−Cl in CCl_4 (average value) $= \dfrac{1304}{4} = \mathbf{326 \text{ kJ mol}^{-1}}$.

34	i.	Inductive effect is a partial shifting/displacement of σ electrons towards a more electronegative atom of σ bond.
	ii.	The **spontaneous formation** of a **dipole molecule of** the **organic compound because** of the **complete transfer of shared pi electrons pairs to other atoms in the influence of attacking reagent present is referred to as Electromeric effect.**
	iii.	Electron withdrawing inductive (-I) effect
	iv.	When an alkyl group is attached to a π system, it acts as an

electron-donor group by the process of hyperconjugation.   1

v.   **heptan-4-one**   1

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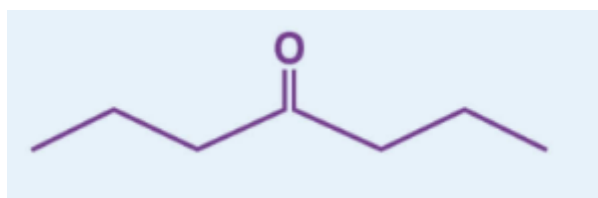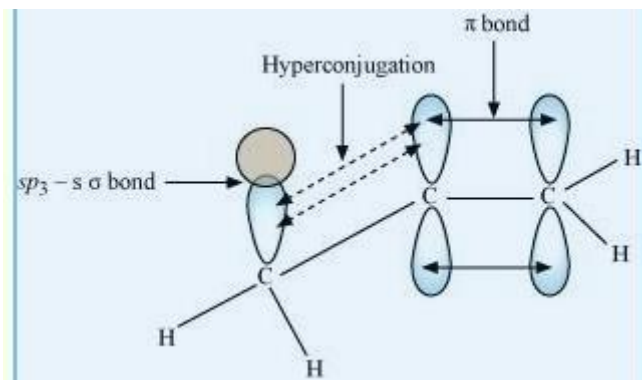
35   a) Decarboxylation:

Sodium salt of carboxylic acids (R-COONa) on heating with soda lime (a mixture of NaOH and CaO), we get an alkane containing one carbon atom less than that of the carboxylic acid.   1

$$\text{e.g. } CH_3COONa \xrightarrow{NaOH/CaO} CH_4 + Na_2CO_3$$

             Sodium acetate   methane
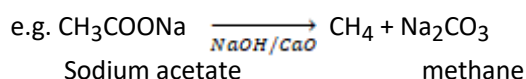
    b) Aromatization:

n-Alkanes having six or more carbon atoms on heating to 773K at 10-20 atmospheric pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina, we get aromatic compounds.

                                                                     1
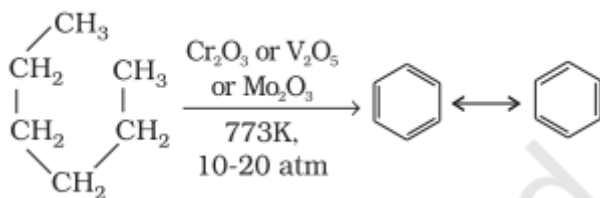
    c) Kharash effect:

    In the presence of peroxide, addition of HBr to unsymmetrical alkenes takes place against Markovnikov rule. This is known as *peroxide or Kharash effect or anti-Markovnikov addition reaction*.

$$\text{e.g. } CH_3-CH=CH_2 + HBr \xrightarrow{Org.peroxide} CH_3-CH_2-CH_2$$
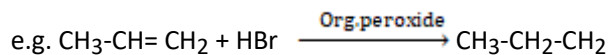
    d) Sulphonation: It is the introduction of sulphonic acid (-SO$_3$H) group to a benzene ring. It is carried out by heating benzene with fuming sulphuric acid (H$_2$S$_2$O$_7$ or oleum).
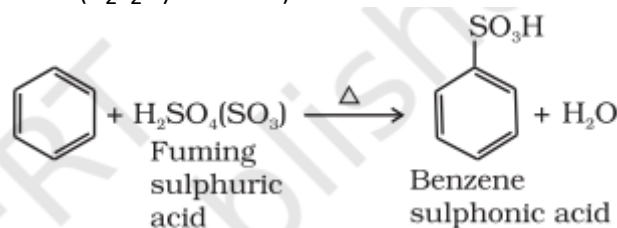
    e) Friedel-Craft's Acylation reaction: The reaction of benzene with an acyl

halide or acid anhydride in the presence of Lewis acids (AlCl$_3$) yields acyl benzene.

$$\text{Benzene} + CH_3COCl \xrightarrow[\triangle]{\text{Anhyd. AlCl}_3} \text{Acetophenone (COCH}_3) + HCl$$

Acetylchloride

Acetophenone

OR

a) What happens when

i. Phenol is reduced to benzene by passing its vapours over heated zinc dust.

$$\text{Phenol (OH)} + Zn \xrightarrow{\triangle} \text{Benzene} + ZnO$$

ii. Ethyne (acetylene) on passing through red hot iron tube at 873K, undergoes cyclic polymerisation to form benzene (C$_6$H$_6$).

iii. n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes.

$$CH_3(CH_2)_4CH_3 \xrightarrow{\text{Anhy. AlCl}_3/\text{HCl}}$$
$$n\text{-Hexane}$$

2-Methylpentane   3-Methylpentane

iv. Benzene on treatment with excess of chlorine in the presence of anhydrous AlCl$_3$ in dark

$$\text{Benzene} + 6Cl_2 \xrightarrow[\text{dark, cold}]{\text{Anhyd. AlCl}_3} \text{Hexachlorobenzene (C}_6Cl_6) + 6HCl$$

v. Propene is treated with HBr

$$CH_3-CH=CH-CH_3 + HBr \longrightarrow CH_3-CH_2-CHCH_3 \; (\text{Br})$$

1

1

OR

1

1

1

1

1

BLUE PRINT							
CHEMISTRY SAMPLE PAPER-2							
CLASS XI							
S.No	Name of the chapters	MCQ	A/R	VSA I	SA I	Case based	LA	Total
		1 Mark	1 Mark	2 Marks	3 Marks	4 Marks	5 Marks	Weig htage
1.	**Some basic concepts of chemistry**	2 (2)		2(1)	3(1)			**7**
2.	**Structure of atom**		1(1)		3(1)		5(1)	**9**
3	**Classification of elements and periodicity in properties**	2(2)	1(1)		3(1)			**6**
4	**Chemical bonding and molecular structure**	2(2)					5(1)	**7**
5	**Chemical thermodynamics**	2(2)		4(2)	3(1)			**9**
6	**Equilibrium**	1(1)		2(1)		4(1)		**7**
7	**Red-ox reactions**	1(1)			3(1)			**4**
8	**Organic chemistry –Some basic principles and Techniques**	2(2)	1(1)	4(2)		4(1)		**11**
9	**Hydrocarbons**	2(2)	1(1)	2(1)			5(1)	**10**
		14	**4**	**14**	**15**	**8**	**15**	**70**

Kendriya vidyalaya sangathan Chennai region

Time: 3 Hrs   Sample paper-2 –XI Chemistry   Max.Mark: 70

 Read the following instructions carefully.

a) There are **35** questions in this question paper with internal choice.

b) SECTION A consists of 18 multiple-choice questions carrying 1 mark each.

c) SECTION B consists of 7 very short answer questions carrying 2 marks each.

d) SECTION C consists of 5 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

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1, The number of significant figure in 0.0016 is

a) 1 b) 2 c) 3 d) 4

2. Equal volume of all gases contain equal no of molecules at constant temperature and pressure This is stated by

a) Gay Lussac law b) Boyle 's Law c)Avogadro law d) None of the above

3. Chloride ion is isoelectronic with

a) $Na+$ b) Mg c) Ar d) Al^{3+}

4.The atomic number of the element Unbinilium is

a) 420   b) 120 c) 123 d) 102

5.The number of sigma bond and pi bond in ethyne is

a) 3 sigma two Pi bond b) only 2 Pi bonds c) one sigma and two pi bond d) Five sigma bonds one pi bonds

6. Which of the following molecule is has zero dipolemonent

a) water   b) $NH3$ c)$NF3$ d) carbon tetra chloride and $CO2$

7. Which is correct about ΔG

a. It is negative for non spontaneous process

b. It is positive for spontaneous process

c. It is zero for a reversible process

d. It is zero for a spontaneous process

8.At what temperature the entropy of perfect crystalline substance is zero

a) O K b)273 K c) O 0 C d) 250 K

9)The P H of aqueous solution of ammonium acetate is

a) equal to zero b) greater than 7 c) equal to 7 d) 14

10.The Red-ox reaction in which a single substance undergoes both oxidation as well as reduction is called

a) Exothermic reaction b) combination reaction c) decomposion reaction d) Disproportionation reaction

11) 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) Hyper conjugation.
12. The type of isomerism not found in alkenes is :
(a) Chain isomerism
(b) Geometrical isomerism
(c) Metamerism
(d) Position isomerism

13.The catalyst used in Friedel – Crafts reaction is
(a) Aluminium Chloride

(b) Anhydrous Aluminium Chloride

(c) Ferric Chloride

(d) Copper .

14. What is the correct decreasing order of boiling point?

a) NeoPentane>Isopentane>Pentane

b)Pentane>Isopentane>NeoPentane

 c)Isopentane>NeoPentane>Pentane

d) None of the above

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

Assertion : An orbit cannot have more than two electrons.

Reason–No two electrons in an atom can have same set of all four Quantum numbers.

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.

16. **Assertion**: Noble gas elements have positive electron gain enthalpy.

   Reason   : Inert gas elements stable octet configuration .

        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.

17. **Assertion**: The reaction between haloalkanes and sodium metal in presence of dry ether alkanes having even number are produced .

   Reason   : propane can be prepared by Wurtz reaction

         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

18. **Assertion**: Resonance hybrid cannot be presented by a single structure

    Reason   : Energy of resonance hybrid is equal to the average of energiesof all canonical forms.

         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

SECTION B

This section contains 7 questions with internal choice in two questions. The following questions are very short answer type and carry 2 marks each.

19. a. What do you mean by limiting reagent.

      b. Molarity changes with temperature. Give reason

20.   a. Explain the term entropy.

       b.Write the mathematical form of first law of thermodynamics .

                        (OR)

     Predict whether entropy change is positive or negative

      a. Heating a substance from 0k to 115K

      b. H_2 (g)----$\rightarrow$ 2H (g)

21.   Derive the Relation Between Cp and Cv for an Ideal Gas.

22. The concentration of hydrogen ions in a sample of soft drink is 3.8×10^{-3} M. What is the pH value?

23. Draw the Newman projection formulae of ethane. Which conformation is stable.

(OR)

What are the conditions for aromaticity?

24. Write IUPAC name of the following

a. $CH_3-CH_2-CO\ CH_2\ CH_2\ COOH$.

b. Draw the bond line structure of 2,4 –dimethyl heptanes

25. Explain heterolytic cleavage with an example .

SECTION C

This section contains 5 questions with internal choice in two questions. The following questions are short answer type and carry 3 marks each.

26.a.Commercially labelled sulphuric acid has 49% H_2SO_4 .Its density is 1.40 g/ml. What is the molarity?

b. The vapour density of a substance is 34 . What is the molar mass?

27. a. What do you mean by dual nature of electron?

b.Calculate the wavelength of an electron moving with the velocity 2.05×10^{7} m/s.

28. a.What are transition metals? Write any four characteristics of transition metals.

(OR)

a. Name the element having the highest electronegativity value.

b. Write general electronic configuration of inner transition elements.

c. The ionisation enthalpy of Boron is less than that of Beryllium.Why?

29. Balance the following red-ox reaction in acid medium by ion electron method.

$Cr_2 O_7{}^{2-} + Fe\ 2+ \longrightarrow Fe^{3+} + Cr^{3+}$
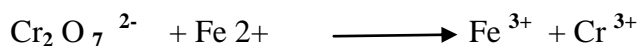
(OR)

a.What is the role of salt bridge in galvanic cell?

b. Calculate the oxidation number of Manganese in Permangante $Mn O_4{}^{-}$ anion

c. Write the cell notation of the following galvanic cell.

$Zn (S) + Cu^{2+} (aq) \longrightarrow Zn^{2+} (aq) + Cu (S)$
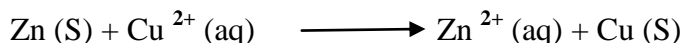
30. Calculate the heat of combustion of ethylene (gas) to from CO_2 (gas) and H_2O (gas) at 298k and 1 atmospheric pressure. The heats of formation of CO_2, H_2O and C_2H_4 are – 393.7, – 241.8, + 52.3 kJ per mole respectively.

SECTION D

The following questions are **case-based** questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

31. According to Arrehenius concept , acids give H+ ions while bases produce OH- ions in their aqueous solutions. Bronsted-Lowry defined an acid as a proton donor and a base as a proton acceptor. When a Bronsted – Lowry acid reacts with a base, it produces its conjugate base and a conjugate acid corresponding to the base with which it reacts. Thus, a conjugate pair of acid - base differs only by a proton. The strength of acids and bases can be measured in terms of their dissociation constants Ka (or pKa) and Kb (or pKb). Larger value of Ka or lower value of pKa corresponds to greater strength of acids. Similarly, larger value of Kb or lower value of pKb corresponds to stronger base. P H finds vital role in cosmetic formulations and buffer solution is used in blood bank.

a. Write the conjugate acid -base pair for the following
i) NH_3 ii) HSO_4^-

b. What are buffer solutions?
c. What are Lewis acids and Lewis Bases?

(OR)

c. which of the following are Lewis acid and bases.

NH_3, BF_3, $AlCl_3$, CH_3NH_2

32. In an organic reaction a covalent bond between two carbon atoms or a carbon and some other atom is broken and a new bond is formed. A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products kinetics) is referred to as reaction mechanism. A species having a carbon atom possessing sextext of electrons and a positive charge is called a *carbocation* (earlier called *carbonium ion*). The CH3+ion is known as a methyl cation or methyl carbonium ion. carbocations are classified as primary, secondary or tertiary depending on whether one, two or three carbons are directly attached to the positively charged carbon. Some other examples of carbocations are: $CH3CH2^+$(ethyl cation, a primary carbocation), $(CH3)2CH^+$ (isopropyl cation, a secondary carbocation), and $(CH3)3C^+$ (*tert*–butyl cation, a tertiary carbocation).Carbocations are highly unstable and reactive species.
. Alkyl radiradicals are classified as primary, secondary, or tertiary. Alkyl radical stability increases as we proceedfromprimary to tertiary:
Organic reactions, which proceed by homolytic fission are called free radical or homopolaror nonpolar reactions.

.a. Write any two reactive intermediates which are unstable.
 b. State the hybridation of carbonium ion.
c. Explain tertiary carbocation is more stabe than secondary and in turn primary .Explain

(OR)

 C. What are electrophiles and nucleophiles .Give an example each.

SECTION E
The following questions are long answer type and carry 5 marks each. Two questions have an internal choice.
33. a. .Calculate the radius of the first orbit of He + .(2)
    b.State Heisenberg uncertainty Give any one significance of it . (2)
    c. Write electronic configuration of Cr $^{3+}$ ion . (Z=24)   1M

(OR)
    a. What is the significance of magneticquantum number? (1)
     b. If n=5 , l=3 what is the designation of the orbital.(1)
     c. State aufbau principle. (1)
     d. Calculate the wave number of yellow radiation having wavelength 5800 A ^{0} (2M)
34.   a .Write two types of hydrogen bonding with its examples . (2M)
     b.Though NH_3 involves Sp^3 hybridaisation ,the shape is pyramidal .Explain with the
help of VSEPR theory. (2M)
    c.Axial bonds in PCl $_5$ are slightly elongated than equatorial bonds .Give reason. (1M)

(OR)

a. Compare the relative stability of O_2, O_2^- O_2^+ in terms of molecular orbital theory.(3)

b. Write the differences between sigma and Pi bond (2)

35.

a. CH ≡ CH $\xrightarrow{\text{red hot iron tube, 873K}}$ X $\xrightarrow{\text{CH3COCl, Anhyd.AlCl3}}$ Y
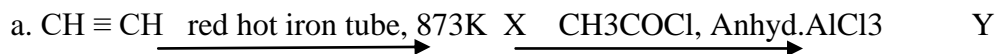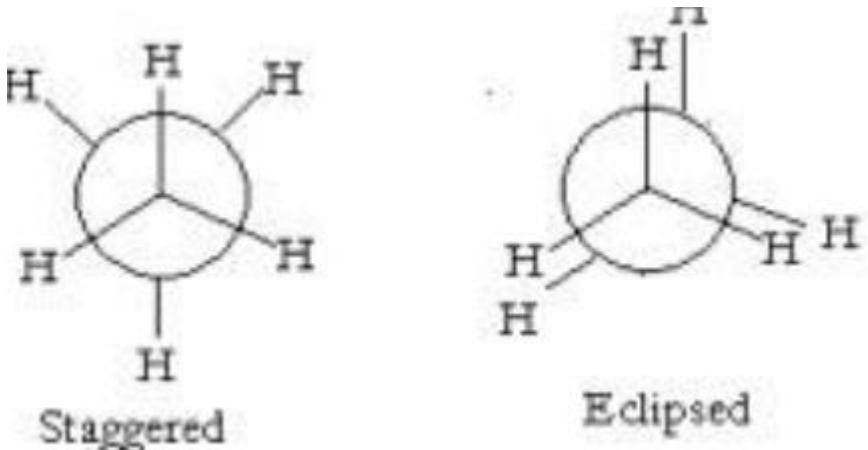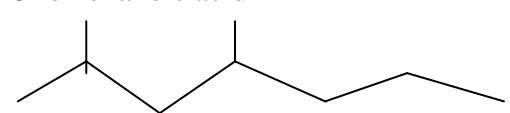
Find X and Y in the above sequence of reaction 2M

b.Explain Markovnikov's rule with an example (2)

c. Convert phenol to benzene. (1)

Scoring key Sample paper-2 chemistry –XI (2022-23)

1	b) 2	1
2	c)Avogadro law	1
3	c) Ar	1
4	b) 120	1
5	a) 3 sigma two Pi bond	1
6	d) carbon tetra chloride and CO_2	1
7	c. It is zero for a reversible process	1
8	a) O K	1
9	c) equal to 7	1
10	d)Disproportionation reaction	1
11	(b) Electromeric effect	1
12	(c) Metamerism	1
13	(b) Anhydrous Aluminium Chloride	1
14	b)Pentane>Isopentane>NeoPentane	1
15	d. A is false but R is true	1
16	a. Both A and R are true and R is the correct explanation of A	1
17	c. A is true but R is false.	1
18	c. A is true but R is false	1
19	a. Reactant consumed fully in a reaction	1
	b. As temperature changed ,volume also changes	1
20	a. Measure of degree of disorder	1
	b.$\Delta U = q + w$	1
	(OR)	
	a. Positive	1
	b. Positive	1
21	At constant volume heat capacity = Cv At constant pressure heat capacity = Cp	
	At constant volume qv= $Cv\Delta T = \Delta U$	½
	At constant pressure qp = $Cp\ \Delta T = \Delta H$ For one mole of an ideal gas	½
	$\Delta H = \Delta U + \Delta (PV) = \Delta U + \Delta (RT)$	½
	$\Delta H = \Delta U + R\Delta T$	
	On substituting the values of ΔH and Δu, the equation is modified as $Cp\ \Delta T = Cv\Delta T + R\Delta T$	½
	or Cp-Cv = R	
22	pH = − log [H+] = − log (3.8 x 10-3) = − log 3.8 + 3 = 3 − 0.5798 = 2.4202 = 2.42	
23	Staggered conformer is more stable	1+1

Staggered　　　　　Eclipsed

(OR)

Planarity, delocalization of pi electrons over planar benzene ring Huckle rule .(Any two) 1+1

24	a. 4-Oxo hexanoic acid b.	
25	In this cleavage the shared pair of electrons goes with any one of the two bonded atom CH_3-Br ==➔ CH_3^+ + Br $^-$	1 1
26	a.　M= $\dfrac{\% \times density \times 10}{molecular\ weight}$ 　　　=$\dfrac{49 \times 1.4 \times 10}{98}$ 　　　= 7M b.68	½ ½ 1 1
27	a. Having both particle as well as wave nature b.　λ = h/mv= $\dfrac{6.626 \times 10^{-34}\ j\text{-}s}{9.1 \times 10^{-31}\ kg \times 2.05 \times 10^{7}\ m/s}$ 　　=3.55×10^{-11} m	1 ½ ½ 1
28	a. Elements having partially filled d orbital either in ground state or oxidation state 　Formation of coloured ion,complex, alloy, showing paramagnetism (any Four) (OR) a. Flourine b, $(n-2)f^{1-14} (n-1)d^{1\ or\ o} ns^2$ c. In boron the differentiating electron to be removed is in p subshell which is less penetrating .	1 2 1 1 1
29	Balancing each half reaction of oxidation and and reduction $Cr_2O_7^{2-}$ + 6Fe 2+ 14 H+ ⟶ 6Fe $^{3+}$ +2 Cr $^{3+}$ +7H_2O (OR) a. .1Salt bridge maintains electrical neutrality2.It prevents accumulation of charges around the electrode . Any one point. b. +7 c. Zn(S) I Zn $^{2+}$ (aq) II Cu^{2+} (aq) I Cu(S)	1=1 1 1 1 1

30.	**Ans.** $C_2H_4 (g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O (g)$ $\Delta H_f(CO_2) = -393.7kJ$ $\Delta H_f(H_2O) = -241.8kJ$ $\Delta H_f(C_2H_4) = +52.3kJ$ $\Delta Hreaction = \sum \Delta H_f^o \, products - \sum \Delta H_f^o \, reactants$ $= [2 \times \Delta H_f^o (CO_2) + 2 \times \Delta H_f^o (H_2O)] - [\Delta H_f^o (C_2H_4) + 3 \times \Delta H_f^o (O_2)]$ $= 2 \times [(-393.7)m + 2 \times (-241.8)] - [(523.0) + 0)]$ $[\therefore \Delta H_f^o \text{ fot elementary substance} = 0]$	1
	$= [-787.4 - 483.6] -523.3$ $= -1323.3 \text{ kJ.}$	1

31	a. Answer: i) Conjugate acid: NH_4^+ Conjugate base: NH_2^-
	 ii) Conjugate acid: H_2SO_4 Conjugate base: SO_4^{2-}
	 b.The solution which resists the change in PH on the addition of small amount of acid or base or dilution
	 c. Electron pair acceptor is Lewis acid
	    Electron pair donor is Lewis base.
	        (OR)
	 c.
	 Answer: Lewis acid: BF_3, $AlCl_3$
	 Lewis base: NH_3, CH_3NH_2
		½
		 ½
		
		 1
		 1
		 1
		
		 1
		 1

32	a. Carbonium ion, carbanion, free radical (any two)
	 b. Sp^2
	 c. Since alkyl groups are electron releasing groups ,positive charge of carbonium ion is dispersed by inductive and hyperconjugation.
	 Greater the no of alkyl groups ,greater is the stability,Hence 3^0 carbonium is more stable than 2^0 and in turn 1^0
	    (OR)
	 c. Electrons loving species are electrophiles . H^+ ,Cl^+
	    Nucleous loving species or electron rich species are nucleophiles NH_3, CN^-
		½+1/2
		 1
		 1
		
		 1
		
		 4x1/2

33	a. $r = 52.9 \, n^2/ Z$ Pm $= 52.9 \, 1^2/2$ Pm	½ ½

	= 26.45 Pm	1
	b. It is impossible to determine the exact position and velocity of sub atomic particles simultaneously.	1
	It rules out the definite path for an electron.	
	It is applicable for micro sized particles only (any one point)	1
	c.$1S^2 2S^2 2P^6 3S^2 3P^6 3d^3$	1
	(OR)	
	a,It signifies the orientation of orbital	1
	b.5f orbital	1
	c.In building up of an atom, electrons enter into various atomic orbitals in the increasing of energy.	1
	d. wave number = $1/\lambda$	
	= $1/ 5800 \times 10^{-10}$ m	½
	=1.72×10^{6} m^{-1}	½
		1
34	a. Intra molecular hydrogen bonding O=nitro phenol	1
	Inter molecular hydrogen bonding water ,ammonia	1
	b.Ammonia has one lone pair of electron .Since the repulsion between bond pair –bond pair is less than lone pair –bond pair , the shape becomes pyramidal.	1
		1
	c.The axial bond pairs suffers more repulsion tha equatorial bond pairs,	1
	(OR)	
	a.Bond order =1/2 [N_b-N_a]	½
	O_2=1/2 [10-6] =2 with Mo configuration	½
	O_2^- =1/2[10=7]=1.5	½
	O_2^{2-} =1/2 [10-8] =1	½
	Increasing order of stability	
	$O_2^{2-} < O_2^- < O_2$	1
	Sigma bond	Pi bond	
	1.axial overlapping of orbits	1.lateral or sidewise overlapping of orbitals	
	2. Strong bond	2. Weak bond	1+1
	3.pure and and hybrid orbitals	3. Only pure orbitals are involved	
	May form sigma bond	
	(any Two)	
35	X= C_6H_6 Y=C_6H_5 CO CH_3	1+1
	b. During hydrohalogenation of alkene, the negative part of adduntum ,HX is added to the carbon having least no of hydrogen	1
	CH_3-CH= CH_2 + HBr $\longrightarrow$ CH3-CH (Br) CH_3	1
		1
	Phenol benzene	

XI CHEMISTRY

Sl No	CHAPTER NAME	1 Mark	2Marks	3 Marks	4Marks	5Marks	TOTAL
1	Some Basic Concepts of Chemistry	11	1	1			7
2	Structure of Atom	11		1	1		9
3	Classification of Elements and Periodicity in Properties	11	2				6
4	Chemical Bonding and Molecular Structure	11	1	1			7
5	Chemical Thermodynamics	1111				1	9
6	Equilibrium	11	1	1			7
7	Redox Reactions	11	1				4
8	Organic Chemistry: Some Basic Principles and Techniques	11			1	1	11
9	Hydrocarbons		1	1		1	10
	Total	18(1)	7(2)	5(3)	2(4)	3(5)	35(70)

KENDRIYA VIDYALAYA SANGATHAN- CHENNAI REGION

SAMPLE PAPER -3
CLASS-XI
SUBJECT:-CHEMISTRY
TIME :3 HOURS   **M M: 70**
General Instruction:

Read the following instructions carefully.

a) There are 33 questions in this question paper. All questions are compulsory.

b) Section A: Q. No. 1 to 16 are objective type questions. Q. No. 1 and 2 are passage based questions carrying 4 marks each while Q. No. 3 to 16 carry 1mark each.

c) Section B: Q. No. 17 to 25 are short answer questions and carry 2 marks each.

d) Section C: Q. No. 26 to 30 are short answer questions and carry 3 marks each.

e) Section D: Q. No. 31 to 33 are long answer questions carrying 5 marks each.

f) There is no overall choice. However, internal choices have been provided.

g) Use of calculators and log tables is not permitted.

SECTION -A (OBJECTIVE TYPE)

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

The following questions are multiple choice questions. Choose the most appropriate answer:

The s-block elements of the Periodic Table are those in which the last electron enters the outermost s-orbital. As the s-orbital can accommodate only two electrons, two groups (1 & 2) belong to the s-block of the Periodic Table. Lithium and beryllium, the first elements of Group 1 and Group 2 respectively exhibit some properties which are different from those of the other members of the respective group. The melting and boiling points of the alkali metals are low indicating weak metallic bonding due to the presence of only a single valence electron in them. The alkali metals and their salts impart characteristic colour to an oxidizing flame. The alkali metals are highly reactive due to their large size and low ionization enthalpy. The reactivity of these metals increases down the group. The alkali metals are strong reducing agents, lithium being the most and sodium the least powerful. The flame test is helpful in their detection in qualitative analysis and estimation by flame photometry.

1.1   Among the following which statement/s is/are not incorrect in respect of   1
      s-block elements-
      (I) Alkaline earth metals are stronger reducing agents than alkali
          metals.
      (II) Cs and Ba are used in making photovoltaic cell.
      (III) Lithium nitrate decomposes to give brown coloured gas NO_2

(IV) $BeCl_2$ is ionic in nature.

(V) On electrolysis of molten NaH , hydrogen gas evolved at anode.

[A] I, IV   [B] III, IV   [C] II, V   [D] III, V

1.2   Ammonical solutions of alkali metals are-   1

    [A] Paramagnetic in nature.

    [B] Convert to hydride on keeping undisturbed for some time.

    [C] Dark green in colour.

    [D] All the above.

OR

The correct set of alkaline earth metals which impart colour to oxidizing flame-

[A] Ca, Mg   [B] Ba, Be   [C] Sr, Ba   [D] Sr, Mg

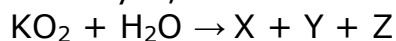1.3   The correct order of density of alkaline earth metals is-   1

    [A] Be<Mg<Ca<Sr<Ba

    [B] Mg<Be<Ca<Sr<Ba

    [C] Ca<Mg<Sr<Be<Ba

    [D] Ca<Mg<Be<Sr<Ba

1.4   Identify X, Y & Z in the following reaction –   1

$KO_2 + H_2O \rightarrow X + Y + Z$

    [A] H_2, K_2O , O_2

    [B] KOH, O_2, H_2

    [C] H_2O_2, O_3, KOH

    [D] None of the above

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

Hydrocarbons are of different types. Depending upon the types of carbon-carbon bonds present, they can be classified into three main categories – (i) saturated (ii) unsaturated and (iii) aromatic hydrocarbons. Saturated hydrocarbons contain carbon-carbon and carbon-hydrogen single bonds. Aromatic hydrocarbons follows Huckel's rule. They show characteristic electrophilic substitution reactions. Hydrocarbons can be prepared by different methods. Alkene and alkyne show characteristic electrophilic addition reactions.

In these questions (Q. No 2.1- 2.4) , a statement of assertion followed by a statement of reason is given. Choose the correct answer out ofthe following choices.

    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

2.1   **Assertion-** n- Hexane cannot be prepared by Wurtz reaction.   1

Reason- Wurtz reaction is not a good method for the preparation of alkane with odd number of carbon atoms.

2.2 **Assertion-** Ethyne on passing through red hot Iron at 773K gives C_6H_6. 1
Reason- It is an example of polymerization reaction.

2.3 **Assertion-** Cyclopentadienyl anion is aromatic in nature. 1
Reason- It has cyclic , planner structure with 6-π electrons.

2.4 **Assertion-** Benzene has 18 sp^2 hybrid orbitals. 1
Reason- Each carbon atom in benzene is sp^2 hybrid.

OR

Assertion- Propyne on reaction with sodium amide gives Sodium propynide and ammonia.
Reason- Propyne is acidic in nature.

Following questions (No. 3 -11) are multiple choice questions carrying 1 mark each:

3 Read the following statements and identify incorrect statements- 1
   (i) Chloronium ion behave as electrophile.
   (ii) In homolytic bond cleavage free radical is formed.
   (iii) Ethoxyethane is functional group isomer of ethanol.
   (iv) In ethyne two sigma and two pi bonds are present.
   [A] i, iv   [B] i , ii   [C] ii, iv   [D] iii, iv

4 Select the correctly matched pair- 1
   [A] Borax – $Na_2B_4O_7.4H_2O$
   [B] Cryolite – Na_3AlCl_6
   [C] Cassiterite – SnO_2
   [D] Galena- PbO

OR

The element of group -13 having least first ionization enthalpy is-
[A] Boron   [B] Thallium   [C] Gallium   [D] Indium

5 What will be the sign of ΔH and ΔS for the reaction: $Cl_{2(g)} \rightarrow 2Cl_{(g)}$ 1
   [A] −ve , +ve   [B] +ve , +ve   [C] -ve , -ve   [D] None

6 Which among the following compounds will show geometrical isomerism- 1
   [A] Propene   [B] Hex-1-ene   [C] Pent-2-ene   [D] But-1-ene

OR

Which among the following statement is not incorrect about conformations of ethane-
   [A] All conformations between eclipsed and staggered conformation are called skew conformations.
   [B] Staggered conformation is less stable than eclipsed conformation.
   [C] Eclipsed form has least torsional strain.
   [D] Both forms have different boiling points.

7 Conjugate base of NH_2^- is- 1
   [A] NH_3 [B] NH^- [C] NH^{2-} [D] NH_4^+

OR

pH of 1×10^{-8} M HCl is-

[A] 8.00   [B] 6.96   [C] 7.32   [D] 7.00

8   Ideal gas equation for 1.5 mol of a gas at temperature T, Pressure P and   1
     volume V will be-

[A] PV= nRT   [B] 2 PV=3 RT   [C] 3 PV= 2 RT   [D] PV = 2.5 RT

OR

Under what conditions a gas follow ideal gas equation-
   [A] High pressure & Low temperature
   [B] High pressure & high temperature
   [C] Low pressure & high temperature
   [D] Low pressure & Low temperature

9   Electronic configuration of Cr (z=24)is-   1
   [A] [Ar] $3d^4 4s^2$
   [B] [Ar] $3d^3 4s^2$
   [C] [Ne] $3d^5 4s^1$
   [D] [Ar] $3d^5 4s^1$

10   In the reaction- $2 F_2 + 2 H_2O \rightarrow 4 H^+ + 4 F^- + O_2$;   1
   [A] F_2 is reducing agent.
   [B] Oxidation number of fluorine changes from -1 to 0.
   [C] Oxidation number of oxygen remains unchanged.
   [D] It is non metal displacement reaction.

11   For which of the following reactions K_p is equal to K_c –   1
   [A] $H_{2(g)} + I_{2(g)} \rightleftharpoons 2 HI_{(g)}$
   [B] $3 H_{2(g)} + N_{2(g)} \rightleftharpoons 2 NH_{3(g)}$
   [C] $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$
   [D] All the above

In the following questions (Q. No. 12 - 16) a statement of assertion followed by a
statement of reason is given. Choose the correct answer out of the following choices.
  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

12   **Assertion-** 3^0 Carbocation is more stable than 2^0 Carbocation.   1
     Reason-   Greater the number of hyper conjugative structures
     morewill stability of carbocation.

13   **Assertion-** Isobutane has higher boiling point than n-Butane.   1
     Reason-   Isobutane has lower surface area than n-Butane.

14   **Assertion-** Reduction involves increase of oxidation number.   1
     Reason-   Increase in oxidation number involve lose of electron.

OR

Assertion- Oxidation number of halogens is always -1.

Reason – Halogens are most electronegative in their respective period.

15   **Assertion-** $AlCl_3$ act as Lewis acid.   1

     Reason - $AlCl_3$ has six electrons on the central atom Al.

16   **Assertion-** Molality depends on temperature.   1

     Reason- Molality is better concentration expressing unit than molarity.

SECTION- B

The following questions, Q.No 17–25 are short answer type and carry 2 marks each-

17   (i) State Modern periodic Law.   2

        (ii) Write IUPAC name and symbol of the element having Z=124.

                 OR

     What do you mean by isoelectronic species? Explain giving one example.

18   Give reason for the following-   2

        (i) BF_3 acts as Lewis acid.

        (ii) CCl_4 cannot be hydrolyzed.

19   Calculate the wavelength of an electron moving with a velocity of   2

     3.05×10^6 m s^{-1}.

     (Mass of electron = 9.1×10^{-31} Kg, h = 6.62×10^{-34} JS)

                 OR

     A golf ball has a mass of 100g, and a speed of 45 m/s. If the speed can be measured within accuracy of 2%, calculate the uncertainty in the position.

20   Write IUPAC name of the following organic compounds-   2

        (i) $CH_3-CH_2-CH=CH-CHO$

        (ii) $CH_3-CH_2-CH(CH_3)-C(CH_3)_3$

                 OR

     Write condensed structural formula of the following compounds-

        (i) Propane-1,2,3-tricarboxylic acid

        (ii) Neopentane

21   (i) Define ionization enthalpy.   2

        (ii) Electron gain enthalpy of fluorine is less negative than chlorine, why?

22   Determine number of moles in the following-   2

        (i) 52 g He

        (ii) 2.24 L of CH_4 at STP

23   Determine oxidation number of underlined bold atom in the following-   2

        (i) **Ni**$(CO)_4$

        (ii) Li**Al**H_4

        (iii) $K_3[$**Fe**$(CN)_6]$

        (iv) **Cr**$_2O_7^{2-}$

24   Define-   2

      (i) mole fraction

      (ii) molarity

25   Complete the following reactions-   2

      (i) $Sn + H_2O \rightarrow$

      (ii) $SiCl_4 + H_2O \rightarrow$

SECTION- C

The following questions, Q. No 26–30 are short answer type and carry 3 marks each-

26   Write short note on the following giving one example of each-   3

      (i) Wurtz Reaction

      (ii) Markovnikov rule

      (iii) Friedel – Craft acylation reaction

OR

     What happens when- (Write chemical equation)

      (i) But-1-ene reacts with HBr in presence of peroxide.

      (ii) Pent-2-ene undergo ozonolysis

      (iii) Phenol heated with zinc dust.

27   (i) What is cause of permanent hardness of water?   3

      (ii) Explain molecular hydrides using suitable example.

      (iii) Explain Clark's method of removal of hardness of water.

OR

     (i) Why ice has lower density than water?

     (ii) Explain Zeolite method for removal of hardness of water.

     (iii) How many hydrogen bonded, interstitial and coordinated water molecules are associated in $CuSO_4.5H_2O$

28   (i) State Le-Chatelier's principle.   3

      (ii) Explain buffer solution giving two examples?

29   (i) State Boyle's Law.   3

      (ii)   Calculate the volume occupied by 4.4 g of CO_2 at 27.0°C and 1 barpressure. $R = 0.083$ bar L K^{-1} mol^{-1} .

30   (i) State Pauli's exclusion principle.   3

      (ii) Write value of 'n' & 'l' for 5d orbital.

      (iii) Draw shape of d_{xy} and d_z^2 orbitals.

SECTION- D

Q.No 31 to 33 are long answer type carrying 5 marks each

31   (a) Using VSEPR theory determine shape and hybridization of the following molecules- SF_4 , CH_4 5

     (b) Using molecular orbital theory determine bond order and magnetic nature of carbon molecule (C_2).

     (c) Why dipole moment of carbon dioxide is zero?

OR

(a) 'Dioxygen molecule has bond order of two and it is paramagnetic in nature'- justify it using molecular orbital theory.
(b) What do you mean by odd electron compounds? Explain giving two examples.
(c) 'All bonds in PCl_5 are not in equal length', justify?

32   (a) Explain inductive effect using suitable example.   5
     (b) Define nucleophile. Write its one example.
     (c) Draw resonance structures of nitrobenzene.
     (d) Using curved arrow notation, show the formation of reactive intermediate when the following covalent bonds undergo heterolytic cleavage- (i) CH_3-CN (ii) CH_3-SCH_3

OR

     (a) Explain hyperconjugation using suitable example.
     (b) Define electrophile. Write its one example.
     (c) Draw resonance structures of aniline.
     (d) Explain the isomerism shown by the following pair of compounds-
         (i) Propanal and Propanone
         (ii) 2-Chloropropane and 1-Chloropropane

33   (a) State Hess Law.   5
     (b) Define state function.
     (c) The combustion of one mole of methanol takes place at 298 K and 1 atm. After combustion CO_2 (g) and H_2O (l) are produced and 726.0 KJ of heat is librated. Calculate standard enthalpy of formation of methanol. The standard enthalpies of formation of CO_2 (g) and H_2O (l) are – 393.0 KJ mol^{-1} and -286.0 KJ mol^{-1} respectively.

OR

     (a) Define entropy.
     (b) What is adiabatic process?
     (c) For the reaction 2A(g) + B (g) → 2D (g),
     ΔU^o = - 20.5 KJ and ΔS^o = - 50.00 JK^{-1}
     Calculate ΔG^o for the reaction and predict whether the reaction is spontaneous or not. (R= 8.314 $Jmol^{-1}K^{-1}$, T=300 K)

KENDRIYA VIDYALAYA SANGATHAN- CHENNAI REGION

SAMPLE PAPER-3
CLASS-XI
SUBJECT:-CHEMISTRY
MARKING SCHEME

TIME:3HOURS   M M:70marks

General Instruction:

Read the following instructions.
a) There are 35 questions in this question paper with internal choice.
b) SECTION A consists of 18 multiple-choice questions carrying 1 mark each.
c) SECTION B consists of 7 very short answer questions carrying 2 marks each.
d) SECTION C consists of 5 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	
1	[b] +ve,+ve	1
2	[d]iii,iv	1
3	[b]Thallium	1
4	(c) 350 kJ	1
5	[c]NH^{2-}	1
6	[b]$2.5h/\pi$	1
7	[d] $[Ar]3d^5 4s^1$	1
8	[b]27.27%	1
9	[b]Polar bond	1
10	. [d]orbital dipole because of lone pair decreases the effect of the resultant N – F bond moments.	1
11	(a)+7	1
12	[d]$ns^{1–2}(n–1)d^{1–10}$	1
13	[b]1–methylcylohex–2–ene.	1
14	[c]Quantity of that substance	1
15	[d] by increasing pressure and decreasing temperature	1
16	(b) $Cl_2(g)$	1
17	[d]Assertion is correct statement but reason is wrong statement.	1

18	[a]Assertion and reason both are correct statements and reason is correct explanation for assertion.	1
	SECTION B	
19	Weight of 1L = 1.97g	1
	Weight of 22.4L = 1.97x 22.4 = 44.1g	1
	Hence the molecular mass = 44.1g/mol	
20	[i]The effect of increased nuclear charge is cancelled by the greater penetration of 2s electron as compared to 2p electron	1
	[ii]When an electron is added to fluorine it goes to a comparitively small 2p orbital and suffers inter electronic repulsion whereas in chlorine the electron moves to 3p orbital which is of bigger size than 2pand so less inter electronic repulsion.	1
21	[i]Properties of elements are periodic functions of their atomic numbers	1
	[ii]Unbiquadium	1
	OR	
	[i]Species having same no of electrons. Eg: Ne, O^{2-}, F^-, Na^+	1
		1
22	$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$	½
	$Cr_2O_7^{2-}(aq) + 6e- \rightarrow 2\ Cr^{3+}(aq)$	½
	$Cr_2O_7^{2-}(aq) + 14H+ (aq) + 6e- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	½
	$6Fe^{2+}(aq) \rightarrow 6Fe^{3+}(aq) + 6e^-$	½
	$6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H+ (aq) \rightarrow 6\ Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$	
23	$O_2: \sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*1s^2, \sigma 2pz^2, \pi 2p_x^2, \pi 2p_y^2, \pi^*2p_x^1, \pi^*2p_y^1$	1
	Unpaired electrons in $\pi^*2p_x^1, \pi^*2p_y^1$ makes oxygen paramagnetic.	1
24	$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$	1
	$3C_2H_2 \xrightarrow[\text{red hot tube,873K}]{} C_6H_6 \xrightarrow[ConcH2SO4]{} C_6H_5SO_3H$	1
25	[i] $Kc = [CH_3COOH(aq)][C_2H_5OH(aq)] / [CH_3COOC_2H_5(aq)]$	1
	[ii] $Kc = [IF_5]^2 / [F_2]^5$	1
	SECTION C	
26	The suppression of the dissociation of a weak electrolyte by the addition of a strong electrolyte having a common ion. Precipitation of Sulphides of Group II.	1
	In order to precipitate the Sulphides of the group II, hydrogen sulphide gas (H_2S) is passed through the original solution in presence of hydrogen chloride (HCl). $H_2S \rightleftharpoons 2H^+ + S^{2-}$	1
	$HCl \rightarrow H^+ + Cl^-$ In the preceding reaction, HCl furnishes H^+ as common ions, which shift the above equilibrium to left according to Le-Chatelier's principle. The addition of HCl to the solution suppresses the ionization of H_2S thereby lowering the concentration of sulphide ions (S^{2-}) in a manner just enough to exceed the solubility product of the group II Sulphides	1
	OR	
	[i]$CuSO_4 + 2H_2O \rightleftharpoons Cu(OH)_2 + H_2SO_4$ (weak base strong acid) $CuSO_4$ is the salt of weak base $Cu(OH)_2$ and a strong acid H_2SO_4. Thus the solution will have free H^+ ions and will, therefore, be acidic. Na_2SO_4, being the salt of a strong acid H_2SO_4 and a strong base. NaOH does not undergo hydrolysis. The solution is, therefore, neutral.	1
		1
	[ii]More the value of Ka, the stronger the acid Their Ka values are $6.7 \times 10^{-4} > 1.8 \times 10^{-5} > 7.2 \times 10^{-10}$	1

172

	∴ HCN < CH₃COOH < HF.	1
27	Sp³d hybridization involving one s orbital three p orbitals and one d orbital of Phosphorus. 5 Cl atoms form covalent bonds with 5 Sp³d hybrid orbitals of Phosphorus .Structure-Trigonal bipyramidal. **.** Three P–Cl bond lie in one plane and make an angle of 120° with each other; these bonds are termed as equatorial bonds. The remaining two P–Cl bonds–one lying above and the other lying below the equatorial plane, make an angle of 90° with the plane. These bonds are called axial bond.	1
	In PCl₅ ,two P–Cl bonds–one lying above and the other lying below the equatorial plane, called as axial bonds make an angle of 90° with the plane. As the axial bond pairs suffer more repulsive interaction from the equatorial bond pairs, they are slightly longer and hence slightly weaker.	1 1
28	[i]CH₃-CH₂-CH=CH₂ $\xrightarrow{HBr/Peroxide}$ CH₃-CH₂-CH₂-CH₂ Br(1-Bromobutane) [ii] CH₃-CH₂-CH=CH- CH₃ $\xrightarrow[ZnH2O]{O3}$ CH₃-CH₂-CHO[propanal] + CH₃- CHO[ethanal] [iii] C₆H₅OH $\xrightarrow[Zn\ dust]{}$] C₆H₆ [benzene] + ZnO	1 1 1
29	Balanced equation→ 4HCl (aq) + MnO₂(s) →2 H₂O (l) + MnCl₂(aq) + Cl₂ (g) 4 moles of HCl reacts with 1 mole of MnO₂ [4x 36.5]g of HCl react with [1x 87]g of MnO₂ 5g of MnO₂ react with 5x4x36.5/87 g of HCl = 8.4g of HCl	1 1 1
30	1/λ = Z² R_H [1/n₁² - 1/n₂²] = Z² R_H [1/2² -1/4²] = 3/4 R_H…………………(1) For a hydrogen atom 1/λ = R_H [1/n₁² - 1/n₂²]………….(2) Equating eqn 1 and eqn2 3/4= [1/n₁² - 1/n₂²] This equation gives n₁ = 1 and n₂ = 2 . Thus the transition n=2 to n=1 in hydrogen atom will have same wavelength as transition, n=4to n=2 in He⁺·	1 1 1
	SECTION D	
31	[i] [c]0 [ii] [d]2 [iii] [c] 2 [iv][c]Assertion is correct statement but reason is wrong statement.	1 1 1 1
32	[i][a] CH₂=CH–C≡CH [ii][b]18sigma 3pi [iii] [a]Methyl chloride [iv][a] Assertion and reason both are correct statements and reason is correct explanation for assertion.	1 1 1 1
	SECTION E	
33	[i]ΔH_R=[2×ΔH_f°(Fe₂O₃(s))]−[4ΔH_f°(Fe(s))+3×ΔH_f°(O₂)] =[2x 824.2]-[0] = 1684.4 kJ mol⁻¹ [ii] ΔH° for formation of CO₂ = -393.5kJmol⁻¹ ΔH° for combustion of C =-393.5kJmol⁻¹ [iii] ΔH=ΔU + pΔV For an appreciable volume change in a gaseous reaction taking place at ideal conditions,	1 1 1

Let V_A represent the volume of gaseous reactants

V_B represent the volume of gaseous products

n_A be the moles of reactant

n_B be the moles of product

At constant pressure and temperature

$pV_A = n_A RT$ 1

$pV_B = n_B RT$ 2

2-1 gives

$pV_B - pV_A = (n_B - n_A)RT$

$p\Delta V = \Delta n_g RT$

$\Delta n_g = n_B - n_A$

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

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

OR

[I] The combustion reaction of ethylene gas is as follows

$C_2H_4 + 3O_2 \rightarrow 2CO_2(g) + 2H_2O(g))$

$\Delta H_f(CO_2) = -393.7 KJ$

$\Delta H_f(H_2O) = -241.8 KJ$

$\Delta H_f(C_2H_4) = +52.7 KJ$

$\Delta HR = \sum \Delta H_f^o(p) - \sum \Delta H_f^o(r)$

$\Delta HR = [2 \times \Delta H_f^o(CO_2) + 2 \times \Delta H_f^o(H_2O)] - [\Delta H_f^o(C_2H_4) + 3 \times \Delta H_f^o(O_2)]$

$\Delta HR = [2 \times -393.7 + 2 \times -241.8] - [523 + 0]$ $\Delta HR = -1323.3 KJ$

[ii] $\Delta H = +61.17 kJmol^{-1}$

$\Delta S = +132 Jk^{-1}mol^{-1} = +0.132 kJk^{-1}mol^{-1}$

$\Delta G = \Delta H - T\Delta S$

Reaction becomes spontaneous when ΔG is negative

At equilibrium $\Delta G = 0$. $\Delta H = T\Delta S$

Hence $T = \Delta H / \Delta S = +61.17 kJmol^{-1} / +0.132 kJk^{-1}mol^{-1}$

$= 463.4 k$

At temperature above 463.4K ΔG becomes negative and the reaction becomes spontaneous.

34	[i]Electrophiles:. Electrophiles are electron deficient. They may be positive ions or neutral molecules.	1

Ex: Br^+, NO_2^+, $AlCl_3$, BF_3

Nucleophiles: attacks the region of low electron density (positive centres) in a substrate molecule. They are electron rich they may be negative ions or neutral molecules.

Ex: Cl^-, CN^-, H_2O, ROH etc.

[ii]Mass of the compound = 0.3780 g

Mass of silver chloride = 0.5740 g

$$\text{Percentage of chlorine} = \frac{35.5}{143.5} \times \frac{\text{Mass of siliver chloride}}{\text{Mass of compound}} \times 100$$

$$= \frac{35.5}{143.5} \times \frac{(0.5740 \text{ g})}{(0.3780 \text{ g})} \times 100 = 37.57 \text{ g}$$

[iii] Steam volatile and insoluble in water.

OR

Inductive Effect: The inductive effect refers to the polarity produced in a molecule as a result of higher electro negativity of one atom compared to another. Atoms or groups which lose electron towards a carbon atom are said to have +1 Effect.

Those atoms or groups which draw electron away from a carbon atom are said to have -I Effect. Common examples of -I effect are:

NO_2, F, Cl, Br, I, OH etc.

Examples of +1 effect are (Electron releasing)

$(CH_3)_3C—$, $(CH_3)_2CH—$, $CH_3CH_2— CH_3—$ etc.

Electromeric effect: The electromeric effect refers to the polarity produced in a multiple bonded compound as it is approached by a reagent.

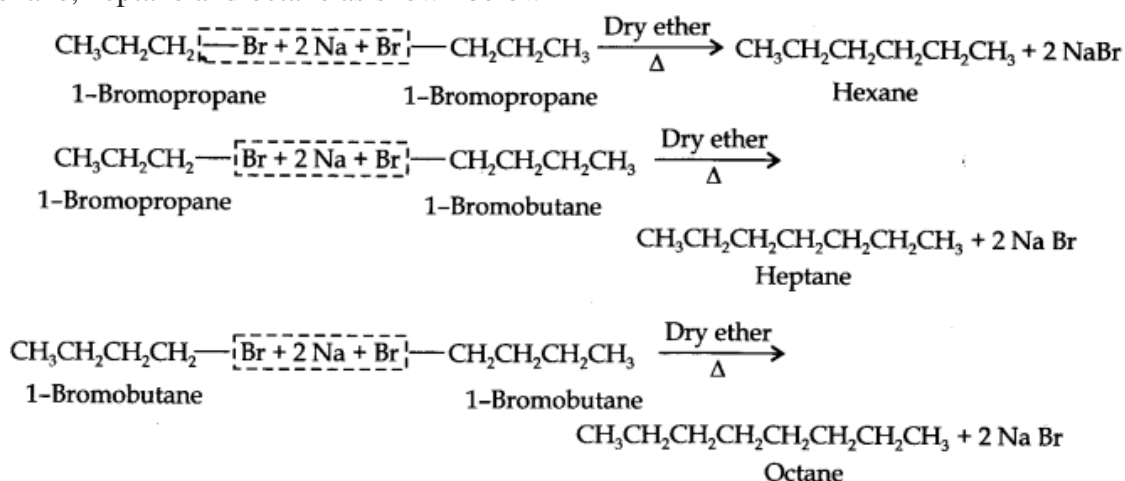[ii] Mass of the compound = 0.468 g

   Mass of barium sulphate= 0.668 g

$$\text{Percentage of sulphur} = \frac{32}{233} \times \frac{\text{Mass of barium sulphate}}{\text{Mass of compound}} \times 100$$

$$= \frac{32}{233} \times \frac{(0.668\ g)}{(0.468\ g)} \times 100 = \mathbf{19.60\%}$$

[iii] **By distillation under reduced pressure**

	1
	1
	1
	1
	1

| 35 | **[i]** For preparation of alkanes containing odd number of carbon atoms, a mixture of two alkyl halides has to be used. Since two alkyl halides can react in three different ways, therefore, a mixture of three alkanes instead of the desired alkane would be formed. For example, Wurtz reaction between '1-bromopropane and 1-bromobutane gives a mixture of three alkanes i.e., hexane, heptane and octane as shown below: | 1 |

$CH_3CH_2CH_2 \!\!—\! Br + 2 Na + Br \!—\! CH_2CH_2CH_3 \xrightarrow[\Delta]{\text{Dry ether}} CH_3CH_2CH_2CH_2CH_2CH_3 + 2\ NaBr$

1-Bromopropane   1-Bromopropane   Hexane

$CH_3CH_2CH_2—\! Br + 2 Na + Br \!—\! CH_2CH_2CH_2CH_3 \xrightarrow[\Delta]{\text{Dry ether}}$

1-Bromopropane   1-Bromobutane

$CH_3CH_2CH_2CH_2CH_2CH_3 + 2\ Na\ Br$

Heptane

$CH_3CH_2CH_2CH_2—\! Br + 2 Na + Br \!—\! CH_2CH_2CH_2CH_3 \xrightarrow[\Delta]{\text{Dry ether}}$

1-Bromobutane   1-Bromobutane

$CH_3CH_2CH_2CH_2CH_2CH_2CH_3 + 2\ Na\ Br$

Octane

[ii]**During the hydrohalogenation of an asymmetric <u>alkene</u>, the acidic <u>hydrogen atom</u> combines with the doubly bonded <u>carbon</u> atom having the most hydrogen substituent's, while the <u>halide</u> group binds to the carbon atom with the most alkyl substituent's."**

 Mechanism steps
Illustration

OR

[i]Alkyl halides (R-X) on heating with alcoholic potash (potassium hydroxide dissolved in alcohol, eliminate one molecule of halogen acid to form alkenes. This reaction is known as

dehydrohalogenation i.e., removal of halogen acid. This is example of β-elimination reaction, since hydrogen atom is eliminated from the β carbon atom (carbon atom next to the carbon to which contains the halogen)

$$CH_3CH_3Cl \xrightarrow{\text{alc KOH,heat}} CH_2=CH_2$$
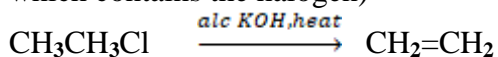
[ii]**Electrophillic substitution in benzene**

(a) Generation of the electrophile During chlorination, alkylation and acylation of benzene, anhydrous $AlCl_3$, being a Lewis acid helps in generation of the electrophile Cl^+, R^+, RCO^+ (acylium ion) respectively by combining with the attacking reagent. In the case of nitration, the electrophile, nitronium ion, NO_2^+ is produced by transfer of a proton (from sulphuric acid) to nitric acid

(b) Formation of Carbocation (arenium ion): Attack of electrophile results in the formation of σ-complex or arenium ion in which one of the carbon is sp3 hybridised. sigma complex (arenium ion) The arenium ion gets stabilized by resonance:

(c) Removal of proton from the carbocation intermediate .

1

1

1

1

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SAMPLE PAPER 4   2022-2023
CHEMISTRY CLASS XI

S.NO	CHAPTERS	1M	2M	3M	4M	5M	Total
1	Some basic concepts of chemistry	2(1)	1(2)				4
2	Stucture of atoms	2(1)	1(2)	1(3)			7
3	Classification of elements	2(1)	1(2)			1(5)	9
4	Chemical bonding and molecular structure	2(1)	1(2)	1(3)	1(4)		11
5	Chemical Thermodynamics	2(1)	1(2)				4
6	Equilibrium	2(1)	1(2)	1(3)			7
7	Redox reactions	2(1)	1(2)				4
8	Organic Chemistry: some basicprinciples	2(1)		1(3)	1(4)	1(5)	14
9	Hydrocarbons	2(1)		1(3)		1(5)	10
		18	14	15	8	15	70

SAMPLE PAPER 4 (2022-23)

CHEMISTRY THEORY

CLASS XI

Time: 3 hours

MM:70

General Instructions: Read the following instructions carefully.

a) There are 35 questions in this question paper with internal choice.

b) SECTION A consists of 18 multiple-choice questions carrying 1 mark each.

c) SECTION B consists of 7 very short answer questions carrying 2 marks each.

d) SECTION C consists of 5 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

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section

1. What will be the molality of the solution containing 18.25 g of HCl gas in 500 g of water?

(i) 0.1 m

(ii) 1 M

(iii) 0.5 m

(iv) 1 m

2. If the concentration of glucose ($C_6H_{12}O_6$) in blood is 0.9 g L–1, what will be the molarity of glucose in blood?

(i) 5 M

(ii) 50 M

(iii) 0.005 M

(Iv) (iv) 0.5 M

3. The pair of ions having same electronic configuration is _____.

(i) Cr3+, Fe3+

(ii) Fe3+, Mn2+

(iii) Fe3+, Co3+

(iv) Sc3+, Cr3+

4. Which of the following statements concerning the quantum numbers are correct?

(i) Angular quantum number determines the three dimensional shape of the orbital.

(ii) The principal quantum number determines the orientation and energy of the orbital.

(iii) Magnetic quantum number determines the size of the orbital.

(iv) Spin quantum number of an electron determines the orientation of the

5. The elements in which electrons are progressively filled in 4f-orbital are called

(i) actinoids

(ii) transition elements

(iii) lanthanoids

(iv) halogens

6. The period number in the long form of the periodic table is equal to

(i) magnetic quantum number of any element of the period.

(ii) atomic number of any element of the period.

(iii) maximum Principal quantum number of any element of the period.

(iv) maximum Azimuthal quantum number of any element of the period.

7. Which of the following species has tetrahedral geometry?

  (i) BH^{4-}

  (ii) NH^{2-}

  (iii) CO_3^{2-}

  (iv) H_3O^+

8. In which of the following substances will hydrogen bond be strongest?

(i) HCl

(ii) H_2O

(iii) HI

(iv) H_2S

9. Enthalpy of sublimation of a substance is equal to

(i) enthalpy of fusion + enthalpy of vapourisation

(ii) enthalpy of fusion

(iii) enthalpy of vapourisation

(iv) twice the enthalpy of vapourisation

10. Which of the following is not correct?

(i) ΔG is zero for a reversible reaction

(ii) ΔG is positive for a spontaneous reaction

(iii) ΔG is negative for a spontaneous reaction

(iv) ΔG is positive for a non-spontaneous reaction

11. We know that the relationship between Kc and Kp is $Kp = K_c(RT)^{\Delta n}$

What would be the value of Δn for the reaction

$$NH_4Cl\ (s) \rightarrow\ NH_3\ (g) + HCl\ (g)$$

(i) 1

(ii) 0.5

(iii) 1.5

(iv) 2

12. For the reaction $H_2(g) + I_2(g) \rightarrow 2HI\ (g)$, the standard free energy is $\Delta G^0 > 0$.

The equilibrium constant (K) would be _____.

(i) K = 0

(ii) K > 1

(iii) K = 1

(iv) K < 1

13 . Which of the following is not an example of redox reaction?

(i) $CuO + H_2 \rightarrow Cu + H_2O$

(ii) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

(iii) $2K + F_2 \rightarrow 2KF$

(iv) $BaCl_2\ +\ H_2SO_4 \rightarrow\ BaSO_4 + 2HCl$

14. Using the standard electrode potential, find out the pair between which redox

reaction is not feasible. E^0 values : $Fe^{3+}/Fe^{2+} = + 0.77$; $I_2/I^- = + 0.54$; $Cu^{2+}/Cu = + 0.34$; $Ag^+/Ag = + 0.80$ V

(i) Fe^{3+} and I^-

(ii) Ag^+ and Cu

(iii) Fe^{3+} and Cu

(iv) Ag and Fe^{3+}

15. Assertion (A) : Energy of resonance hybrid is equal to the average of energies of all canonical forms.

Reason (R) : Resonance hybrid cannot be presented by a single structure.

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

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

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct

16. Assertion (A) : Pent- 1- ene and pent- 2- ene are position isomers.

Reason (R) : Position isomers differ in the position of functional group or a substituent.

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

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

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.is not correct but R is correct.

17. Assertion (A) : Toluene on Friedal Crafts methylation gives o– and p–xylene.

Reason (R) : CH3-group bonded to benzene ring increases electron density at o– and p– position.

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

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

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

18 . Assertion (A) : Nitration of benzene with nitric acid requires the use of concentrated sulphuric acid.Reason (R) : The mixture of concentrated sulphuric acid and concentrated nitric acid produces the electrophile, NO2+.

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

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

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

SECTION B

This section contains 7 questions with internal choice in two questions. The following questions are very short answer type and carry 2 marks each.

19. What will be the mass of one atom of C-12 in grams?

20. Arrange s, p and d sub-shells of a shell in the increasing order of effective nuclear charge (Zeff) experienced by the electron present in them.

Or

Calculate the total number of angular nodes and radial nodes present in 3p orbital.

21. Explain why the electron gain enthalpy of fluorine is less negative than that of chlorine.

Or

All transition elements are d-block elements, but all d-block elements are not transition elements. Explain.

22. Distinguish between a sigma and a pi bond.

23. If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1bar and 100°C is 41kJ mol–1. Calculate the internal energy change, when 1 mol of water is vapourised at 1 bar pressure and 100°C.

24. The following concentrations were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500K. $[N_2] = 1.5 \times 10^{-2}$M. $[H_2] = 3.0 \times 10^{-2}$ M and [NH3] = 1.2×10^{-2}M. Calculate equilibrium constant.

25. What is Disproportionation reaction?

SECTION C

This section contains 5 questions with internal choice in 2 questions. The following questions are short answer type and carry 3 marks each.

26. Calculate energy of one mole of photons of radiation whose frequency is 5×10^{14} Hz.

27. What is meant by hybridisation of atomic orbitals? Describe the shapes of sp, sp2 , sp3 hybrid orbitals.

28. At 473 K, equilibrium constant Kc for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3}. If decomposition is depicted as, PCl_5 (g)$\rightarrow$ PCl_3 (g) + Cl_2 (g) Δ_rH 0 = 124.0 kJ mol^{-1}
a) write an expression for Kc for the reaction.
b) what is the value of Kc for the reverse reaction at the same temperature ?
c) what would be the effect on Kc if (i) more PCl_5 is added (ii) pressure is increased (iii) the temperature is increased.

29. Write bond line formulas for : Isopropyl alcohol, 2,3-Dimethylbutanal, Heptan-4- one.

30. Draw the cis and trans structures of hex-2-ene. Which isomer will have higher b.p. and why?

SECTION D

The following questions are case-based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

31. Read the passage and answer the questions

Molecular orbitals are formed by the overlap of atomic orbitals. Two atomic orbitalscombine to form two molecular orbitals called bonding molecular orbital (BMO)and anti bonding molecular orbital (ABMO). Energy of anti bonding orbital is raisedabove the parent atomic orbitals that have combined and the energy of the bondingorbital is lowered than the parent atomic orbitals. Energies of various molecular orbitals for elements hydrogen to nitrogen increase in the order :

Different atomic orbitals of one atom combine with those atomic orbitals of the second atom which have comparable energies and proper orientation. Further, if the overlapping is head on, the molecular orbital is called 'Sigma', (σ) and if the overlap is lateral, the molecular orbital is called 'pi', (π). The molecular orbitals are filled with electrons according to the same rules as followed for filling of atomic orbitals. However, the order for filling is not the same for all molecules or their ions. Bond order is one of the most important parameters to compare the strength of bonds.

Answer the following .

a. Calculate the bond order for Hydrogen molecule.

b. Calculate the bond order for He

c. Calculate the bond order and magnetic nature of Oxygen molecule

    or

Calculate the bond order and magnetic nature of Flourine molecule

32. The Lewis structure or dot structure, dash structure, condensed structure and bond line structural formulas are some of the specific types. The Lewis structures, however, can be simplified by representing the two-electron covalent bond by a dash (–). Such a structural formula focuses on the electrons involved in bond formation. A single dash represents a single bond, double dash is used for double bond and a triple dash represents triple bond. Lone- pairs of electrons on heteroatoms (e.g., oxygen, nitrogen, sulphur, halogens etc.) may or may not be shown. Thus, ethane (C_2H_6), ethene (C_2H_4), ethyne (C_2H_2) and methanol (CH_3OH) can be represented by the following structural formulas. Such structural representations are called complete structural formulas. For simplification, organic chemists use another way of representing the structures, in which only lines are used. In this bond-line structural representation of organic compounds, carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are drawn in a zig-zag fashion. The only atoms specifically written are oxygen, chlorine, nitrogen etc. The terminals denote methyl ($-CH_3$) groups (unless indicated otherwise by a functional group), while the line junctions denote carbon atoms bonded to appropriate number of hydrogens required to satisfy the valency of the carbon atoms.

a. How many sigma and pi bonds are there in but- 2-ene?

b. The terminal group denote which group in bond line formula?

C Represent the bond line formula of 2- bromo butane.

                Or

Represent the bond line formula of cyclopropane.

33. The first ($\Box iH1$) and the second ($\Box iH2$) ionization enthalpies (in kJ mol–1)and the ($\Box egH$) electron gain nthalpy (in kJ mol–1) of a few elements aregiven below:Elements
$\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box$ $\Box$

	$\Box H1$	$\Box H2$	$\Box egH$
I	520	7300	–60
II	419	3051	–48

III	1681	3374	–328
IV	1008	1846	–295
V	2372	5251	+48
VI	738	1451	–40

Which of the above elements is likely to be :

(a) the least reactive element.

(b) the most reactive metal.

(c) the most reactive non-metal.

(d) the least reactive non-metal.

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

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

Or

Predict the formulas of the stable binary compounds that would be formed by the combination of the following pairs of elements.

(a) Lithium and oxygen   (b) Magnesium and nitrogen

(c) Aluminium and iodine   (d) Silicon and oxygen

(e) Phosphorus and fluorine

34.a). What is metamerism?

b). What type isomerism is shown by propanone and propanal

c). Identify the type of isomerism in propa-1-ol and propan-2-ol

d). In which C-C bond of bromopropane the inductive effect is least?

e). Write the resonance structure of acetate ion.

Or

a. Give a brief description of the principles of the following techniques taking an example in each case.

(a) Crystallisation   (b) Distillation   (c) Chromatography

b.What is the difference between distillation, distillation under reduced pressure and steam distillation ?

35.a). Write IUPAC names of the products obtained by addition reactions of HBr to hex-1-ene

(i) in the absence of peroxide and   (ii) in the presence of peroxide

b). How will you convert ethanoic acid into benzene.

c). Write Friedel craft alkylation and acylation reaction.

SAMPLE PAPER 4 (2022-23)

CHEMISTRY THEORY

CLASS XI

ANSWER KEY

(SECTION A each correct answer 1 mark)

1. IV-
2. III
3. II
4. I
5. III
6. III
7. I
8. II
9. I
10. II
11. IV
12. IV
13. IV
14. IV
15. I
16. I
17. I
18. I

SECTION B

19. 1.992648 × 10–23 g ≈ 1.99 × 10–23 g   (2)

20. d < p < s   OR   For 3p orbital n = 3, l = 1   (2)
    Number of angular nodes = l = 1
    Number of radial nodes = n – l – 1 = 3–1–1=1

21. The added electron in fluorine goes to second quantum level. Due to small lsize of fluorine it experiences repulsion from other electrons much more in comparison to that in chlorine because in chlorine, the electron is added to 3rd quantum level in which larger space is available for movement.   (2)

                    Or

    Elements with fully filled d orbitals are not transition elements.   (2)

22.   Sigma(σ) bond : This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap.   (1)
      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   (1)

23. (i) The change, substituting the.The equation for enthalpy $\Delta H = \Delta U + \Delta n_g RT$ (1)

= 41.00 kJ mol^{-1} – 3.096 kJ mol.= 37.904 kJ mol^{-1} (1)

24. The equilibrium constant for the reaction, (1)
    $N_2(g) + 3H_2(g)$ $2NH_3(g)$ can be written

   Write kc Substitute and final answer 1.06×10^{3} (refer TEXT BOOK (1)

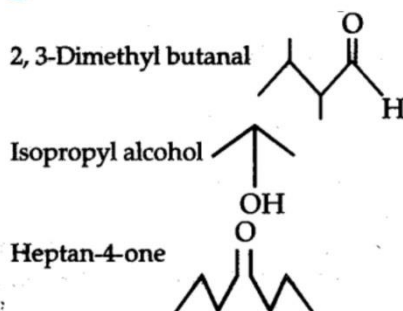25. Definition (1)
    Example (1)

SECTION C

26. E = hV (1)

   Substituting the value and calculating 199.51 KJmol-1 (2)

27. correct explanation (1)
    Correct shape (2)

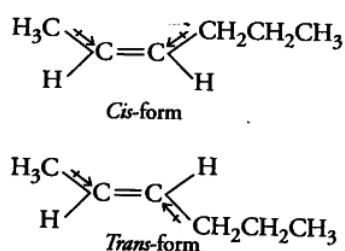28 a).kc= [PCl_3] [Cl_2]/ [PCl_5] (1)
   b) Kc" = 1/kc (1)
   c)no change / no change /kc will increase (1)

29.
                                                    (Each correct Answer 1 mark)

2, 3-Dimethyl butanal
Isopropyl alcohol
Heptan-4-one

30. (2)

Cis-form
Trans-form

Cis- form is more polar than trans-form i.e., cis-form has higher dipole moment than trans-form. Thus, the boiling point of cis-isomer is greater than that of trans-isomer because of the greater dipole-dipole interactions between the molecules in it. further more trans-isomer of hex-2-ene is almost non-polar (1)

31.a) Bond order for H2 is 1
   b) Bond order for He is 0   (each 1 mark)
   c) Bond order for O2 is 2   (each 2 mark)
   or
   Bond order for F2 is 1

32. a) 1 pi bond and 11 sigma bond (1)
   b) methyl group (1)
   c) (2)

OR

(1 mark for each correct answer)

33. a) The element   V has highest first IE and p ositive electron gain enthalpy and hence least reactive. Since inert gases have positive electron gain enthalpy so the element must be a inert gas. So may be He

   b)The element II which has least first IE and low negative electron gain enthalpy is most reactive so it must be K

   c) The element III   which has   high first IE and very high negative   EG is most reactive   non metal so it must be fluorine

   d) The   element IV has a high   negative electron gain enthalpy   but so high first IE .So it the least reactive non metal ,it is Iodine

   e) The element VI   has low first IE but higher than   that of alkali metal. So It is Alkaline Earth metal and forms   binary halide. It is Mg

OR

a) Li_2O
b) Mg_3N_2
c) AlI_3
d) SiO_2
e) PF_3 or PF_5

34. a) Metamers are the isomers having the same molecular formula but different alkyl groups on two sides of functional groups.... (1)

   b) Functional isomerim (1)

   c) C_2 and C_3 (1)
   d) Refer NCERT text book (2)

OR

(1 mark for each correct answer)

(a) Crystallisation Crystallisation is one of the most commonly used techniques for the purification of solid organic compounds. Principle: It is based on the difference in the solubilities of the compound and the impurities in a given solvent. The impure compound gets dissolved in the solvent in which it is sparingly soluble at room temperature but appreciably soluble at higher temperature. The solution is concentrated to obtain a nearly saturated solution. On cooling the solution, the pure compound crystallises out and is removed by filtration.

(b) Distillation This method is used to separate volatile liquids from non-volatile impurities or a mixture of those liquids that have a sufficient difference in their boiling points. Principle: It is based on the fact that liquids having different boiling points vaporise at different temperatures. The vapours are then cooled and the liquids so formed are collected separately down

(c) Chromatography It is one of the most useful methods for the separation and purification of organic compounds. Principle: It is based on the difference in movement of individual components of a mixture through the stationary phase under the influence of mobile phase.

(2)

b) Distillation : It is used for the purification of compounds that are associated with non-volatile impurities or those liquids, which do not decompose on boiling. In other words, distillation is used to separate volatile liquids from non-volatile impurities or a mixture of those liquids that have sufficient difference in boiling points.

Distillation under reduced pressure : This method is used to purify a liquid that tends to decompose on boiling. Under the conditions of reduced pressure, the liquid will boil at a low temperature than its boiling point and will, therefore, not decompose

 Steam distillation : It is used to purify an organic compound, which is steam volatile and immiscible in water. On passing steam, the compound gets heated up and the steam gets condensed to water. After some time, the mixture of water and liquid starts to boil and passes through the condenser. This condensed mixture of water and liquid is then separated by using a separating funnel

 35. a) Refer NCERT Text book (Problem 13.12)   (2)
      b) Refer NCERT Text book (Problem 13.14)   (2)
      b) Refer NCERT Text book   (page number 392)   (1)