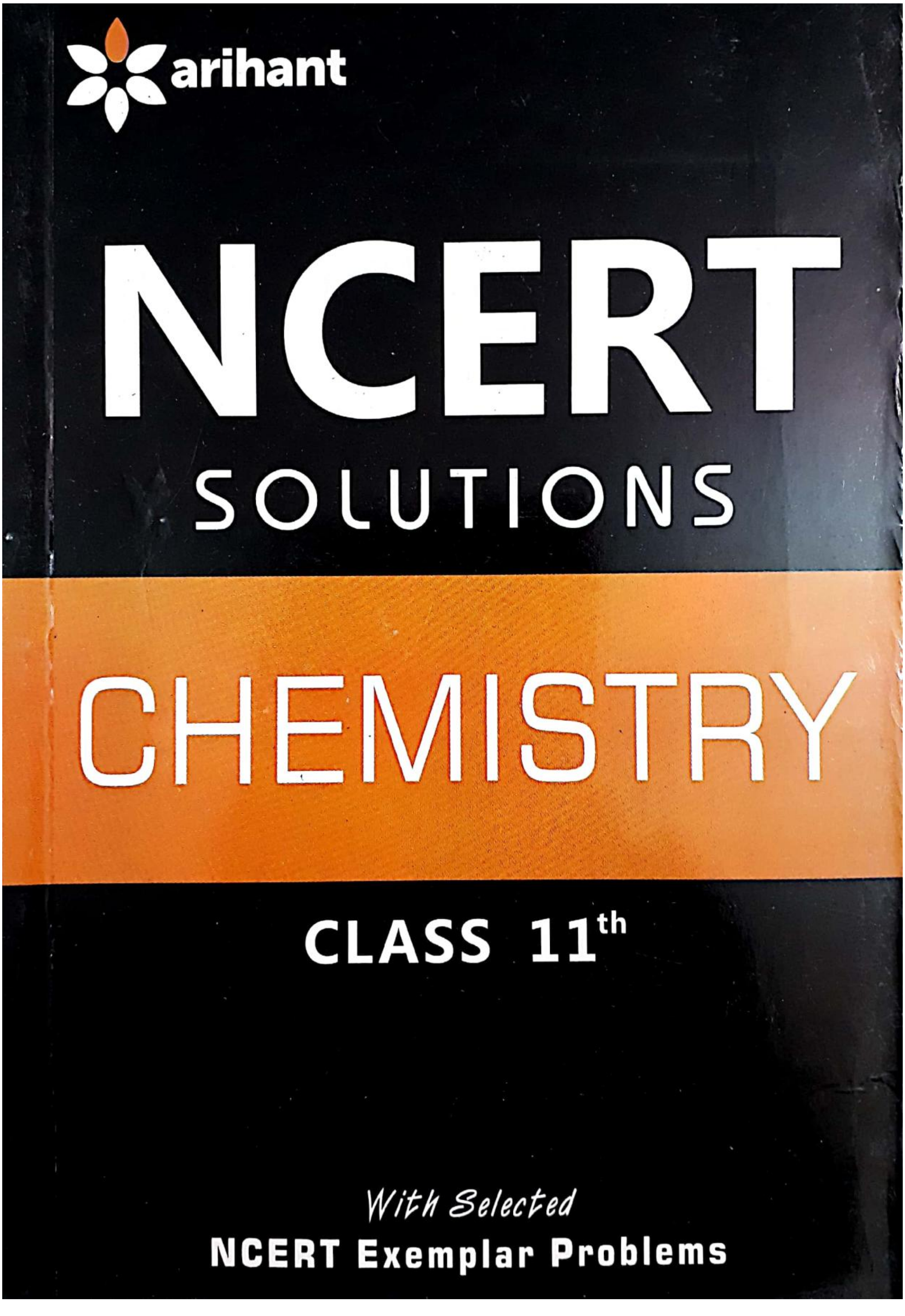


arihant

NCERT
SOLUTIONS

CHEMISTRY

CLASS 11th

With Selected
NCERT Exemplar Problems

NCERT SOLUTIONS

CHEMISTRY

CLASS 11th

by

Purnima Sharma

arihant
ARIHANT PRAKASHAN, MEERUT

Preface

Feeling the immense importance and value of NCERT books, we are presenting this book, having the NCERT Exercises Solutions.

For the overall benefit of the students we have made this book unique in such a way that it presents not only solutions but also detailed explanations. Through these detailed and through explanations, students can learn the concepts which will enhance their thinking and learning abilities.

We have introduced some **Additional Features** with the solutions which are given below :

Thinking Process (💡) Before giving solutions to questions we have discussed the points that tell how to approach to solve a problem. Here we have tried to cover all those loopholes which may lead to confusion. All formulae and hints are discussed in full detail.

Note We have provided notes also to solutions in which special points are mentioned which are of great value for the students.

This book also covers Solutions to selected problems of **NCERT Exemplar Problems.**

With the hope that this book will be of great help to the students, we wish great success to our readers.

Purnima Sharma

Contents

Course Structure

Class XI (Theory)

Paper One Time: 3 Hrs Max Marks: 70

	Class XI	Weightage
Unit I	Some Basic Concepts of Chemistry	5
Unit II	Structure of Atom	6
Unit III	Classification of Elements and Periodicity in Properties	4
Unit IV	Chemical Bonding and Molecular Structure	5
Unit V	States of Matter: Gases and Liquids	4
Unit VI	Thermodynamics	6
Unit VII	Equilibrium	6
Unit VIII	Redox Reactions	3
Unit IX	Hydrogen	3
Unit X	s -Block Elements	5
Unit XI	Some p -Block Elements	5
Unit XII	Organic Chemistry: Some basic Principles and Techniques	7
Unit XIII	Hydrocarbons	8
Unit XIV	Environmental Chemistry	3

Unit I **Some Basic Concepts of Chemistry**

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**

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**

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

Unit IV **Chemical Bonding and Molecular structure**

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

Unit V **States of Matter: Gases and Liquids**

Three states of matter, intermolecular interactions, types of bonding, melting and boiling points, role of gas laws in elucidating the concept of the molecule, Boyle's law, Charles law, Gay Lussac's law, Avogadro's law, ideal behaviour, empirical derivation of gas equation, Avogadro's number, ideal gas equation. Deviation from ideal behaviour, liquification of gases, critical temperature, kinetic energy and molecular speeds (elementary idea) Liquid State- vapour pressure, viscosity and surface tension (qualitative idea only, no mathematical derivations)

Unit VI **Chemical Thermodynamics**

Concepts of System and types of systems, surroundings, work, heat, energy, extensive and intensive properties, state functions. First law of thermodynamics -internal energy and enthalpy, heat capacity and specific heat, measurement of 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 of Thermodynamics (brief introduction) Introduction of entropy as a state function, Gibbs energy change for spontaneous and non - spontaneous processes, criteria for equilibrium. Third law of thermodynamics (brief introduction).

Unit VII **Equilibrium**

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, Henderson Equation, hydrolysis of salts (elementary idea), buffer solution, solubility product, common ion effect (with illustrative examples).

Unit VIII **Redox Reactions**

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 IX **Hydrogen**

Position of hydrogen in periodic table, occurrence, isotopes, preparation, properties and uses of hydrogen, hydrides-ionic covalent and interstitial; physical and chemical properties of water, heavy water, hydrogen peroxide - preparation, reactions and structure and use; hydrogen as a fuel.

Unit X ***s*-Block Elements**

(Alkali and Alkaline Earth Metals)

Group 1 and Group 2 Elements General introduction, electronic configuration, occurrence, anomalous properties of the first element of each group, diagonal relationship, trends in the variation of properties (such as ionization enthalpy, atomic and ionic radii), trends in chemical reactivity with oxygen, water, hydrogen and halogens, uses.

Preparation and Properties of Some Important Compounds: Sodium carbonate, sodium chloride, sodium hydroxide and Sodium hydrogencarbonate, biological importance of sodium and potassium. Calcium oxide and Calcium carbonate and their industrial uses, biological importance of Magnesium and Calcium.

Unit XI **Some p -Block Elements**

General Introduction to p -Block Elements, Group 13 Elements General introduction, electronic configuration, occurrence, variation of properties, oxidation states, trends in chemical reactivity, anomalous properties of first element of the group, Boron - physical and chemical properties, some important compounds, borax, boric acid, boron hydrides, Aluminium: Reactions with acids and alkalies, uses.

Group 14 Elements General introduction, electronic configuration, occurrence, variation of properties, oxidation states, trends in chemical reactivity, anomalous behaviour of first elements Carbon -catenation, allotropic forms, physical and chemical properties; uses of some important compounds: oxides. Important compounds of silicon and a few uses: silicon tetrachloride, silicones, silicates and Zeolites, their uses.

Unit XII **Organic Chemistry**

Some Basic Principles and Technique General introduction, methods of purification, qualitative and quantitative analysis, classification and IUPAC nomenclature of organic compounds. 100 Electronic displacements in a covalent bond: inductive effect, electromeric effect, resonance and hyper conjugation. Homolytic and heterolytic fission of a covalent bond: free radicals, carbocations, carbanions, electrophiles and nucleophiles, types of organic reactions.

Unit XIII **Hydrocarbons**

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

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

Unit XIV **Environmental Chemistry**

Environmental pollution - air, water and soil pollution, chemical reactions in atmosphere, smog, major atmospheric pollutants, acid rain, ozone and its reactions, effects of depletion of ozone layer, greenhouse effect and global warming- pollution due to industrial wastes, green chemistry as an alternative tool for reducing pollution, strategies for control of environment pollution.

Practicals

Evaluation Scheme for Examination Marks

Evaluation Scheme	
Volumetric Analysis	10
Salt Analysis	8
Content Based Experiment	6
Class Record, Project Viva	6
Total	**30**

Chapter 1

Some Basic Concepts of Chemistry

Important Results

1. Seven **basic SI units** for physical quantities are:
Length-metre (m), mass-kilogram (kg), time-second (s), temperature-kelvin (K), electric current-Ampere (A), Luminous intensity-Candela (Cd) and amount of substance-Mole (mol).
2. **Some useful conversion factors**

$$1\text{ pm} = 10^{-12}\text{ m},\ 1\text{ Å} = 10^{-10}\text{ m},\ 1\text{ nm} = 10^{-9}\text{ m}$$

$$1\text{ L} = 10^{-3}\text{ m}^3 = 1\text{ dm}^3;\ 760\text{ torr} = 101325\text{ Pa} = \text{Nm}^{-2}$$

$$1\text{ atm} = 1.01325\text{ bar}$$

$$1\text{ bar} = 10^5\text{ Nm}^{-2} = 10^5\text{ Pa};\ 1\text{ atm} = 760\text{ mm Hg} = 760\text{ torr}$$

$$1\text{ Calorie} = 4.184\text{ J},\ 1\text{ eV} = 1.6022 \times 10^{-19}\text{ J}$$

3. $\text{Mole} = \dfrac{\text{Mass (g)}}{\text{Molar mass (g mol}^{-1})}$
4. 1 mole of a substance $= N_0$ molecules $= 6.022 \times 10^{23}$ molecules
1 mole of an element $= N_0$ atoms $= 6.022 \times 10^{23}$ atoms
5. $1\text{ amu (or u)} = \dfrac{\text{Atomic mass}}{N_0}$ (N_0 = Avogadro number $= 6.022 \times 10^{23}$)
6. At STP ($T = 273$ K and $p = 1$ atm) 1 mole of an ideal gas occupies volume 22.4 L.
7. Molarity = concentration in mol L^{-1}.

$$\text{Molarity} = \frac{\text{Number of moles}}{\text{Volume in litres}}$$

8. Normality = concentration in g equi. L^{-1}.
   (i) Normality of an acid = molarity × basicity (basicity is the number of ionisable H^+ ions.
   (ii) Normality of a base = molarity × acidity (acidity is the number of ionisable OH^- ions).
9. Molality = concentration in mol per kg solvent.

10. Molality $= \dfrac{\text{Number of moles}}{\text{Mass of solvent (kg)}}$

11. Mass per cent $= \dfrac{\text{Mass of solute } \times 100}{\text{Mass of solution}}$

12. **Percentage composition** Mass % of an element

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

13. Mole fraction of the component 1 in the mixture of 1 and 2 with number of moles n_1 and n_2,

$$x_1 = \frac{n_1}{n_1 + n_2}; x_1 + x_2 = 1$$

So, $$x_1 = 1 - x_2$$

14. Empirical formula represents the simplest whole number ratio of various atoms present in a compound.

15. Molecular formula represents exact number of different types of atoms present in a molecule of a compound.

16. Molecular formula = $n \times$ empirical formula and

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

17. In a reaction, when the reactants are not present in the amounts as required by a balanced chemical reaction, in this case, one reactant is in excess over the other. The reactant which is present in lesser amount gets consumed first. This reactant is known as **limiting reagent** because it limits the amount of product.

18. Average molar mass of an element

$$\overline{M} = \frac{\text{Sum of isotopic molar mass} \times \text{\% abundance}}{100} \text{ or } \frac{\Sigma A_i \times P_i}{100}$$

where, P_i is the per cent abundance of isotope with atomic mass A_i.

or $$\overline{M} = \Sigma f_i \times A_i$$

where, f_i = fractional abundances of isotopes and A_i = their corresponding mass numbers.

Exercises

Question 1. **Calculate the molecular mass of the following.**
(i) H_2O (ii) CO_2 (iii) CH_4

(i) Molecular mass of a molecule is the sum of atomic masses of all the atoms present in the molecule.

(ii) Molecular mass of H = 1.0079
Molecular mass of O = 16.00
Molecular mass of C = 12.01

Solution.

(i) Molecular mass of H_2O = 2 × Atomic mass of hydrogen + 1 × Atomic mass of oxygen

$$= 2 \times 1.0079 \text{ u} + 1 \times 16.00 \text{ u} = 18.0158 \text{ u}$$

(ii) Molecular mass of CO_2 = 1 × Atomic mass of carbon + 2 × Atomic mass of oxygen

$$= 1 \times 12.01 \text{ u} + 2 \times 16.00 \text{ u} = 44.01 \text{ u}$$

(iii) Molecular mass of CH_4 = 1 × Atomic mass of carbon + 4 × Atomic mass of hydrogen

$$= 1 \times 12.01 \text{ u} + 4 \times 1.0079 \text{ u} = 16.0416$$

Question 2. Calculate the mass per cent of different elements present in sodium sulphate, Na_2SO_4.

Solution. Mass per cent of an element

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

Molar mass of $Na_2SO_4 = (2 \times 22.99) + 32.06 + (4 \times 16.00) = 142.04$ g

$$\text{Mass per cent of sodium} = \frac{45.98 \times 100}{142.04} = 32.37$$

$$\text{Mass per cent of sulphur} = \frac{32.06 \times 100}{142.04} = 22.57$$

$$\text{Mass per cent of oxygen} = \frac{64 \times 100}{142.04} = 45.06$$

Question 3. Determine the empirical formula of an oxide of iron which has 69.9% iron and 30.1% dioxygen by mass.

(i) Empirical formula shows the number of moles of different elements present in a molecule, so first find the relative number of moles of each element by dividing the mass percentage by respective atomic masses.

(ii) Divide the mole value obtained in above step by the smallest number, to obtain the simplest ratio.

(iii) Write the empirical formula by mentioning the numbers after writing the symbols of respective elements.

Solution.

Element	Symbol	% by mass	Atomic mass	Relative number of moles of element	Simple molar ratio	Simple whole number molar ratio
Iron	Fe	69.9	55.85	$\frac{69.9}{55.85} = 1.25$	$\frac{1.25}{1.25} = 1$	1 × 2 = 2
Oxygen	O	30.1	16.00	$\frac{30.1}{16.00} = 1.88$	$\frac{1.88}{1.25} = 1.5$	1.5 × 2 = 3

∴ Empirical formula = Fe_2O_3

Note *In case the ratios are not whole numbers, they may be converted into whole number by multiplying by the suitable coefficient.*

Question 4. **Calculate the amount of carbon dioxide that could be produced when**

(i) 1 mole of carbon is burnt in air.

(ii) 1 mole of carbon is burnt in 16 g of dioxygen.

(iii) 2 moles of carbon are burnt in 16 g of dioxygen.

(i) In order to find the moles of different elements/compounds taking part in the reaction, write a balanced chemical equation for combustion of carbon in dioxygen (air).

(ii) Calculate the amount of CO_2 produced with the help of information available from the balanced chemical equation.

Solution.

$$\begin{array}{cccc} C(s) & +\,O_2(g) & \longrightarrow & CO_2(g) \\ 1\text{ mol} & 1\text{ mol} & & 1\text{ mol} \\ & 32\text{ g} & & 44\text{ g} \end{array}$$

(i) According to the equation when 1 mole of carbon is burnt completely, CO_2 produced is 44 g.

(ii) 1 mole of carbon requires 32 g dioxygen from the reaction. But we have only 16g dioxygen. Hence, dioxygen is the limiting reagent. So, the amount of CO_2 produced by 16 g dioxygen is 22 g.

(iii) In this case again, dioxygen is the limiting reagent. 16 g dioxygen can react only with 0.5 mole of carbon and produce 22 g CO_2.

Note *Limiting reagent limits the amount of product formed because it is present in lesser amount and gets consumed first.*

Question 5. **Calculate the mass of sodium acetate, CH_3COONa required to make 500 mL of 0.375 molar aqueous solution. Molar mass of sodium acetate is 82.0245 g mol^{-1}.**

Solution. $$\text{Molarity} = \frac{w \times 1000}{m \times \text{volume of solution (mL)}}$$

where, w = mass of solute and m = molar mass of solute.

Given, molarity of the solution = 0.375 M

Molar mass of solute, m = 82.0245 g mol^{-1}

Volume of solution = 500 mL

Mass of solute = ?

$$\therefore \text{ Mass of solute, } w = \frac{0.375 \times 82.0245 \times 500}{1000} = 15.379\text{ g} \approx 15.38\text{ g}$$

Question 6. **Calculate the concentration of nitric acid in mol per litre in a sample which has a density, 1.41 g mL^{-1} and the mass per cent of nitric acid in it being 69%.**

(i) We know that molarity $= \dfrac{w \times 1000}{m \times V}$ so in order to calculate molarity, we require mass and molar mass of solute and volume of the solution. To calculate mass convert mass per cent into gram.

(ii) Calculate, molar mass of nitric acid by adding atomic masses of different atoms and volume of solution by using the formula, $d = \frac{m}{V}$.

(iii) Now put these values in the formula of molarity.

Solution. $$\text{Molarity} = \frac{w \times 1000}{m \times \text{volume of solution (mL)}}$$

Given, $d = 1.41 \text{ g mL}^{-1}$, mass % of $HNO_3 = 69\%$

69% HNO_3 means 100 g of its solution contains 69 g HNO_3 (nitric acid). Hence, mass of HNO_3 (solute) = 69 g.

Molar mass of nitric acid,

$HNO_3 = 1.0079 + 14.0067 + (3 \times 16.00) = 63.0146 \text{ g mol}^{-1}$

$$\text{Density, } d = \frac{m}{V} \text{ or } V = \frac{m}{d} = \frac{100 \text{ g}}{1.41 \text{ g mL}^{-1}}$$

$$\text{Molarity} = \frac{w \times 1000}{m \times \text{volume of solution (mL)}}$$

$$= \frac{69 \times 1000 \times 1.41}{63.0146 \times 100} = 15.439 \text{ M}$$

Note *Concentration of a substance in mol per litre is known as molarity.*

Question 7. **How much copper can be obtained from 100 g of copper sulphate ($CuSO_4$)?**

Solution. Molar mass of $CuSO_4 = 63.54 + 32.06 + (4 \times 16)$

$= 159.6 \text{ g mol}^{-1}$

$$159.6 \text{ g } CuSO_4 \text{ contains} = 63.54 \text{ g Cu}$$

$$1 \text{ g } CuSO_4 \text{ contains} = \frac{63.54}{159.6} \text{ g Cu}$$

$$\therefore \quad 100 \text{ g } CuSO_4 \text{ contains} = \frac{63.54 \times 100}{159.6} = 39.81 \text{ g Cu}$$

Question 8. **Determine the molecular formula of an oxide of iron in which the mass per cent of iron and oxygen are 69.9 and 30.1 respectively. Given that molar mass of the oxide is 159.89 mol^{-1}.**

(i) We know that molecular formula = (empirical formula)$_n$ so find the empirical formula.

(ii) Then, find the value of n by using the formula

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

(iii) Multiply empirical formula by n to get the molecular formula.

Solution. Calculation of empirical formula (see solution of Q. 3 as similar data is given). Empirical formula mass of

$$Fe_2O_3 = (2 \times 55.85) + (3 \times 16.00) = 159.7 \text{ g mol}^{-1}$$

$$n = \frac{\text{Molar mass}}{\text{Empirical formula mass}} = \frac{159.8}{159.7} = 1$$

Hence, molecular formula is same as empirical formula; Fe_2O_3.

Question 9. Calculate the atomic mass (average) of chlorine using the following data.

Isotope	% natural abundance	Molar mass
^{35}Cl	75.77	34.9689
^{37}Cl	24.23	36.9659

Solution. Average atomic mass is the sum of the products of fractional abundances (f_i) of the isotopes and their corresponding mass number (A_i).

Average atomic mass, $\overline{A} = \Sigma f_i \cdot A_i = f_1 \times A_1 + f_2 \times A_2 + \ldots\ldots$

Isotope	% natural abundance	Fractional abundance	Molar mass
^{35}Cl	75.77	0.7577	34.9689
^{37}Cl	24.23	0.2423	36.9659

Average atomic mass,

$$\overline{A} = 0.7577 \times 34.9689 + 0.2423 \times 36.9659$$
$$= 26.4959 + 8.9568 = 35.4527$$

Question 10. **In three moles of ethane (C_2H_6), calculate the following.**

(i) Number of moles of carbon atoms.
(ii) Number of moles of hydrogen atoms.
(iii) Number of molecule of ethane.

Solution.

(i) 1 mole of ethane, C_2H_6 contains 2 moles of carbon atoms.
$\therefore$ 3 moles of ethane, C_2H_6 will contain $2 \times 3 = 6$ moles of C-atoms.

(ii) 1 mole of ethane, C_2H_6 contains 6 moles of H-atoms.
$\therefore$ 3 moles of ethane, C_2H_6 will contain $3 \times 6 = 18$ moles of H-atoms.

(iii) 1 mole of ethane $= 6.022 \times 10^{23}$ molecules of ethane.
$\therefore$ 3 moles of ethane $= 3 \times 6.022 \times 10^{23} = 18.066 \times 10^{23}$ molecules of ethane.

Question 11. **What is the concentration of sugar ($C_{12}H_{22}O_{11}$) in mol L^{-1} if its 20g are dissolved in enough water to make a final volume up to 2 L?**

To find molar concentration, calculate the molar mass of the sugar, by adding atomic masses of different elements as molarity $= \frac{w}{m \times V}$.

Solution. Molar mass of the sugar, $C_{12}H_{22}O_{11}$,

$$m = (12 \times 12.01) + (22 \times 1.0079) + (11 \times 16.00)$$
$$= 342.2938 \text{ g mol}^{-1} \approx 342$$

Given, $w = 20\text{ g}, V = 2\text{ L}$

$$\text{Molarity} = \frac{w}{m \times V\text{ (L)}} = \frac{20}{342 \times 2} = 0.0292\text{ mol L}^{-1}$$

$$= 0.0292\text{ M}$$

Question 12. If the density of methanol is 0.793 kg L^{-1}, what is its volume needed for making 2.5 L of its 0.25 M solution?

(i) In case of dilution, volume is calculated by using molarity equation, $M_1V_1 = M_2V_2$, we have M_2, V_2 but not M_1, so calculate molarity of the given solution from density.

(ii) Then, find volume (V_1) needed by using molarity equation, $M_1V_1 = M_2V_2$

Solution. Given, $d = 0.793\text{ kg L}^{-1} = 0.793 \times 10^3\text{ g L}^{-1}$

Final volume, $V_2 = 2.5\text{ L}$

Final molarity, $M_2 = 0.25\text{ M}$

Molarity of initial solution $M_1 = ?$

Initial volume $V_1 = ?$

Molar mass of methanol,

$$CH_3OH = (1 \times 12.01) + (4 \times 1.0079) + 16.00 = 32.0416 \approx 32$$

$$\text{Molarity} = \frac{0.793 \times 10^3\text{ g L}^{-1}}{32\text{ g mol}^{-1}} = 24.781\text{ mol L}^{-1}$$

$$M_1V_1 = M_2V_2$$

$$24.781 \times V_1 = 0.25 \times 2.5$$

$$V_1 = \frac{0.25 \times 2.5}{24.781} = 0.02522\text{ L} = 25.22\text{ mL}$$

Question 13. Pressure is determined as force per unit area of the surface. The SI unit of pressure, pascal is as shown below.

$$1\text{ Pa} = 1\text{ Nm}^{-2}$$

If the mass of air at sea level is 1034 g cm^{-2}, calculate the pressure in pascal.

(i) The SI unit of mass is kilogram and of length is m so convert gram to kilogram and cm^2 to m^2 as pressure is to be calculated in SI units.

(ii) Write $1\text{ kg ms}^{-2} = 1\text{ N}$ and $1\text{ Nm}^{-2} = 1\text{ Pa}$ to obtain pressure in pascal.

Solution. Pressure is the force or weight per unit area.

$$\text{Pressure} = \frac{1034\text{ g} \times 9.8\text{ ms}^{-2}}{\text{cm}^2}$$

$$= \frac{1034\text{ kg} \times 100 \times 100 \times 9.8\text{ ms}^{-2}}{1000\text{ m}^2}$$

$$= 101332.0\text{ Nm}^{-2} \qquad (1\text{ N} = 1\text{ kg ms}^{-2})$$

$$= 1.01332 \times 10^5\text{ Pa}$$

Question 14. What is the SI unit of mass? How is it defined?

Solution. SI unit of mass is kilogram (kg). It is equal to the mass of international prototype of the kilogram.

Question 15. **Match the following prefixes with their multiples.**

	Prefixes	Multiples
(i)	micro	10^6
(ii)	deca	10^9
(iii)	mega	10^{-6}
(iv)	giga	10^{-15}
(v)	femto	10

Solution. Micro $= 10^{-6}$, deca $= 10$, mega $= 10^6$,
giga $= 10^9$ and femto $= 10^{-15}$.

Question 16. **What do you mean by significant figures?**

Solution. The number of significant figures in a given data is the number of all certain digits plus one uncertain digit. For example, 3.015 has four significant figures.

Note *All measured quantities are reported in such a way that only the last digit is uncertain* (*usually by* ± 1).

Question 17. **A sample of drinking water was found to be severely contaminated with chloroform, $CHCl_3$, supposed to be carcinogenic in nature. The level of contamination was 15ppm (by mass).**

(i) Express this in per cent by mass.

(ii) Determine the molarity of chloroform in the water sample.

Solution.

(i) 15 ppm means 15 parts in one million (10^6) parts.

Therefore, % by mass $= \frac{15 \times 100}{10^6} = 1.5 \times 10^{-3}$ %

(ii) Molar mass of $CHCl_3 = 12.01 + 1.0079 + (3 \times 35.45)$

$$M_{CHCl_3} = 119.367 \approx 119 \text{ g mol}^{-1}$$

1.5×10^{-3}% means 1.5×10^{-3} g chloroform is present in 100 g sample.

$$\text{Molarity, } M = \frac{w \times 1000}{m \times \text{volume of sample}}$$

(For water, density = 1 g cm^{-3}, so mass = volume)

$$M = \frac{1.5 \times 10^{-3} \times 1000}{119 \times 100} = 0.000126 = 1.26 \times 10^{-4} \text{ M}$$

Question 18. **Express the following in scientific notation:**

(i) 0.0048 **(ii) 234000** **(iii) 8008**

(iv) 5000 **(v) 6.0012**

(i) To convert a digit into scientific notation ($N \times 10^n$) shift the decimal point just after a non-zero digit.

(ii) If shifting is towards right, n has negative value and if shifting is towards left, n has positive value.

Solution. (i) 4.8×10^{-3} (ii) 2.34×10^5 (iii) 8.008×10^3
(iv) 5.0×10^3 (v) 6.0012×10^0

Note *In scientific notation any number can be expressed in the form of* $N \times 10^n$. *Where n is an exponent having positive or negative values and N can vary between 1 to 10.*

Question 19. How many significant figures are present in the following?
(i) 0.0025 (ii) 208 (iii) 5005 (iv) 126000 (v) 500.0 (vi) 2.0034

(a) All non-zero digits are significant.
(b) Zeros present to left/right of a number are non-significant however, zeros present after decimal points are significant.
(c) Zeros present between two non-zero digits are significant.

Solution. (i) 2 (ii) 3 (iii) 4 (iv) 3 (v) 4 (vi) 5

Question 20. Round up the following up to three significant figures :
(i) 34.216 (ii) 10.4107 (iii) 0.04597 (iv) 2808

To round up a number, left the last digit as such, if the digit next to it is less than 5 and increase it by 1, if the next digit is greater than 5.

Solution. (i) 34.2 (ii) 10.4 (iii) 0.0460 (iv) 2810

Question 21. The following data are obtained when dinitrogen and dioxygen react together to form different compounds.

	Mass of dinitrogen	Mass of dioxygen
(i)	14 g	16 g
(ii)	14 g	32 g
(iii)	28 g	32 g
(iv)	28 g	80 g

(a) Which law of chemical combination is obeyed by the above experimental data? Give its statement.

(b) Fill in the blanks in the following conversions.

(i) 1 km = ... mm = ... pm
(ii) 1 mg = ... kg = ... ng
(iii) 1 mL = ... L = ... dm^3

Solution.

(a) On fixing the mass of dinitrogen as 28 g, the masses of dioxygen combined are 32, 64, 32 and 80 in the given four oxides. These are in the simple whole number ratio *i.e.,* 2 : 4 : 2 : 5. Hence, the given data obey the law of multiple proportions.

Law of multiple proportions This law was proposed by Dalton in 1803. According to this law, if two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element are in the ratio of small whole numbers.

(b) (i) $1\text{ km} = 1\text{ km} \times \dfrac{1000\text{ m}}{1\text{ km}} \times \dfrac{100\text{ cm}}{1\text{ m}} \times \dfrac{10\text{ mm}}{1\text{ cm}} = 10^6\text{mm}$

$$1\text{ km} = 1\text{ km} \times \frac{1000\text{ m}}{1\text{ km}} \times \frac{1\text{ pm}}{10^{-12}\text{ m}} = 10^{15}\text{ pm}$$

$$\therefore 1\text{ km} = 10^6\text{ mm} = 10^{15}\text{ pm}$$

(ii) $1\text{ mg} = 1\text{ mg} \times \dfrac{1\text{ g}}{1000\text{ mg}} \times \dfrac{1\text{ kg}}{1000\text{ g}} = 10^{-6}\text{ kg}$

$$1\text{ mg} = 1\text{ mg} \times \frac{1\text{ g}}{1000\text{ mg}} \times \frac{1\text{ ng}}{10^{-9}\text{ g}} = 10^6\text{ ng}$$

$$\therefore 1\text{ mg} = 10^{-6}\text{ kg} = 10^6\text{ ng}$$

(iii) $1\text{ mL} = 1\text{ mL} \times \dfrac{1\text{ L}}{1000\text{ mL}} = 10^{-3}\text{ L}$

$$1\text{ mL} = 1\text{ cm}^3 = 1\text{ cm}^3 \times \frac{1\text{ dm} \times 1\text{ dm} \times 1\text{ dm}}{10\text{ cm} \times 10\text{ cm} \times 10\text{ cm}} = 10^{-3}\text{ dm}^3$$

$$\therefore \quad 1\text{ mL} = 10^{-3}\text{ L} = 10^{-3}\text{ dm}^3$$

Question 22. If the speed of light is $3.0 \times 10^8\text{ms}^{-1}$, calculate the distance covered by light in 2.00 ns.

Solution. $2.00\text{ ns} = 2.00 \times 10^{-9}\text{ s}$ $(1\text{ ns} = 10^{-9}\text{ s})$

Distance covered = Speed × Time

$$= 3.0 \times 10^8\text{ ms}^{-1} \times 2.0 \times 10^{-9}\text{ s}$$
$$= 6.0 \times 10^{-1}\text{ m} = 0.6\text{ m}$$

Question 23. In a reaction, $A + B_2 \longrightarrow AB_2$, identify the limiting reagent, if any, in the following reaction mixtures.

(i) 300 atoms of A + 200 molecules of B
(ii) 2 moles of A + 3 moles of B
(iii) 100 atoms of A + 100 molecules of B
(iv) 5 moles of A + 2.5 moles of B
(v) 2.5 moles of A + 5 moles of B

Limiting reagent is the reagent that is consumed first in the reaction, so compare the amounts of A and B to find the limiting reagent.

Solution. $A + B_2 \longrightarrow AB_2$

(i) According to the above reaction, 1 atom of A reacts with 1 molecule of B.

$\therefore$ 200 atoms of A will react with 200 molecules of B. In this case, B is the limiting reagent, so A is in excess.

(ii) According to the above reaction, 1 mole of A reacts with 1 mole of B.

$\therefore$ 2 moles of A will react with 2 moles of B. In this case A is limiting reagent and B is in excess.

(iii) No limiting reagent.

(iv) 2.5 moles of B requires only 2.5 moles of A to react. So, B is limiting reagent and A is in excess.

(v) 2.5 moles of A requires only 2.5 moles of B to react. So, A is limiting reagent and B is in excess.

Question 24. Dinitrogen and dihydrogen react with each other to produce ammonia according to the following chemical equation,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

(i) Calculate the mass of ammonia produced if 2.00×10^3 g dinitrogen reacts with 1.00×10^3 g of dihydrogen.

(ii) Will any of the two reactants remain unreacted?

(iii) If yes, which one and what would be its mass?

Solution.

$$\begin{array}{cccc} N_2(g) + & 3H_2(g) & \longrightarrow & 2NH_3(g) \\ 1\text{ mol} & 3\text{ mol} & & 2\text{ mol} \\ 28\text{ g} & 6\text{ g} & & 34\text{ g} \end{array}$$

28 g N_2 reacts with 6 g H_2

1 g N_2 reacts with $\frac{6}{28}$ g H_2

$\therefore$ 2000 g N_2 will react with $\frac{2000 \times 6}{28} = 428.57$ g H_2

Hence, N_2 is the limiting reagent and H_2 is in excess. N_2 limits the amount of ammonia produced.

28 g N_2 produces 34 g NH_3

1 g N_2 produces $\frac{34}{28}$ g NH_3

2000 g N_2 will produce $\frac{34}{28} \times 2000 = 2428.57$ g NH_3

(ii) H_2 is in excess so it will remain unreacted.

(iii) Amount of H_2 remain unreacted $= 1000 - 428.57 = 571.43$ g

Question 25. How are 0.50 mole Na_2CO_3 and 0.50 M Na_2CO_3 different?

Solution. Molar mass of $Na_2CO_3 = (2 \times 22.99) + 12.01 + (3 \times 16)$

$$= 105.99 \approx 106 \text{ g mol}^{-1}$$

0.50 mole $Na_2CO_3 = 0.50 \times 106 = 53$ g Na_2CO_3

0.50 M Na_2CO_3 means 53 g Na_2CO_3 is present in 1 L of the solution.

Question 26. If ten volumes of dihydrogen gas react with five volumes of dioxygen gas, how many volumes of water vapour would be produced?

(i) In order to find the moles of H_2 and O_2 generally utilised to obtain water, write a balanced chemical equation for the production of water vapours from H_2 and O_2.

(ii) Apply Gay-Lussac's law of gaseous volume to calculate the volume of water vapours produced.

Solution. $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$

$\quad\quad 2\text{ V} \quad\quad 1\text{ V} \quad\quad\quad\quad 2\text{ V}$

According to Gay-Lussac's law of gaseous volume, 2 volumes of dihydrogen react with 1 volume of O_2 to produce 2 volumes of water vapour. Therefore, 10 volumes of dihydrogen on reaction with 5 volumes of dioxygen will produce 10 volumes of water vapour.

Question 27. **Convert the following into basic units.**

(i) 28.7 pm **(ii) 15.15 μs** **(iii) 25365 mg**

The basic units for length is meter (m), for time is second (s) and for mass is kilogram (kg).

Solution.

(i) $28.7\text{ pm} \times \frac{10^{-12}\text{ m}}{1\text{ pm}} = 2.87 \times 10^{-11}\text{ m}$

(ii) $15.15\ \mu\text{s} \times \frac{10^{-6}\text{ s}}{1\ \mu\text{s}} = 1.515 \times 10^{-5}\text{ s}$

(iii) $25365\text{ mg} \times \frac{1\text{ g}}{1000\text{ mg}} \times \frac{1\text{ kg}}{1000\text{ g}} = 2.5365 \times 10^{-2}\text{ kg}$

Question 28. **Which one of the following will have the largest number of atoms?**

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

(i) We know that number of atoms = moles × N_A × atomicity, so first calculate the number of moles by using the formula,

$$\text{Moles of a substance} = \frac{\text{Mass of a substance }(g)}{\text{Molar mass}}$$

(ii) Then, find number of atoms from moles of the substance and compare them.
(Atomic masses : Au = 197, Na = 23, Li = 7, Cl = 35.5 u)

Solution.

(i) $1\text{ g Au} = \frac{1}{197}\text{ mol atoms of Au} = \frac{1}{197} \times 6.022 \times 10^{23}\text{ atoms of Au.}$

(ii) $1\text{ g Na} = \frac{1}{23}\text{ mole atoms of Na} = \frac{1}{23} \times 6.022 \times 10^{23}\text{ atoms of Na.}$

(iii) $1\text{ g Li} = \frac{1}{7}\text{ mole atoms of Li} = \frac{1}{7} \times 6.022 \times 10^{23}\text{ molecules of Li.}$

(iv) $1\text{ g } Cl_2 = \frac{1}{71}\text{ mole molecules of } Cl_2$

$$= \frac{1}{71} \times 6.022 \times 10^{23}\text{ molecules of } Cl_2.$$

$$= \frac{2}{71} \times 6.022 \times 10^{23} \text{ atoms of Cl}$$

(1 molecule of chlorine contains 2 atoms).

Therefore, 1 g of Li has largest number of atoms.

Note *If a substance exists in atomic form, it contains mole atoms and if a substance exists in molecular form, it contains mole molecules.*

Question 29. Calculate the molarity of a solution of ethanol in water in which the mole fraction of ethanol is 0.040.

(i) Molarity is the number of moles of solute present in 1 L of solution, so find moles of H_2O in 1 L solution of ethanol in water.

(ii) Then, find mole fraction of H_2O by using the formula $x_1 + x_2 = 1$ and moles of ethanol by using the formula, $x_{H_2O} = \dfrac{n_{H_2O}}{n_{C_2H_5OH} + n_{H_2O}}$

(iii) $n_{C_2H_5OH}$ gives the molarity of solution as moles of solute in 1L solution is equal to its molarity.

Solution. Molarity is defined as the moles of solute (ethanol) in 1 L of the solution.

1 L of ethanol solution (as it is diluted) = 1 L of water

Number of moles of H_2O in 1 L water $= \dfrac{1000 \text{ g}}{18} = 55.55$ moles

For a binary solution (binary solution contains two components)

$$x_1 + x_2 = 1$$

Hence,

$$x_{H_2O} = 1 - x_{C_2H_5OH}$$

$$x_{H_2O} = 1 - 0.040 = 0.96$$

$$x_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{C_2H_5OH}}$$

$$0.96 = \frac{55.55}{55.55 + n_{C_2H_5OH}}$$

$$53.328 + 0.96\, n_{C_2H_5OH} = 55.55$$

$$0.96\, n_{C_2H_5OH} = 55.55 - 53.328 = 2.222$$

$$n_{C_2H_5OH} = \frac{2.222}{0.96} = 2.3145 \text{ mol}$$

Question 30. What will be the mass of one ^{12}C atom in gram?

Solution. Mass of 1 atom of $^{12}C = \dfrac{\text{Atomic mass of C}}{\text{Avogadro's number}}$

$$= \frac{12 \text{ g}}{6.022 \times 10^{23}} = 1.9927 \times 10^{-23} \text{ g}$$

Question 31. How many significant figures should be present in the answer of the following calculations?

(i) $\dfrac{0.02856 \times 298.15 \times 0.112}{0.5785}$

(ii) 5×5.364

(iii) $0.0125 + 0.7864 + 0.0215$

Solution.

(i) In multiplication and division, the least precise term 0.112 has 3 significant figures. Hence, the answer should not have more than three significant figures.

(ii) In multiplication, 5 is the exact number and the other number has 4 significant figures. Hence, the answer should have 4 significant figures.

(iii) In addition (or in subtraction), the answer cannot have more digits to the decimal point than either of the original members. Hence, the answer should have 4 significant figures.

Question 32. Use the data given in the following table to calculate the molar mass of naturally occurring argon.

Isotope	Isotopic molar mass	Abundance
^{36}Ar	35.96755 g mol^{-1}	0.337%
^{38}Ar	37.96272 g mol^{-1}	0.063%
^{40}Ar	39.9624 g mol^{-1}	99.600%

Solution. Average molar mass of

$$Ar = \Sigma f_i \times A_i = (0.00337 \times 35.96755) + (0.00063 \times 37.96272) + (0.99600 \times 39.9624)$$

$$= 0.121 + 0.024 + 39.803 = 39.948 \text{ g mol}^{-1}$$

Question 33. Calculate the number of atoms in each of the following.

(i) 52 moles of Ar (ii) 52 u of He (iii) 52 g of He

Solution.

(i) 1 mol of Ar $= 6.022 \times 10^{23}$ atoms.

$$52 \text{ moles of Ar} = 52 \times 6.022 \times 10^{23} \text{ atoms}$$
$$= 313.144 \times 10^{23} \text{ atoms}$$
$$= 3.131 \times 10^{25} \text{ atoms}$$

(ii) 4 u of He = 1 He atom

$$\therefore \quad 52 \text{ u of He} = \frac{52}{4} \text{ He atoms} = 13 \text{ He atoms.}$$

(iii) 1 mol atom of He = 4 g $= 6.022 \times 10^{23}$ atoms.

$$52 \text{ g of He} = \frac{52 \times 6.022 \times 10^{23}}{4} \text{ atoms}$$
$$= 78.286 \times 10^{23} \text{ atoms}$$
$$= 7.8286 \times 10^{24} \text{ atoms.}$$

Question 34. **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.**

(i) To find empirical formula, moles are required which are calculated by dividing the percentage of elements by their atomic mass and percentage is obtained from the mass of elements, so first calculate the amount of C and H in the given masses of CO_2 and H_2O by using the formulae $w_C\% = \frac{12}{44} \times$ wt. of CO_2, $w_H\% = \frac{2}{18} \times$ wt. of H_2O Then, calculate the per cent of C and H and empirical formula (by finding simplest ratio of moles of different elements).

(ii) At STP volume of 1 mole gas = 22.4 L thus, calculate the molar mass of the gas at STP by unitary method.

(iii) Since molecular formula = (empirical formula)$_n$, so calculate n by using the formula, $n = \frac{\text{Molar mass}}{\text{Empirical formula mass}}$ and then find molecular formula [by using molecular formula = (empirical formula)$_n$]

Solution.

(i) $44 \text{ g } CO_2 = 12 \text{ g carbon}$

$$3.38 \text{ g } CO_2 = \frac{12}{44} \times 3.38 \text{ g} = 0.9218 \text{ g carbon}$$

$$18 \text{ g } H_2O = 2 \text{ g hydrogen}$$

$$0.690 \text{ g } H_2O = \frac{2}{18} \times 0.690 \text{ g} = 0.0767 \text{ g hydrogen}$$

Total mass of compound = 0.9218 + 0.0767 = 0.9985 g (because compound contains only carbon and hydrogen).

$$\% \text{ of C in the compound} = \frac{0.9218}{0.9985} \times 100 = 92.32$$

$$\% \text{ of H in the compound} = \frac{0.0767}{0.9985} \times 100 = 7.68$$

Calculation for empirical formula

Element	Per cent by mass	Atomic mass	Relative number of moles of elements	Simplest molar ratio
C	92.32	12	$\frac{92.32}{12} = 7.69$	$\frac{7.69}{7.68} = 1$
H	7.68	1	$\frac{7.68}{1} = 7.68$	$\frac{7.69}{7.68} = 1$

Hence, empirical formula = CH

(ii) **Calculation for molar mass of the gas**

10.0 L of the given gas at STP weigh = 11.6 g

$\therefore$ 22.4 L of the given gas at STP will weigh

$$= \frac{11.6 \times 22.4}{10} = 25.984 \text{ g}$$

Molar mass = 25.984 ≈ 26 g mol^{-1}

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

$$\therefore \quad n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{26}{13} = 2$$

Hence, molecular formula = $n \times \text{CH} = 2 \times \text{CH} = C_2H_2$

Question 35. Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction,

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

What mass of $CaCO_3$ is required to react completely with 25 mL of 0.75 M HCl?

(i) To calculate the mass of $CaCO_3$ required to react completely with 25 mL of 0.75 M HCl first we will calculate the mass of HCl in 25 mL of 0.75 M HCl.

(ii) Now calculate the mass of $CaCO_3(g)$ by using the information available from a balanced chemical equation.

Solution.

(i) Calculation for mass of HCl in 25 mL of 0.75 M HCl

$$\text{Molarity} = \frac{w \times 1000}{m \times \text{vol (mL)}}$$

$$0.75 = \frac{w \times 1000}{36.5 \times 25}$$

(Molar mass of HCl = 1 + 35.5 = 36.5 g/mol)

$$w = 0.75 \times 36.5 \times 25 / 1000 = 0.6844 \text{ g}$$

(ii) Calculation for required mass of $CaCO_3$ to react completely with 0.6844 g HCl.

$$\underset{100\text{ g}}{CaCO_3(s)} + \underset{2 \times 36.5 = 73\text{ g}}{2HCl(aq)} \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

According to balanced chemical equation,

73 g HCl completely reacts with 100 g $CaCO_3$

1 g HCl completely reacts with $\frac{100}{73}$ g $CaCO_3$

$\therefore$ 0.6844 g HCl will completely reacts with $\frac{100 \times 0.6844}{73}$

$= 0.9375$ g

Note *The amount of substance present in a given volume of a solution is expressed in number of ways e.g., mass per cent, mole fraction, molarity and molality.*

Question 36. Chlorine is prepared in the laboratory by treating manganese dioxide (MnO_2) with aqueous hydrochloric acid according to the reaction,

$$4HCl(aq) + MnO_2(s) \longrightarrow 2H_2O(l) + MnCl_2(aq) + Cl_2(g)$$

How many grams of HCl reacts with 5.0 g of manganese dioxide?

Solution. $\underset{4 \times 36.5}{4\ HCl(aq)} + \underset{87\ g}{MnO_2(s)} \longrightarrow 2H_2O(l) + MnCl_2(aq) + Cl_2(g)$

According to balanced chemical equation,

$$87\ g \text{ of } MnO_2 \text{ react with } 4 \times 36.5\ g\ HCl$$

$$5\ g \text{ of } MnO_2 \text{ will react with } \frac{4 \times 36.5 \times 5}{87} = 8.39\ g\ HCl$$

Note *Amounts of one reactant required to react a particular amount of another reactant can be determined by using stoichiometric calculations.*

Selected NCERT Exemplar Problems

Short Answer Type

Question 1. How many significant figures should be present in the answer of the following calculation?

$$\frac{2.5 \times 1.25 \times 3.5}{2.01}$$

Solution. Least precise term 2.5 or 3.5 has two significant figures. Hence, the answer should have two significant figures.

$$\frac{2.5 \times 1.25 \times 3.5}{2.01} = 5.4415 \approx 5.4$$

Question 2. What is the difference between molality and molarity?

Solution. **Molality** It is defined as the number of moles of solute dissolved in 1 kg of solvent. It is independent of temperature.

Molarity It is defined as the number of moles of solute dissolved in 1 L of solution. It depends upon temperature (because, volume of solution $\propto$ temperature.)

Question 3. 45.4L of dinitrogen reacted with 22.7L of dioxygen and 45.4 L of nitrous oxide was formed. The reaction is given below

$$2N_2(g) + O_2(g) \longrightarrow 2N_2O(g)$$

Which law is being obeyed in this experiment? Write the statement of the law.

Solution.

$$\begin{array}{ccccc} 2N_2(g) & + & O_2(g) & \longrightarrow & 2N_2O(g) \\ 2\ V & & 1\ V & & 2\ V \\ \frac{45.4}{22.7} = 2 & & \frac{22.7}{22.7} = 1 & & \frac{45.4}{22.7} = 2 \end{array}$$

Hence, the ratio between the volumes of the reactants and the product in the given question is simple *i.e.,* 2 : 1 : 2. It proves the Gay-Lussac's law of gaseous volumes.

Gay-Lussac's law of gaseous volumes When gases combine or are produced in a chemical reaction, they do so in a simple ratio by volume provided all gases are at same temperature and pressure.

Question 4. Hydrogen gas is prepared in the laboratory by reacting dil. HCl with granulated zinc. Following reaction takes place

$$\mathrm{Zn + 2HCl \longrightarrow ZnCl_2 + H_2}$$

Calculate the volume of hydrogen gas liberated at STP when 32.65 g of zinc reacts with HCl. 1 mole of gas occupies 22.7 L volume at STP, atomic mass of Zn = 65.3 u

Solution.

$$\underset{65.3\text{ g}}{\mathrm{Zn}} + 2\mathrm{HCl} \longrightarrow \mathrm{ZnCl_2} + \underset{1\text{ mol} = 22.7\text{ L at STP (given)}}{\mathrm{H_2}}$$

65.3 g Zn when reacts with HCl it produces $= 22.7\text{ L } H_2$ at STP

32.65 g Zn when reacts with HCl it will produce

$$\frac{22.7 \times 32.65}{65.3} = 11.35\text{ L H}_2 \text{ at STP.}$$

Question 5. The density of 3 molal solution of NaOH is 1.110 g mL^{-1}. Calculate the molarity of the solution.

Solution. 3 molal solution of NaOH means 3 moles of NaOH are dissolved in 1 kg solvent. So, the mass of solution

$= 1000$ g solvent + 120 g NaOH $= 1120$ g solution

(Molar mass of NaOH $= 23 + 16 + 1 = 40$ g;
3 moles of NaOH $= 3 \times 40 = 120$ g)

$$\text{Volume of solution} = \frac{\text{Mass of solution}}{\text{Density of solution}} \qquad \left(\because d = \frac{m}{V}\right)$$

$$V = \frac{1120\text{ g}}{1.110\text{ gmL}^{-1}} = 1009\text{ mL}$$

$$\text{Molarity} = \frac{\text{Moles of solute} \times 1000}{\text{Volume of solution (mL)}} = \frac{3 \times 1000}{1009} = 2.973\text{ M}$$

Question 6. If 4 g of NaOH dissolves in 36 g of H$_2$O, calculate the mole fraction of each component in the solution. Also, determine the molarity of the solution (Specific gravity of solution is 1 g mL^{-1}).

Solution. Number of moles of NaOH,

$$n_{\mathrm{NaOH}} = \frac{4}{40} = 0.1\text{ mol} \qquad \left\{n = \frac{\text{Mass (g)}}{\text{Molar mass (g mol}^{-1})}\right\}$$

Similarly, $$n_{\mathrm{H_2O}} = \frac{36}{18} = 2\text{ mol}$$

Mole fraction of NaOH,

$$x_{\mathrm{NaOH}} = \frac{\text{Moles of NaOH}}{\text{Moles of NaOH + moles of H}_2\text{O}}$$

$$x_{NaOH} = \frac{0.1}{0.1+2} = 0.0476$$

Similarly, $$x_{H_2O} = \frac{n_{H_2O}}{n_{NaOH} + n_{H_2O}} = \frac{2}{0.1+2} = 0.9524$$

Total mass of solution = mass of solute + mass of solvent

$$= 4 + 36 = 40\text{ g}$$

$$\text{Volume of solution} = \frac{\text{Mass of solution}}{\text{Sp. gravity}} = \frac{40\text{ g}}{1\text{ g mL}^{-1}} = 40\text{ mL}$$

$$\text{Molarity} = \frac{\text{Moles of solute} \times 1000}{\text{Volume of solution (mL)}} = \frac{0.1 \times 1000}{40} = 2.5\text{ M}$$

Question 7. **The reactant which is entirely consumed in the reaction is known as limiting reagent. In the reaction,**

$$2A + 4B \longrightarrow 3C + 4D,$$

when 5 moles of A react with 6 moles of B then,

(i) which is the limiting reagent?

(ii) calculate the amount of C formed.

Solution. $2A + 4B \longrightarrow 3C + 4D$

According to the given reaction, 2 moles of A react with 4 moles of B.

Hence, 5 moles of A will react with 10 moles of B $\left(\frac{5 \times 4}{2} = 10\text{ moles}\right)$

(i) It indicates that reactant B is limiting reagent as it will consume first in the reaction because we have only 6 moles of B.

(ii) Limiting reagent decide the amount of product produced.
According to the reaction,

4 moles of B produces 3 moles of C

$\therefore$ 6 moles of B will produce $\frac{3 \times 6}{4} = 4.5$ moles of C.

Long Answer Type

Question 8. **A vessel contains 1.6 g of dioxygen at STP (273.15 K, 1 atm pressure). The gas is now transferred to another vessel at constant temperature, where pressure becomes half of the original pressure. Calculate**

(i) volume of the new vessel.

(ii) number of molecules of dioxygen.

Solution.

(i) $p_1 = 1\text{ atm}, p_2 = \frac{1}{2} = 0.5\text{ atm}, T_1 = 273.15, \quad V_2 = ?, V_1 = ?$

32 g dioxygen occupies = 22.4 L volume at STP

$\therefore$ 1.6 g dioxygen will occupy $= \frac{22.4\text{ L} \times 1.6\text{ g}}{32\text{ g}} = 1.12\text{ L}$

$$V_1 = 1.12\text{ L}$$

From Boyle's law (as temperature is constant),

$$p_1V_1 = p_2V_2$$

$$V_2 = \frac{p_1V_1}{p_2} = \frac{1\text{ atm} \times 1.12\text{ L}}{0.5\text{ atm}} = 2.24\text{ L}$$

(ii) Number of moles of dioxygen $= \frac{\text{mass of dioxygen}}{\text{molar mass of dioxygen}}$

$$n_{O_2} = \frac{1.6}{32} = 0.05\text{ mol}$$

1 mole molecule of dioxygen $= 6.022 \times 10^{23}$ molecules of dioxygen

$\therefore$ 0.05 mole molecules of dioxygen

$$= 6.022 \times 10^{23} \times 0.05 \text{ molecule of } O_2$$

$$= 0.3011 \times 10^{23} \text{ molecules}$$

$$= 3.011 \times 10^{22} \text{ molecules}$$

Question 9. Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction,

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

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

Solution. Molar mass of $CaCO_3 = 40 + 12 + 3 \times 16 = 100\text{ g mol}^{-1}$

Moles of $CaCO_3$ in 1000 g,

$$n_{CaCO_3} = \frac{\text{Mass }(g)}{\text{Molar mass}}$$

$$n_{CaCO_3} = \frac{1000\text{ g}}{100\text{ g mol}^{-1}} = 10\text{ mol}$$

$$\text{Molarity} = \frac{\text{Moles of solute (HCl)} \times 1000}{\text{Volume of solution}}$$

(Moles of HCl in 250 mL of 0.76 M HCl $= n_{HCl}$)

$$0.76 = \frac{n_{HCl} \times 1000}{250}$$

$$n_{HCl} = \frac{0.76 \times 250}{1000} = 0.19\text{ mol.}$$

$$\underset{1\text{ mol}}{CaCO_3(s)} + \underset{2\text{ mol}}{2HCl(aq)} \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

According to the equation,

1 mole of $CaCO_3$ reacts with 2 moles HCl

$\therefore$ 10 moles of $CaCO_3$ will react with $\frac{10 \times 2}{1} = 20$ moles HCl.

But we have only 0.19 moles HCl, so HCl is limiting reagent and it limits the yield of $CaCl_2$.

2 moles of HCl produces 1 mole of $CaCl_2$

0.19 mole of HCl will produce $\frac{1 \times 0.19}{2} = 0.095$ mol $CaCl_2$

Molar mass of $CaCl_2 = 40 + (2 \times 35.5) = 111\,\text{g mol}^{-1}$

$\therefore$ 0.095 mole of $CaCl_2 = 0.095 \times 111 = 10.54$ g

Question 10. A box contains some identical red coloured balls, labelled as A, each weighing 2 g. Another box contains identical blue coloured balls, labelled as B, each weighing 5 g. Consider the combinations AB, AB_2, A_2B and A_2B_3 and show that law of multiple proportions is applicable.

Solution.

Combination	Mass of A (g)	Mass of B (g)
AB	2	5
AB_2	2	10
A_2B	4	5
A_2B_3	4	15

Mass of B which is combined with fixed mass of A (say 1 g) will be 2.5 g, 5 g, 1.25 g and 3.75 g. They are in the ratio 2 : 4 : 1 : 3 which is simple whole number ratio. Hence, the law of multiple proportions is applicable.

Chapter 2

Structure of Atom

Important Results

1. Relation between frequency (ν) and wavelength (λ).

$$\nu = \frac{c}{\lambda} \quad (c = \text{velocity of light, } 3.0 \times 10^8 \text{ ms}^{-1})$$

Einstein's equation $E = mc^2$

Planck's equation $E = h\nu = \frac{hc}{\lambda}$

(h = Planck's constant $= 6.626 \times 10^{-34}$ Js)

Photoelectric effect $h\nu = h\nu_0 + \frac{1}{2}mv^2$

(where, $h\nu$ = energy of striking photon, $h\nu_0 = W_0$ = work function and $\frac{1}{2}mv^2$ = kinetic energy of an ejected electron.)

Rydberg formula $\bar{\nu} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]; n_2 > n_1$

(where, R = Rydberg constant $= 1.09678 \times 10^7 \text{ m}^{-1}$)

For			
	$n_1 = 1; n_2 = 2, 3, 4$	Lyman series (UV)	
	$n_1 = 2; n_2 = 3, 4, 5$	Balmer series (visible)	
	$n_1 = 3; n_2 = 4, 5, 6$	Paschen series	IR
	$n_1 = 4; n_2 = 5, 6, 7$	Brackett series	
	$n_1 = 5; n_2 = 6, 7, 8$	Pfund series	
	$n_1 = 6; n_2 = 7, 8, 9$	Humphries series	

2. The frequency of radiation absorbed or emitted when transition occurs between two stationary states,

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

(where, E_1 and E_2 are the energies of lower and higher allowed energy states respectively.)

3. Energy of the stationary states, $E_n = -R_H\left(\frac{1}{n^2}\right)$ where, $n = 1, 2, 3, \ldots$

4. Energy of the stationary states for H and H like species (one electron system)

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

5. Radius of nth orbit, $r_n = \frac{n^2 a_0}{Z}$

where, a_0 (Bohr's radius of H-atom) $= \frac{h^2}{4\pi^2 me^2 k} = 0.529$ Å

For H like species, $r_n = \frac{0.529\,(n^2)}{Z}\text{ Å} = \frac{52.9\,(n^2)}{Z}\text{ pm}$

6. de-Broglie equation, $\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2m(\text{KE})}}$

7. Heisenberg's uncertainty principle, $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$ or $\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$

(where, Δx and Δv are uncertainty in position and velocity respectively.)

8. Angular momentum, $mvr = \frac{nh}{2\pi}$

9. Velocity in nth orbital, $v_n = 2.182 \times 10^6 \frac{Z}{n}$

10. Ionisation energy $(\text{IE})_H = \Delta E \propto Z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

11. The position of an electron in an atom is determined by four quantum numbers (n, l, m, s)

n (principal quantum number) $= 1, 2, 3, \ldots, n$

l (angular quantum number) $= 0, 1, 2 \ldots, (n-1)$

l	0	1	2	3	4
Sub-shell	s	p	d	f	g

m (magnetic quantum number) $= -l$ to $+l$

s (spin quantum number) $= +\frac{1}{2}$ or $-\frac{1}{2}$

12. Sub-shell indicated $= nl$

e.g., $\left.\begin{matrix} n=3 \\ l=2 \end{matrix}\right] 3d \quad \left.\begin{matrix} n=1 \\ l=0 \end{matrix}\right] 1s$

13. l also describes the shapes of the orbital occupied by the electron. s-spherical, p-dumb-bell and d-double dumb-bell.

14. Total values of $m = (2l + 1)$ = total number of orbitals in a sub-shell

= number of spectral lines when placed in a magnetic field or electric field.

15. For a hydrogen atom wavefunction, there are $n - l - 1$ radial nodes, $(n - 1)$ total nodes

16. Electrons in various orbitals are filled on the basis of

(i) Aufbau rule (ii) Hund's rule (iii) Pauli's exclusion rule

EC of Cr(24) — [Ar] $3d^5 4s^1$

EC of Cu (29) — [Ar] $3d^{10} 4s^1$

Exercises

Question 1. **(i) Calculate the number of electrons which will together weigh one gram.**

(ii) Calculate the mass and charge of one mole of electrons.

(i) 1 mole species = 6.022×10^{23} species

(ii) Mass of 1 e^- = 9.11×10^{-31} kg

(iii) Charge on 1 e^- = 1.602×10^{-19} C

Solution.

(i) Mass of one electron $= 9.11 \times 10^{-28}$ g (or 9.11×10^{-31} kg)

$$\text{Number of electrons in 1 g} = \frac{1}{9.11 \times 10^{-28}} = 1.0976 \times 10^{27} \text{ electrons}$$

(ii) Mass of 1 electron $= 9.11 \times 10^{-31}$ kg

$$\therefore \text{Mass of 1 mole of electrons} = 9.11 \times 10^{-31} \times 6.022 \times 10^{23}$$

$$= 54.86 \times 10^{-8} = 5.486 \times 10^{-7} \text{ kg}$$

Charge on 1 electron $= 1.602 \times 10^{-19}$ C

$$\therefore \text{Charge on 1 mole of electrons} = 1.602 \times 10^{-19} \times 6.022 \times 10^{23}$$

$$= 9.647 \times 10^4 \text{ C}$$

Question 2. **(i) Calculate the total number of electrons present in one mole of methane.**

(ii) Find (a) the total number and (b) the total mass of neutrons in 7 mg of ^{14}C. (Assume that mass of a neutron = 1.675×10^{-27} kg)

(iii) Find (a) the total number and (b) the total mass of protons in 34 mg of NH_3 at STP. (Mass of 1 p = 1.6726×10^{-27} kg.)

Will the answer change if the temperature and pressure are changed?

Solution.

(i) 1 molecule of methane (CH_4) contains

$6 + 4 = 10$ electrons

[6 from C and 1 from each H atom]

$\therefore$ 1 mol molecule of methane will contain

$$6.022 \times 10^{23} \times 10 = 6.022 \times 10^{24} \text{ electrons}$$

(ii) (a) 1mol $^{14}C = 14\ g = 6.022 \times 10^{23}$ carbon atoms

Number of neutrons in 1 carbon atom

$= \text{mass number} - \text{atomic number} = 14 - 6 = 8$ neutrons

$\therefore$ 6.022×10^{23} carbon atoms will contain $6.022 \times 10^{23} \times 8$ neutrons

14 g carbon-14 have $6.022 \times 10^{23} \times 8$ neutrons

$\therefore$ 7 mg or 7×10^{-3} g carbon-14 will have

$$\frac{7 \times 10^{-3} \times 6.022 \times 10^{23} \times 8}{14} \text{ neutrons}$$

$$= 24.088 \times 10^{20} \text{ neutrons} = 2.4088 \times 10^{21} \text{ neutrons}$$

(b) Mass of 1 neutron $= 1.675 \times 10^{-27}$ kg

Mass of 2.4088×10^{21} neutrons

$$= 2.4088 \times 10^{21} \times 1.675 \times 10^{-27} \text{ kg} = 4.0347 \times 10^{-6} \text{ kg}$$

(iii) 1 mole of NH_3 contains protons $= 7 + 3 = 10$ moles of protons (7 in N and 1 in each H atom) $= 6.022 \times 10^{23} \times 10$ protons

(a) 1 mole of NH_3 or 17 g NH_3 contains 6.022×10^{24} protons

34 mg or 34×10^{-3} g NH_3 will contain

$$\frac{34 \times 10^{-3} \times 6.022 \times 10^{24}}{17} = 12.044 \times 10^{21} \text{ protons}$$

$$= 1.2044 \times 10^{22} \text{ protons}$$

(b) Mass of 1 proton $= 1.6726 \times 10^{-27}$ kg

$\therefore$ Mass of 1.2044×10^{22} protons

$$= 1.2044 \times 10^{22} \times 1.6726 \times 10^{-27} \text{ kg}$$

$$= 2.01447 \times 10^{-5} \text{ kg}$$

There is no effect of temperature and pressure change. The answer will remain the same.

Question 3. **How many neutrons and protons are there in the following nuclei?**

$$^{13}_{6}C,\ ^{16}_{8}O,\ ^{24}_{12}Mg,\ ^{56}_{26}Fe,\ ^{88}_{38}Sr$$

(i) The digit written as subscript represents the atomic number (Z) and that as superscript represents the mass number (A) of the element.

(ii) Number of neutrons $= A - Z$ and number of protons $= Z$

Solution.

Nucleus	Atomic number (Z)	Mass number (A)	Number of protons $= Z$	Number of neutrons $= A - Z$
$^{13}_{6}C$	6	13	6	$13 - 6 = 7$
$^{16}_{8}O$	8	16	8	$16 - 8 = 8$
$^{24}_{12}Mg$	12	24	12	$24 - 12 = 12$
$^{56}_{26}Fe$	26	56	26	$56 - 26 = 30$
$^{88}_{38}Sr$	38	88	38	$88 - 38 = 50$

Question 4. Write the complete symbol for the atom with the given atomic number (Z) and atomic mass (A)

(i) $Z = 17, A = 35$ (ii) $Z = 92, A = 233$ (iii) $Z = 4, A = 9$

See the symbols of atoms having atomic number 17, 92 and 4 respectively in the Periodic Table as the atomic number is a fundamental property of an element, *i.e.*, certain for each element.

Solution. (i) ${}^{35}_{17}\text{Cl}$ (ii) ${}^{233}_{92}\text{U}$ (iii) ${}^{9}_{4}\text{Be}$

Question 5. Yellow light emitted from a sodium lamp has a wavelength (λ) of 580 nm. Calculate the frequency (ν) and wave number ($\overline{\nu}$) of the yellow light.

Solution. Frequency, $\nu = \frac{c}{\lambda}$

$$1 \text{ nm} = 10^{-9} \text{ m}$$

$$580 \text{ nm} = 580 \times 10^{-9} \text{ m} = 580 \times 10^{-7} \text{ cm}$$

$$\nu = \frac{3.0 \times 10^{8} \text{ ms}^{-1}}{580 \times 10^{-9} \text{ m}} = 5.17 \times 10^{14} \text{ s}^{-1}$$

(Velocity of light $= 3 \times 10^{8} \text{ ms}^{-1}$)

Wave number, $\overline{\nu} = \frac{1}{\lambda} = \frac{1}{580 \times 10^{-7} \text{ cm}}$

$$= 1.724 \times 10^{4} \text{ cm}^{-1}$$

Question 6. Find energy of each of the photons which

(i) correspond to light of frequency 3×10^{15} Hz.

(ii) have wavelength of 0.50 Å.

Solution.

(i) Energy, $E = h\nu$

[h = Planck's constant $= 6.626 \times 10^{-34}$ Js and $\nu = 3 \times 10^{15}$ Hz $= 3 \times 10^{15}$cps]

Energy, $E = 6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^{15} \text{ s}^{-1}$

$$= 19.878 \times 10^{-19} \text{ J} = 1.9878 \times 10^{-18} \text{ J}$$

(ii) Energy, $E = \frac{hc}{\lambda}$ $\left(\because \nu = \frac{c}{\lambda}\right)$

$$\lambda = 0.50 \text{ Å} = 0.50 \times 10^{-10} \text{ m}$$

Energy, $E = \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^{8} \text{ ms}^{-1}}{0.50 \times 10^{-10} \text{ m}}$

$$= 39.756 \times 10^{-16} \text{ J}$$

$$= 3.975 \times 10^{-15} \text{ J}$$

Question 7. **Calculate the wavelength , frequency and wave number of a light wave whose period is 2.0×10^{-10}s.**

Solution. Frequency, $\nu = \dfrac{1}{\text{Time period}} = \dfrac{1}{2.0 \times 10^{-10}\ \text{s}} = 5 \times 10^{9}\ \text{s}^{-1}$

Wavelength, $\lambda = \dfrac{c}{\nu} = \dfrac{3.0 \times 10^{8}\ \text{ms}^{-1}}{5 \times 10^{9}\ \text{s}^{-1}} = 0.6 \times 10^{-1}\ \text{m} = 6.0 \times 10^{-2}\ \text{m}$

Wave number, $\bar{\nu} = \dfrac{1}{\lambda} = \dfrac{1}{6.0 \times 10^{-2}\ \text{m}} = 16.66\ \text{m}^{-1}$

Question 8. **What is the number of photons of light with a wavelength of 4000 pm that provide 1 J of energy?**

(i) Number of photons is calculated by dividing total energy by energy of 1 photon, so first calculate the energy of 1 photon by applying, $E = \dfrac{hc}{\lambda}$

(ii) Then, calculate the number of photons by using the formula.

$$N = \frac{\text{Total energy}}{\text{Energy of one photon}}$$

Solution. Energy, $E = \dfrac{hc}{\lambda} = \dfrac{6.626 \times 10^{-34}\ \text{Js} \times 3.0 \times 10^{8}\ \text{ms}^{-1}}{4000 \times 10^{-12}\ \text{m}}$

(1 pm $= 10^{-12}$ m)

$= 4.9695 \times 10^{-17}\ \text{J}$

Number of photons, $N = \dfrac{1\ \text{J}}{4.9695 \times 10^{-17}\ \text{J}} = 2.0122 \times 10^{16}$ photons

Question 9. **A photon of wavelength 4×10^{-7} m strikes on metal surface, the work function of the metal being 2.13 eV. Calculate**

(i) the energy of the photon (eV).

(ii) the kinetic energy of the emission.

(iii) the velocity of the photoelectron (1 eV = 1.6020×10^{-19} J).

Direct formula based question.

(i) Calculate the energy of a photon by using, $E = \dfrac{hc}{\lambda}$ in joule and convert it in eV.

(ii) Calculate the kinetic energy of ejected electron, KE = $h\nu - h\nu_0$ where, $E = h\nu$ and $h\nu_0$ = work function.

(iii) Calculate the velocity of electron by using the formula, KE = $\dfrac{1}{2} mv^2$.

Solution.

(i) Energy of a photon,

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\ \text{Js} \times 3.0 \times 10^{8}\ \text{ms}^{-1}}{4 \times 10^{-7}\ \text{m}}$$

$$E = 4.969 \times 10^{-19}\ \text{J}$$

$$(1.602 \times 10^{-19}\ \text{J} = 1\ \text{eV})$$

$$4.969 \times 10^{-19}\ \text{J} = \frac{4.969 \times 10^{-19}}{1.602 \times 10^{-19}} = 3.10\ \text{eV}$$

(ii) Kinetic energy of an ejected electron, $\text{KE} = h\nu - h\nu_0$

$h\nu = 3.10\ \text{eV}$ (energy of striking photon)

$h\nu_0 = W_0 = 2.13\ \text{eV}$ (work function of the metal)

$$\text{KE} = \frac{1}{2} mv^2 = 3.10 - 2.13 = 0.97\ \text{eV}$$

(iii) $\text{KE} = \frac{1}{2} mv^2 = 0.97\ \text{eV}$

$$\frac{1}{2} mv^2 = 0.97 \times 1.602 \times 10^{-19}\ \text{J} \qquad (1\ \text{eV} = 1.602 \times 10^{-19}\ \text{J})$$

$$\frac{1}{2} \times 9.11 \times 10^{-31}\ \text{kg} \times v^2 = 0.97 \times 1.602 \times 10^{-19}\ \text{J}$$

$(\because$ Mass of 1 $e^- = 9.11 \times 10^{-31}$ kg)

$$v^2 = \frac{0.97 \times 1.602 \times 10^{-19} \times 2\ \text{J}}{9.11 \times 10^{-31}\ \text{kg}} = 0.341 \times 10^{12}$$

$$v^2 = 0.341 \times 10^{12}\ (\text{ms}^{-1})^2$$

$$v = 0.584 \times 10^6 = 5.84 \times 10^5\ \text{ms}^{-1}$$

Note *Minimum energy required to eject the electron is $h\nu_0$. It is also called work function, W_0.*

Question 10. Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-1}.

Solution. Given, wavelength, $\lambda = 242\ \text{nm} = 242 \times 10^{-9}$ m

$$\text{Energy, } E = h\nu = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\ \text{Js} \times 3.0 \times 10^8\ \text{ms}^{-1}}{242 \times 10^{-9}\ \text{m}}$$

$$E = 0.0821 \times 10^{-17}\ \text{J/atom}$$

This energy is sufficient for ionization of one Na atom, so it is the ionization energy of Na.

$$E = 6.02 \times 10^{23} \times 0.0821 \times 10^{-17}\ \text{J/mol}$$

$$E = 4.945 \times 10^5\ \text{J/mol} = 4.945 \times 10^2\ \text{kJ/mol}$$

Question 11. A 25 watt bulb emits monochromatic yellow light of wavelength 0.57 μm. Calculate the rate of emission of quanta per second.

Solution. 25 watt = 25 Js^{-1} (1 watt = 1 Js^{-1})

Wavelength, $\lambda = 0.57\ \mu\text{m} = 0.57 \times 10^{-6}$ m (1 μm = 10^{-6} m)

Energy of one photon, $E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ Js} \times 3.0 \times 10^{8} \text{ ms}^{-1}}{0.57 \times 10^{-6} \text{ m}}$

$$E = 34.87 \times 10^{-20} \text{ J}$$

Number of photons emitted per second

$$= \frac{\text{Total energy per second}}{\text{Energy of one photon}}$$

$$= \frac{25 \text{ Js}^{-1}}{34.87 \times 10^{-20} \text{ J}} = 0.7169 \times 10^{20} \text{ photons per second}$$

$$= 7.169 \times 10^{19} \text{ photons per second}$$

Question 12. Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800 Å. Calculate threshold frequency (v_0) and work function (W_0) of the metal.

Solution. Threshold wavelength, $\lambda_0 = 6800 \text{ Å} = 6800 \times 10^{-10} \text{ m}$

Threshold frequency, $\nu_0 = \frac{c}{\lambda_0} = \frac{3.0 \times 10^{8} \text{ ms}^{-1}}{6800 \times 10^{-10} \text{ m}} = 4.41 \times 10^{14} \text{ s}^{-1}$

Work function, $W_0 = h\nu_0 = 6.626 \times 10^{-34} \text{ Js} \times 4.41 \times 10^{14} \text{ s}^{-1}$

$$= 29.22 \times 10^{-20} \text{ J} = 2.922 \times 10^{-19} \text{ J}$$

Note *For each metal, there is a characteristic minimum frequency,* ν_0 *which is also know as threshold frequency below which photoelectric effect is not observed.*

Question 13. What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with $n = 4$ to an energy level with $n = 2$?

Solution. Wave number, $\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

(Rydberg constant, $R = 109677 \text{ cm}^{-1}$)

$$\frac{1}{\lambda} = 109677\left(\frac{1}{2^2} - \frac{1}{4^2}\right) \text{cm}^{-1}$$

$$\frac{1}{\lambda} = 109677\left(\frac{3}{16}\right) \text{cm}^{-1}$$

$$\frac{1}{\lambda} = 20564.4 \text{ cm}^{-1}$$

$$\lambda = \frac{1}{20564.4} \text{ cm} = 486 \times 10^{-7} \text{ cm}$$

$$= 486 \times 10^{-9} \text{ m} = 486 \text{ nm}$$

The colour corresponding to this wavelength is blue.

Note *n_2 is always greater than n_1. If $n_1 = 1, 2 \ldots$ then $n_2 = n_1 + 1$, $n_1 + 2 \ldots$*

Question 14. How much energy is required to ionize a H-atom if the electron occupies $n = 5$ orbit? Compare your answer with the ionization enthalpy of H-atom (energy required to remove the electron from $n = 1$ orbit).

(i) Find ΔE when $n_i = 5$ and $n_f = \infty$.
(ii) Find $\Delta E'$ when $n_i = 1$ and $n_f = \infty$ and compare them.

Solution. Energy change, $\Delta E = E_f - E_i$

$$\Delta E = 2.18 \times 10^{-18}\ \text{J}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

When $n_i = 5$ and $n_f = \infty$, energy change,

$$\Delta E = 2.18 \times 10^{-18}\ \text{J}\left(\frac{1}{5^2} - \frac{1}{\infty}\right) = 0.0872 \times 10^{-18}\ \text{J}$$

When $n_i = 1$ and $n_f = \infty$, energy change,

$$\Delta E' = 2.18 \times 10^{-18}\ \text{J}\left(\frac{1}{1^2} - \frac{1}{\infty}\right)$$

$$\Delta E' = 2.18 \times 10^{-18}\ \text{J}$$

$$\frac{\Delta E'}{\Delta E} = \frac{2.18 \times 10^{-18}}{0.0872 \times 10^{-18}} = 25$$

Hence, energy required to remove an electron from first orbit is 25 times than that required to remove an electron from fifth orbit.

Question 15. What is the maximum number of emission lines when the excited electron of a H-atom in $n = 6$ drops to the ground state?

Solution. Number of lines produced when electron from nth shell drops to ground state $= \dfrac{n(n-1)}{2}$

When $n = 6$, number of lines produced $= \dfrac{6(6-1)}{2} = \dfrac{6 \times 5}{2} = 15$

Question 16. (i) The energy associated with the first orbit in the hydrogen atom is -2.18×10^{-18} J atom^{-1}. What is the energy associated with the fifth orbit?

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

Solution.

(i) Energy in nth orbit, $E_n = \dfrac{-2.18 \times 10^{-18}}{n^2}$ J

Energy in fifth orbit, $E_5 = \dfrac{-2.18 \times 10^{-18}}{5^2}$ J $= -0.0872 \times 10^{-18}$ J

$= -8.72 \times 10^{-20}$ J

(ii) For H atom, radius of nth orbit, $r_n = 0.529 \times n^2$ Å

$\therefore$ Radius of 5th Bohr orbit, $r_5 = 0.529 \times 5^2 = 13.225$ Å $= 1.3225$ nm

Question 17. Calculate the wave number for the longest wavelength transition in the Balmer series of atomic hydrogen.

(i) For longest wavelength (λ), wave number ($\bar{\nu}$) should be minimum, *i.e.*, the difference between n_1 and n_2 is minimum.

(ii) For Balmer series, $n_1 = 2$, so $n_2 = 3$

(iii) Put the values of n_1 and n_2 in the formula, $\bar{\nu} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$ to calculate wave number for the longest wavelength in the Balmer series.

Solution. Wave number, $\bar{\nu} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

$$\bar{\nu} = 109677\left(\frac{1}{2^2} - \frac{1}{3^2}\right)\text{cm}^{-1}$$

$$\bar{\nu} = 15232.91\ \text{cm}^{-1}$$

$$= 1.523 \times 10^4\ \text{cm}^{-1} = 1.523 \times 10^6\ \text{m}^{-1}$$

Question 18. 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 the light emitted when the electron returns to the ground state? The ground state electron energy is -2.18×10^{-11} erg.

(i) Find energy required to shift electron from E_1 to E_5 by using the formula $\Delta E = E_5 - E_1$.

(ii) Find λ of emitted light when electron returns to E_1 (ground state) by using the formula $\Delta E = \frac{hc}{\lambda}$.

Solution. $\Delta E = E_5 - E_1 = 2.18 \times 10^{-11}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$ erg

(n_i = 1st orbit and n_f = 5th orbit)

$$\Delta E = 2.18 \times 10^{-11}\left(\frac{1}{1^2} - \frac{1}{5^2}\right)\text{erg}$$

$$\Delta E = 2.18 \times 10^{-11} \times \frac{24}{25} = 2.0928 \times 10^{-11}\ \text{erg}$$

$$= 2.0928 \times 10^{-18}\ \text{J} \qquad (1\ \text{erg} = 10^{-7}\ \text{J})$$

When electron returns to ground state, it emits energy equals to ΔE hence,

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

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34}\ \text{Js} \times 3.0 \times 10^{8}\ \text{ms}^{-1}}{2.0928 \times 10^{-18}\ \text{J}}$$

$$= 9.498 \times 10^{-8}\ \text{m} = 949.8 \times 10^{-10}\ \text{m} = 949.8\ \text{Å}$$

Question 19. **The electron energy in hydrogen atom is given by $E_n = (-2.18 \times 10^{-18})/n^2$ J. Calculate the energy required to remove an electron completely from the $n = 2$ orbit. What is the longest wavelength of light in cm that can be used to cause this transition?**

(i) $\Delta E = E_\infty - E_2$ (as the electron is removed completely from the orbit)

(ii) $\Delta E = \frac{hc}{\lambda}$ or $\lambda = \frac{hc}{\Delta E}$

Solution. Energy required to shift an electron from $n = 2$ to $n = \infty$.

$$\Delta E = E_\infty - E_2 = 0 - \left(-\frac{2.18 \times 10^{-18}\ \text{J atom}^{-1}}{2^2}\right)$$

$$= 0.545 \times 10^{-18}\ \text{J atom}^{-1}$$

$$= 5.45 \times 10^{-19}\ \text{J atom}^{-1}$$

$$\text{Wavelength, } \lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34}\ \text{Js} \times 3.0 \times 10^{8}\ \text{ms}^{-1}}{5.45 \times 10^{-19}\ \text{J}}$$

$$= 3.647 \times 10^{-7}\ \text{m} = 3.647 \times 10^{-5}\ \text{cm}$$

Question 20. **Calculate the wavelength of an electron moving with velocity of $2.05 \times 10^7\ \text{ms}^{-1}$.**

Solution. We know that mass of an electron, $m = 9.1 \times 10^{-31}$ kg,

h = Planck's constant $= 6.626 \times 10^{-34}$ Js and

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ \text{Js}}{9.11 \times 10^{-31}\ \text{kg} \times 2.05 \times 10^{7}\ \text{ms}^{-1}}$$

$$\lambda = 0.35 \times 10^{-10}\ \text{m} \qquad (1\ \text{J} = 1\ \text{kgm}^2\text{s}^{-2})$$

$$\lambda = 3.5 \times 10^{-11}\ \text{m}$$

Question 21. **The mass of an electron is 9.1×10^{-31} kg. If its KE is 3.0×10^{-25} J, calculate its wavelength.**

Wavelength depends upon the mass and velocity of electron, so first calculate the velocity of electron from the formula of kinetic energy ($\text{KE} = \frac{1}{2}mv^2$) then, calculate the wavelength by using the formula $\lambda = \frac{h}{mv}$.

Solution. $\text{KE} = \frac{1}{2}mv^2$

$$v^2 = \frac{2\text{KE}}{m} \text{ or } v = \sqrt{\frac{2\text{KE}}{m}}$$

$$v = \sqrt{\frac{2 \times 3.0 \times 10^{-25}\ \text{J}}{9.1 \times 10^{-31}\ \text{kg}}} \qquad (1\ \text{J} = 1\ \text{kg m}^2\text{s}^{-2})$$

$$v = \sqrt{0.6593 \times 10^{6}} = 0.8119 \times 10^{3} = 812.0\ \text{ms}^{-1}$$

$$\text{Wavelength, } \lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ \text{Js}}{9.1 \times 10^{-31}\ \text{kg} \times 812.0\ \text{ms}^{-1}}$$

$$\lambda = 0.0008967 \times 10^{-3}\ \text{m}$$

$$\lambda = 8967\ \text{Å}$$

Question 22. **Which of the following are isoelectronic species, *i.e.*, those having the same number of electrons?**

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

Solution. Isoelectronic species have the same number of electrons but different atomic numbers

Calculation of number of electrons have been shown below

(Number of positive charge shows, number of electrons lost and number of negative charges shows number of electrons gained by an atom).

$_{11}Na^+ = 11 - 1 = 10\, e^-$, $_{19}K^+ = 19 - 1 = 18\, e^-$

$_{12}Mg^{2+} = 12 - 2 = 10\, e^-$, $_{20}Ca^{2+} = 20 - 2 = 18\, e^-$

$_{16}S^{2-} = 16 + 2 = 18\, e^-$, $_{18}Ar = 18\, e^-$

Hence, isoelectronic species are

(i) Na^+ and Mg^{2+} (ii) K^+, Ca^{2+}, S^{2-} and Ar

Question 23. **(i) Write the electronic configurations of the following ions:**

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

(ii) What are the atomic numbers of elements whose outermost electrons are represented by

(a) $3s^1$ (b) $2p^3$ (c) $3p^5$?

(iii) Which atoms are indicated by the following configurations?

(a) [He] $2s^1$ (b) [Ne] $3s^2 3p^3$ (c) [Ar] $4s^2\ 3d^1$

(i) First write the electronic configuration of neutral atom of the given ions and then remove or add the electrons as the ion have a charge. (If it has positive charge, remove electrons and if it has negative charge, add the electrons equal to the charge.)

(ii) To find the total number of electrons, which is equal to atomic number in case of netural atom, fill the orbitals in order of their increasing energies up to the given outer orbital configuration.

Solution.

(i) (a) $_1H = 1s^1$; $H^- = 1s^2$

(b) $_{11}Na = 1s^2 2s^2 2p^6 3s^1$; $Na^+ = 1s^2\ 2s^2\ 2p^6$

(c) $_8O = 1s^2 2s^2 2p^4$; $O^{2-} = 1s^2 2s^2 2p^6$

(d) $_9F = 1s^2 2s^2 2p^5$; $F^- = 1s^2 2s^2 2p^6$

(ii) To obtain atomic number of an element fill the orbitals in order of their increasing energies up to the given outer orbital configuration.

(a) $1s^2 2s^2 2p^6 3s^1$ (Z = 11)

(b) $1s^2 2s^2 2p^3$ (Z = 7)
(c) $1s^2 2s^2 2p^6 3s^2 3p^5$ (Z = 17)

(iii) (a) [He] $2s^1$; It represents ${}_3$Li (lithium)
(b) [Ne] $3s^2 3p^3$; It represents ${}_{15}$P (phosphorus)
(c) [Ar] $4s^2 3d^1$; It represents ${}_{21}$Sc (scandium)

Question 24. **What is the lowest value of *n* that allows *g* orbitals to exist?**

(i) Value of $l = 0$ to $(n - 1)$
(ii) $l = 0$ means *s* orbital, $l = 1$ means *p* orbitals, $l = 2$ means *d* orbitals $l = 3$ means *f* orbitals and $l = 4$ means *g* orbitals

Solution. For *g* subshell $l = 4$ and to have $l = 4$ minimum value of $n = 5$ [because the value of $l = 0$ to $(n - 1)$]

Question 25. **An electron is in one of the 3*d*-orbitals. Give the possible values of *n*, *l* and m_l for this electron.**

(i) For *s*, *p*, *d* and *f* orbitals, value of *l* is 0, 1, 2 and 3 respectively.
(ii) $m_l = -l$ to $+l$ including 0.

Solution. For 3*d*-electron,

$$n = 3, \quad l = 2, \quad m_l = -2, -1, 0, +1, +2 \text{ (any one)}$$

Question 26. **An atom of an element contains 29 electrons and 35 neutrons. Deduce**

(i) the number of protons
(ii) the electronic configuration of the element.

Solution.

(i) For a neutral atom;
Number of electrons = number of protons = Z (At. no.)
29 electrons = 29 protons.

(ii) ${}_{29}Z = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ (The element is copper.)

Question 27. **Give the number of electrons in the species H_2^+, H_2 and O_2^+.**

(i) Count the total number of electrons by adding electrons present in each atom of a molecule.
(ii) Then remove or add electrons according to charge (positive or negative) to count the electrons in an ion.

Solution.

$$H_2 = {}_1H + {}_1H = 1 + 1 = 2e^-$$
$$H_2^+ = 2 - 1 = 1e^-$$
$$O_2 = {}_8O + {}_8O = 8 + 8 = 16e^-$$
$$O_2^+ = 16 - 1 = 15e^-$$

Question 28. (i) An atomic orbital has $n = 3$. What are the possible values of l and m_l?

(ii) List the quantum numbers (m_l and l) of electrons for $3d$-orbital.

(iii) Which of the following orbitals are possible?

$1p$, $2s$, $2p$ and $3f$

(a) l has the values 0 to $(n - 1)$
(b) m has the values $-l$ to $+l$
(c) The value of l never be equal to n or greater than it.

Solution.

(i) For $n = 3$

$l = 0, 1, 2$
$l = 0$; $m_l = 0$
$l = 1$; $m_l = -1, 0, +1$
$l = 2$; $m_l = -2, -1, 0, +1, +2$

(ii) For $3d$-orbital, $l = 2$; $m_l = -2, -1, 0, +1, +2$

(iii) $1p$ is not possible because if $n = 1$ then $l = 0$ only and for p, $l = 1$
$2s$ is possible because if $n = 2$ then $l = 0$ and 1 and for s, $l = 0$.
$2p$ is possible because if $n = 2$ then $l = 0$ and 1 and for p, $l = 1$
$3f$ is not possible because if $n = 3$ then $l = 0, 1$ and 2 for f, $l = 3$

Question 29. Using s, p, d notations, describe the orbital with the following quantum numbers,

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

n represents the main shell and 0, 1, 2, 3 ...... values of l represent the s, p, d, f ...... orbitals respectively.

Solution. Subshell notations

	n	l	Subshell notation
(a)	1	0	$1s$
(b)	3	1	$3p$
(c)	4	2	$4d$
(d)	4	3	$4f$

Question 30. Explain, giving reasons, which of the following sets of quantum numbers are not possible?

(a) $n = 0, l = 0, m_l = 0, m_s = +\frac{1}{2}$ (b) $n = 1, l = 0, m_l = 0, m_s = -\frac{1}{2}$

(c) $n = 1, l = 1, m_l = 0, m_s = +\frac{1}{2}$ (d) $n = 2, l = 1, m_l = 0, m_s = -\frac{1}{2}$

(e) $n = 3, l = 3, m_l = -3, m_s = +\frac{1}{2}$ (f) $n = 3, l = 1, m_l = 0, m_s = +\frac{1}{2}$

(i) n always be a positive integer.
(ii) $n \neq l$

Solution.

(a) is not possible as $n \neq 0$
(b) is possible (1*s*)
(c) is not possible because if $n = 1$, $l = 0$ only $(l \neq 1)$
(d) is possible (2*p*)
(e) is not possible because if $n = 3$, $l = 0, 1$ and 2 $(l \neq 3)$
(f) is possible (3*p*)

Question 31. **How many electrons in an atom may have the following quantum numbers?**

(a) $n = 4, m_s = -\frac{1}{2}$ **(b)** $n = 3, l = 0$

(i) Total number of electrons in a shell $(n) = 2n^2$.
(ii) Total number of electrons in an orbital = 2.

Solution.

(a) Total electrons if $n = 4 = 2n^2 = 2 \times 4^2 = 32$

Half of the total electrons, *i.e.*, 16 electrons have $m_s = -\frac{1}{2}$

(b) $n = 3, l = 0$ it is 3*s*-orbital and it can have two electrons.

Question 32. **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.**

Solution. According to Bohr model for H-atom, the angular momentum of an electron in a given stationary state,

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

or

$$2\pi r = \frac{nh}{mv}$$

From de-Broglie equation, wavelength, $\lambda = \frac{h}{mv}$

Hence, $$2\pi r = n\lambda$$

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

Question 33. **What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum?**

(i) Since, the $\bar{v}$ of He^+ is same as that of $\bar{v}$ of H, find the value of $\bar{v}$ of He^+ spectrum for Balmer transition by using the formula $\bar{v} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$.

(ii) Write the same expression for H-atom and find the value of n_1 and n_2 by putting the value of $\bar{v}$ of He^+ spectrum in Eq. (2).

Solution. Wave number, $\bar{\nu} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ and $\bar{\nu} = \frac{1}{\lambda}$

For He$^+$ spectrum (for Balmer transition)

$$\bar{\nu} = R \times (2)^2\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$$\bar{\nu} = R \times 4 \times \frac{3}{16} = \frac{3}{4}R \qquad ...(1)$$

For H spectrum, $$\bar{\nu} = R \times 1^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad ...(2)$$

$$\frac{3}{4}R = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\frac{3}{4} = \frac{1}{n_1^2} - \frac{1}{n_2^2}$$

Hence, $n_1 = 1$ and $n_2 = 2$. In H-spectrum, the transition from $n = 2$ to $n = 1$ have same wavelength as the Balmer transition from $n = 3$ to $n = 2$ of He$^+$ spectrum.

Question 34. Calculate the energy required for the process

$$\text{He}^+(g) \longrightarrow \text{He}^{2+}(g) + e^-$$

The ionization energy for the H-atom in the ground state is 2.18×10^{-18} J atom^{-1}.

Solution. Energy of electron in unielectron atomic system,

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

For H-atom, ionization energy (IE) = $E_\infty - E_1$

$$\text{IE} = 0 - \left(-\frac{2\pi^2 me^4 1^2}{1^2h^2}\right) \qquad \text{(where, Z = 1 and } n = 1 \text{ for H-atom)}$$

$$\text{IE} = 2.18 \times 10^{-18} \text{ J atom}^{-1}$$

For He$^+$, $\text{IE} = E_\infty - E_1 = 0 - \left(\frac{-2\pi^2 me^4 2^2}{1^2 n^2}\right) = 4 \times \frac{2\pi^2\, me^4}{h^2}$

$$= 4 \times 2.18 \times 10^{-18} \text{ J atom}^{-1} = 8.72 \times 10^{-18} \text{ J atom}^{-1}$$

∴ The energy required for the process He$^+$ ⟶ He^{2+} + e$^-$ is 8.72×10^{-18} atoms^{-1}.

Question 35. If the diameter of a carbon atom is 0.15 nm, calculate the number of carbon atoms which can be placed side by side in a straight line across length of scale of length 20 cm long.

Solution. Diameter of a carbon atom $= 0.15$ nm $= 0.15 \times 10^{-9}$ m

Length along which atoms are to be placed $= 20$ cm $= 0.2$ m

Number of carbon atom which can be placed in the given length

$$= \frac{0.2 \text{ m}}{0.15 \times 10^{-9} \text{ m}} = \frac{0.2 \times 10^{9}}{0.15 \text{ m}} = 1.33 \times 10^{9} \text{ atoms}$$

Question 36. **2×10^{8} atoms of carbon are arranged side by side. Calculate the radius of carbon atom if the length of this arrangement is 2.4 cm.**

Radius depends upon diameter d as $r = \frac{d}{2}$, so first calculate the diameter by dividing total length with number of carbon atoms present and then calculate radius.

Solution. Total length = 2.4 cm

Number of carbon atoms along the length = 2×10^{8}

$\therefore$ Diameter of 1 carbon atom $= \frac{2.4 \text{ cm}}{2 \times 10^{8}} = 1.2 \times 10^{-8}$ cm

$$\text{Radius of 1 carbon atom} = \frac{d}{2} = \frac{1.2 \times 10^{-8} \text{ cm}}{2}$$
$$= 0.60 \times 10^{-8} \text{ cm} = 0.060 \times 10^{-7} \text{ cm}$$
$$= 0.060 \times 10^{-9} \text{ m} = 0.060 \text{ nm}$$

Question 37. **The diameter of zinc atom is 2.6 Å. Calculate (a) radius of zinc atom in pm and (b) number of atoms present in a length of 1.6 cm if the zinc atoms are arranged side by side lengthwise.**

Solution. Diameter of Zn atom = 2.6 Å = 2.6×10^{-10} m

$$\text{Radius of Zn atom} = \frac{2.6 \times 10^{-10} \text{ m}}{2} = 1.3 \times 10^{-10} \text{ m}$$
$$= 130 \times 10^{-12} \text{ m} = 130 \text{ pm}$$

Given, length = 1.6 cm = 1.6×10^{-2} m

Number of Zn atoms in 1.6×10^{-2} m

$$= \frac{1.6 \times 10^{-2} \text{ m}}{2.6 \times 10^{-10} \text{ m}} = 0.6154 \times 10^{8} \text{ atoms} = 6.154 \times 10^{7} \text{ atoms}$$

Question 38. **A certain particle carries 2.5×10^{-16} C of static electric charge. Calculate the number of electrons present in it.**

Solution. Charge on 1 electron = 1.6022×10^{-19} C

Total charge = 2.5×10^{-16} C

$$\text{Number of electrons present in particle} = \frac{2.5 \times 10^{-16}}{1.6022 \times 10^{-19}}$$
$$= 1.5603 \times 10^{3} = 1560.3 \text{ electrons}$$

Question 39. **In Milikan's experiment, static electric charge on the oil drops has been obtained by shining X-rays. If the static electric charge on the oil drop is -1.282×10^{-18} C, calculate the number of electrons present on it.**

Solution. Number of electrons $= \dfrac{\text{Total charge in oil drop}}{\text{Charge on 1 electron}}$

$$= \frac{-1.282 \times 10^{-18}\ \text{C}}{-1.6022 \times 10^{-19}\ \text{C}} = 0.800 \times 10$$

$$= 8.0 \text{ electrons}$$

Question 40. **In Rutherford's experiment, generally the thin foil of heavy atoms, like gold, platinum, etc., have been used to be bombarded by the α-particles. If the thin foil of light atoms like aluminium, etc., is used, what difference would be observed from the above results?**

Solution. Heavy atoms such as gold, platinum have heavy nucleus. Heavy nucleus contains large amount of positive charge. When a beam of α-particles is shot at a thin gold foil, most of them pass through without much effect. Some however, are deflected back or by small angles due to enormous repulsive force of heavy nucleus. If light aluminium foil is used, the number of α-particles deflected back or those deflected by small angles will be negligible.

Question 41. **Symbols ${}^{79}_{35}\text{Br}$ and ${}^{79}\text{Br}$ can be written, whereas symbols ${}^{35}_{79}\text{Br}$ and ${}^{35}\text{Br}$ are not acceptable. Answer briefly.**

Solution. The composition of any atom can be represented by using the normal element symbol (X) with superscript on the left hand side as the mass number (*A*) and subscript (*Z*) on the left hand side as the atomic number, *i.e.*, ${}^{A}_{Z}\text{X}$. Hence, the symbols ${}^{35}_{79}\text{Br}$ and ${}^{35}\text{Br}$ are not acceptable.

Question 42. **An element with mass number 81 contains 31.7% more neutrons as compared to protons. Assign the atomic symbol.**

Solution. We know that mass number of the element, $A = p + n = 81$ ...(i)

Let the number of protons, $p = x$

Then, number of neutrons, $n = x + \dfrac{31.7}{100}x = 1.317x$

(as number of neutrons are 31.7% more than the protons)

Hence, from Eq. (i) $\quad x + 1.317x = 81$

$$2.317x = 81 \quad \text{or} \quad x = \frac{81}{2.317} = 34.958 \approx 35$$

Therefore, number of protons = 35 and the symbol is ${}^{81}_{35}\text{Br}$

(Number of protons = Atomic number)

Question 43. **An ion with mass number 37 possesses one unit of negative charge. If the ion contains 11.1% more neutrons than the electrons, find the symbol of the ion.**

Solution. Let the number of electrons in an ion = x

$\therefore$ Number of neutrons, $n = x + \frac{11.1}{100} x = 1.111x$

(As the number of neutrons are 11.1% more than the number of electrons)

In the neutral atom, number of electrons, $e^- = x - 1$

(as the ion carries – 1 charge)

Similarly, number of protons, $p = x - 1$

we know that, mass number $= n + p = 37$

or $1.111x + x - 1 = 37$

$2.111x = 37 + 1 = 38$

$$x = \frac{38}{2.111} = 18.0009 \approx 18$$

Number of protons = atomic number $= 18 - 1 = 17$

Therefore, the symbol of the ion is ${}^{37}_{17}\mathrm{Cl}^-$.

Question 44. **An ion with mass number 56 contains 3 units of positive charge and 30.4% more neutrons than the electrons. Assign the symbol to this ion.**

Solution. Let the number of electrons in an ion = x

$\therefore$ Number of neutrons $= x + \frac{30.4}{100} x = 1.304\,x$

($\because$ Number of neutrons are 30.4% more than the number of electrons).

In the neutral atom, number of electrons $= x + 3$ ($\because$ The ion carries + 3 charge.)

So, number of protons $= x + 3$

We know that, mass number $= n + p = 1.304x + x + 3 = 56$

$$2.304x = 53, \quad x = \frac{53}{2.304} = 23.003 \approx 23$$

$\therefore$ Number of protons $= 23 + 3 = 26$ = atomic number

Therefore, the symbol of the ion is ${}^{56}_{26}\mathrm{Fe}^{3+}$.

Question 45. **Arrange the following type of radiations in increasing order of frequency.**

(a) Radiation from microwave oven
(b) Amber light from traffic signal
(c) Radiation from FM radio
(d) Cosmic rays from outer space and
(e) X-rays.

Solution. The order of frequency is radiation from FM radio < microwaves < amber colour < X-rays < cosmic rays.

Question 46. **Nitrogen laser produces a radiation at a wavelength of 337.1 nm. If the number of photons emitted is 5.6×10^{24}, calculate the power of this laser.**

If *n* photons are emitted by a laser, the total energy of the photons emitted is equal to the power of the laser.

Solution. Energy of 1 photon,

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

$$= \frac{6.626 \times 10^{-34}\ \text{Js} \times 3.0 \times 10^{8}\ \text{ms}^{-1}}{337.1 \times 10^{-9}\ \text{m}} \qquad (1\ \text{nm} = 10^{-9}\ \text{m})$$

$$= 0.05896 \times 10^{-17}\ \text{J}$$

$$\text{Energy of } 5.6 \times 10^{24} \text{ photons} = 0.05896 \times 10^{-17} \times 5.6 \times 10^{24}\ \text{J}$$

$$= 0.3302 \times 10^{7}\ \text{J} = 3.302 \times 10^{6}\ \text{J}$$

Question 47. **Neon gas is generally used in sign boards. If it emits strongly at 616 nm, calculate**

(a) the frequency of emission.
(b) distance travelled by this radiation in 30 s.
(c) energy of quantum.
(d) number of quanta present if it produces 2 J of energy.

Solution.

(a) Frequency, $\nu = \frac{c}{\lambda}$

$$\lambda = 616\ \text{nm} = 616 \times 10^{-9}\ \text{m}$$

$$\nu = \frac{3.0 \times 10^{8}\ \text{ms}^{-1}}{616 \times 10^{-9}\ \text{m}} = 4.870 \times 10^{14}\ \text{s}^{-1}$$

(b) Distance travelled = Speed × Time

$$= 3.0 \times 10^{8}\ \text{ms}^{-1} \times 30\ \text{s} = 9.0 \times 10^{9}\ \text{m}$$

(c) Energy of quantum (or photon),

$$E = h\nu = 6.626 \times 10^{-34}\ \text{Js} \times 4.870 \times 10^{14}\ \text{s}^{-1}$$

$$= 32.268 \times 10^{-20}\ \text{J} = 32.27 \times 10^{-20}\ \text{J}$$

(d) Number of quanta present $= \frac{\text{Total energy produced}}{\text{Energy of 1 quanta}}$

$$= \frac{2\ \text{J}}{32.27 \times 10^{-20}\ \text{J}} = 6.197 \times 10^{18} \approx 6.2 \times 10^{18}\ \text{quanta}$$

Question 48. **In astronomical observations, signals observed from the distant stars are generally weak. If the photon detector receives a total of 3.15×10^{-18} J from the radiations of 600 nm, calculate the number of photons received by the detector.**

Solution. Energy of 1 photon, $E = \frac{hc}{\lambda}$

Given, wavelength, $\lambda = 600 \text{ nm} = 600 \times 10^{-9} \text{ m}$

$$\text{Energy of 1 photon, } E = \frac{6.626 \times 10^{-34} \text{ Js} \times 3.0 \times 10^{8} \text{ ms}^{-1}}{600 \times 10^{-9} \text{ m}} = 3.313 \times 10^{-19} \text{ J}$$

$$\text{Number of photons} = \frac{\text{Total energy received}}{\text{Energy of 1 photon}}$$

$$= \frac{3.15 \times 10^{-18} \text{ J}}{3.313 \times 10^{-19} \text{ J}} = 0.9507 \times 10^{1} \text{ photons}$$

$$\approx 10 \text{ photons}$$

Question 49. **Lifetimes of the molecules in the excited states are often measured by using pulsed radiation source of duration nearly in the nanosecond range. If the radiation source has the duration of 2ns and the number of photons emitted during the pulse source is 2.5×10^{15}, calculate the energy of the source.**

Solution. Frequency, $\nu = \frac{1}{\text{period}} = \frac{1}{2\text{ns}} = \frac{1}{2 \times 10^{-9} \text{ s}} = 0.5 \times 10^{9} \text{ s}^{-1}$

Energy of the source = Energy of 1 photon × number of photons produced

$$E_{\text{source}} = h\nu \times N$$

$$= 6.626 \times 10^{-34} \text{ Js} \times 0.5 \times 10^{9} \text{ s}^{-1} \times 2.5 \times 10^{15} = 8.28 \times 10^{-10} \text{ J}$$

Question 50. **The longest wavelength doublet absorption transition is observed at 589 and 589.6 nm. Calculate the frequency of each transition and energy difference between two excited states.**

Solution.

(i) Given, wavelength $\lambda_1 = 589 \text{ nm} = 589 \times 10^{-9} \text{ m}$

$\lambda_2 = 589.6 \text{ nm} = 589.6 \times 10^{-9} \text{ m}$

Frequency of wavelength 589 nm

$$\nu_1 = \frac{c}{\lambda_1} = \frac{3.0 \times 10^{8} \text{ ms}^{-1}}{589 \times 10^{-9} \text{ m}} = 5.093 \times 10^{14} \text{ s}^{-1}$$

Frequency of wavelength 589.6 nm

$$\nu_2 = \frac{c}{\lambda_2} = \frac{3.0 \times 10^{8} \text{ ms}^{-1}}{589.6 \times 10^{-9} \text{ m}} = 5.088 \times 10^{14} \text{ s}^{-1}$$

(ii) Energy difference between two excited states,

$$\Delta E = h\nu_1 - h\nu_2 = h(\nu_1 - \nu_2)$$

$$\Delta E = 6.626 \times 10^{-34} \text{ Js} (5.093 \times 10^{14} \text{s}^{-1} - 5.088 \times 10^{14} \text{s}^{-1})$$

$$\Delta E = 6.626 \times 10^{-34} \text{ Js} \times 0.005 \times 10^{14} \text{ s}^{-1}$$

$$\Delta E = 3.31 \times 10^{-22} \text{ J}$$

Question 51. **The work function for caesium atom is 1.9 eV. Calculate**

(a) the threshold wavelength.

(b) the threshold frequency of the radiation. If the caesium element is irradiated with a wavelength 500 nm, calculate the kinetic energy and the velocity of the ejected photoelectron.

(i) As we know the value of work function (W_0) and h, calculate the threshold frequency ν_0 by using the formula $W_0 = h\nu_0$.

(ii) Calculate λ_0 by using $\lambda_0 = \frac{c}{\nu_0}$

(iii) To calculate $KE = h(\nu - \nu_0)$ calculate ν of the striking and then calculate v by using the formula $KE = \frac{1}{2}mv^2$.

Solution.

(a) Work function $W_0 = h\nu_0$

$W_0 = 1.9 \text{ eV} = 1.9 \times 1.602 \times 10^{-19}$ J

Threshold frequency,

$$\nu_0 = \frac{W_0}{h} = \frac{1.9 \times 1.602 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ Js}}$$

$$\nu_0 = 4.59 \times 10^{14} \text{ s}^{-1}$$

(b) Threshold wavelength,

$$\lambda_0 = \frac{c}{\nu_0} = \frac{3.0 \times 10^8 \text{ ms}^{-1}}{4.59 \times 10^{14} \text{ s}^{-1}}$$

$$= 6.536 \times 10^{-7} \text{ m}$$

$$= 653.6 \times 10^{-9} \text{ m} = 653.6 \text{ nm}$$

(c) KE of ejected photoelectron $= h(\nu - \nu_0)$

λ of striking radiation = 500 nm = 500×10^{-9} m

$$\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^8 \text{ ms}^{-1}}{500 \times 10^{-9} \text{ m}} = 6.0 \times 10^{14} \text{ s}^{-1}$$

$$KE = 6.626 \times 10^{-34} \text{ Js } (6.0 \times 10^{14} \text{ s}^{-1} - 4.59 \times 10^{14} \text{s}^{-1})$$

$$KE = 9.34 \times 10^{-20} \text{ J}$$

(d) $KE = \frac{1}{2}mv^2$ (Mass of an electron $= 9.11 \times 10^{-31}$ kg)

$$9.34 \times 10^{-20} \text{ J} = \frac{1}{2} \times 9.11 \times 10^{-31} \text{ kg} \times v^2$$

$\therefore$ $v^2 = 2.050 \times 10^{11} \text{ m}^2\text{s}^{-2}$ ($\because 1 \text{ J} = 1 \text{ kg m}^2\text{s}^{-2}$)

or $v = \sqrt{20.50 \times 10^{10} \text{ m}^2\text{s}^{-2}}$

or $v = 4.527 \times 10^5 \text{ ms}^{-1}$

Note *Minimum energy required to eject an electron is also known as work function, W_0 ($W_0 = h\nu_0$).*

Question 52. **Following results are observed when sodium metal is irradiated with different wavelengths. Calculate**

(a) threshold wavelength **(b) Planck's constant.**

λ (nm)	**500**	**450**	**400**
$v \times 10^5$ (ms^{-1})	**2.55**	**4.35**	**5.20**

(i) To find the value of λ_0, ν_0 is required, so first calculate the value of ν for all the three experiments by using the formula, $\nu = \frac{c}{\lambda}$ and make three equation by substituting the values of ν and v in the formula. $KE = h(\nu - \nu_0) = \frac{1}{2}mv^2$.

(ii) Divide Eq. (ii) by Eq. (i) and obtain ν_0.

(iii) Find λ_0 by using the formula, $\lambda_0 = \frac{c}{\nu_0}$

(iv) Find h by putting the value of ν_0 in Eq. (iii).

Solution. Kinetic energy, $KE = h(\nu - \nu_0) = \frac{1}{2}mv^2$

On substituting the given results of the three experiments, we get

For Ist experiment $\lambda = 500$ nm $= 500 \times 10^{-9}$ m;

$$\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^8 \text{ ms}^{-1}}{500 \times 10^{-9} \text{ m}} = 6 \times 10^{14} \text{s}^{-1}$$

$$h(6 \times 10^{14} \text{ s}^{-1} - \nu_0) = \frac{1}{2} m (2.55 \times 10^5 \text{ ms}^{-1})^2 \quad \text{...(i)}$$

For 2nd experiment $\lambda = 450$ nm $= 450 \times 10^{-9}$ m;

$$\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^8 \text{ ms}^{-1}}{450 \times 10^{-9} \text{ m}} = 6.67 \times 10^{14} \text{ s}^{-1}$$

$$h(6.67 \times 10^{14} \text{s}^{-1} - \nu_0) = \frac{1}{2} \text{m} (4.35 \times 10^5 \text{ ms}^{-1})^2 \quad \text{...(ii)}$$

For 3rd experiment $\lambda = 400$ nm $= 400 \times 10^{-9}$ m;

$$\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^8 \text{ ms}^{-1}}{400 \times 10^{-9} \text{ m}} = 7.5 \times 10^{14} \text{ s}^{-1}$$

$$h(7.5 \times 10^{14} \text{ s}^{-1} - \nu_0) = \frac{1}{2} m (5.20 \times 10^5 \text{ ms}^{-1})^2 \quad \text{...(iii)}$$

On dividing Eq. (ii) by Eq. (i), we get

$$\frac{h(6.67 \times 10^{14} \text{s}^{-1} - \nu_0) = \frac{1}{2} m (4.35 \times 10^5 \text{ ms}^{-1})^2}{h(6 \times 10^{14} \text{ s}^{-1} - \nu_0) = \frac{1}{2} m (2.55 \times 10^5 \text{ ms}^{-1})^2}$$

$$\frac{6.67 \times 10^{14} \text{ s}^{-1} - \nu_0}{6 \times 10^{14} \text{ s}^{-1} - \nu_0} = \frac{(4.35)^2}{(2.55)^2} = 2.91$$

$$6.67 \times 10^{14} \text{ s}^{-1} - \nu_0 = 17.46 \times 10^{14} \text{s}^{-1} - 2.91 \nu_0$$

$$2.91\nu_0 - \nu_0 = 17.46 \times 10^{14}\ \text{s}^{-1} - 6.67 \times 10^{14}\ \text{s}^{-1}$$
$$1.91\nu_0 = 10.79 \times 10^{14}\text{s}^{-1}$$
$$\nu_0 = \frac{10.79 \times 10^{14}\text{s}^{-1}}{1.91} = 5.649 \times 10^{14}\ \text{s}^{-1}$$
$$\lambda_0 = \frac{c}{\nu_0} = \frac{3.0 \times 10^{8}\ \text{ms}^{-1}}{5.649 \times 10^{14}\ \text{s}^{-1}} = 5.31 \times 10^{-7}\ \text{m}$$

On substituting the value of ν_0 in Eq. (iii), we get

$$h\,(7.5 \times 10^{14}\text{s}^{-1} - 5.649 \times 10^{14}\text{s}^{-1})$$
$$= \frac{1}{2} \times 9.11 \times 10^{-31}\ \text{kg} \times (5.20 \times 10^{5}\ \text{ms}^{-1})^2$$
$$h\,(1.851 \times 10^{14}\text{s}^{-1}) \times 2 = 9.11 \times 10^{-31}\ \text{kg} \times (5.20 \times 10^{5}\ \text{ms}^{-1})^2$$
$$h \times 3.702 \times 10^{14}\ \text{s}^{-1} = 246.33 \times 10^{-21}\ \text{kg m}^2\text{s}^{-2}$$
$$h = \frac{246.33 \times 10^{-21}\ \text{kg m}^2\text{s}^{-2}}{3.702 \times 10^{14}\ \text{s}^{-1}}$$
$$h = 6.6539 \times 10^{-34}\ \text{Js} \qquad (1\ \text{J} = 1\ \text{kg m}^2\text{s}^{-2})$$

Question 53. The ejection of the photoelectron from the silver metal in the photoelectric effect experiment can be stopped by applying the voltage of 0.35 V when the radiation 256.7 nm is used. Calculate the work function for silver metal.

We know that energy of incident radiation is related to work function as E of incident radiation = work function + KE, so first calculate E from $E = \frac{hc}{\lambda}$ and use KE of electron = potential applied (as applied potential gives the kinetic energy of electron) to calculate work function.

Solution. Energy of incident radiation, $h\nu = h\nu_0 + \text{KE}$

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\ \text{Js} \times 3.0 \times 10^{8}\ \text{ms}^{-1}}{256.7 \times 10^{-9}\ \text{m}}$$
$$= 7.74 \times 10^{-19}\ \text{J} = \frac{7.74 \times 10^{-19}\ \text{eV}}{1.602 \times 10^{-19}} = 4.83\ \text{eV}$$

Applied potential gives the kinetic energy to electron, *i.e.*,

$$\text{eV}_0 = \frac{1}{2} mv^2_{\text{max}} = \text{KE}$$
$$= \frac{1}{2} mv^2_{\text{max}} = 1.6 \times 10^{-19} \times 0.35 = 0.56 \times 10^{19}\ \text{J}$$
$$= \frac{0.56 \times 10^{-19}}{1.6 \times 10^{-19}}\ \text{eV} = 0.35\ \text{eV}$$

$\therefore \quad \text{KE} = 0.35\ \text{eV}$

Work function, W_0 or $h\nu_0 = h\nu - \text{KE}$

$$= 4.83\ \text{eV} - 0.35\ \text{eV} = 4.48\ \text{eV}$$

Question 54. **If the photon of the wavelength 150 pm strikes an atom and one of its inner bound electrons is ejected out with a velocity of 1.5×10^7 ms^{-1}, calculate the energy with which it is bound to the nucleus.**

The energy ($h\nu_0$) with which an electron is bound to the nucleus is calculated by using the formula $h\nu = h\nu_0 + \text{KE}$, so first find $h\nu$ of incident radiation and KE of electron by using the formula $\text{KE} = \frac{1}{2}mv^2$.

Then, substitute the values of $h\nu$ and KE to find $h\nu_0$ (*i.e.*, energy with which electron is bound to the nucleus).

Solution. Energy of incident radiation $h\nu = h\nu_0 + \frac{1}{2}mv^2$

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\ \text{Js} \times 3.0 \times 10^{8}\ \text{ms}^{-1}}{150 \times 10^{-12}\ \text{m}} \qquad (1\ \text{pm} = 10^{-12}\ \text{m})$$

$$E = 13.25 \times 10^{-16}\ \text{J}$$

$$\text{KE of ejected electron} = \frac{1}{2}mv^2 = \frac{1}{2} \times 9.11 \times 10^{-31}\ \text{kg} \times (1.5 \times 10^{7}\ \text{ms}^{-1})^2$$

$$\text{KE} = 1.025 \times 10^{-16}\ \text{J}$$

$$W_0 = h\nu_0 = h\nu - \frac{1}{2}mv^2$$

$$= 13.25 \times 10^{-16}\ \text{J} - 1.025 \times 10^{-16}\ \text{J} = 12.225 \times 10^{-16}\ \text{J}$$

$$= \frac{12.225 \times 10^{-16}}{1.602 \times 10^{-19}}\ \text{eV} = 7.63 \times 10^{3}\ \text{eV}$$

Note *Energy with which the electron was bound to the nucleus = work function for the metal.*

Question 55. **Emission transitions in the Paschen series end at orbit $n = 3$ and start from orbit n and can be represented as $v = 3.29 \times 10^{15}$ (Hz) $\left[\frac{1}{3^2} - \frac{1}{n^2}\right]$. Calculate the value of n if the transition is observed at 1285 nm. Find the region of the spectrum.**

Solution. Frequency, $\nu = \frac{c}{\lambda} = 3.29 \times 10^{15}\ \text{Hz}\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$

$$\nu = \frac{3.0 \times 10^{8}\ \text{ms}^{-1}}{1285 \times 10^{-9}\ \text{m}} = 3.29 \times 10^{15}\ \text{Hz}\left(\frac{1}{9} - \frac{1}{n^2}\right)$$

$$\frac{3.0 \times 10^{8}\ \text{ms}^{-1}}{1285 \times 10^{-9}\ \text{m} \times 3.29 \times 10^{15}\ \text{Hz}} = \left(\frac{1}{9} - \frac{1}{n^2}\right)$$

$$0.0709 = 0.1111 - \frac{1}{n^2}$$

$$\frac{1}{n^2} = 0.1111 - 0.0709 = 0.0402 \approx 0.04 = \frac{1}{25}$$

$$n^2 = 25 \text{ or } n = 5$$

∴ The electrons jumps from $n = 5$ to $n = 3$ *i.e.*, the transition occurs in Paschen series and lies in infra-red region.
Moreover the radiation 1285 nm lies in the infrared region.

Question 56. Calculate the wavelength for the emission transition if it starts from the orbit having radius 1.3225 nm and ends at 211.6 pm. Name the series to which this transition belongs and the region of the spectrum.

(i) Rydberg formula for finding λ is $\bar{\nu} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$. To calculate λ by using this formula, n_1 and n_2 are required, so first find the values of energy levels n_1 and n_2 by using the formula, $r_n = \frac{52.9\, n^2}{Z}$ pm, then calculate λ by using Rydberg formula.

(ii) On the basis of value of n_1, also give the name of series as for Lyman series $n_1 = 1$, for Balmer series $n_1 = 2$, for Paschen series $n_1 = 3$ and so on.

Solution. Radius of *n*th orbit of H like species,

$$r_n = \frac{52.9\,(n^2)}{Z}\ \text{pm}$$

$$r_1 = 1.3225\ \text{nm} = 1322.5\ \text{pm}$$

$$= \frac{52.9\, n_1^2}{Z}$$

$$r_2 = 211.6\ \text{pm} = \frac{52.9\, n_2^2}{Z}$$

$$\frac{r_1}{r_2} = \frac{1322.5}{211.6} = \frac{n_1^2}{n_2^2}$$

$$\frac{n_1^2}{n_2^2} = 6.25 \text{ or } \frac{n_1}{n_2} = 2.5$$

If $n_1 = 5$, $n_2 = 2$, so, the transition (emission transition) is from 5th orbit to 2nd orbit and it belongs to Balmer series.

$$\bar{\nu} = \frac{1}{\lambda} = 1.09677 \times 10^7 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{m}^{-1}$$

$$\frac{1}{\lambda} = 1.09677 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{5^2}\right) \text{m}^{-1}$$

$$\frac{1}{\lambda} = 1.09677 \times 10^7 \times \frac{21}{100} = 2.303 \times 10^6\ \text{m}^{-1}$$

$$\lambda = 0.434 \times 10^{-6}\ \text{m} = 434 \times 10^{-9}\ \text{m} = 434\ \text{nm}$$

It belongs to visible region.

Note *In the above Rydberg formula if $n_1 = 1, 2, \ldots$ then $n_2 = n_1 + 1$, $n_1 + 2 \ldots$. For Balmer series, spectral region is visible.*

Question 57. Dual behaviour of matter proposed by de-Broglie led to the discovery of electron microscope often used for the highly magnified images of biological molecules and other type of materials. If the velocity of the electron in this microscope is 1.6×10^6 ms^{-1}, calculate de-Broglie wavelength associated with this electron.

Solution. de-Broglie wavelength, $\lambda = \frac{h}{mv}$

$$\lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{9.11 \times 10^{-31} \text{ kg} \times 1.6 \times 10^6 \text{ ms}^{-1}} \quad (1\text{ J} = 1 \text{ kg m}^2\text{s}^{-2})$$

$$= 0.455 \times 10^{-9} \text{ m} = 4.55 \times 10^{-10} \text{ m} = 455 \text{ pm}.$$

Question 58. Similar to electron diffraction, neutron diffraction microscope is also used for the determination of the structure of molecules. If the wavelength used here is 800 pm, calculate the characteristic velocity associated with the neutron (mass of neutron = 1.675×10^{-27} kg).

Solution. Wavelength, $\lambda = \frac{h}{mv}$

Mass of neutron, $m = 1.675 \times 10^{-27}$ kg

$$\lambda = 800 \text{ pm} = 800 \times 10^{-12} \text{ m} = \frac{6.626 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}}{1.675 \times 10^{-27} \text{ kg} \times v}$$

$$v = \frac{6.626 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}}{1.675 \times 10^{-27} \text{ kg} \times 800 \times 10^{-12} \text{ m}}$$

$$= 0.494 \times 10^3 \text{ ms}^{-1} = 4.94 \times 10^2 \text{ ms}^{-1}$$

Question 59. If the velocity of the electron in Bohr's first orbit is 2.19×10^6 ms^{-1}, calculate the de-Broglie wavelength associated with it.

Solution. We know that, mass of electron = 9.11×10^{-31} kg

$$h = 6.626 \times 10^{-34} \text{ J-s}$$

Wavelength, $\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}}{9.11 \times 10^{-31} \text{ kg} \times 2.19 \times 10^6 \text{ m s}^{-1}}$

$$\lambda = 3.32 \times 10^{-10} \text{ m} = 332 \text{ pm}$$

Question 60. The velocity associated with a proton moving in a potential difference of 1000 V is 4.37×10^5 ms^{-1}. If the hockey ball of mass 0.1 kg is moving with this velocity, calculate the wavelength associated with this velocity.

Solution. Wavelength associated with the velocity of hockey ball

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}}{0.1 \text{ kg} \times 4.37 \times 10^5 \text{ m s}^{-1}}$$

$$= 15.16 \times 10^{-39} \text{ m} = 1.516 \times 10^{-38} \text{ m}$$

Question 61. If the position of the electron is measured within an accuracy of ± 0.002 nm, calculate the uncertainty in the momentum of the electron. Suppose the momentum of the electron is $\frac{h}{4\pi_m \times 0.05 \text{ nm}}$, is there any problem in defining this value.

Solution. $\Delta x = 0.002 \text{ nm} = 0.002 \times 10^{-9} \text{ m} = 2.00 \times 10^{-12} \text{ m}$

From Heisenberg's uncertainty principle,

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

$$\Delta p = \frac{h}{4\pi \, \Delta x} = \frac{6.626 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}}{4 \times 3.14 \times 2.00 \times 10^{-12} \text{ m}}$$

$$\Delta p = 2.638 \times 10^{-23} \text{ kg m s}^{-1}$$

$$\text{Actual momentum} = \frac{h}{4\pi \times 0.05 \text{ nm}} = \frac{6.626 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}}{4 \times 3.14 \times 0.05 \times 10^{-9} \text{ m}}$$

$$= 1.055 \times 10^{-24} \text{ kg m s}^{-1}$$

It cannot be defined as the actual value of momentum is smaller than uncertainty.

Question 62. The quantum numbers of six electrons are given below. Arrange them in order of increasing energies. If any of these combination(s) has/have the same energy lists :

1. $n = 4, l = 2, m_l = -2, m_s = -\frac{1}{2}$
2. $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$
3. $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$
4. $n = 3, l = 2, m_l = -2, m_s = -\frac{1}{2}$
5. $n = 3, l = 1, m_l = -1, m_s = +\frac{1}{2}$
6. $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$

Energy of the orbitals in multielectron atom depends upon the values of n and l. The lower the value of $(n + l)$ for an orbital, the lower is its energy. If two orbitals have the same $(n + l)$ value, the orbital with lower value of n, has the lower energy.

Solution.	**Subshell notation**	$n + l$
1. $n = 4, l = 2, m_l = -2, m_s = -\frac{1}{2}$	4d	$4 + 2 = 6$
2. $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$	3d	$3 + 2 = 5$
3. $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$	4p	$4 + 1 = 5$
4. $n = 3, l = 2, m_l = -2, m_s = -\frac{1}{2}$	3d	$3 + 2 = 5$
5. $n = 3, l = 1, m_l = -1, m_s = +\frac{1}{2}$	3p	$3 + 1 = 4$
6. $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$	4p	$4 + 1 = 5$

$$5 < 2 = 4 < 3 = 6 < 1$$

$$3p < 3d = 3d < 4p = 4p < 4d$$

(Arrangement of orbitals in order of their increasing energies.)

Question 63. **The bromine atom possesses 35 electrons. It contains 6 electrons in $2p$-orbital, 6 electrons in $3p$-orbital and 5 electron in $4p$-orbital. Which of these electron experiences the lowest effective nuclear charge?**

Solution. Effective nuclear charge decreases as the distance of the orbitals increases from the nucleus. Hence, $4p$ electrons experience the lowest effective nuclear charge.

Question 64. **Among the following pairs of orbitals which orbital will experience the larger effective nuclear charge?**

(i) $2s$ and $3s$, (ii) $4d$ and $4f$, (iii) $3d$ and $3p$

As the distance between the nucleus and orbital increases, effective nuclear charge decreases.

Solution.

(i) $2s$-orbital experiences larger effective nuclear charge than $3s$ because $2s$ is closer to nucleus than $3s$.

(ii) Similarly $4d$-orbital experiences larger effective nuclear charge than $4f$-orbital.

(iii) In $3d$ and $3p$-orbitals, $3p$-orbital experiences larger effective nuclear charge.

Question 65. **The unpaired electrons in Al and Si are present in $3p$-orbital. Which electrons will experience more effective nuclear charge from the nucleus?**

Solution. ${}_{13}\text{Al} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^1$

${}_{14}\text{Si} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^2$

Si (+4) has greater nuclear charge than aluminium (+3). Hence, $3p$ unpaired electrons of Si experience greater effective nuclear charge than Al.

Question 66. **Indicate the number of unpaired electrons in**

(a) P (b) Si (c) Cr (d) Fe (e) Kr

Solution.

(a) ${}_{15}\text{P} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^3$	3 unpaired electrons
(b) ${}_{14}\text{Si} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^2$	2 unpaired electrons
(c) ${}_{24}\text{Cr} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$	6 unpaired electrons
(d) ${}_{26}\text{Fe} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$	4 unpaired electrons
(e) ${}_{36}\text{Kr} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6$	No unpaired electron

Note *Either exactly half-filled or fully filled orbitals are more stable due to symmetrical distribution of electrons and maximum exchange energy.*

Question 67. (a) How many subshells are associated with $n = 4$?

(b) How many electrons will be present in the subshells having m_s value of $-\frac{1}{2}$ for $n = 4$?

Solution.

(a) $n = 4$, $l = 0, 1, 2, 3$, $s\ p\ d\ f$ (4 subshells)

(b) Number of orbitals in 4th shell $= n^2 = 4^2 = 16$

The maximum number of electrons present in any orbital is two and each orbital has one electron with $m_s = -\frac{1}{2}$. Hence, there are 16 electrons with $m_s = -\frac{1}{2}$.

Selected NCERT Exemplar Problems

Short Answer Type

Question 1. Arrange s, p and d-subshells of a shell in the increasing order of effective nuclear charge (Z_{eff}) experienced by the electron present in them.

Solution. s-orbital is spherical in shape, it shields the electrons from the nucleus more effectively than p-orbital which in turn shields more effectively than d-orbital. Therefore, the effective nuclear charge (Z_{eff}) experienced by electrons present in them is $d < p < s$.

Question 2. Show the distribution of electrons in oxygen atom (atomic number 8) using orbital diagram.

Solution. ${}_8O = 1s^2\ \ 2s^2\ \ \ 2p^4$

Question 3. Nickel atom can lose two electrons to form Ni^{2+} ion. The atomic number of Ni is 28. From which orbital will nickel lose two electrons?

Solution. ${}_{28}Ni = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^8, 4s^2$; Nickel will lose 2 electrons from $4s$ (outer most shell) to form Ni^{2+} ion.

Question 4. Which of the following orbitals are degenerate?

$$3d_{xy}, 4d_{xy}, 3d_{z^2}, 3d_{yz}\ 4d_{z^2}$$

Solution. The orbitals which belongs to same subshell and same shell are called degenerate orbitals. ($3d_{xy}$, $3d_{z^2}$, $3d_{yz}$) and ($4d_{xy}$, $4d_{yz}$, $4d_{z^2}$) are the two sets of degenerate orbitals.

Question 5. Calculate the total number of angular nodes and radial nodes present in $3p$-orbital.

Solution. For $3p$-orbital, principal quantum number, $n = 3$ and azimuthal quantum number, $l = 1$

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

Question 6. **Wavelengths of different radiations are given below.**

$$\lambda(A) = 300\ \text{nm}, \lambda(B) = 300\ \mu\text{m}, \lambda(C) = 3\ \text{nm}, \lambda(D) = 30\ \text{Å}$$

Arrange these radiations in the increasing order of their energies.

Solution.

(A) $\lambda = 300\ \text{nm} = 300 \times 10^{-9}\ \text{m}$
(B) $\lambda = 300\ \mu\text{m} = 300 \times 10^{-6}\ \text{m}$
(C) $\lambda = 3\ \text{nm} = 3 \times 10^{-9}\ \text{m}$
(D) $\lambda = 30\ \text{Å} = 30 \times 10^{-10}\ \text{m} = 3 \times 10^{-9}\ \text{m}$

$$\text{Energy,} \quad E = \frac{hc}{\lambda}$$

$$\text{Therefore,} \quad E \propto \frac{1}{\lambda}$$

Increasing order of energy is $B < A < C = D$

Question 7. **The Balmer series in the hydrogen spectrum corresponds to the transition from $n_1 = 2$ to $n_2 = 3, 4 \ldots$. This series lies in the visible region. Calculate the wave number of line associated with the transition in Balmer series when the electron moves to $n = 4$ orbit. ($R_H = 109677\ \text{cm}^{-1}$)**

Solution. From Rydberg formula,

$$\text{Wave number, } \bar{\nu} = 109677\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]\text{cm}^{-1}$$

Given $n_i = 2$ and $n_f = 4$ (Transition in Balmer series)

$$\bar{\nu} = 109677\left[\frac{1}{2^2} - \frac{1}{4^2}\right]\text{cm}^{-1}$$

$$\bar{\nu} = 109677\left[\frac{1}{4} - \frac{1}{16}\right]\text{cm}^{-1}$$

$$\bar{\nu} = 109677 \times \left[\frac{4-1}{16}\right]\text{cm}^{-1}$$

$$\bar{\nu} = 20564.44\ \text{cm}^{-1}$$

Question 8. **According to de-Broglie, matter should exhibit dual behaviour, that is both particle and wave like properties. However, a cricket ball of mass 100 g does not move like a wave when it is thrown by a bowler at a speed of 100 km/h. Calculate the wavelength of the ball and explain why it does not show wave nature?**

Solution. Given, $m = 100\ \text{g} = 0.1\ \text{kg}$

$$v = 100\ \text{km/h} = \frac{100 \times 1000}{60 \times 60} = \frac{1000}{36}\ \text{ms}^{-1}$$

From de-Broglie equation, wavelength, $\lambda = \frac{h}{mv}$

$$\lambda = \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{0.1 \text{ kg} \times \frac{1000}{36} \text{ ms}^{-1}} = 238.5 \times 10^{-36} \text{ m}$$

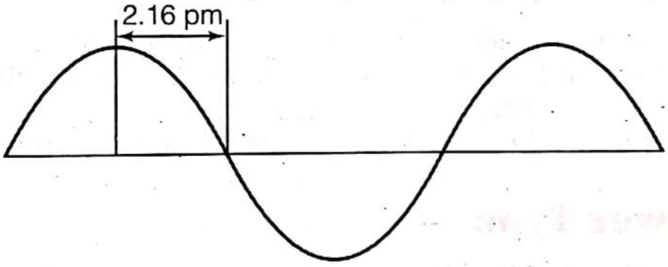
As the wavelength is very small so wave nature cannot be detected.

Question 9. **Out of electron and proton which one will have, a higher velocity to produce matter waves of the same wavelength? Explain it.**

Solution. From de-Broglie equation, wavelength, $\lambda = \frac{h}{mv}$

For same wavelength for two different particles, *i.e.*, electron and proton, $m_1v_1 = m_2v_2$ (h is constant). Lesser the mass of the particle, greater will be the velocity. Hence, electron will have higher velocity.

Question 10. **A hypothetical electromagnetic wave is shown in Fig. Find out the wavelength of the radiation.**



Solution. **Wavelength** It is the distance between two successive peaks or two successive troughs of a wave.

Therefore, $\lambda = 4 \times 2.16 \text{ pm} = 8.64 \text{ pm}$

Question 11. **Table-Tennis ball has a mass 10 g and a speed of 90 m/s. If speed can be measured within an accuracy of 4% what will be the uncertainty in speed and position?**

Solution. $m = 10 \text{ g} = 10 \times 10^{-3} \text{ kg}$

Uncertainty in speed $(\Delta v) = 4\%$ of $90 \text{ ms}^{-1} = \frac{4 \times 90}{100} = 3.6 \text{ ms}^{-1}$

From Heisenberg uncertainty principle,

$$\Delta x \cdot \Delta v = \frac{h}{4\pi m} \text{ or } \Delta x = \frac{h}{4\pi m \, \Delta v}$$

Uncertainty in position,

$$\Delta x = \frac{6.626 \times 10^{-34} \text{ kgm}^2\text{s}^{-1}}{4 \times 3.14 \times 10 \times 10^{-3} \text{ kg} \times 3.6 \text{ ms}^{-1}} = 1.46 \times 10^{-33} \text{ m}$$

Question 12. **The effect of uncertainty principle is significant only for motion of microscopic particles and is negligible for the macroscopic particles. Justify the statement with the help of a suitable example.**

Solution. If uncertainty principle is applied to an object of mass, say about a milligram (10^{-6} kg), then

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

$$\Delta v \cdot \Delta x = \frac{6.626 \times 10^{-34}\ \text{kgm}^2\text{s}^{-1}}{4 \times 3.14 \times 10^{-6}\ \text{kg}}$$

$$= 0.52 \times 10^{-28}\ \text{m}^2\text{s}^{-1}$$

The value of $\Delta v \cdot \Delta x$ obtained is extremely small and is insignificant. Therefore, for milligram-sized or heavier objects, the associated uncertainties are hardly of any real consequence.

Question 13. Hydrogen atom has only one electron, so mutual repulsion between electrons is absent. However, in multielectron atoms mutual repulsion between the electrons is significant. How does this affect the energy of an electron in the orbitals of the same principal quantum number in multielectron atoms?

Solution. In hydrogen atom, the energy of an electron is determined by the value of n and in multielectron atom, it is determined by $n + l$. Hence, for a given principal quantum, electrons of s, p, d and f-orbitals have different energy (for s, p, d and f, $l = 0, 1, 2$ and 3 respectively.)

Long Answer Type

Question 14. Threshold frequency, ν_0 is the minimum frequency which a photon must possess to eject an electron from a metal. It is different for different metals. When a photon of frequency $1.0 \times 10^{15}\ \text{s}^{-1}$ was allowed to hit a metal surface, an electron having 1.988×10^{-19} J of kinetic energy was emitted. Calculate the threshold frequency of this metal. Show that an electron will not be emitted if a photon with a wavelength equal to 600 nm hits the metal surface.

Solution. We know that $h\nu = h\nu_0 + \text{KE}$

or $h\nu - \text{KE} = h\nu_0 = (6.626 \times 10^{-34}\ \text{Js} \times 1 \times 10^{15}\ \text{s}^{-1}) - 1.988 \times 10^{-19}\ \text{J}$

$$h\nu_0 = 6.626 \times 10^{-19} - 1.988 \times 10^{-19}\ \text{J}$$

$$h\nu_0 = 4.638 \times 10^{-19}\ \text{J}$$

$$\nu_0 = \frac{4.638 \times 10^{-19}\ \text{J}}{6.626 \times 10^{-34}\ \text{Js}} = 0.699 \times 10^{15}\ \text{s}^{-1}$$

When, $\lambda = 600\ \text{nm} = 600 \times 10^{-9}\ \text{m}$

$$\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^{8}\ \text{ms}^{-1}}{6.0 \times 10^{-7}\ \text{m}} = 0.5 \times 10^{15}\ \text{s}^{-1}$$

Thus, $\nu < \nu_0$. Hence, no electron will be emitted.

Question 15. When an electric discharge is passed through hydrogen gas, the hydrogen molecules dissociate to produce excited hydrogen atoms. These excited atoms emit electromagnetic radiation of discrete frequencies which can be given by the general formula

$$\bar{\nu} = 109677\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$

What points of Bohr's model of an atom can be used to arrive at this formula? Based on these points derive the above formula giving description of each step and each term.

Solution. The two important points of Bohr's model that can be used to derive the given formula are as follows

(i) Electrons revolve around the nucleus in a circular path of fixed radius and energy. These paths are called orbits, stationary states or allowed energy states.

(ii) Energy is emitted or absorbed when an electron moves from higher stationary state to lower stationary state or from lower stationary state to higher stationary state respectively.

Derivation The energy of the electron in the nth stationary state is given by the expression,

$$E_n = -R_H\left(\frac{1}{n^2}\right) \qquad n = 1, 2, 3 \ldots \qquad \ldots\text{(i)}$$

where R_H is called Rydberg constant and its value is 2.18×10^{-18} J.

The energy of the lowest state, also called the ground state, is

$$E_1 = -2.18 \times 10^{-18}\left(\frac{1}{1^2}\right) = -2.18 \times 10^{-18} \text{ J} \qquad \ldots\text{(ii)}$$

The energy gap between the two orbits is given by the equation,

$$\Delta E = E_f - E_i \qquad \ldots\text{(iii)}$$

On combining equations (i) and (iii)

$$\Delta E = \left(-\frac{R_H}{n_f^2}\right) - \left(-\frac{R_H}{n_i^2}\right)$$

where, n_i and n_f stand for initial orbit and final orbit.

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

Frequency, ν associated with the absorption and emission of the photon can be calculated as follows

$$\nu = \frac{\Delta E}{h} = \frac{R_H}{h}\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$

$$\nu = \frac{2.18 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ Js}}\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$

$$\nu = 3.29 \times 10^{15}\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right] \text{Hz}$$

$$\bar{\nu} = \frac{\nu}{c} = \frac{3.29 \times 10^{15}}{3 \times 10^{8}\ \mathrm{ms^{-1}}}\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$

$$\bar{\nu} = 1.09677 \times 10^{7}\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]\mathrm{m^{-1}}$$

$$\bar{\nu} = 109677\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]\mathrm{cm^{-1}}$$

Question 16. Calculate the energy and frequency of the radiation emitted when an electron jumps from $n = 3$ to $n = 2$ in a hydrogen atom.

Solution. Wave number, $\bar{\nu} = 109677\ \mathrm{cm^{-1}}\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$

$$\bar{\nu} = 109677 \times \frac{5}{36} = 15232.9\ \mathrm{cm^{-1}}$$

$$\bar{\nu} = \frac{1}{\lambda} \text{ or } \lambda = \frac{1}{\bar{\nu}} = \frac{1}{15232.9} = 6.564 \times 10^{-5}\ \mathrm{cm}$$

Wavelength, $\lambda = 6.564 \times 10^{-7}\ \mathrm{m}$

Energy, $E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\ \mathrm{Js} \times 3.0 \times 10^{8}\ \mathrm{ms^{-1}}}{6.564 \times 10^{-7}\ \mathrm{m}} = 3.028 \times 10^{-19}\ \mathrm{J}$

Frequency, $\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^{8}\ \mathrm{ms^{-1}}}{6.564 \times 10^{-7}\ \mathrm{m}} = 0.457 \times 10^{15}\ \mathrm{s^{-1}}$

$\nu = 4.57 \times 10^{14}\ \mathrm{s^{-1}}$

Question 17. Why was a change in the Bohr model of atom required, due to which important development(s), concept of movement of an electron in an orbit was replaced by the concept of probability of finding electron in an orbital? What is the name given to the changed model of atom?

Solution. In Bohr model, an electron is regarded as a charged particle moving in well defined circular orbits about the nucleus. An orbit 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 uncertainty principal. Further more, the wave character of the electron is not considered in Bohr model. Therefore, concept of movement of an electron in an orbit was replaced by the concept of probability of finding electron in an orbital due to de-Broglie concept of dual nature of electron and Heisenberg's uncertainty principle. The changed model is called quantum mechanical model of the atom.

Chapter 3

Classification of Elements & Periodicity in Properties

Important Results

1. Periodic Table is an arrangement of elements with similar properties placed together.
2. Earlier attempts to classify elements :
   - (i) **Dobereiner's Triads** Dobereiner (1829) classified the elements into groups of three elements having similarity in physical and chemical properties. He also noticed that atomic mass of central element was the arithmetic mean of other two elements.
   - (ii) **Newland's Law of Octaves** Newland arranged the elements in such a manner that the eighth element starting from a given one has properties which are a repetition of those of the first, if arranged in order of increasing atomic weight.
   - (iii) **Mendeleev's Periodic Table** (1869) Mendeleev arranged the elements known at that time on the basis of his famous periodic law given as
     - (a) Atomic weight is the fundamental property of elements.
     - (b) The physical and chemical properties of elements are periodic function of their atomic weight.
3. **Modern Periodic Law** (1972) Moseley modified Mendeleev's periodic law and proposed modern periodic law as "the physical and chemical properties of the elements are periodic functions of their atomic numbers".
4. **Long form of Periodic Table** It was based on Bohr-Bury concept of electronic configuration. It contains 7 periods and 18 groups. Each period starts with filling of electrons in new principal quantum number and completes after the outermost shell is completely filled. Four types of elements can be recognized in the Periodic Table on the basis of their electronic configurations. These are *s*-block, *p*-block, *d*-block and *f*-block elements. Hydrogen with one electron in the *s*-orbital occupies a unique position in the Periodic Table.

5. Metals comprise more than 78% of the known elements. Non-metals, which are located at the extreme right of the Periodic Table, are less than twenty in number. Elements which lie at the border line between metals and non-metals are called metalloids or semi-metals.
6. Metallic character increases with increasing atomic number in a group whereas decreases from left to right in a period. The physical and chemical properties of elements vary periodically with their atomic numbers.
7. Periodic trends are observed in atomic sizes, ionization enthalpies, electron gain enthalpies, electronegativity and valence.
8. The atomic radii decreases while going from left to right in a period and increases with atomic number in a group. The size of isoelectronic species decreases with increase in the nuclear charge.
9. Ionization enthalpies generally increase across a period and decrease down a group. However, the elements having extra stable configuration have extra ordinarily high ionization enthalpies. Electronegativity also shows a similar trend.
10. Electron gain enthalpies in general, become more negative across a period and less negative down a group.
11. There is some periodicity in valence, for example, among representative elements, the valence is either equal to the number of electrons in the outermost shell or eight minus this number.
12. Chemical reactivity is the highest at the two extremes of a period and is lowest in the centre. The reactivity on the left extreme of a period is because of the ease of electron loss (or low ionization enthalpy) and reactivity on the right extreme of a period is because of the ease of gain of electron.
13. Oxides of the elements on the left are basic and of the elements on the right are acidic in nature. Oxides of elements in the centre are amphoteric or neutral.

Exercises

Question 1. What is the basic theme of organisation in the Periodic Table?

Solution. The basic theme of organisation in the Periodic Table is to simplify and systematise the study of physical and chemical properties of all the elements and their innumerable compounds.

Question 2. Which important property did Mendeleev use to classify the elements in his Periodic Table and did he stick to that?

Solution. Mendeleev used atomic weight as the basis of classification of elements in the Periodic Table. He arranged 63 elements known at that time in the Periodic Table on the basis of the order of their

increasing atomic weights and he placed elements with similar nature in same group.
He stuck to this basis sincerely as some places were left vacant for new elements which were not discovered at that time. For example Ga (gallium) and Ge (germanium) were not known at that time. He left vacant space for them and named them as eka-aluminium and eka-silicon. He predicted not only the existence of these two elements but also described some of their general physical properties. These elements were discovered later.
However, he also found some elements that did not fit in his scheme of classification on the basis of atomic weight. In such cases, he ignored the order of atomic weights *e.g.*, iodine is placed after tellurium due to its similarity in properties with other halogens although its atomic weight is lower (=126.9) than that of tellurium (=127.6).

Question 3. **What is the basic difference in approach between the Mendeleev's periodic law and the modern periodic law?**

Solution. **Mendeleev periodic law** It states that the properties of the elements are a periodic function of their atomic weights.
Modern periodic law It states that the properties of the elements are a periodic function of their atomic numbers.
Thus, change in the base of classification of elements from atomic weight to atomic number is the basic difference between Mendeleev's periodic law and the modern periodic law.

Question 4. **On the basis of quantum numbers, justify that sixth period of the Periodic Table should have 32 elements.**

Solution. In the modern Periodic Table, each period starts with the filling of a new principal energy level. Sixth period begins with filling of principal quantum number, $n = 6$. According to **Aufbau principle**, in the ground state of the atoms, the orbitals are filled in order of their increasing energies. Therefore, in sixth period, electrons enter in $6s, 4f, 5d$ and $6p$ subshells. Total 16 orbitals (2 + 7 + 5 + 3 respectively) are present in these subshells. According to Pauli's exclusion principle each orbital can accomodate maximum two electrons, therefore 16 orbitals can have 32 electrons and hence, 6th period have 32 elements.

Question 5. **In terms of period and group where would you locate the element with $Z = 114$?**

First write electronic configuration of the given element. Highest value of n shows the period of element and group number = 10 + number of electrons in ns and np shells.

Solution. $_{114}Z = {}_{86}[\text{Rn}]\ 7s^2, 5f^{14}, 6d^{10}, 7p^2$

In the Periodic Table, the element with $Z = 114$ is located in
Block – p-block (as last electron enters in p-subshell).
Period – 7th (as $n = 7$ for valence shell)
Group – 14th (for p-block elements, group number = 10 + number of electrons in the valence shell).

Question 6. Write the atomic number of the element present in the third period and seventeenth group of the Periodic Table.

Solution. General configuration for 17th group elements is ns^2np^5. In the third period, the principal quantum number for valence shell is three, so the electronic configuration of valence shell for the given element is $3s^2, 3p^5$. Third period starts from atomic number, $Z = 11$ and end at $Z = 18$. Hence, the atomic number of the given element is $10 + 7 = 17$.

Question 7. Which element do you think would have been named by
(i) Lawrence Berkeley laboratory (ii) Seaborg's group?

Solution.

(i) Lawrencium ($Z = 103$) and Berkelium ($Z = 97$).
(ii) Seaborgium ($Z = 106$).

Question 8. Why do elements in the same group have similar physical and chemical properties?

Solution. Same group elements have similar electronic configuration therefore, have similar physical and chemical properties.

Question 9. What does atomic radius or ionic radius mean to you?

Solution. **Atomic radius** Atomic radius means size of the atom. It can be measured by X-ray or other spectroscopic methods. In case of non-metals, it is called covalent radius and if the element is metal, it is called metallic radius.

Covalent radius is defined as one half the distance between the nuclei of two covalently bonded atoms of the same element in a molecule. For example, the bond distance in the Cl_2 molecule is 198 pm and half of this distance, 99 pm is taken as the atomic radius of chlorine.

Metallic radius is defined as one half the distance between the two adjacent atoms in the metallic lattice. For example, the distance between two adjacent copper atoms in solid copper is 256 pm; hence, the metallic radius of Cu is 128 pm.

Ionic radius Ionic radius means size of the ion (cation or anion). It can be estimated by measuring the distances between cations and anions in ionic crystal. A cation is always smaller than its parent atom because effective nuclear charge increases as a result of loss of one or more electrons. An anion is always larger than its parent atom because effective nuclear charge decreases as a result of addition of one or more electrons. For example; ionic radius of fluoride ion ($F^- = 136$ pm) is greater than atomic radius of fluorine atom ($F = 72$ pm). On the other hand, the atomic radius of sodium (186 pm) is larger than ionic radius of Na^+ ion (95 pm).

Question 10. How do atomic radius vary in a period and in a group? How do you explain the variation?

Solution. Atomic size decreases as we move from left to right in a period. It is because within a period the electrons enter in the same valence shell and the effective nuclear charge increases with increase in atomic number. As a result of this increased effective nuclear charge, the attraction of the nucleus for outer electrons increases and hence, the atomic size decreases.

Within a group atomic size of the elements increases regularly with increase in atomic number. As we move down a group, number of shells increases by one and the valence shell electrons are farther and farther away from the nucleus. Due to this, nuclear attraction for valence electrons decreases and hence, the size increases.

Question 11. What do you understand by isoelectronic species? Name a species that will be isoelectronic with each of the following atoms or ions.

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

Solution. Isoelectronic species have the same number of electrons but different nuclear charges. In case of isoelectronic species as the nuclear charge increases, their size decreases.

(i) F^- has 10 electrons (9 + 1).

(ii) Ar has 18 electrons.

(iii) Mg^{2+} has 10 electrons (12–2) and (iv) Rb^+ has 36 electrons (37–1).

N^{3-}, O^{2-}, Ne, Na^+ and Al^{3+} are some species which are isoelectronic with F^- and Mg^{2+}.

$P^{3-}, S^{2-}, Cl^-, K^+$ and Ca^{2+} are some species which are isoelectronic to Ar.

Similarly, Br^-, Kr and Sr^{2+} are isoelectronic with Rb^+.

Question 12. Consider the following species :

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

(a) What is common in them?

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

(i) Find number of electrons in each ion. For each positive charge remove one electron and for each negative charge add one electron.

(ii) Ionic radii of isoelectronic species varies inversely with atomic number.

Solution.

(i) All the given species have same number of electrons ($10e^-$). Therefore, all are isoelectronic.

(ii) The ionic radii of isoelectronic species decreases with increase in atomic number (as magnitude of the nuclear charge increases with increase in atomic number). Therefore, their ionic radii increase in the order

Isoelectronic ions $= Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$

Atomic number, $Z = 13 \quad 12 \quad 11 \quad 9 \quad 8 \quad 7$

Question 13. Explain why cations are smaller and anions larger in radii than their parent atoms?

Solution. Cations are always smaller in radii than their parent atoms because by the loss of one or two electrons effective nuclear charge increases. Due to this forces of attraction of nucleus for electrons increases and hence, ionic radii decreases. On the other hand, anions are always larger in radii than their parent atoms because by the addition of one or two electrons effective nuclear charge decreases. Due to this, forces of attraction between nucleus and valence shell electrons decreases and hence, ionic radii of anion increases.

Question 14. What is the significance of the terms – 'isolated gaseous atom' and 'ground state' while defining the ionization enthalpy and electron gain enthalpy?

Hint Requirements for comparison purposes.

Solution. **Ionization enthalpy** It is the minimum amount of energy required to remove an electron from an isolated gaseous atom (X) in its ground state.

$$X(g) \longrightarrow X^+(g) + e^-$$

The force by which an electron is attracted by nucleus is also affected by the presence of other atoms within its molecule or in the neighbourhood. Therefore, ionization enthalpy is determined in gaseous state because in gaseous state interatomic distances are larger and interatomic forces of attractions are minimum. Further more, ionization enthalpy is determined at a low pressure because it is not possible to isolate a single atom but interatomic attractions can be further reduced by reducing pressure. Due to these reasons, the term isolated gaseous atom in ground state has been included in definition of ionization enthalpy.

Electron gain enthalpy It is the energy released when an isolated gaseous atom (X) in ground state gains an electron to form gaseous anion.

$$X(g) + e^- \longrightarrow X^-(g)$$

The most stable state of an atom is ground state. If isolated gaseous atom is in excited state, comparatively lesser energy will be released on addition of an electron. So, electron gain enthalpies of gaseous atoms must be determined in their ground states. Therefore, the terms ground state and isolated gaseous atom (explained above) has been also included in the definition of electron gain enthalpy.

Question 15. Energy of an electron in the ground state of the hydrogen atom is -2.18×10^{-18} J. Calculate the ionization enthalpy of atomic hydrogen in terms of J mol^{-1}.

Hint Apply the idea of mole concept to derive the answer.

(i) We know that the amount of energy required to remove an electron from the ground state (E_1) to infinity (E_∞) is called ionization energy, so IE is calculated by using $\Delta E = E_\infty - E_1$. Calculate the ionization enthalpy per hydrogen atom.

(ii) Since, the energy is obtained in J, convert it into per mole of hydrogen atoms by applying mole concept.

Solution. Ionization energy is the amount of energy required to remove the electron from the ground state (E_1) to infinity (E_∞).

$$E_1 = -2.18 \times 10^{-18}\ \text{J}$$

$$E_\infty = 0$$

$$\Delta E = E_\infty - E_1 = 0 - (-2.18 \times 10^{-18}\ \text{J}) = 2.18 \times 10^{-18}\ \text{J}$$

Ionization enthalpy per hydrogen atom $= 2.18 \times 10^{-18}$ J

$\therefore$ Ionization enthalpy per mole of hydrogen atoms

$$= 2.18 \times 10^{-18} \times 6.022 \times 10^{23}\ \text{J mol}^{-1}$$

$$= 13.12 \times 10^{5}\ \text{J mol}^{-1}$$

Note *Energy of an electron at infinity* = 0.

Question 16. **Among the second period elements the actual ionization enthalpies are in the order**

$$\text{Li} < \text{B} < \text{Be} < \text{C} < \text{O} < \text{N} < \text{F} < \text{Ne}$$

Explain why

(i) Be has higher $\Delta_i H$ than B?

(ii) O has lower $\Delta_i H$ than N and F?

Solution.

(i) Be has higher $\Delta_i H$ (ionization enthalpy) than boron. In both the cases, the electron to be removed belongs to the same principal shell. In $_4\text{Be} = (1s^2, 2s^2)$, it is 2*s*-electron while in boron $_5\text{B} = (1s^2, 2s^2, 2p^1)$ it is 2*p*-electron. The penetration of a 2*s*-electron to the nucleus is more than that of a 2*p*-electron. It means 2*s*-electrons are more strongly attracted by the nucleus than 2*p*-electrons. Therefore, higher amount of energy is required to remove a 2*s*-electron than a 2*p*-electron. Hence, Be has higher $\Delta_i H$ than B.

(ii) O has lower $\Delta_i H$ than N and F

$$_7\text{N} = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1;$$

$$_8\text{O} = 1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1;$$

$$_9\text{F} = 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$$

Across a period ionization enthalpy increases as we move from left to right due to decrease in atomic size. But $\Delta_i H$ of nitrogen is greater than oxygen. It is becasue of the more stable electronic configuration (exactly half filled orbitals are more stable) of nitrogen, so it is difficult to remove an electron from nitrogen than from oxygen. That's why oxygen has lower ionization enthalpy than nitrogen and fluorine.

Question 17. **How would you explain the fact that the first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium?**

Solution. First ionization enthalpy of sodium ($Na = 1s^2, 2s^2, 2p^6, 3s^1$) is lower than that of magnesium ($Mg = 1s^2, 2s^2\ 2p^6, 3s^2$) because the electron to be removed in both the cases is from 3*s*-orbital but the nuclear charge is lower in Na than that of magnesium $\left(\text{IE} \propto \frac{1}{\text{atomic size}}\right)$.

After the removal of first electron Na^+ acquires inert gas (Ne) configuration ($Na^+ = 1s^2, 2s^2, 2p^6$) and hence, removal of second electron from sodium is difficult. While in case of magnesium, after the removal of first electron, the electronic configuration of Mg^+ is $1s^2, 2s^2, 2p^6, 3s^1$. In this case $3s^1$ electron is easy to remove in comparison to remove an electron from inert gas configuration. Therefore, IE_2 of Na is higher than that of magnesium.

Note *The species having exactly half-filled or fully filled orbitals have extra ordinarily high ionization enthalpies.*

Question 18. **What are the various factors due to which the ionization enthalpy of the main group elements tends to decrease down a group?**

Solution. The ionization enthalpy of the main group elements decreases regularly on moving down the group due to the following two factors:

(i) **Atomic size** On moving down the group, atomic size increases due to addition of new higher energy shell. As a result of this forces of attraction of nucleus for valence electrons decreases and ionization enthalpy also decreases.

(ii) **Screening effect** On moving down the group, screening effect or shielding effect increases, so ionization enthalpy decreases (because forces of attraction between nucleus and electrons decreases).

Question 19. **The first ionization enthalpy values (in $kJ\ mol^{-1}$) of group 13 elements are**

B	Al	Ga	In	Tl
801	577	579	558	589

How would you explain this deviation from the general trend?

Solution. In general on moving down the group (13th group) from B to Al, the ionization enthalpy decreases with increase in atomic size and screening effect as expected. But IE_1 of Ga is slightly higher (only 2 $kJ\ mol^{-1}$) than IE_1 of Al. It is due to imperfect shielding of the valence electrons by 3*d*-electrons. As a result of this effective nuclear charge in Ga is slightly more than that of Al. That's why (IE_1) $\Delta_i H_1$ of Ga is slightly more than that of Al.

On moving from In to Tl, $\Delta_i H_1$ of Tl is larger than that of In. It is due to the fact that effective nuclear charge outweighs the shielding effect of all the electrons present in 4*f* and 5*d*-electrons.

Note *d- and f-electrons shield the valence shell electrons from nucleus less effectively than s- and p- electrons.*

Question 20. Which of the following pairs of elements would have a more negative electron gain enthalpy?

(i) O or F (ii) F or Cl

Solution.

(i) Oxygen and fluorine both belong to second period. Electron gain enthalpy generally becomes more negative across a period as we move from left to right. On moving from oxygen to fluorine, the effective nuclear charge increases and atomic size decreases with increase in atomic number. Due to this, forces of attraction of the nucleus increases for the incoming electron. That's why electron gain enthalpy becomes more negative for fluorine than that of oxygen. Furthermore fluorine attain stable gas configuration by picking up an electron.

$$\underset{2,7}{F(g)} + e^- \longrightarrow \underset{2,8}{F^-(g)}$$

Therefore, electron gain enthalpy of fluorine is much more negative (-328 kJ mol^{-1}) than that of oxygen (-141 kJ mol^{-1}).

(ii) Within a group, electron gain enthalpy becomes less negative down a group. But electron gain enthalpy of chlorine is more negative (-349 kJ mol^{-1}) than that of the fluorine (-328 kJ mol^{-1}). This is due to small size of fluorine as the electron–electron repulsions in relatively compact 2*p*-orbital is greater than that in the larger 3*p*-orbital and hence, the incoming electron feels greater repulsion in fluorine than in the chlorine. That's why chlorine have more negative electron gain enthalpy than that of fluorine.

Question 21. Would you expect the second electron gain enthalpy of O as positive, more negative or less negative than the first? Justify you answer.

Solution. $O(g) + e^-(g) \longrightarrow O^-(g);$ $\Delta_{e_g} H = -141 \text{ kJ mol}^{-1}$

$O^-(g) + e^-(g) \longrightarrow O^{2-}(g);$ $\Delta_{e_g} H = +780 \text{ kJ mol}^{-1}$

When an electron is added to oxygen atom to form O^- ion, energy is released. Hence, first electron gain enthalpy of oxygen is negative. But when another electron is added to O^- ion to form O^{2-} ion, it feels stronger electrostatic repulsion. Hence, addition of second electron takes place with absorption of energy. That's why the second electron gain enthalpy of oxygen is positive.

Question 22. What is the basic difference between the terms electron gain enthalpy and electronegativity?

Solution. Electron gain enthalpy is the tendency of an isolated gaseous atom to accept an extra electron to form a gaseous anion while electronegativity is the tendency of an atom of an element to attract the shared pair of electrons towards itself in a covalent bond. Unlike electron gain enthalpy, electronegativity is not a measurable quantity.

Question 23. How would you react to the statement that the electronegativity of N on Pauling scale is 3.0 in all the nitrogen compounds?

Solution. The statement that electronegativity of N on Pauling scale is 3.0 in all the nitrogen compounds is wrong because electronegativity of any given element is not constant. It varies depending on the element to which it is bound. It increases as the oxidation state of the element increases or percentage of *s*-character of hybrid orbital increases.

Question 24. Describe the theory associated with the radius of an atom as it

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

Solution.

(a) When an atom gains an electron to form anion, its radius increases. In an anion per electron nuclear forces decreases due to increase in number of electrons and as a result of decrease in effective nuclear charge, radius of an anion increases. For example, ionic radius of Cl^- ion is greater than the radius of its parent atom Cl.

$$Cl + e^- \longrightarrow Cl^-$$

Electrons	17	18
Nuclear charge	17	17

(b) When an atom loses an electron to form cation, its radius decreases. In a cation per electron nuclear forces increases due to decrease in number of electrons. As a result of this, effective nuclear charge increases and the radius of cation decreases. For example, ionic radius of Na^+ is smaller than the radius of its parent atom Na.

$$Na \longrightarrow Na^+ + 1e^-$$

Electrons	11	10
Nuclear charge	11	11

Question 25. Would you expect the first ionization enthalpies for two isotopes of the same element to be the same or different? Justify your answer.

Solution. First ionization enthalpies of two isotopes of the same element are expected to be same because ionization enthalpy depends upon the electronic configuration and effective nuclear charge. Isotopes of an element have same electronic configuration and thus, the same nuclear charge.

Question 26. What are the major differences between metals and non-metals?

Solution. Metals are usually solids at room temperature (mercury is an exception, Gallium and caesium also have very low melting points). Metals usually have very high melting and boiling points. They are good conductors of heat and electricity. They are malleable and ductile. They are electropositive in nature (having a tendency to form cations by the lose of 1, 2 or 3 electrons). Metals have low ionization enthalpies, less electronegativity, less negative electron gain enthalpies. They act as strong reducing agent, form basic and amphoteric oxides. Their compounds are usually ionic in nature.

Non-metals are usually solids or gases at room temperature with low melting and boiling points (boron and carbon are exceptions). They are poor conductors of heat and electricity. Most non-metallic solids are brittle. They are electronegative in nature, have high ionization enthalpies and high negative electron gain enthalpies. They act as strong oxidising agent, form acidic or neutral oxides. Their compounds are usually covalent in nature.

Question 27. Use the Periodic Table to answer the following questions.

(a) Identify an element with five electrons in the outer subshell.

(b) Identify an element that would tend to lose two electrons.

(c) Identify an element that would tend to gain two electrons.

(d) Identify the group having metal, non-metal, liquid as well as gas at the room temperature.

Solution.

(a) General electronic configuration of elements having five electrons in the outer sub shell is ns^2np^5. This configuration belongs to halogen family, *i.e.*, F, Cl, Br, I, At.

(b) Elements of second group are known as alkaline earth metals (Mg, Ca, Sr, Ba, etc). Their general electronic configuration for valence shell is ns^2. These elements form dipositive cations by the lose of two electrons easily.

(c) 16th group elements such as O, S, Se, etc., have a tendency to accept two electrons because by the gain of two electrons they attain noble gas configuration. Their general electronic configuration for valence shell is ns^2np^4.

(d) Group 1 or 17 of the Periodic Table contains metal, non-metal, liquid as well as gas at the room temperature, *e.g.*, H_2 is a non-metal and in gaseous state at room temperature. All other elements of this group are metals. Cs is a liquid metal.

Similary, Br_2 is a liquid non-metal while other elements of this group are gaseous non-metals. Iodine can form I^+ so it has some what metallic properties.

Question 28. **The increasing order of reactivity among group 1 elements is Li < Na < K < Rb < Cs whereas that among group 17 elements is F > Cl > Br > I. Explain.**

Solution. Chemical reactivity of alkali metals is exhibited by the loss of an electron leading to the formation of cation. The tendency to lose an electron depends upon the ionization enthalpy and ionization enthalpy decreases down the group. Hence, the reactivity increases down the group (Li < Na < K < Rb < Cs).

On the other hand, chemical reactivity of halogens is shown by the gain of an electron leading to the formation of anion. The tendency to gain an electron depends upon their electrode potentials. Their electrode potentials decrease from fluorine to iodine. Therefore, reactivity decreases down the group (F > Cl > Br > I). Furthermore, the tendency to gain an electron is also related to electron gain enthalpy. Electron gain enthalpy becomes less and less negative as we move from chlorine to iodine. Hence, reactivity decreases from chlorine to iodine. Fluorine has less electron gain enthalpy but it is the most reactive due to its low bond dissociation enthalpy.

Group-17	F	Cl	Br	I	At
$\Delta_{eq}H$ (kJ mol^{-1})	–328	–349	–325	–245	–270

$\longrightarrow$ Reactivity decreases

Question 29. **Write the general outer electronic configuration of *s*-, *p*-, *d*- and *f*-block elements.**

Solution. *s*-block elements – ns^{1-2} $(n = 2 - 7)$

p-block elements – ns^2np^{1-6} $(n = 2 - 7)$

d-block elements – $(n-1)\,d^{1-10}\,ns^{0-2}$ $(n = 3 - 7)$

f-block elements – $(n-2)\,f^{1-14}\,(n-1)\,d^{0-1}\,ns^2$ $(n = 6 - 7)$

Question 30. **Assign the position of the element having outer electronic configuration.**

(i) ns^2np^4 for $n = 3$

(ii) $(n-1)\,d^2ns^2$ for $n = 4$, and

(iii) $(n-2)\,f^7\,(n-1)\,d^1ns^2$ for $n = 6$, in the Periodic Table.

Solution.

(i) ns^2np^4 for $n = 3$

$n = 3$ means element belongs to third period. Since, last electron enters in the *p*-orbital, it belongs to *p*-block. For *p*-block elements, the group number = 10 + valence shell electrons = 10 + (2 + 4) = 16

Hence, the element belongs to 16th group.

The complete electronic configuration of the element is as follows,

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^4$$

Thus, the element is sulphur.

(ii) $(n-1)d^2\ ns^2$ for $n=4$

$n=4$ means the element belongs to fourth period. Since, last electron enters in d-orbital, the given element belongs to d-block. For d-block elements, group number = number of d-electrons + number of ns electrons $=2+2=4$

Hence, the element belongs to 4th group.

The complete electronic configuration of the element is as follows,

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^2, 4s^2$$

Thus, the element is titanium.

(iii) $(n-2)f^7\ (n-1)d^1\ ns^2$ for $n=6$

$n=6$ means, the element belongs to sixth period.

Since, last electron enters in f-orbital, the given element belongs to f-block and all f-block elements are the members of third group. Hence, the element belongs to third group.

The complete configuration of the element is as follows,

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^6, 4f^7, 5d^1, 6s^2$$

Thus, the element is gadolinium (Gd).

Question 31. **The first ($\Delta_i H_1$) and the second ($\Delta_i H_2$) ionization enthalpies (in kJ mol^{-1}) and the ($\Delta e_g H$) electron gain enthalpy (in kJ mol^{-1}) of a few elements are given below :**

Elements	ΔH_1	ΔH_2	$\Delta e_g H$
I	520	7300	− 60
II	419	3051	− 48
III	1681	3374	− 328
IV	1008	1846	− 295
V	2372	5251	+48
VI	738	1451	− 40

Which of the above elements is likely to be

(a) the least reactive element

(b) the most reactive metal

(c) the most reactive non-metal

(d) the least reactive non-metal

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

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

Solution.

(a) The least reactive element is element (V) because it has highest $\Delta_i H_1$ (first ionization enthalpy) and positive electron gain enthalpy ($\Delta e_g H$). The element (V) is an inert gas because inert gases have positive electron gain enthalpy. The given values for element (V) match with He.

(b) The most reactive metal is element (II) because it has the least $\Delta_i H_1$ (first ionization enthalpy) and low negative electron gain enthalpy ($\Delta e_g H$). The given values for element II match with K.

(c) The most reactive non-metal is element (III) because it has high $\Delta_i H_1$ (first ionization enthalpy) and a very high negative electron gain enthalpy ($\Delta e_g H$). The given values for element III match with F.

(d) The least reactive non-metal is element IV. The element IV has not so high $\Delta_i H_1$ but it has high negative electron gain enthalpy ($\Delta e_g H$). The given values for element IV match with I, (iodine).

(e) The metal which can form a stable binary halide of the formula MX_2 is element (VI). Element VI is alkaline earth metal because it has low $\Delta_i H_1$ but higher than that of alkali metals. Moreover, the difference between $\Delta_i H_1$ and $\Delta_i H_2$ is very less. The given values for element VI match with Mg.

(f) Element I has low $\Delta_i H_1$ but a very high $\Delta_i H_2$. It has less negative electron gain enthalpy. So, element (I) is alkali metal. The given values for element I match with Li. Lithium forms predominantly stable covalent halide of the formula MX.

Question 32. **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
(f) Element 71 and fluorine

Solution.

	Element	Group number	Electrons in valence shell	Valency	Formulae of binary compound
(a)	Lithium	Group-1	1	1	Li_2O
	Oxygen	Group-16	6	8 − 6 = 2	
(b)	Magnesium	Group-2	2	2	Mg_3N_2
	Nitrogen	Group-15	5	8 − 5 = 3	
(c)	Aluminium	Group-13	3	3	AlI_3
	Iodine	Group-17	7	8 − 7 = 1	
(d)	Silicon	Group-14	4	4	SiO_2
	Oxygen	Group-16	6	8 − 6 = 2	
(e)	Phosphorus	Group-15	5	3 or 5	PF_3 or PF_5
	Fluorine	Group-17	7	8 − 7 = 1	
(f)	Element 71, (Lutetium)	Group-3	3	3	LuF_3
	Fluorine	Group-17	7	8 − 7 = 1	

Note (i) *In case of s- and p-block elements (representative elements), the valency of an atom is generally equal to either the number of valence electrons or equal to eight minus the number of valence electrons.*

(ii) *In case of lathanoids (inner-transition elements) there is involvement of d- and f-electrons with valence shell electrons in bond formation. Common valence for lanthanoids is* 3.

(iii) *Electronic configuration of* $_{71}\text{Lu} = [\text{Xe}]\,4f^{14}, 5d^1, 6s^2$; (*Valency* = 3).

Question 33. In the modern Periodic Table, the period indicates the value of

(a) atomic number (b) atomic mass

(c) principal quantum number (d) azimuthal quantum number

Solution. (c) In the modern Periodic Table, the period indicates the value of principal quantum number.

Question 34. Which of the following statements related to the modern Periodic Table is incorrect?

(a) The *p*-block has 6 columns, because a maximum of 6 electrons can occupy all the orbitals in a *p*-shell.

(b) The *d*-block has 8 columns because a maximum of 8 electrons can occupy all the orbitals in a *d*-subshell.

(c) Each block contains a number of columns equal to the number of electrons that can occupy that subshell.

(d) The block indicates value of azimuthal quantum number (l) for the last subshell that received electrons in building up the electronic configuration.

Solution. Statement (b) is incorrect. The correct statement (b) is; the *d*-block has 10 columns, because a maximum of 10 electrons can occupy all the orbitals in a *d*-subshell.

All other given statements are correct.

Question 35. Anything that influences the valence electrons will affect the chemistry of the element. Which one of the following factors does not affect the valence shell?

(a) Valence principal quantum number (n)

(b) Nuclear charge (Z)

(c) Nuclear mass

(d) Number of core electrons

Solution. (c) Nuclear mass (protons + neutrons) does not affect the valence shell, only protons, *i.e.*, nuclear charge affects the valence shell.

Question 36. The size of isoelectronic species; F^-, Ne and Na^+ is affected by

(a) nuclear charge (Z)

(b) valence principal quantum number (n)

(c) electron-electron interaction in the outer orbitals

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

Solution. (a) The size of isoelectronic species; F^-, Ne and Na^+ is affected by nuclear charge (Z). With increase in nuclear charge (atomic number), the size of the isoelectronic species decreases.

Question 37. Which one of the following statements is incorrect in relation to ionization enthalpy?

(a) Ionization enthalpy increases for each successive electron.

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

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

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

Solution. Correct statement (d) is; removal of electron from orbitals bearing lower n value is difficult than from orbital having higher n value, due to decrease in effective nuclear charge with increase in the value of n.

Question 38. Considering the elements B, Al, Mg and K, the correct order of their metallic character is

(a) B > Al > Mg > K (b) Al > Mg > B > K

(c) Mg > Al > K > B (d) K > Mg > Al > B

Solution. (d) In a group, metallic character increases from top to bottom as ionisation energy decreases and in a period metallic character decreases from left to right as tendency to lose electron decreases. Therefore, the correct order is K > Mg > Al > B.

Question 39. Considering the elements B, C, N, F and Si, the correct order of their non-metallic character is

(a) B > C > Si > N > F (b) Si > C > B > N > F

(c) F > N > C > B > Si (d) F > N > C > Si > B

Solution. (c) Non-metallic character in a group decreases from top to bottom but it increases in a period when we move from left to right. This is because ionisation energy increases in a period and decreases in a group. Therefore, among B, C, N, F and Si, the non-metallic character decreases in the order F > N > C > B > Si.

Question 40. Considering the elements F, Cl, O and N, the correct order of their chemical reactivity in terms of oxidizing property is

(a) F > Cl > O > N (b) F > O > Cl > N

(c) Cl > F > O > N (d) O > F > N > Cl

Solution. (b) In a group oxidising power (*i.e.*, tendency to gain electron) decreases from top to bottom as the size increases but when we move left to right in a period it increases because size decreases. Therefore, among F, Cl, O and N, the oxidising power decreases in the order

$$F > O > Cl > N$$

Note *Oxygen is more electronegative than chlorine. Hence, O is stronger oxidising agent than Cl.*

Selected NCERT Exemplar Problems

Short Answer Type

Question 1. **Explain why the electron gain enthalpy of fluorine is less negative than that of chlorine?**

Solution. Electron gain enthalpy of F is less negative than that of Cl because when an electron is added to F, the added electron goes to the smaller $n = 2$ quantum level and suffers repulsion from other electrons present in this level. In case of Cl, the added electron goes to the larger $n = 3$ quantum level and suffers much less repulsion from other electrons.

Question 2. **All transition elements are *d*-block elements, but all *d*-block elements are not transition elements. Explain.**

Solution. Elements in which the last electron enters in the *d*-orbitals, are called *d*-block elements or transition elements. These elements have the general outer electronic configuration $(n-1)\,d^{1-10}\,ns^{0-2}$. Zn, Cd and Hg having the electronic configuration, $(n-1)\,d^{10}ns^2$ do not show most of the properties of transition elements. The *d*-orbitals in these elements are completely filled in the ground state as well as in their common oxidation states. Therefore, they are not regarded as transition elements. Thus, on the basis of properties, all transition elements are *d*-block elements but on the basis of electronic configuration, all *d*-block elements are not transition elements.

Question 3. **Among the elements B, Al, C and Si,**

(i) Which element has the highest first ionization enthalpy?
(ii) Which element has the most metallic character? Justify your answer in each case.

Solution.

Period	Group-13	Group-14
2nd period	Boron	Carbon
3rd period	Aluminium	Silicon

(i) Ionization enthalpy increases along a period (as we move from left to right in a period) with decrease in atomic size and decreases down the group with increase in atomic size. Hence, carbon has the highest first ionization enthalpy.

(ii) Metallic character decreases across a period but increases on moving down the group. Hence, aluminium has the most metallic character.

Question 4. **Choose the correct order of atomic radii of fluorine and neon (in pm) out of the options given below and justify your answer.**

(i) 72, 160 (ii) 160, 160 (iii) 72, 72 (iv) 160, 72

Solution. Atomic radius of F is expressed in terms of covalent radius while atomic radius of neon is usually expressed in terms of van der Waals' radius. van der Waals' radius of an element is always larger than its covalent radius. Therefore, atomic radius of F is smaller than atomic radius of Ne (F = 72 pm, Ne = 160 pm).

Question 5. **Illustrate by taking examples of transition elements and non-transition elements that oxidation states of elements are largely based on electronic configuration.**

Solution. Oxidation state of an element depends upon the electrons present in the outer most shell or eight minus the number of valence shell electrons (outermost shell electrons). For example,

Alkali metals (Group 1 elements) General valence shell electronic configuration —ns^1; Oxidation state = + 1.

Alkaline earth metals (Group 2 elements) General valence shell electronic configuration —ns^2; Oxidation state = + 2.

Alkali metals and alkaline earth metals belong to *s*-block elements.
Elements of group 13 to group 18 are known as *p*-block elements.

Group 13 elements General valence shell electronic configuration — $ns^2\ np^1$; Oxidation states = + 3 and + 1.

Group 14 elements General valence shell electronic configuration — $ns^2\ np^2$; Oxidation states = + 4 and + 2.

Group 15 elements General valence shell electronic configuration — $ns^2\ np^3$; Oxidation states = – 3, + 3 and + 5. Nitrogen shows + 1, + 2, + 4 oxidation states also.

Group 16 elements General valence shell electronic configuration — $ns^2\ np^4$; Oxidation states = – 2, + 2, + 4 and + 6.

Group 17 elements General valence shell electronic configuration — ns^2np^5; Oxidation states = – 1. Cl, Br and I also show + 1, + 3, + 5 and + 7 oxidation states.

Group 18 elements General valence shell configuration —ns^2np^6. Oxidation state = zero.

Transition elements or d-block elements General electronic configuration – $(n-1)\,d^{1-10}\,ns^{1-2}$. These elements show variable oxidation states due to involvement of not only *ns* electrons but *d*- or *f*-electrons (inner-transition elements) as well. Their most common oxidation states are + 2 and + 3.

Question 6. **Nitrogen has positive electron gain enthalpy whereas oxygen has negative. However, oxygen has lower ionization enthalpy than nitrogen. Explain.**

Solution. EC of $_7\text{N} = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$. Nitrogen has stable configuration because *p*-orbital is half-filled. Therefore, addition of extra electron to any of the *p*-orbital requires energy.

EC of $_8\text{O} = 1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$. Oxygen has $2p^4$ electrons, so process of adding an electron to the *p*-orbital is exothermic.

Oxygen has lower ionization enthalpy than nitrogen because by removing one electron from 2*p*-orbital, oxygen acquires stable configuration, *i.e.*, $2p^3$. On the other hand, in case of nitrogen it is not easy to remove one of the three 2*p*-electrons due to its stable configuration.

Question 7. **First member of each group of representative elements (*i.e.*, *s*- and *p*-block elements) shows anomalous behaviour. Illustrate with two examples.**

Solution. First member of each group of representative elements (*i.e.*, *s*- and *p*-block elements) shows anomalous behaviour due to (i) small size (ii) high ionization enthalpy (iii) high electronegativity and (iv) absence of *d*- orbitals. For example in *s*- block elements, Lithium shows anomalous behaviour from rest of the alkali metals.

(i) Compounds of lithium have significant covalent character. While compounds of other alkali metals are predominantly ionic.

(ii) Lithium reacts with nitrogen to form lithium nitride while other alkali metals do not form nitrides.

In *p*-block elements, first member of each group has four orbitals, one 2*s*- and three 2*p*-orbitals in their valence shell. So, these elements show a maximum covalency of four while other members of the same group or different group show a maximum covalency beyond four due to availability of vacant *d*- orbitals.

Question 8. **p-block elements form acidic, basic and amphoteric oxides. Explain each property by giving two examples and also write the reactions of these oxides with water.**

Solution. In *p*-block, when we move from left to right in a period, the acidic character of the oxides increases due to increase in electronegativity. For example,

(i) **2nd period** $B_2O_3 < CO_2 < N_2O_3$ acidic nature increases.

(ii) **3rd period** $Al_2O_3 < SiO_2 < P_4O_{10} < SO_3 < Cl_2O_7$ acidic character increases.

On moving down the group, acidic character decreases and basic character increases. For example

(i) **Nature of oxides of 13 group elements**

$$\underset{\text{Weakly acidic}}{B_2O_3} \quad \underbrace{Al_2O_3 \;\; Ga_2O_3}_{\text{Amphoteric}} \quad \underset{\text{Basic}}{In_2O_3} \quad \underset{\text{Strongly basic}}{Tl_2O}$$

(ii) **Nature of oxides of 15 group elements**

N_2O_5	P_4O_{10}	As_4O_{10}	Sb_4O_{10}	Bi_2O_3
Strongly acidic	Moderately acidic	Amphoteric	Amphoteric	Basic

Among the oxides of same element, higher the oxidation state of the element, stronger is the acid. For example, SO_3 is a stronger acid than SO_2.

B_2O_3 is weakly acidic and on dissolution in water, it forms orthoboric acid. Orthoboric acid does not act as a protonic acid (it does not ionize) but acts as a weak Lewis acid.

$$\underset{\text{Boron trioxide}}{B_2O_3} + 3H_2O \rightleftharpoons \underset{\text{Orthoboric acid}}{2H_3BO_3}$$

$$B(OH)_3 + H{-}OH \longrightarrow [B(OH)_4]^- + H^+$$

Al_2O_3 is amphoteric in nature. It is insoluble in water but dissolves in alkalies and reacts with acids.

$$\underset{\text{Aluminium trioxide}}{Al_2O_3} + 2NaOH \xrightarrow{\Delta} \underset{\text{Sodium meta aluminate}}{2NaAlO_2} + H_2O$$

$$Al_2O_3 + 6HCl \xrightarrow{\Delta} \underset{\text{Aluminium chloride}}{2AlCl_3} + 3H_2O$$

Tl_2O is as basic as NaOH due to its lower oxidation state (+ 1).

$$Tl_2O + 2HCl \longrightarrow 2TlCl + H_2O$$

P_4O_{10} on reaction with water gives orthophosphoric acid

$$\underset{\text{Phosphorus pentoxide}}{P_4O_{10}} + 6H_2O \longrightarrow \underset{\text{Orthophosphoric acid}}{4H_3PO_4}$$

Cl_2O_7 is strongly acidic in nature, and on dissolution in water, it gives perchloric acid.

$$\underset{\text{Dichlorine heptoxide}}{Cl_2O_7} + H_2O \longrightarrow \underset{\text{Perchloric acid}}{2HClO_4}$$

Question 9. **Arrange the elements N, P, O and S in the order of**

(i) increasing first ionization enthalpy.

(ii) increasing non-metallic character.

Give reason for the arrangement assigned.

Solution.

	Group 15	Group 16
2nd period	N	O
3rd period	P	S

(i) Ionization enthalpy of nitrogen $({}_7N = 1s^2, 2s^2, 2p^3)$ is greater than oxygen $({}_8O = 1s^2, 2s^2, 2p^4)$ due to extra stable exactly half-filled $2p$-orbitals. Similarly, ionization enthalpy of phosphorus $({}_{15}P = 1s^2, 2s^2, 2p^6, 3s^2, 3p^3)$ is greater than sulphur $({}_{16}S = 1s^2, 2s^2, 2p^6, 3s^2, 3p^4)$.

On moving down the group, ionization enthalpy decreases with increasing atomic size. So, the order is

$S < P < O < N \rightarrow$ First ionization enthalpy increases.

(ii) Non-metallic character across a period (left to right) increases but on moving down the group it decreases. So, the order is

$P < S < N < O \rightarrow$ Non-metallic character increases.

Question 10. **How does the metallic and non-metallic character vary on moving from left to right in a period?**

Solution. As we move from left to right in a period, the number of valence electrons increases by one at each succeeding element but the number of shells remains same. Due to this effective nuclear charge increases. More is the effective nuclear charge, more is the attraction between nuclei and electron. Hence, the tendency of the element to lose electrons decreases, this results in decrease in metallic character. Furthermore, the tendency of an element to gain electrons increases with increase in effective nuclear charge, so non-metallic character increases on moving from left to right in a period.

Question 11. Among alkali metals which element do you expect to be least electronegative and why?

Solution. On moving down the group, electronegativity decreases because atomic size increases. Fr has the largest size, therefore it is least electronegative.

Long Answer Type

Question 12. Discuss the factors affecting electron gain enthalpy and the trend in its variation in the Periodic Table.

Solution. Electron gain enthalpy of an element is equal to the energy released when an electron is added to valence shell of an isolated gaseous atom.

$$A(g) + e^- \longrightarrow A^-(g); \qquad \Delta e_g H = \text{negative}$$

Factors Affecting Electron Gain Enthalpy

(i) **Effective nuclear charge** Electron gain enthalpy increases with increase in effective nuclear charge because attraction of nucleus towards test electron (incoming electron) increases.

(ii) **Size of an atom** Electron gain enthalpy decreases with increase in the size of valence shell.

(iii) **Type of subshell** More closer is the subshell to the nucleus, easier is the addition of electron in that subshell.
Electron gain enthalpy (in decreasing order) for addition of electron in different subshell (n-same) is

$$s > p > d > f$$

(iv) **Nature of configuration** Half-filled and completely-filled subshell have stable configuration, so addition of electron in them is not energetically favourable.

Variation in the Periodic Table As a general rule, electron gain enthalpy becomes more and more negative with increase in the atomic number across a period. The effective nuclear charge increases from left to right across a period and consequently it will be easier to add an electron to a smaller atom.

Electron gain enthalpy becomes less negative as we go down a group because the size of the atom increases and the added electron would be farther from the nucleus.

Electron gain enthalpy of O or F is less than that of the succeeding element (S or Cl) because the added electron goes to the smaller $n = 2$ level and suffers repulsion from other electrons present in this level. For the $n = 3$ level (S or Cl), the added electron occupies a larger region of space and suffers much less repulsion from electrons present in this level.

Question 13. **Justify the given statement with suitable examples–"the properties of the elements are a periodic function of their atomic numbers".**

Solution. There are numerous physical properties of elements such as melting points, boiling points, heats of fusion and vaporization, energy of atomization, etc., which show periodic variations. The cause of periodicity in properties is the repetition of similar outer electronic configurations after certain regular intervals. For example, all the elements of 1st group (alkali metals) have similar outer electronic configuration, *i.e.*, ns^1.

$${}_{3}\text{Li} = 1s^2, 2s^1$$
$${}_{11}\text{Na} = 1s^2, 2s^2, 2p^6, 3s^1$$
$${}_{19}\text{K} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$$
$${}_{37}\text{Rb} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 5s^1$$
$${}_{55}\text{Cs} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^6, 6s^1$$
$${}_{87}\text{Fr} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 4f^{14}$$
$$5s^2, 5p^6, 5d^{10}, 6s^2, 6p^6, 7s^1$$

Therefore, due to similar outermost shell electronic configuration all alkali metals have similar properties. For example sodium and potassium both are soft and reactive metals. They all form basic oxides and their basic character increases down the group. They all form unipositive ion by the lose of one electron.

Similarly, all the elements of 17th group (halogens) have similar outermost shell electronic configuration, *i.e.*, ns^2np^5 and thus possess similar properties.

$${}_{9}\text{F} = 1s^2, 2s^2, 2p^5$$
$${}_{17}\text{Cl} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^5$$
$${}_{35}\text{Br} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^5$$
$${}_{53}\text{I} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^5$$
$${}_{85}\text{At} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}$$
$$4f^{14}, 5s^2, 5p^6, 5d^{10}, 6s^2, 6p^5$$

Question 14. **Write the drawbacks in Mendeleev's Periodic Table that led to its modification.**

Solution. The main drawbacks of Mendeleev's Periodic Table are

(i) Some elements having similar properties were placed in different groups whereas some elements having dissimilar properties were placed in the same group. For example alkali metals such as Li, Na, K, etc., (IA group) are grouped together with coinage metals such as Cu, Ag, Au (IB group) though their properties are quite different. Chemically similar elements such as Cu(IB group) and Hg (IIB group) have been placed in different groups.

(ii) Some elements with higher atomic weights are placed before the elements with lower atomic weights in order to maintain the similar chemical nature of elements. For example,

$$^{39.9}_{18}\text{Ar and } ^{39.1}_{19}\text{K; } ^{58.9}_{27}\text{Co and } ^{58.7}_{28}\text{Ni, etc.}$$

(iii) Isotopes did not find any place in the Periodic Table. However, according to Mendeleev's classification, these should be placed at different places in the Periodic Table.

(All the above three defects were however removed when modern periodic law based on atomic number was given.)

(iv) Position of hydrogen in the Periodic Table is not fixed but is controversial.

(v) Position of elements of group VIII could not be made clear which have been arranged in three triads without any justification.

(vi) It could not explain the even and odd series in IV, V and VI long periods.

(vii) Lanthanides and actinides which were discovered later on have not been given proper positions in the main frame of Periodic Table.

Chapter 4

Chemical Bonding and Molecular Structures

Important Results

1. The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.
2. The atoms of different elements combine with each other in order to complete their respective octets (*i.e.,* 8 electrons in their outermost shell) or duplet (*i.e.,* outermost shell containing 2 electrons) in case of hydrogen, lithium and beryllium (**Octet rule**).
3. Lewis symbols are the simple symbols to denote the valence shell electrons in an atom. The valence shell electrons are shown as dots surrounding the symbol of the atom.
4. An ionic bond is formed when a metal atom transfers one or more electrons to a non-metal atom. As a result of this transfer, the metal atom converts into cation and non-metal into anion.
5. Ionic solids are good conductor of electricity in fused state and in aqueous state. These are soluble in polar solvents, insoluble in non-polar solvents and have high melting and boiling point due to strong electrostatic forces of attraction.
6. The energy given off when gaseous positive and negative ions come together to form 1 mole of the solid ionic compound is called lattice energy (U). It can be calculated using **Born-Haber cycle.**
7. If duplet (2) or octet (8) is completed by sharing of electrons between two electronegative elements, the bond formed is known as covalent bond. In single, double and triple covalent bonds, the number of shared pair of electrons between the two atoms are one, two and three.
8. Formal charge (F.C.) on an atom in a Lewis structure

$$\begin{aligned}&= \text{(total number of valence electrons in the free atom)}\\ &\quad - \text{[total number of non-bonding (lone pairs) electrons]}\\ &\quad - \frac{1}{2}\text{[total number of bonding (shared) electrons]}\end{aligned}$$

9. Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule.
10. Bond angle is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion.
11. Bond enthalpy is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in the gaseous state. The unit of bond enthalpy is kJ mol^{-1}.
12. **Bond order** In the Lewis representation of a molecule or ion, the number of bonds present between two atoms is called bond order. Isoelectronic molecules and ions have identical bond orders, *e.g.*, F_2 and O_2^{2-} have bond order 1. N_2, CO and NO^+ have bond order 3. With increase in bond order, bond enthalpy increases, bond length decreases and stability increases.
13. 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 written. These structures are called canonical structures. The phenomenon is called resonance.
14. The actual structure is in between of all these contributing structures and is called resonance hybrid. The difference in the energy of the resonance hybrid and the most stable contributing structure (having least energy) is called **resonance energy**.
15. Non-polar covalent bond is formed between the two similar atoms. In this bond the electron cloud is completely symmetrical. Polar covalent bond is formed between two dissimilar atoms having different electronegativities, *e.g.*, in HCl, HBr, etc. In this bond, electron cloud is unsymmetrical (more towards more electronegative atom). Due to this, more electronegative atom acquires slightly negative charge and less electronegative atom acquires slightly positive charge ($\overset{\delta+}{H} — \overset{\delta-}{Cl}$).
16. As a result of polarisation, the molecule possesses the dipole moment, which can be defined as the product of the magnitude of the charge and the distance between the centres of positive and negative charge.
    Dipole moment, μ = charge (Q) × distance of separation (r)
17. It is usually expressed in Debye unit. $1 D = 3.33564 \times 10^{-30}$ Cm (where, C is coulomb and m is meter.)
18. **Fajan's rule**
    (i) The smaller the size of the cation and the larger the size of the anion, the greater is the polarizing power and hence, greater the covalent character of an ionic bond. That's why LiCl is more covalent than KCl and LiI is more covalent than LiCl.
    (ii) If two cations have same size and charge then the one with 18 electrons in outermost shell has greater polarizing power than the other with 8 electrons in outermost shell. That's why CuCl is more covalent than NaCl.

(iii) Larger the charge on the cation, greater is its polarizing power. Similarly, greater the charge on the anion, more easily it gets polarized.

19. **The Valence Shell Electron Pair Repulsion (VSEPR) theory**–The VSEPR theory used for predicting the geometrical shapes of the molecules is based on the assumption that electron pairs repel each other and therefore, tend to remain as far apart as possible. According to this model, molecular geometry is determined by repulsions between lone pairs-lone pairs, lone pairs – bond pairs and bond pairs – bond pairs.

20. The valence bond (VB) approach to covalent bonding is basically concerned with the energetics of covalent bond formation and discusses bond formation in terms of overlap of orbitals.

21. For explaining the characteristic shapes of polyatomic molecules, Pauling introduced the concept of hybridization of atomic orbitals. sp, sp^2, sp^3 hybridizations of atomic orbitals of Be, B, C, N and O are used to explain the formation and geometrical shapes of molecules like $BeCl_2$, BCl_3, CH_4, C_2H_2, C_2H_4, NH_3 and H_2O.

22. The molecular orbital (MO) theory describes bonding in terms of the combination and arrangement of atomic orbitals to form molecular orbitals associated with molecule. The number of molecular orbitals are always equal to the number of atomic orbitals from which they are formed.

23. Bonding molecular orbitals increase electron density between the nuclei and are lower in energy than the individual atomic orbitals. Similarly, antibonding molecular orbitals have a region of zero electron density between the nuclei and have more energy than the individual atomic orbitals.

24. The increasing order of energies of various molecular orbitals for B_2, C_2, N_2, etc., is

$$\sigma 1s < \overset{*}{\sigma} 1s < \sigma 2s < \overset{*}{\sigma} 2s < (\pi 2p_x \approx \pi 2p_y) < \sigma 2p_z < (\overset{*}{\pi} 2p_x \approx \overset{*}{\pi} 2p_y) < \overset{*}{\sigma} 2p_z$$

The increasing order of energies of various molecular orbitals for O_2 and F_2 is

$$\sigma 1s < \overset{*}{\sigma} 1s < \sigma 2s < \overset{*}{\sigma} 2s < \sigma 2p_z < (\pi 2p_x \approx \pi 2p_y) < (\overset{*}{\pi} 2p_x \approx \overset{*}{\pi} 2p_y) < \overset{*}{\sigma} 2p_z$$

25. Hydrogen bond is formed when a hydrogen atom finds itself between two highly electronegative atoms such as F, O or N. It may be intermolecular (existing between two or more molecules) or intramolecular (within the same molecule). H-bonds have a powerful effect on the structure and properties of many compounds.

Exercises

Question 1. **Explain the formation of a chemical bond.**

Solution. Kossel and Lewis approach to chemical bonding was based on the inertness of noble gases. Inertness of noble gases is due to the presence of 8 electrons in their outermost shell (called octet) except He (2 electrons in its outermost shell). Atoms of all other elements have less than eight electrons in their outermost shell, hence they are reactive chemically.

Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds. Atoms combine with one another in a number of different ways, *i.e.*, by transference of electrons (ionic bond) or by sharing of electrons (covalent bond), etc. For example, in case of sodium and chlorine, a chemical bond is formed by the transfer of an electron from sodium to chlorine.

Question 2. **Write Lewis dot symbols for atoms of the following elements : Mg, Na, B, O, N, Br.**

(i) Write the electronic configuration of each element to find the number of valence electrons *i.e.*, electrons present in the outer shell.
(ii) Represent the valence electrons by dots around the symbols of the element to write Lewis dot symbols.

Solution. $_{12}\text{Mg} = 2, 8, 2$; Lewis symbol = $\ddot{\text{Mg}}$

$_{11}\text{Na} = 2, 8, 1$; Lewis symbol = $\dot{\text{Na}}$

$_{5}\text{B} = 2, 3$; Lewis symbol = $\cdot\dot{\text{B}}\cdot$

$_{8}\text{O} = 2, 6$; Lewis symbol = $:\ddot{\text{O}}:$

$_{35}\text{Br} = 2, 8, 18, 7$; Lewis symbol = $\cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{Br}}}:$

(Lewis symbols are simple notations to represent valence electrons in an atom.)

Question 3. **Write the Lewis structure for the following atoms and ions S and S^{2-}; Al and Al^{3+}; H and H^{-}.**

(i) Write the electronic configuration of each element to find the number of valence electrons *i.e.*, electrons present in the outer shell.
(ii) Represent the valence electrons by dots around the symbols of the element to write Lewis dot symbols.

Solution. ${}_{16}S = 2, 8, 6;$ Lewis symbol = $:\overset{\bullet\bullet}{S}:$

$S^{2-} = (16 + 2)$ electrons; Lewis symbol = $[\underset{\bullet\bullet}{\overset{\bullet\bullet}{:S:}}]^{2-}$

${}_{13}Al = 2, 8, 3;$ Lewis symbol = $\underset{\bullet\bullet}{Al}\bullet$

$Al^{3+} = (13 - 3) = 10$ electrons; Lewis symbol = $[Al]^{3+}$

${}_{1}H = 1;$ Lewis symbol = $\overset{\bullet}{H}$

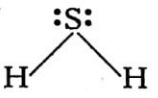
$H^{-} = (1 + 1) = 2$ electrons; Lewis symbol = $[\overset{\bullet\bullet}{H}]^{-}$

Question 4. **Draw the Lewis structures for the following molecules and ions.**

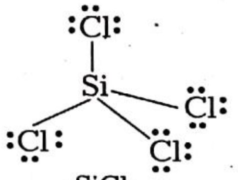
H_2S, $SiCl_4$, BeF_2, CO_3^{2-}, HCOOH

In Lewis structures, all the elements (except H) have 8 electrons in their outer shell. H has only 2 electrons.

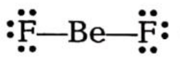
Solution.



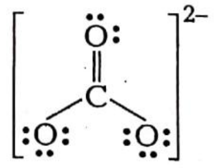
H_2S



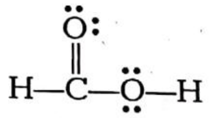
$SiCl_4$



BeF_2



CO_3^{2-}



HCOOH

Question 5. **Define octet rule. Write its significance and limitations.**

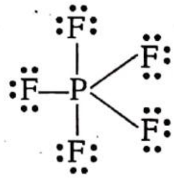
Solution. **Octet rule** Atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shell.

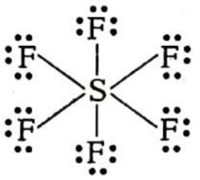
Significance of octet rule It helps to explain why different atoms combine with each other to form ionic or covalent compounds.

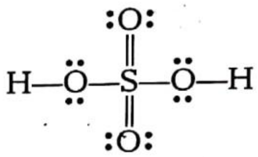
Limitations of octet rule It is quite useful for understanding the structures of most of the organic compounds and applies mainly to second period elements of the Periodic Table. Some exceptions to the octet rule are

(a) In some compounds, there are less than eight valence electrons around the central atom, *e.g.*, Li : Cl, H : Be : H; $\text{Cl}\,\overset{\text{Cl}}{\overset{\bullet\bullet}{:B:}}\,\text{Cl}$. In LiCl, BeH_2 and BCl_3, central atoms Li, Be and B have only 2, 4 and 6 electrons respectively.

(b) In some compounds there are more than eight valence electrons around the central atom, *e.g.*,







In PF_5, SF_6 and H_2SO_4, central atoms P, S and S have 10, 12 and 12 electrons respectively.

(c) In molecules with an odd number of electrons like NO (nitric oxide) and NO_2 (nitrogen dioxide), the octet rule is not satisfied for all the atoms.

(d) Octet rule is based upon the chemical inertness of noble gases. However, some noble gases such as Xe and Kr also form a number of compounds, *e.g.*, XeF_2, XeF_4, XeF_6, KrF_2, $XeOF_2$, etc.

(e) It does not explain the shape of the molecules.

(f) It does not explain about the energy of a molecule and the relative stability of the molecules.

Question 6. **Write the favourable factors for the formation of ionic bond.**

Ionic bond is formed between ions *i.e.*, cation and anion. Thus, factors which favour the formation of these ions, also favour the formation of ionic bond.

Solution. The favourable conditions for forming stable ionic bond are

(i) Low ionization enthalpy of element forming cation.

(ii) More negative electron gain enthalpy of element forming anion.

(iii) High lattice enthalpy of the ionic compound formed.

Question 7. **Discuss the shape of the following molecules using the VSEPR model.**

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

(i) Find the number of bonds formed (*i.e.*, bond pairs of electrons) and lone pairs (*i.e.*, non bonding pairs) around the central atom.

(ii) If lone pairs are absent and the number of bond pairs is 2, the molecule is linear, if 3, the molecule is trigonal planar, if 4, the molecule is tetrahedral and if 5, it is trigonal bipyramidal.

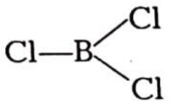
(iii) If there is 1 lone pair and 3 bond pairs, the molecule is pyramidal and if there is 2 lone pairs and two bond pairs, the molecule has angular or V shape.

Solution. According to VSEPR theory, 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 each other. The order of their repulsions is as follows

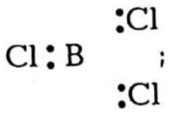
$$lp - lp > lp - bp > bp - bp$$

(i) **$BeCl_2$** : Cl **:** Be **:** Cl; The central atom Be has only 2 valence electrons which are bonded to Cl, so there are only 2 bond pairs and no lone pairs. It is of the type AB_2 and hence, the shape is linear.

(ii) **BCl_3** :

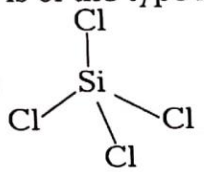


or

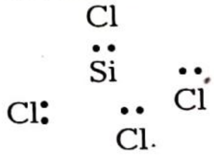


The central atom B has only 3 valence electrons which are bonded with three Cl atoms, so it contains only 3 bond pairs and no lone pair. It is of the type AB_3 and hence, the shape is trigonal planar.

(iii) **$SiCl_4$** :

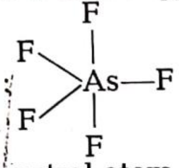


or

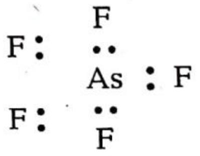


Similarly, the central atom Si has only 4 bond pairs and no lone pair. It is of the type AB_4 and hence, the shape is tetrahedral.

(iv) **AsF_5** :

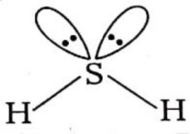


or

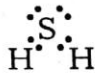


The central atom As has only 5 bond pairs and no lone pair. It is of the type AB_5 and hence, the shape is trigonal bipyramidal.

(v) **H_2S** :

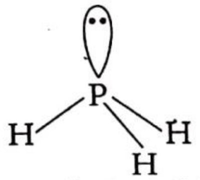


or

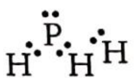


The central atom S has 6 valence electrons. Out of these, only two are used in bond formation with two H atoms while four (two pairs) remains as non-bonding electrons (*i.e.*, lone pairs). So it contains 2 bond pairs and 2 lone pairs. It is of the type AB_2L_2 and hence, the shape is bent or V shaped.

(vi) **PH_3** :



or

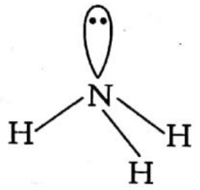


The central atom P has 5 valence electrons. Out of which three are utilized in bonding with H atoms and one pair remains as lone pair. So, it contains 3 bond pairs and 1 lone pair. It is of the type AB_3L and hence, the shape is pyramidal.

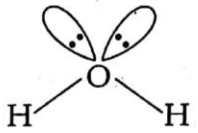
Question 8. Although geometries of NH_3 and H_2O molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. Discuss.

The size of lone pair is larger than the bond pair, so more the number of lone pairs of electrons, lesser is the bond angle.

Solution.



NH_3
bp = 3
lp = 1



H_2O
bp = 2
lp = 2

In H_2O molecule there is lone pair-lone pair repulsion due the presence of two lone pairs of electrons while in NH_3 molecule there found only lone pair-bond pair repulsion. According to VSEPR theory, the former one is more stronger and hence, the bond angle in water is less than that of ammonia (NH_3).

Question 9. How do you express the bond strength in terms of bond order?

Solution. With increase in bond order, bond enthalpy increases. Therefore, greater the bond order, higher is the bond strength, *i.e.*, bond strength $\propto$ bond order,

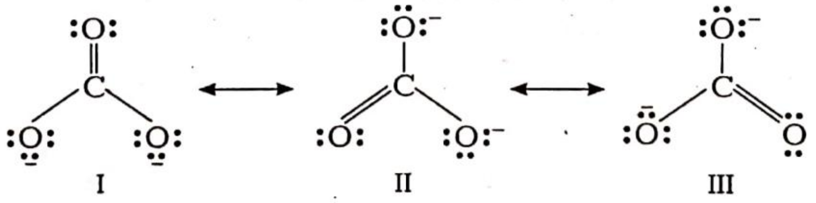
Question 10. Define the bond length.

Solution. **Bond length** It is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule. It is measured by spectroscopic, X-ray diffraction and electron diffraction techniques. In an ionic compound, the bond length is the sum of their ionic radii, $d = r_+ + r_-$ and in a covalent molecule, it is the sum of their covalent radii, *e.g.*, for HBr, $d = r_{H^+} + r_{Br^-}$.

Question 11. Explain the important aspects of resonance with reference to the CO_3^{2-} ion.

Solution. When a single Lewis structure of a molecule cannot describe its all properties, a number of structures, called canonical structures, are written. The actual structure, known as resonance hybrid, is in between of all these canonical forms. This phenomenon is called resonance.

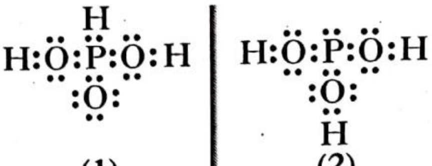
According to experimental findings, all carbon to oxygen bonds in CO_3^{2-} are equivalent, while in a single Lewis structure, there are two single bonds and one double bond between carbon and oxygen. So, a single Lewis structure is inadequate for the representation of CO_3^{2-} ion. The carbonate ion is best described as a hybrid of the canonical or resonance forms I, II and III.



Resonance in CO_3^{2-} ion

All canonical forms have similar energy, same positions of atoms and same number of bonded and non-bonded pairs of electrons.

Question 12. **H_3PO_3 can be represented by structures 1 and 2 shown below. Can these two structures be taken as the canonical forms of the resonance hybrid representing H_3PO_3? If not, give reasons for the same.**



(1) (2)

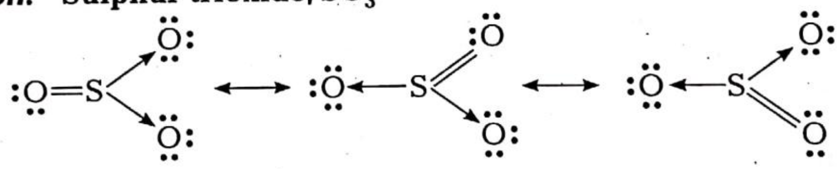
Resonating structures or canonical forms differ only in the arrangement of electrons, but not in the positions of atoms.

Solution. No. These two structures cannot be taken as the canonical forms of the resonance hybrid because positions of the atoms have been changed.

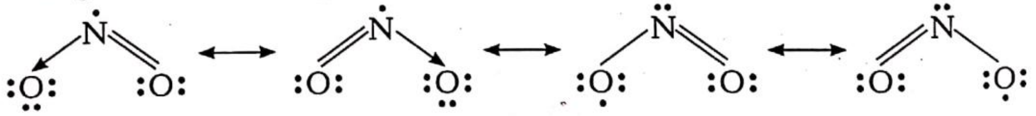
Question 13. **Write the resonance structures for SO_3, NO_2 and NO_3^-.**

Draw the possible structures in which octet (duplet in case of H) of all the atoms is complete and which differ only in the positions of electrons, but not in the position of atoms or nuclei.

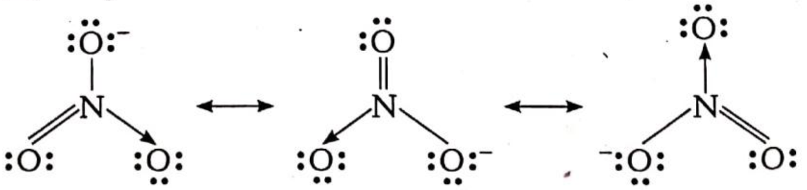
Solution. **Sulphur trioxide, SO_3**



Nitrogen dioxide, NO_2



Nitrate ion, NO_3^-

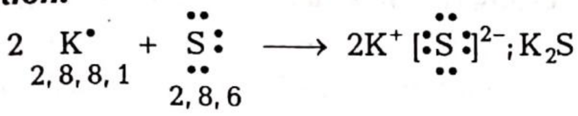


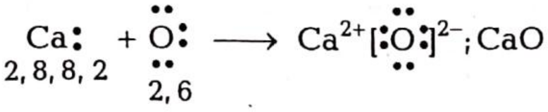
Question 14. **Use Lewis symbols to show electron transfer between the following atoms to form cations and anions :**

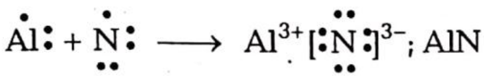
(a) K and S **(b) Ca and O** **(c) Al and N**

Metals lose electrons to complete their octet while non-metals gain electrons to complete octet. So write the Lewis symbol *i.e.*, symbols with valence electrons to show the transfer of electron from metal to non-metal.

Solution.

(a) 
$$2\,\underset{2,8,8,1}{K^{\bullet}} + \underset{2,8,6}{:\!\ddot{\underset{\cdot\cdot}{S}}\!:} \longrightarrow 2K^{+}[:\!\ddot{\underset{\cdot\cdot}{S}}\!:]^{2-}; K_2S$$

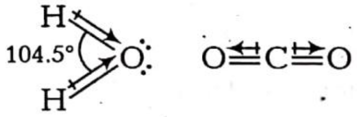
(b) 
$$\underset{2,8,8,2}{Ca:} + \underset{2,6}{\ddot{\underset{\cdot\cdot}{O}}\!:} \longrightarrow Ca^{2+}[:\!\ddot{\underset{\cdot\cdot}{O}}\!:]^{2-}; CaO$$

(c) 
$$\dot{Al}\!: + \dot{\underset{\cdot\cdot}{N}}\!: \longrightarrow Al^{3+}[:\!\ddot{\underset{\cdot\cdot}{N}}\!:]^{3-}; AlN$$

Question 15. **Although both CO_2 and H_2O are triatomic molecules, the shape of the H_2O molecule is bent while that of CO_2 is linear. Explain this on the basis of dipole moment.**

For symmetrical or regular structures dipole moment is zero. Unsymmetrical structures have some dipole moment.

Solution. The net dipole moment of CO_2 is zero. This is because the two equal bond dipoles ($\overset{\delta^+}{C}—\overset{\delta^-}{O}$) point in opposite directions and cancel the effect of each other. Hence, CO_2 is linear. On the other hand, H_2O molecule is found to have a net dipole moment (1.84 D) which suggests that the two O—H dipoles are not in a straight line opposing each other, *i.e.*, H_2O does not have linear structure, but they (O—H) must be inclined to each other at certain angle. Thus, H_2O molecule has a bent structure in which the two O—H bonds are oriented at an angle of 104.5°.



Question 16. **Write the significance/applications of dipole moment.**

Solution. The applications of dipole moment are :

(i) The dipole moment helps to predict whether a molecule is polar or non-polar. As $\mu = q \times d$, greater is the magnitude of dipole moment, higher will be the polarity of the bond. For non-polar molecules, the dipole moment is zero.

(ii) The percentage of ionic character can be calculated as

$$\text{Percentage of ionic character} = \frac{\mu_{\text{observed}}}{\mu_{\text{ionic}}} \times 100$$

(iii) Symmetrical molecules have zero dipole moment although they have two or more polar bonds. (In determination of symmetry).

(iv) It helps to distinguish between *cis*- and *trans*-isomers. Usually *cis*-isomer has higher dipole moment than *trans*-isomer.

(v) It helps to distinguish between *ortho*, *meta* and *para* isomers. Dipole moment of *para* isomer is zero. Dipole moment of *ortho* isomer is greater than that of *meta* isomer.

Question 17. **Define electronegativity. How does it differ from electron gain enthalpy?**

Solution. Electronegativity of an element is the tendency of its atom to attract the shared pair of electrons towards itself in a covalent bond. Electron gain enthalpy of an element may be defined as the energy released when a neutral isolated gaseous atom accepts an extra electron to form the gaseous negative ion, *i.e.*, anion.

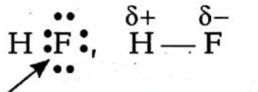
$$\underset{\text{Neutral gaseous atom}}{X(g)} + e^- \longrightarrow \underset{\text{Anion}}{X^-(g)}; \qquad \Delta H = \Delta e_g H$$

Greater the amount of energy released in the above process, higher is the electron gain enthalpy of the element.

Electronegativity differs from electron gain enthalpy because electronegativity is a property of an atom in the bonded state while electron gain enthalpy relates to atoms in their isolated gaseous states.

Question 18. **Explain with the help of suitable example polar covalent bond.**

Solution. When covalent bond is formed between two dissimilar atoms, for example, HF (heteronuclear molecule), the shared pair of electrons between the two atoms gets displaced more towards more electronegative atom, fluorine. As a result, hydrogen atom becomes slightly positively charged and fluorine becomes slightly negatively charged. This type of bond is called polar covalent bond.



$$\mathrm{H}\,\overset{\bullet\bullet}{\underset{\bullet\bullet}{:\mathrm{F}:}},\quad \overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}}$$

attracted more towards fluorine

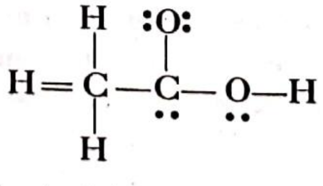
Question 19. **Arrange the bonds in order of increasing ionic character in the molecules; LiF, K_2O, N_2, SO_2 and ClF_3.**

(i) Ionic character $\propto$ lattice energy $\propto \frac{1}{\text{size of ion}} \propto$ charge on ion.

(ii) A non-polar molecule like N_2 has almost negligible ionic character.

Solution. $N_2 < SO_2 < ClF_3 < K_2O < LiF$

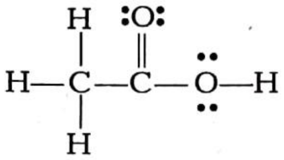
Question 20. **The skeletal structure of CH_3COOH as shown below is correct, but some of the bonds are shown incorrectly. Write the correct Lewis structure for acetic acid.**



$$\begin{array}{ccccccc} & & \mathrm{H} & & :\mathrm{O}: & & \\ & & | & & | & & \\ \mathrm{H} & = & \mathrm{C} & - & \underset{\bullet\bullet}{\mathrm{C}} & - & \underset{\bullet\bullet}{\mathrm{O}}-\mathrm{H} \\ & & | & & & & \\ & & \mathrm{H} & & & & \end{array}$$

Complete the octet (or duplet in case of H) of all the atoms to correct the structure.

Solution. The correct Lewis structure for acetic acid is



Question 21. Apart from tetrahedral geometry, another possible geometry for CH_4 is square planar with the four H-atoms at the corners of the square and the C atom at its centre. Explain, why CH_4 is not square planar?

Solution. Electronic configuration of carbon
In ground state : ${}_6C$— $1s^2, 2s^2, 2p_x^1, 2p_y^1$

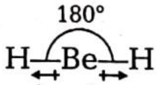
In excited state : $1s^2, \underbrace{2s^1, 2p_x^1, 2p_y^1, 2p_z^1}_{sp^3 \text{ hybridized}}$

In CH_4 molecule, carbon is sp^3 hybridized, so it is tetrahedral in shape. For square planar dsp^2 hybridization is required which is not possible in carbon due to absence of *d*-orbitals. Furthermore according to VSEPR theory, the four bonded electron pairs around carbon atom arranged themselves in a regular tetrahedron geometry. For tetrahedral structure, the bond angle is 109°28′ while in square planar structure, the bond angle is 90°. Therefore, in tetrahedral structure repulsions between bonded electron pairs is less than that of the square planar.

Question 22. Explain why BeH_2 molecule has a zero dipole moment although the Be—H bonds are polar?

Dipole moment is the vector sum of all the bond dipoles.

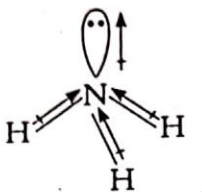
Solution. BeH_2 molecule is linear. The two equal bond dipoles point in opposite directions and cancel the effect of each other. That's why its dipole moment is zero.



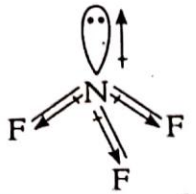
BeH_2 molecule, $\mu = 0$

Question 23. Which out of NH_3 and NF_3 has higher dipole moment and why?

Solution. NH_3 has higher dipole moment than NF_3, although both the molecules are pyramidal in shape. In NH_3, the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the three N—H bonds, while in NF_3, the orbital dipole due to lone pair is in the direction opposite to the resultant dipole moment of three N—F bonds. Hence, resultant dipole in NF_3 decreases.



NH_3, ($\mu = 4.90 \times 10^{-30}$ cm)



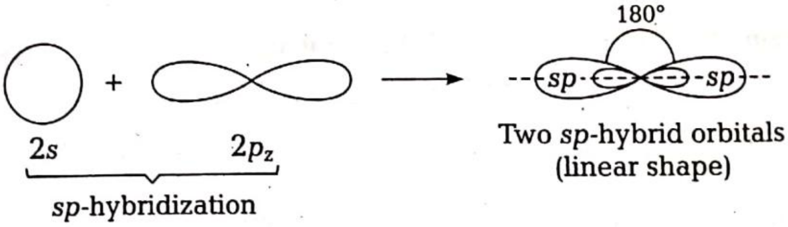
NF_3, ($\mu = 0.80 \times 10^{-30}$ cm)

Note *Dipole moment is represented by an arrow pointing towards the more electronegative atom.*

Question 24. What is meant by hybridization of atomic orbitals? Describe the shapes of *sp*, sp^2 and sp^3 hybrid orbitals.

Solution. **Hybridization** To explain the shape of polyatomic molecules like CH_4, H_2O, etc., Pauling introduced the concept of hybridization. It is defined as the mixing of atomic orbitals of nearly same energy, resulting in the formation of new set of orbitals of equal energies and identical shapes. The new orbitals thus, formed are known as hybrid orbitals. The number of hybrid orbitals is equal to the number of atomic orbitals mixed.

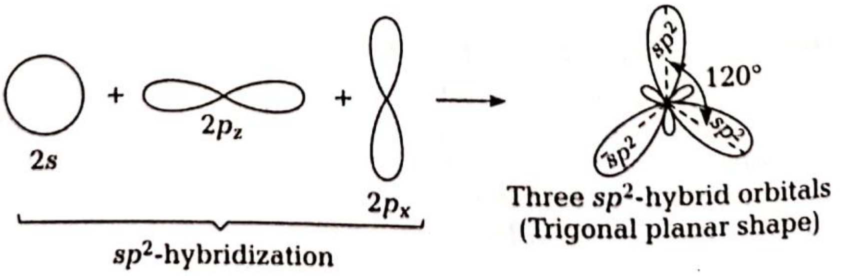
sp-**hybridization** It involves the mixing of one *s* and one *p* (p_z) orbital resulting in the formation of two *sp* hybridized orbitals. These two *sp* hybridized orbitals are oriented in opposite direction (linear arrangement) and make an angle of 180° with one another. Examples, in BeH_2, BeF_2 and C_2H_2, Be and C are *sp*-hybridized.



Two *sp*-hybrid orbitals (linear shape)

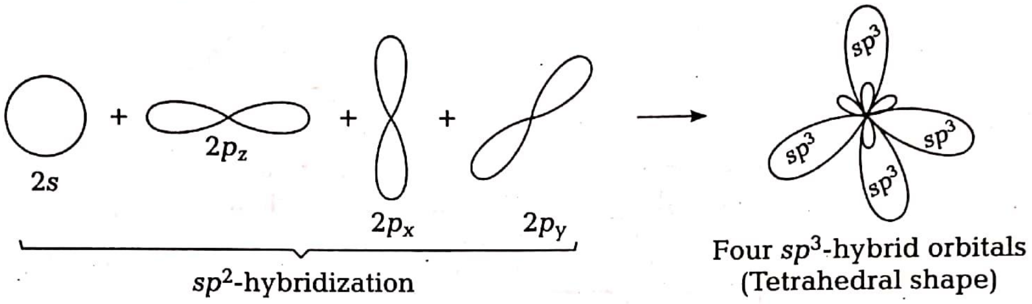
sp hybridization is also called diagonal hybridization.

sp^2-**hybridization** It involves the mixing of one *s* and two *p*-orbitals resulting in the formation of three sp^2 hybridized orbitals. These three sp^2 hybridized orbitals are oriented in trigonal planar arrangement and make an angle of 120° with one another. Examples, in BH_3 and BF_3 boron is sp^2 hybridized and in C_2H_4, carbon is sp^2-hybridized.



Three sp^2-hybrid orbitals (Trigonal planar shape)

sp^3-hybridization It involves the mixing of one *s* and three *p*-orbitals resulting in the formation of four sp^3-hybridized orbitals. These four sp^3-hybridized orbitals are oriented towards the four corners of a regular tetrahedron and make an angle of 109°28′ with one another. **Examples** In methane (CH_4), ethane (C_2H_6) and all compounds of carbon containing C—C single bonds, carbon is sp^3 hybridized.



Question 25. **Describe the change in hybridization (if any) of the Al atom in the following reaction.**

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

Solution. Electronic configuration of Al

In ground state $_{13}Al = 1s^2, 2s^2, 2p^6, 3s^2, 3p_x^1$

In excited state $= 1s^2, 2s^2, 2p^6, 3s^1, 3p_x^1, 3p_y^1$

In the formation of $AlCl_3$, Al undergoes sp^2-hybridization and it is trigonal planar in shape. While in the formation of $AlCl_4^-$, Al undergoes sp^3-hybridization. It means empty $3p_z$-orbital also involved in hybridization. Thus, the shape of $AlCl_4^-$ ion is tetrahedral.

Question 26. **Is there any change in the hybridization of B and N atoms as a result of the reaction?**

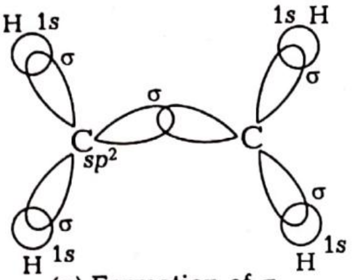
$$BF_3 + NH_3 \longrightarrow F_3B \cdot NH_3$$

Find the number of lone pairs and bond pairs on the central atom to find hybridization.

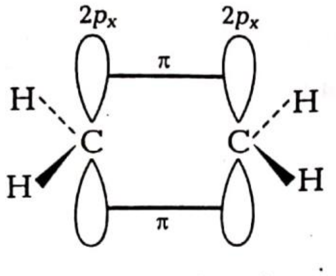
Solution. In BF_3, there are 3 bond pairs and 0 lone pairs, so boron is sp^2 hybridized and in NH_3, there are 3 bond pairs and 1 lone pair, so nitrogen is sp^3 hybridized. After the reaction, hybridization of boron changes to sp^3 but hybridization of nitrogen remains the same because N shares its lone pair with electron deficient B.

Question 27. Draw diagrams showing the formation of a double bond and a triple bond between the carbon atoms in C_2H_4 and C_2H_2.

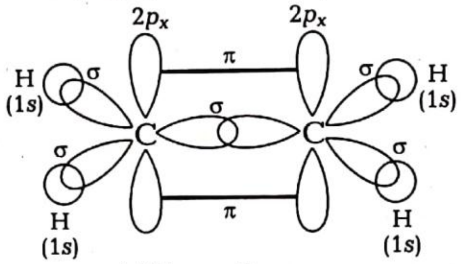
Solution. **Formation of C_2H_4 (ethylene)**



(a) Formation of σ-bonds in ethene, C_2H_4

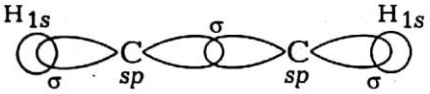


(b) Formation of π-bonds in ethene

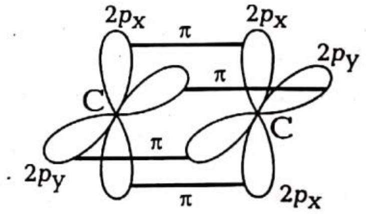


(c) Formation σ- and π-bonds in ethene (5σ, 1π)

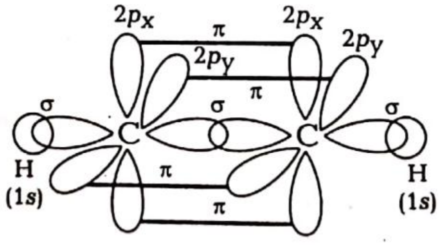
Formation of C_2H_2 (acetylene)



(a) Formation of σ-bonds in ethyne, C_2H_2



(b) Formation of π-bonds in ethyne



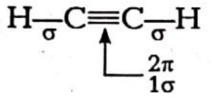
(c) Formation of σ- and π bonds in ethyne (3σ, 2π)

Question 28. What is the total number of sigma and pi bonds in the following molecules?

(a) C_2H_2 (b) C_2H_4

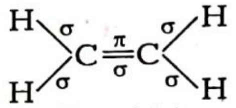
As each single bond is a σ-bond, a double bond contains one σ and one π-bond and a triple bond contains one σ and two π-bonds, so draw structure of the given molecules and count the number of σ and π-bonds.

Solution. (a) C_2H_2



(3σ and 2π)

(b) C_2H_4



(5σ and 1π)

Question 29. Considering *x*-axis as the internuclear axis, which out of the following will not form a sigma bond and why?

(a) 1*s* and 1*s* (b) 1*s* and $2p_x$ (c) $2p_y$ and $2p_y$ (d) 1*s* and 2*s*

Axial overlapping results in the formation of σ bonds.

Solution. Only (c) will not form a σ-bond. Because on taking *x*-axis as the internuclear axis,. $2p_y$ and $2p_y$ orbitals overlap sideway (lateral overlapping) resulting in the formation of a π-bond.

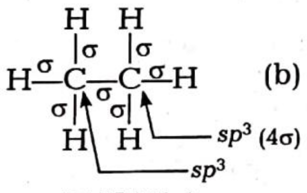
Question 30. Which hybrid orbitals are used by carbon atoms in the following molecules?

(a) $CH_3—CH_3$ (b) $CH_3CH=CH_2$
(c) CH_3CH_2OH (d) CH_3CHO
(e) CH_3COOH

Find number of σ-bonds and find hybridization as 4σ ⇒ sp^3-hybridization, 3σ ⇒ sp^2-hybridization, 2σ ⇒ *sp*-hybridization.

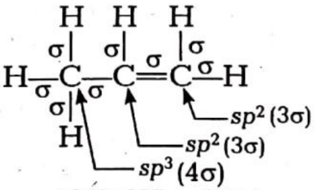
Solution.

(a)



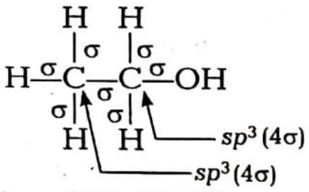
(C_2H_6) (4σ)

(b)



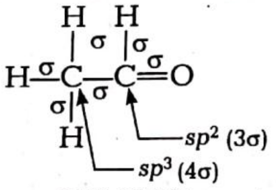
($CH_3CH=CH_2$)

(c)



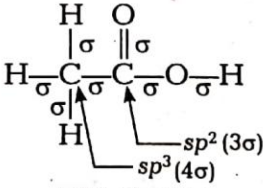
(CH_3CH_2OH)

(d)



(CH_3CHO)

(e)

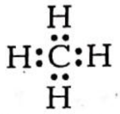


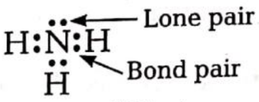
(CH_3CHO)

(If a carbon atom is bonded by only single bonds, it is sp^3 hybridized, if it is bonded by double bond, it is sp^2 hybridized and if it is bonded by one triple bond, it is *sp* hybridized.)

Question 31. What do you understand by bond pairs and lone pairs of electrons? Illustrate by giving one example of each type.

Solution. Covalent bond is formed by mutual sharing of electrons. The shared pair of electrons present between the bonded atoms are called are called lone pairs of electrons. For example, ammonia, NH_3 contains 3 bond pairs and 1 lone pair of electrons, water H_2O contains 2 bond pairs and 2 lone pairs of electrons and CH_4 contains only 4 bond pairs.


(CH_4 – 4bp)



(NH_3 – 1 lp and 3bp)


(H_2O – 2lp and 2bp)

Question 32. Distinguish between a sigma and a pi bond.

Solution.

S. No.	Sigma (σ) bond	Pi (π) bond
1.	It is formed by the axial overlapping (end to end overlapping) of atomic orbitals.	It is formed by the sideways overlapping (lateral overlapping) of atomic orbitals.
2.	It involves overlapping of s-s, s-p and p-p atomic orbitals.	It involves overlapping of p-p atomic orbitals.
3.	In σ-bond, the overlapping of orbitals takes place to a larger extent, so, it is a stronger bond.	In π-bond, the overlapping of orbitals takes place to a smaller extent, so, it is a weaker bond.
4.	Free rotation about a σ-bond is possible.	Free rotation about a π-bond is not possible.
5.	A σ-bond may exist either alone or along with π-bonds.	It is always present along with a sigma bond.
6.	Electron cloud of sigma bond is symmetrical about internuclear axis.	Electron cloud of π-bond is unsymmetrical. It consists of electron clouds below and above the internuclear axis.
7.	In the formation of σ-bond, hybridized orbitals or unhybridised orbitals are involved.	In the formation of π-bond, only unhybridized orbitals are involved.

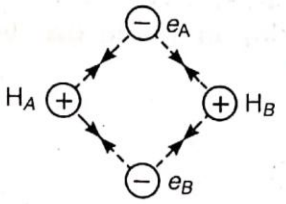
Question 33. Explain the formation of H_2 molecule on the basis of valence bond theory.

Solution. **Formation of H_2 molecule** Consider two hydrogen atoms A and B, each containing one electron in its 1s-subshell. When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive forces and repulsive forces begin to operate.

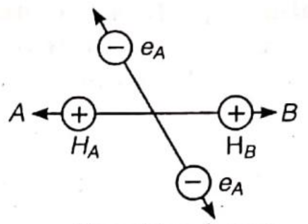
(i) Attractive forces arises between nucleus of A and electron of B and *vice-versa, i.e.,* $N_A - e_B$, $N_B - e_A$.

(ii) Repulsive forces arises between nuclei of two atoms A and B, *i.e.,* $N_A - N_B$.

(iii) Repulsive forces arises between electrons of two atoms A and B, *i.e.,* $e_A - e_B$.

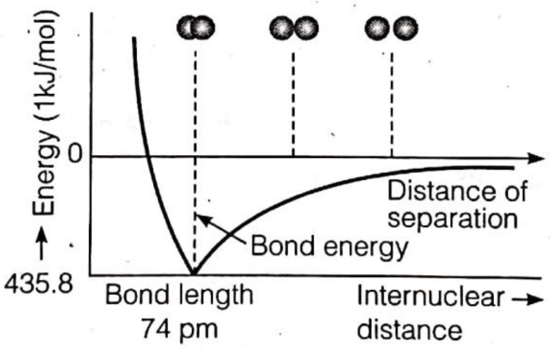


Attractive forces



Repulsive forces

Repulsive forces tend to push them apart while attractive forces tend to bring the two atoms close to each other . As the two atoms start to come closer to each other from infinite distance, the energy of the system starts decreasing as the forces of attraction exceed the forces of repulsion. Ultimately at a certain equilibrium distance, the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage, the two H-atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm. In the formation of H_2 molecule, the released energy is called bond enthalpy. The energy changes taking place during the formation of H_2 molecule are shown graphically in the following figure.



The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H-atoms. The minimum in the curve corresponds to the most stable state of H_2.

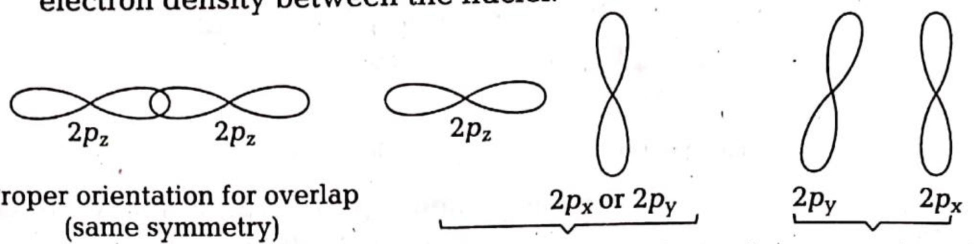
Question 34. **Write the important conditions required for the linear combination of atomic orbitals to form molecular orbitals.**

Solution. Conditions for the combination of atomic orbitals :

(i) **The combining atomic orbitals must have comparable energies.** For example 1*s*-orbital can combine with another 1*s*-orbital but not with 2*s*-orbital because 2*s*-orbital have higher energy than that of 1*s*-orbital. Such combinations are possible if the atoms are different (heteronuclear diatomic molecules).

(ii) **The combining atomic orbitals must have the same symmetry about the molecular axis.** For example $2p_z$-orbital of one atom can combine with $2p_z$-orbital of another atom. It cannot combine with the $2p_x$ or $2p_y$ orbitals because of their different symmetries.

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



Proper orientation for overlap (same symmetry)

Improper orientation (no overlapping)

Improper orientation (no overlapping)

Question 35. Use molecular orbital theory to explain why the Be_2 molecule does not exist?

A positive bond order means a stable molecule (*i.e.*, it exists) while a negative or zero bond order means an unstable molecule (*i.e.*, it does not exist). Write MO electronic configuration of Be_2 to find its bond order from the formula

$$BO = \frac{1}{2}[N_b - N_a]$$

where, N_b = number of electrons in bonding molecular orbitals and N_a = number of electrons in antibonding molecular orbitals. (represented by*)

Solution. Electronic configuration of $_4Be$—$1s^2, 2s^2$

Electronic configuration of Be_2 molecule $(4 + 4 = 8)$,

$$\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2$$

Bond order $= \frac{1}{2}[N_b - N_a] = \frac{1}{2}(4 - 4) = 0$

Hence, Be_2 does not exist.

Question 36. Compare the relative stability of the following species and indicate their magnetic properties.

$$O_2, O_2^+, O_2^- \text{ (superoxide)}, O_2^{2-} \text{ (peroxide)}.$$

(i) Bond order is directly proportional to stability so calculate bond order by writing MO configuration and using the formula $BO = \frac{1}{2}(N_b - N_a)$. Now compare the stability by comparing bond order.

(ii) Also find whether all the electrons are paired (*i.e.*, it is diamagnetic) or not (*i.e.* it is paramagnetic).

Solution. Electronic configurations of O_2, O_2^+, O_2^- and O_2^{2-} species are as follows

$O_2\ (16e^-)$ — $\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, (\pi 2p_x^2 \approx \pi 2p_y^2)(\overset{*}{\pi} 2p_x^1 \approx \overset{*}{\pi} 2p_y^1)$

Bond order $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 6) = 2$

O_2 is paramagnetic because it has two unpaired electrons.

O_2^+ ion is formed by the lose of one electron by O_2 molecule.

O_2^+ $(15e^-)$ — $\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, (\pi\, 2p_x^2 \approx \pi\, 2p_y^2)\ (\overset{*}{\pi} 2p_x^1 \approx \overset{*}{\pi} 2p_y)$

Bond order $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 5) = 2.5$

O_2^+ is paramagnetic because it has one unpaired electron.

O_2^- ion is formed by the gain of one electron by O_2 molecule.

O_2^- $(17e^-)$ — $\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, (\pi\, 2p_x^2 \approx \pi\, 2p_y^2), (\overset{*}{\pi} 2p_x^2 \approx \overset{*}{\pi} 2p_y^1)$

Bond order $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 7) = 1.5$

O_2^- is paramagnetic because it has one unpaired electron.

O_2^{2-} ion is formed by the gain of 2 electrons by O_2 molecule.

O_2^{2-} $(18e^-)$ — $\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, (\pi\, 2p_x^2 \approx \pi\, 2p_y^2), (\overset{*}{\pi} 2p_x^2 \approx \overset{*}{\pi} 2p_y^2)$

Bond order $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 8) = 1$

O_2^{2-} is diamagnetic because all electrons are paired.

Relative stability of the above species in decreasing order

$$O_2^+ > O_2 > O_2^- > O_2^{2-}$$

Question 37. **Write the significance of a plus and a minus sign shown in representing the orbitals.**

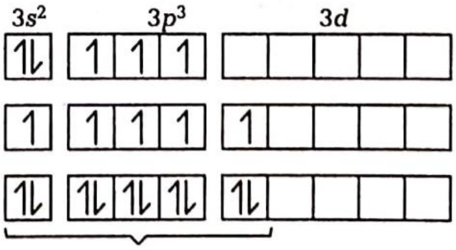
Solution. Orbitals are represented by wave functions. A plus sign in an orbital represents a positive wave function and a minus sign represents a negative wave function. Combination of two wave functions having similar sign gave bonding molecular orbital while that having opposite sign, gave antibonding molecular orbital.

Question 38. **Describe the hybridization in case of PCl_5. Why are the axial bonds longer as compared to the equatorial bonds?**

Find the number of unpaired electrons present in excited state in P atom from its electronic configuration and give hybridization on this basis.

Solution. Electronic configuration of phosphorus

In ground state, ${}_{15}P = 1s^2, 2s^2, 2p^6, 3s^2, 3p^3$

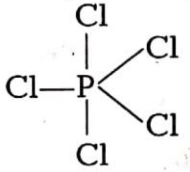


In excited state ${}_{15}P$ =

Formation of PCl_5 =

sp^3d hybrid orbitals (filled by electrons donated by 5 Cl atoms)

In the formation of PCl_5 molecule, the five orbitals, *i.e.*, one *s*, three *p* and one *d*-orbitals, are available for hybridization to yield five sp^3d hybridized orbitals. These five sp^3d hybridized orbitals are directed towards the five corners of a trigonal bipyramidal.



In PCl_5, three P—Cl bonds lie in one plane and make an angle of 120° with each other. These bonds are known as equatorial bonds. The remaining two P—Cl bonds, one lying above and other lying below the equatorial plane make an angle of 90° with the plane. These bonds are known as axial bonds. Axial P—Cl bonds are longer than equatorial P—Cl bonds because of the greater repulsion on axial bond pair electrons by equatorial bond pair electrons.

Question 39. **Define hydrogen bond. Is it weaker or stronger than the van der Waals' forces?**

Solution. Whenever in a molecule H-atom is linked with an atom of electronegative element like F, O or N, the shared pair electrons of the covalent bond are shifted towards the more electronegative atom. Due to this H-atom acquires partial positive charge and more electronegative atom acquires partial negative charge. This partially positively charged hydrogen of one molecule forms a bond with the other partially negatively charged more electronegative atom. This bond is known as hydrogen bond, *e.g.*, in HF molecule hydrogen acquires partial positive charge and F acquires partial negative charge due to the shifting of shared pair of electrons towards F. This partial positive charged H-atom of one molecule forms a hydrogen bond with partial negative charged F atom of another molecule.

$$\overset{+\delta}{H}—\overset{-\delta}{F}\cdots\overset{+\delta}{H}—\overset{-\delta}{F}\cdots\cdots\overset{+\delta}{H}—\overset{-\delta}{F}$$

Hydrogen bond

Thus, H-bond can be defined as the attractive force which binds H-atom of one molecule with the electronegative atom like F, O or N of another molecule.

Hydrogen bond is stronger than van der Waals' forces.

Question 40. **What is meant by the term bond order? Calculate the bond order of N_2, O_2, O_2^+ and O_2^-.**

Solution. **Bond order** is defined as one half the difference between the number of electrons present in the bonding and antibonding orbitals, *i.e.*,

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

A positive bond order means a stable molecule while a negative or zero bond order means an unstable molecule.

$$\text{Stability of a molecule} \propto \text{bond order}$$

$$\text{Bond length} \propto \frac{1}{\text{bond order}}$$

Bond order values 1,2 or 3 correspond to single, double or triple bonds respectively.

Calculation of the bond order of N_2, O_2, O_2^+ and O_2^-

Electronic configuration of N_2 (14 electrons)

$$\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, (\pi\, 2p_x^2 \approx \pi\, 2p_y^2), \sigma 2p_z^2$$

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2} \times (10 - 4) = 3$$

E.C. of O_2 (16 electrons)

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

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 6) = 2$$

E.C. of O_2^+ (15 electrons)

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

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 5) = 2.5$$

E.C. of O_2^- (17 electrons)

$$= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, (\pi\, 2p_x^2 \approx \pi\, 2p_y^2), (\dot{\pi} 2p_x^2 \approx \dot{\pi} 2p_y^1)$$

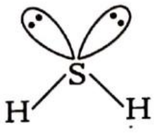
$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 7) = 1.5$$

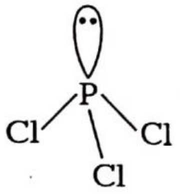
Selected NCERT Exemplar Problems

Short Answer Type

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

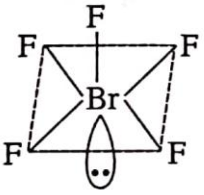
Solution. **H_2S**—Central atom is sulphur. There are 6 electrons in its valence shell ($_{16}S = 2, 8, 6$). Two electrons are shared with two H-atoms and the remaining four electrons are present as two lone pairs. Hence, total pairs of electrons are four (2 bond pairs and 2 lone pairs). Due to the presence of 2 lone pairs the shape becomes distorted tetrahedral or angular or bent (non-linear).





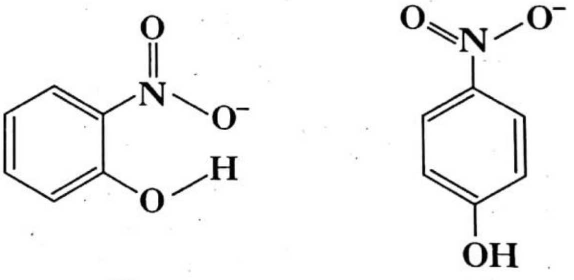
PCl_3—Central atom is phosphorus. There are 5 electrons in its valence shell ($_{15}P = 2, 8, 5$). Three electrons are shared with three Cl-atoms and the remaining two electrons are present as one lone pair. Hence, total pairs of electrons are four (1 lone pair and 3 bond pairs). Due to the presence of one lone pair, the shape becomes pyramidal (non-planar).

Question 2. Explain the shape of BrF_5^-.



Solution. The central atom Br has seven electrons in the valence shell. Five of these will form bonds with five fluorine atoms and the remaining two electrons are present as one lone pair. Hence, total pairs of electrons are six (5 bond pairs and 1 lone pair). To minimize repulsion between lone pairs and bond pairs, the shape becomes square pyramidal.

Question 3. Structures of molecules of two compounds are given below.



(I) (II)

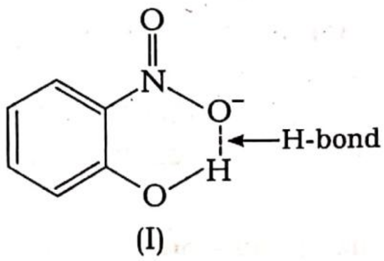
(a) Which of the two compounds will have intermolecular hydrogen bonding and which compound is expected to show intramolecular hydrogen bonding ?

(b) The melting point of a compound depends on, among other things, the extent of hydrogen bonding. On this basis explain which of the above two compounds will show higher melting point ?

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

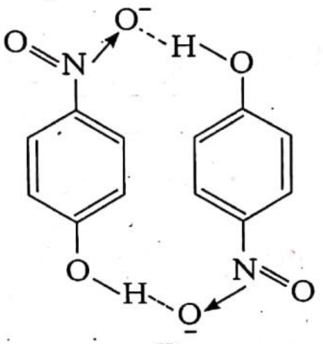
Solution.

(a) Compound (I) will form intramolecular H-bonding. Intramolecular H-bonding is formed when H-atom, in between the two highly electronegative atoms, is present within the same molecule. In *ortho*-nitrophenol (compound I), H-atom is in between the two oxygen atoms.



(I)

Compound (II) forms intermolecular H-bonding. In *para*-nitrophenol (II) there is a gap between NO_2 and OH group. So, H-bond exists between H-atom of one molecule and O-atom of another molecule as depicted below.

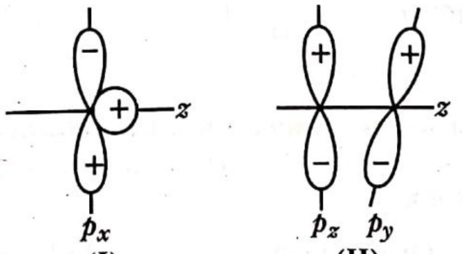


(II)

(b) Compound (II) will have higher melting point because large number of molecules are joined together by H-bonds.

(c) Due to intramolecular H-bonding compound (I) is not able to form H-bond with water, so it is less soluble in water. While molecules of compound II form H-bonding with H_2O easily, so it is soluble in water.

Question 4. Why does the type of overlap given in the following figure not result in bond formation?

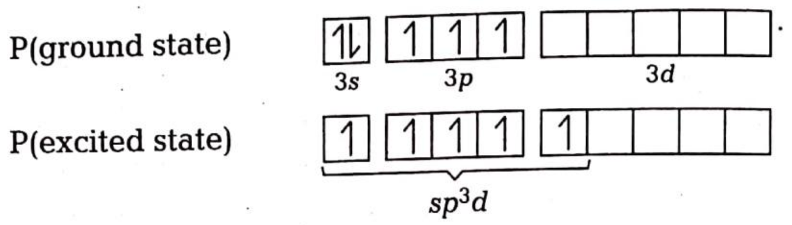


(I) (II)

Solution. In the figure (I) area of ++ overlap is equal to +– overlap, so net overlap is zero, while in figure II there is no overlap due to different symmetry.

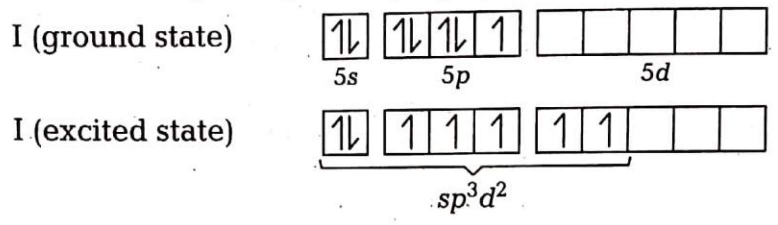
Question 5. Explain why PCl_5 is trigonal bipyramidal whereas IF_5 is square pyramidal?

Solution. PCl_5—The ground state and the excited state outer electronic configurations of phosphorus (Z = 15) are represented below:



In PCl_5, P is sp^3d hybridized, therefore, its shape is trigonal bipyramidal.

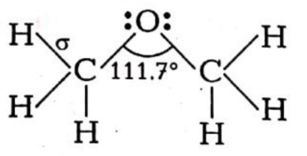
IF_5—The ground state and the excited state outer electronic configurations of iodine (Z = 53) are represented below.



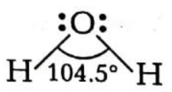
In IF_5, I is sp^3d^2 hybridized, therefore, shape of IF_5 is square pyramidal.

Question 6. In both water and dimethyl ether $(CH_3-\ddot{\underset{..}{O}}-CH_3)$, oxygen atom is central atom, and has the same hybridization, yet they have different bond angles. Which one has the greater bond angle? Give reason.

Solution. Dimethyl ether has greater bond angle than that of water, however in both the molecules central atom oxygen is sp^3 hybridized with two lone pairs. In dimethyl ether, bond angle is greater (111.7°) due to the greater repulsive interaction between the two bulky alkyl (methyl) groups than that between two H-atoms.



Dimethyl ether



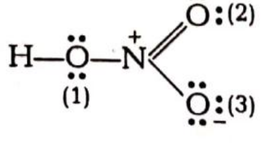
Water

Actually C of CH_3 group is attached to three H-atoms through σ-bonds. These three C—H bond pair of electrons increases the electronic charge density on carbon atom.

Question 7. Write Lewis structure of the following compounds and show formal charge on each atom :

HNO_3, NO_2, H_2SO_4

Solution. (a) **HNO_3 :**



Formal charge on an atom in a Lewis structure

$$= [\text{total number of valence electrons in free atom}] - [\text{total number of non-bonding (lone pairs) electrons}] - \frac{1}{2}[\text{total number of bonding or shared electrons}]$$

Formal charge on $H = 1 - 0 - \frac{1}{2} \times 2 = 0$

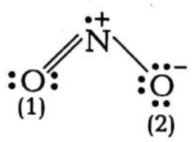
Formal charge on $N = 5 - 0 - \frac{1}{2} \times 8 = 1$

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

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

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

NO_2 :

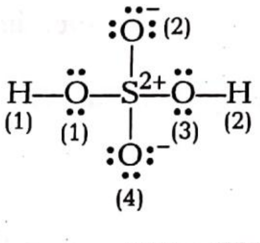


Formal charge on $O(1) = 6 - 4 - \frac{1}{2} \times 4 = 0$

Formal charge on $N = 5 - 1 - \frac{1}{2} \times 6 = +1$

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

H_2SO_4 :



Formal charge on H(1) or H(2) $= 1 - 0 - \frac{1}{2} \times 2 = 0$

Formal charge on O(1) or O(3) $= 6 - 4 - \frac{1}{2} \times 4 = 0$

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

Formal charge on $S = 6 - 0 - \frac{1}{2} \times 8 = +2$

Question 8. What is the effect of the following processes on the bond order in N_2 and O_2?

(i) $N_2 \longrightarrow N_2^+ + e^-$ (ii) $O_2 \longrightarrow O_2^+ + e^-$

Solution. According to molecular orbital theory, electronic configurations and bond order of N_2, N_2^+, O_2 and O_2^+ species are as follows:

$N_2\ (14e^-) = \sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2, (\pi 2p_x^2 \approx \pi 2p_y^2), \sigma 2p_z^2$

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}(10-4) = 3$$

$N_2^+\ (13e^-) = \sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2, (\pi 2p_x^2 \approx \pi 2p_y^2)\ \sigma 2p_z^1$

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}(9-4) = 2.5$$

$O_2\ (16e^-) = \sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2, \sigma 2p_z^2, (\pi 2p_x^2 \approx \pi 2p_y^2), (\overset{*}{\pi}2p_x^1 \approx \overset{*}{\pi}2p_y^1)$

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}(10-6) = 2$$

$O_2^+\ (15e^-) = \sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2, \sigma 2p_z^2, (\pi 2p_x^2 \approx \pi 2p_y^2), (\overset{*}{\pi}2p_x^1 \approx \overset{*}{\pi}2p_y)$

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}(10-5) = 2.5$$

(i) $\underset{\text{B.O.} = 3}{N_2} \longrightarrow \underset{\text{B.O.} = 2.5}{N_2^+} + e^-$

Thus, bond order decreases.

(ii) $\underset{\text{B.O} = 2}{O_2} \longrightarrow \underset{\text{B.O} = 2.5}{O_2^+} + e^-$

Thus, bond order increases.

Question 9. **Give reasons for the following.**

(i) Covalent bond are directional bonds while ionic bonds are non-directional.

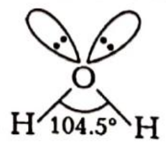
(ii) Water molecule has bent structure whereas carbon dioxide molecule is linear.

(iii) Ethyne molecule is linear.

Solution.

(i) A covalent bond is formed by the overlap of atomic orbitals. The direction of overlapping gives the direction of bond. In ionic bond, the electrostatic field of an ion is non-directional. Each positive ion is surrounded by a number of anions in any direction depending upon its size and *vice-versa*. That's why covalent bonds are directional bonds while ionic bonds are non-directional.

(ii) In H_2O, oxygen atom is sp^3 hybridised with two lone pairs. The four sp^3 hybridised orbitals acquire a tetrahedral geometry with two corners occupied by hydrogen atoms while other two by the lone pairs. The bond angle is reduced to 104.5° from 109.5° due to greater repulsive forces between $lp-lp$ and the molecule thus acquires a V-shape or bent structure (angular structure).



In CO_2 molecule, carbon atom is *sp*-hybridised. The two *sp* hybrid orbitals are oriented in opposite direction forming an angle of 180°.

$$O\overset{\pi}{\underset{\sigma}{=}}C\overset{\pi}{\underset{\sigma}{=}}O$$

That's why H_2O molecule has bent structure whereas CO_2 molecule is linear.

(iii) In ethyne molecule, both the carbon atoms are *sp* hybridised, having two unhybridised orbitals, *i.e.*, $2p_x$ and $2p_y$. The two *sp* hybrid orbitals of both the carbon atoms are oriented in opposite direction forming an angle of 180°.

$$H—C\underset{2\pi\text{-bond}}{\overset{\sigma}{\equiv}}C—H$$

That's why ethyne molecule is linear.

Question 10. Arrange the following bonds in order of increasing ionic character giving reason.

N—H, F—H, C—H and O—H

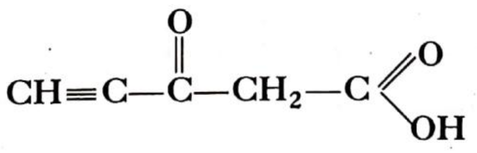
Solution. Greater is the electronegativity difference between the two bonded atoms, greater is the ionic character.

	N—H	F—H	C—H	and	O—H
Electronegativity difference	(3.0 – 2.1) = 0.9	(4.0 – 2.1) = 1.9	(2.5 – 2.1) = 0.4		(3.5 – 2.1) = 1.4

Therefore, increasing order of ionic character of the given bonds is as follows :

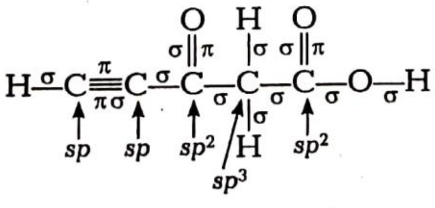
C—H < N—H < O—H < F—H

Question 11. Predict the hybridization of each carbon in the molecule of organic compound given below. Also indicate the total number of sigma and pi-bonds in this molecule.



$$CH\equiv C-\overset{\overset{O}{\|}}{C}-CH_2-C{\genfrac{}{}{0pt}{}{/\!\!/ O}{\backslash OH}}$$

Solution.

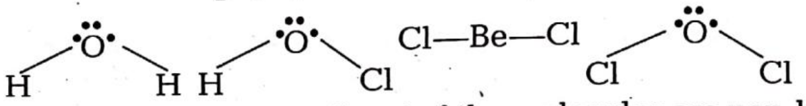


σ-bonds = 11
π-bonds = 4

Question 12. Group the given molecules as linear and non-linear molecules.

$$H_2O, HOCl, BeCl_2, Cl_2O$$

Solution.



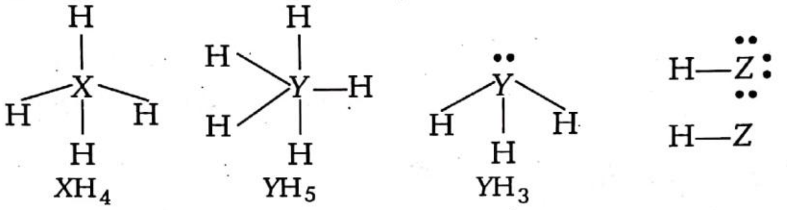
Therefore, only $BeCl_2$ is linear and rest of the molecules are non-linear.

Question 13. (i) X, Y and Z elements have 4, 5 and 7 valence electrons. Draw the structure of XH_4, YH_5, YH_3 and H—Z.

(ii) Which of these compounds has the highest dipole moment?

Solution.

(i)



(ii) Z has seven electrons in its valence shell. It is the most electronegative element .Therefore, HZ will have the highest dipole moment.

Question 14. What is meant by the term average bond enthalpy? Why is there difference in bond enthalpy of O—H bond in ethanol (C_2H_5OH) and water?

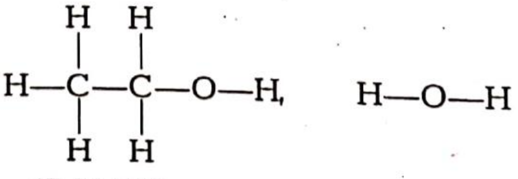
Solution. All the similar bonds in a molecule do not have the same bond enthalpies. For example in H_2O(H—O—H) molecule after the breaking of first O—H bond the second O—H bond undergoes some change because of changed chemical environment. Therefore, in polyatomic molecules the term mean or average bond enthalpy is used. It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken. For example,

$$H_2O(g) \longrightarrow H(g) + OH(g); \qquad \Delta_a H_1^\circ = 502 \text{ kJ mol}^{-1}$$

$$OH(g) \longrightarrow H + O(g); \qquad \Delta_a H_2^\circ = 427 \text{ kJ mol}^{-1}$$

$$\text{Average O—H bond enthalpy} = \frac{502 + 427}{2} = 464.5 \text{ kJ mol}^{-1}$$

The bond enthalpies of O—H bond in C_2H_5OH and H_2O are different because of the different chemical (electronic) environment around oxygen atom.



H_3C—CH_2—O—H, H—O—H

(C_2H_5OH) (H_2O)

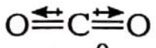
Long Answer Type

Question 15. (i) Discuss the significance/applications of dipole moment.

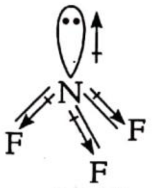
(ii) Represent diagrammatically the bond moments and the resultant dipole moment in CO_2, NF_3 and $CHCl_3$.

Solution.

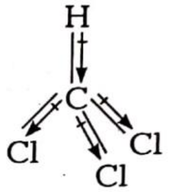
(i) Refer Q. 16 of Exercises.

(ii) 

$\mu = 0$



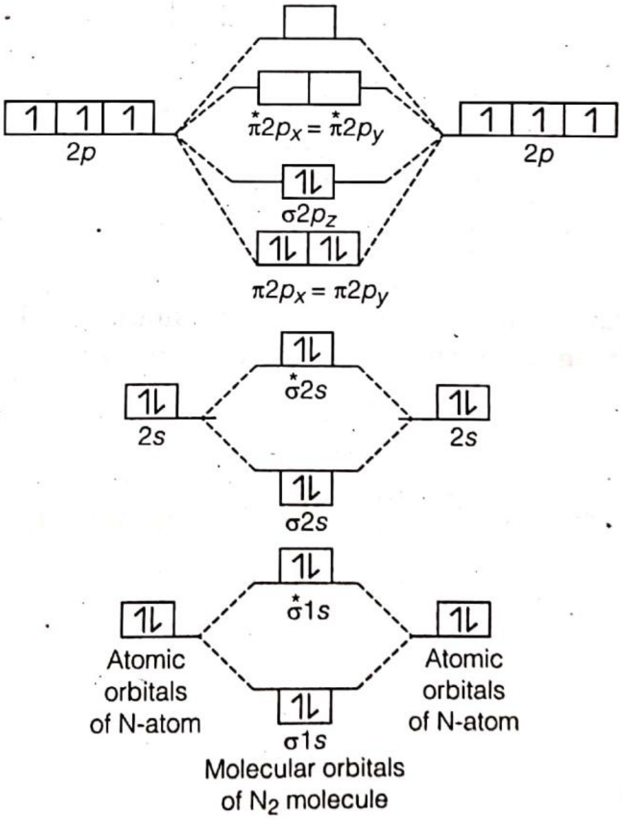
$\mu = 0.24$ D



$\mu = 1.03$ D

Question 16. Use the molecular orbital energy level diagram to show that N_2 would be expected to have a triple bond; F_2, a single bond and Ne_2, no bond.

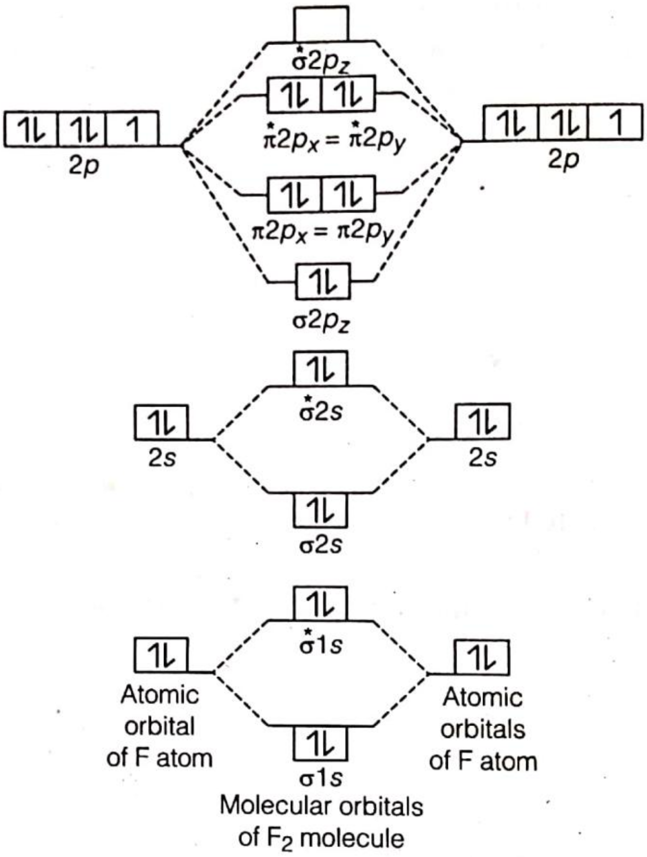
Solution. **Formation of N_2 molecule, $_7N = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$**



$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}(10 - 4) = 3$$

Bond order value of 3 means that N_2 contains a triple bond.

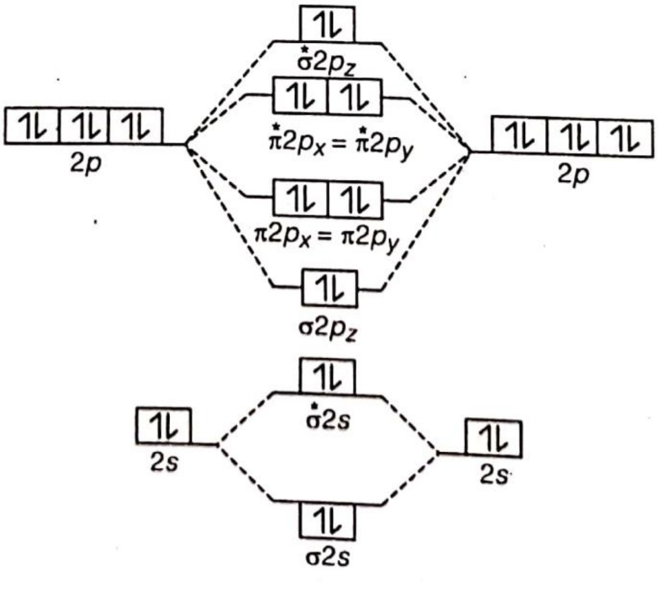
Formation of F_2 molecule, ${}_9F = 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$

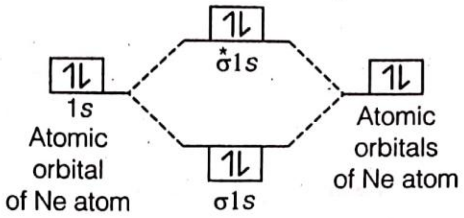


Bond order $= \frac{1}{2}[N_b - N_a] = \frac{1}{2}(10 - 8) = 1$

Bond order value 1 means that F_2 contains single bond.

Formation of Ne_2 molecule ${}_{10}Ne = 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^2$





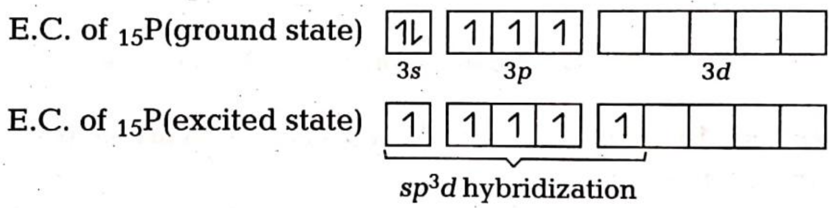
Molecular orbitals of Ne_2 molecule

Bond order $= \frac{1}{2}[N_b - N_a] = \frac{1}{2}(10 - 10) = 0$

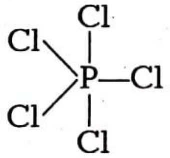
Bond order value zero means that there is no formation of bond between two Ne atoms. Hence, Ne_2 molecule does not exist.

Question 17. **Describe the hybridization in the case of PCl_5 and SF_6. The axial bonds are longer as compared to equatorial bonds in PCl_5 whereas in SF_6 both axial bonds and equatorial bonds have the same bond length. Explain.**

Solution. **Formation of PCl_5**



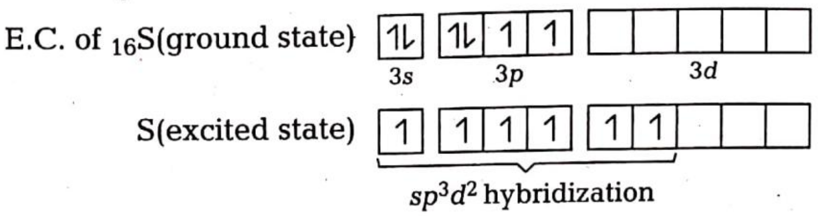
In PCl_5, phosphorus is sp^3d hybridized to produce a set of five sp^3d hybrid orbitals which are directed towards the five corners of a trigonal bipyramidal. These five sp^3d hybrid orbitals overlap with singly occupied p-orbitals of Cl atoms to form five P—Cl sigma bonds.



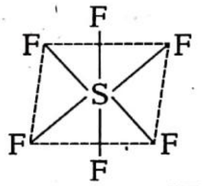
(Trigonal bipyramidal)
PCl_5

Three P—Cl bonds lie in one plane and make an angle of 120° with each other. These bonds are called equatorial bonds. The remaining two P—Cl bonds one lying above and other lying below the plane make an angle of 90° with the equatorial plane. These bonds are called axial bonds. Axial bonds are slightly longer than equatorial bonds because axial bond pairs suffer more repulsive interaction from the equatorial bond pairs.

Formation of SF_6



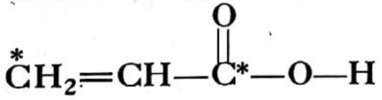
In SF_6, sulphur is sp^3d^2 hybridized to produce a set of six sp^3d^2 hybrid orbitals which are directed towards the six corners of a regular octahedron. These six sp^3d^2 hybrid orbitals overlap with singly occupied orbitals of fluorine atoms to form six S—F sigma bonds. Thus, SF_6 molecule has a regular octahedral geometry and all S—F bonds have same bond length.



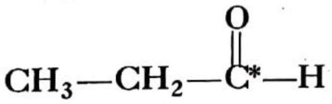
Octahedral geometry of SF_6 molecule.

Question 18. (i) Discuss the concept of hybridization. What are its different types in a carbon atom?

(ii) What is the type of hybridization of carbon atoms marked with star?

(a) 
$\overset{*}{C}H_2{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C^*}{-}O{-}H$

(b) $CH_3{-}\overset{*}{C}H_2{-}OH$

(c) 
$CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C^*}{-}H$

(d) $\overset{*}{C}H_3{-}CH{=}CH{-}CH_3$

(e) $CH_3{-}\overset{*}{C}{\equiv}CH$

Solution. **Hybridization** It can be defined as the process of intermixing of the orbitals of slightly different energy or of same energy to produce entirely new orbitals of equivalent energy, identical shapes and symmetrically disposed in plane. New orbitals formed are called hybrid orbitals.

Only the orbitals of an isolated single atom can undergo hybridization.

The hybrid orbitals generated are equal in number to that of the pure atomic orbitals which mix up.

Hybrid orbitals do not make π, pi-bonds. If there are π-bonds, equal number of atomic orbitals must be left unhybridised for π-bonding.

Like atomic orbitals, hybrid orbitals cannot have more than two electrons of opposite spins.

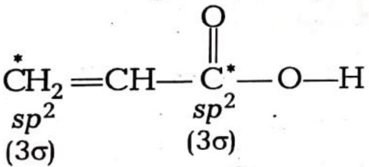
Types of hybridization in carbon atoms

(i) (a) Diagonal or *sp*-hybridization—All compounds of carbon containing $C{\equiv}C$ triple bond like ethyne (C_2H_2).

(b) Trigonal or sp^2-hybridization—All compounds of carbon containing $C{=}C$ (double bond) like ethene (C_2H_4).

(c) Tetrahedral or sp^3-hybridization—All compounds of carbon containing C—C single bonds only like ethane (C_2H_6).

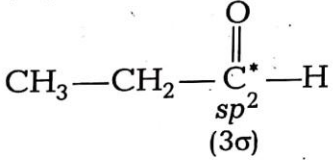
(ii) (a)



$$\underset{\substack{sp^2\\(3\sigma)}}{\overset{*}{C}H_2}=CH-\underset{\substack{sp^2\\(3\sigma)}}{\overset{\overset{O}{\|}}{C^*}}-O-H$$

(b) $CH_3\underset{\substack{sp^3\\(4\sigma)}}{\overset{*}{C}H_2}OH$

(c)



$$CH_3-CH_2-\underset{\substack{sp^2\\(3\sigma)}}{\overset{\overset{O}{\|}}{C^*}}-H$$

(d) $\underset{\substack{sp^3\\(4\sigma)}}{\overset{*}{C}H_3}-CH{=}CH-CH_3$

(e) $CH_3-\underset{\substack{sp\\(2\sigma)}}{\overset{*}{C}}{\equiv}CH$

Chapter 5

States of Matter

Important Results

1. At STP/NTP, $T = 273.15\,K$; $p = 1\,atm = 101.325\,kPa$; $V = 22.4\,L\,mol^{-1}$.
2. $1\,Pa = 1\,Nm^{-2}$; $1\,atm = 1.01325 \times 10^5\,Nm^{-2}$ (SI)
3. **Boyle's law** $p_1V_1 = p_2V_2$ (at constant T)

   Charles' law $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ (at constant p)
4. **Gay Lussac's law** $p \propto T$ (at constant V).
5. **Avogadro law** $V \propto n$ (at constant T and p)
6. **Ideal gas equation** $pV = nRT$ or $p = \frac{nRT}{V} = \frac{mRT}{MV} = \frac{dRT}{M}$

   where, d = density in gL^{-1}.
7. **Dalton's law of partial pressure**

   $$p_{total} = p_1 + p_2 + p_3 + \ldots..$$

   where, p_1, p_2 ..... are partial pressures.

   $$p_1 = p_{total} \cdot x_1 \text{ etc. } x_1 = \text{mole fraction.}$$

   $$p_{dry\ gas} = p_{total} - \text{aqueous tension}$$
8. **Graham's law**

   $$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} = \frac{V_1t_2}{V_2t_1}$$

   where, d = vapour density; V_1 = volume of gas-1 diffusing in time t_1 and V_2 = volume of gas-2 diffusing in time t_2.

   If two gases diffuse under different pressures then

   $$\frac{r_1}{r_2} = \frac{p_1}{p_2}\sqrt{\frac{M_2}{M_1}} = \frac{p_1}{p_2}\sqrt{\frac{d_2}{d_1}}$$
9. **Kinetic theory**

   $$pV = \frac{1}{3}Mu^2 \qquad \text{where, } u = \text{root mean square velocity}$$

   $$KE = \frac{3}{2}n\,RT$$

   $$\text{Average KE} = \frac{3}{2}\frac{RT}{N_0} = \frac{3}{2}KT \text{ where, } K = \frac{R}{N_0} = \text{Boltzmann's constant}$$

10. **van der Waals' equation**

$$\left[p + \frac{n^2a}{V^2}\right][V - nb] = nRT$$

where, a and b are van der Waals' constants.

11. $\frac{n^2a}{V^2}$ = internal pressure and is called pressure correction. It is a measure of force of attraction between gas molecules. Gases which can be liquified easily have high value of a.

nb is the volume correction due to finite size of the molecules; b is called excluded volume. ($b \approx 4V$, where, V is the volume of a spherical molecule).

12. Units of $a = \text{atm L}^2 \text{ mol}^{-2}$; units of $b = \text{L mol}^{-1}$.

13. **Compressibility factor** $Z = \frac{pV}{nRT}$

$Z = 1$ for ideal gas, $Z \neq 1$ for real (non-ideal) gas.

14. **Boyle's temperature** is a temperature at which real gas obeys the gas laws over a wide range of pressure.

15. **Surface tension** (γ) Surface tension of a liquid is defined as the work (energy) required to expand the surface of a liquid by unit area.

$$\gamma = \text{force/length; dyne/cm, Nm}^{-1}$$

16. Surface tension is due to intermolecular attractive forces. It decreases with rise in temperature.

17. **Viscosity** It is defined as the resistance in flow of liquid and decreases with increase in temperature.

$$F = \eta A \frac{du}{dz};$$

where, η is the proportionality constant and is called coefficient of viscosity, F = force required to maintain the flow of layers, A = area of contact and du/dz is velocity gradient.

It is expressed in poise (dynes/cm^2 s)

$$1 \text{ poise} = 10^{-1} \text{kg m}^{-1}\text{s}^{-1}$$

Exercises

Question 1. **What will be the minimum pressure required to compress 500 dm^3 of air at 1 bar to 200 dm^3 at 30° C?**

Apply Boyle's law, $p_1V_1 = p_2V_2$ to calculate p_2 as temperature remains constant.

Solution. $p_1 = 1\text{ bar}, p_2 = ?, V_1 = 500\text{ dm}^3, V_2 = 200\text{ dm}^3$

$$p_1V_1 = p_2V_2$$

$$p_2 = \frac{p_1V_1}{V_2} = \frac{1\text{ bar} \times 500\text{ dm}^3}{200\text{ dm}^3} = 2.5\text{ bar}$$

Question 2. A vessel of 120 mL capacity contains a certain amount of gas at 35° C and 1.2 bar pressure. The gas is transferred to another vessel of volume 180 mL at 35°C. What would be its pressure ?

Apply Boyle's law, $p_1V_1 = p_2V_2$ to calculate p_2 as temperature remains constant.

Solution. $p_1 = 1.2\text{ bar}, p_2 = ?, V_1 = 120\text{ mL}, V_2 = 180\text{ mL}$

From Boyle's law, $p_1V_1 = p_2V_2$

$$p_2 = \frac{p_1V_1}{V_2} = \frac{1.2\text{ bar} \times 120\text{ mL}}{180\text{ mL}}$$

$$p_2 = 0.8\text{ bar.}$$

Question 3. Using the equation of state $pV = nRT$; show that at a given temperature, density of a gas is proportional to gas pressure p.

Solution.

$$pV = nRT$$

$$pV = \frac{m}{M}RT \qquad \left\{n = \frac{m}{M} = \frac{\text{Mass of gas }(g)}{\text{Molar mass of gas}}\right\}$$

or

$$p = \frac{mRT}{VM} \text{ or } p = \frac{dRT}{M} \qquad \left(\because \text{ Density, } d = \frac{m}{V}\right)$$

or

$$d = \frac{pM}{RT}; \text{ If } T = \text{constant, } d \propto p$$

Question 4. At 0° C, the density of a certain oxide of a gas at 2 bar is same as that of dinitrogen at 5 bar. What is the molecular mass of the oxide ?

Molar mass is related to the density by the formula, $d = \frac{Mp}{RT}$. Since, d is same and R and T are constant, $M_1p_1 = M_2p_2$. As M_2p_2 and p_1 are given, calculate M_1 (mass of gaseous oxide).

Solution. Density, $d = \frac{Mp}{RT}$

When T and d are same and R is constant,
then p_1M_1 (gaseous oxide) $= p_2M_2$ (nitrogen).

$$2\text{ bar} \times M_1 = 5\text{ bar} \times 28\text{ u} \qquad (\text{Molar mass of } N_2 = 28\text{ u})$$

Molecular mass of unknown oxide, $M_1 = \frac{5\text{ bar} \times 28}{2\text{ bar}} = 70\text{ u}$

Question 5. **Pressure of 1 g of an ideal gas *A* at 27°C is found to be 2 bar. When 2 g of another ideal gas *B* is introduced in the same flask at same temperature, the pressure becomes 3 bar. Find a relationship between their molecular masses.**

(i) In order to compare the molecular masses of gas A and B, write two equations for A and B gases by using the relation, $pV = nRT$.

(ii) Find the moles of A and B from their masses and pressure of B by subtracting pressure of A from total pressure.

(iii) Now, find the relation between M_A and M_B by comparing the two equations.

Solution. $pV = nRT$

For A gas, $p_A V = n_A RT$ ...(i)

Similarly for B gas, $p_B V = n_B RT$ ...(ii)

Number of moles of A gas; $n_A = \frac{1}{M_A}$ (M_A = molar mass of gas A)

Number of moles of B gas; $n_B = \frac{2}{M_B}$ (M_B = molar mass of gas B)

Pressure of gas A, $p_A = 2$ bar

Total pressure, $p_{\text{total}} = p_A + p_B = 3$ bar

Pressure of gas B, $p_B = p_{\text{total}} - p_A = 3 - 2 = 1$ bar

V, R and T are same for both the gases.

Hence, from Eqs. (i) and (ii),

$$\frac{p_A}{p_B} = \frac{n_A}{n_B} = \frac{1 \times M_B}{M_A \times 2}$$

$$\frac{M_B}{M_A} = \frac{2p_A}{p_B}$$

$$\frac{M_B}{M_A} = \frac{2 \times 2}{1}$$

$$M_B = 4\,M_A$$

Question 6. **The drain cleaner, Drainex contains small bits of aluminium which react with caustic soda to produce dihydrogen. What volume of dihydrogen at 20°C and 1 bar will be released when 0.15 g of aluminium reacts ?**

(i) To find the volume of dihydrogen, by using the equation $pV = nRT$, number of moles of hydrogen produced are required, so write a balanced chemical reaction between Al and NaOH and find the number of moles of H_2 produced from 0.15 g Al.

(ii) Find V_{H_2} by using the relation $pV = nRT$.

Solution.

$$\begin{array}{lcl} 2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaAlO}_2 + & & 3\text{H}_2 \\ & & 3 \text{ mol} \\ 2 \times 27 \text{ g} & & \\ 0.15 \text{ g} & & \frac{0.15 \times 3}{2 \times 27} = 0.00833 \text{ mol} \end{array}$$

$$pV = nRT$$

$$V_{H_2} = \frac{0.00833\text{ mol} \times 0.0821\text{ dm}^3\text{ atm K}^{-1}\text{ mol}^{-1} \times 293\text{ K}}{1 \times 0.987\text{ atm}}$$

(1 bar = 0.987 atm)

$$V_{H_2} = 0.203\text{ dm}^3$$

$$V_{H_2} = 203\text{ mL}$$

Note *Temperature must be in kelvin. If it is given in* °C, *convert it into* K.

Question 7. **What will be the pressure exerted by a mixture of 3.2 g of methane and 4.4 g of carbon dioxide contained in a 9 dm^3 flask at 27°C ?**

Solution. Moles of CH_4,

$$n_{CH_4} = \frac{\text{Mass of } CH_4}{\text{Molar mass of } CH_4} \qquad [\text{Molar mass of } CH_4 = 12 + 4 \times 1 = 16]$$

$$= \frac{3.2}{16} = 0.2\text{ mol}$$

Similarly, moles of CO_2,

$$n_{CO_2} = \frac{4.4}{44} = 0.1\text{ mol} \qquad [\text{Molar mass of } CO_2 = 12 + 2 \times 16 = 44]$$

Total moles = 0.2 + 0.1 = 0.3 mol

$$pV = nRT$$

$$\text{Pressure, } p = \frac{nRT}{V}$$

$$= \frac{0.3\text{ mol} \times 0.0821\text{ dm}^3\text{ atm K}^{-1}\text{ mol}^{-1} \times 300\text{ K}}{9\text{ dm}^3} = 0.821\text{ atm}$$

In terms of SI units :

$$\text{Pressure, } p = \frac{0.3\text{ mol} \times 8.314\text{ Pa m}^3\text{ K}^{-1}\text{ mol}^{-1} \times 300}{9 \times 10^{-3}\text{ m}^3}$$

$$p = 8.314 \times 10^4\text{ Pa}$$

Question 8. **What will be the pressure of the gaseous mixture when 0.5 L of H_2 at 0.8 bar and 2.0 L of dioxygen at 0.7 bar are introduced in a 1L vessel at 27° C ?**

(i) Calculate the total number of moles of H_2 and O_2 by using the relation $pV = nRT$.

(ii) Calculate the total pressure exerted by mixture of gas again by applying $pV = nRT$.

Solution. $pV = nRT$

$$\text{Moles of } H_2,\ n_{H_2} = \frac{pV}{RT} = \frac{0.8 \times 0.5}{RT} = \frac{0.40}{RT}$$

$$\text{Similarly, moles of } O_2,\ n_{O_2} = \frac{pV}{RT} = \frac{0.7 \times 2}{RT} = \frac{1.4}{RT}$$

$$\text{Total number of moles} = \frac{0.40}{RT} + \frac{1.4}{RT} = \frac{1.8}{RT}$$

$$\text{Total pressure, } p_{\text{total}} = \frac{nRT}{V} = \frac{1.8 \times RT}{RT \times 1} = 1.8 \text{ atm}$$

Question 9. Density of a gas is found to be 5.46 g/dm^3 at 27°C and 2 bar pressure. What will be its density at STP ?

STP mean at 1 bar and 273 K so compare the density at 27°C and 2 bar with the density at STP by using the relation $d = \frac{pM}{RT}$.

Solution. Density, $d = \frac{pM}{RT}$

For same gas at different temperatures and pressures :

$$\frac{d_2}{d_1} = \frac{p_2 T_1}{p_1 T_2}$$

$$d_1 = 5.46 \text{ g / dm}^3, d_2 = ?$$

$$T_1 = 27^\circ\text{C} = 300\text{K}, T_2 = 0^\circ\text{C} = 273 \text{ K}$$

$$p_1 = 2 \text{ bar}, p_2 = 1 \text{ bar}$$

$$d_2 = \frac{p_2 T_1 d_1}{p_1 T_2} = \frac{1 \times 300 \times 5.46}{2 \times 273} = 3 \text{ g dm}^{-3}$$

Question 10. 34.05 mL of phosphorus vapour weighs 0.0625 g at 546°C and 0.1 bar pressure. What is the molar mass of phosphorus ?

Solution. $pV = nRT$

$$pV = \frac{mRT}{M}$$

(m = mass of phosphorus (g) and

M = molar mass of phosphorus)

$$M = \frac{mRT}{pV}$$

$$M = \frac{0.0625 \text{ g} \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 819 \text{ K}}{0.1 \times 0.987 \text{ atm} \times 0.03405 \text{ L}}$$

$$M = 1250.4 \text{ g mol}^{-1}$$

Question 11. A student forgot to add the reaction mixture to the round bottomed flask at 27°C but instead he/she placed the flask on the flame. After a lapse of time, he realized his mistake, and using a pyrometer he found the temperature of the flask was 477°C. What fraction of air would have been expelled out ?

Apply Charles' law as pressure remains constant, $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ to find a relation between V_1 and V_2 and then calculate the fraction of air expelled by using the formula,

$$\text{Fraction of air expelled} = \frac{\text{Volume expelled}}{\text{Total volume}}$$

Solution. Suppose volume of the air in flask = $V\,\text{cm}^3$ at 27° C = 300 K

$$V_1 = V\,\text{cm}^3,\quad V_2 = ?,\ T_1 = 300\,\text{K},\ T_2 = 750\,\text{K}$$

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

$$\frac{V}{300} = \frac{V_2}{750} \text{ or } 300\,V_2 = 750\,V$$

$$V_2 = 2.5\,V \qquad \text{(final volume)}$$

Volume expelled = $2.5\,V - V = 1.5\,V$

$$\text{Fraction of air expelled} = \frac{1.5\,V}{2.5\,V} = 0.6$$

Alternatively, using $pV = nRT$

$$n \propto \frac{1}{T}$$

$$\frac{n_2}{n_1} = \frac{T_1}{T_2} = \frac{300}{750}$$

$$\frac{n_2}{n_1} = 0.4$$

$\therefore$ Fraction of air expelled = 0.6

Question 12. Calculate the temperature of 4.0 mole of a gas occupying 5 dm^3 at 3.32 bar. ($R = 0.083$ bar $\text{dm}^3\ \text{K}^{-1}\ \text{mol}^{-1}$).

Solution. Apply ideal gas equation, $pV = nRT$

Pressure, $p = 3.32$ bar

Volume, $V = 5\,\text{dm}^3$

Number of moles, $n = 4$ mol

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

Temperature, $T = ?$

$$T = \frac{pV}{Rn} = \frac{3.32\ \text{bar} \times 5\ \text{dm}^3}{0.083\ \text{bar dm}^3\ \text{K}^{-1}\ \text{mol}^{-1} \times 4\ \text{mol}}$$

$$T = 50\ \text{K}$$

Question 13. Calculate the number of electrons present in 1.4 g of dinitrogen gas.

(i) Convert the given mass into mole with the help of the formula,

$$\text{Moles} = \frac{\text{Mass}}{\text{Molecular mass}}$$

(ii) 1 mol = 6.022×10^{23} molecule

Solution. $n_{N_2} = \dfrac{1.4}{28} = 0.05$ mol

$\because$ 1 mol = 6.022×10^{23} molecules

$0{\cdot}05$ mol = $0.05 \times 6.022 \times 10^{23} = 0.3011 \times 10^{23}$ molecules

1 molecule of N_2 contains = 14 electrons

$\therefore$ 0.3011×10^{23} molecules will contain

$$= 0.3011 \times 10^{23} \times 14 = 4.2154 \times 10^{23} \text{ electrons}$$

Question 14. **How much time would it take to distribute one Avogadro number of wheat grains if 10^{10} grains are distributed each second ?**

(i) 1 $N_A = 6.022 \times 10^{23}$ where, N_A = Avogadro's number.

(ii) Convert time into yr.

Solution. Time required $= \dfrac{\text{Total grains}}{\text{Grains distributed}}$

$$= \frac{6.022 \times 10^{23}}{10^{10}} = 6.022 \times 10^{13} \text{ s}$$

$$= \frac{6.022 \times 10^{13}}{365 \times 24 \times 60 \times 60} = 1.909 \times 10^{6} \text{ yr}$$

Question 15. **Calculate the total pressure in a mixture of 8g of dioxygen and 4 g of dihydrogen confined in a vessel of 1 dm^3 at 27°C.**
$R = 0.083$ bar dm^3 K^{-1} mol^{-1}.

To calculate the total pressure exerted by a mixture of gases first find total number of moles of gas and then apply the relation, $pV = nRT$.

Solution. Moles of O_2, $n_{O_2} = \dfrac{\text{Mass}}{\text{Mol. wt.}} = \dfrac{8}{32} = 0.25$ mol

[mol. wt. of $O_2 = 16 + 16 = 32$]

Moles of H_2, $n_{H_2} = \dfrac{4}{2} = 2.0$ mol [mol. wt. of $H_2 = 1 + 1 = 2$]

Total number of moles = 0.25 + 2.0 = 2.25 mol

$p = ?;\ n = 2.25 \text{ mol};\ V = 1\,\text{dm}^3;\ R = 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$

$T = 27^\circ\text{C} = 300\text{ K}$

$pV = nRT$

Pressure, $$p = \frac{nRT}{V} = \frac{2.25 \text{ mol} \times 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{1\,\text{dm}^3}$$

$p = 56.025$ bar

Question 16. **Pay load is defined as the difference between the mass of displaced air and the mass of the balloon. Calculate the pay load when a balloon of radius 10 m, mass 100 kg is filled with helium at 1.66 bar at 27° C. (Density of air = 1.2 kg m^{-3} and $R = 0.083$ bar dm^3 K^{-1} mol^{-1}).**

(i) To calculate the pay load, mass of displaced air, and mass of balloon with He are required, so calculate mass of air displaced by using the formula,

Mass of air displaced = $V \times d$

and V = volume of air displaced = volume of balloon = $\dfrac{4}{3}\pi r^3$.

$\therefore$ Mass of air displaced = $\dfrac{4}{3}\pi r^3 \cdot d$

(ii) Then, calculate the mass of helium filled in the balloon by using the relation, $pV = \frac{m}{M} RT$ and use the relation,

Pay load = Mass of displaced air–Mass of balloon with He (to calculate pay load.)

Solution. Radius, $R_{\text{balloon}} = 10\,\text{m}$

$$V_{\text{balloon}} = \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (10)^3 = 4190.476\ \text{m}^3.$$

$$V_{\text{balloon}} = V_{\text{displaced air (by balloon)}}$$

$\therefore$ Mass of displaced air = $V_{\text{displaced air}} \times$ density of air

$$m_{\text{displaced air}} = 4190.476\ \text{m}^3 \times 1.2\ \text{kg m}^{-3}$$

$$m = 5028.57\ \text{kg}$$

Mass of He filled in balloon, $m_{\text{He}} = \frac{pVM}{RT}$ $\left(pV = \frac{mRT}{M}\right)$

$$m_{\text{He}} = \frac{1.66\ \text{bar} \times 4190.476 \times 10^3\ \text{dm}^3 \times 4 \times 10^{-3}\ \text{kg mol}^{-1}}{0.083\ \text{bar dm}^3\ \text{K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}$$

$$m_{\text{He}} = 1117.46\ \text{kg}$$

Total mass of filled balloon, m_{balloon}

= mass of balloon + mass of He filled in the balloon

$m_{\text{balloon}} = 100\ \text{kg} + 1117.46\ \text{kg} = 1217.46\ \text{kg}$

Pay load = mass of displaced air – mass of balloon

= 5028.57 kg – 1217.46 kg = 3811.11 kg

Question 17. **Calculate the volume occupied by 8.8 g of CO_2 at 31.1°C and 1 bar pressure. $R = 0.083\ \text{bar LK}^{-1}\ \text{mol}^{-1}$.**

Solution. $pV = nRT$

$$pV = \frac{m}{M} RT$$

$p = 1\ \text{bar}$, $V = ?$, $m = 8.8\ \text{g}$

$M = 44\ \text{g mol}^{-1}$ (CO_2)

$R = 0.083\ \text{bar LK}^{-1}\ \text{mol}^{-1}$ and $T = 304.1\ \text{K}$

Volume occupied by 8.8 g of CO_2,

$$V = \frac{mRT}{pM} = \frac{8.8\ \text{g} \times 0.083\ \text{bar LK}^{-1}\ \text{mol}^{-1} \times 304.1\ \text{K}}{1\ \text{bar} \times 44\ \text{g mol}^{-1}}$$

$$V = 5.048\ \text{L}$$

Question 18. **2.9 g of a gas at 95° C occupied the same volume as 0.184 g of dihydrogen at 17° C, at the same pressure. What is the molar mass of the gas?**

(i) Since, two gases are given write two separate equations (for unknown gas and for H_2) by using the relation, $pV = \frac{m}{M} RT$.

(ii) To calculate the molar mass of unknown gas compare both the equations at the same volume and pressure.

Solution. $pV = nRT$

$$pV = \frac{mRT}{M}$$

Unknown gas; $\quad$ H_2 gas

$$p_1V_1 = \frac{m_1RT_1}{M_1}; \quad p_2V_2 = \frac{m_2RT_2}{M_2}$$

$$p_1V_1 = p_2V_2$$

Hence,
$$\frac{m_1RT_1}{M_1} = \frac{m_2RT_2}{M_2}$$

$$\frac{2.9\text{ g} \times R \times 368\text{ K}}{M_1} = \frac{0.184\text{ g} \times R \times 290\text{ K}}{2\text{ g mol}^{-1}}$$

Molar mass of unknown gas, $M_1 = \dfrac{2.9\text{ g} \times 368\text{ K} \times 2\text{ g mol}^{-1}}{0.184\text{ g} \times 290\text{ K}} = 40\text{ g mol}^{-1}$

Question 19. A mixture of dihydrogen and dioxygen at one bar pressure contains 20% by weight of dihydrogen. Calculate the partial pressure of dihydrogen.

(i) To calculate the partial pressure, total pressure and mole fraction of hydrogen is required, so first calculate number of moles of H_2 and O_2 in the given mixture and mole fraction of hydrogen.

(ii) Then, calculate p_{H_2} by using the formula $p_A = p_{\text{total}} \times x_A$.

Solution. A mixture of H_2 and O_2 contains 20% by weight of H_2 means $H_2 = 20\text{ g}$ and $O_2 = 80\text{ g}$

Moles of hydrogen, $n_{H_2} = \dfrac{20}{2} = 10\text{ mol}$

Moles of oxygen, $n_{O_2} = \dfrac{80}{32} = 2.5\text{ mol}$

Mole fraction of hydrogen, $x_{H_2} = \dfrac{n_{H_2}}{n_{H_2} + n_{O_2}} = \dfrac{10}{10 + 2.5} = 0.8$

Partial pressure of H_2, $p_{H_2} = p_{\text{total}} \times x_{H_2}$

$$p_{H_2} = 1\text{ bar} \times 0.8$$

$$p_{H_2} = 0.8\text{ bar.}$$

Question 20. What would be the SI unit for the quantity pV^2T^2/n?

Solution. $\dfrac{pV^2T^2}{n} = \dfrac{(\text{Nm}^{-2})\,(\text{m}^3)^2\,(\text{K})^2}{\text{mol}} = \text{Nm}^4\,\text{K}^2\,\text{mol}^{-1}$

Question 21. In terms of Charles' law explain why – 273°C is the lowest possible temperature?

Solution. According to Charles' law, $V_t = V_0\left[1 + \dfrac{t}{273}\right]$

At $t = -273°\text{C}$, $\quad V_t = V_0\left[1 - \dfrac{273}{273}\right] = 0$

Thus, at – 273°C, volume of a gas becomes equal to zero and below this the volume become negative which is meaningless.

Question 22. Critical temperature for carbon dioxide and methane are 31.1°C and – 81.9°C respectively. Which of these has stronger intermolecular forces and why ?

Solution. Critical temperature is the temperature above which the gas cannot be liquified, how so ever high pressure we may apply. Higher the critical temperature, more easily the gas can be liquified, *i.e.*, stronger are the intermolecular forces. Hence, CO_2 has stronger intermolecular forces than CH_4.

Question 23. Explain the physical significance of van der Waals' parameters.

Solution. a is a measure of magnitude of intermolecular forces of attraction while b is a measure of the effective volume of the gas molecules. Value of a and b depends upon the characteristics of a gas.

Selected NCERT Exemplar Problems

Short Answer Type

Question 1. If 1 g of each of the following gases are taken at STP, which of the gases will occupy (a) greatest volume and (b) smallest volume?

$$CO, H_2O, CH_4, NO$$

Solution. Volume of 1 mole of the gas = 22.4 L at STP

Volume occupied by 28 g CO (1 mol CO) = 22.4 L at STP

$(\because$ Molar mass of CO $= 12 + 16 = 28\text{ g mol}^{-1})$

$\therefore$ Volume occupied by 1 g CO $= \frac{22.4}{28}$ L at STP

Similarly, volume occupied by 1 g $H_2O = \frac{22.4}{18}$ L at STP

$(\because$ Molar mass of $H_2O = (2 \times 1) + 16 = 18\text{ g mol}^{-1})$

Volume occupied by 1 g $CH_4 = \frac{22.4}{16}$ L at STP

$(\because$ Molar mass of $CH_4 = 12 + (4 \times 1) = 16\text{ g mol}^{-1})$

Volume occupied by 1 g NO $= \frac{22.4}{30}$ L at STP

$(\because$ Molar mass of NO $= 14 + 16 = 30\text{ g mol}^{-1})$

Thus, 1 g CH_4 will occupy maximum volume and 1 g of NO will occupy minimum volume at STP.

Question 2. The behaviour of matter in different states is governed by various physical laws. According to you what are the factors that determine the state of matter?

Solution. Temperature, pressure, mass and volume are some factors which determine the state of matter.

Question 3. What will be the molar volume of nitrogen and argon at 273.15 K and 1 atm?

Solution. Every gas has 22.4 L molar volume at 273.15 K and 1atm pressure (STP).

Question 4. A gas that follows Boyle's law, Charles' law and Avogadro's law is called an ideal gas. Under what conditions a real gas would behave ideally?

Solution. At low pressure and high temperature, a real gas behaves as an ideal gas.

Question 5. Two different gases '*A*' and '*B*' are filled in separate containers of equal capacity under the same conditions of temperature and pressure. On increasing the pressure slightly the gas '*A*' liquefies but gas *B* does not liquify even on applying high pressure until it is cooled. Explain this phenomenon.

Solution. A gas cannot be liquified above critical temperature. So, gas '*A*' is below its critical temperature whereas gas '*B*' is above its critical temperature.

Question 6. One of the assumptions of kinetic theory of gases states that "there is no force of attraction between the molecules of a gas." How far is this statement correct? Is it possible to liquefy an ideal gas? Explain.

Solution. This statement is correct only for ideal gases. It is not possible to liquefy an ideal gas because there is no intermolecular forces of attractions between the molecules of an ideal gas.

Question 7. The magnitude of surface tension of liquid depends on the attractive forces between the molecules. Arrange the following in increasing order of surface tension :

water, alcohol (C_2H_5OH) and hexane [$CH_3(CH_2)_4CH_3$)].

Solution. In hexane, there are only London forces between the molecules. These forces are very weak. H-bondng is stronger in H_2O in comparison to C_2H_5OH. Hence, the increasing order of surface tension is

Hexane < alcohol < water

Question 8. Name the energy which arises due to motion of atoms or molecules in a body. How is this energy affected when the temperature is increased?

Solution. The energy which arises due to motion of atoms or molecules in a body is know as thermal energy. It is a measure of average kinetic energy of the particles. It increases with increase in temperature.

Question 9. Name two intermolecular forces that exist between HF molecules in liquid state.

Solution. HF are polar covalent molecules. In liquid state, there are dipole-dipole interactions and H-bonding.

Question 10. Compressibility factor, Z of a gas is given as $Z = \frac{pV}{nRT}$

(i) What is the value of Z for an ideal gas?
(ii) For real gas what will be the effect on value of Z above Boyle's temperature?

Solution.

(i) For ideal gas, compressibility factor, $Z = 1$.
(ii) Above Boyle's temperature, real gases show positive deviation.
So, $Z > 1$

Question 11. For real gases the relation between p, V and T is given by van der Waals' equation

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

where, 'a' and 'b' are van der Waals' constants, 'nb' is approximately equal to the total volume of the molecules of a gas. 'a' is the measure of magnitude of intermolecular attraction.

(i) Arrange the following gases in the increasing order of 'b'. Give reason.

$$O_2, CO_2, H_2, He$$

(ii) Arrange the following gases in the decreasing order of magnitude of 'a'. Give reason.

$$CH_4, O_2, H_2$$

Solution.

(i) Molar volume occupied by the gas molecules $\propto$ size of the molecules and van der Waals' constant 'b' represents molar volume of the gas molecules. Hence, value of 'b' increases in the following order

$$H_2 < He < O_2 < CO_2$$

(ii) van der Waals' constant 'a' is the measure of magnitude of intermolecular attraction. The magnitude of intermolecular attractions increases with increase in size of electron cloud in a molecule. Hence, for the given gases magnitude of 'a' decreases in the following order:

$$CH_4 > O_2 > H_2$$

Greater the size of electron cloud, greater is the polarisability of the molecule and greater is the dispersion forces or London forces.

Question 12. The relation between pressure exerted by an ideal gas (p_{ideal}) and observed pressure (p_{real}) is given by the equation,

$$p_{\text{ideal}} = p_{\text{real}} + \frac{an^2}{V^2}$$

(i) If pressure is taken in Nm^{-2}, number of moles in mol and volume in m^3, calculate the unit of 'a'.

(ii) What will be the unit of 'a' when pressure is in atmosphere and volume in dm^3?

Solution. $p_{\text{ideal}} = p_{\text{real}} + \frac{an^2}{V^2}$.

(i) $a = \frac{pV^2}{n^2}$

If units of $p = \text{Nm}^{-2}$, units of $V = \text{m}^3$, units of $n = \text{mol}$

then, units of $a = \frac{\text{Nm}^{-2}\,(\text{m}^3)^2}{(\text{mol})^2} = \text{Nm}^4\,\text{mol}^{-2}$

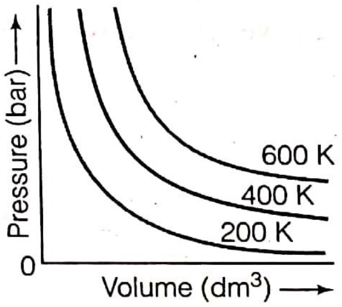
(ii) If units of $p = \text{atm}$, units of $V = \text{dm}^3$, units of $n = \text{mol}$

then, units of $a = \frac{pV^2}{n^2} = \frac{\text{atm.}\,(\text{dm}^3)^2}{(\text{mol})^2} = \text{atm dm}^6\,\text{mol}^{-2}$

Question 13. Explain the effect of increasing the temperature of a liquid, on intermolecular forces operating between its particles. What will happen to the viscosity of a liquid if its temperature is increased?

Solution. As the temperature of a liquid increases, kinetic energy of the molecules increases which can overcome intermolecular forces. So, the liquid can flow more easily, this results in decrease in viscosity of the liquid.

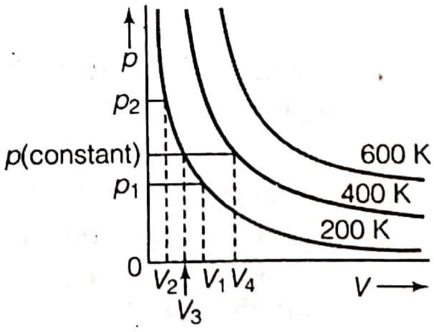
Question 14. The variation of pressure with volume of the gas at different temperatures can be graphically represented as shown in figure. On the basis of this graph answer the following questions:



(i) How will the volume of a gas change if its pressure is increased at constant temperature?

(ii) At a constant pressure, how will the volume of a gas change if the temperature is increased from 200 K to 400 K?

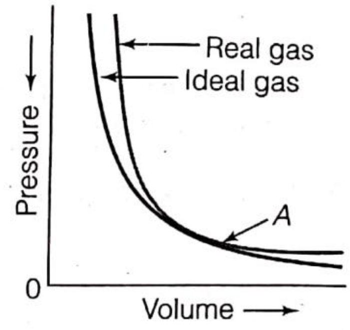
Solution.



(i) The volume of a gas will decrease if the pressure on the gas is increased keeping the temperature constant. For example at 200 K when pressure increases from p_1 to p_2, volume of the gas decreases, $V_2 < V_1$.

(ii) On increasing temperature, the volume of a gas will increase if pressure is kept constant. At constant p when we increase the temperature from 200 K to 400 K, the volume of the gas increases, $V_4 > V_3$.

Question 15. Pressure *versus* volume graph for a real gas and an ideal gas are shown in figure. Answer the following questions on the basis of this graph.



(i) Interpret the behaviour of real gas with respect to ideal gas at low pressure.
(ii) Interpret the behaviour of real gas with respect to ideal gas at high pressure.
(iii) Mark the pressure and volume by drawing a line at the point where real gas behaves as an ideal gas.

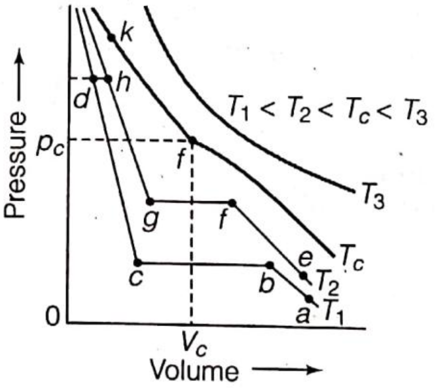
Solution.

(i) At low pressure, the real gas shows very small deviation from ideal behaviour because the two curves almost coincide at low pressure.
(ii) At high pressure, the real gas show large deviations from ideal behaviour as the curves are far apart.
(iii) At point 'A', both the curves intersect each other. At this point real gas behaves as an ideal gas. p_1 and V_1 are the pressure and volume which corresponds to this point A.

Long Answer Type

Question 16. Isotherms of carbon dioxide at various temperatures are represented in figure.

Answer the following questions based on this figure.



(i) In which state will CO_2 exist between the points a and b at temperature T_1?
(ii) At what point will CO_2 start liquefying when temperature is T_1?
(iii) At what point will CO_2 be completely liquefied when temperature is T_2?
(iv) Will condensation take place when the temperature is T_3?
(v) What portion of the isotherm at T_1 represent liquid and gaseous CO_2 at equilibrium?

Solution.

(i) Gaseous state

(ii) At point *b*, the plot becomes linear, this shows the phase transition, *i.e.*, liquification of CO_2 starts and at point *c*, it gets completely liquified.

(iii) Similarly, at temperature T_2, g is the point at which CO_2 will be completely liquified.

(iv) Condensation will not take place at T_3 temperature because $T_3 > T_c$ (critical temperature).

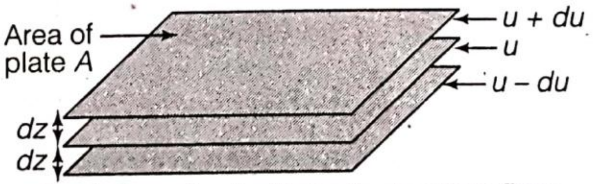
(v) Between *b* and *c*, liquid and gaseous CO_2 are in equilibrium.

Question 17. **Why does sharp glass edge become smooth on heating it up to its melting point in a flame? Explain which property of liquids is responsible for this phenomenon?**

Solution. Sharp glass edges are heated to make them smooth. Because on heating glass melts and the surface of the liquid tends to take the rounded shape at the edges which has minimum surface area. This is called fire polishing of glass.

Question 18. **Explain the term 'Laminar flow'. Is the velocity of molecules same in all the layers in laminar flow? Explain your answer.**

Solution. When a liquid flows over a fixed surface, the layer of molecules in the immediate contact of surface is stationary. The velocity of the upper layers increases as the distance of layers from the fixed layer increases. This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called laminar flow. In laminar flow, the velocity of molecules is not same in all the layers because every layer offers some resistance or friction to the layer immediately below it.



Gradation of velocity in the laminar flow

Chapter 6

Thermodynamics

Important Results

1. A part of the universe which is under investigation is called system and everything else in the universe except system is called surroundings.
2. In an open system, there is exchange of energy and matter between system and surrounding. In a closed system, there is no exchange of matter, but exchange of energy between system and surrounding. In an isolated system, there is no exchange of energy or matter between the system and the surrounding.
3. The state of a system is described by its measurable properties such as T, V, p etc., of the system. These properties of the system are called state variables.
4. A physical quantity is said to be a state function if its value depends only upon the initial state and final state of the system and does not depend upon the path by which this state has been attained. p, T, V, internal energy (U), enthalpy (H), entropy (S) and free energy (G) etc., are some examples of state functions.
5. **Thermodynamic processes**—Isothermal process is carried out at constant temperature, isobaric process is carried out at constant pressure, isochoric process is carried out at constant volume and in adiabatic process, there is no exchange of heat between system and surroundings.
6. Heat absorbed by the system = + ve, heat lost by the system = –ve.

   Work done on the system = +ve and work done by the system = –ve

   Mechanical work, $W = -p_{ex}\,\Delta V$; where, ΔV is the change in volume of the system by the application of external pressure.
7. Internal energy, U is the energy associated with every substance, depending on the chemical nature, temperature, pressure and volume. It is a state function.
8. First law of thermodynamics is also called law of conservation of energy.

$$\Delta U = q + W$$

For reversible change under constant temperature, $\Delta U = 0$

$$W_{max} = q = p\Delta V = 2.303\ nRT \log \frac{V_2}{V_1}$$

For isochoric process, $\Delta V = 0, p\Delta V = 0, \Delta U = q$
For adiabatic change, $q = 0, \Delta U = W_{ad}$

9. The thermodynamic quantity $U + pV$ is called the heat content or enthalpy of the system. Enthalpy change of a system is equal to the heat absorbed or evolved by the system at constant pressure.

$$\Delta H = \Delta U + p\Delta V$$
$$\Delta H = \Delta U + \Delta n_g RT \quad (\Delta n_g = n_{\text{products}} - n_{\text{reactants}})$$

10. Heat capacity of a system is defined as the amount of heat required to raise the temperature of the system through 1° C.

Heat capacity of the system, $C = \frac{q}{\Delta T}$ (where, q is the heat supplied to a system and ΔT rise in temperature).

11. Specific heat capacity or specific heat c, of a substance is defined as the amount of heat required to raise the temperature of 1 g of the substance through 1° C.

$$q = mc\Delta T \text{ or } q = C\,\Delta T$$

12. Molar heat capacity of a substance is defined as the amount of heat required to raise the temperature of one mole of the substance through 1° C.

$$C_m = \frac{C}{n}$$

13. Relationship between C_p and C_V for an ideal gas

For 1 mole of an ideal gas, $C_p - C_V = R$
For n mole of an ideal gas, $C_p - C_V = nR$

14. Enthalpy of reaction, $\Delta_r H$ = sum of enthalpies of products – sum of enthalpies of reactants $= \Sigma a_i H$ (products) $- \Sigma b_i H$ (reactants)

(where, Σ (sigma) represents summation, a_i and b_i represents coefficients of the products and reactants.)

15. Standard enthalpies of formation,

$\Delta_r H^\circ$ = (sum of the standard enthalpies of formation of products) – (sum of the standard enthalpies of formation of reactants)

$$\Delta_r H^\circ = \Sigma a_i \Delta_f H^\circ \text{ (products)} - \Sigma b_i \Delta_f H^\circ \text{ (reactants)}$$

16. **Hess's law of constant heat summation :** If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature.

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 \ldots\ldots$$

17. The standard enthalpy of reaction, $\Delta_r H^\circ$ is related to bond enthalpies of the reactants and products in gas phase reaction as:

$\Delta_r H^\circ = \Sigma$ bond enthalpies (reactants) $- \Sigma$ bond enthalpies (products)

18. Entropy is a measure of disorder or randomness. For a spontaneous change, total entropy change is positive. Therefore, for an isolated

system, $\Delta U = 0$, $\Delta S > 0$. Change in entropy, $\Delta S = \frac{q_{\text{rev}}}{T}$ for a reversible process. $\frac{q_{\text{rev}}}{T}$ is independent of path.

19. Gibbs energy, G is related to entropy and enthalpy changes of the system by the equation;

$$\Delta_r G = \Delta_r H - T\Delta_r S$$

For a spontaneous change, $\Delta G_{\text{sys}} < 0$ and at equilibrium, $\Delta G_{\text{sys}} = 0$.

20. Relation between Gibbs energy and equilibrium constant,

$$\Delta_r G^\circ = -RT \ln K$$

$$\Delta_r G^\circ = -2.303\, RT \log K_c$$

$\Delta_r G^\circ$ can be calculated from $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$

Exercises

Question 1. Choose the correct answer. 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.

Solution. (ii) A thermodynamic state function is a quantity whose value is independent of path. Its value depends only upon the state of the system.

Question 2. For the process to occur under adiabatic conditions, the correct condition is

(i) $\Delta T = 0$ (ii) $\Delta p = 0$ (iii) $q = 0$ (iv) $w = 0$

Solution. (iii) For the process to occur under adiabatic conditions, $q = 0$, *i.e.*, heat cannot flow from system to surroundings or *vice-versa*.

Question 3. The enthalpies of all the elements in their standard states are

(i) unity (ii) zero (iii) < 0 (iv) different for each element.

Solution. (ii) The enthalpies of all elements in their standard states are taken as zero. The standard state of an elementary substance means the most stable form of that substance at 298 K temperature and 1 bar pressure.

Question 4. ΔU° of combustion of methane is $-X$ kJ mol^{-1}. The value of ΔH° is

(i) $= \Delta U^\circ$ (ii) $> \Delta U^\circ$ (iii) $< \Delta U^\circ$ (iv) $= 0$

(i) ΔH° (enthalpy change) is related to ΔU° (internal energy change) by the following relation;

$$\Delta H^\circ = \Delta U^\circ + \Delta n_g RT$$

So, first find Δn_g by writing a balanced chemical equation for the combustion of methane and using the formula Δn_g = total moles of gaseous products – total moles of gaseous reactants.

(ii) If $\Delta n_g = 0$, then $\Delta H = \Delta U$; If $\Delta n_g > 0$, then $\Delta H > \Delta U$: similarly if $\Delta n_g < 0$ then $\Delta H < \Delta U$

Solution. $CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(l)$

$$\Delta n_g = (n_p - n_r) = 1 - 3 = -2$$
$$\Delta H^\circ = \Delta U^\circ + \Delta n_g RT$$
$$\Delta H^\circ = -X - 2RT$$

Hence, $\Delta H^\circ < \Delta U^\circ$ [option (iii) is correct]

Question 5. **The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, $-890.3\ \text{kJ mol}^{-1}$, $-393.5\ \text{kJ mol}^{-1}$ and $-285.8\ \text{kJ mol}^{-1}$ respectively. Enthalpy of formation of $CH_4(g)$ will be**

(i) $-74.8\ \text{kJ mol}^{-1}$ **(ii) $-52.27\ \text{kJ mol}^{-1}$**
(iii) $+74.8\ \text{kJ mol}^{-1}$ **(iv) $+52.26\ \text{kJ mol}^{-1}$**

(i) Write the required equation for the formation of 1 mole of methane.

(ii) Apply Hess's law to calculate $\Delta_f H^\circ$ for methane.

Solution. Required equation for the formation of 1 mole of methane, CH_4 is given by :

$$C(s) + 2H_2\,(g) \longrightarrow CH_4(g); \qquad \Delta_f H^\circ = ?$$

Given, the enthalpy of combustion of 1 mole of methane is

(i) $CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(l)$; $\Delta H = -890.3\ \text{kJ mol}^{-1}$

the enthalpy of combustion of 1 mole of graphite is

(ii) $C(s) + O_2\,(g) \longrightarrow CO_2\,(g)$; $\Delta H = -393.5\ \text{kJ mol}^{-1}$

The enthalpy of combustion of 1 mole of dihydrogen is

(iii) $H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l)$; $\Delta H = -285.8\ \text{kJ mol}^{-1}$

Multiplying Eq. (iii) by 2, we get

(iv) $2H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O\,(l)$; $\Delta H = -571.6\ \text{kJ mol}^{-1}$

Adding Eqs. (ii) and (iv), we get

(v) $C(s) + 2H_2(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$; $\Delta H = -965.1\ \text{kJ mol}^{-1}$

Reversing Eqs. (i),

(vi) $CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g)$; $\Delta H = +890.3\ \text{kJ mol}^{-1}$

Adding Eqs. (v) and (vi), we get required equation

$$C(s) + 2H_2(g) \longrightarrow CH_4(g); \qquad \Delta H = -74.8\ \text{kJ mol}^{-1}$$

Hence, option (i) is correct.

Question 6. A reaction, $A + B \longrightarrow C + D + q$ 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.

For a reaction to be spontaneous, ΔG must be negative.

Solution. (iv) $\Delta G = \Delta H - T\Delta S$

For the given reaction, $\Delta H = -\text{ve}$ as it is exothermic, $\Delta S = +\text{ve}$ then $\Delta G = -\text{ve}$. So, the reaction will be spontaneous at all temperatures.

Question 7. In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process ?

Solution. Given, $q = +\ 701$ J (heat is absorbed, hence q is positive.)

$W = -\ 394$ J (work is done by the system, hence W is negative.)

By first law of thermodynamics;

Internal energy change, $\Delta U = q + W$

$$= +\ 701\text{ J} + (-\ 394\text{ J}) = +\ 307\text{ J}.$$

Hence, internal energy of the system increases by 307 J.

Question 8. The reaction of cyanamide, $NH_2CN\,(s)$, with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be $-\ 742.7\text{ kJ mol}^{-1}$ at 298 K. Calculate the enthalpy change for the reaction at 298 K ($R = 8.314 \times 10^{-3}\text{ kJ K}^{-1}\text{ mol}^{-1}$)

$$NH_2CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(l)$$

(i) Enthalpy change ΔH is related to internal energy ΔU as $\Delta H = \Delta U + \Delta n_g RT$

(ii) We have ΔU, R and T, so first calculate Δn_g and then ΔH from all other values.

Solution. $NH_2CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(l)$

Difference of moles of gaseous products and reactants,

$$\Delta n_g = n_p - n_r = 2 - \frac{3}{2} = \frac{1}{2} = 0.5\text{ mol}$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Delta H = -\ 742.7\text{ kJ mol}^{-1} + (0.5\text{ mol} \times 8.314 \times 10^{-3}\text{ kJ mol}^{-1} \times 298\text{ K})$$

$$\Delta H = (-\ 742.7\text{ kJ} + 1238.786 \times 10^{-3}\text{ kJ})\ \text{mol}^{-1}$$

$$= -\ 741.46\text{ kJ mol}^{-1}$$

Question 9. 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 $24\text{ J mol}^{-1}\text{ K}^{-1}$. Molar mass of Al = 27 g mol^{-1}.

Solution. Given, mass of Al $= 60.0\text{g}$

Molar mass of Al $= 27\text{ g mol}^{-1}$

Molar heat capacity, $C = 24\text{ J mol}^{-1}\text{ K}^{-1}$

$$\Delta T = 55°\text{C} - 35°\text{C} = 20°\text{C or } 20\text{K}$$

$$\text{Heat, } q = n\,.\,C.\,\Delta T$$

$$q = \frac{60}{27} \times 24\text{ J mol}^{-1}\text{ K}^{-1} \times 20\text{K} \qquad \left(n = \frac{60}{27}\text{ mol}\right)$$

$$= 1066.66\text{ J} = 1.067\text{ kJ}$$

Question 10. Calculate the enthalpy change on freezing of 1.0 mole of water at 10.0° C to ice at – 10.0° C. $\Delta_{\text{fus}}H = 6.03\text{ kJ mol}^{-1}$ at 0° C.

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

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

Conversion of 1 mole of water at 10°C to ice at –10°C involves the following steps:

1 mol $H_2O(l)$ at 10°C $\longrightarrow$ 1 mol $H_2O(l)$ at 0°C $\Delta H_1 = C_pH_2O(l) \times \Delta T$

1 mol $H_2O(l)$ at 0°C $\longrightarrow$ 1 mol $H_2O(s)$ at 0°C $\Delta H_2 = \Delta H_{\text{freezing}}$

1 mol $H_2O(s)$ at 0°C $\longrightarrow$ 1 mol $H_2O(s)$ at 10°C $\Delta H_3 = C_pH_2O(s) \times \Delta T$;

$\Delta T = 10\text{K}$ and we know that according to Hess's law, total enthalpy change, $\Delta H = H_1 + H_2 + H_3$ so first calculate ΔH_1, ΔH_2, ΔH_3 and then ΔH.

Solution. Enthalpy change for the conversion of 1 mole liquid water at 10°C into 1 mole liquid water at 0°C,

$$\Delta H_1 = C_P\,\text{H}_2\text{O}(l) \times \Delta T$$

$$= -75.3\text{ J mol}^{-1}\text{ K}^{-1} \times 10\text{K} = -753\text{ J mol}^{-1}$$

Enthalpy of fusion,

$$\Delta H_2 = \Delta H_{\text{freezing}} = -\Delta H_{\text{fusion}} = -6.03\text{ kJ mol}^{-1}$$

Enthalpy change for the conversion of 1 mole of ice at 0°C to 1 mole of ice at 10°C,

$$\Delta H_3 = C_p\text{H}_2\text{O}(s) \times \Delta T = -36.8\text{ J mol}^{-1}\text{ K}^{-1} \times 10\text{K}$$

$$= -368\text{ J mol}^{-1}$$

$$\Delta H_{\text{total}} = -(0.753 + 6\cdot 03 + 0.368)\text{ kJ mol}^{-1} = -7.151\text{ kJ mol}^{-1}$$

Note *Heat is evolved in the process of cooling (freezing) so each step will have a negative sign with* ΔH.

Question 11. Enthalpy of combustion of carbon to CO_2 is – 393.5 kJ mol^{-1}. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas. (Molar mass of $CO_2 = 44\text{ g mol}^{-1}$).

Solution. The reaction for the combustion of carbon into CO_2 is

$$\text{C}(s) + \text{O}_2(g) \longrightarrow \underset{44\text{ g}}{\text{CO}_2(g)};\ \Delta H = -393.5\text{ kJ mol}^{-1}$$

Heat released in the formation of 44 g CO_2 = 393.5 kJ

∴ Heat released in the formation of 35.2 g CO_2

$$= \frac{393.5 \text{ kJ} \times 35.2\text{g}}{44\text{g}} = 314.8 \text{ kJ}.$$

Question 12. Enthalpies of formation of $CO(g)$, $CO_2(g)$, $N_2O(g)$ and $N_2O_4(g)$ are $-110, -393$, 81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H$ for the reaction,

$$N_2O_4(g) + 3CO(g) \longrightarrow N_2O(g) + 3CO_2(g)$$

Solution. Heat of reaction, $\Delta_r H^\circ = \Sigma \Delta_f H^\circ_{\text{products}} - \Sigma \Delta_f H^\circ_{\text{reactants}}$

$$= [\Delta_f H^\circ (N_2O) + 3\Delta_f H^\circ (CO_2)] - [\Delta_f H^\circ (N_2O_4) + 3\Delta_f H^\circ (CO)]$$
$$= [81 + (3 \times -393)] - [9.7 + (3 \times -110)] \text{ kJ}$$
$$= -777.7 \text{ kJ} \approx -778 \text{ kJ}.$$

Question 13. Given, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$;

$$\Delta_r H^\circ = -92.4 \text{ kJ mol}^{-1}$$

What is the standard enthalpy of formation of NH_3 gas ?

Standard enthalpy of formation means heat released in the formation of 1 mole of substance.

Solution. Given, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ $\Delta_r H^\circ = -92.4$ kJ mol^{-1}

Chemical reaction for the enthalpy of formation of $NH_3(g)$ is as follows :

$$\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \longrightarrow NH_3(g)$$

Therefore, $$\Delta_f H^\circ = \frac{-92.4}{2} = -46.2 \text{ kJ mol}^{-1}$$

Question 14. Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the following data :

$$CH_3OH(l) + \frac{3}{2} O_2(g) \longrightarrow CO_2(g) + 2H_2O(l); \ \Delta_r H^\circ = -726 \text{ kJ mol}^{-1}$$
$$C_{(\text{graphite})} + O_2(g) \longrightarrow CO_2(g); \qquad \Delta_c H^\circ = -393 \text{ kJ mol}^{-1}$$
$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l); \qquad \Delta_f H^\circ = -286 \text{ kJ mol}^{-1}$$

Firstly write the required chemical equation for the formation of 1 mole of methanol (l) and then calculate $\Delta_f H^\circ$ for the formation of methanol by adding all the equation in such a way so that it give the required equation (*i.e.*, apply Hess's Law)

Solution. Required reaction for the formation of methanol is as follows

$$C(s) + 2H_2(g) + \frac{1}{2} O_2(g) \longrightarrow CH_3OH(l); \qquad \Delta_f H^\circ = ?$$

Given, enthalpy for the combustion of methanol;

(i) $CH_3OH(l) + \frac{3}{2} O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$; $\Delta_r H^\circ = -726$ kJ mol^{-1}

Enthalpy for the formation of 1 mole of $CO_2(g)$;

(ii) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta_f H^\circ = -393$ kJ mol^{-1}

Enthalpy for the formation of 2 moles of $H_2O(l)$;

(iii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$; $\quad \Delta_f H^\circ = -286 \text{ kJ mol}^{-1}$

Multiplying Eq. (iii) by 2 [because 2 moles $H_2O(l)$ are formed in equation (i)] we get,

(iv) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$; $\quad \Delta_f H^\circ = -572 \text{ kJ mol}^{-1}$

Summing up the Eqs. (ii) and (iv), we get

(v) $C(s) + 2H_2(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$; $\quad \Delta_f H^\circ = -965 \text{ kJ mol}^{-1}$

Reversing Eq. (i), we get

(vi) $CO_2(g) + 2H_2O(l) \longrightarrow CH_3OH(l) + \frac{3}{2}O_2(g)$; $\quad \Delta_f H^\circ = +726 \text{ kJ mol}^{-1}$

Adding Eqs. (v) and (vi) we get required equation :

$C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(l)$; $\quad \Delta_f H^\circ = -239 \text{ kJ mol}^{-1}$

Question 15. **Calculate the enthalpy change for the process :**

$$CCl_4(g) \longrightarrow C(g) + 4Cl(g)$$

and calculate the bond enthalpy of C — Cl in $CCl_4(g)$.

$$\Delta_{vap}H^\circ(CCl_4) = 30.5 \text{ kJ mol}^{-1}.$$
$$\Delta_f H^\circ(CCl_4) = -135.5 \text{ kJ mol}^{-1}.$$
$$\Delta_a H^\circ(C) = 715.0 \text{ kJ mol}^{-1},$$

where, $\Delta_a H^\circ$ is enthalpy of atomisation, $\Delta_a H^\circ(Cl_2) = 242 \text{ kJ mol}^{-1}$.

Solution. Given,

(i) $CCl_4(l) \longrightarrow CCl_4(g)$; $\quad \Delta_{vap}H^\circ = +30.5 \text{ kJ mol}^{-1}$

(ii) $C(s) + 2Cl_2(g) \longrightarrow CCl_4(l)$; $\quad \Delta_f H^\circ = -135.5 \text{ kJ mol}^{-1}$

(iii) $C(s) \longrightarrow C(g)$; $\quad \Delta_a H^\circ = 715.0 \text{ kJ mol}^{-1}$

(iv) $Cl_2(g) \longrightarrow 2Cl(g)$; $\quad \Delta_a H^\circ = 242 \text{ kJ mol}^{-1}$

Multiplying Eq. (iv) by 2, we get

(v) $2Cl_2(g) \longrightarrow 4Cl(g)$; $\quad \Delta_a H^\circ = 484.0 \text{ kJ mol}^{-1}$

Adding Eqs. (iii) and (v), we get

(vi) $C(s) + 2Cl_2(g) \longrightarrow C(g) + 4Cl(g)$; $\quad \Delta H = 1199 \text{ kJ mol}^{-1}$

Reversing Eqs. (i) and (ii), we get

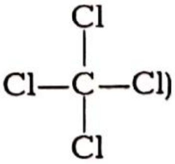
(vii) $CCl_4(g) \longrightarrow CCl_4(l)$; $\quad \Delta H = -30.5 \text{ kJ mol}^{-1}$

(viii) $CCl_4(l) \longrightarrow C(s) + 2Cl_2(g)$; $\quad \Delta H = +135.5 \text{ kJ mol}^{-1}$

Adding Eqs. (vi), (vii) and (viii), we get

$CCl_4(g) \longrightarrow C(g) + 4Cl(g)$; $\quad \Delta H = 1304 \text{ kJ mol}^{-1}$

Bond enthalpy of C — Cl bond in $CCl_4 = \frac{1304}{4} = 326 \text{ kJ mol}^{-1}$.

(∵ There are four C — Cl bonds in CCl_4,  $Cl{-}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}{-}Cl$)

Question 16. For an isolated system, $\Delta U = 0$, what will be ΔS ?

Solution. For an isolated system, $\Delta U = 0$ and for a spontaneous process, total entropy change must be positive. For example, consider the diffusion of two gases A and B into each other in a closed container which is isolated from the surroundings. The two gases A and B are separated by a movable partition. When partition is removed, the gases begin to diffuse into each other and the system becomes more disordered. It shows that $\Delta S > 0$ and $\Delta U = 0$ for this process.

Moreover, $$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{\Delta H}{T} = \frac{\Delta U + p\Delta V}{T} = \frac{p\Delta V}{T} \qquad (\because \Delta U = 0)$$

i.e., $T\Delta S$ or $\Delta S > 0$

Question 17. For the reaction at 298 K,

$$2A + B \longrightarrow C$$

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

At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range ?

For a reaction to be spontaneous, $\Delta G \leq 0$. So, calculate the temperature at which $\Delta G = 0$ by using the relation, $\Delta G = \Delta H - T\Delta S$

Solution. Given, $\Delta H = 400 \text{ kJ mol}^{-1}$, $\Delta S = 0.2 \text{ kJ K}^{-1}\text{mol}^{-1}$,

Gibbs free energy, $\Delta G = \Delta H - T\Delta S$

$$0 = 400 \text{ kJ mol}^{-1} - T \times 0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\text{Temperature, } T = \frac{400 \text{ kJ mol}^{-1}}{0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}} = 2000 \text{ K}$$

Therefore, above 2000K, the reaction will become spontaneous.

Note *If $\Delta G < 0$, the process is spontaneous and if $\Delta G > 0$, the process is non-spontaneous.*

Question 18. For the reaction, $2\text{Cl}(g) \longrightarrow \text{Cl}_2(g)$, what are the signs of ΔH and ΔS ?

Solution. In the given reaction, a molecule of Cl_2 is formed from its two gaseous atoms and the energy is released with the formation of bond. Hence, ΔH is –ve. In this reaction, randomness (entropy) also decreases because 2 mol atoms of Cl have more randomness than one mole molecules of chlorine. Hence, ΔS is –ve.

Question 19. For the reaction,

$$2A(g) + B(g) \longrightarrow 2D(g); \quad \Delta U^\circ = -10.5 \text{ kJ and } \Delta S^\circ = -44.1 \text{ JK}^{-1}.$$

Calculate ΔG° for the reaction, and predict whether the reaction may occur spontaneously.

$(R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}, T = 298 \text{ K})$

(i) We know that $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ so first find ΔH° by using the formula, $\Delta H^\circ = \Delta U^\circ + \Delta n_g RT$ and then ΔG° by putting the values of ΔH°, T and ΔS°.

(ii) For a spontaneous reaction $\Delta G^\circ \leq 0$

Solution. $2A(g) + B(g) \longrightarrow 2D(g); \Delta n_g = n_p - n_r = 2 - 3 = -1$

$$\Delta H^\circ = \Delta U^\circ + \Delta n_g RT$$
$$\Delta H^\circ = -10.5 \text{ kJ} + (-1 \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298\text{K})$$
$$\Delta H^\circ = -10.5 + (-2.477) \text{ kJ mol}^{-1}$$
$$\Delta H^\circ = -12.977 \text{ kJ mol}^{-1}$$
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$\Delta G^\circ = -12.977 \text{ kJ mol}^{-1} - (298 \text{ K} \times -44.1 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})$$
$$\Delta G^\circ = -12.977 \text{ kJ mol}^{-1} + 13.14 \text{ kJ mol}^{-1} = +0.165 \text{ kJ mol}^{-1}$$

The reaction will not occur spontaneously because ΔG° is positive.

Question 20. **The equilibrium constant for a reaction is 10. What will be the value of ΔG°? $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}, T = 300 \text{ K}$.**

Solution. $\Delta G^\circ = -2.303 \, RT \log K_c$

Given, $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}, T = 300 \text{ K}, K_c = 10$

$$\Delta G^\circ = -2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times \log 10 \qquad (\log 10 = 1)$$
$$= -5744.14 \text{ J mol}^{-1}$$

Question 21. **Comment on the thermodynamic stability of NO(g), given**

$$\frac{1}{2}\text{N}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{NO}(g); \quad \Delta_r H^\circ = 90 \text{ kJ mol}^{-1}$$
$$\text{NO}(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{NO}_2(g); \Delta_r H^\circ = -74 \text{ kJ mol}^{-1}$$

Solution. NO(g) is unstable because formation of NO is endothermic (energy is absorbed), but $NO_2(g)$ is formed because its formation is exothermic (energy is released). Therefore, unstable NO(g) converts into stable $NO_2(g)$.

Question 22. **Calculate the entropy change in surroundings when 1.00 mole of $H_2O(l)$ is formed under standard conditions.**

$$\Delta_f H^\circ = -286 \text{ kJ mol}^{-1}.$$

Solution. Enthalpy change for the formation of 1 mole of $H_2O(l)$,

$$\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l); \qquad \Delta_f H^\circ = -286 \text{ kJ mol}^{-1}$$

Energy released in the above reaction, is absorbed by the surroundings. It means $q_{\text{surr}} = +286 \text{ kJ mol}^{-1}$.

$$\Delta S = \frac{q_{\text{surr}}}{T} = \frac{+286 \text{ kJ mol}^{-1}}{298 \text{ K}}$$
$$= 0.9597 \text{ kJ K}^{-1}\text{mol}^{-1} = 959.7 \text{ JK}^{-1}\text{mol}^{-1}$$

Selected NCERT Exemplar Problems

Short Answer Type

Question 1. 18.0 g water completely vaporises at 100°C and 1 bar pressure and the enthalpy change in the process is 40.79 kJ mol^{-1}. What will be the enthalpy change for vaporising two moles of water under the same conditions? What is the standard enthalpy of vaporisation for water?

Solution. 18.0 g $H_2O = 1$ mol H_2O

Enthalpy change for vaporising 1 mole of $H_2O = 40.79$ kJ

∴ Enthalpy change for vaporising 2 moles of $H_2O = 2 \times 40.79$ kJ

$$= 81.58 \text{ kJ}$$

Standard enthalpy of vaporisation at 100°C and 1 bar pressure,

$$\Delta_{vap}H^\circ = +40.79 \text{ kJ mol}^{-1}$$

Question 2. Standard molar enthalpy of formation, $\Delta_f H^\circ$ is just a special case of enthalpy of reaction, $\Delta_r H^\circ$. Is the $\Delta_r H^\circ$ for the following reaction same as $\Delta_f H^\circ$? Give reason for your answer.

$$CaO(s) + CO_2(g) \longrightarrow CaCO_3(s); \quad \Delta_f H^\circ = -178.3 \text{ kJ mol}^{-1}$$

Solution. The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states (reference states) is called standard molar enthalpy of formation, $\Delta_f H^\circ$.

$$Ca(s) + C(s) + \frac{3}{2}O_2(g) \longrightarrow CaCO_3(s); \ \Delta_f H^\circ$$

This reaction is different from the given reaction.

Hence, $\Delta_r H^\circ \neq \Delta_f H^\circ$

Question 3. The value of $\Delta_f H^\circ$ for NH_3 is – 91.8 kJ mol^{-1}. Calculate the enthalpy change for the following reaction,

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$$

Solution. Given, $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g); \ \Delta_f H^\circ = -91.8 \text{ kJ mol}^{-1}$

($\Delta_f H^\circ$ means enthalpy of formation of 1 mole of NH_3)

∴ Enthalpy change for the formation of 2 moles of NH_3

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g); \ \Delta_r H^\circ = 2 \times -91.8 = -183.6 \text{ kJ mol}^{-1}$$

and for the reverse reaction,

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g); \quad \Delta_r H^\circ = +183.6 \text{ kJ mol}^{-1}$$

Question 4. The enthalpy of atomisation for the reaction, $CH_4(g) \longrightarrow C(g) + 4H(g)$ is 1665 kJ mol^{-1}. What is the bond energy of C—H bond?

Solution. In CH_4, there are four C—H bonds. The enthalpy of atomisation of 1 mole of CH_4 means dissociation of four moles of C—H bond.

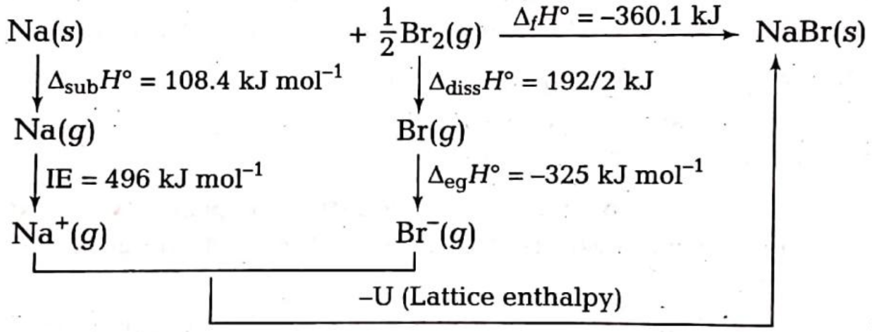
$$\therefore \text{C—H bond energy per mol} = \frac{1665 \text{ kJ}}{4 \text{ mol}} = 416.25 \text{ kJ mol}^{-1}$$

Question 5. Use the following data to calculate $\Delta_{\text{lattice}}H^\circ$ for NaBr.

$\Delta_{\text{sub}}H^\circ$ for sodium metal = 108.4 kJ mol^{-1}
Ionization enthalpy of sodium = 496 kJ mol^{-1}
Electron gain enthalpy of bromine = – 325 kJ mol^{-1}
Bond dissociation enthalpy of bromine = 192 kJ mol^{-1}

$$\Delta_f H^\circ \text{ for NaBr}(s) = -360.1 \text{ kJ mol}^{-1}$$

Solution. Born Haber cycle for the formation of NaBr is as



By applying Hess's law,

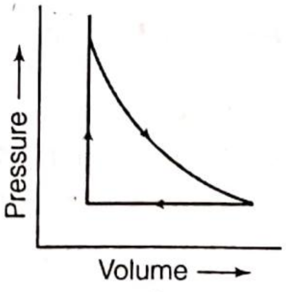
$$\Delta_f H^\circ = \Delta_{\text{sub}}H^\circ + \text{IE} + \Delta_{\text{diss}}H^\circ + \Delta_{\text{eq}}H^\circ + U$$
$$-360.1 = 108.4 + 496 + 96 + (-325) - U$$
$$U = +735.5 \text{ kJ mol}^{-1}$$

Question 6. At 298 K, K_p for the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 0.98. Predict whether the reaction is spontaneous or not.

Solution. $\Delta_r G^\circ = -2.303\, RT \log K_p$

Here $K_p = 0.98$, *i.e.*, $K_p < 1$ therefore, $\Delta_r G^\circ$ is positive. Hence, the reaction is non-spontaneous.

Question 7. A sample of 1.0 mole of a monoatomic ideal gas is taken through a cyclic process of expansion and compression as shown in figure. What will be the value of ΔH for the cycle as a whole?



Solution. The net enthalpy change, ΔH for a cyclic process is zero as enthalpy change is a state function.

Question 8. Which quantity out of $\Delta_r G$ and $\Delta_r G^\circ$ will be zero at equilibrium?

Solution. $\Delta_r G = \Delta_r G^\circ + RT \ln K$

At equilibrium, $0 = \Delta_r G^\circ + RT \ln K$ $(\because \Delta_r G = 0)$

or $\Delta_r G^\circ = -RT \ln K$

$\Delta_r G^\circ = 0$ when $K = 1$

For all other values of K, $\Delta_r G^\circ$ will be non-zero.

Question 9. Predict the change in internal energy for an isolated system at constant volume.

Solution. For isolated system there is no transfer of energy as heat or work, so according to the first law of thermodynamics,

$$\Delta U = q + W$$
$$\Delta U = 0 + 0 = 0$$

Question 10. Expansion of a gas in vacuum is called free-expansion. Calculate the work done and the change in internal energy when 1 L of ideal gas expands isothermally into vacuum until its total volume is 5 L?

Solution. Workdone, $W = -p_{\text{ext}}(V_2 - V_1)$

As $p_{\text{ext}} = 0$, so $W = -0(5-1) = 0$

For isothermal expansion, $\Delta U = 0$ as $\Delta T = 0$

Question 11. Heat capacity (C_p) is an extensive property but specific heat (C) is an intensive property. What will be the relation between C_p and C for 1 mole of water?

Solution. For water, molar heat capacity, $C_p = 18 \times$ specific heat, C

Specific heat, $C = 4.18 \text{ Jg}^{-1}\text{K}^{-1}$ (for water)

Heat capacity, $C_p = 18 \times 4.18 \text{ JK}^{-1} = 75.3 \text{ JK}^{-1}$

Question 12. If the combustion of 1 g of graphite produces 20.7 kJ of heat, what will be molar enthalpy change? Give the significance of sign also.

Solution. Molar enthalpy change for the combustion of graphite, ΔH

= enthalpy of combustion of 1 g graphite × molar mass

$$\Delta H = -20.7 \text{ kJ g}^{-1} \times 12 \text{ g mol}^{-1}$$
$$\Delta H = -2.48 \times 10^2 \text{ kJ mol}^{-1}$$

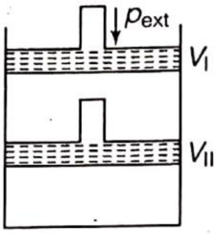
Negative sign in the value of ΔH indicates that the reaction is exothermic.

Question 13. The enthalpy of vaporisation of CCl_4 is 30.5 kJ mol^{-1}. Calculate the heat required for the vaporisation of 284 g of CCl_4 at constant pressure (molar mass of CCl_4 = 154 g mol^{-1})

Solution. 1 mol of CCl_4 = 154 g

$$\Delta_{\text{vap}}H \text{ for } 154 \text{ g } CCl_4 = 30.5 \text{ kJ}$$
$$\therefore \quad \Delta_{\text{vap}}H \text{ for } 284 \text{ g } CCl_4 = \frac{30.5 \times 284}{154} \text{ kJ} = 56.25 \text{ kJ}$$

Question 14. What will be the work done on an ideal gas enclosed in a cylinder, when it is compressed by a constant external pressure, p_{ext} in a single step as shown in figure ? Explain graphically.



Solution. Suppose total volume of the gas is V_i and pressure of the gas inside cylinder is p. After compression by constant external pressure, (p_{ext}) in a single step, final volume of the gas becomes V_f.

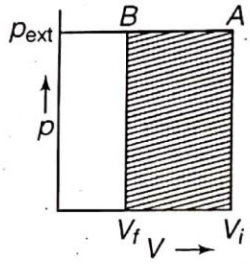
Then, volume change, $\Delta V = (V_f - V_i)$

If W is the work done on the system by movement of the piston, then

$$W = p_{ext}\ (-\Delta V)$$
$$W = -p_{ext}\ (V_f - V_i)$$

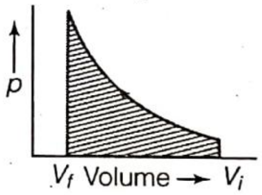
This can be calculated from p-V graph as shown in the side figure. Work done is equal to the shaded area ABV_fV_i.

The negative sign in this expression is required to obtain conventional sign for W, which will be positive, Because in case of compression work is done on the system, so ΔV will be negative.

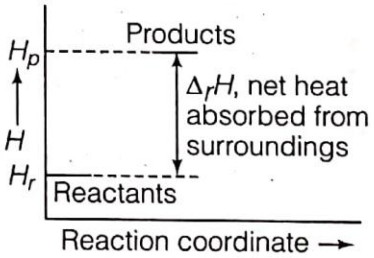


Question 15. How will you calculate the work done on an ideal gas in a compression, when change in pressure is carried out in infinite steps?

Solution. When compression is carried out in infinite steps with change in pressure, it is a reversible process. Work done on the gas is represented by the shaded area.

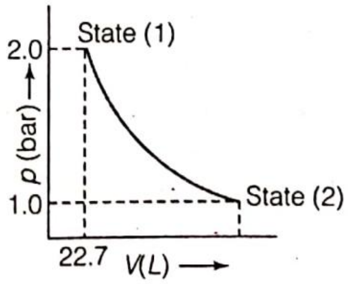


Question 16. Enthalpy diagram for a particular reaction is given in figure. Is it possible to decide spontaneity of a reaction from given diagram. Explain.



Solution. No, enthalpy is one of the contributing factors in deciding spontaneity but it is not the only factor. Another contributory factor, entropy factor has also to be taken into consideration.

Question 17. 1.0 mole of a monoatomic ideal gas is expanded from state (1) to state (2) as shown in figure. Calculate the work done for the expansion of gas from state (1) to state (2) at 298 K.



Solution. The given diagram represents that the process is carried out in infinite steps, hence it is isothermal reversible expansion of the ideal gas from pressure 2.0 atm to 1.0 atm at 298 K.

$$W = -2.303\, nRT \log \frac{p_1}{p_2}$$

$$W = -2.303 \times 1\,\text{mol} \times 8.314\ \text{JK}^{-1}\text{mol}^{-1} \times 298\,\text{K} \log 2 \qquad \left(\because \frac{p_1}{p_2} = \frac{2}{1}\right)$$

$$W = -2.303 \times 1 \times 8.314 \times 298 \times 0.3010\ \text{J}$$

$$W = -1717.46\ \text{J}$$

Long Answer Type

Question 18. **Extensive properties depend on the quantity of matter but intensive properties do not. Explain whether the following properties are extensive or intensive. Mass, internal energy, pressure, heat capacity, molar heat capacity, density, mole fraction, specific heat, temperature and molarity.**

Solution. Extensive properties—mass, internal energy, heat capacity.
Intensive properties—pressure, molar heat capacity, density, mole fraction, specific heat, temperature and molarity.
Ratio of two extensive properties is always intensive.

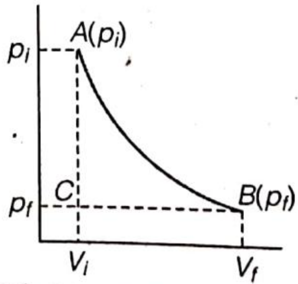
$$\frac{\text{Extensive}}{\text{Extensive}} = \text{Intensive}$$

So, mole fraction and molarity are intensive properties.

Question 19. **Graphically show the total work done in an expansion when the state of an ideal gas is changed reversibly and isothermally from (p_i, V_i) to $(p_f \cdot V_f)$. With the help of a pV plot compare the work done in the above case with that carried out against a constant external pressure p_f.**

Solution.

(i) Reversible work is represented by the combined areas ABC and BCV_iV_f.



(ii) Work against constant pressure, p_f is represented by the area BCV_iV_f
Work (i) > work (ii)

Chapter 7

Equilibrium

Important Results

1. Equilibrium is a dynamic process. It is established in a system when reactants combine to form products at the same rate at which products combine to form reactants.

2. Chemical equilibrium can be approached from either sides. A catalyst can hasten the approach of equilibrium but does not alter the state of equilibrium.

3. Systems can be homogeneous or heterogeneous.

4. For a reaction in equilibrium,

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{(in terms of active masses)}$$

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} \quad \text{(in terms of partial pressures)}$$

5. Partial pressure of solid is taken as unity and in the calculation of partial pressure of solids, their number of moles are not considered. Molar concentration of pure solid or pure liquid is constant.

6. $K_p = K_c\,(RT)^{\Delta n_g}$ and $\Delta n_g = (c + d) - (a + b)$

While calculating Δn_g, take only gaseous species

7. For,

$$A + B \rightleftharpoons C + D; \qquad K_c = K$$

$$C + D \rightleftharpoons A + B; \qquad K_c' = \frac{1}{K}$$

$$2A + 2B \rightleftharpoons 2C + 2D; \qquad K_c'' = K^2$$

$$\frac{A}{2} + \frac{B}{2} \rightleftharpoons \frac{C}{2} + \frac{D}{2}; \qquad K_c''' = \sqrt{K}$$

8. Reaction quotient, Q_c for reversible reaction,

$$A + B \rightleftharpoons C + D; \qquad Q_c = \frac{[C]\,[D]}{[A]\,[B]}$$

Q is taken before equilibrium is attained.

If $Q_c = K_c$ then system is in equilibrium.

If $Q_c > K_c$ then system proceeds in backward side to attain equilibrium.

If $Q_c < K_c$ then system proceeds in forward side to attain equilibrium.

9. Relationship between equilibrium constant (K_c), reaction quotient (Q_c) and Gibbs energy (G),

$$\Delta G = \Delta G^\circ + RT \ln Q_c$$

At equilibrium when $\Delta G = 0$ and $Q_c = K_c$ then, $\Delta G^\circ = -RT \ln K_c$

$$\Delta G^\circ = -2.303\, RT \log K_c$$

10. $\Delta G^\circ = -nFE^\circ_{\text{cell}}$ (where E°_{cell} = standard emf and n is the number of electrons.)

and $E^\circ_{\text{cell}} = \dfrac{2.303RT}{nF} \log K_c$

11. **Le-Chatelier's principle** It states that a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.

Or

If a stress is applied to a reaction mixture at equilibrium, reaction occurs in that direction that relieves the stress.

12. **Acid-Base Theory**
    (i) **Arrhenius concept** Acid ionises in water to give H_3O^+ ion while base ionises to give OH^- ion.
    (ii) **Bronsted-Lowry's protonic concept** Acid is H^+ ion donor and base is H^+ ion acceptor. HCl and Cl^- is a conjugate acid-base pair. If acid is weak, its conjugate base is strong and *vice-versa*.

    A substance that can accept H^+ ion as well as can donate H^+ ion is called amphiprotic.

$$H_3O^+ \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\text{Amphiprotic}}{H_2O} \rightleftharpoons H^+ + OH^-$$

    (iii) **Lewis concept** Lewis acid is an electron pair acceptor, and Lewis base is an electron pair donor. All Lewis bases are Bronsted-Lowry bases and *vice-versa*.

13. Ionic product of water, $K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$ at 298 K.

14. In a mixture of acid and base, resultant is

    (a) acidic mixture if N_1V_1 (acid) > N_2V_2 (base)

$$[H_3O^+] = \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$$

    (b) basic mixture if N_2V_2 (base) > N_1V_1 (acid)

$$[OH^-] = \frac{N_2V_2 - N_1V_1}{V_1 + V_2}$$

(c) neutral mixture if N_1V_1 (acid) = N_2V_2 (base)

$$K_a \cdot K_b = K_w = 1 \times 10^{-14}$$

where, K_a is the ionization constant of acid and K_b is the ionization constant of base.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-;\ K_a \quad (A^- + H_2O \rightleftharpoons HA + OH^-;\ K_b)$$

15. $pK_a + pK_b = pK_w = 14$

$$pH = -\log[H_3O^+]$$

$$pOH = -\log[OH^-]$$

$$pK_a = -\log K_a \text{ and } pK_b = -\log K_b$$

$$pH + pOH = 14 = pK_w$$

16. Acidic solution has $pH < 7$, basic solution has $pH > 7$ and neutral solution has $pH = 7$.

17. For a weak acid by Ostwald dilution law,

$$K_a = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2$$

and for a weak base, $K_b = \dfrac{C\alpha^2}{(1-\alpha)} = C\alpha^2$

$$[H^+] = \sqrt{K_aC},\ pH = \frac{1}{2}[pK_a - \log C]$$

$$[OH^-] = \sqrt{K_bC},\ pOH = \frac{1}{2}[pK_b - \log C]$$

18. Hydrolysis of salts and pH of their solutions

(i) **Salt of strong acid and weak base,** *e.g.*, NH_4Cl, its aqueous solution is acidic due to hydrolysis of cation.

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

Degree of hydrolysis, $h = \sqrt{\dfrac{K_w}{K_bC}}$

Hydrolysis constant, $K_h = \dfrac{K_w}{K_b}$

$$pH = 7 - \frac{pK_b}{2} - \frac{\log C}{2}$$

(ii) **Salt of weak acid and strong base,** *e.g.*, CH_3COONa, its aqueous solution is basic due to anionic hydrolysis.

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

Degree of hydrolysis, $h = \sqrt{\dfrac{K_w}{K_a \cdot C}}$

$$K_h = K_w / K_a$$

$$pH = 7 + \frac{pK_a}{2} + \frac{\log C}{2}$$

(iii) **Salt of weak acid and weak base**, *e.g.*, CH_3COONH_4, its aqueous solution may be neutral or weakly acidic or basic depending upon the nature of acid and base.

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

Degree of hydrolysis, $h = \sqrt{\dfrac{K_w}{K_a \, . \, K_b}}$

$$K_h = \frac{K_w}{K_a \, . \, K_b}$$

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

$$pH = 7 \text{ if } pK_a = pK_b$$
$$pH < 7 \text{ if } pK_a < pK_b$$
$$pH > 7 \text{ if } pK_a > pK_b$$

For amphiprotic anion (as HCO_3^-)

$$pH = \frac{pK_1 + pK_2}{2}$$

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

20. Solubility product of the sparingly soluble salt, A_xB_y with solubility (s mol L^{-1}) in saturated solution,

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

$$K_{sp} = x^x \, . \, y^y \, (s)^{x+y}$$

$$s = (K_{sp} / x^x \cdot y^y)^{1/x+y}$$

21. **Common-ion effect** Ionization of weak electrolyte is decreased in the presence of common-ion.

22. Salt analysis of inorganic mixture depends on common-ion effect and values of solubility products. Solute AB is precipitated if $[A^+][B^-] > K_{sp}$.

Exercises

Question 1. A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.

(a) What is the initial effect of change on vapour pressure ?

(b) How do rates of evaporation and condensation change initially ?

(c) What happens when equilibrium is restored finally and what will be the final vapour pressure ?

Solution. $$\underset{\text{Low pressure}}{A(l)} \longrightarrow \underset{\text{High pressure}}{A(g)}$$

If volume is increased at constant temperature, pressure decreases, since, $p \propto \frac{1}{V}$ at constant temperature.

(a) Decrease in pressure shift the equilibrium in the direction of high pressure *i.e.*, more vapours are formed hence vapour pressure increases.

(b) Rate of evaporation increases and rate of condensation decreases.

(c) When equilibrium is restored finally the rate of evaporation again becomes equal to the rate of condensation and the final vapour pressure becomes equal to the vapour pressure that was before the sudden increase in the volume of the container.

Question 2. **What is K_c for the following equilibrium when the equilibrium concentration of each substance is**

$$[SO_2] = 0.60\text{ M}, [O_2] = 0.82\text{ M and } [SO_3] = 1.90\text{ M ?}$$

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Solution. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Given, $[SO_2] = 0.60\text{ M}$, $[O_2] = 0.82\text{ M}$, $[SO_3] = 1.90\text{ M}$

Equilibrium constant, $$K_c = \frac{[SO_3]^2}{[SO_2]^2 \cdot [O_2]} = \frac{(1.90\text{ M})^2}{(0.60\text{ M})^2\,(0.82\text{ M})}$$
$$= 12.2289\text{ M}^{-1} \approx 12.23\text{ M}^{-1}$$

Question 3. **At a certain temperature and total pressure of 10^5 Pa, iodine vapour contains 40% by volume of I atoms.**

$$I_2(g) \rightleftharpoons 2I(g)$$

Calculate K_p for the equilibrium.

K_p depends upon the partial pressures of reactants and products so find their partial pressures from the percentage given and then, calculate K_p.

Solution. Given, $I_2(g) \rightleftharpoons 2I(g)$

I atoms in iodine vapours = 40% by volume

So, iodine vapours of I_2 molecules = 60% by volume

Partial pressure of iodine atoms, $p_1 = \frac{40}{100} \times 10^5 = 0.40 \times 10^5$ Pa

Similarly, partial pressure of iodine molecules (I_2),

$$p_2 = \frac{60}{100} \times 10^5 = 0.60 \times 10^5\text{ Pa}$$

According to equation,

$$K_p = \frac{p_I^2}{p_{I_2}} = \frac{(0.40 \times 10^5\text{ Pa})^2}{(0.60 \times 10^5\text{ Pa})} = 0.2666 \times 10^5\text{ Pa} \approx 2.67 \times 10^4\text{ Pa}$$

Question 4. Write the expression for the equilibrium constant, K_c for each of the following reactions.

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

(ii) $2Cu(NO_3)_2(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$

(iii) $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$

(iv) $Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$

(v) $I_2(s) + 5F_2 \rightleftharpoons 2IF_5$

K_c shows the ratio of the product of concentrations of the products to the product of concentrations of the reactants, each raised to a power equal to the corresponding stoichiometric coefficient.

Solution. (i) $K_c = \dfrac{[NO]^2\,[Cl_2]}{[NOCl]^2}$

(ii) $K_c = [NO_2]^4[O_2]$

(because molar concentrations of pure solids are constant)

(iii) $K_c = \dfrac{[CH_3COOH(aq)]\,[C_2H_5OH(aq)]}{[CH_3COOC_2H_5(aq)]\,[H_2O(l)]}$

(iv) $K_c = \dfrac{1}{[Fe^{3+}(aq)]\,.\,[OH^-(aq)]^3}$ (because $[Fe(OH)_3(s)] = 1$)

(v) $K_c = \dfrac{[IF_5]^2}{[F_2]^5}$ (because $[I_2(s)] = 1$)

Question 5. Find out the value of K_c for each of the following equilibria from the value of K_p:

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g);\ K_p = 1.8 \times 10^{-2}$ at 500 K

(ii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g);\ K_p = 167$ at 1073 K

(a) First find Δn_g by subtracting the moles of gaseous reactants from the moles of gaseous products for each equation, as K_p and K_c are related as $K_p = K_c\,(RT)^{\Delta n_g}$

(b) Then, calculate K_c in each case.

Solution. (i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g);\ K_p = 1.8 \times 10^{-2}$ at 500 K

$$\Delta n_g = n_p - n_r = 3 - 2 = 1$$

$$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{1.8 \times 10^{-2}}{0.0821 \times 500} = 4.38 \times 10^{-4}$$

(ii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2\,(g);\quad K_p = 167$ at 1073 K

$$\Delta n_g = n_p - n_r = 1$$

$$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{167}{0.0821 \times 1073} = 1.89$$

Question 6. For the following equilibrium, $K_c = 6.3 \times 10^{14}$ at 1000 K

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

Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_c for the reverse reaction ?

Solution. For the reaction, $NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$;

$$K_c = 6.3 \times 10^{14} \text{ at } 1000 \text{ K}$$

$$K_c = \frac{[NO_2][O_2]}{[NO][O_3]} = 6.3 \times 10^{14} \quad \ldots(i)$$

For reverse reaction,

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

$$K_c' = \frac{[NO][O_3]}{[NO_2][O_2]} \quad \ldots(ii)$$

From Eqs. (i) and (ii), we get

$$K_c' = \frac{1}{K_c} = \frac{1}{6.3 \times 10^{14}} = 1.587 \times 10^{-15}$$

Question 7. Explain, why pure liquids and solids can be ignored while writing the equilibrium constant expression ?

Solution. Molar concentration of a pure solid or liquid (if in excess) is constant (*i.e.*, independent of the amount present) . That's why pure liquids and solids can be ignored while writing the equilibrium constant expression.

Question 8. Reaction between N_2 and O_2 takes place as follows :

$$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$$

If a mixture of 0.482 mol N_2 and 0.933 mol O_2 is placed in a 10 L reaction vessel and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$, determine the composition of equilibrium mixture.

(i) Find the equilibrium concentrations of reactants and products in the given equation by assuming $2x$ mol of N_2 and x mol of O_2 are disappeared and $2x$ mol of N_2O are appeared.

(ii) Find the value of x to determine the concentration of reaction mixture.

Solution.	$2N_2(g)$ +	$O_2(g)$ $\rightleftharpoons$	$2N_2O(g)$
Initial conc.	0.482	0.933	0
Equilibrium conc.	$(0.482 - 2x)$	$(0.933 - x)$	$2x$
Active mass	$\left(\frac{0.482 - 2x}{10}\right)$	$\left(\frac{0 \cdot 933 - x}{10}\right)$	$\left(\frac{2x}{10}\right)$

$$K_c = 2.0 \times 10^{-37}$$

K_c is very-very small, which means negligible amounts of N_2 and O_2 react.

$$[N_2]_{eq} = \frac{0.482 - 2x}{10} = \frac{0.482}{10} = 0.0482$$

Similarly, $$[O_2]_{eq} = \frac{0.933 - x}{10} = \frac{0.933}{10} = 0.0933$$

$$K_c = \frac{[N_2O]^2}{[N_2]^2[O_2]}$$

$$K_c = 2.0 \times 10^{-37} = \frac{[4x^2/100]}{(0.0482)^2(0.0933)}$$

$$x^2 = 10{\cdot}837 \times 10^{-40} \quad \text{or} \quad x = 3.292 \times 10^{-20}$$

$$[N_2O] = \frac{2x}{10} = \frac{2 \times 3.292 \times 10^{-20}}{10} = 6.58 \times 10^{-21}\ \text{mol L}^{-1}$$

Question 9. **Nitric oxide reacts with Br_2 and gives nitrosyl bromide as per reaction given below :**

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$$

When 0.087 mole of NO and 0.0437 mole of Br_2 are mixed in a closed container at constant temperature, 0.0518 mole of NOBr is obtained at equilibrium. Calculate the equilibrium amount of NO and Br_2.

Find the value of x as in the previous *Q.* and then, substitute the value of x to calculate the equilibrium concentration of NO and Br_2.

Solution.	$2NO$	+	Br_2	$\longrightarrow$	$2NOBr$
Initial conc.	0.087		0.0437		0
Equilibrium conc.	(0.087 − 2x)		(0·0437 − x)		2x

Given, $2x = 0.0518$ = moles of NOBr formed

$$x = 0.0259 \text{ mol}$$

Moles of NO at equilibrium $= (0.087 - 2x)$

$$= 0.087 - 0.0518 = 0.0352 \text{ mol}$$

Moles of Br_2 at equilibrium $= (0.0437 - x)$

$$= 0.0437 - 0.0259 = 0.0178 \text{ mol}$$

Question 10. **At 450 K, $K_p = 2.0 \times 10^{10}$/bar for the given reaction at equilibrium,**

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

What is K_c at this temperature?

K_p and K_c are related as $K_p = K_c(RT)^{\Delta n_g}$ so calculate Δn_g by subtracting moles of gaseous reactants from the moles of gaseous products and then, calculate K_c.

Solution. $$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$$K_p = K_c(RT)^{\Delta n_g}$$

$$\Delta n_g = 2 - 3 = -1$$

$K_p = 2.0 \times 10^{10}\ \text{bar}^{-1}$, $R = 0.0831\ \text{L bar K}^{-1}\text{mol}^{-1}$ and $T = 450\ \text{K}$

$$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{K_p}{(RT)^{-1}} \qquad (\because \Delta n_g = -1)$$

$$K_c = K_p \times RT = 2.0 \times 10^{10}\ \text{bar}^{-1} \times 0.0831\ \text{L bar K}^{-1}\ \text{mol}^{-1} \times 450\ \text{K}$$

$$K_c = 7.479 \times 10^{11}\text{L mol}^{-1}$$

Question 11. A sample of HI(g) is placed in flask at a pressure of 0.2 atm. At equilibrium, the partial pressure of HI(g) is 0.04 atm. What is K_p for the given equilibrium ?

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

Solution. $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

Initial pressure	0.2 atm	0	0
Equili. pressure	0.04 atm	0.08 atm	0.08 atm

(Decrease in pressure of HI = 0.2 – 0.04 = 0.16 atm; so equilibrium pressure of H_2 is $\frac{0.16}{2} = 0.08$ atm, and for I_2 is $\frac{0.16}{2} = 0.08$ atm as two moles of HI on dissociation gives 1 mol H_2 and 1 mol I_2)

$$K_p = \frac{p_{H_2} \cdot p_{I_2}}{p_{HI}^2} = \frac{0.08\ \text{atm} \times 0.08\ \text{atm}}{(0.04\ \text{atm})^2} = 4.0$$

Question 12. A mixture of 1.57 moles of N_2, 1.92 moles of H_2 and 8.13 moles of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 1.7×10^2. Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction ?

To predict the direction of a reaction calculate Q_c, reaction quotient. If $Q_c = K_c$, the reaction mixture is at equilibrium ;If $Q_c > K_c$ the reaction will proceed in the direction of reactants; If $Q_c < K_c$, the reaction will proceed in the direction of the products.

Solution. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$Q_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

Given, $[NH_3] = \frac{8.13}{20}\ \text{M} = 0.4065\ \text{M}$; $[N_2] = \frac{1.57}{20}\ \text{M} = 0.0785\ \text{M}$

$$[H_2] = \frac{1.92}{20}\ \text{M} = 0.096\ \text{M}$$

$$Q_c = \frac{[0.4065\ \text{M}]^2}{[0.0785\ \text{M}]\,[0.096\ \text{M}]^3} = 2.379 \times 10^3\ \text{M}^{-2}$$

$Q_c \neq K_c$, so the reaction mixture is not in equilibrium. $Q_c > K_c$, it indicates that the reaction will proceed in the direction of reactants.

Question 13. **The equilibrium constant expression for a gas reaction is,**

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

Write the balanced chemical equation corresponding to this expression.

Solution. The expression shows that 4NO and $6H_2O$ are reactants and $4NH_3$ and $5O_2$ are products. Thus, the balanced chemical equation is

$$4NO + 6H_2O \longrightarrow 4NH_3 + 5O_2$$

Question 14. **One mole of H_2O and one mole of CO are taken in 10 L vessel and heated to 725 K. At equilibrium, 40% of water (by mass) reacts with CO according to the equation,**

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Calculate the equilibrium constant for the reaction.

Solution.	$H_2O(g)$	+ $CO(g)$	$\rightleftharpoons$ $H_2(g)$	+ $CO_2(g)$
Initial conc.	1	1	0	0
Equili. conc.	$(1-x)$	$(1-x)$	x	x

H_2O reacted = 40% of 1 mol of H_2O = 0.4 mol

$$x = 0.4 \text{ mol}$$

$$(1-x) = 1 - 0.4 = 0.6 \text{ mol}$$

$$K_c = \frac{[H_2]\,[CO_2]}{[H_2O]\,[CO]} = \frac{0.4 \times 0.4}{0.6 \times 0.6} = 0.444$$

Question 15. **At 700 K, equilibrium constant for the reaction,**

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

is 54.8. If 0.5 mol L^{-1} of HI(*g*) is present at equilibrium at 700 K, what are the concentration of $H_2(g)$ and $I_2(g)$ assuming that we initially started with HI(*g*) and allowed it to reach equilibrium at 700 K ?

(i) As we started the reaction with HI, so equilibrium constant for the dissociation of HI ($2HI \rightleftharpoons H_2 + I_2$) is required. Thus, calculate equilibrium constant for backward reaction (K_c') $\left(K'_c = \frac{1}{K_c}\right)$

(ii) and then calculate $[H_2]$ and $[I_2]$.

Solution. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$; $K_c = 54.8$

$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$; $K_c' = \frac{1}{K_c} = \frac{1}{54.8}$

$$K_c' = \frac{[H_2]\,[I_2]}{[HI]^2} = \frac{1}{54.8}$$

Given, $[HI] = 0.5 \text{ mol } L^{-1}$

According to equation, $[H_2] = [I_2] = [x]$

$$\frac{x\,.\,x}{[0.5]^2} = \frac{1}{54.8}$$

$$x^2 = \frac{[0.5]^2}{54.8} = 0.00456$$

$$x = 0.0675\ \text{M}$$

$$[H_2] = [I_2] = x = 0.0675\ \text{M}$$

Question 16. **What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M ?**

$$2\text{ICl}(g) \rightleftharpoons I_2(g) + Cl_2(g)\,; \qquad K_c = 0.14$$

Solution.

	$2\text{ICl}(g) \rightleftharpoons$	$I_2(g) +$	$Cl_2(g)$
Initial conc.	0.78 M	0	0
Equili conc.	$0.78 - 2x$	x	x

$$K_c = \frac{[I_2][Cl_2]}{[\text{ICl}]^2} = \frac{x \,.\, x}{(0.78 - 2x)^2} = 0.14$$

or $$\frac{x}{(0.78 - 2x)} = \sqrt{0.14} = 0.374 \quad \text{or} \quad x = 0.29172 - 0.748x$$

or $$1.748x = 0.29172 \quad \text{or} \quad x = \frac{0.29172}{1.748} = 0.1668$$

$$[\text{ICl}]_{\text{equili}} = 0.45$$

Question 17. K_p **= 0.04 atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of** C_2H_6 **when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium ?**

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$$

(i) Find the equilibrium concentration of all reactants and products in the given equation by assuming decrease in pressure of C_2H_6 is p and increase in pressure of C_2H_4 equal to H_2 is p.

(ii) Find the value of p to calculate $p_{C_2H_6}$.

Solution.

	$C_2H_6(g) \rightleftharpoons$	$C_2H_4(g) +$	$H_2(g)$
Initial pressure	4.0 atm	0	0
Equili. pressure	$(4.0 - p)$ atm	p	p

$$K_p = \frac{p_{C_2H_4} \cdot p_{H_2}}{p_{C_2H_6}} = \frac{p.p}{4.0 - p}$$

$$0.04 = \frac{p^2}{4.0 - p} \quad \text{or} \quad 0.16 - 0.04p = p^2$$

$$p = \frac{-0.04 \pm \sqrt{0.0016 - 4\,(-0.16)}}{2}$$

$$p = \frac{-0.04 \pm 0.80}{2}$$

$$p = 0.38 \qquad \text{(by taking positive value)}$$

Hence, $$p_{C_2H_6} = 4.0 - 0.38 = 3.62\ \text{atm}$$

Question 18. Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as

$$CH_3COOH(l) + C_2H_5OH\,(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

(i) Write the concentration ratio (reaction quotient), Q_c, for this reaction (Note : Water is not in excess and is not a solvent in this reaction.)

(ii) At 293 K, if one starts with 1.00 mole of acetic acid and 0.18 mole of ethanol, there is 0.171 mole of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(iii) Starting with 0.5 mole of ethanol and 1.0 mole of acetic acid and maintaining it at 293 K, 0.214 mole of ethyl acetate is found after sometime. Has equilibrium been reached?

Solution. $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

(i) $Q_c = \dfrac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$

Here, H_2O is not in excess that's why its concentration is not constant.

(ii) $$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Initial conc.	1.00 mol	0.180 mol	0	0
Equili. conc.	(1 − x) mol	(0.180 − x) mol	x mol	x mol

Given, $[CH_3COOC_2H_5]_{\text{equili.}} = 0.171\text{ mol} = x$

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$$

$$K_c = \frac{0.171 \times 0.171}{(1-0.171) \times (0.180 - 0.171)}$$

$$K_c = \frac{0.171 \times 0.171}{0.829 \times 0.009} = 3.919 \approx 3.92$$

(iii) $$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Initial conc.	1.0 mol	0.5 mol	0	0
After *t* time, conc.	(1.0 − 0.214) = 0.786 mol	(0.5 − 0.214) = 0.286 mol	0.214 mol	0.214 mol

$$Q_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$$

$$Q_c = \frac{0.214 \times 0.214}{0.786 \times 0.286} = 0.2037 \approx 0.204$$

$Q_c \neq K_c$, hence, equilibrium has not been reached.

Question 19. A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be 0.5×10^{-1} mol L^{-1}. If value of K_c is 8.3×10^{-3}, what are the concentration of PCl_3 and Cl_2 at equilibrium?

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

Solution. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

At equili. $0.05\,M$ $\quad x \quad x$

Given, $[PCl_5]_{equili.} = 0.5 \times 10^{-1}\ \text{mol L}^{-1}\ (= 0.05\ \text{mol L}^{-1})$

$$K_c = 8.3 \times 10^{-3}$$

$$K_c = 8.3 \times 10^{-3} = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$8.3 \times 10^{-3} = \frac{x^2}{0.05} \quad \text{(because } [PCl_3] = [Cl_2])$$

$$x^2 = 0.415 \times 10^{-3} = 4.15 \times 10^{-4}$$

$$x = 2.037 \times 10^{-2} \approx 2.04 \times 10^{-2}\ \text{mol L}^{-1}$$

Hence, $[PCl_3] = [Cl_2] = 2.04 \times 10^{-2}\ \text{mol L}^{-1}$

Question 20. One of the reaction that takes place in producing steel from iron ore is the reduction of iron(II) oxide by carbon monoxide to give iron metal and CO_2.

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)\ ;$$

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

What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are; $p_{CO} = 1.4$ atm and $p_{CO_2} = 0.80$ atm ?

(i) First find Q_p by the given initial partial pressures of [CO] and [CO_2].

(ii) Compare Q_p and K_c to find the equilibrium partial pressure of [CO] and [CO_2].

Solution. $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)\ ;\ K_p = 0.265$ at 1050 K

Initial pressure $\quad 1.4$ atm $\quad 0.80$ atm

$$Q_p = \frac{p_{CO_2}}{p_{CO}} = \frac{0.80}{1.4} = 0.571 \qquad [\because \text{Fe and FeO are solids.}]$$

$Q_p > K_p$, the reaction will go in reverse direction. Due to this pressure of CO_2 will decrease and that of CO will increase to attain equilibrium. Hence, $p_{CO_2} = (0.80 - p)$ and $p_{CO} = (1.4 + p)$

(Suppose p is the decrease in pressure of CO_2 and p is the increase in pressure of CO).

$$K_p = \frac{p_{CO_2}}{p_{CO}} = 0.265 = \frac{(0.80 - p)}{(1.4 + p)}$$

$$1.265\,p = 0.80 - 0.371$$

$$1.265\,p = 0.429$$

$$p = \frac{0.429}{1.265} = 0.339\ \text{atm}$$

Hence, at equilibium,

$$p_{CO_2} = 0.80 - 0.339 = 0.461\ \text{atm}$$

and $\quad p_{CO} = 1.4 + 0.339 = 1.739$ atm.

Question 21. **Equilibrium constant, K_c for the reaction,**

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \text{ at 500 K is 0.061}$$

At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L^{-1} N_2, 2.0 mol L^{-1} H_2 and 0.5 mol L^{-1} NH_3. Is the reaction at equilibrium ? If not in which direction does the reaction tend to proceed to reach equilibrium ?

Find Q_c and compare it with K_c. If $Q_c = K_c$, the reaction is in equilibrium, if $Q_c < K_c$, the reaction will go in forward direction and if $Q_c > K_c$, the reaction will go in backward direction.

Solution. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $K_c = 0.061$ at 500 K

Given, $[N_2] = 3.0 \text{ mol } L^{-1}$, $[H_2] = 2.0 \text{ mol } L^{-1}$

and $[NH_3] = 0.5 \text{ mol } L^{-1}$ at time t

So,

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[0.5]^2}{[3.0][2.0]^3}$$

$$Q_c = 0.0104$$

Because $Q_c \neq K_c$, equilibrium has not been attained.
Because $Q_c < K_c$ $(0.0104 < 0.061)$, the reaction will proceed from left to right, *i.e.*, towards formation of more products.

Question 22. **Bromine monochloride, BrCl decomposes into bromine and chlorine and reaches the equilibrium,**

$$2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$$

for which $K_c = 32$ at 500 K. If initially pure BrCl is present at a concentration of 3.3×10^{-3} mol L^{-1}, what is its molar concentration in the mixture at equilibrium?

(i) First find equilibrium concentration for all reactants and products given in the equation by assuming x mole of BrCl decomposes.
(ii) Find x by the expression of K_c and then find $[BrCl]_{\text{equilibrium}}$.

Solution. $2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$; $K_c = 32$ at 500 K

	$2BrCl(g)$	$Br_2(g)$	$Cl_2(g)$
Initial conc.	3.30×10^{-3} mol L^{-1}	0	0
Equili. conc.	$(3.30 \times 10^{-3} - x)$ mol L^{-1}	$\frac{x}{2}$ mol L^{-1}	$\frac{x}{2}$ mol L^{-1}

$$K_c = \frac{[Br_2][Cl_2]}{[BrCl]^2} = \frac{x/2 \times x/2}{(3.30 \times 10^{-3} - x)^2} = 32$$

$$\frac{x^2}{4 \times (3.30 \times 10^{-3} - x)^2} = 32$$

$$\frac{x}{2 \times (3.30 \times 10^{-3} - x)} = \sqrt{32} = 5.656$$

$$\frac{x}{3.30 \times 10^{-3} - x} = 2 \times 5.656 = 11.312$$

$$x = 11.312(3.30 \times 10^{-3} - x)$$

$$x = 0.03732 - 11.312x$$
$$x + 11.312\,x = 0.03732$$
$$x = \frac{0.03732}{12.312} = 3.032 \times 10^{-3}\ \text{mol L}^{-1}$$
$$[\text{BrCl}]_{\text{equili.}} = (3.30 \times 10^{-3} - 3.032 \times 10^{-3})\,\text{mol L}^{-1} = 2.68 \times 10^{-4}\ \text{mol L}^{-1}$$

Question 23. **At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90.55% CO by mass.**

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

Calculate K_c for this reaction at the above temperature.

(i) Since, the percentage by mass is given, so calculate the number of moles of CO and CO_2 to calculate their mole fractions.

(ii) Then, calculate the partial pressures of CO and CO_2 by using the formula $p_A = x_A \cdot p_{\text{total}}$

(iii) Calculate K_p by using the formula, $K_p = \dfrac{p^2_{CO}}{p_{CO_2}}$ and K_c by using the formula, $K_p = K_c(RT)^{\Delta n_g}$

Solution. 90.55% CO by mass means 90.55 g CO and 9.45 g CO_2 are present in 100 g mixture.

No. of moles of CO, $n_{CO} = \dfrac{90.55}{28} = 3.234$ mol

(Molar mass of CO = 28 g mol^{-1})

No. of moles of CO_2, $n_{CO_2} = \dfrac{9.45}{44} = 0.215$ mol

(Molar mass of CO_2 = 44 g mol^{-1})

Partial pressure of CO, $p_{CO} = x_{CO} \cdot p_{\text{total}} \left(x_{CO} = \dfrac{3.234}{3.234 + 0.215} = 0.938 \right)$

$$p_{CO} = 0.938 \times 1\,\text{atm} = 0.938\ \text{atm}$$

Similarly, $p_{CO_2} = x_{CO_2} \cdot p_{\text{total}} \left(x_{CO_2} = \dfrac{0.215}{3.234 + 0.215} = 0.062 \right)$

$$p_{CO_2} = 0.062 \times 1\,\text{atm} = 0.062\ \text{atm}$$

$$C(s) + CO_2(g) \rightleftharpoons 2\,CO(g)$$

$$K_p = \frac{p^2_{CO}}{p_{CO_2}} = \frac{(0.938)^2}{0.062} = 14{,}19$$

$$\Delta n_g = 2 - 1 = 1$$

$$K_p = K_c\,(RT)^{\Delta n_g}$$

$$K_c = \frac{K_p}{RT} \qquad (\because \Delta n_g = 1)$$

$$K_c = \frac{14.19}{0.0821 \times 1127} = 0{,}15336 \approx 0.153$$

Question 24. **Calculate (a) ΔG° and (b) the equilibrium constant for the formation of the NO_2 from NO and O_2 at 298 K.**

$$NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$$

where, $\Delta_f G^\circ(NO_2) = 52.0$ kJ/mol,

$\Delta_f G^\circ(NO) = 87.0$ kJ/mol, $\Delta_f G^\circ(O_2) = 0$ kJ/mol

(i) Calculate the $\Delta_r G^\circ$ by using the formula $\Delta_r G^\circ = \Sigma\Delta_f G^\circ_p - \Sigma\Delta_f G^\circ_r$ (p = products and r = reactants.)

(ii) Calculate the equilibrium constant, K_c by using the formula, $\Delta G^\circ = -2.303RT \log K_c$.

Solution. (a) $NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$;

$$\Delta_r G^\circ = \Sigma\Delta_f G^\circ_{\text{products}} - \Sigma\Delta_f G^\circ_{\text{reactants}}$$

$$\Delta_r G^\circ = \Delta_f G^\circ(NO_2) - \left(\Delta_f G^\circ(NO) + \frac{1}{2}\Delta_f G^\circ(O_2)\right)$$

$$\Delta_r G^\circ = 52.0 - \left(87.0 + \frac{1}{2}\times 0\right) \text{ kJ mol}^{-1}$$

$$\Delta_r G^\circ = -35.0 \text{ kJ mol}^{-1}$$

(b) $\Delta_r G^\circ = -2.303\, RT \log K_c$

$$-35000 \text{ J mol}^{-1} = -2.303 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298\text{ K} \times \log K_c$$

$$\log K_c = \frac{35000}{5705.85} = 6.134$$

$$K_c = \text{antilog } 6.134$$

$$K_c = 1.361 \times 10^6$$

Question 25. **Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume ?**

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

(b) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

(c) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

Solution. According to Le-Chatelier's principle, on decreasing pressure equilibrium shifts in that direction where pressure increases (*i.e.*, number of moles in gaseous state are more). Therefore, number of moles of reaction products in (a) increases (b) decreases (c) remains the same. (If $\Delta n_g = 0$, there is no effect of change in pressure).

Question 26. **Which of the following reactions will get affected by increasing the pressure? Also, mention whether change will cause the reaction to go into forward or backward direction.**

(i) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

(ii) $CH_4(g) + 2S_2(g) \rightleftharpoons CS_2(g) + 2H_2S(g)$

(iii) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

(iv) $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$

(v) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(vi) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

According to Le-Chatelier's principle, increase in pressure shifts the equilibrium in the direction where pressure decreases (*i.e.*, number of moles are less), Furthermore, if $n_p \neq n_r$, the change in pressure affects the equilibrium.

Solution. (i) $n_p > n_r$, the reaction will go in backward direction.

(ii) $n_p = n_r$, the reaction will not be affected by increasing pressure.

(iii) $n_p > n_r$, the reaction will go in backward direction.

(iv) $n_p < n_r$, the reaction will go in forward direction.

(v) $n_p > n_r$, the reaction will go in backward direction.

(vi) $n_p > n_r$, the reaction will go in backward direction.

Question 27. The equilibrium constant for the following reaction is 1.6×10^5 at 1024 K

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

Solution. $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$; $K_p = 1.6 \times 10^5$ at 1024 K

$$\therefore \quad 2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)\ ;\ K'_p = \frac{1}{1.6 \times 10^5} \text{ at } 1024 \text{ K}$$

Initial pressure	10.0 bar	0	0
Equili. pressure	$(10 - x)$	$\frac{x}{2}$	$\frac{x}{2}$

$$K_p = \frac{p_{H_2} \cdot p_{Br_2}}{p^2_{HBr}} = \frac{\frac{x}{2} \cdot \frac{x}{2}}{(10 - x)^2}$$

$$\frac{1}{1.6 \times 10^5} = 0.625 \times 10^{-5} = \frac{\frac{x}{2} \cdot \frac{x}{2}}{10 \times 10}$$

[$(10 - x) \approx 10$ because magnitude of K_p is small.)]

$$2 \times 2 \times 10 \times 10 \times 0.625 \times 10^{-5} = x^2 \quad \text{or} \quad x = 0.050$$

$$p_{H_2} = p_{Br_2} = \frac{x}{2} = \frac{0.050}{2} = 0.025 \text{ bar} = 2.5 \times 10^{-2} \text{ bar}$$

$$p_{HBr} = 10 - 0.050 = 9.95 \approx 10 \text{ bar}$$

Question 28. Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction,

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

(a) Write an expression of K_p for the above reaction.

(b) How will the values of K_p and composition of equilibrium mixture be affected by

(i) increasing the pressure

(ii) increasing the temperature

(iii) using a catalyst?

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

(a) $K_p = \dfrac{p_{CO} \cdot p^3_{H_2}}{p_{CH_4} \cdot p_{H_2O}}$

(b)(i) Increase in pressure shifts the equilibrium in the direction where pressure decreases (*i.e.*, number of moles are less). This is backward direction. K_p remains unaffected from pressure change.

(ii) Since, ΔH = +ve (endothermic reaction), reaction takes place with absorption of heat. Hence, increase in temperature shifts the equilibrium in the direction where heat is absorbed (*i.e.*, forward). It also increases the value of K_p.

(iii) No effect, since catalyst affects rate of both directions equally.

Question 29. Describe the effect of

(a) addition of H_2 (b) addition of CH_3OH

(c) removal of CO (d) removal of CH_3OH

on the equilibrium of the reaction,

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$$

Solution. $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$

According to Le-Chatelier's principle,

(a) Addition of H_2 (increase in concentration of reactants) shifts the equilibrium in forward direction (more product is formed).

(b) Addition of CH_3OH (increase in concentration of product) shifts the equilibrium in backward direction.

(c) Removal of CO also shifts the equilibrium in backward direction.

(d) Removal of CH_3OH shifts the equilibrium in forward direction.

Question 30. At 473K, equilibrium constant K_c for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3}. If decomposition is depicted as,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g); \qquad \Delta H^\circ = 124.0 \text{ kJ mol}^{-1}$$

(a) Write an expression for K_c for the reaction.

(b) What is the value of K_c for the reverse reaction at the same temperature?

(c) What would be the effect on K_c if (i) more PCl_5 is added (ii) pressure is increased (iii) the temperature is increased ?

Solution. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$; $K_c = 8.3 \times 10^{-3}$

(a) $K_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]}$

(b) For the reverse reaction, $K_c' = \dfrac{1}{K_c} = \dfrac{1}{8.3 \times 10^{-3}} = 120.48$

(c) (i) Addition of PCl_5 have no effect on K_c because K_c is constant at constant temperature.

(ii) K_c does not change with pressure.

(iii) The given reaction is endothermic, hence on increasing the temperature, K_f will increase, this results in increase in K_c $\left(K_c = \dfrac{K_f}{K_b}\right)$.

Question 31. Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H_2. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that $p_{CO} = p_{H_2O} = 4.0$ bar, what will be the partial pressure of H_2 at equilibrium? $K_p = 10.1$ at 400°C.

Solution.

	$CO(g)$	$+ H_2O(g)$	$\rightleftharpoons CO_2(g)$	$+ H_2(g)$
Initial pressure	4.0 bar	4.0 bar	0	0
At equili.	$(4.0 - p)$	$(4.0 - p)$	p	p

$$K_p = \frac{p_{CO_2} \cdot p_{H_2}}{p_{CO} \cdot p_{H_2O}} = \frac{p \cdot p}{(4 - p) \cdot (4 - p)}$$

$$10.1 = \frac{p^2}{(4 - p)^2}$$

$$\sqrt{10.1} = \frac{p}{(4 - p)}$$

$$3.17 = \frac{p}{(4 - p)}$$

$$p = 12.71 - 3.17p$$

$$4.17p = 12.71$$

$$p = \frac{12.71}{4.17} = 3.04 \text{ bar}$$

Hence, $$p_{H_2} = 3.04 \text{ bar}$$

Question 32. **Predict which of the following reaction will have appreciable concentration of reactants and products ?**

(a) $Cl_2(g) \rightleftharpoons 2Cl(g)$; $K_c = 5 \times 10^{-39}$

(b) $Cl_2(g) + 2NO(g) \rightleftharpoons 2NOCl(g)$; $K_c = 3.7 \times 10^{8}$

(c) $Cl_2(g) + 2NO_2(g) \rightleftharpoons 2NO_2Cl(g)$; $K_c = 1.8$

When the value of K_c is greater than 10^3, only product predominates. If $K_c < 10^{-3}$, only reactant predominates, and if the value of K_c lies between 10^{-3} to 10^3, both reactants and products are present in appreciable concentration.

Solution. For the reaction (c) equilibrium constant, K_c is neither high nor very low so the reactants and products will be present in appreciable concentrations.

Question 33. **The value of K_c for the reaction,**

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

is 2.0×10^{-50} at 25°C. If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2}, what is the concentration of O_3?

Solution. $$3O_2(g) \rightleftharpoons 2O_3(g)$$

Equili. conc. $\quad 1.6 \times 10^{-2} \quad ?$

$$K_c = \frac{[O_3]^2}{[O_2]^3}$$

$$2.0 \times 10^{-50} = \frac{[O_3]^2}{[1.6 \times 10^{-2}]^3}$$

$$[O_3]^2 = 2.0 \times 10^{-50} \times [1.6 \times 10^{-2}]^3$$

$$[O_3]^2 = 8.192 \times 10^{-56}$$

$$[O_3] = 2.86 \times 10^{-28} \text{ mol L}^{-1}$$

Question 34. **The reaction,**

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

is at equilibrium at 1300 K in a 1L flask. It also contains 0.30 mole of CO, 0.10 mole of H_2 and 0.02 mole of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration of CH_4 in the mixture. The equilibrium constant, K_c for the reaction at the given temperature is 3.90.

Solution. $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$; $K_c = 3.90$ at 1300 K.

$$K_c = \frac{[CH_4] \cdot [H_2O]}{[CO]\,[H_2]^3}$$

$$3.90 = \frac{[CH_4]\,[0.02]}{[0.30]\,[0.10]^3}$$

(Molar concentration means number of moles present in 1 L and volume of the flask is 1 L.)

$$[CH_4] = \frac{3.90 \times 0.30 \times (0.10)^3}{0.02} = 0.0585\ \text{M}$$

$$[CH_4]_{eq} = 5.85 \times 10^{-2}\text{M}$$

Question 35. What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species.

$$HNO_2,\ CN^-,\ HClO_4,\ F^-,\ OH^-,\ CO_3^{2-} \text{ and } S^{2-}$$

$\text{Acid} - H^+ \longrightarrow$ Conjugate base

$\text{Base} + H^+ \longrightarrow$ Conjugate acid.

Solution. An acid-base pair differ by a proton is known as conjugate acid-base pair.

$$\underset{\text{Acid}}{HNO_2} \rightleftharpoons \underset{\text{Conjugate base}}{NO_2^-} + H^+$$

$$\underset{\text{Base}}{CN^- + H^+} \rightleftharpoons \underset{\text{Conjugate acid}}{HCN}$$

$$\underset{\text{Acid}}{HClO_4} \rightleftharpoons \underset{\text{Conjugate base}}{ClO_4^-} + H^+$$

$$\underset{\text{Base}}{F^- + H^+} \rightleftharpoons \underset{\text{Conjugate acid}}{HF}$$

$$\underset{\text{Base}}{OH^- + H^+} \rightleftharpoons \underset{\text{Conjugate acid}}{H_2O}$$

$$\underset{\text{Acid}}{OH^-} \rightleftharpoons \underset{\text{Conjugate base}}{O^{2-}} + H^+$$

$$\underset{\text{Base}}{CO_3^{2-} + H^+} \rightleftharpoons \underset{\text{Conjugate acid}}{HCO_3^-}$$

$$\underset{\text{Base}}{S^{2-} + H^+} \rightleftharpoons \underset{\text{Conjugate acid}}{HS^-}$$

Question 36. Which of the following are Lewis acids ?

$$H_2O,\ BF_3,\ H^+,\ NH_4^+$$

Lewis acids have a tendency to accept electrons. Electron deficient or positively charged species have such tendency.

Solution. BF_3, H^+ and NH_4^+ act as Lewis acids.

Question 37. What will be the conjugate bases for the Bronsted acids: HF, H_2SO_4 and HCO_3^-?

$\text{Acid} \rightleftharpoons$ Conjugate base $+ H^+$

Solution.

$$HF \rightleftharpoons F^- + H^+$$
$$H_2SO_4 \rightleftharpoons HSO_4^- + H^+$$
$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$$

Question 38. **Write the conjugate acids for the Bronsted bases NH_2^-, NH_3 and $HCOO^-$.**

Base $+ H^+ \rightleftharpoons$ Conjugate acid

Solution.

$$NH_2^- + H^+ \rightleftharpoons NH_3$$
$$NH_3 + H^+ \rightleftharpoons NH_4^+$$
$$HCOO^- + H^+ \rightleftharpoons HCOOH$$

Question 39. **The species, H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and base.**

Solution.

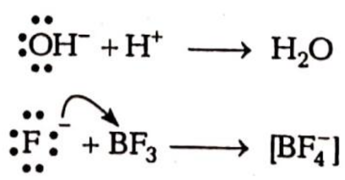
Species	Conjugate acid	Conjugate base
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{2-}
HSO_4^-	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	NH_2^-

Question 40. **Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base?**

(a) OH^- **(b) F^-**
(c) H^+ **(d) BCl_3**

Lewis acids have a tendency to accept electrons and Lewis bases have a tendency to donate electrons.

Solution. **OH^- and F^- are electron rich species and can donate electron pair. Hence, these act as Lewis base.**



$$:\ddot{\underset{\cdot\cdot}{O}}H^- + H^+ \longrightarrow H_2O$$
$$:\ddot{\underset{\cdot\cdot}{F}}:^- + BF_3 \longrightarrow [BF_4^-]$$

H^+ and BCl_3 are electron deficient species and can accept electron pair. Hence, these act as Lewis acid.

$$H_3N\!: + H^+ \longrightarrow NH_4^+$$

$$H_3N\!: + BCl_3 \longrightarrow H_3N \rightarrow BCl_3$$

Question 41. The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3} M. What is its pH?

Solution.

$$pH = -\log [H^+]$$
$$pH = -\log [3.8 \times 10^{-3}]$$
$$pH = -(-3\log 10 + \log 3.8)$$
$$pH = +3 - 0.5798 = 2.4202 \approx 2.42$$

Question 42. The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

Solution.

$$pH = 3.76 = -\log [H^+]$$
$$\log [H^+] = -3.76$$

[Before taking antilog add -1 in characteristic (-3) and $+1$ in mantissa (0.76), *i.e.*, $-3.76 - 1 + 1 = \bar{4}.24$]

$$\log[H^+] = \bar{4}.24 \text{ or } [H^+] = \text{antilog } \bar{4}.24$$
$$[H^+] = 1.738 \times 10^{-4} \text{ M}$$

Question 43. The ionization constant of HF, HCOOH and HCN at 298 K are 6.8×10^{-4}, 1.8×10^{-4} and 4.8×10^{-9} respectively. Calculate the ionization constants of the corresponding conjugate base.

To find K_b of a conjugate base, use the formula $K_a \cdot K_b = K_w = 1 \times 10^{-14}$.

Solution. If K_a is the ionization constant of a weak acid (HA) and K_b is the ionization constant of its conjugate base (A^-) then $K_a \cdot K_b = K_w$

$$K_b\,(F^-) = \frac{1 \times 10^{-14}}{K_a\,(HF)} = \frac{1 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.47 \times 10^{-11}$$

$$K_b\,(HCOO^-) = \frac{1 \times 10^{-14}}{K_a\,(HCOOH)} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.56 \times 10^{-11}$$

$$K_b\,(CN^-) = \frac{1 \times 10^{-14}}{K_a\,(HCN)} = \frac{1 \times 10^{-14}}{4.8 \times 10^{-9}} = 2.08 \times 10^{-6}$$

Question 44. The ionization constant of phenol is 1.0×10^{-10}. What is the concentration of phenolate ion in 0.05 M solution of phenol ? What will be its degree of ionization if the solution is also 0.01 M in sodium phenolate?

Solution.

$$\underset{\text{phenol}}{C_6H_5OH} + H_2O \rightleftharpoons \underset{\text{phenolate}}{C_6H_5O^-} + H_3O^+$$

$$K_a = \frac{[C_6H_5O^-]\,[H_3O^+]}{[C_6H_5OH]}$$

By Ostwald dilution law,

$$[C_6H_5O^-] = [H_3O^+] = \sqrt{K_a \cdot C}$$

$$= \sqrt{1.0 \times 10^{-10} \times 0.05} = 2.24 \times 10^{-6} \text{ M}$$

When mixture contains 0.05 M phenol and 0.01 M phenolate ion (from sodium phenolate) then

$$K_a = \frac{[C_6H_5O^-][H_3O^+]}{[C_6H_5OH]}$$

$$1.0 \times 10^{-10} = \frac{[0.01] \times [H_3O^+]}{[0.05]}$$

$$[H_3O^+] = \frac{0.05 \times 1.0 \times 10^{-10}}{0.01} = 5 \times 10^{-10} \text{ M}$$

$$[H_3O^+] = C \cdot \alpha = 5 \times 10^{-10} \quad \text{or} \quad \alpha = \frac{5 \times 10^{-10}}{C}$$

$$\alpha = \frac{5 \times 10^{-10}}{0.05} = 1 \times 10^{-8}$$

Question 45. The first ionization constant of H_2S is 9.1×10^{-8}. Calculate the concentration of HS^- ion in its 0.1 M solution. How will this concentration be affected if the solution is 0.1 M in HCl also? If the second dissociation constant of H_2S is 1.2×10^{-13}, calculate the concentration of S^{2-} under both conditions.

(i) H_2S, being a weak acid, dissociates as $H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$

so, calculate $[HS^-]$ by using the formula, $K_a = \dfrac{[H_3O^+][HS^-]}{[H_2S]}$

(ii) HCl being a strong acid dissociates completely, so calculate $[HS^-]$ in the presence of 0.1 M HCl by taking $[H^+]$ concentration as 0.1 M.

(iii) Calculate $[S^{2-}]$ ion concentration by using the equation,

$$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-}$$

(iv) Calculate $[S^{2-}]$ ion concentration in the presence of 0.1 M HCl.

Solution. (i) $H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$

$$K_a = \frac{[H_3O^+]\,[HS^-]}{[H_2S]}$$

$$[H_3O^+] = [HS^-] = \sqrt{K_{a_1} . C}$$

$$= \sqrt{9.1 \times 10^{-8} \times 0.1} = 9.54 \times 10^{-5} \text{ M}$$

(ii) In the presence of 0.1 M HCl, $[H_3O^+] = 0.1$ M

$$K_{a_1} = \frac{[H_3O^+]\,[HS^-]}{[H_2S]}$$

$$9.1 \times 10^{-8} = \frac{[0.1]\,[HS^-]}{[0.1]}$$

$$[HS^-] = 9.1 \times 10^{-8}\ M$$

Hence, concentration of $[HS^-]$ is decreased in the presence of 0.1 M HCl due to common-ion effect.

(iii) For second dissociation constant,

$$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-} \quad \text{(In absence of HCl)}$$

$$[HS^-] = 9.54 \times 10^{-5}\ M$$

$$K_{a_2} = \frac{[H_3O^+]\,[S^{2-}]}{[HS^-]}$$

$$[H_3O^+] = [S^{2-}] = \sqrt{K_{a_2} \cdot C}$$

$$= \sqrt{1.2 \times 10^{-13} \times 9.54 \times 10^{-5}} = 3.38 \times 10^{-9} M$$

(iv) In the presence of 0.1 M HCl,

$$K_{a_2} = \frac{[H_3O^+]\,[S^{2-}]}{[HS^-]} = 1.2 \times 10^{-13} = \frac{[0.1]\,[S^{2-}]}{[9.1 \times 10^{-8}]}$$

$$[S^{2-}] = 1.092 \times 10^{-19} M$$

Question 46. **The ionization constant of acetic acid is 1.74×10^{-5}. Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.**

Solution.

$$\begin{array}{lcccl} CH_3COOH + H_2O & \rightleftharpoons & CH_3COO^- & + H_3O^+ & \\ C & & 0 & 0 & \text{Initially} \\ C - C\alpha & & C\alpha & C\alpha & \text{At time } t \end{array}$$

$$K_a = \frac{[CH_3COO^-]\,[H_3O^+]}{[CH_3COOH]}$$

Given, $K_a = 1.74 \times 10^{-5}$, $[CH_3COOH] = 0.05$ M

$$[CH_3COO^-] = [H_3O^+] = \sqrt{K_a \cdot [CH_3COOH]}$$

$$[CH_3COO^-] = [H_3O^+] = \sqrt{1.74 \times 10^{-5} \times 0.05}$$

$$[CH_3COO^-] = [H_3O^+] = \sqrt{17.4 \times 10^{-6} \times 5.0 \times 10^{-2}}$$

$$= 9.33 \times 10^{-4}\ M$$

$$[CH_3COO^-] = [H_3O^+] = C \cdot \alpha$$

Degree of dissociation, $\alpha = \frac{[H_3O^+]}{C} = \frac{9.33 \times 10^{-4}}{0.05} = 1.86 \times 10^{-2}$

$$pH = -\log [H_3O^+]$$

$$pH = -\log [9.33 \times 10^{-4}]$$

$$pH = 4 - 0.9699 = 3.0301$$

Question 47. 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.

(i) Organic acids are weak acids, so dissociate as $HA \rightleftharpoons H^+ + A^-$ and their K_a is calculated as, $K_a = \frac{[H^+][A^-]}{[HA]}$.

(ii) To calculate K_a, $[H^+]$ and $[A^-]$ are required. Calculate $[H^+]$ by using the formula, $pH = -\log[H^+]$ and calculate $[A^-]$ by using the equation $HA \rightleftharpoons H^+ + A^-$

(iii) Then, calculate K_a by using the formula, $K_a = \frac{[H^+][A^-]}{[HA]}$

(iv) Calculate pK_a by using the formula $pK_a = -\log K_a$

Solution. $HA \rightleftharpoons H^+ + A^-$

$$pH = 4.15 = -\log[H^+]$$

$$\log[H^+] = -4.15$$

$$\log[H^+] = \bar{5}.85 \text{ or } [H^+] = \text{antilog } \bar{5}.85 = 7.079\times10^{-5}$$

$$[H^+] = [A^-] = 7.079\times10^{-5}\text{ M}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(7.079\times10^{-5})(7.079\times10^{-5})}{0.01}$$

$$K_a = 5011.22\times10^{-10} = 5.0\times10^{-7}$$

$$pK_a = -\log K_a = -\log[5.0\times10^{-7}]$$

$$pK_a = 7 - 0.699 = 6.301$$

Question 48. Assuming complete dissociation, calculate the pH of the following solutions :

(a) 0.003 M HCl **(b) 0.005 M NaOH**
(c) 0.002 M HBr **(d) 0.002 M KOH**

$pH = -\log[H_3O^+]$
$pOH = -\log[OH^-]$
$pH + pOH = 14$

Solution. (a) $0.003\text{ M HCl} = 0.003\text{ M }[H_3O^+]$

$$pH = -\log[H_3O^+]$$

$$pH = -\log[0.003] = -\log[3.0\times10^{-3}]$$

$$pH = 3 + (-0.4771) = 2.52$$

(b) $0.005\text{ M NaOH} = 0.005\text{ M }[OH^-]$

$$pOH = -\log[OH^-] = -\log[0.005]$$

$$pOH = -\log[5.0\times10^{-3}] = 3 + (-0.6990)$$

$$pOH = 2.30$$

$$pH + pOH = 14 \quad \text{or} \quad pH = 14 - 2.30 = 11.70$$

(c) 0.002 M HBr

$$pH = -\log [H_3O^+] = -\log [0.002]$$

$$pH = 3 + (-0.3010) = 2.699 \approx 2.70$$

(d) 0.002 M KOH

$$pOH = -\log [0.002] = 2.70$$

$$pH + pOH = 14 \quad \text{or} \quad pH = 14 - 2.70 = 11.30$$

Question 49. Calculate the pH of the following solutions :

(a) 2 g of TlOH dissolved in water to give 2 L of solution.

(b) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL solution.

(c) 0.3 g of NaOH dissolved in water to give 200 mL of solution.

(d) 1 mL of 13.6 M HCl is diluted with water to give 1 L of solution.

(i) To find pH of the given solution, first find concentration of solution in mol L^{-1}.

(ii) To find pH of the given acidic solution use the formula $pH = -\log [H_3O^+]$.

(iii) To find pH of the given basic solution, first find pOH of the solution by using the formula $pOH = -\log [OH^-]$ and then find pH by using the formula $pH + pOH = 14$.

Solution. (a) Molecular mass of TlOH = 204 + 16 + 1 = 221 g mol^{-1}

Conc. in mol L^{-1} (molarity)

$$= \frac{\text{Mass of TlOH (g)}}{\text{Molar mass of TlOH} \times \text{Volume of solution (L)}}$$

$$= \frac{2}{221 \times 2} = 0.00452 = 4.52 \times 10^{-3}\ M$$

$$pH = -\log [OH^-] = -\log [4.52 \times 10^{-3}]$$

$$pOH = 3 + (-0.6551) = 2.344$$

$$pH + pOH = 14 \quad \text{or} \quad pH = 14 - 2.334 = 11.656 \approx 11.66$$

(b) Molecular mass of $Ca(OH)_2 = 40 + [(16 + 1) \times 2] = 74$ g mol^{-1}

$$\text{Molarity, } M = \frac{\text{Mass of } Ca(OH)_2 (g) \times 1000}{\text{Molar mass of } Ca(OH)_2 \times \text{Volume of solution (mL)}}$$

$$M = \frac{0.3 \times 1000}{74 \times 500} = 0.0081$$

One mole of $Ca(OH)_2$ gives 2 moles of OH^-. So

$$[OH^-] = 2 \times 0.0081 = 0.0162\ M$$

$$pOH = -\log [OH^-] = -\log [0.0162]$$

$$pOH = -\log [1.62 \times 10^{-2}] = 2 + (-0.2095) = 1.7905 \approx 1.79$$

$$pH + pOH = 14 \quad \text{or } pH = 14 - 1.79 = 12.21$$

(c) Molecular mass of NaOH = 23 + 16 + 1 = 40

$$M = \frac{\text{Mass of NaOH (g)} \times 1000}{\text{Molar mass of NaOH} \times \text{Volume of solution (mL)}}$$

$$= \frac{0.3 \times 1000}{40 \times 200} = 0.0375$$

$$\text{pOH} = -\log [0.0375] = -\log [3.75 \times 10^{-2}]$$

$$\text{pOH} = 2 + (-0.5740) = 1.426 \approx 1.43$$

$$\text{pH} + \text{pOH} = 14 \quad \text{or} \quad \text{pH} = 14 - 1.43 = 12.57$$

(d) In case of dilution $M_1V_1 = M_2V_2$

$$13.6 \times 1 \text{ (mL)} = M_2 \times 1000 \text{ (mL)}$$

$$M_2 = \frac{13.6 \times 1}{1000} = 0.0136 = 1.36 \times 10^{-2} \text{M}$$

$$\text{pH} = -\log [1.36 \times 10^{-2}] = 2 + (-0.1335) = 1.8665$$

$$\text{pH} = 1.87$$

Question 50. The degree of ionization of a 0.1 M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK_a of bromoacetic acid.

(i) Find K_a by using the formula $K_a = C \cdot \alpha^2$ (for weak acid).
(ii) Find pK_a by using the formula p$K_a = -\log K_a$.
(iii) To find pH of the solution, find $[H_3O^+]$ concentration, by using the relation $[H_3O^+] = C\alpha$.

Solution. $CH_2(Br)COOH + H_2O \rightleftharpoons CH_2(Br)COO^- + H_3O^+$

	$CH_2(Br)COOH$	$CH_2(Br)COO^-$	H_3O^+
Initial conc.	C	0	0
Equili. conc.	$C - C\alpha$ $C(1-\alpha)$	$C\alpha$	$C\alpha$

$$K_a = \frac{C\alpha \, . \, C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

$$K_a = C\alpha^2 \qquad \text{[For weak acid } (1-\alpha) \approx 1]$$

$$K_a = 0.1 \times (0.132)^2 = 0.00174 \approx 1.74 \times 10^{-3}$$

$$\text{p}K_a = -\log K_a$$

or

$$\text{p}K_a = -\log [1.74 \times 10^{-3}]$$

$$\text{p}K_a = 3 + (-0.2405) = 2.7595$$

$$\text{pH} = -\log [H_3O^+]$$

$$\text{pH} = -\log [1.32 \times 10^{-2}]$$

$$\text{(because } [H_3O^+] = C\alpha = 0.1 \times 0.132 = 0.0132)$$

$$\text{pH} = 2 + (-0.1206) = 1.8794 \approx 1.88$$

Question 51. The pH of 0.005 M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate its ionization constant and pK_b.

(i) As codeine is a weak base, its ionization constant is related to OH^- as

$$K_b = \frac{[OH^-]^2}{[\text{Codeine}]}$$

(ii) Calculate $[OH^-]$ from pOH with the help of the formula

$$pOH = -\log[OH^-]$$

(iii) $pK_b = -\log K_b$

Solution. Codeine $(C_{18}H_{21}NO_3) + H_2O \rightleftharpoons \text{Codeine } H^+ + OH^-$

$$pH = 9.95 \text{ or } pOH = 14 - 9.95 = 4.05$$

$$pOH = -\log[OH^-]$$

$$\log[OH^-] = -4.05 = \bar{5}.95$$

$$[OH^-] = \text{antilog } \bar{5}.95 = 8.913 \times 10^{-5}$$

$$K_b = \frac{[\text{codeine } H^+][OH^-]}{[\text{codeine}]} = \frac{[OH^-]^2}{[\text{codeine}]} \quad (\text{because } [\text{codein } H^+] = [OH^-])$$

$$K_b = \frac{(8.913 \times 10^{-5})^2}{0.005} = 1.588 \times 10^{-6}$$

$$pK_b = -\log[K_b] = -\log[1.588 \times 10^{-6}]$$

$$pK_b = 6 + (-0.2009) = 5.7991 \approx 5.80$$

Question 52. What is the pH of 0.001 M aniline solution? The ionization constant of aniline is 4.27×10^{-10}. Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline.

(i) Find $[OH^-]$ ion concentration by using the formula $[OH^-] = \sqrt{K_b C}$.

(ii) To find pH of the solution first find pOH and then pH (pH + pOH = 14).

(iii) Find α by using the formula $\alpha = \sqrt{K_b / C}$ (for weak base).

(iv) Find K_a by using the formula $K_a \cdot K_b = K_w = 10^{-14}$.

Solution. $C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$

$$K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]} = \frac{[OH^-]^2}{[C_6H_5NH_2]}$$

$$[OH^-] = \sqrt{K_b \cdot C} = \sqrt{4.27 \times 10^{-10} \times 0.001}$$

$$[OH^-] = 6.534 \times 10^{-7}$$

$$pOH = -\log[6.534 \times 10^{-7}]$$

$$pOH = 7 + (-0.8152) = 6.18$$

$$pH + pOH = 14$$

or

$$pH = 14 - 6.18 = 7.82$$

$$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$$

	$C_6H_5NH_2$	$C_6H_5NH_3^+$	OH^-
Initial conc.	C	0	0
Equili. conc.	$C - C\alpha$	$C\alpha$	$C\alpha$

$$K_b = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} \quad [(1-\alpha) \approx 1 \text{ for weak base}]$$

$$K_b = C\alpha^2 \quad \text{or} \quad \alpha = \sqrt{K_b / C}$$

$$\text{Degree of ionization, } \alpha = \sqrt{\frac{4.27 \times 10^{-10}}{0.001}} = 6.53 \times 10^{-4}$$

K_a of conjugate acid of aniline,

$$K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{4.27 \times 10^{-10}} = 2.34 \times 10^{-5}$$

Question 53. Calculate the degree of ionization of 0.05 M acetic acid if its pK_a value is 4.74. How is the degree of dissociation affected when its solution also contains (a) 0.01 M (b) 0.1 M in HCl ?

(i) α is related to K_a as $\alpha = \sqrt{K_a / C}$, so first find K_a from pK_a as p$K_a = -\log(K_a)$ and then calculate α.

(ii) To find α in the presence of 0.01 M HCl or 0.1 M HCl, calculate $C\alpha$ for acetate ions by taking $[H^+]$ ion concentrations 0.01 M or 0.1 M.

Solution.

$$pK_a = -\log K_a,$$

$$4.74 = -\log K_a$$

$$\log K_a = -4.74 = \bar{5}\cdot 26$$

$$K_a = \text{antilog } \bar{5}.26 = 1.82 \times 10^{-5}$$

$$\alpha = \sqrt{K_a / C} \quad \text{or} \quad \alpha = \sqrt{\frac{1.82 \times 10^{-5}}{0.05}} \qquad (C = 0.05 \text{ given})$$

$$\alpha = \sqrt{\frac{1.82 \times 10^{-5}}{5.0 \times 10^{-2}}} = \sqrt{0.364 \times 10^{-3}} = \sqrt{3.64 \times 10^{-4}}$$

$$\alpha = 1.908 \times 10^{-2}$$

(a) **In the presence of 0.01 M H^+**

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

	CH_3COOH	CH_3COO^-	H^+
Initial conc.	0.05 M	0	0
Equili. conc.	$0.05 - C\alpha$ ≈ 0.05	$C\alpha$	$(C\alpha + 0.01)$ ≈ 0.01

[CH_3COOH is a weak acid and HCl is a strong acid, so we can assume that $(C\alpha + 0.01) \approx 0.01$]

$$\therefore \quad K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$1.82 \times 10^{-5} = \frac{C\alpha \times 0.01}{0.05}$$

or $$C\alpha = \frac{1.82 \times 10^{-5} \times 0.05}{0.01} = 9.1 \times 10^{-5}$$

$$C\alpha = 9.1 \times 10^{-5} \quad \text{or} \quad \alpha = \frac{9.1 \times 10^{-5}}{0.05} = 1.82 \times 10^{-3}$$

(b) **In the presence of 0.1 M HCl** similarly, $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

$$1.82 \times 10^{-5} = \frac{C\alpha \times 0.1}{0.05} \quad ([H^+] = (C\alpha + 0.1\,M) \approx 0.1\,M)$$

(because 0.1 M HCl = 0.1 M H^+ ions)

$$C\alpha = \frac{1.82 \times 10^{-5} \times 0.05}{0.1} = 0.91 \times 10^{-5}$$

$$\alpha = \frac{0.91 \times 10^{-5}}{0.05} = 1.82 \times 10^{-4}$$

In the presence of strong acid, dissociation of weak acid *i.e.*, CH_3COOH decreases due to common ion effect.

Question 54. The ionization constant of dimethylamine is 5.4×10^{-4}. Calculate its degree of ionization in its 0.02 M solution. What percentage of dimethylamine is ionized if the solution is also 0.1 M in NaOH?

Solution. Given, K_b for dimethylamine = 5.4×10^{-4}

C for dimethylamine = 0.02 M

$$\alpha = \sqrt{K_b / C} = \sqrt{\frac{5.4 \times 10^{-4}}{0.02}} = 1.64 \times 10^{-1} = 0.164$$

In the presence of 0.1 M NaOH,

$$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2\overset{+}{N}H_2 + OH^-$$

	$(CH_3)_2NH$	$(CH_3)_2\overset{+}{N}H_2$	OH^-
Initial conc.	0.02 M	0	0
Equili. conc.	$(0.02 - C\alpha)$ ≈ 0.02	$C\alpha$	$C\alpha + 0.1$ ≈ 0.1 (0.1 from 0.1 M NaOH)

$$K_b = \frac{[(CH_3)_2\overset{+}{N}H_2]\,[OH^-]}{[(CH_3)_2NH]}$$

or $$5.4 \times 10^{-4} = \frac{C\alpha \times 0.1}{0.02}$$

$$C\alpha = \frac{5.4 \times 10^{-4} \times 0.02}{0.1} = 108 \times 10^{-6}$$

$$\alpha = \frac{108 \times 10^{-6}}{0.02} = 54 \times 10^{-4} = 5.4 \times 10^{-3}$$

$$\alpha = 0.54\%$$

Question 55. Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below :

(a) Human muscle-fluid, 6.83 (b) Human stomach fluid, 1.2

(c) Human blood, 7.38 (d) Human saliva, 6.4

Solution. (a) **pH of human muscle fluid** $= 6.83$

$$\text{pH} = -\log[\text{H}^+]$$

or $\log[\text{H}^+] = -6.83 = \bar{7}.17$

or $[\text{H}^+] = \text{antilog } \bar{7}.17 = 1.479 \times 10^{-7}\text{M}$

(b) **pH of human stomach fluid** $= 1.2$

$\log[\text{H}^+] = -1.2 = \bar{2}.80$ or $[\text{H}^+] = \text{antilog } \bar{2}.80$

$\therefore$ $[\text{H}^+] = 6.31 \times 10^{-2}\text{M}$

(c) **pH of human blood** $= 7.38$

$\log[\text{H}^+] = -7.38 = \bar{8}.62$

or $[\text{H}^+] = \text{antilog } \bar{8}.62 = 4.169 \times 10^{-8}\text{M}$

(d) **pH of human saliva = 6.4**

$\log[\text{H}^+] = -6.4 = \bar{7}.60$

$[\text{H}^+] = \text{antilog } \bar{7}.60 = 3.981 \times 10^{-7}\text{M}$

Question 56. The pH of milk, black coffee, tomato juice, lemon juice and egg white are 6.8, 5.0, 4.2, 2.2 and 7.8 respectively. Calculate the corresponding hydrogen ion concentration in each.

Solution. (a) **pH of milk** $= 6.8$

$\log[\text{H}^+] = -6.8 = \bar{7}.20$

$[\text{H}^+] = \text{antilog } \bar{7}.20 = 1.585 \times 10^{-7}\text{M}$

(b) **pH of black coffee** $= 5.0$

$\log[\text{H}^+] = -5.0$

$[\text{H}^+] = 10^{-5}\text{M}$

(c) **pH of lemon juice** $= 2.2$

$\log[\text{H}^+] = -2.2 = \bar{3}.8$

$[\text{H}^+] = \text{antilog } \bar{3}.8 = 6.310 \times 10^{-3}\text{M}$

(d) **pH of tomato juice** $= 4.2$

$\log[\text{H}^+] = -4.2 = \bar{5}.80$

$[\text{H}^+] = \text{antilog } \bar{5}.80 = 6.310 \times 10^{-5}\text{M}$

(e) **pH of egg white** $= 7.8$

$\log[\text{H}^+] = -7.8 = \bar{8}.20$

$[\text{H}^+] = \text{antilog } \bar{8}.20 = 1.585 \times 10^{-8}\text{M}$

Question 57. If 0.561 g of KOH is dissolved in water to give 200mL of solution at 298 K, calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?

Solution. Concentration of aq. KOH in mol L^{-1}, *i.e.*,

$$\text{Molarity, } M = \frac{\text{Mass of KOH (g)} \times 1000}{\text{Molar mass (KOH)} \times \text{Volume of solution (mL)}}$$

$$M = \frac{0.561 \times 1000}{56 \times 200}$$

(Molar mass of KOH = 39 + 16 + 1 = 56 g mol^{-1})

$$M = 0.05 \text{ mol L}^{-1}$$

$$\underset{0.05\text{ M}}{\text{KOH}} \rightleftharpoons \underset{0.05\text{ M}}{K^+} + \underset{0.05\text{ M}}{OH^-}$$

$$\therefore \quad [K^+] = 0.05 \text{ M} \quad \text{and} \quad [OH^-] = 0.05 \text{ M}$$

$$[H^+] \cdot [OH^-] = K_w = 1.0 \times 10^{-14}$$

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.05} = 20 \times 10^{-14} \text{ M} = 2.0 \times 10^{-13} \text{M}$$

$$\text{pH} = -\log[H^+] = -\log[2.0 \times 10^{-13}]$$

$$= -\log 2 - \log 10^{-13}$$

$$= -0.3010 + 13 = 12.7$$

Question 58. The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

(i) First find concentration of $Sr(OH)_2$ solution in mol per litre as concentration is given in g/L.
(ii) We have the $[OH^-]$, so find $[H^+]$ ion concentration, with the help of $[H^+][OH^-] = 10^{-14}$
(iii) Find pH of the solution from $[H^+]$.

Solution. Solubility of $Sr(OH)_2$ = 19.23 g/L at 298 K

$$\text{Molarity, } M = \frac{19.23 \text{ (g)}}{121.6 \text{ g mol}^{-1} \times 1\text{L}}$$

(Molar mass of $Sr(OH)_2$ = 87.6 + 2 (16 + 1) = 121.6 g mol^{-1})

$$M = 0.1581 \text{ mol L}^{-1}$$

$$\underset{0.1581\text{ M}}{Sr(OH)_2} \longrightarrow \underset{0.1581\text{ M}}{Sr^{2+}} + \underset{2 \times 0.1581\text{ M}}{2OH^-}$$

$$[Sr^{2+}] = 0.1581 \text{ M}$$

$$[OH^-] = 0.3162 \text{ M}$$

$$[H^+]\cdot[OH^-]=10^{-14} \quad (K_w=10^{-14}=[H^+]\cdot[OH^-])$$

$$[H^+]=\frac{10^{-14}}{0.3162}=3.16\times10^{-14}$$

$$pH=-\log[H^+]=-\log[3.16\times10^{-14}]$$

$$pH=14-0.4997=13.5003\approx13.5$$

Question 59. **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 0.01 M in HCl also ?**

Solution.

$$\underset{\substack{\text{Propanoic acid}\\(0.05-C\alpha)}}{CH_3CH_2COOH}+H_2O \rightleftharpoons \underset{C\alpha}{CH_3CH_2COO^-}+\underset{C\alpha}{H_3O^+};\ K_a=1.32\times10^{-5}$$

From Ostwald's dilution law,

$$\alpha=\sqrt{K_a/C}=\sqrt{\frac{1.32\times10^{-5}}{0.05}}$$

$$\alpha=0.016248$$

$$[H_3O^+]=C\alpha=0.05\times0.016248$$

$$[H_3O^+]=0.0008124=8.124\times10^{-4}$$

$$pH=-\log[H_3O^+]=-\log(8.124\times10^{-4})$$

$$pH=4-0.9098=3.0902\approx3.09$$

When the solution contains 0.01 M HCl

$$K_a=\frac{[CH_3CH_2COO^-][H_3O^+]}{CH_3CH_2COOH}$$

$$1.32\times10^{-5}=\frac{C\alpha\times0.01}{(0.05-C\alpha)}$$

($[H_3O^+]=0\cdot01$ M from HCl. In the presence of 0.01 M HCl dissociation of propanoic acid decreases.)

$$C\alpha=\frac{1.32\times10^{-5}\times(0.05-C\alpha)}{0.01} \quad [\text{as } (0.05-C\alpha)\approx0.05]$$

$$C\alpha=6.60\times10^{-5}$$

Degree of ionization, $\alpha=\dfrac{6.60\times10^{-5}}{0.05}=1.32\times10^{-3}$

Question 60. **The pH of 0.1M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.**

As we have pH, find $[H_3O^+]$ to calculate K_a and α.

$$\alpha=\frac{[H_3O^+]}{C}$$

Solution. $HCNO + H_2O \rightleftharpoons H_3O^+ + CNO^-$

$$pH = 2.34$$
$$pH = -\log [H_3O^+]$$
$$\log [H_3O^+] = -2.34 = \overline{3}.66$$
$$[H_3O^+] = \text{antilog } \overline{3}.66 = 4.571 \times 10^{-3} M$$
$$[H_3O^+] = C\alpha = 4.571 \times 10^{-3}$$

Degree of ionization, $\alpha = \dfrac{4.571 \times 10^{-3}}{0.1} = 4.571 \times 10^{-2}$

Ionization constant, $K_a = \dfrac{[H_3O^+][CNO^-]}{[HCNO]}$

$$= \frac{4.571 \times 10^{-3} \times 4.571 \times 10^{-3}}{0.1} = 2.089 \times 10^{-4}$$

Question 61. The ionization constant of nitrous acid is 4.5×10^{-4}. Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.

(i) Sodium nitrite is a salt of weak acid and strong base. Hence, to calculate pH of its aqueous solution use the formula $pH = 7 + \dfrac{pK_a + \log C}{2}$,

(ii) Degree of hydrolysis, $h = \sqrt{\dfrac{K_w}{K_a C}}$ (for a salt of weak acid + strong base)

Solution. Given, $[NaNO_2] = 0.04$ M

K_a of $HNO_2 = 4.5 \times 10^{-4}$

$$\therefore \quad pK_a = -\log K_a = -\log (4.5 \times 10^{-4})$$
$$pK_a = 4 - 0.6532 = 3.3468 \approx 3.35$$
$$pH = 7 + \frac{pK_a + \log C}{2}$$
$$pH = 7 + \frac{3.35 + \log 0.04}{2} = 7.98$$
$$pH = 7.98$$

Degree of hydrolysis, $h = \sqrt{\dfrac{K_w}{K_a C}} = \sqrt{\dfrac{10^{-14}}{4.5 \times 10^{-4} \times 0.04}}$

$$h = 2.36 \times 10^{-5}$$

Alternatively, $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$

	NO_2^-	HNO_2	OH^-
Initial conc.	C	0	0
After hydrolysis conc.	$(C - Ch)$	Ch	Ch

$$[OH^-] = Ch = 0.04 \times 2.36 \times 10^{-5}$$
$$[OH^-] = 9.44 \times 10^{-7}$$

$$pOH = -\log[9.44 \times 10^{-7}]$$
$$pOH = 7 - 0.9750 = 6.03$$
$$pH + pOH = 14 \quad \text{or} \quad pH = 14 - 6.03 = 7.97$$

Question. 62. A 0.02 M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine.

(i) Pyridinium hydrochloride is a salt of weak base (pyridine) and strong acid (hydrochloric acid). Therefore, to calculate K_b first calculate pK_b by using the formula,

$$pH = 7 - \frac{pK_b}{2} - \frac{\log C}{2}$$

(ii) Calculate K_b by using the formula $pK_b = -\log K_b$

Solution. $C_6H_5N^+HCl^- + H_2O \rightleftharpoons C_6H_5N^+HOH^- + HCl$

(Solution is acidic due to hydrolysis)

$$pH = 7 - \frac{pK_b}{2} - \frac{\log C}{2}$$
$$3.44 = 7 - \frac{pK_b}{2} - \frac{\log 0.02}{2}$$
$$pK_b = 8.82$$
$$pK_b = 8.82 = -\log pK_b$$
$$\log K_b = -8.82 = \bar{9}.18$$
$$K_b = \text{antilog } \bar{9}.18 = 1.5 \times 10^{-9}$$

Alternatively,

(i) Find $[H_3O^+]$ ion conc. by using the formula $pH = -\log[H_3O^+]$.

(ii) Calculate K_a by using the formula, $K_a = \dfrac{[C_6H_5N^+Cl^-]\,[H_3O^+]}{[C_6H_5N \cdot HCl]}$.

(iii) Calculate pK_a from K_a and then pK_b by using the formula

$$pK_a + pK_b = 14.$$

(iv) Calculate K_b from pK_b.

$$C_6H_5N \cdot HCl + H_2O \rightleftharpoons C_6H_5N^+Cl^- + H_3O^+$$
$$K_a = \frac{[C_6H_5N^+Cl^-]\,[H_3O^+]}{[C_6H_5N \cdot HCl]}$$
$$pH = 3.44 = -\log[H_3O^+]$$
$$\log[H_3O^+] = -3.44 = \bar{4}.56$$
$$[H_3O^+] = \text{antilog } \bar{4}.56 = 3.63 \times 10^{-4} M$$
$$[H_3O^+] = [C_6H_5N^+Cl^-] = 3.63 \times 10^{-4}$$

Hence, $$K_a = \frac{3.63 \times 10^{-4} \times 3.63 \times 10^{-4}}{0.02} = 6.588 \times 10^{-6}$$

$$pK_a = -\log K_a = -\log 6.588 \times 10^{-6}$$
$$pK_a = 6 + (-0.8187) = 5.18$$
$$pK_a + pK_b = 14$$
$$pK_b = 14 - 5.18 = 8.82$$

$$-\log K_b = -8.82$$

or
$$\log K_b = -8.82 = \overline{9}.18$$
$$K_b = \text{antilog } \overline{9}.18 = 1.5 \times 10^{-9}$$

Question 63. Predict if the solutions of the following salts are neutral, acidic or basic :

NaCl, KBr, NaCN, NH_4NO_3, $NaNO_2$ and KF

The solution of a salt of strong acid and strong base is neutral while that of weak acid and strong base is basic. A solution of salt of strong acid and weak base is acidic.

Solution.

	Salt	Acid	Base	Hydrolysis reaction	Nature of solution
(i)	NaCl	HCl	NaOH	$H_2O \rightleftharpoons H^+ + OH^-$ No hydrolysis	Neutral
(ii)	KBr	HBr	KOH	No hydrolysis	Neutral
(iii)	NaCN	HCN	NaOH	$CN^- + H_2O \rightleftharpoons HCN + OH^-$	Basic
(iv)	NH_4NO_3	HNO_3	NH_4OH	$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$	Acidic
(v)	$NaNO_2$	HNO_2	NaOH	$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$	Basic
(vi)	KF	HF	KOH	$F^- + H_2O \rightleftharpoons HF + OH^-$	Basic

Question 64. 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 ?

(i) To calculate pH of the solution first find $[H_3O^+]$ ion concentration by using the formula, $[H_3O^+] = \sqrt{K_a C}$.
(ii) Calculate pH by using the formula, $pH = -\log [H_3O^+]$.
(iii) Sodium chloroacetate is a salt of strong base and weak acid therefore,

$$pH = 7 + \frac{pK_a + \log C}{2}$$

Solution. $CH_2ClCOOH + H_2O \rightleftharpoons CH_2ClCOO^- + H_3O^+$

$$K_a = 1.35 \times 10^{-3} \qquad \text{(given)}$$

$$pK_a = -\log K_a = -\log [1.35 \times 10^{-3}]$$
$$= 3 - 0.13 = 2.87$$

By Oswald's dilution law,

$$[H_3O^+] = \sqrt{K_a \cdot C} = \sqrt{1.35 \times 10^{-3} \times 0.1}$$

$$[H_3O^+] = 1.16 \times 10^{-2} M$$

$$\text{pH of acid} = -\log [H_3O^+] = -\log (1.16 \times 10^{-2}) M$$

$$pH = 2 - 0.06 = 1.94$$

0.1 M $CH_2ClCOONa$ (sod. chloroacetate) is basic due to hydrolysis.

$$CH_2ClCOO^- + H_2O \rightleftharpoons CH_2ClCOOH + OH^-$$

For a salt of strong base + weak acid,

$$pH = 7 + \frac{pK_a + \log C}{2} = 7 + \frac{2.87 + \log 0.1}{2}$$

$$pH = 7 + \frac{2.87 + (-1)}{2} = 7 + \frac{1.87}{2} = 7 + 0.935 \approx 7.94$$

$$pH = 7.94$$

Alternatively To find pH of 0.1 M sodium salt solution use the formula,

$$pH = -\frac{1}{2}[\log K_w + \log K_a - \log C]$$

$$pH = -\frac{1}{2}[\log 10^{-14} + \log (1.35 \times 10^{-3}) - \log 0.1]$$

$$pH = -\frac{1}{2}[-14 + (-3 + 0.1303) - (-1)]$$

$$pH = -\frac{1}{2}[-15.8697] = 7.93485 \approx 7.94$$

Question 65. Ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature?

Solution. $K_w = [H_3O^+] \cdot [OH^-] = 2.7 \times 10^{-14}$ at 310 K

$$H_2O + H_2O \rightleftharpoons [H_3O^+][OH^-]$$

$$[H_3O^+] = [OH^-]$$

Therefore, $[H_3O^+] = \sqrt{2.7 \times 10^{-14}} = 1.643 \times 10^{-7} M$

$$pH = -\log [H_3O^+] = -\log 1.643 \times 10^{-7}$$

$$pH = 7 + (-0.2156) = 6.7844$$

Question 66. Calculate the pH of the resultant mixtures :

(a) 10 mL of 0.2 M $Ca(OH)_2$ + 25 mL of 0.1 M HCl

(b) 10 mL of 0.01 M H_2SO_4 + 10 mL of 0.01 M $Ca(OH)_2$

(c) 10 mL of 0.1 M H_2SO_4 + 10 mL of 0.1 M KOH

Compare millimoles (MV) of acid and base, to find the nature of solution.

(i) If millimoles of acid are more, the resultant mixture is acidic.

(ii) If millimoles of base are more, the resultant mixture is basic.

(iii) If millimoles of acid and base are equal, the resultant mixture, is neutral. Then calculate the pH.

Solution. (a) Base, $Ca(OH)_2$ = Acid, HCl

$$M_1V_1 = M_2V_2$$

Given, $M_1 = [OH^-] = 2 \times 0.2 = 0.4$ M

$V_1 = 10$ mL, $M_2 = 0.1$ M, $V_2 = 25$ mL

$$M_1V_1 = M_2V_2$$
$$0.4 \times 10 = 0.1 \times 25$$
$$4 > 2.5$$

$M_1V_1 > M_2V_2$ hence, solution is basic.

$$[OH^-] = \frac{M_1V_1 - M_2V_2}{V_1 + V_2} = \frac{4 - 2.5}{10 + 25} = 0.043 \text{ M}$$

$$pOH = -\log[4.3 \times 10^{-2}] = 2 - 0.6335 = 1.3665$$

$$pH = 14 - pOH = 14 - 1.3665 = 12.6335 \approx 12.63$$

(b) Similarly, base, $Ca(OH)_2$ = Acid, H_2SO_4

$$M_1V_1 = M_2V_2$$
$$(2 \times 0.01) \times 10 = (2 \times 0.01) \times 10$$

Because $M_1V_1 = M_2V_2$, hence solution is neutral.

$\therefore$ $pH = 7$

(c) Acid, H_2SO_4 = Base, KOH

$$M_1V_1 = M_2V_2$$
$$(2 \times 0.1)\, 10 = 0.1 \times 10$$

Because $M_1V_1 > M_2V_2$, hence solution is acidic,

$$[H^+] = \frac{M_1V_1 - M_2V_2}{V_1 + V_2}$$
$$= \frac{(0.2 \times 10) - (0.1 \times 10)}{10 + 10} = \frac{2 - 1}{20} = 0.05 \text{ M}$$

$$pH = -\log[0.05] = -\log[5.0 \times 10^{-2}]$$
$$pH = 2 - 0.6990 = 1.301 \approx 1.30$$
$$pH = 1.30$$

Question 67. **Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298 K from their solubility product constants.**

$[K_{sp}(Ag_2CrO_4) = 1.1 \times 10^{-12}, K_{sp}(BaCrO_4) = 1.2 \times 10^{-10},$
$K_{sp}[Fe(OH)_3] = 1.0 \times 10^{-38}, K_{sp}(PbCl_2) = 1.6 \times 10^{-5}$
$K_{sp}(Hg_2I_2) = 4.5 \times 10^{-29}]$

Determine also the molarities of individual ions.

Solution. (a) $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$; $K_{sp} = 1.1 \times 10^{-12}$

$$\underset{s}{} \qquad \underset{2s}{} \qquad \underset{s}{\phantom{CrO_4^{2-}}}$$

$$K_{sp} = [Ag^+]^2 \cdot [CrO_4^{2-}]$$
$$K_{sp} = [2s]^2 \cdot [s] = 4s^3$$
$$s^3 = \frac{K_{sp}}{4}$$

or $$s^3 = \frac{1.1 \times 10^{-12}}{4} = 0.275 \times 10^{-12}$$

$$3 \log s = \log 2.75 \times 10^{-13}$$

$$3 \log s = -13 + 0.4393 = -12.5607$$

$$\log s = \frac{-12.5607}{3} = -4.1869 = \bar{5}.8131$$

$$s = \text{antilog } \bar{5}.8131 = 6.503 \times 10^{-5} \text{ M}$$

$$[Ag^+] = 2s = 2 \times 6.503 \times 10^{-5}$$

$$= 13.006 \times 10^{-5} \approx 1.3 \times 10^{-4} \text{ M}$$

$$[CrO_4^{2-}] = s = 6.503 \times 10^{-5} \text{ M}$$

(b) $BaCrO_4 \rightleftharpoons Ba^{2+} + CrO_4^{2-}$; $K_{sp} = 1.2 \times 10^{-10}$

$s \quad\quad s \quad\quad s$ (Solubility of $BaCrO_4$ is s mol L^{-1})

$$K_{sp} = 1.2 \times 10^{-10} = [Ba^{2+}] \cdot [CrO_4^{2-}] = s^2$$

$$s = \sqrt{1.2 \times 10^{-10}} = 1.1 \times 10^{-5} \text{ M}$$

$$[Ba^{2+}] = [CrO_4^{2-}] = 1.1 \times 10^{-5} \text{ M}$$

(c) $Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$; $K_{sp} = 1.0 \times 10^{-38}$

$s \quad\quad s \quad\quad 3s$ (Solubility of $Fe(OH)_3$ is s mol L^{-1})

$$K_{sp} = [Fe^{3+}][OH^-]^3$$

$$K_{sp} = s \cdot (3s)^3 = 27s^4 \quad \text{or} \quad s^4 = \frac{K_{sp}}{27}$$

$$s^4 = \frac{1.0 \times 10^{-38}}{27} = 0.037 \times 10^{-38}$$

$$4 \log s = \log 3.7 \times 10^{-40}$$

$$4 \log s = -40 + 0.5682 = -39.4318$$

$$\log s = \frac{-39.4318}{4} = -9.8579 = \overline{10}.1421$$

$$s = \text{antilog } \overline{10}.1421 = 1.387 \times 10^{-10}$$

$$s \approx 1.39 \times 10^{-10}$$

$$[Fe^{3+}] = 1.39 \times 10^{-10} \text{ M}$$

$$[OH^-] = 3s = 3 \times 1.39 \times 10^{-10} = 4.17 \times 10^{-10} \text{ M}$$

(d) $PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-$; $K_{sp} = 1.6 \times 10^{-5}$

$s \quad\quad s \quad\quad 2s$ (Solubility of $PbCl_2$ is s mol L^{-1})

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

$$K_{sp} = s \cdot (2s)^2 = 4s^3$$

$$s^3 = \frac{K_{sp}}{4} = \frac{1.6 \times 10^{-5}}{4} = 0.4 \times 10^{-5}$$

$$3 \log s = \log 0.4 \times 10^{-5} = \log 4.0 \times 10^{-6}$$

$$3 \log s = -6 + 0.6021 = -5.3979$$

$$\log s = \frac{-5.3979}{3} = -1.7993 = \bar{2}.2007$$

$$s = \text{antilog } \bar{2}.2007 = 1.585 \times 10^{-2}$$

$$\approx 1.59 \times 10^{-2} \text{ M}$$

$\therefore$ Solubility of $PbCl_2 = 1.59 \times 10^{-2}$ M

$$[Pb^{2+}] = 1.59 \times 10^{-2} \text{ M}$$

$$[Cl^-] = 2 \times 1.59 \times 10^{-2} \text{ M} = 3.18 \times 10^{-2} \text{ M}$$

(e) $Hg_2I_2 \rightleftharpoons Hg_2^{2+} + 2I^-; K_{sp} = 4.5 \times 10^{-29}$

$s \quad s \quad 2s$ (Solubility of Hg_2I_2 is s mol L^{-1})

$$K_{sp} = [Hg_2^{2+}][I^-]^2$$

$$K_{sp} = s \cdot (2s)^2 = 4s^3$$

$$s^3 = \frac{K_{sp}}{4} = \frac{4.5 \times 10^{-29}}{4} = 1.125 \times 10^{-29}$$

$$3 \log s = \log (1.125 \times 10^{-29})$$

$$3 \log s = -29 + 0.0512 = -28.9488$$

$$\log s = \frac{-28.9488}{3} = -9.6496$$

$$\log s = -9.6496 = \overline{10}.3504$$

$$s = \text{antilog } \overline{10}.3504 = 2.241 \times 10^{-10} \text{ M}$$

Solubility of $Hg_2I_2 = 2.241 \times 10^{-10}$ M

$$[Hg_2^{2+}] = 2.241 \times 10^{-10} \text{M}$$

$$[I^-] = 2 \times 2.241 \times 10^{-10} \text{ M} = 4.482 \times 10^{-10} \text{M}$$

Question 68. The solubility product constant of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.

Solution. $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}; \quad K_{sp} = 1.1 \times 10^{-12}$

$s \quad 2s \quad s$

(Solubility of Ag_2CrO_4 is s mol L^{-1})

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

$$K_{sp} = (2s)^2 \cdot s = 4s^3$$

or $$s^3 = \frac{K_{sp}}{4} = \frac{1.1 \times 10^{-12}}{4} = 0.275 \times 10^{-12}$$

$$s^3 = 2.75 \times 10^{-13}$$

$$3 \log s = \log 2.75 \times 10^{-13}$$

$$3 \log s = -13 + 0.4393 = -12.5607$$

$$\log s = \frac{-12.5607}{3} = -4.1869 = \bar{5}.8131$$

$$s = \text{antilog } \bar{5}.8131 = 6.503 \times 10^{-5}\ \text{M}$$

Solubility of $[Ag_2CrO_4] = 6.503 \times 10^{-5}$ M

$$\underset{s}{AgBr} \rightleftharpoons \underset{s}{Ag^+} + \underset{s}{Br^-};\ K_{sp} = 5.0 \times 10^{-13}$$

(Solubility of AgBr is s mol L^{-1})

$$K_{sp} = [Ag^+][Br^-] = s \cdot s = s^2$$

or $$s = \sqrt{K_{sp}} = \sqrt{5.0 \times 10^{-13}} = \sqrt{50 \times 10^{-14}}$$

$$s = 7.07 \times 10^{-7}\ \text{M}$$

Ratio of their solubilities

$$\frac{s\,(Ag_2CrO_4)}{s\,(AgBr)} = \frac{6.50 \times 10^{-5}\ \text{M}}{7.07 \times 10^{-7}\ \text{M}} = 91.93 \approx 92$$

Ag_2CrO_4 is 92 times more soluble than AgBr.

Question 69. **Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead precipitation of copper iodate? (For cupric iodate $K_{sp} = 7.4 \times 10^{-8}$)**

(i) For precipitation, ionic product > K_{sp}, so first find concentration, (mol L^{-1}) of Cu^{2+} ions and IO_3^- ions in mixture and then ionic product of $[Cu^{2+}]$ and $[IO_3^-]$.

(ii) If ionic product $> K_{sp}$, precipitation of $Cu(IO_3)_2$ will take place, otherwise not.

Solution. $$2NaIO_3 + Cu(ClO_3)_2 \longrightarrow 2NaClO_3 + \underset{\text{copper iodate}}{Cu(IO_3)_2}$$

$$[Cu^{2+}]_{mix} = \frac{0.002}{2} = 0.001\ \text{M}$$

$$[IO_3^-]_{mix} = \frac{0.002}{2} = 0.001\ \text{M}$$

(Due to mixing of equal volumes, molar concentrations of each species is halved.)

$$Cu(IO_3)_2 \rightleftharpoons Cu^{2+} + 2IO_3^-$$

$Cu(IO_3)_2$ is precipitated if $[Cu^{2+}] \cdot [IO_3^-]^2 > K_{sp}$

$$[Cu^{2+}].[IO_3^-]^2 = (1.0 \times 10^{-3}) \times (1.0 \times 10^{-3})^2 = 1 \times 10^{-9}$$

It is less than K_{sp} of $Cu(IO_3)_2$ (7.4×10^{-8}). Hence, there will be no precipitation.

Question 70. **The ionization constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water?**

(i) In order to find the hydrolysis constant of silver benzoate, first write the equation of ionization of benzoic acid and ionization of silver benzoate and find a relation of K_3 (hydrolysis constant) with $K_1 (K_{sp})$ and K_a.

(ii) Find $[H^+]$ concentration to find s (solubility of silver benzoate) in buffer.

(iii) Find solubility of silver benzoate in aqueous solution and compare them.

Solution.

$$C_6H_5COOAg(s) \rightleftharpoons C_6H_5COO^- + Ag^+; \quad K_1 = K_{sp}$$

$$C_6H_5COO^- + H^+ \rightleftharpoons C_6H_5COOH; \quad K_2 = \frac{1}{K_a}$$

$$C_6H_5COOAg\,(s) + H^+ \rightleftharpoons C_6H_5COOH + Ag^+; \quad K_3 = \frac{K_{sp}}{K_a}$$

$$K_3 = \frac{[C_6H_5COOH]\,[Ag^+]}{[H^+]} = \frac{s \cdot s}{[H^+]} = \frac{s^2}{[H^+]} = \frac{K_{sp}}{K_a}$$

where, s is the solubility of C_6H_5COOAg.

In a buffer of pH = 3.19

$$\log [H^+] = -3.19 = \bar{4}.81$$

$$[H^+] = \text{antilog}\,\bar{4}.81 = 6.46 \times 10^{-4}$$

$$\frac{s^2}{[H^+]} = \frac{K_{sp}}{K_a} \text{ or } s^2 = \frac{K_{sp} \times [H^+]}{K_a}$$

$$s = \sqrt{\frac{2.5 \times 10^{-13} \times 6.46 \times 10^{-4}}{6.46 \times 10^{-5}}}$$

$$s = \sqrt{2.5 \times 10^{-13} \times 10}$$

$$s = 1.6 \times 10^{-6}\ \text{M (in buffer)}$$

In aqueous solution, solubility of C_6H_5COOAg :

$$K_{sp} = [C_6H_5COO^-]\,[Ag^+] = s \cdot s = s^2$$

$$s = \sqrt{K_{sp}} = \sqrt{2.5 \times 10^{-13}} = 5 \times 10^{-7}\text{M}$$

$$\frac{s_{(C_6H_5COOAg)} \text{ in buffer}}{s_{(C_6H_5COOAg)} \text{ in aqueous solution}} = \frac{1.6 \times 10^{-6}}{5.0 \times 10^{-7}} = 3.2$$

C_6H_5COOAg is 3.2 times more soluble in buffer than in pure water.

Question 71. What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide ? (For iron sulphide, $K_{sp} = 6.3 \times 10^{-18}$)

Solution. FeS is at the point of precipitation when

$$[Fe^{2+}]\,[S^{2-}] = K_{sp}$$

$$[Fe^{2+}] = [S^{2-}] = \sqrt{K_{sp}} = \sqrt{6.3 \times 10^{-18}}$$

$$[Fe^{2+}] = [S^{2-}] = 2.51 \times 10^{-9}\ M$$

Since, equimolar solutions are to be mixed, hence on mixing concentration is halved. Thus, in original solution

$$[FeSO_4] = [Na_2S] = 2 \times 2.51 \times 10^{-9}\ M = 5.02 \times 10^{-9} M$$

Question 72. What is the minimum volume of water required to dissolved 1g of calcium sulphate at 298 K ? (For calcium sulphate, K_{sp} is 9.1×10^{-6}).

Solution. $CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$; $K_{sp} = 9.1 \times 10^{-6}$

$s \quad s \quad s$

where s is the solubility of $CaSO_4$.

$$K_{sp} = [Ca^{2+}][SO_4^{2-}] = s \cdot s = s^2$$

$$s = \sqrt{K_{sp}} = \sqrt{9.1 \times 10^{-6}}$$

$$s = 3.017 \times 10^{-3}\ M$$

$\therefore$ $CaSO_4$ solubility $= 3.017 \times 10^{-3} mol\ L^{-1}$

$= 3.017 \times 10^{-3} \times 136\ gL^{-1}$

(Molar mass of $CaSO_4 = 136\ g\ mol^{-1}$)

$= 410.3 \times 10^{-3} gL^{-1}$

410.3×10^{-3} g $CaSO_4$ is dissolved in 1 L.

Therefore, 1 g $CaSO_4$ is dissolved in $\dfrac{1 \times 1}{410.3 \times 10^{-3}} = 2.437\ L$

Question 73. The concentration of sulphide ion in 0.1 M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19} M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following : $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$, in which of these solutions precipitation will take place ?

(Given, K_{sp} of FeS $= 6.3 \times 10^{-18}$, K_{sp} of MnS $= 2.5 \times 10^{-13}$

K_{sp} of ZnS $= 1.6 \times 10^{-24}$, K_{sp} of CdS $= 8.0 \times 10^{-27}$)

For precipitation, ionic product > solubility product, so calculate ionic product of each salt and compare it with solubility product.

Solution. $[S^{2-}] = 1 \times 10^{-19}$ M

10 mL of S^{2-} is mixed with 5 mL of 0.04 M solution of different solutes so that final volume of solution is 15 mL.

$$\therefore \quad [S^{2-}]_{mix} = \frac{10 \times 10^{-19}}{15} = 6.67 \times 10^{-20}\ M$$

$$[M^{2+}] = \frac{5 \times 0.04}{15} = 1.33 \times 10^{-2}\ M$$

where, $[M^{2+}] = Fe^{2+}, Mn^{2+}, Zn^{2+}$ or Cd^{2+}

$$[M^{2+}][S^{2-}] = 1.33 \times 10^{-2} \times 6.67 \times 10^{-20}$$

Ionic product of $[M^{2+}][S^{2-}] = 8.87 \times 10^{-22}$

IP of $[M^{2+}][S^{2-}] > K_{sp}$ of ZnS and CdS

So, these ($CdCl_2$ and $ZnCl_2$) are precipitated as CdS and ZnS.

Selected NCERT Exemplar Problems

Short Answer Type

Question 1. The ionization of hydrogen chloride in water is given below

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

Label two conjugate acid-base pairs in this ionization.

Adds proton

Solution. $HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

Acid	Base	Conjugate acid	Conjugate base
$HCl(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$Cl^-(aq)$

Loses proton

Question 2. Ionization constant of a weak base MOH, is given by the expression

$$K_b = \frac{[M^+][OH^-]}{[MOH]}$$

Values of ionization constant of some weak bases at a particular temperature are given below :

Base	Dimethyl amine	Urea	Pyridine	Ammonia
K_b	5.4×10^{-4}	1.3×10^{-14}	1.77×10^{-9}	1.77×10^{-5}

Arrange the bases in decreasing order of the extent of their ionization at equilibrium. Which of the above base is the strongest?

Solution. Greater the ionization constant (K_b) of a base, greater is its ionization. Hence, dimethyl amine is the strongest base.

	Dimethyl amine >	ammonia >	pyridine >	urea
K_b	5.4×10^{-4}	1.77×10^{-5}	1.77×10^{-9}	1.3×10^{-14}

Question 3. Conjugate acid of a weak base is always stronger. What will be the decreasing order of basic strength of the following conjugate bases?

$$OH^-, RO^-, CH_3COO^-, Cl^-$$

Solution. Conjugate acids of the given bases are, H_2O, ROH, CH_3COOH and HCl. Order of acidic strength is

$$HCl > CH_3COOH > H_2O > ROH$$

Hence, order of basic strength of their conjugate bases is

$$R\bar{O} > \bar{O}H > CH_3CO\bar{O} > Cl^-$$

Question 4. **Arrange the following in increasing order of pH.**

$$KNO_3(aq), CH_3COONa(aq), NH_4Cl(aq), C_6H_5COONH_4(aq)$$

Solution. (i) KNO_3 is a salt of strong acid-strong base, hence its aqueous solution is neutral; $pH = 7$

(ii) CH_3COONa is a salt of weak acid and strong base, hence, its aqueous solution is basic; $pH > 7$.

(iii) NH_4Cl is a salt of strong acid and weak base, hence its aqueous solution is acidic; $pH < 7$.

(iv) $C_6H_5COONH_4$ is a salt of weak acid, C_6H_5COOH and weak base, NH_4OH. But NH_4OH is slightly stronger than C_6H_5COOH. Hence, pH is slightly > 7.

Therefore, increasing order of pH of the given salts is,

$$NH_4Cl < KNO_3 < C_6H_5COONH_4 < CH_3COONa$$

Question 5. **On the basis of the equation $pH = -\log[H^+]$, the pH of 10^{-8} mol dm^{-3} solution of HCl should be 8. However, it is observed to be less than 7.0. Explain the reason.**

Solution. Concentration 10^{-8} mol dm^{-3} indicates that the solution is very dilute. So, we cannot neglect the contribution of H_3O^+ ions produced from H_2O in the solution. Total $[H_3O^+] = 10^{-8} + 10^{-7}$ M. From this we get the value of pH close to 7 but less than 7 because the solution is acidic.

Question 6. **pH of a solution of a strong acid is 5.0. What will be the pH of the solution obtained after diluting the given solution 100 times?**

Solution. $pH = 5$

$$[H^+] = 10^{-5} \text{ mol L}^{-1}$$

On diluting the solution 100 times, $[H^+] = \dfrac{10^{-5}}{100} = 10^{-7} \text{ mol L}^{-1}$

Total H^+ ion concentration = H^+ ions from acid + H^+ ion from water

$$[H^+] = 10^{-7} + 10^{-7} = 2 \times 10^{-7} \text{ M}$$

$$pH = -\log[2 \times 10^{-7}]$$

$$pH = 7 - 0.3010 = 6.699$$

Question 7. **A sparingly soluble salt gets precipitated only when the product of concentration of its ions in the solution (K_{sp}) becomes greater than its solubility product. If the solubility of $BaSO_4$ in water is 8×10^{-4}mol dm^{-3}, calculate its solubility in 0.01 mol dm^{-3} of H_2SO_4.**

Solution.

$$\underset{(1-s)}{BaSO_4(s)} \rightleftharpoons \underset{s}{Ba^{2+}(aq)} + \underset{s}{SO_4^{2-}(aq)}$$

At equili.

$$K_{sp} \text{ for } BaSO_4 = [Ba^{2+}][SO_4^{2-}] = s \times s = s^2$$

But $s = 8 \times 10^{-4}$ mol dm^{-3}

$\therefore$ $K_{sp} = (8 \times 10^{-4})^2 = 64 \times 10^{-8}$

In the presence of 0.01 M H_2SO_4, the expression for K_{sp} will be

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

$$K_{sp} = (s) \cdot (s + 0.01)$$

(0.01 M SO_4^{2-} ions from 0.01 M H_2SO_4)

$$64 \times 10^{-8} = s \cdot (s + 0.01)$$

$$s^2 + 0.01\,s - 64 \times 10^{-8} = 0$$

$$s = \frac{-0.01 \pm \sqrt{(0.01)^2 + (4 \times 64 \times 10^{-8})}}{2}$$

$$= \frac{-0.01 \pm \sqrt{10^{-4} + (256 \times 10^{-8})}}{2}$$

$$= \frac{-0.01 \pm \sqrt{10^{-4}\,(1 + 256 \times 10^{-4})}}{2}$$

$$= \frac{-0.01 \pm 10^{-2}\sqrt{1 + 0.0256}}{2} = \frac{10^{-2}\,(-1 \pm 1.012719)}{2}$$

$$= 5 \times 10^{-3}\,(-1 + 1.012719) = 6.4 \times 10^{-5} \text{ mol dm}^{-3}$$

Note $s <<< 0.01$, so, $s + 0.01 \approx 0.01$ and $64 \times 10^{-8} = s \times 0.01$

$$s = \frac{64 \times 10^{-8}}{0.01} = 6.4 \times 10^{-5}$$

Question 8. Calculate the pH of a solution formed by mixing equal volumes of two solutions, *A* and *B* of a strong acid having pH= 6 and pH=4 respectively.

Solution. pH of solution $A = 6$. Hence, $[H^+] = 10^{-6}$ mol L^{-1}

pH of solution $B = 4$. Hence, $[H^+] = 10^{-4}$ mol L^{-1}

On mixing 1 L of each solution, molar concentration of total H^+ is halved.

$$\text{Total, } [H^+] = \frac{10^{-6} + 10^{-4}}{2} \text{ mol L}^{-1}$$

$$[H^+] = \frac{1.01 \times 10^{-4}}{2} = 5.05 \times 10^{-5} \text{ mol L}^{-1}$$

$$[H^+] = 5.0 \times 10^{-5} \text{ mol L}^{-1}$$

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

$$pH = -\log (5.0 \times 10^{-5})$$

$$pH = -[\log 5 + (-5 \log 10)]$$

$$pH = -\log 5 + 5$$

$$pH = 5 - \log 5 = 5 - 0.6990$$

$$pH = 4.3010 \approx 4.3$$

Question 9. Calculate the volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution (K_{sp} of $PbCl_2 = 3.2 \times 10^{-8}$, atomic mass of Pb = 207 u).

Solution. Suppose solubility of $PbCl_2$ in water is s mol L^{-1}.

$$\underset{(1-s)}{PbCl_2(s)} \rightleftharpoons \underset{s}{Pb^{2+}(aq)} + \underset{2s}{2Cl^-(aq)}$$

$$K_{sp} = [Pb^{2+}] \cdot [Cl^-]^2$$

$$K_{sp} = [s]\,[2s]^2 = 4s^3$$

$$3.2 \times 10^{-8} = 4s^3$$

$$s^3 = \frac{3.2 \times 10^{-8}}{4} = 0.8 \times 10^{-8}$$

$$s^3 = 8.0 \times 10^{-9}$$

Solubility of $PbCl_2$, $s = 2 \times 10^{-3}$ mol L^{-1}

Solubility of $PbCl_2$ in g $L^{-1} = 278 \times 2 \times 10^{-3} = 0.556$ g L^{-1}

(∵ Molar mass of $PbCl_2 = 207 + (2 \times 35.5) = 278$)

0.556 g of $PbCl_2$ dissolve in 1 L of water.

$\therefore$ 0.1 g of $PbCl_2$ will dissolve in $\frac{1 \times 0.1}{0.556}$ L of water

$= 0.1798$ L $= 179.8$ mL

Question 10. Following data is given for the reaction,

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g); \quad \Delta_f H^\circ[CaO(s)] = -635.1 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ[CO_2(g)] = -393.5 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ[CaCO_3(s)] = -1206.9 \text{ kJ mol}^{-1}$$

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

Solution. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$\Delta_r H^\circ = \Delta_f H^\circ[CaO(s)] + \Delta_f H^\circ[CO_2(g)] - \Delta_f H^\circ[CaCO_3(s)]$$

$$\therefore \quad \Delta_r H^\circ = -635.1 + (-393.5) - (-1206.9) = 178.3 \text{ kJ mol}^{-1}$$

Because ΔH value is positive, so the reaction is endothermic. Hence, according to Le-Chatelier's principle, reaction will proceed in forward direction on increasing temperature.

Long Answer Type

Question 11. How can you predict the following stages of a reaction by comparing the value of K_c and Q_c?

(i) Net reaction proceeds in the forward direction.
(ii) Net reaction proceeds in the backward direction.
(iii) No net reaction occurs.

Solution. (i) If $Q_c < K_c$, the reaction will proceed in the direction of the products (forward reaction).

(ii) $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse reaction).

(iii) If $Q_c = K_c$, the reaction mixture is already at equilibrium.

Question 12. On the basis of Le-Chatelier's principle, explain how temperature and pressure can be adjusted to increase the yield of ammonia in the following reaction?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \quad \Delta H = -92.38 \text{ kJ mol}^{-1}$$

What will be the effect of addition of argon to the above reaction mixture at constant volume?

Solution. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \Delta H = -92.38 \text{ kJ mol}^{-1}$

It is an exothermic process. According to Le-Chatelier's principle, low temperature is favourable for high yield of ammonia, but practically very low temperatures slow down the reaction. So, optimum temperature, 700 K is favourable in attainment of equilibrium.

Similarly, high pressure about 200 atm is favourable for high yield of ammonia. On increasing pressure, reaction goes in the forward direction because the number of moles decreases in the forward direction.

At constant volume addition of argon does not affect the equilibrium because it does not change the partial pressures of the reactants or products involved in the reaction and the equilibrium remains undisturbed.

Question 13. Write a relation between ΔG and Q and define the meaning of each term and answer the following :

(a) Why a reaction proceeds forward when $Q < K$ and no net reaction occurs when $Q = K$?

(b) Explain the effect of increase in pressure in terms of reaction quotient Q for the reaction.

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

Solution. $\Delta G = \Delta G^\circ + RT \ln Q$

ΔG° = change in free energy as the reaction proceeds
ΔG = standard free energy
Q = reaction quotient
R = gas constant
T = absolute temperature

(a) Since, $\Delta G^\circ = -RT \ln K$

$$\therefore \quad \Delta G = -RT \ln K + RT \ln Q$$

$$\Delta G = RT \ln \frac{Q}{K}$$

If $Q < K$, ΔG will be negative and the reaction proceeds in the forward direction.

If $Q = K$, $\Delta G = 0$ reaction is in equilibrium and there is no net reaction.

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

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

On increasing pressure, volume decreases. If we doubled the pressure, volume will be halved but the molar concentrations will be doubled. Then

$$Q_c = \frac{2[CH_4]\cdot 2[H_2O]}{2[CO]\{2[H_2]\}^3} = \frac{1}{4}\frac{[CH_4][H_2O]}{[CO][H_2]^3} = \frac{1}{4}K_c$$

Therefore, Q_c is less than K_c, so Q_c will tend to increase to reestablish equilibrium and the reaction will go in forward direction.