CHEMISTRY

HIGHER SECONDARY - FIRST YEAR

VOLUME - I

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Untouchability is a crime
Untouchability is inhuman

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PREFACE

Where has chemistry come from ? Throughout the history of the human race, people have struggled to make sense of the world around them. Through the branch of science we call chemistry we have gained an understanding of the matter which makes up our world and of the interactions between particles on which it depends. The ancient Greek philosophers had their own ideas of the nature of matter, proposing atoms as the smallest indivisible particles. However, although these ideas seems to fit with modern models of matter, so many other Ancient Greek ideas were wrong that chemistry cannot truly be said to have started there.

Alchemy was a mixture of scientific investigation and mystical quest, with strands of philosophy from Greece, China, Egypt and Arabia mixed in. The main aims of alchemy that emerged with time were the quest for the **elixir of life** (the drinking of which would endue the alchemist with immortality), and the search for the **philosopher's stone**, which would turn base metals into gold. Improbable as these ideas might seem today, the alchemists continued their quests for around 2000 years and achieved some remarkable successes, even if the elixir of life and the philosopher's stone never appeared.

Towards the end of the eighteenth century, pioneering work by Antoine and Marie Lavoisier and by John Dalton on the chemistry of air and the atomic nature of matter paved the way for modern chemistry. During the nineteenth century chemists worked steadily towards an understanding of the relationships between the different chemical elements and the way they react together. A great body of work was built up from careful observation and experimentation until the relationship which we now represent as the periodic table emerged. This brought order to the chemical world, and from then on chemists have never looked back.

Modern society looks to chemists to produce, amongst many things, healing drugs, pesticides and fertilisers to ensure better crops and chemicals for the many synthetic materials produced in the twenty-first century. It also looks for an academic understanding of how matter works and how the environment might be protected from the source of pollutants. Fortunately, chemistry holds many of the answers !

Following the progressing trend in chemistry, it enters into other branches of chemistry and answers for all those miracles that are found in all living organisms. The present book is written after following the revised syllabus, keeping in view with the expectations of National Council of Educational Research & Training (NCERT). The questions that are given in each and every chapter can be taken only as model questions. A lot of self evaluation questions, like, choose the best answer, fill up the blanks and very short answer type questions are given in all chapters. **While preparing for the examination, students should not restrict themselves, only to the questions/problems given in the self evaluation. They must be prepared to answer the questions and problems from the entire text.**

Learning objectives may create an awareness to understand each and every chapter.

Sufficient reference books are suggested so as to enable the students to acquire more informations about the concepts of chemistry.

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Chairperson
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& XI Std Chemistry Text Book Writing Committee

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Syllabus : Higher Secondary - First Year Chemistry
INORGANIC CHEMISTRY

Unit I - Chemical Calculations

Significant figures - SI units - Dimensions - Writing number in scientific notation - Conversion of scientific notation to decimal notation - Factor label method - Calculations using densities and specific gravities - Calculation of formula weight - Understanding Avogadro's number - Mole concept-mole fraction of the solvent and solute - Conversion of grams into moles and moles into grams - Calculation of empirical formula from quantitative analysis and percentage composition - Calculation of molecular formula from empirical formula - Laws of chemical combination and Dalton's atomic theory - Laws of multiple proportion and law of reciprocal proportion - Postulates of Dalton's atomic theory and limitations - Stoichiometric equations - Balancing chemical equation in its molecular form - Oxidation reduction-Oxidation number - Balancing Redox equation using oxidation number - Calculations based on equations. - Mass/Mass relationship - Methods of expressing concentration of solution - Calculations on principle of volumetric analysis - Determination of equivalent mass of an element - Determination of equivalent mass by oxide, chloride and hydrogen displacement method - Calculation of equivalent mass of an element and compounds - Determination of molar mass of a volatile solute using Avogadro's hypothesis.

Unit 2 - Environmental Chemistry

Environment - Pollution and pollutants - Types of pollution - Types of pollutants - Causes for pollution - Effects of pollution - General methods of prevention of environmental pollution.

Unit 3 - General Introduction to Metallurgy

Ores and minerals - Sources from earth, living system and in sea - Purification of ores-Oxide ores sulphide ores magnetic and non magnetic ores - Metallurgical process - Roasting-oxidation - Smelting-reduction - Bessemerisation - Purification of metals-electrolytic and vapour phase refining - Mineral wealth of India.

Unit 4 - Atomic Structure - I

Brief introduction of history of structure of atom - Defects of Rutherford's model and Niels Bohr's model of an atom - Sommerfeld's extension of atomic structure - Electronic configuration and quantum numbers - Orbitals-shapes of s, p and d orbitals. - Quantum designation of electron - Pauli's exclusion principle - Hund's rule of maximum multiplicity - Aufbau principle - Stability of orbitals - Classification of elements based on electronic configuration.

Unit 5 - Periodic Classification - I

Brief history of periodic classification - IUPAC periodic table and IUPAC nomenclature of elements with atomic number greater than 100 - Electronic configuration and periodic table - Periodicity of properties Anomalous periodic properties of elements.

Unit 6 - Group-1s Block elements

Isotopes of hydrogen - Nature and application - Ortho and para hydrogen - Heavy water - Hydrogen peroxide - Liquid hydrogen as a fuel - Alkali metals - General characteristics - Chemical properties - Basic nature of oxides and hydroxides - Extraction of lithium and sodium - Properties and uses.

Unit 7 - Group - 2s - Block elements

General characteristics - Magnesium - Compounds of alkaline earth metals.

Unit 8 -p- Block elements

General characteristics of p-block elements - Group-13. Boron Group - Important ores of Boron - Isolation of Born-Properties - Compounds of Boron-Borax, Boranes, diboranes, Borazole-preparation. properties - Uses of Boron and its compounds - Carbon group - Group -14 - Allotropes of carbon - Structural difference of graphite and diamond - General physical and chemical properties of oxides, carbides, halides and sulphides of carbon group - Nitrogen - Group-15 - Fixation of nitrogen - natural and industrial - HNO_3-Ostwald process - Uses of nitrogen and its compounds - Oxygen - Group-16 - Importance of molecular oxygen-cell fuel - Difference between nascent oxygen and molecular oxygen - Oxides classification, acidic basic, amphoteric, neutral and peroxide - Ozone preparation, property and structure - Factors affecting ozone layer.

Physical Chemistry

Unit 9 - Solid State - I

Classification of solids-amorphous, crystalline - Unit cell - Miller indices - Types of lattices belong to cubic system.

Unit 10 - Gaseous State

Four important measurable properties of gases - Gas laws and ideal gas equation - Calculation of gas constant "R" - Dalton's law of partial pressure - Graham's law of diffusion - Causes for deviation of real gases from ideal behaviour - Vanderwaal's equation of state - Critical phenomena - Joule-Thomson effect and inversion temperature - Liquefaction of gases - Methods of Liquefaction of gases.

Unit 11 - Chemical Bonding

Elementary theories on chemical bonding - Kossel-Lewis approach - Octet rule - Types of bonds - Ionic bond - Lattice energy and calculation of lattice energy using Born-Haber cycle - Properties of electrovalent compounds - Covalent bond - Lewis structure of Covalent bond - Properties of covalent compounds - Fajan's rules - Polarity of Covalent bonds - VSEPR Model - Covalent bond through valence bond approach - Concept of resonance - Coordinate covalent bond.

Unit 12 - Colligative Properties

Concept of colligative properties and its scope - Lowering of vapour pressure - Raoul's law - Ostwald - Walker method - Depression of freezing point of dilute solution - Beckmann method - Elevation of boiling point of dilute solution - Cotrell's method - Osmotic pressure - Laws of Osmotic pressure - Berkley-Hartley's method - Abnormal colligative properties Van't Hoff factor and degree of dissociation.

Unit 13 - Thermodynamics - I

Thermodynamics - Scope - Terminology used in thermodynamics - Thermodynamic properties - nature - Zeroth law of thermodynamics - Internal energy - Enthalpy - Relation between "H and "E - Mathematical form of First law - Enthalpy of transition - Enthalpy of formation - Enthalpy of combustion -

Enthalpy of neutralisation - Various sources of energy-Non-conventional energy resources.

Unit 14 - Chemical Equilibrium - I

Scope of chemical equilibrium - Reversible and irreversible reactions - Nature of chemical equilibrium - Equilibrium in physical process - Equilibrium in chemical process - Law of chemical equilibrium and equilibrium constant - Homogeneous equilibria - Heterogeneous equilibria.

Unit 15 - Chemical Kinetics - I

Scope - Rate of chemical reactions - Rate law and rate determining step - Calculation of reaction rate from the rate law - Order and molecularity of the reactions - Calculation of exponents of a rate law - Classification of rates based on order of the reactions.

ORGANIC CHEMISTRY

Unit 16 - Basic Concepts of Organic Chemistry

Catenation - Classification of organic compounds - Functional groups - Nomenclature - Isomerism - Types of organic reactions - Fission of bonds - Electrophiles and nucleophiles - Carbonium ion Carbanion - Free radicals - Electron displacement in covalent bond.

Unit 17 - Purification of Organic compounds

Characteristics of organic compounds - Crystallisation - Fractional Crystallisation - Sublimation - Distillation - Fractional distillation - Steam distillation - Chromotography.

Unit 18 - Detection and Estimation of Elements

Detection of carbon and hydrogen - Detection of Nitrogen - Detection of halogens - Detection of sulphur - Estimation of carbon and hydrogen - Estimation of Nitrogen - Estimation of sulphur - Estimation of halogens.

Unit 19 - Hydrocarbons

Classification of Hydrocarbons - IUPAC nomenclature - Sources of alkanes - General methods of preparation of alkanes - Physical properties -

Chemical properties - Conformations of alkanes - Alkenes - IUPAC nomenclature of alkenes - General methods of preparation - Physical properties - Chemical properties - Uses - Alkynes - IUPAC Nomenclature of alkynes - General methods of preparation - Physical properties - Chemical properties - Uses.

Unit 20 - Aromatic Hydrocarbons

Aromatic Hydrocarbons - IUPAC nomenclature of aromatic hydrocarbons - Structure of Benzene - Orientation of substituents on the benzene ring - Commercial preparation of benzene - General methods of preparation of Benzene and its homologues - Physical properties - Chemical properties - Uses - Carcinogenic and toxic nature.

Unit 21 - Organic Halogen Compounds

Classification of organic hydrogen compounds - IUPAC nomenclature of alkyl halides - General methods of preparation - Properties - Nucleophilic substitution reactions - Elimination reactions - Uses - Aryl halide - General methods of preparation - Properties - Uses - Aralkyl halides - Comparison arylhalides and aralkyl halides - Grignard reagents - Preparation - Synthetic uses.

CHEMISTRY PRACTICALS FOR STD XI

I. Knowledge of using Burette, Pipette and use of logarithms is to be demonstrated.

II. Preparation of Compounds.

1. Copper Sulphate Crystals from amorphous copper sulphate solutions

2. Preparation of Mohr's Salt

3. Preparation of Aspirin

4. Preparation of Iodoform

5. Preparation of tetrammine copper (II) sulphate

III. Identification of one cation and one anion from the following. (Insoluble salt should not be given)

Cation : Pb^{++}, Cu^{++}, Al^{++}, Mn^{2+}, Zn^{++}, Ca^{++}, Ba^{++}, Mg^{++}, NH_4^+.

Anions : Borate, Sulphide, Sulphate, Carbonate, Nitrate, Chloride, Bromide.

IV. Determination of Melting point of a low melting solid.

V. Acidimetry Vs Alkalimetry

1. Preparation of Standard solution of Oxalic acid and Sodium Carbonate solution.

2. Titration of HCl Vs NaOH

3. Titration of HCl Vs Na_2CO_3

4. Titration of Oxalic acid Vs NaOH

CONTENTS

INORGANIC CHEMISTRY

1. CHEMICAL CALCULATION

OBJECTIVES

* *Know the method of finding formula weight of different compounds.*

* *Recognise the value of Avogadro number and its significance.*

* *Learn about the mole concept and the conversions of grams to moles.*

* *Know about the empirical and molecular formula and understand the method of arriving molecular formula from empirical formula.*

* *Understand the stoichiometric equation.*

* *Know about balancing the equation in its molecular form.*

* *Understand the concept of reduction and oxidation.*

* *Know about the method of balancing redox equation using oxidation number.*

1.1 Formula Weight (FW) or Formula Mass

The formula weight of a substance is the sum of the atomic weights of all atoms in a formula unit of the compound, whether molecular or not.

Sodium chloride, NaCl, has a formula weight of 58.44 amu (22.99 amu from Na plus 35.45 amu from Cl). NaCl is ionic, so strictly speaking the expression "molecular weight of NaCl" has no meaning. On the other hand, the molecular weight and the formula weight calculated from the molecular formula of a substance are identical.

Solved Problem

Calculate the formula weight of each of the following to three significant figures, using a table of atomic weight (AW): (a) chloroform $CHCl_3$ (b) Iron (III) sulfate $Fe_2 (SO_4)_3$.

Solution

a. 1 x AW of C $\quad\quad\quad$ = $\quad$ 12.0 amu

$\quad$ 1 x AW of H $\quad\quad\quad$ = $\quad$ 1.0 amu

$\quad$ 3 x AW of Cl = 3 x 35.45 $\quad$ = $\quad$ <u>106.4 amu</u>

Formula weight of $CHCl_3$ $\quad$ = $\quad$ <u>119.4 amu</u>

The answer rounded to three significant figures is 119 amu.

b. Iron(III)Sulfate

2 x Atomic weight of Fe = 2 x 55.8 = 111.6 amu

3 x Atomic weight of S = 3 x 32.1 = 96.3 amu

3 x 4 Atomic weight of O =12x16= 192.0 amu

Formula weight of $Fe_2 (SO_4)_3$ = 399.9 amu

The answer rounded to three significant figures is 4.00×10^2 amu.

Problems for Practice

Calculate the formula weights of the following compounds

a. NO_2 b. glucose $(C_6H_{12}O_6)$ c. NaOH   d. $Mg(OH)_2$

e. methanol $(CH_3 OH)$ f. PCl_3 g. $K_2 CO_3$

1.2 Avogadro's Number (N_A)

The number of atoms in a 12-g sample of carbon - 12 is called Avogadro's number (to which we give the symbol N_A).

Recent measurements of this number give the value 6.0221367×10^{23}, which is 6.023×10^{23}.

A mole of a substance contains Avogadro's number of molecules. A dozen eggs equals 12 eggs, a gross of pencils equals 144 pencils and a mole of ethanol equals 6.023×10^{23} ethanol molecules.

Significance

The molecular mass of SO_2 is 64 g mol^{-1}. 64 g of SO_2 contains 6.023×10^{23} molecules of SO_2. $2.24 \times 10^{-2}m^3$ of SO_2 at S.T.P. contains 6.023×10^{23} molecules of SO_2.

Similarly the molecular mass of CO_2 is 44 g mol^{-1}. 44g of CO_2 contains 6.023×10^{23} molecules of CO_2. $2.24 \times 10^{-2}m^3$ of CO_2 at S.T.P contains 6.023×10^{23} molecules of CO_2.

1.3 Mole concept

While carrying out reaction we are often interested in knowing the number of atoms and molecules. Some times, we have to take the atoms or molecules of different reactants in a definite ratio.

Eg. Consider the following reaction

$$2 H_2 + O_2 \rightarrow 2H_2O$$
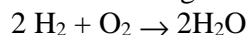
In this reaction one molecule of oxygen reacts with two molecules of hydrogen. So it would be desirable to take the molecules of H_2 and oxygen in the ratio 2:1, so that the reactants are completely consumed during the reaction. But atoms and molecules are so small in size that is not possible to count them individually.

In order to overcome these difficulties, the concept of mole was introduced. According to this concept number of particles of the substance is related to the mass of the substance.

Definition

The mole may be defined as the amount of the substance that contains as many specified elementary particles as the number of atoms in 12g of carbon - 12 isotope.

(i.e) one mole of an atom consists of Avogadro number of particles.

One mole	=	6.023×10^{23} particles
One mole of oxygen molecule	=	6.023×10^{23} oxygen molecules
One mole of oxygen atom	=	6.023×10^{23} oxygen atoms
One mole of ethanol	=	6.023×10^{23} ethanol molecules

In using the term mole for ionic substances, we mean the number of formula units of the substance. For example, a mole of sodium carbonate, Na_2CO_3 is a quantity containing 6.023×10^{23} Na_2CO_3 units. But each formula unit of Na_2CO_3 contains $2 \times 6.023 \times 10^{23}$ Na^+ ions and one CO_3^{2-} ions and $1 \times 6.023 \times 10^{23}$ CO_3^{2-} ions.

When using the term mole, it is important to specify the formula of the unit to avoid any misunderstanding.

Eg. A mole of oxygen atom (with the formula O) contains 6.023×10^{23} Oxygen atoms. A mole of oxygen molecule (formula O_2) contains 6.023×10^{23} O_2 molecules (i.e) $2 \times 6.023 \times 10^{23}$ oxygen.

Molar mass

The molar mass of a substance is the mass of one mole of the substance. The mass and moles can be related by means of the formula.

$$\text{Molar mass} = \frac{\text{Mass}}{\text{mole}}$$

Eg. Carbon has a molar mass of exactly 12g/mol.

Problems

Solved Problems

1. What is the mass in grams of a chlorine atom, Cl?
2. What is the mass in grams of a hydrogen chloride, HCl?

Solution

1. The atomic weight of Cl is 35.5 amu, so the molar mass of Cl is 35.5 g/mol. Dividing 35.5 g (per mole) by 6.023×10^{23} gives the mass of one atom.

$$\text{Mass of a Cl atom} = \frac{35.5 \text{ g}}{6.023 \times 10^{23}}$$
$$= 5.90 \times 10^{-23} \text{ g}$$

2. The molecular weight of HCl equal to the atomic weight of H, plus the atomic weight of Cl, (ie) $(1.01 + 35.5)$ amu $= 36.5$ amu. Therefore 1 mol of HCl contains 36.5 g HCl

$$\text{Mass of an HCl molecule} = \frac{36.5 \text{ g}}{6.02 \times 10^{23}}$$
$$= 6.06 \times 10^{-23} \text{g}$$

Problems For Practice

1. What is the mass in grams of a calcium atom, Ca?
2. What is mass in grams of an ethanol molecule, C_2H_5OH?
3. Calcualte the mass (in grams) of each of the following species.

a. Na atom b. S atom c. CH_3Cl molecule d. Na_2SO_3 formula unit

1.3.1 Mole Calculations

To find the mass of one mole of substance, there are two important things to know.

i. How much does a given number of moles of a substance weigh?

ii. How many moles of a given formula unit does a given mass of substance contain.

Both of them can be known by using dimensional analysis.

To illustrate, consider the conversion of grams of ethanol, C_2H_5OH, to moles of ethanol. The molar mass of ethanol is 46.1 g/mol, So, we write

1 mol C_2H_5OH = 46.1 g of C_2 H_5OH

Thus, the factor converting grams of ethanol to moles of ethanol is 1mol C_2H_5OH/46.1g C_2H_5OH. To covert moles of ethanol to grams of ethanol, we simply convert the conversion factor (46.1 g C_2H_5OH/1 mol C_2H_5OH).

Again, suppose you are going to prepare acetic acid from 10.0g of ethanol, C_2H_5OH. How many moles of C_2H_5OH is this? you convert 10.0g C_2H_5OH to moles C_2H_5OH by multiplying by the appropriate conversion factor.

$$10.0g\ C_2H_5\ OH\ x\ \frac{1\ mol\ C_2H_5OH}{46.1\ g\ C_2H_5OH}$$

$$=\ 0.217\ mol\ C_2H_5\ OH$$

1.3.2 Converting Moles of Substances to Grams

Solved Problems

1. ZnI_2, can be prepared by the direct combination of elements. A chemist determines from the amounts of elements that 0.0654 mol ZnI_2 can be formed.

Solution

The molar mass of ZnI_2 is 319 g/mol. (The formula weight is 319 amu, which is obtained by summing the atomic weight in the formula) Thus

$$0.0654\ mol\ ZnI_2\ \ x\ \frac{319\ g\ ZnI_2}{1\ mol\ ZnI_2}$$

$$=\ 20.9\ gm\ ZnI_2$$

Problems for Practice

1. H_2O_2 is a colourless liquid. A concentrated solution of it is used as a source of oxygen for Rocket propellant fuels. Dilute aqueous solutions are used as a bleach. Analysis of a solution shows that it contains 0.909 mol H_2O_2 in 1.00 L of solution. What is the mass of H_2O_2 in this volume of solution?.

2. Boric acid, H_3BO_3 is a mild antiseptic and is often used as an eye wash. A sample contains 0.543 mol H_3BO_3. What is the mass of boric acid in the sample?.

3. CS_2 is a colourless, highly inflammable liquid used in the manufacture of rayon and cellophane. A sample contains 0.0205 mol CS_2. Calculate the mass of CS_2 in the sample.

Converting Grams of Substances to Moles

In the preparation of lead(II)chromate $PbCrO_4$, 45.6 g of lead(II)chromate is obtained as a precipitate. How many moles of $PbCrO_4$ is this?

The molar mass of $PbCrO_4$ is 323 g/mol (i.e) 1 mol $PbCrO_4$ = 323 g $PbCrO_4$

Therefore,

$$\frac{45.6 \text{ g } PbCrO_4 \times 1 \text{ mol.}PbCrO_4}{323 \text{ g } PbCrO_4}$$

= 0.141 mol $PbCrO_4$

Problems for Practice

1. Nitric acid, HNO_3 is a colourless, corrosive liquid used in the manufacture of Nitrogen fertilizers and explosives. In an experiment to develop new explosives for mining operations, a 28.5 g sample of HNO_3 was poured into a beaker. How many moles of HNO_3 are there in this sample of HNO_3?

2. Obtain the moles of substances in the following.
   a. 3.43 g of C   b. 7.05 g Br_2
   c. 76g C_4H_{10} d. 35.4 g Li_2CO_3
   e. 2.57 g As   f. 7.83 g P_4
   g. 41.4 g N_2H_4 h. 153 g $Al_2(SO_4)_3$

Calculation of the Number of Molecules in a Given Mass

Solved Problem

How many molecules are there in a 3.46 g sample of hydrogen chloride, HCl?

Note: The number of molecules in a sample is related to moles of compound (1 mol HCl = 6.023 x 10^{23} HCl molecules). Therefore if you first convert grams HCl to moles, then you can convert moles to number of molecules).

Solution

$$3.46\text{g HCl x} \frac{1\,\text{mol HCl}}{36.5\text{g HCl}} \text{ x } \frac{6.023 \times 10^{23}\,\text{HCl molecules}}{1\,\text{mol HCl}}$$

$$= 5.71 \times 10^{22} \text{ HCl molecules}$$

Problems for Practice

1. How many molecules are there in 56mg HCN?

2. Calculate the following
a. Number of molecules in 43g NH_3
b. Number of atoms in 32.0 g Br_2
c. Number of atoms in 7.46 g Li

1.4 Calculation of Empirical Formula from Quantitative Analysis and Percentage composition

Empirical Formula

"An empirical formula (or) simplest formula for a compound is the formula of a substance written with the smallest integer subscripts".

For most ionic substances, the empirical formula is the formula of the compound. This is often not the case for molecular substances. For example, the formula of sodium peroxide, an ionic compound of Na^+ and O_2^{2-}, is Na_2O_2. Its empirical formula is NaO. Thus empirical formula tells you the ratio of numbers of atoms in the compound.

Steps for writing the Empirical formula

The percentage of the elements in the compound is determined by

suitable methods and from the data collected, the empirical formula is determined by the following steps.

i.   Divide the percentage of each element by its atomic mass. This will give the relative number of moles of various elements present in the compound.

ii. Divide the quotients obtained in the above step by the smallest of them so as to get a simple ratio of moles of various elements.

iii. Multiply the figures, so obtained by a suitable integer of necessary in order to obtain whole number ratio.

iv. Finally write down the symbols of the various elements side by side and put the above numbers as the subscripts to the lower right hand of each symbol. This will represent the empirical formula of the compound.

Solved Problem

A compound has the following composition Mg = 9.76%, S = 13.01%, 0 = 26.01, H_2O = 51.22, what is its empirical formula?

[Mg = 24, S = 32, O = 16, H = 1]

Solution

Element	%	Relative No. of moles	Simple ratio moles	Simplest whole No. ratio
Magnesium	9.76	$\dfrac{9.76}{24} = 0.406$	$\dfrac{0.406}{0.406} = 1$	1
Sulphur	13.01	$\dfrac{13.01}{32} = 0.406$	$\dfrac{0.406}{0.406} = 1$	1
Oxygen	26.01	$\dfrac{26.01}{16} = 1.625$	$\dfrac{1.625}{0.406} = 4$	4
Water	51.22	$\dfrac{51.22}{18} = 2.846$	$\dfrac{2.846}{0.406} = 7$	7

Hence the empirical formula is Mg $SO_4.7H_2O$.

Problems for Practice

1. A substance on analysis, gave the following percentage composition, Na = 43.4%, C = 11.3%, 0 = 43.3% calculate its empirical formula [Na = 23, C = 12, O = 16].

Ans:- Na_2CO_3

2. What is the simplest formula of the compound which has the following percentage composition: Carbon 80%, hydrogen 20%.

Ans:- CH_3

3. A compound on analysis gave the following percentage composition: C - 54.54%, H = 9.09%, 0 = 36.36%

Ans:- C_2H_4O

1.4.1   Molecular Formula from Empirical Formula

The molecular formula of a compound is a multiple of its empirical formula.

Example

The molecular formula of acetylene, C_2H_2 is equivalent to $(CH)_2$, and the molecular formula of benzene, C_6H_6 is equivalent to $(CH)_6$. Therefore, the molecular weight is some multiple of the empirical formula weight, which is obtained by summing the atomic Weights from the empirical formula. For any molecular compound.

Molecular Weight = n x empirical formula weight.

Where `n' is the whole number of empirical formula units in the molecule. The molecular formula can be obtained by multiplying the subscripts of the empirical formula by `n' which can be calculated by the following equation

$$n \ = \ \frac{Molecular \ Weight}{Empirical \ formula \ Weight}$$

Steps for writing the molecular formula

i.   Calculate the empirical formula

ii. Find out the empirical formula mass by adding the atomic mass of all the atoms present in the empirical formula of the compound.

iii. Divide the molecular mass (determined experimentally by some

suitable method) by the empirical formula mass and find out the value of n which is a whole number.

iv. Multiply the empirical formula of the compound with n, so as to find out the molecular formula of the compound.

Solved Problem

1. A compound on analysis gave the following percentage composition C = 54.54%, H, 9.09% 0 = 36.36. The vapour density of the compound was found to be 44. Find out the molecular formula of the compound.

Solution

Calculation of empirical formula

Element	%	Relative No. of moles	Simple ratio moles	Simplest whole No. ratio
C	54.54	$\dfrac{54.54}{12} = 4.53$	$\dfrac{4.53}{2.27} = 2$	2
H	9.09	$\dfrac{9.09}{1} = 9.09$	$\dfrac{9.09}{2.27} = 4$	4
O	36.36	$\dfrac{36.36}{16} = 2.27$	$\dfrac{2.27}{2.27} = 1$	1

Empirical formula is $C_2 H_4 O$.

Calculation of Molecular formula

Empirical formula mass $= 12 \times 2 + 1 \times 4 + 16 \times 1 = 44$

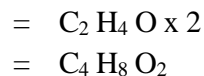Molecular mass $= 2 \times$ Vapour density

$= 2 \times 44 = 88$

$$n = \frac{\text{Molecular mass}}{\text{Empirical Formula mass}} = \frac{88}{44} = 2$$

Molecular formula $=$ Empirical formula x n

$$= C_2 H_4 O \times 2$$
$$= C_4 H_8 O_2$$

2. A compound on analysis gave the following percentage composition: Na=14.31% S = 9.97%, H = 6.22%, O = 69.5%, calcualte the molecular formula of the compound on the assumption that all the hydrogen in the compound is present in combination with oxygen as water of crystallisation. Molecular mass of the compound is 322 [Na = 23, S = 32, H = 1, 0 = 16].

Solution :- Calculation of empirical formula

Element	%	Relative No. of moles	Simple ratio moles	Simplest whole No. ratio
Na	14.31	$\dfrac{14.31}{23} = 0.62$	$\dfrac{0.62}{0.31} = 2$	2
S	9.97	$\dfrac{19.97}{32} = 0.31$	$\dfrac{0.31}{0.31} = 1$	1
H	6.22	$\dfrac{6.22}{1} = 6.22$	$\dfrac{6.22}{0.31} = 20$	20
O	69.5	$\dfrac{69.5}{16} = 4.34$	$\dfrac{4.34}{0.31} = 14$	14

The empirical formula is $Na_2 SH_{20}O_{14}$

Calculation of Molecular formula

Empirical formula mass $= (23 \times 2) + 32 + (20 \times 1) + (16 \times 14)$

$$= 322$$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{322}{322} = 1$$

Hence molecular formula $= Na_2 SH_{20} O_{14}$

Since all hydrogens are present as H_2O in the compound, it means 20 hydrogen atoms must have combined. It means 20 hydrogen atoms must have combined with 10 atoms of oxygen to form 10 molecules of water of crystallisation. The remaining (14 - 10 = 4) atoms of oxygen should be present with the rest of the compound.

Hence, molecular formula = $Na_2SO_4.10H_2O$.

Problems for Practice

1. An organic compound was found to have contained carbon = 40.65%, hydrogen = 8.55% and Nitrogen = 23.7%. Its vapour - density was found to be 29.5. What is the molecular formula of the compound?
Ans:- C_2H_5NO

2. A compound contains 32% carbon, 4% hydrogen and rest oxygen. Its vapour density is 75. Calculate the empirical and molecular formula.
Ans:- $C_2H_3O_3$, $C_4H_6O_6$

3. An acid of molecular mass 104 contains 34.6% carbon, 3.85% hydrogen and the rest is oxygen. Calcualte the molecualr formula of the acid.

4. What is the simplest formula of the compound which has the following percentage composition: carbon 80%, Hydrogen 20%, If the molecular mass is 30, calcualte its molecular formula.

1.5 Stoichiometry Equations

Stoichiometry

Stoichiometry is the calculation of the quantities of reactants and products involved in the chemical reaction. It is the study of the relationship between the number of mole of the reactants and products of a chemical reaction. A stoichiometric equation is a short scientific representation of a chemical reaction.

Rules for writing stoichiometric equations

i. In order to write the stoichiometric equation correctly, we must know the reacting substances, all the products formed and their chemical formula.

ii. The formulae of the reactant must be written on the left side of

arrow with a positive sign between them.

iii. The formulae of the products formed are written on the right side of the arrow mark. If there is more than one product, a positive sign is placed between them. The equation thus obtained is called skeleton equation. For example, the Chemical reaction between Barium chloride and sodium sulphate producing $BaSO_4$ and $NaCl$ is represented by the equation as

$$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + NaCl$$
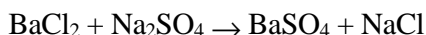
This skeleton equation itself is a balanced one. But in many cases the skeleton equation is not a balanced one.

For example, the decomposition of Lead Nitrate giving Lead oxide, NO_2 and oxygen. The skeletal equation for this reaction is

$$Pb(NO_3)_2 \rightarrow PbO + NO_2 + O_2$$

iv. In the skeleton equation, the numbers and kinds of particles present on both sides of the arrow are not equal.

v. During balancing the equation, the formulae of substances should not be altered, but the number of molecules with it only be suitably changed.

vi. Important conditions such as temperature, pressure, catalyst etc., may be noted above (or) below the arrow of the equation.

vii. An upward arrow ($\uparrow$) is placed on the right side of the formula of a gaseous product and a downward arrow ($\downarrow$) on the right side of the formulae of a precipitated product.

viii.   All the reactants and products should be written as molecules including the elements like hydrogen, oxygen, nitrogen, fluorine chlorine, bromine and iodine as H_2, O_2, N_2, F_2, Cl_2, Br_2 and I_2.
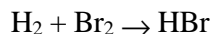
1.5.1   Balancing chemical equation in its molecular form

A chemical equation is called balanced equation only when the numbers and kinds of molecules present on both sides are equal. The several steps involved in balancing chemical equation are discussed below.
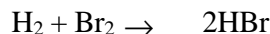
Example 1

Hydrogen combines with bromine giving HBr

$$H_2 + Br_2 \rightarrow HBr$$

This is the skeletal equation. The number of atoms of hydrogen on the left side is two but on the right side it is one. So the number of molecules of HBr is to be multiplied by two. Then the equation becomes

$$H_2 + Br_2 \rightarrow \quad 2HBr$$

This is the balanced (or) stoichiometric equation.

Example 2

Potassium permanganate reacts with HCl to give KCl and other products. The skeletal equation is

$$KMnO_4 + HCl \rightarrow KCl + MnCl_2 + H_2O + Cl_2$$
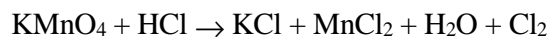
If an element is present only one substance in the left hand side of the equation and if the same element is present only one of the substances in the right side, it may be taken up first while balancing the equation.

According to the above rule, the balancing of the equation may be started with respect to K, Mn, O (or) H but not with Cl.
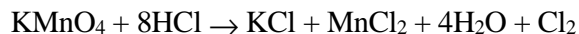
There are

| **L.H.S.**	**R.H.S**
$K = 1$	1
$Mn = 1$	1
$O = 4$	1

So the equation becomes

$$KMnO_4 + HCl \rightarrow KCl + MnCl_2 + 4H_2O + Cl_2$$
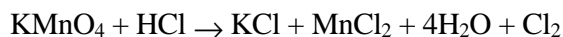
Now there are eight hydrogen atoms on the right side of the equation, we must write 8 HCl.

$$KMnO_4 + 8HCl \rightarrow KCl + MnCl_2 + 4H_2O + Cl_2$$

Of the eight chlorine atoms on the left, one is disposed of in KCl and two in $MnCl_2$ leaving five free chlorine atoms. Therefore, the above equation becomes

$$KMnO_4 + 8HCl \rightarrow KCl + MnCl_2 + 4H_2O + 5/2\ Cl_2$$
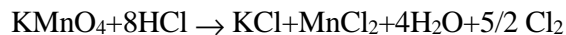
Equations are written with whole number coefficient and so the

equation is multiplied through out by 2 to become

$$2KMnO_4 + 16\ HCl \rightarrow 2KCl + 2\ MnCl_2 + 8H_2O + 5Cl_2$$

### 1.5.2 Redox reactions [Reduction - oxidation]

In our daily life we come across process like fading of the colour of the clothes, burning of the combustible substances such as cooking gas, wood, coal, rusting of iron articles, etc. All such processes fall in the category of specific type of chemical reactions called reduction - oxidation (or) redox reactions. A large number of industrial processes like, electroplating, extraction of metals like aluminium and sodium, manufactures of caustic soda, etc., are also based upon the redox reactions. Redox reactions also form the basis of electrochemical and electrolytic cells. According to the classical concept, oxidation and reduction may be defined as,

Oxidation is a process of addition of oxygen (or) removal of hydrogen

Reduction is a process of removal of oxygen (or) addition of hydrogen.

Example

Reaction of Cl_2 and H_2S

Oxidation

$$H_2S\ +\ Cl_2\ \rightarrow\ 2HCl\ +\ S$$
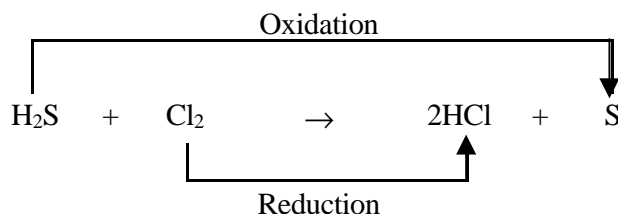
Reduction

In the above reaction, hydrogen is being removed from hydrogen sulphide (H_2S) and is being added to chlorine (Cl_2). Thus, H_2S is oxidised and Cl_2 is reduced.

Electronic concept of oxidation and Reduction

According to electronic concept, oxidation is a process in which an atom taking part in chemical reaction loses one or more electrons. The loss of electrons results in the increase of positive charge (or) decrease of negative of the species. For example.

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \text{ [Increase of positive charge]}$$

$$Cu \rightarrow Cu^{2+} + 2e^- \text{ [Increse of positive charge]}$$

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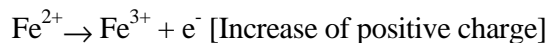
The species which undergo the loss of electrons during the reactions are called reducing agents or reductants. Fe^{2+} and Cu are reducing agents in the above example.

Reduction

Reduction is a process in which an atom (or) a group of atoms taking part in chemical reaction gains one (or) more electrons. The gain of electrons result in the decrease of positive charge (or) increase of negative charge of the species. For example,

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \text{ [Decrease of positive charges]}$$

$$Zn^{2+} + 2e^- \rightarrow Zn \text{ [Decrease of positive charges]}$$
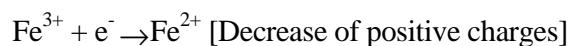
The species which undergo gain of electrons during the reactions are called oxidising agents (or) oxidants. In the above reaction, Fe^{3+} and Zn^{2+} are oxidising agents.

Oxidation Number (or) Oxidation State

Oxidation number of the element is defined as the residual charge which its atom has (or) appears to have when all other atoms from the molecule are removed as ions.

Atoms can have positive, zero or negative values of oxidation numbers depending upon their state of combination.

General Rules for assigning Oxidation Number to an atom

The following rules are employed for determining oxidation number of the atoms.

1. The oxidation number of the element in the free (or) elementary state is always Zero.
Oxidation number of Helium in $He = 0$
Oxidation number of chlorine in $Cl_2 = 0$

2. The oxidation number of the element in monoatomic ion is equal to the charge on the ion.

3. The oxidaton number of fluorine is always - 1 in all its compounds.

4. Hydrogen is assigned oxidation number +1 in all its compounds except in metal hydrides. In metal hydrides like NaH, MgH_2, CaH_2, LiH,

etc., the oxidation number of hydrogen is -1.

5. Oxygen is assigned oxidation number -2 in most of its compounds, however in peroxides like H_2O_2, BaO_2, Na_2O_2, etc its oxidation number is -1. Similarly the exception also occurs in compounds of Fluorine and oxygen like OF_2 and O_2F_2 in which the oxidation number of oxygen is +2 and +1 respectively.

6. The oxidation numbers of all the atoms in neutral molecule is Zero. In case of polyatomic ion the sum of oxidation numbers of all its atoms is equal to the charge on the ion.

7. In binary compounds of metal and non-metal the metal atom has positive oxidation number while the non-metal atom has negative oxidation number. Example. Oxidation number of K in KI is +1 but oxidation number of I is - I.

8. In binary compounds of non-metals, the more electronegative atom has negative oxidation number, but less electronegative atom has positive oxidation number. Example : Oxidation number of Cl in ClF_3 is positive (+3) while that in ICl is negative (-1).

Problem

Calculate the oxidation number of underlined elements in the following species.

$\underline{C}O_2$, $\underline{Cr}_2O_7^{2-}$, $\underline{Pb}_3O_4$, $\underline{P}O_4^{3-}$
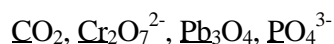
Solution

1. C in CO_2. Let oxidation number of C be x. Oxidation number of each O atom = -2. Sum of oxidation number of all atoms = x+2 (-2) $\Rightarrow$ x - 4.

As it is neutral molecule, the sum must be equal to zero.

$\therefore$ x-4 = 0 (or) x = + 4

2. Cr in $Cr_2O_7^{2-}$ Let oxidation number of Cr = x. Oxidation number of each oxygen atom =-2. Sum of oxidation number of all atoms

$$2x + 7(-2) = 2x - 14$$

Sum of oxidation number must be equal to the charge on the ion.

Thus, 2x - 14 = -2

$$2x = +12$$
$$x = 12/2$$
$$x = 6$$

Problems for Practice

Calculate the oxidation number of underlined elements in the following species.

a. $\underline{Mn}SO_4$ b. $\underline{S}_2O_3$ c. $H\underline{N}O_3$ d. $K_2\underline{Mn}O_4$ e. $\underline{N}H_4^+$
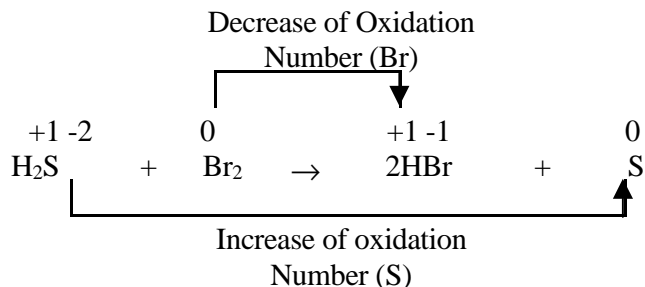
Oxidation and Reduction in Terms of Oxidation Number

Oxidation

"A chemical process in which oxidation number of the element increases".

Reduction

"A chemical process in which oxidation number of the element decreases".

Eg.   Reaction between H_2S and Br_2 to give HBr and Sulphur.

Decrease of Oxidation
Number (Br)

$$\overset{+1\ -2}{H_2S} \quad + \quad \overset{0}{Br_2} \quad \rightarrow \quad \overset{+1\ -1}{2HBr} \quad + \quad \overset{0}{S}$$

Increase of oxidation
Number (S)

In the above reaction, the oxidation number of bromine decreases from 0 to -1, thus it is reduced. The oxidation number of S increases from -2 to 0. Hence H_2S is oxidised.

Under the concept of oxidation number, oxidising and reducing agent can be defined as follows.

i.   Oxidising agent is a substance which undergoes decrease in the oxidation number of one of its elements.

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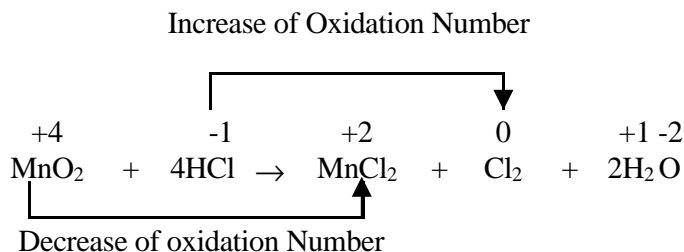ii. Reducing agent is a substance which undergoes increase in the oxidation number of one of its elements.

In the above reaction H_2S is reducing agent while Br_2 is oxidising agent.

Solved Problem

Identify the oxidising agent, reducing agent, substance oxidised and substance reduced in the following reactions.

$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$

Solution

Increase of Oxidation Number

$$\overset{+4}{MnO_2} \; + \; \overset{-1}{4HCl} \; \rightarrow \; \overset{+2}{MnCl_2} \; + \; \overset{0}{Cl_2} \; + \; \overset{+1\;-2}{2H_2O}$$

Decrease of oxidation Number

As it is clear, manganese decrease its oxidation number from +4 to +2. Hence, MnO_2 gets reduced and it is an oxidising agent. Chlorine atom in HCl increases its oxidation number from -1 to 0. Thus, HCl gets oxidised and it is reducing agent.

**Balancing Redox reaction by Oxidation Number Method**

The various steps involved in the balancing of redox equations according to this method are :

1. Write skeleton equation and indicate oxidation number of each element and thus identify the elements undergoing change in oxidation number.

2. Determine the increase and decrease of oxidation number per atom. Multiply the increase (or) decrease of oxidation number of atoms undergoing the change.

3. Equalise the increase in oxidation number and decrease in oxidation number on the reactant side by multiplying the respective formulae with

suitable integers.

4. Balance the equation with respect to all atoms other than O and H atoms.

5. Balance oxygen by adding equal number of water molecules to the side falling short of oxygen atoms.

6. H atoms are balanced depending upon the medium in same way as followed in ion electron method.

Let us balance the following equations by oxidation number method.

$$MnO_2 + \underline{Cl^-} \rightarrow Mn^{2+} + Cl_2 + H_2O$$

in acidic medium

Step 1

$$MnO_2 + Cl^- \rightarrow Mn^{2+} + Cl_2 + H_2O$$

Step 2

Step 3

Equalise the increase / decrease in O.N by multiply MnO_2 by 1 and Cl^{-1} by 2.

$$MnO_2 + 2\,Cl^- \rightarrow Mn^{2+} + Cl_2 + H_2O$$

Step 4

Balance other atoms except H and O. Here they are all balanced.

Step 5

Balance O atoms by adding H_2O molecules to the side falling short of oxygen atoms.

$$MnO_2 + 2Cl^- \rightarrow Mn^{2+} + Cl_2 + H_2O + H_2O$$

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Step 6

Balance H atoms by adding H^+ ions to the side falling short of H atoms

$$MnO_2 + 2Cl^- + 4H^+ \rightarrow Mn^{2+} + Cl_2 + 2H_2O$$
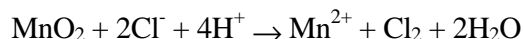
Problems for practice

Balance the following equations

1. $Mg + NO_3^- \rightarrow Mg^{2+} + N_2O + H_2O$

                 (in acidic medium)

2. $Cr^{3+} + Na_2O_2 \rightarrow CrO_4^- + Na^+$

3. $S^{2-} + NO_3^- \rightarrow NO + S$

4. $FeS + O_2 \rightarrow Fe_2O_3 + SO_2$ (molecular form)

5. $Cl_2 + OH^- \rightarrow Cl^- + ClO_3^- + H_2O$

1.6 Calculations based on chemical equations

Stoichiometric problems are solved readily with reference to the equation describing the chemical change. From a stoichiometric chemical equation, we know how many molecules of reactant react and how many molecules of products are formed. When the molecular mass of the substances are inserted, the equation indicates how many parts by mass of reactants react to produce how many parts by mass of products. The parts by mass are usually in kg. So it is possible to calculate desired mass of the product for a known mass of the reactant or vice versa.

1.6.1 Mass / Mass Relationship

Example 1

Calculate the mass of CO_2 that would be obtained by completely dissolving 10kg of pure $CaCO_3$ in HCl.

    $CaCO_3 + 2\ HCl \rightarrow CaCl_2 + H_2O + CO_2$
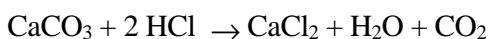
    100 kg x 10^{-3} 44 kg x 10^{-3}

100 kg of $CaCO_3$ produces 44 x 10^{-3} kg of CO_2

$$44 \times 10^{-3}$$

$$10 \text{ kg of CaCO}_3 \text{ produces} = \frac{}{100 \times 10^{-3}} \times 10$$

$$= 4.4 \text{ kg of CO}_2$$

Example 2

Calculate the mass of oxygen obtained by complete decomposition of 10kg of pure potassium chlorate (Atomic mass K=39, O=16 and Cl = 35.5)

$$2KClO_3 \rightarrow 2 KCl + 3O_2$$
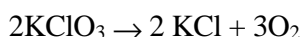
Molecular mass of $KClO_3 = 39+35.5+48=122.5$

Molecular Mass of $O_2 = 16 + 16 = 32$.

According to the Stoichiometric equation written above $(2 \times 122.5) \times 10^{-3}$ kg of $KClO_3$ on heating gives $(3 \times 32) \times 10^{-3}$ kg of oxygen.

$$10 \text{kg of KClO}_3 \text{ gives} = \frac{3 \times 32 \times 10^{-3}}{2 \times 122.5 \times 10^{-3}} \times 10$$

$$= 3.92 \text{ kg of O}_2$$

Example 3

Calculate the mass of lime that can be prepared by heating 200 kg of limestone that is 90% pure $CaCO_3$

$$\begin{array}{ccc} CaCO_3 & \rightarrow & CaO + CO_2 \\ 100 \text{ kg} \times 10^{-3} & & 56 \text{ kg} \times 10^{-3} \end{array}$$
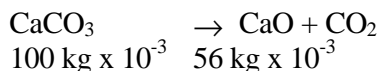
$$200 \text{ kg of 90\% pure CaCO}_3 = 200 \times \frac{90}{100}$$

$$= 180 \text{ kg pure CaCO}_3$$

100×10^{-3} kg of pure $CaCO_3$ on heating gives 56×10^{-3} kg of Ca0

$$\begin{array}{l} 180 \text{ kg of CaCO}_3 = \\ \text{gives on heating} \end{array} \frac{56 \times 10^{-3} \times 180}{100 \times 10^{-3}}$$

$$= 100.8 \text{ kg CaO}$$

1.7 Methods of Expressing the concentration of solution

The concentration of a solution refers to the amount of solute present in the given quantity of solution or solvent. The concentration of a solution may be expressed quantitatively in any of the following ways.

1. Strength

The Strength of a solution is defined as the amount of the solute in grams, present in one litre of the solution. It is expressed in $g\ L^{-1}$.

$$\text{Strength} = \frac{\text{Mass of solute in grams}}{\text{Volume of solution in litres}}$$

If X gram of solute is present in $V\ cm^3$ of a given solution then

$$\text{Strength} = \frac{X \times 1000}{V}$$

2. Molarity (M)

Molarity of a solution is defined as the number of gram-moles of solute dissolved in 1 litre of a solution

$$\text{Molarity} = \frac{\text{No. of moles of solute}}{\text{Volume of Solution in litres}}$$

If `X' grams of the solute is present in $V\ cm^3$ of a given solution, then,

$$\text{Molarity} = \frac{X}{\text{Mol. mass}} \times \frac{1000}{V}$$

Molarity is represented by the symbol M. Molarity can also be calculated from the strength as follows

$$\text{Molarity} = \frac{\text{Strength in grams per litre}}{\text{Molecular mass of the solute}}$$

Example

A 0.1M solution of Sugar, $C_{12}H_{22}O_{11}$ (mol.mass = 342), means that 34.2 g of sugar is present in one litre (1000 cm^3) of the solution.

3. Normality

Normality of a solution is defined as the number of gram equivalents of the solute dissolved per litre of the given solution.

$$\text{Normality} = \frac{\text{Number of gram-equivalents of solute}}{\text{Volume of Solution in litre}}$$

If X grams of the solute is present in V cm^3 of a given solution, then,

$$\text{Normality} = \frac{X}{\text{Eq.mass}} \times \frac{1000 \text{ mL}}{V}$$

Normality is represented by the symbol N. Normality can also be calculated from strength as follows

$$\text{Normality} = \frac{\text{Strength in grams per litre}}{\text{Eq.mass of the solute}}$$

Example

A 0.1N (or decinormal) solution of H_2SO_4 (Eq.mass = 49), means that 4.9 g of H_2SO_4 is present in one litre (1000 cm^3) of the solution.

4. Molality (m)

Molality of a solution is defined as the number of gram-moles of solute dissolved in 1000 grams (or 1 kg) of a Solvent. Mathematically,

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kilograms}}$$

"If X grams of the solute is dissolved in b grams of the solvent", then

$$\text{Molality} \quad = \quad \frac{X}{\text{Mol. mass}} \quad x \quad \frac{1000g}{bg}$$

Molality is represented by the symbol 'm'.

Example

A 0.1m Solution of glucose $C_6H_{12}O_6$ (Mol.mass = 180), means that 18g of glucose is present in 1000g (or one kilogram) of water.

5. Mole Fraction

Mole fraction is the ratio of number of moles of one component (Solute or Solvent) to the total number of moles of all the components (Solute and Solvent) present in the Solution. It is denoted by X. Let us suppose that a solution contains 2 components A&B and suppose that n_A moles of A and n_B moles of B are present in the solution. Then,

$$\text{Mole fraction of A, } X_A = \frac{n_A}{n_A + n_B} \quad .....(1)$$

$$\text{Mole fraction of B, } X_B = \frac{n_B}{n_A + n_B} \quad ......(2)$$

Adding 1 & 2 we get,

$$X_A + X_B = \frac{n_A}{n_A+n_B} + \frac{n_B}{n_A+n_B} = \frac{n_A+n_B}{n_A+n_B}$$

Thus, sum of the two mole fractions is one. Therefore, if mole fraction of one component in a binary solution is known, that of the other can be calculated.

Solved Problems

1. 4.5g of urea (molar mass = 60g mol^{-1}) are dissolved in water and solution is made to 100 ml in a volumetric flask. Calculate the molarity of solution.

Solution

Mass of Urea $=$ 4.5g

$$\text{Moles of Urea} = \frac{\text{Mass}}{\text{Molar Mass}} = \frac{4.5g}{60gmol^{-1}}$$

$$= 0.075mol$$

Volume of Solution $= 1000$ ml $= \dfrac{100}{1000}$ L

$$= 0.1L$$

$$\text{Molarity of Solution} = \frac{\text{Mass of Solute in g}}{\text{Volume of Solution in litres}}$$

$$= \frac{0.075}{0.12} \text{ mol} = 0.75M$$

2. Calculate the normality of solution containing 3.15g of hydrated oxalic acid ($H_2C_2O_4.2H_2O$) in 250ml of solution (Mol.mass = 126).

Solution

Mass of oxalic acid $=$ 3.15g

$$\text{Equivalent mass of oxalic acid} = \frac{\text{Mol.mass}}{\text{Basicity}}$$

$$= \frac{126}{2} = 63 \text{ g equiv}^{-1}$$

$$\text{Equivalents of oxalic acid} = \frac{\text{Mass of solute}}{\text{Eq.Mass}}$$

$$\frac{3.15g}{63 \text{ g equiv}^{-1}} = 0.05 \text{ equiv}^{-1}$$

Volume of solution = 250ml $= \frac{250}{1000} L = 0.25L$

$$\text{Normality} = \frac{\text{Equivalent of Solute}}{\text{Volume of solution inL}}$$

$$= \frac{0.05 \text{ equiv}}{0.25 \text{ L}} = 0.2N$$

3. Calculate the molality of an aqueous solution containing 3.0g of urea (mol.mass=60) in 250g of water.

Solution

Mass of solute $= 3.0g$

$$\text{Moles of solute} = \frac{\text{Mass of solute}}{\text{Molar Mass}}$$

$$= \frac{3.0 \text{ g}}{60 \text{ g mol}^{-1}} = 0.05 \text{ mol}$$

Mass of Solvent $= 250g$

$$= \frac{250}{1000} = 0.25 \text{ kg}$$

$$\text{Molality of Solution} = \frac{\text{Moles of Solute}}{\text{Mass of Solvent in kg.}}$$

$$= \frac{0.05 \text{ Mol}}{0.25 \text{ kg}} = 0.2m$$

Problems for practice

1. Calculate the volume of 14.3m NH_3, solution needed to prepare 1L of 0.1M solution.

Ans:-6.77 mL

2. How would you make up 425 mL of 0.150M HNO_3 from 68.0% HNO_3? The density of 68.0% HNO_3 is1.41g/mL.

Ans: 4.25 mL

3. Calculate the molarity of a solution obtained by mixing 100 mL of 0.3 M H_2SO_4 and 200 mL of 1.5M H_2SO_4
Ans:1.1M

4. Calculate the molality of a solution by dissolving 0.850g of ammonia (NH_3) in 100g of water.
Ans:0.5m

1.8 Calculations based on Principle of Volumetric Analysis

1.8.1   Volumetric Analysis

An important method for determining the amount of a particular substance is based on measuring the volume of reactant solution. Suppose substance A in solution reacts with substance B. If you know the volume and concentration of a solution of B that just reacts with substance A in a sample, you can determine the amount of A.

Titration is a procedure for determining the amount of substance A by adding a carefully measured volume of a solution of A with known concentration of B untill the reaction of A and B is just completed. Volumetric analysis is a method of analysis based on titrations.

Law

"Equal volume of equinormal solutions exactly neutralise the other solution having same concentration and volume".

$V_1 N_1 = V_2 N_2$

V_1, V_2 -   Volume of solutions.

N_1, N_2 -   Strength of solutions.

Solved problem

Calculating the volume of reactant solution needed

1. What volume of 6M HCl and 2M HCl should be mixed to get one litre of 3M HCl?

Solution

Suppose the volume of 6M HCl required to obtain 1L of 3M HCl = XL

Volume of 2M HCl required $=$ (1-x)L

Applying the molarity equation

M_1V_1 $+$ M_2V_2 $=$ M_3V_3
6MHCl+ 2MHCl= 3MHCl
6x+2(1-x) $=$ 3x1
6x+2-2x $=$ 3
4x $=$ 1
x $=$ 0.25L

hence, volume of 6M HCl required $=$ 0.25L

Volume of 2M HCl required $=$ 0.75L

2. How much volume of 10M HCl should be diluted with water to prepare 2.00L of 5M HCl.

Solution

N_1V_1 $=$ N_2V_2

10N HCl $=$ 5N HCl

$10xV_1$ $=$ 5 x 2.00

$\therefore V_1$ $=$ $\dfrac{5 \times 2.00}{10}$

$=$ 1.00L

Problems for Practice

1. NiSO$_4$ reacts with Na$_3$PO$_4$ to give a yellow green precipitate of Ni$_3$(PO$_4$)$_2$ and a solution of Na$_2$SO$_4$.

$3NiSO_4(aq) + 2Na_3PO_4(aq) \rightarrow Ni_3(PO_4)_{2\ (s)} + 3Na_2SO_4(aq)$
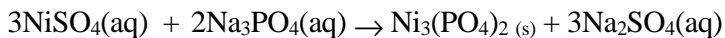
How many mL of 0.375M $NiSO_4$ will react with 45.7 mL of 0.265M Na_3PO_4?

2. What volume of 0.250M HNO_3 reacts with 42.4 mL of 0.150M Na_2CO_3 in the following reaction?

$2HNO_{3(aq)} + Na_2CO_{3(aq)} \rightarrow 2NaNO_{3(aq)} + H_2O_{(aq)} + CO_{2(g)}$
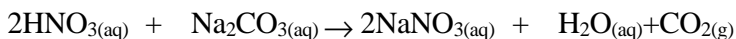
3. A flask contains 53.1 mL of 0.150M $Ca(OH)_2$ solution. How many mL of 0.350M Na_2CO_3 are required to react completely with $Ca(OH)_2$ in the following reaction.

$Na_2CO_{3(aq)} + Ca(OH)_{2(aq)} \rightarrow CaCO_{3(aq)} + 2NaOH_{(aq)}$
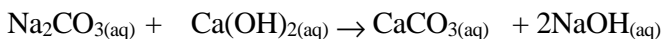
1.8.2 Determination of equivalent masses of elements

Equivalent masses can be determined by the following methods:

1. Hydrogen displacement method
2. Oxide method
3. Chloride method
4. Metal displacement method

Hydrogen displacement method

This method is used to determine the equivalent mass of those metals such as magnesium, zinc and aluminium which react with dilute acids and readily displace hydrogen.

$Mg + 2HCl \longrightarrow MgCl_2 + H_2$

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$
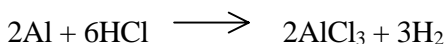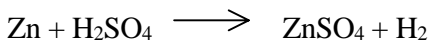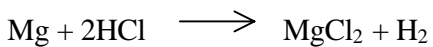
From the mass of the metal and the volume of hydrogen displaced, the equivalent mass of the metal can be calculated.

Problem 1

0.548 g of the metal reacts with dilute acid and liberates 0.0198 g of hydrogen at S.T.P. Calculate the equivalent mass of the metal.

0.548 g of the metal displaces 0.0198 g of hydrogen

The mass of the metal which will displace

$$1.008 \text{ g of hydrogen} = \frac{1.008 \times 0.548}{0.0198} \text{ g of metal}$$

The equivalent mass of the metal $= 27.90$ g equiv^{-1}

Oxide Method

This method is employed to determine the equivalent mass of those elements which readily form their oxides eg. magnesium, copper etc. Oxide of an element can be formed by direct method or by indirect method.

Magnesium forms its oxide directly on heating

$$2Mg + O_2 \rightarrow 2\,MgO$$
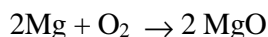
In the case of copper, its oxide is obtained in an indirect manner i.e. copper is dissolved in concentrated nitric acid and the copper(II) nitrate formed after evaporation is strongly heated to give copper (II) oxide.

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2\,NO_2$$

$$2Cu(NO_3)_2 \rightarrow 2CuO + 4\,NO_2 + O_2$$

Calculations

Mass of the element taken $= w_1$ g

Mass of the oxide of the element $= w_2$ g

Mass of oxygen $= (w_2\text{-}w_1)$ g

$(w_2 - w_1)$ g of oxygen has combined with w_1 g of the metal.

$\therefore 8$ g of oxygen will combine with $\dfrac{w_1}{w_2 - w_1} \times 8$

This value represents the equivalent mass of the metal.

Problem 2

0.635 g of a metal gives on oxidation 0.795g g of its oxide. Calculate the equivalent mass of the metal.

Mass of the metal oxide   =   0.795g

Mass of the metal   =   0.635g

Mass of oxygen   =   0.795 - 0.635 = 0.16g

0.16 g of oxygen has combined with 0.635 g of a metal

∴ 8 g of oxygen will combine with

$$\frac{8 \times 0.635}{0.16} = 31.75 \text{ of the metal}$$

Equivalent mass of the metal = 31.75g equiv^{-1}

Chloride Method

The equivalent mass of those elements which readily form their chlorides can be determined by chloride method. For example, a known mass of pure silver is dissolved completely in dilute nitric acid. The resulting silver nitrate solution is treated with pure hydrochloric acid when silver chloride is precipitated. It is then filtered, dried and weighed. Thus from the masses of the metal and its chloride, the equivalent mass of the metal can be determined as follows :

Calculations

Mass of the metal   = w_1 g

Mass of the metal chloride = w_2 g

Mass of chlorine   = $(w_2 - w_2)$ g

$(w_2 - w_1)$ g of chlorine has combined with w_1 of the metal

35.46 g of chlorine will combine with

$$\frac{35.46 \times w_1}{(w_2 - w_1)} \text{ g of the metal}$$

This value gives the equivalent mass of the metal.

Uses of volumetric laws

If the volume of the acid is represented as V_1, the normality of the acid as N_1, volume of base as V_2 the normality of the base as N_2, then from the law of volumetric analysis it follows that

$$V_1 \times N_1 = V_2 \times N_2$$

All volumetric estimations are based on the above relationship. If any three quantities are known, the fourth one can readily be calculated using the above expression.

1.8.3 Equivalent mass of acid, base, salt, oxidising agent and reducing agent

Acids contain one or more replaceble hydrogen atoms. The number of replaceble hydrogen atoms present in a molecule of the acid is referred to its basicity.

Equivalent mass of an acid is the number of parts by mass of the acid which contains 1.008 part by mass of replaceble hydrogen atom.

$$\text{Equivalent mass of an acid} = \frac{\text{molar mass of the acid}}{\text{No. of replaceble hydrogen atom}}$$

(or)

$$= \frac{\text{molar mass of the acid}}{\text{basicity of the acid}}$$

For example, the basicity of sulphuric acid is 2.

$$\text{Equivalent mass of } H_2SO_4 = \frac{\text{Molar mass of } H_2SO_4}{2}$$

$$= \frac{98}{2} = 49$$

2. Equivalent mass of the base

Equivalent mass of a base is the number of parts by mass of the base which contains one replaceable hydroxyl ion or which completely neutralises one gram equivalent of an acid. The number of hydroxyl ions present in one mole of a base is known as the acidity of the base. Sodium hydroxide, potassium hydroxide, ammonium hydroxide are examples of monoacidic bases.

Calcium hydroxide is a diacidic base

In general,

equivalent mass of a base $=$ $\dfrac{\text{molar mass of the base}}{\text{acidity of the base}}$

Equivalent mass of KOH $= 56/1 = 56$

3. Equivalent mass of a salt

Equivalent mass of a salt is a number of parts by mass of the salt that is produced by the neutralisation of one equivalent of an acid by a base.

In the case of salt like potassium chloride, the salt formed by the neutralisation of one equivalent of an acid by a base.

$$KOH + HCl \rightarrow KCl + H_2O$$
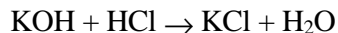
Therefore, the equivalent mass of the salt is equal to its molar mass.

4. Equivalent mass of an oxidising agent

The equivalent mass of an oxidising agent is the number of parts by mass which can furnish 8 parts by mass of oxygen for oxidation either directly or indirectly.

For example, potassium permanganate is an oxidising agent. In acid medium potassium permanganate reacts as follows

$$\underset{316}{2\ KMnO_4}\ + 3\ H_2SO_4 \ \rightarrow\ K_2SO_4 + 2\ MnSO_4 + 3\ H_2O + \underset{80}{5\ [O]}$$
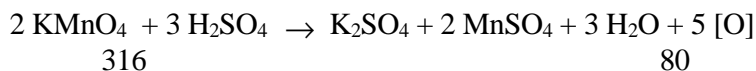
80 parts by mass of oxygen are made available from 316 parts by mass of $KMnO_4$
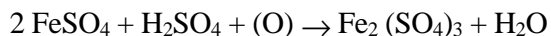
8 parts by mass of oxygen will be furnished by

$$\dfrac{316 \times 8}{80} = 3.16$$

Equivalent mass of $KMnO_4 = 31.6$g equiv^{-1}

5. Equivalent mass of a reducing agent

The equivalent mass of a reducing agent is the number of parts by mass of the reducing agent which is completely oxidised by 8 parts by mass of oxygen or with one equivalent of any oxidising agent.

(i) Ferrous sulphate reacts with an oxidising agent in acid medium according to the equation

$2 FeSO_4 + H_2SO_4 + (O) \rightarrow Fe_2 (SO_4)_3 + H_2O$

2 x 152g   16g

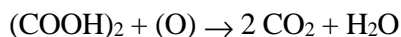16 parts by mass of oxygen oxidised 304 parts by mass of ferrous sulphate

8 parts by mass of oxygen will oxidise 304/16 x 8 parts by mass of ferrous sulphate.

The equivalent mass of ferrous sulphate (anhydrous) is 152.
The equivalent mass of crystalline ferrous sulphate, $FeSO_4$ $7H_2O$ is $152 + 126 = 278$

126 is the mass corresponding to 7 moles of water.

(ii) In acid medium, oxalic acid is oxidised according to the equation

$(COOH)_2 + (O) \rightarrow 2 CO_2 + H_2O$

16 Parts by mass of oxygen oxidised 90 parts by mass of anhydrous oxalic acid.

8 parts by mass of oxygen will oxidise 90/16 x 8 = 45 parts by mass of anhydrous oxalic acid.

$\therefore$ Equivalent mass of anhydrous oxalic acid = 45 g equiv^{-1}

But equivalent mass of crystalline oxalic acid, $(COOH)_2$. $2H_2O$=126/2

$= 63$ g equiv^{-1}.

1.8.4   Determination of Molecular Mass Victor-Meyer's Method Principle

In this method a known mass of a volatile liquid or solid is converted into its vapour by heating in a Victor-Meyer's tube. The vapour displaces its own volume of air. The volume of air displaced by the vapour is measured at the experimental temperature and pressure. The volume of the vapour at s.t.p is then calculated. From this the mass of $2.24 \times 10^{-2} m^3$ of the vapour at S.T.P. is calculated. This value represents the molecular mass of the substance.
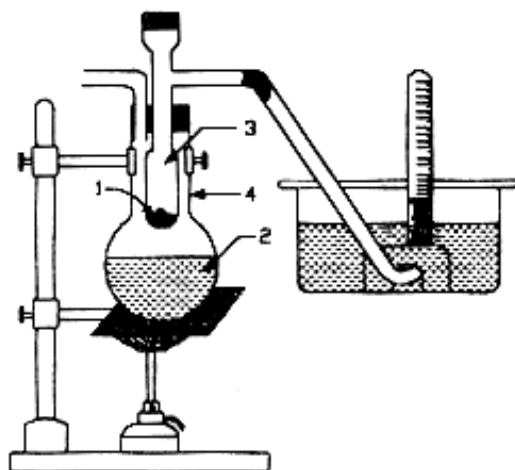
1. Sample tube
2. Liquid of boiling point higher than that of the volatile substance
3. Victor-Meyer tube
4. Outer jacket

Figure 1.1 Determination of molecular mass by victor-Meyers method

The apparatus consists of an inner Victor-Meyer tube, the lower end of which is in the form of a bulb. The upper end of the tube has a side tube which leads to a trough of water. The Victor-Meyer tube is surrounded by an outer jacket. In the outer jacket is placed a liquid which boils at a temperature at least 30 K higher than the boiling point of the volatile substance under study. A small quantity of glass wool or asbestos fiber covers the bottom of the Victor-Meyer tube to prevent breakage when the bottle containing the substance is dropped in.

Procedure

The liquid in the outer jacket is allowed to boil and when no more air escapes from the side tube, a graduated tube filled with water is inverted over the side tube dipping in a trough full of water. A small quantity of the substance is exactly weighed in a small stoppered bottle and quickly dropped in the heated Victor-Meyer tube and corked immediately.

The bottle falls on the asbestos pad and its content suddenly changes into vapour, blow out the stopper and displace an equal volume of air which collects in the graduated tube. The volume of air in the graduated tube is measured by taking it out by closing its mouth with the thumb and dipping

it in a jar full of water. When the water levels outside and inside the tube are the same, the volume of air displaced is noted. The atmospheric pressure and laboratory temperature are noted.

Calculations

Mass of the volatile substance = wg

Volume of air displaced = Volume of vapour = V_1 m^3

Laboratory temperature = T_1 K

Let the atomospheric pressure be P

Pressure of dry vapour = Atomospheric pressure - aqueous tension at. T_1 K

Let the aqueous tension be p Nm^{-2} at that temperature.

Pressure of dry vapour = P_1 = [P-p]

Standard temperature = T_0 = 273 K

Standard pressure = P_0 = 1.013 x 10^5 Nm^{-2}

Let the volume of the vapour at standard temperature and pressure be V_0 m^3

From the gas equation, it follows

$$\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1}$$

$$V_0 = \frac{P_1 V_1}{T_1} \times \frac{T_0}{P_0}$$

The mass of V_0 m^3 of vapour at s.t.p is w g.

The mass of 2.24 x 10^{-2} m^3 of the vapour at s.t.p. is

$$\frac{2.24 \times 10^{-2} \times W}{V_0}$$

The value thus calculatd gives the molecular mass

Molecular mass   =   2 x vapour density

$$\text{Vapour density} = \frac{\text{Molecular mass}}{2}$$

Problem

In the determination of molecular mass by Victor-Meyer's Method 0.790 g of a volatile liquid displaced $1.696 \times 10^{-4} m^3$ of moist air at 303 K and at 1×10^5 Nm^{-2} pressure. Aqueous tension at 303 K is 4.242×10^3 Nm^{-2}. Calculate the molecular mass and vapour density of the compound.

Mass of the organic compound   =   0.79 g

Volume of Vapour   = $V_1 = 1.696 \times 10^{-4} m^3$

Volume of air displaced   =   Volume of vapour.

P_1 = (atmospheric pressure - aqueous tension)

$= (1.0 \times 10^5) - (4.242 \times 10^3) = 0.958 \times 10^5$ Nm^{-2}

$T_1 = 303$ K

Lab Values

$V_1 = 1.696 \times 10^{-4}$ Nm^{-2}

$P_1 = 0.958 \times 10^{-5} \times 10^5$ Nm^{-2}

$T_1 = 303$ K

Values at S.T.P

$V_o = ?$

$P_o = 1.013 \times 10^5$ Nm^{-2}

$T_0 = 273$ K

$$\frac{P_1 V_1}{T_1} = \frac{P_0 V_0}{T_0}$$

$$V_0 = \frac{P_1 V_1 T_0}{P_0 T_1}$$

$$V_0 = \frac{0.958 \times 10^5 \times 1.696 \times 10^{-4}}{1.013 \times 10^5} \times \frac{273}{303}$$

$V_0 = 1.445 \times 10^{-4} \ m^3$

The mass of $1.445 \times 10^{-4} m^3$ of vapour at S.T.P = 0.79 g.

The mass of $2.24 \times 10^{-2} m^3$ of vapour at S.T.P is

$$= \frac{2.24 \times 10^{-2} \times 0.79}{1.445 \times 10^{-4}}$$

The molecular mass of the substance = 122.46

$$\text{Vapour density of the compound} = \frac{\text{molecular mass}}{2}$$

$$= \frac{122.46}{2} = 61.23$$

Questions

A. Choose the best answer :

1. The volume occupied by 16g of oxygen at S.T.P.
   a) 22.4 L   b) 44.8 L   c) 11.2 L d)   5.6 L

2. Avogadro's number represents the number of atoms in
   a) 12g of C^{12} b) 320g of S
   c) 32g of Oxygen   d) 12.7g of iodine.

3. The value of gram molecular volume of ozone at S.T.P is
   a) 22.4 L   b) 2.24 L   c) 11.2 L d)   67.2 L

4. The number of atoms present in 0.5 gram- atoms of Nitrogen is same as the atoms in
   a) 12g of C   b) 32g of S
   c) 8g of the oxygen   d) 24g of magnesium.

5. The number of gram-atoms of oxygen in 128g of oxygen is
   a) 4   b) 8   c) 128   d) $8 \times 6.02 \times 10^{23}$

6. The total number of moles present in 111 g of $CaCl_2$ is
   a) One mole b) Two moles   c) Three moles   d) Four moles

7. Which of the following weighs the most?
   a) One gram-atom of nitrogen   b) One mole of water
   c) One mole of Sodium   d) One molecule of H_2SO_4

8. Which of the following contains same number of carbon atoms as are in 6.0g of carbon (C-12)?
   a) 6.0g ethane b) 8.0g methane c) 21.0g Propane d) 28.0g CO

9. Which of the following contains maximum number of atoms?
   a) 2.0g hydrogen b) 2.0g oxygen c) 2.0g nitrogen d) 2.0g methane

10. Which one among the following is the standard for atomic mass?
    a) H   b) $^{12}_6C$ c) $^{14}_6C$ d) $^{16}_8O$

11. Which of the following pair of species have same number of atoms under similar conditions ?
    a) 1L each of SO_2 and CO_2 b) 2L each of O_3 and O_2
    c) 1L each of NH_3 and Cl_2 d) 1L each of NH_3 and 2L of SO_2

12. 2.0 g of oxygen contains number of atoms same as in
    a) 4 g of S   b) 7 g of nitrogen
    c) 0.5 g of H_2 d) 12.3 g of Na

13. The number of gm-molecules of oxygen in 6.02 x 10^{24} CO molecules is
    a) 1 gm-molecule   b) 0.5 gm-molecule
    c) 5 gm-molecule   d) 10 gm-molecule

14. Hydrogen phosphate of certain metal has a formula $MHPO_4$, the formula of metal chloride is
    a) MCl   b) MCl_3 c) MCl_2 d) MCl_4

15. A compound contains 50% of X (atomic mass 10) and 50% Y (at. mass 20). Which formulate pertain to above date ?
    a) XY   b) X_2Y c) X_4Y_3 d) $(X_2)_3 Y_3$

16. Which of the following compound has / have percentage of carbon same as that in ethylene (C_2H_4) ?
    a) propene   b) Cyclohexane c) Ethyne   d) Benzene

17. 5L of 0.1 M solution of sodium Carbonate contains
    a) 53 g of Na_2CO_3 b) 106 g of Na_2CO_3
    c) 10.6 of Na_2CO_3 d) 5 x 10^2 millimoles of Na_2CO_3

B. Fill in the blanks

1. One mole of a triatomic gas contains _____ atoms.
2. One mole of Sulphuric acid contains _____Oxygen atoms.
3. 11.2 L of carbon dioxide at S.T.P contains_____ oxygen atoms.
4. Equal volumes of different gases under similar conditions of temperature and pressure contain equal number of _____

5. A decimolar solution of NaOH contains ___ of NaOH per litre of the solution.
6. 7 g of CO contains _____O atoms.
7. The mass of 1 x 10^{22} formula units of $CuSO_4$ $5H_2O$ is _____

C. Match the following

Column A		Column B
1. CaC_2	a.	106 g
2. Law of multiple proportions	b.	6.02 x 10^{23} Ne atoms
3. Hydrargyrum	c.	Molarity of solution
4. 2 gm-equivalents of Na_2CO_3	d.	0.01 moles of solute in one L of solution
5. 22.4 L at S.T.P	e.	Liquid element
6. Number of gm-molecules per litre of solution	f.	Calcium carbide
7. 1 gm-atom of rhombic sulphur	g.	$(NH_4)_2SO_4.Fe(SO_4).6H_2O$
8. Centimolar solution	h.	1/8 gm-molecules
9. Mohr's Salt	i.	John Dalton

D. Answer the following

1. Can two different compounds have same molecular formula ? Illustrate your answer with two examples.
2. What are the essentials of a chemical equation ?
3. What are the informations conveyed by a chemical equation ?
4. Balance the following equations
   i. $Fe + H_2O \rightarrow Fe_3O_4 + H_2$
   ii. $Fe_2 (SO_4)_3 + NH_3 + H_2O \rightarrow Fe(OH)_3 + (NH_4)_2 SO_4$
   iii. $KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + H_2O + O_2$
   iv. $K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O + O_2$

SUMMARY

SI units and different scientific notation. Molecular mass, Mole

concept, Avogardo number and its significance are dealt. The application of the various concepts are explained by solving problems. By knowing the percentage composition of elements in a compound, empirical formula and molecular formula can be calculated.

It is important to write the stoichiometric equation. So, the method of balancing the any equation explained and given or practice. And also the method of balancing redox equation using oxidation number is dealt.

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2. GENERAL INTRODUCTION TO METALLURGY

OBJECTIVES

- *Know the ores and minerals of elements*

- *Learn the purification methods of ores*

- *Understand the different metallurgical processes*

- *Know the importance of purification of metals*

- *Understand clearly the extraction of Cu, Au, Ag, Pb, Zn and Al*

- *Gain knowledge about the mineral wealth of India and Tamilnadu*

2.1 Ores and minerals

Metals occur in nature sometimes in **free or native state,** but most of these occur in nature in the form of **chemical combination,** i.e., in the form of their stable compounds which are associated with **gangue or matrix.** The earthy impurities such as sand, clay, rocks etc. associated with ore are collectively known as **gangue or matrix.** Thus a large number of metals in nature occur in the combined form along with other elements, but some metals, such as Ag, Au, Pt etc. occur in the **native form (metallic state)** in some regions. Ag occurs in **native (or free)** as well as in the form of **compounds.** The natural material in which the metal or their compounds occur in the earth is known as **mineral**. Thus a mineral is a naturally occurring material present in earth's crust which contains metal in the native (or free state) or in combined state.

A mineral may be a single compound or a complex mixture of various compounds. When a mineral contains sufficient amount of a metal in combined state, from which it can be readily and profitably separated on commercial scale, then the mineral is said to be an ore of the metal**. Thus all ores are minerals, but all minerals are not ores.** A mineral from which a metal can be profitably extracted is called an **ore.** For example, clay (Al_2O_3 2 SiO_2 2 H_2O) and bauxite ($Al_2 O_3$ $2H_2O$) are two minerals of aluminium, but aluminium, can be profitably extracted only from bauxite and not from the clay. **Hence bauxite is an ore of aluminium, while clay is a mineral.** The biggest source of metal is the

earth's crust and the process of taking out the ores from the earth crust is called **mining**.

In the combined state ores are generally found in the form of oxides, sulphides, carbonates, sulphates, chlorides and silicates. The important ores are given in Table 2.1.

Table 2.1 Classification of ores

Ore	Ore or Mineral	Composition	Metal Present
Oxide ores	Bauxite	$Al_2O_3 .2H_2O$	Al
	Cuprite	Cu_2O	Cu
	Haematite	Fe_2O_3	Fe
	Zincite	ZnO	Zn
	Tinstone or Casseterite	SnO_2	Sn
	Pyrolusite	MnO_2	Mn
	Pitch Blende	U_3O_8	U
Sulphide ores	Copper Pyrites	Cu_2S, Fe_2S_3 or $Cu_2S . FeS_2$	Cu
	Copper Glance	Cu_2S	Cu
	Zinc Blende	ZnS	Zn
	Cinnabar	HgS	Hg
	Galena	PbS	Pb
	Argentite or Silver Glance	Ag_2S	Ag
Carbonate ores	Magnesite	$MgCO_3$	Mg
	Dolomite	$CaCO_3.MgCO_3$	Mg
	Calamine	$ZnCO_3$	Zn
	Malachite	$CuCO_3.Cu(OH)_2$	Cu
	Limestone	$CaCO_3$	Ca

Halide ores	Rock Salt	NaCl	Na
	Carnallite	$KCl.MgCl_2.6H_2O$	Mg
	Horn Silver	AgCl	Ag
	Sylvine	KCl	K
	Cryolite	$3\ NaF.AlF_3$ or Na_3AlF_6	Al
Sulphate ores	Epsom Salt	$MgSO_4.7H_2O$	Mg
	Gypsum	$CaSO_4.2H_2O$	Ca
	Barytes	$BaSO_4$	Ba
	Anglesite	$PbSO_4$	Pb
Silicate ores	Asbestos	$CaSiO_3.3MgSiO_3$	Mg
	Felspar	$K_2O.Al_2O_3.6SiO_2$ or $KAlSi_3O_8$	Al
	Mica	$K_2O.3Al_2O_3.6SiO_22H_2O$	Al
Phosphate ores	Phosphorite	$Ca_3(PO_4)_2$	P

2.2 Sources from earth, living systems and in sea

Sources from earth

Nearly 80 elements are obtained from mineral deposits on or beneath the surface of the earth.

(a) Metals which are sufficiently unreactive to occur uncombined (ie in elementary form) are present in group 10 and 11 of the 2nd and 3rd transition series (e.g Pt, Au, Ag; free Ag is also found in nature).

(b) Metalloids (e.g Ge, As, Sb) and neighbouring metals, all of which have relatively large ionization energies, generally occur as sulphides.

(c) The more strongly metallic elements that form positive ions readily are found as oxides (transition metals), carbonates (group 2 metals) or chlorides (group 1 metals).

(i) Three noble metals (Cu, Ag, Au), Hg and six platinum metals (Ru, Os, Rh, Ir, Pd and Pt) occur in nature in free state. All other metals are found in combined state in the nature.

(ii) The composition of earth's crust is : O (49.1%), Si (26%), Al(7.5%), Fe(4.2%), Ca (3.2%), Na (2.4%), Mg (2.3%) and H (1.0%) by weight.

(iii) In combined state metals are found as (a) Oxides- Mg, Cu, Zn, Al, Mn, Fe, etc. (b)Carbonates-Na, Cu, Mg, Ca, Ba, Zn, Fe etc. (c) Phosphates- Ca, Pb, Fe etc (d) Silicates- Li, Cu, Zn, Al, Mn, Ni, etc and (e) Sulphates- Fe, Cu, Pb, Hg etc.

Source from sea

Four elements such as Na, Mg, Cl_2 and Br_2 can be extracted from the oceans or salt brines, where they are present as monoatomic ions (Na^+, Mg^{2+}, Cl^-, Br^-).

Source from living system

Table 3.2 represents the descending mass abundance of elements. About 30 percent of enzymes have a metal atom at the active site. A large number of biomolecules contain metal ions ; many of these molecules are proteins. In addition metal ions in the form of crystalline minerals or amorphous solids are important as structural materials in many organisms.

Table 2.2 Descending mass abundance of the elements

| Earth Crust	Oceans	Humans
O	O	H
Si	H	O
Al	Cl	C
Fe	Na	N
Ca	Mg	Na
Mg	S	K
Na	Ca	Ca
K	K	Mg
Ti	C	P
H	Br	S
P	B	Cl

2.3 Purification of ores

The ore is generally associated with rock impurities like clay, sand etc. called '**gangue or matrix**'. The purification of ore means removal of gangue from the powdered ore. This process is otherwise called concentration of the ore or ore dressing. Thus, the percentage of the ore in the concentrated ore is higher than that in the original ore. The purification or concentration of ore can be brought about in the following ways, depending upon the type of ore.

(i) **Gravity separation process** or **hydraulic washing**

This method is especially suitable for heavy 'oxide' ores like haematite, tinstone, etc. In this, the powdered ore is placed on a sloping floor (or platform) and washed by directing on it a strong current of water. The lighter sandy, and earthy impurities are washed away; while the heavier ore particles are left behind.

(ii) **Froth flotation process**

This method is especially suitable   for sulphide ores like zinc blende (ZnS), and copper pyrites (CuFeS$_2$). This process is based on the fact that the sulphide ore particles are only moistened by **oil;** while those of oxide, and gangue particles are moistened only by **water**. In this process, the powdered ore is mixed with water and a little pine oil (a foaming agent) and the whole mixture is then stirred vigorously by blowing compressed air. The oil forms a foam (or froth) with air. The ore particles stick to the froth, which rises to the surface; while the rocky, and earthy impurities (gangue) are left in water Fig**.** 2.1. The froth is skimmed off, collected, and allowed to subside to get concentrated ore.
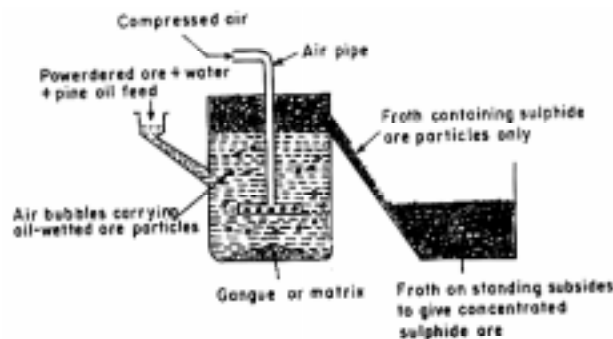
Fig. 2.1 Froth flotation process

(iii)**Electromagnetic separation process**

This method is meant for separating **magnetic impurities from non-magnetic ore particles,** e.g., tinstone (a tin ore) in which tinstone is non- magnetic; while impurities iron, manganese and tungstates are magnetic. The powdered ore (containing the associated magnetic impurities) is made to fall (from a hopper) on a belt moving over electromagnetic roller. The magnetic impurities fall from the belt in a heap near the magnet, due to attraction; while the non-magnetic concentrated ore falls in separate heap, away from the magnet, due to the influence of centrifugal force Fig. 2.2.
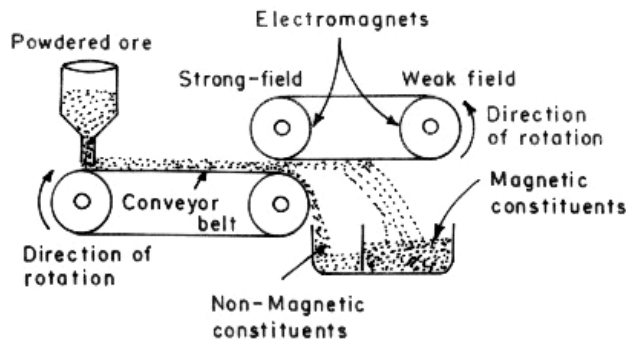
Fig. 2.2 Electromagnetic separation method

(iv)**Chemical method**

This method is employed in case where the ore is to be in a very pureform, e.g., aluminium extraction. Bauxite (Al_2O_3), an ore of aluminium, contains SiO_2 and Fe_2O_3 as impurities. When bauxite ore is treated with NaOH, the Al_2O_3 goes into solution as sodium meta-aluminate leaving behind the undissolved impurities [Fe_2O_3, SiO_2, $Fe(OH)_3$,etc.], which are then filtered off.

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$
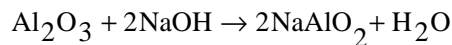
Sod. meta. aluminate
(In solution form)

The filtrate (containing sodium meta-aluminate) on dilution, and stirring gives a precipitate of aluminium hydroxide, which is filtered, and ignited to get pure alumina.

$$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 + NaOH$$
$$\text{Ppt}$$

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$
$$\text{Pure}$$
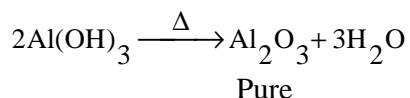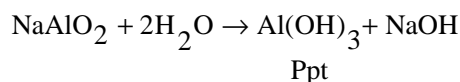
2.4 Metallurgical processes

Metallurgy is a branch of chemistry which deals with,

(i) Extraction of metals from ores

(ii) Refining of crude metal

(iii) Producing alloys and the study of their constitution, structure and properties.

(iv) The relationship of physical and mechanical treatment of metals to alloys.

The extraction of metals cannot be carried out by any universal method because extraction of each metal requires different methods of extraction. This depends upon the nature and preparation of metals. In general, noble metals such as Au, Ag, etc are usually extracted by electrolysis of their chlorides, oxides or hydroxides. Heavy metals, e.g. Cu, Zn, Fe, Pb, Sn, etc., are extracted by making use of roasting and smelting methods.

2.4.1 Roasting- oxidation

Roasting is one of the oxidation method where ore is converted into metal oxide. In the process of roasting, the ore either alone or with the addition of suitable material, is subjected to the action of heat in excess of air at temperature below its melting point. Roasting is usually carried out in a reverber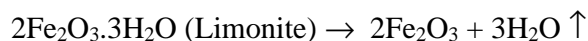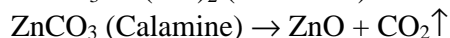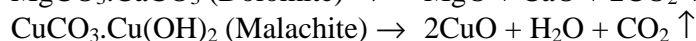atory fur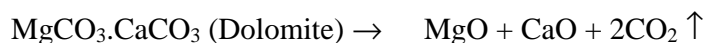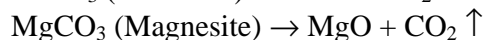nace or in a blast furnace. During roastin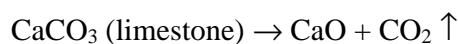g (a) Volatile impurities like S, As, Sb etc. get oxidized and escape out as volatile gases SO_2, As_2O_3 and Sb_2O_3 (b) The sulphide ores decompose to their oxides evolving SO_2 (c) The moisture is removed. Mass becomes porous and thus it can easily be reduced. Roasting may be of many types.

Oxidising Roasting – In this type of roasting S, As, and Sb impurities are removed in the form of their volatile oxides as SO_2, As_2O_3 and Sb_2O_3 etc. due to combined action of heat and air. The ore is simultaneously converted into its oxides. This type of roasting is carried out for ores like copper pyrites, zinc blende and lead ores (PbS) etc.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$
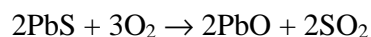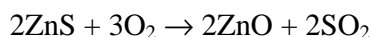
Calcination

Another method of conversion of ore into metal oxide (oxidation) is called calcination. It is the process in which the ore is subjected to the action of heat at high temperature in the absence of air below its melting point. The process of calcination is carried out in the case of carbonate and hydrated ore. As a result of calcination (a) The moisture is removed. (b) Gases may be expelled. (c) Volatile impurities are removed. (d) The mass becomes porous. (e) Thermal decomposition of the ore takes place. For example,

$CaCO_3$ (limestone) $\rightarrow CaO + CO_2 \uparrow$
$MgCO_3$ (Magnesite) $\rightarrow MgO + CO_2 \uparrow$

$MgCO_3.CaCO_3$ (Dolomite) $\rightarrow \quad MgO + CaO + 2CO_2 \uparrow$
$CuCO_3.Cu(OH)_2$ (Malachite) $\rightarrow 2CuO + H_2O + CO_2 \uparrow$
$ZnCO_3$ (Calamine) $\rightarrow ZnO + CO_2 \uparrow$

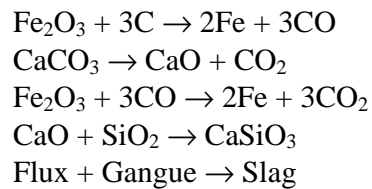$2Fe_2O_3.3H_2O$ (Limonite) $\rightarrow 2Fe_2O_3 + 3H_2O \uparrow$

The name calcination originated from the ore calcite which on thermal decomposition gives quick lime. Calcination is usually carried out in reverberatory furnace.
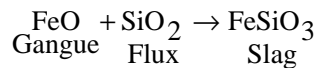
2.4.2 Smelting – Reduction

Smelting is one of reduction method where the metal oxide is converted into metal. It is the process used for all operations where the metal is separated by fusion from the ore. The process of smelting is that in which ore is melted with a flux and often with a reducing agent, and it involves, calcination, roasting and reduction. In general, the process of separation of a metal or its sulphide mixture from its ore in fused state is

called smelting. Smelting is generally carried out in a blast furnace and high temperature is produced by burning coal or by using electric energy.
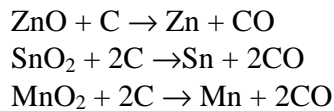
In smelting, the roasted or calcined ore is mixed with coke and then heated in a furnace. As a result, (carbon and CO produced by the incomplete combustion) carbon reduces the oxide to the metal. For example, in the extraction of iron, haematite ore(Fe_2O_3) is smelted with coke and limestone (flux). As a result of reduction, iron is obtained in fused or molten state.

$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$

$CaCO_3 \rightarrow CaO + CO_2$

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

$CaO + SiO_2 \rightarrow CaSiO_3$

$Flux + Gangue \rightarrow Slag$

Similarly, in the extraction of copper from **copper pyrites,** the ore is mixed with coke and heated in blast furnace (smelted). Infusible impurity FeO is converted to $FeSiO_3$(slag) and is removed. A mixture containing sulphide of copper and iron, called **matte** is formed in the molten state.

$$\underset{Gangue}{FeO} + \underset{Flux}{SiO_2} \rightarrow \underset{Slag}{FeSiO_3}$$

Other Examples

$ZnO + C \rightarrow Zn + CO$

$SnO_2 + 2C \rightarrow Sn + 2CO$

$MnO_2 + 2C \rightarrow Mn + 2CO$

2.4.3 Bessemerisation

It is the process used for the manufacture of steel from pig iron. Steel is an alloy of carbon and iron and contains 0.15-1.5% of carbon with traces of sulphur, phosphorus, manganese and silicon as impurities. Depending upon the carbon content, steel are classified into three classes namely mild carbon steel (0.15-0.3%), medium carbon steel (0.3-0.8%) and high carbon steel (0.8-1.50).

The process was discovered by Henry Bessemer in England (1856). The principle involved in this process is that cold air blowed through refractory lined vessel known as converter containing molten pig iron at about 2 atmospheric pressure, oxidizing the impurities and simultaneously converting pig iron to steel.

This process mainly differs in the use of acidic and basic refractory linings of the converters. In this process low phosphorus pig iron (below 0.09%) is treated by acidic Bessemer process and high phosphorus pig iron (more than 1.5%) is treated in basic.

The converter is a pear shaped furnace about 6m high and 3m in diameter. It is made of steel plates and is lined inside with silica or magnesia (MgO), depending upon the nature of impurities present in the pig iron. If the impurities present in the pig iron are basic, e.g., manganese, a lining of silica brick is used and the process is known as **acid Bessemer process**. If impurities are acidic, e.g., sulphur, phosphorus etc., a basic lining of lime (CaO) or magnesia (MgO) is used in the converter and process is then known as **basic Bessemer process.** The capacity of the converter is from 10-25 tonnes of charge at a time. The converter is mounted on shafts or trunnions, one of which is hollow and serves as a wind pipe and upon which the converter can rotate in any position. The converter is also provided with a number of holes at the bottom through which a hot blast of air can be introduced.

The molten pig iron is mixed in mixers and then charged into converter. About 15-16 tonnes of iron can be charged at a time. The converter is first set in the horizontal position and after charging the converter is adjusted in vertical position. After charging a blast of cold air is admitted through the hole provided at the bottom at a pressure of about 2-3 kg/cm^3. The blast is continued for about 15 minutes during which the impurities are oxidized. Mn is oxidized to MnO and Si is oxidized to SiO_2. Carbon is also oxidized to CO. The resulting oxides of Mn and Si (MnO and SiO_2) combine together to form slag of manganese silicate Fig.3.4.1.
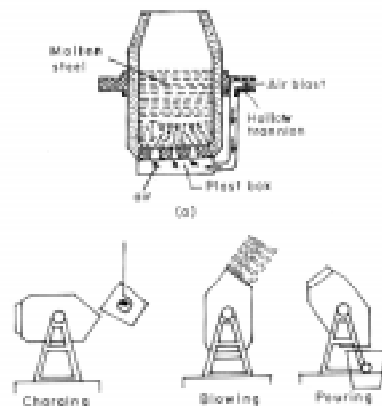
**Fig. 2.3 Bessemer Converter and Bessemer Process**

2.4.4 Purification of metals

(a) Electrolytic refining

This is one of the most convenient and important method of refining and gives a metal of high purity. This method is applicable to many metals such as **Cu, Ag, Pb, Au, Ni, Sn, Zn etc.** The blocks of impure metal form the anode and thin sheets of pure metal form the cathode. A solution of a salt of the metal is taken as an electrolyte. On passing an electric current through the solution pure metal dissolves from the anode and deposits on cathode. By this process, more metal ions undergo reduction and pure metal is deposited at the cathode. The insoluble impurities either dissolve in the electrolyte or fall at the bottom and collect as **anode mud**. For example, in the refining of copper, impurities like Fe and Zn dissolve in the electrolyte, while Au, Ag and Pt are left behind as anode mud.

(i) **Copper:** During the electrolytic refining of a copper, a thick block of impure copper is made anode, and thin plate of pure copper is made cathode. Copper sulphate solution is used as an electrolyte. On passing electric current, following reactions take place:

1) Cu^{2+} ions (from copper sulphate solution) go to the cathode (negative electrode), where they are reduced to copper, which gets deposited on the cathode.

$$Cu^{2+} + 2e^- \rightarrow Cu$$
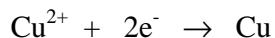
2) Copper (of impure anode) forms copper ions, and these go into solution of electrolyte.

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

Thus, the net result is transfer of pure copper from anode to the cathode. Impurities like zinc, iron, etc., go into solution; while noble impurities like silver, gold, etc., are left behind as anode mud. Copper is refined to 99.98% pure copper by electrolytic refining (Fig. 2.4).

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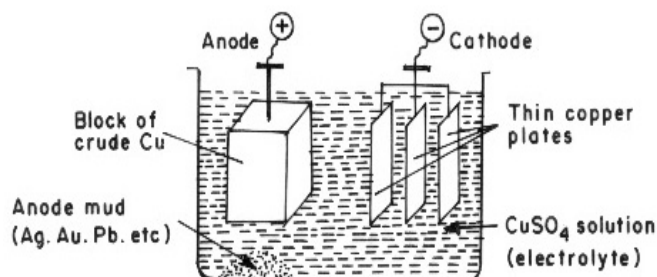
Fig. 2.4 Electrolytic refining of copper

(b) Zone refining

This method is employed for preparing highly pure metal (such as silicon, tellurium, germanium), which are used as semiconductors. It is based on the principle that melting point of a substance is lowered by the presence of impurities. Consequently, when an impure molten metal is cooled, crystals of the pure metal are solidified, and the impurities remain behind the remaining metal. (Fig. 2.5).
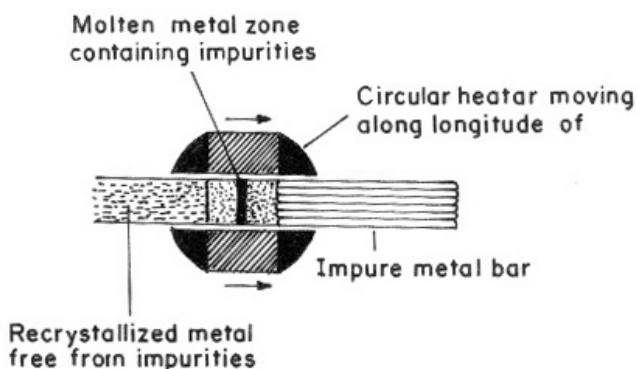
Fig. 2.5 Zone refining

The process consists in casting the impure metal in the form of a bar. A circular heater fitted around this bar is slowly moved longitudinally from one end to the other. At the heated zone, the bar melts, and as the heater moves on, pure metal crystallizes, while the impurities pass into the adjacent molten part. In this way, the impurities are swept from one end of the bar to the other. By repeating the process, ultra pure metal can be obtained.

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(c) Mond's process

Thermal methods include methods as carbonyl method, decomposition of hydrides etc. The carbonyl method is used for the refining of metals like Ni and Fe. For example, in case of nickel, the impure metal is heated with CO. The nickel carbonyl thus formed is then decomposed (after distilling off the impurities) to get pure nickel metal and CO. The process is known as **Mond's process.**

$$Ni + 4CO \rightarrow Ni(CO)_4 \rightarrow Ni + 4CO$$

It is based on the following facts:

(a) Only nickel (and not Cu, Fe, etc.) forms a volatile carbonyl, $Ni(CO)_4$, when CO is passed over it at 50^0C.

(b) the nickel carbonyl decomposes at 180^0C to yield pure nickel.

Questions

A. Fillup the blanks

1. The earthy impurities associated with ores are ……………..
2. Froth flotation process is suitable for concentrating …………… ores.
3. Highly pure metals are obtained by ………… process.
4. Gangue + flux $\rightarrow$ ……………………..
5. A mineral from which metal can be profitably extracted is called ……………
6. A mixture containing sulphides of copper and iron is called …………….
7. ………………… is used as a foaming agent.

B. Write in one or two sentence

1. Distinguish between ore and mineral with suitable example ?
2. What are the elements obtained from sea water source?
3. What are the different methods of concentration of ores?
4. What is gravity separation ?
5. Name the ores which are concentrated by froth floatation process.
6. Define Metallurgy.
7. What are the major steps involved in the metallurgical process ?
8. What is calcination? Give example.

9. What is the principle involved in Bessemer process ?
10. What is meant by electrolytic refining? Give example.
11. What is anode mud?
12. What do you understand by the following terms (i) roasting (ii) smelting

C. Explain briefly on the following
1. Write short note on source of element in living system.
2. Explain froth flotation process with neat diagram.
3. How electrolytic separation process is useful in the separation of magnetic impurities from nonmagnetic ores? Draw the diagram.
4. How the impurities of ore are removed by chemical method?
5. What is roasting ? Explain different types of roasting with suitable example.
6. What is smelting ? Explain the process with example.
7. What is Zone refining ? Describe the principle involved in the purification of the metal by this method.
8. How nickel is extracted by Mond's process? Write the various reactions involved in the process.
9. Write short note on mineral wealth of India.
10. Give a brief account of the mineral wealth of Tamil Nadu.

SUMMARY
*   This chapter explains and summarizes the salient features of metallurgy
*   Different types of ores and their purification methods
*   Chemistry behind roasting, smelting and bessemerisation processes
*   Various methods of refining process

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3. ATOMIC STRUCTURE - I

OBJECTIVES

- *Know about the history of structure of atom.*

- *Recognise the merits and demerits of Niels Bohr's model of an atom.*

- *Learn about Sommerfield's atom model.*

- *Analyse the significance of quantum number.*

- *Learn about the shapes of orbitals.*

- *Understand the quantum designation of electron.*

- *Know the application of Pauli's exclusion principle, Hund's rule and Aufbau principle.*

- *Understand the stability of different orbitals and its application in writing the electronic configuration.*

- *Know about the classification of elements based on electronic configuration.*

3.1 Brief introduction of history of structure of atom

The introduction of the atomic theory by John Dalton in 1808 marks the inception of a modern era in chemical thinking. According to this theory, all matter is composed of very small particles called atoms. The atoms were regarded to be structureless, hard, impenetrable particles which cannot be subdivided. Dalton's ideas of the structure of matter were born out by a considerable amount of subsequent experimental evidences towards the end of the nineteenth century. Early in the twentieth century, it has been proved that an atom consists of smaller particles such as electrons, protons and neutrons. The proton, a positively charged particle, is present in the central part of the atom called nucleus. The electron, a negatively charged particle, is present around the nucleus. The neutron, a neutral particle, is also present in the nucleus of the atom. Since the atom is electrically neutral, the number of positive charges on the nucleus is exactly balanced by an equal number of orbital electrons.

Thomson's Model of atom

In 1904 Sir J. J. Thomson proposed the first definite theory as to the internal structure of the atom. According to this theory the atom was assumed to consist of a sphere of uniform distribution of about 10^{-10}m positive charge with electrons embedded in it such that the number of electrons equal to the number of positive charges and the atom as a whole is electrically neutral.

This model of atom could account the electrical neutrality of atom, but it could not explain the results of gold foil scattering experiment carried out by Rutherford.

Rutherford's Scattering Experiment

Rutherford conducted a scattering experiment in 1911 to find out the arrangement of electrons and protons. He bombarded a thin gold foil with a stream of fast moving positively charged α-particles emanating from radium.

Rutherford's Nuclear model of a atom

This model resulted from conclusion drawn from experiments on the scattering of alpha particles from a radio active source when the particles were passed through thin sheets of metal foil. According to him

(i) Most of the space in the atom is empty as most of the α-particles passed through the foil.

(ii) A few positively charged α-particles are deflected. The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had thought. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α-particles. This very small portion of the atom was called **nucleus** by Rutherford.

(iii)Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The diameter of the atom is about 10^{-10} m while that of nucleus is 10^{-15}m. One can appreciate this difference in size by realizing that

if a cricket ball represents a nucleus, then radius of the atom would be about 5 km.

On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom. According to this model:

(a) An atom consists of a tiny positively charged nucleus at its centre.

(b) The positive charge of the nucleus is due to protons. The mass of the nucleus, on the other hand, is due to protons and some neutral particles each having mass nearly equal to the mass of proton. This neutral particle, called neutron, was discovered later on by Chadwick in 1932. Protons and neutrons present in the nucleus are collectively also known as nucleons. The total number of nucleons is termed as **mass number(A)** of the atom.

(c) The nucleus is surrounded by electrons that move around the nucleus with very high speed in circular paths called **orbits**. Thus, Rutherford's model of atom resembles the solar system in which the sun plays the role of the nucleus and the planets that of revolving electrons.

(d) The number of electrons in an atom is equal to the number of protons in it. Thus, the total positive charge of the nucleus exactly balances the total negative charge in the atom making it electrically neutral. The number of protons in an atom is called its atomic number**(Z).**

(e) Electrons and the nucleus are held together by electrostatic forces of attraction.

3.2 Defects of Rutherford's model

According to Rutherford's model, an atom consists of a positive nucleus with the electrons moving around it in circular orbits. However it had been shown by J. C. Maxwell that whenever an electron is subjected to acceleration, it emits radiation and loses energy. As a result of this, its orbit should become smaller and smaller Fig. 3.1.   and finally it should drop into the nucleus by following a spiral path. This means that atom would collapse and thus Rutherford's model failed to explain stability of atoms.
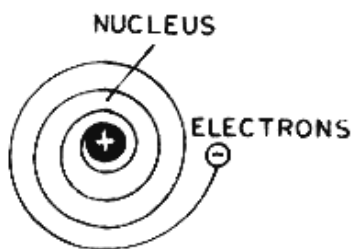
Fig. 3.1 Failure of Rutherford's atom model

Another drawback of the Rutherford's model is that it says nothing about the electronic structure of the atoms i.e., how the electrons are distributed around the nucleus and what are the energies of these electrons. Therefore, this model failed to explain the existence of certain definite lines in the hydrogen spectrum.

**Postulates of Bohr's model of an atom**

To overcome the above defects of Rutherford's model, Niels Bohr in 1913 gave a modification based on Quantum theory of radiation. The important postulates are:

(1) The electrons revolve round the nucleus only in certain selected circular paths called orbits. These orbits are associated with definite energies and are called energy shells or energy levels or quantum levels. These are numbered as 1, 2, 3, 4 ….. etc. (starting from the nucleus) are designated as K, L, M, N ….etc. (Fig. 3.2).

(2) As long as an electron remains in a particular orbit, it does not lose or gain energy. This means that energy of an electron in a particular path remains constant. Therefore, these orbits are also called stationary states.

(3) Only those orbits are permitted in which angular momentum of the electron is a whole number multiple of $h/2\pi$, where 'h' is Planck's constant. An electron moving in a circular orbit has an angular momentum equal to mvr where m is the mass of the electron and v, the angular momentum, mvr is a whole number multiple of $h/2\pi$ i.e.,

$$mvr = nh/2\pi \text{ where } n = 1, 2, 3……$$

In other words, angular velocity of electrons in an atom is quantised.

(4) If an electron jumps from one stationary state to another, it will absorb or emit radiation of a definite frequency giving a spectral line of that frequency which depends upon the initial and final levels. When an electron jumps back to the lower energy level, it radiates same amount of energy in the form of radiation.
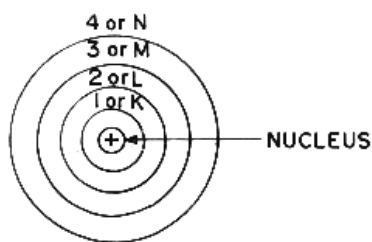
Fig. 3.2 Bohr's orbits

Limitation of Bohr's Theory

(i) According to Bohr, the radiation results when an electron jumps from one energy orbit to another energy orbit, but how this radiation occurs is not explained by Bohr.

(ii) Bohr Theory had explained the existence of various lines in H-spectrum, but it predicted that only a series of lines exist. At that time this was exactly what had been observed. However, as better instruments and techniques were developed, it was realized that the spectral line that had been thought to be a single line was actually a collection of several lines very close together (known as fine spectrum). Thus for example, the single H∞-spectral line of Balmer series consists of many lines very close to each other.

(iii)Thus the appearance of the several lines implies that there are several energy levels, which are close together for each quantum number n. This would require the existence of new quantum numbers.

(iv) Bohr's theory has successfully explained the observed spectra for hydrogen atom and hydrogen like ions (e.g. He^+, Li^{2+}, Be^{3+} etc.), it can not explain the spectral series for the atoms having a large number of electrons.

(v) There was no satisfactory justification for the assumption that the electron can rotate only in those orbits in which the angular momentum of the electron (mvr) is a whole number multiple of h/2π, i.e. he could not give any explanation for using the principle of quantisation of angular momentum and it was introduced by him arbitrarily.

(vi) Bohr assumes that an electron in an atom is located at a definite distance from the nucleus and is revolving round it with definite velocity, i.e. it is associated with a fixed value of momentum. This is against the Heisenberg's Uncertainty Principle according to which it is impossible to determine simultaneously with certainty the position and the momentum of a particle.

(vii) No explanation for Zeeman effect: If a substance which gives a line emission spectrum, is placed in a magnetic field, the lines of the spectrum get split up into a number of closely spaced lines. This phenomenon is known as Zeeman effect. Bohr's theory has no explanation for this effect.

(viii) No explanation of the Stark effect: If a substance which gives a line emission spectrum is placed in an external electric field, its lines get spilt into a number of closely spaced lines. This phenomenon is known as Stark effect. Bohr's theory is not able to explain this observation as well.

3.3 Electronic configuration and quantum numbers

Quantum Numbers

The quantum numbers are nothing but the details that are required to locate an electron in an atom. In an atom a large number of electron orbitals are permissible. An orbital of smaller size means there is more chance of finding the electron near the nucleus. These orbitals are designated by a set of numbers known as quantum numbers. In order to specify energy, size, shape and orientation of the electron orbital, three quantum numbers are required these are discussed below.

1. The principal quantum number (n)

The electrons inside an atom are arranged in different energy levels called electron shells or orbits. Each shell is characterized by a quantum

number called principal quantum number. This is represented by the letter 'n' and 'n' can have values, 1,2,3,4 etc. The first level is also known as K level. Second as L level, third as M level, fourth as N level and so on. The first or K level is the orbit nearest to the nucleus and next one is second or L level and so on.

2. The subsidiary or azimuthal quantum number (l)

According to Sommerfield, the electron in any particular energy level could have circular path or a variety of elliptical paths about the nucleus resulting in slight differences in orbital shapes with slightly differing energies due to the differences in the attraction exerted by the nucleus on the electron. This concept gave rise to the idea of the existence of sub-energy levels in each of the principal energy levels of the atom. This is denoted by the letter 'l' and have values from 0 to n-1.

Thus, if n=1, l=0 only one value (one level only) s level.

n=2, l=0 and 1 (2 values or 2 sub- levels) s and p level.

n=3, l=0, 1 and 2 (3 values or 3 sub-levels) s, p and d level.

n=4, l=0, 1, 2 and 3 (4 values or 4 sub-levels) s, p, d and f level.

3. Magnetic quantum number (m)

In a strong magnetic field a sub-shell is resolved into different orientations in space. These orientations called orbitals have slight differences in energy. This explains the appearance of additional lines in atomic spectra produced when atoms emit light in magnetic field. Each orbitals is designated by a magnetic quantum number m and its values depends on the value of 'l'. The values are -'l' through zero to +'l' and thus there are (2l+1) values.

Thus when l=0, m= 0 (only one value or one orbital)

l=1, m= -1, 0, +1 (3 values or 3 orbitals)

l=2, m= -2, -1, 0, +1, +2 (5 values or 5 orbitals)

l=3, m= -3,-2, -1, 0, +1, +2, +3 (7 values or 7 orbitals).

The three quantum numbers labeling an atomic orbital can be used equally well to label electron in the orbital. However, a fourth quantum

number, the spin quantum number, (*s*) is necessary to describe an electron completely.

4. Spin quantum number (*s*)

The electron in the atom rotates not only around the nucleus but also around its own axis and two opposite directions of rotation are possible (clock wise and anticlock wise). Therefore the spin quantum number can have only two values +1/2 or –1/2. For each values of m including zero, there will be two values for *s*.

To sum up, the four quantum numbers provide the following informations:

1. n identifies the shell, determines the size of the orbital and also to a large extent the energy of the orbit.

2. There are n subshells in the nth shell. *l* identifies the subshell and determines the shape of the orbital. There are ($2l$+1) orbitals of each type in a subshell i.e., one s orbital (*l*=0), three p orbitals (*l*=1), and five d orbitals (*l*=2) per subshell. To some extent *l* also determines the energy of the orbital in a multi-electron atom.

3. m_l designates the orientation of the orbital. For a given value of *l*, m_l has ($2l$+1) values, the same as the number of orbitals per subshell. It means that the number of orbitals is equal to the number of ways in which they are oriented.

4. m_s refers to orientation of the spin of the electron.

Example 1

What is the total number of orbitals associated with the principal quantum number n=3 ?

Solution

For n = 3, the possible values of *l* are 0,1 and 2. Thus, there is one 3s orbital (n = 3, *l* = 0 and m_l = 0); there are three p orbitals (n = 3, *l* = 1 and m_l = -1, 0, 1) there are five 3d orbitals (n = 3, *l* = 2, m_l = -2, -1, 0, 1, 2).

Therefore, the total number of orbitals is 1+3+5 = 9.

Example 2

Using s, p, d, f notations, describe the orbital with the following quantum numbers (a) n=2, $l = 1$ (b) n = 4, $l = 0$ (c) n = 5, $l = 3$ (d) n = 3, $l = 2$.

Solution

	n	l	orbital
(a)	2	1	2p
(b)	4	0	4s
(c)	5	3	5f
(d)	3	2	3d

3.4 Shapes or boundary surfaces of Orbitals

s-orbitals: For s-orbital $l = 0$ and hence, m can have only one value, i.e., m = 0. This means that the probability of finding the electron in s-orbital is the same in all directions at a particular distance. In other words s-orbitals are spherically symmetrical.

The electron cloud picture of 1s-orbital is spherical. The *s*-orbitals of higher energy levels are also spherically symmetrical. However, they are more diffused and have spherical shells within them where probability of finding the electron is zero. These are called nodes. In 2*s*-orbital there is one spherical node. In the ns orbital, number of nodes are (n-1).

p-orbitals: For p-orbitals $l = 1$ and hence 'm' can have three possible values +1, 0, -1. This means that there are three possible orientations of electron cloud in a *p*-sub-shell. The three orbitals of a *p*-sub-shell are designated as p_x, p_y and p_z respectively along x-axis, y-axis and z-axis respectively. Each *p*-orbital has two lobes, which are separated by a point of zero probability called node. Each *p*-orbital is thus dumb bell shaped.

In the absence of magnetic field these three *p*-orbitals are equivalent in energy and are, therefore, said to be three-fold degenerate or triply degenerate. In the presence of an external magnetic field, the relative energies of the three *p* orbitals vary and depend on their orientation or

magnetic quantum number. This probably accounts for the splitting of a single spectral line into a number of closely spaced lines in presence of a magnetic field (fine structure).

d-orbitals: For *d*-orbitals $l = 2$, m = 0, ±1, ±2 indicating that d-orbitals have five orientations, i.e., there are five *d*-orbitals which are named as d_{xy}, d_{yz}, d_{zx}, d_z^2 and $d_{x^2-y^2}$. All these five orbitals, in the absence of magnetic field, are equivalent in energy and are, therefore, said to be five-fold degenerate

The three orbitals namely d_{xy}, d_{yz} and d_{zx} have their lobes lying symmetrically between the coordinate axes indicated in the subscript to d, e.g. the lobes of d_{xy} orbital are lying between the x-and y-axes. This set of three orbitals is known as t$_{2g}$ set. $d_{x^2-y^2}$ and d_z^2 orbitals have their lobes along the axes (i.e. along the axial directions), e.g., the lobes of d   orbital lie along the x and y-axes, while those of d_z^2 orbital lie along the z-axis. This set is known as e$_g$ set.

3.5 Pauli's exclusion principle

The filling of electron into the orbitals of different atoms takes place according to the Aufbau principle, which is based on the Pauli's exclusion principle and the Hund's rule of maximum multiplicity.

The distribution of quantum numbers among the electrons in a given atom is governed by Pauli's Exclusion principle, which states that *"it is impossible for any two electrons in a given atom to have all the four quantum numbers identical"* i.e., in an atom, two electrons can have maximum three quantum numbers (n, *l* and m) the same and the fourth (*s*) will definitely be having a different value. Thus if s = +1/2 for one electron, s should be equal to –1/2 for the other electron. In other words the two electrons in the same orbital should have opposite spins (↑↓).

Uses of the principle

The greatest use of the principle is that it is helpful in determining the maximum number of electrons that a main energy level can have. Let us illustrate this point by considering K and L shells.

(a) K-shell: For this shell n = 1. For n = 1, $l = 0$ and m = 0. Hence *s* can have a value either +1/2 or –1/2. The different values of n, *l*, m and s

given above give the following two combinations of the four quantum numbers, keeping in view the exclusion principle. Combination (i) is for one electron and combination (ii) is for the other electron.

(i) n = 1, l = 0, m = 0

   s = +1/2 (1st electron)

(ii) n = 1, l = 0, m = 0,

   s = -1/2 (2nd electron)

   (Two electrons in l = 0 sub-shell i.e., 1s-orbital)

These two combinations show that in K shell there is only one sub-shell corresponding to l = 0 value (s-sub-shell) contains only two electrons with opposite spins.

(b) L-shell: For this shell n = 2. For n = 2 the different values of l, m and s give the following eight combinations of four quantum numbers.

(i)   n= 2, l = 0, m = 0, s = +1/2

(ii)   n = 2, l = 0, m = 0, s = -1/2

(iii)   n = 2, l = 1, m = 0, s = +1/2

(iv)   n = 2, l = 1, m = 0, s = -1/2

(v)   n = 2, l = 1, m = +1, s = +1/2

(vi)   n = 2, l = 1, m = +1, s = -1/2

(vii)   n = 2, l = 1, m = -1, s = +1/2

(viii) n = 2, l = 1, m = -1, s = -1/2

Eight combinations given above show that L shell is divided into two sub-shells corresponding to l = 0 (s sub-shell) and l = 1 (p sub-shell) and this shell cannot contain more than 8 electrons, i.e., its maximum capacity for keeping the electrons is eight.

3.6 Hund's rule of maximum multiplicity

Hund's rule of maximum multiplicity states, that in filling p, d or f orbitals, as many unpaired electrons as possible are placed before pairing of electrons with opposite spin is allowed. Pairing of electrons requires energy. Therefore **no pairing occurs until all orbitals of a given sub-level are half filled.** This is known as Hund's rule of maximum multiplicity. It states that when electrons enter sub-levels of fixed (n+1) values , available orbitals are singly occupied (Table 3.1).

Table 3.1 Representation of arrangements of electrons

Atomic Number	Element	1s	2s	$2p_x$	$2p_y$	$2p_z$	Number of unpaired electrons
1	H	↑					1
2	He	↑↓					0
3	Li	↑↓	↑				1
4	Be	↑↓	↑↓				0
5	B	↑↓	↑↓	↑	↑		1
6	C	↑↓	↑↓	↑	↑		2
7	N	↑↓	↑↓	↑	↑	↑	3
8	O	↑↓	↑↓	↑↓	↑	↑	2
9	F	↑↓	↑↓	↑↓	↑↓	↑	1
10	Ne	↑↓	↑↓	↑↓	↑↓	↑↓	0

Thus, if three electrons are to be filled in the p- level of any shell, one each will go into each of the three (p_x, p_y, p_z) orbitals. The fourth electron entering the p- level will go to p_x orbital which now will have two electrons with opposite spins (as shown above) and said to be paired. The unpaired electrons play an important part in the formation of bonds.

3.7 Aufbau Principle

The word 'aufbau' in German means 'building up'. The building up of orbitals means the filling up of orbitals with electrons. The principles states: **In the ground state of the atoms, the orbitals are filled in**

order of their increasing energies. In other words, electrons first occupy the lowest-energy orbital available to them and enter into higher energy orbitals only after the lower energy orbitals are filled. The order in which the energies of the orbitals increase and hence the order in which the orbitals are filled is as follows:

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

This order may be remembered by using the method given in Fig. 3.3. Starting from the top, the direction of the arrows gives the order of filling of orbitals. Alternatively, the order of increase of energy of orbitals can be calculated from (n +1) rule, explained below:

The lower the value of (n+1) for an orbital, the lower is its energy. If two orbitals have the same (n+1) value, the orbital with lower value of n has the lower energy.
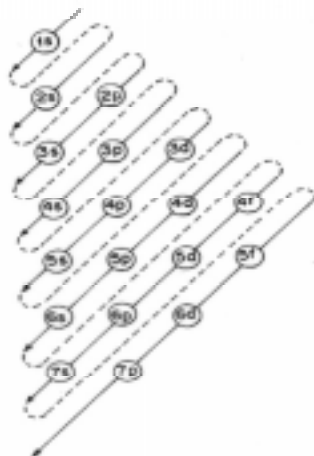
Fig. 3.3 Order of filling of orbitals

It may be noted that different subshells of a particular shell have different energies in case of many-electron atoms. However in hydrogen atom, they have the same energy.

3.8 Stability of orbitals

According to Hund's rule atoms having half-filled or completely-filled orbitals are comparatively more stable and hence more energy is

needed to remove an electron from such atoms. The ionization potential or ionization enthalpy of such atom is, therefore, relatively higher than expected normally from their position in the periodic table.

The extraordinary stability of half-filled and completely filled electron configuration can be explained in terms of symmetry and exchange energy. The half-filled and completely filled electron configurations have symmetrical distribution of electrons and this symmetry leads to stability. Moreover, in such configuration electron can exchange their positions among themselves to maximum extent. This exchange leads to stabilization for example, half-filled $2p$ orbital is Nitrogen and completely filled orbitals in Neon are given as follows.

Thus the $p^3, p^6, d^5, d^{10}, f^7$ and f^{14} configuration which are either completely filled or exactly half-filled are more stable.

Further, it may be noted that chromium and copper have five and ten electrons in $3d$ orbitals rather than four and nine electrons respectively as expected. Therefore, to acquire more stability one of the 4s electron goes into $3d$ orbitals so that $3d$ orbitals get half-filled or completely filled in chromium and copper respectively.

Chromium

Expected configuration : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^4, 4s^2$

Actual configuration   : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$

Electron exchange

Copper

Expected configuration : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^9, 4s^2$

Actual configuration   : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$

Electron exchange

Questions

A. Choose the best answer

1. Atomic mass of an element is not necessarily a whole number because :
   (a) It contains electrons, protons and neutrons
   (b) It contains allotropic forms
   (c) Atoms are no longer considered indivisible
   (d) It contains isotopes (e) None of these.

2. No two electrons in an atom will have all four quantum numbers equal. The statement is known as

   (a) Exclusion principle   (b) Uncertainity principle
   (c) Hund's rule   (d) Aufbau principle
   (e) Newlands law.

3. When the 3d orbital is complete, the new electron will enter the

   (a) 4p orbital (b) 4f orbital (c) 4s orbital

   (d) 4d orbital (e) 5s orbital.

4. The preference of three unpaired electrons in the nitrogen atom can be explained by : (a) Pauling's exclusion principle   (b) Aufbau principle (c) Uncertainty principle (d) Hund's rule (e) None of these.

5. The number of orbitals in a p-sub-shell is

   (a) 1 (b) 2 (c) 3 (d) 6 (e) 5.

6. The nucleus of an atom contains :

   (a) Electrons and protons (b) Neutrons and protons

   (c) Electrons, protons and neutrons (d) Neutrons and electrons

   (e) None of these.

7. Which is the lightest among the following? (a) An atom of hydrogen (b) An electron (c) A neutron (d) A proton (e) An alpha particle.

8. Which of the following has no neutrons in the nucleus? (a) Deuterium (b) Helium (c) Hydrogen (d) Tritium (e) An alpha particle.

9. When the value of the azimuthal quantum number is 3, the magnetic quantum number can have values :

   (a) +1,-1 (b) +1,0, 1 (c) +2,+1,0, -1,-2

   (d) +3,+2, +1,0, -1,-2,-3 (e) +3,-3.

10. 2p orbitals have :

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

   (d) $n = 2, l =1$ (e) $n =1, l =1$.

11. The atomic number of an element is 17 and its mass number is 37. The number of protons, electrons and neutrons present in the neutral atom are :

   (a) 17, 37,20 (b) 20,17,37 (c) 17, 17, 20 (d) 17, 20,17 (e) 37, 20, 17.

12. The maximum number of electrons that can be accommodated in the nth level is : (a) n^2 (b) n+1 (c) n-1 (d) $2n^2$ (e) 2 + n.

13. The magnetic quantum number decides : (a) The distance of the orbital from the nucleus (b) The shape of the orbital (c) The orientation of the orbital in space (d) The spin of the electron (e) None of these.

B. Fill up the blanks

1. The decomposition of an electrolyte by passage of electricity is known as ……………….

2. When cathode rays are focused on thin metal foil, it gets heated up to ……………

3. Cathode rays produce ……………on the walls of the discharge tube.

4. The radiations which were not influenced by a magnet were called………….

5. Neutrons are discovered by ………… ……………..

C. Write in one or two sentence

1. What is the charge of an electron, proton and a neutron ?

2. What is atomic number?

3. What is the maximum number of electrons that an orbital can have?

4. How many orbitals are there in the second orbit? How are they designated?

5. Sketch the shape of s and p-orbital indicating the angular distribution of electrons.

6. What are the charge and mass of an electron?

7. What is an orbital?

8. Give the order of filling of electrons in the following orbitals 3p, 3d,4p, 3d and 6s.

9. What is meant by principal quantum number?

10. How many protons and neutrons are present in $^{18}_{8}O$?

11. What are the particles generally present in the nuclei of atoms?

12. The atomic mass of an element is 24 and its atomic number is 12. Show how the atom of the element is constituted?

13. How will you experimentally distinguish between a ray of neutron and ray of proton?

14. What is the principal defect of Bohr atom model?

15. Write the complete symbol for : (a) The nucleus with atomic number 56 and mass number 138 ; (b) The nucleus with atomic number 26 and mass number 55 ; (c) The nucleus with atomic number 4 and mass number 9.

16. An atomic orbital has n = 3. What are the possible values of l ?

17. An atomic orbital has l= 3. What are the possible values of m?

18. Give the electronic configuration of chromium. (Z=24).

19. Which energy level does not have p-orbital?

20. An atom of an element has 19 electrons. What is the total number of p-orbital?

21. How many electrons can have s+ ½ in a d-sub-shell?

22. Write the values of l and m for p-orbitals.

23. Which quantum accounts for the orientation of the electron orbital?

24. What is shape of the orbital with (i) n = 2 and l = 0 ; (ii) n = 2 and l = 1?

25. Give the values for all quantum numbers for 2p electrons in nitrogen (Z = 7).

26. Give the electronic configuration of Mn^{2+} and Cu. Atomic number of Cu = 29 and Mn = 25.

27. Explain why the electronic configuration of Cr andCu are written as $3d^5$, $4s^1$ and $3d^{10}$ $4s^1$ instead of $3d^4$ $4s^2$ and $3d^9$ $4s^2$?

D. Explain briefly on the following

1. Describe Aufbau principle. Explain its significance in the electronic build up of atoms.

2. Using the s, p, d, notation, describe the orbital with the following quantum numbers? (a) n = 1, l=0; (b) n = 2,l = 0; (c) n = 3, l = 1; (d) n = 4, l =3.

3. Using the a Aufbau principle, write the electronic configuration in the ground state of the following atoms : Boron (Z = 5) Neon (Z = 10) and Aluminium (Z = 13).

4. What is Rutherford's α- ray scattering experiment? What are its conclusions?

5. What are the postulates of Bohr theory of atom?

6. Explain the various quantum numbers which completely specify the electron of an atom.

SUMMARY

- The model of the nuclear atom developed by Thomson, Rutherford and their defects are explained.

- Niel's Bohr model and sommerfield's extension were mentioned with diagrammatic representation.

- The location of electron in an atom through four quantum numbers are explained including their significance.

- Occupancy of electrons following Hund's rule Aufbau principle, Pauli's exclusion principle are explained with represnetation.

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4. PERIODIC CLASSIFICATION-I

OBJECTIVES

- *Recall the history of periodic classification.*

- *Understand the IUPAC periodic table and the nomenclature of elements with atomic number greater than 100.*

- *Understand the electronic configuration of the elements and the classification based on it.*

- *Analyse the periodicity of properties like atomic radii, ionisation potential, electron affinity electronegativity etc.*

- *Know the anamolous periodic properties of elements and to reason it.*

4.1 Brief history of periodic classification

More than one hundred and nine elements are known today,. The periodic table of elements is an important landmark in the history of chemistry. It would be difficult to study individually the chemistry of all the elements and their numerous compounds. The periodic table provides a systematic and extremely useful framework for organizing a lot of information available on the chemical behaviour of the elements into a few simple and logical patterns. This gave rise to the necessity of classifying the elements into various groups or families having similar properties. This classification has resulted in the formulation of periodic table. Periodic table may be defined as the arrangements of various elements according to their properties in a tabular form.

All earlier attempts on the classification of elements were based on atomic mass. Several chemists have for long tried to classify the elements and to find patterns in their properties.

Dobereiner's Triads

In 1829, *John Dobereiner* (German Chemist) classified elements having similar properties into groups of three. These groups were called triads. According to this law when elements are arranged in the order of increasing atomic mass in a triad, the atomic mass of the middle element

was found to be approximately equal to the arithmetic mean of the other two elements. For example lithium, sodium and potassium constituted one triad. However, only a limited number of elements could be grouped into traids.

Table 4.1 Doberenier's Triads

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

Newlands Law of Octaves

In 1865, John Newlands (English Chemist) observed that if the elements were arranged in order of their increasing atomic weights, the eighth element starting from a given one, possessed properties similar to the first, like the eighth note in an octave of music. He called it the law of octaves. It worked well for the lighter elements but failed when applied to heavier elements.

Lother-Meyer's Arrangement

In 1869, **J. Lother-Meyer** in Germany gave a more detailed and accurate relationship among the elements., Lother-Meyer plotted atomic volumes versus atomic weights of elements and obtained a curve. He pointed out that elements occupying similar positions in the curve possessed similar properties.

Mendeleev's Periodic Table

In 1869, Dimitriv Mendeleev (Russian Chemist) arranged the 63 chemical elements, then known, according to their increasing order of atomic weights. He gave his famous scheme of the periodic classification of elements known as the periodic law. The law states that " the properties of the elements are the periodic function of their atomic

weights". It means that when elements are arranged in order of increasing atomic weights, the elements was similar properties recur after regular intervals. On the basis of this periodic law Mendeleev constructed a periodic table in such a way that the elements were arranged horizontally in order of their increasing atomic weights. Mendeleev, while studying his Periodic Table had found that in certain cases the regularity in behaviour between two succeeding elements was not observed. In order to overcome this he had kept gaps between such elements and had predicted that the gaps would be filled by new elements, to be discovered in future, For example, both gallium and germanium were not discovered at the time when Mendeleev proposed the periodic table. Mendeleev named these elements as eka-aluminium and eka-silicon because he believed that they would be similar to aluminium and silicon respectively. These elements were discovered later and Mendeleev's prediction proved remarkably correct. The discoveries / synthesis of new elements have continued even to the present day, raising their number to 120. The elements with atomic numbers upto 92 (i.e. uranium) are found in nature. The rest known as transuranium elements have been synthesized in the laboratories, which are highly unstable. They decay radioactively.

The modified periodic table is essentially similar to that of Mendeleev with a separate column added for noble gases, which were not discovered until the closing years of the nineteenth century. The general plan of the modified Mendeleev's periodic table is improved.

The Mendeleev's modified periodic table consists of:

(1) Nine vertical columns called groups. These are numbered from I to VIII and zero. (The members of zero group were not discovered at the time of Mendeleev). Each group from I to VII is further sub-divided into two sub-groups designated as A and B. Group VIII consists of three sets, each one containing three elements. Group zero consists of inert gases.

(2) Seven horizontal rows, called periods. These are numbered from 1 to 7. First period contains two elements. Second and third periods contain eight elements each. These periods are called short periods. Fourth and fifth contains eighteen elements each. These periods are called long periods. Sixth period contains thirty two elements and is called longest

period. Seventh period is incomplete and contains nineteen elements according to early classification.

4.2 IUPAC periodic table and IUPAC nomenclature of elements with atomic number greater than 100

Modern Periodic Law

In 1913, a British Physicist Henry Moseley showed that the atomic number is a more fundamental property of an element than its atomic weight. This observation led to the development of modern periodic law. The modern periodic law states that " the physical and chemical properties of the elements are periodic function of their atomic numbers."

This means that when the elements are arranged in order of increasing atomic numbers, the elements with similar properties recur after regular intervals. The periodic repetition is called periodicity. The physical and chemical properties of the elements are related to the arrangement of electrons in the outermost shell. Thus, if the arrangement of electrons in the outermost shell (valence shell) of the atoms is the same, their properties will also be similar. For example, the valence shell configurations of alkali metals show the presence of one electron in the s-orbital of their valence shells.

Similar behaviour of alkali metals is attributed to the similar valence shell configuration of their atoms. Similarly, if we examine the electronic configurations of other elements, we will find that there is repetition of the similar valence shell configuration after certain regular intervals with the gradual increase of atomic number. Thus we find that the periodic repetition of properties is due to the recurrence of similar valence shell configuration after certain intervals. It is observed that similarity in properties is repeated after the intervals of 2, 8, 18, or 32 in their atomic numbers.

Long form of the Periodic Table: The periodic table is constructed on the basis of repeating electronic configurations of the atoms when they are arranged in the order of increasing atomic numbers. The long form of the Periodic table is given in a modified form in page number 70. Readers are advised to follow the periodic table closely while studying the structural features of the long form of the Periodic Table.

Structural Features of the Long form of the periodic Table: The long form of the periodic table consists of horizontal rows called periods and vertical columns called groups.

Periods: In terms of electronic structure of the atom, a period constitutes a series of elements whose atoms have the same number of electron shell i.e., principal quantum number (n). There are seven periods and each period starts with a different principal quantum number.

The first period corresponds to the filling of electrons in the first energy shell (n = 1). Now this energy level has only one orbital (1s) and, therefore, it can accommodate two electrons. This means that there can be only two elements (hydrogen, $1s^1$ and helium, $1s^2$) in the first period.

The second period starts with the electron beginning to enter the second energy shell (n = 2). Since there are only four orbitals (one 2s- and three 2p- orbitals) to be filled, it can accommodate eight electrons. Thus, second period has eight elements in it. It starts with lithium (Z = 3) in which one electron enters the 2s-orbital. The period ends with neon (Z = 10) in which the second shell is complete ($2s^2 2p^6$).

The third period begins with the electrons entering the third energy shell (n = 3). It should be noted that out of nine orbitals of this energy level (one s, three p and five d) the five 3d-orbitals have higher energy than 4s-orbitals. As such only four orbitals (one 3s and three 3p) corresponding to n = 3 are filled before fourth energy level begins to be filled. Hence, third period contains only eight elements from sodium (Z = 11) to argon (Z = 18).

The fourth period corresponding to n = 4 involves the filling of one 4s and three 4p-orbitals (4d and 4f orbitals have higher energy than 5s-orbital and are filled later). In between 4s and 4p-orbitals, five 3d-orbitals are also filled which have energies in between these orbitals. Thus, altogether nine orbitals (one 4s, five 3d and three 4p) are to be filled and therefore, there are eighteen elements in fourth period from potassium (Z = 19) to krypton (Z = 36). The elements from scandium (Z = 21) to zinc (Z = 30) are called 3d- transition series.

The fifth period beginning with 5s-orbital (n=5) is similar to fourth period. There are nine orbitals (one 5s, five 4d and three 5p) to be filled and, therefore, there are eighteen elements in fifth period from rubidium (Z = 37) to xenon (Z = 54).

The sixth period starts with the filling of 6s-orbitals (n= 6). There are sixteen orbitals (one 6s, seven 4f, five 5d, and three 6p) in which filling of electrons takes place before the next energy level starts. As such there are thirty two elements in sixth period starting from cesium (Z = 55) and ending with radon (Z = 86). The filling up of 4f orbitals begins with cerium (Z = 58) and ends at lutetium (Z = 71). It constitutes the first f-inner transition series which is called lanthanide series.

The seventh period begins with 7s-orbital (n = 7). It would also have contained 32 elements corresponding to the filling of sixteen orbitals (one 7s, seven 5f, five 6d and three 7p), but it is still incomplete. At present there are 23 elements in it. The filling up of 5f- orbitals begins with thorium (Z = 90) and ends up at lawrencium (Z = 103). It constitutes second f-inner transition series which is called actinide series. It mostly includes man made radioactive elements. In order to avoid undue extension of the periodic table the 4f and 5f- inner transition elements are placed separately.

The number of elements and the corresponding orbitals being filled are given below.

Table 4.2

Period	Principal Valence shell (=n)	Orbitals being filled up	Electrons to be accommo- dated	Number of electrons
First	N = 1	1s	2	2
Second	N = 2	2s, 2p	2+6	8
Third	n = 3	3s, 3p	2+6	8
Fourth	n = 4	4s, 3d, 4p	2 +10+6	18
Fifth	n = 5	5s, 4d, 5p	2+10+6	18
Sixth	n = 6	6s, 4f, 5d, 6p	2+14+10+6	32
Seventh	n = 7	7s, 5f, 6d, 7p	2+14+10+6	32

The first three periods containing 2, 8 and 8 elements respectively are called short periods, the next three periods containing 18, 18 and 32 elements respectively are called long periods.

Groups

A vertical column in the periodic table is known as group. A group consists of a series of elements having similar configuration of the outer energy shell. There *are* eighteen vertical columns in long from of the periodic table. According to the recommendations of the **International Union of Pure and Applied Chemistry** (IUPAC), these groups are numbered from 1 to 18. Previously, these were numbered from I to VII as A and B, VIII and zero groups elements. The elements belonging to the same group are said to constitute a family. For example, elements of group 17 (VII A) constitute halogen family.

IUPAC Nomenclature for Elements with Z > 100

The elements beyond uranium (Z = 92) are all synthetic elements and are known as transuranium elements. The elements beyond fermium are known as transfermium elements. These elements fermium (Z = 100), mendelevium (Z = 101), nobelium (Z = 102) and lawrencium (Z = 103) are named after the names of famous scientists. Although names and symbols to many of these elements have been assigned by these are still not universally accepted. Also some of these elements have been assigned two names/symbols. For example, element with atomic number 104 is called either Kurchatovium (Ku) or Rutherfordium (Rf) while element with atomic number 107 is called Neilsbohrium (Ns) or Borium (Bh). But the following elements have been assigned only one official name. For example element with atomic number 105 is called Dubnium, with atomic number 106 as Seaborgium, with atomic number 108 as Hassnium and with atomic number 109 is named as Meiternium. To overcome all these difficulties, IUPAC nomenclature has been recommended for all the elements with Z > 100. It was decided by IUPAC that the names of elements beyond atomic number 100 should use Latin words for their numbers. The names of these elements are derived from their numerical roots.

Numerical → roots	0	1	2	3	4	5	6	7	8	9
	nil	un	bi	tri	quad	pent	hex	sept	oct	en

Table 4.3

Atomic number	Name of the element	Symbol
101	Unnilunnium	Unu
102	Unnilbium	Unb
103	Unniltrium	Unt
104	Unnilquadium	Unq
105	Unnilpentium	Unp
106	Unnilhexium	Unh
107	Unnilseptium	Uns
108	Unniloctium	Uno
109	Unnilennium	Une
110	Ununnilium	Uun
111	Unununium	Uuu
112	Ununbium	Uub
113	Ununtrium	Uut
114	Ununquadium	Uuq
115	Ununpentium	Uup
116	Ununhexium	Uuh
117	Ununseptium	Uus
118	Ununoctium	Uuo
119	Ununennium	Uue
120	Unbinilium	Ubn

PERIODIC CHART OF THE ELEMENTS

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4.3 Electronic configuration and periodic table

There is a close connection between the electronic configuration of the elements and the long form of the Periodic Table. We have already learnt that an electron in an atom is characterized by a set of four quantum numbers and the principal quantum number (n) defines the main energy level known as the **Shell**. The electronic configuration of elements can be best studied in terms of variations in periods and groups of the periodic table.

(a) Electronic Configuration in periods

Each successive period in the periodic table is associated with the filling up of the next higher principal energy level (n=1, n=2,etc.). It can be readily seen that the number of elements in each period is twice the number of atomic orbitals available in the energy level that is being filled. The first period starts with the filling of the lowest level (1s) and has thus the two elements-hydrogen ($1s^1$) and helium ($1s^2$) when the first shell (K) is completed. The second period starts with lithium and the third electron enters the 2s orbital. The next element, beryllium has four electrons and has the electronic configuration $1s^2 2s^2$. Starting from the next element boron, the 2p orbitals are filled with electrons when the L shell is completed at neon ($2s^2 2p^6$). Thus there are 8 elements in the second period. The third period (n=3) begins at sodium, and the added electron enters a 3s orbital. Successive filling of 3s and 3p orbitals gives rise to the third period of 8 elements from sodium to argon.

The fourth period (n=4) starts at potassium with the filling up of 4s orbital. Now you may note that before the 4p orbital is filled, filling up of 3d orbitals becomes energetically favourable and we come across the so-called 3d Transition Series of elements. The fourth period ends at krypton with the filling up of the 4p orbitals. Altogether we have 18 elements in this fourth period. The fifth period (n=5) beginning with rubidium is similar to the fourth period and contains the 4d transition series starting at yttrium (Z=39). This period ends at xenon with filling up of the 5p orbitals. The sixth period (n=6) contains 32 elements and successive electrons enter 6s, 4f, 5d and 6p orbitals, in that order. Filling up of the 4f orbitals begins with cerium (Z=58) and ends at lutetium (Z=71) to give the 4f-inner transition series, which is called the **Lanthanoid Series**. The seventh period (n=7) is similar to the sixth

period with the successive filling up of the 7s, 5f, 6d and 7p orbitals and includes most of the man-made radioactive elements. This period will end at the element with atomic number 118 which would belong to the noble gas family. Filling up of the 5f orbitals after actinium (Z=89) gives the 5f-inner transition series known as the **Actinoid Series**. The 4f- and 5f- transition series of elements are placed separately in the periodic table to maintain its structure and to preserve the principle of classification by keeping elements with similar properties in a single column.

(b) Groupwise/electronic configuration

Elements in the same vertical column or group have similar electronic configurations, have the same number of electrons in the outer orbitals, and similar properties. Group 1 (the alkali metals) is an example.

Thus it can be seen that the properties of an element have periodic dependence upon the atomic number and not on relative atomic mass (Table 4.4).

Table 4.4 Types of elements : Electronic configuration of alkali metals

Atomic number	Symbol	Electronic configuration
3	Li	$1s^2 2s^1$ or [He] $2s^1$
11	Na	$1s^2 2s^2 2p^6 3s^1$ or [Ne] $3s^1$
19	K	$1s^2 2s^2 2p^6 3s^2\, 3p^6 4s^1$ or [Ar] $4s^1$
37	Rb	$1s^2 2s^2 2p^6 3s^2\, 3p^6 4s^2\, 3d^{10} 4p^6 5s^1$ or [Kr] $5s^1$
55	Cs	$1s^2 2s^2 2p^6 3s^2\, 3p^6 4s^2\, 3d^{10} 4p^6 5s^2\, 4d^{10} 5p^6 6s^1$ or [Xe] $6s^1$

Types of elements: *s-*, *p-*,*d-*, *f-* Blocks

The aufbau principle and the electronic configuration of atoms provide a theoretical foundation for the periodic classification. The

elements in a vertical column of the periodic table constitute a group or family and exhibit similar chemical behaviour. Strictly, helium belongs to the s-block but its positioning in the p-block along with other group 18 elements is justified because it has a completely filled valence shell ($1s^2$) and as a result, exhibits properties characteristic of other noble gases. The other exception is hydrogen. It has a lone s- electron and hence can be placed in group 1 (alkali metals). It can also gain an electron to achieve a noble gas arrangement and hence it can behave similar to a group 17 (halogen family) elements. Because it is a special case, we shall place hydrogen separately at the top of the Periodic Table. We will briefly discuss the salient features of the four types of elements marked in the periodic table.

s-Block Elements

The elements of group 1 (alkali metals) and group 2 (alkaline earth metals) which have ns^1 and ns^2 outermost electronic configuration belong to the **s-block elements.** They are all reactive metals with low ionization enthalpies. They lose the outermost electron(s) readily to form 1+ (in the case of alkali metal) or 2+ ions (in the case of alkaline earth metals). The metallic character and the reactivity increase as we go down the group. The compounds of the *s*-block elements, with the exception of those of beryllium are predominantly ionic.

p-Block Elements

The ***p*-Block Elements** comprise those belonging to groups 13 to 18 and together with the s-block elements are called the **Representative Elements or Main Group Elements.** The outermost electronic configuration varies from ns^2np^1 to ns^2np^6 in each period. Each period ends in a noble gas with a closed shell ns^2np^6 configuration. All the orbitals in the valence shell of the **noble gases** are completely filled by electrons and it is very difficult to alter this stable arrangement by the addition or removal of electrons. The noble gases thus exhibit very low chemical reactivity. Preceding the noble gas family are two chemically important groups of nonmetals. They are the **halogens** (groups 17) and **chalcogens** (group 16). These two groups of elements have higher negative electron gain enthalpies and readily add one or two electrons respectively to attain the stable noble gas configuration. The nonmetallic

character increases as we move from left to right across a period and metallic character increases as we go down the group.

The *d*-block Elements (Transition Elements)

These are the elements of group 3 to 12 in the center of the periodic table. These elements are characterized by filling of inner d orbitals by electrons and are therefore referred to as ***d*-Block Elements**. These elements have the outer electronic configuration $(n-1)\,d^{1-10}\,ns^{1-2}$. They are all metals. They mostly form colored ions and exhibit variable valency. However, Zn, Cd and Hg, which have the $(n-1)d^{10}\,ns^2$ electronic configuration, do not show most of the properties of transition elements in a way, transition metals form a bridge between the chemically active metals of s-block elements and less active metals of groups 13 and 14 and thus take their familiar name "transition elements"

The *f*-Block Elements (Inner-Transition elements)

The two rows of elements at the bottom of the periodic table, called the **Lanthanoids** $_{58}$Ce-$_{71}$Lu and **Actinoids.** $_{90}$Th-$_{103}$Lr are characterized by the outer electronic configuration $(n-2)\,f^{1-14}\,(n-1)\,d^{0-10}ns^2$. The last electron added to each element is an f-electron. These two series of elements are hence called the inner transition elements (f-Block Elements). They are all metals within each series, the properties of the elements are quite similar. The chemistry of the early actinoids is more complicated than the corresponding lanthanoids, due to the large number of oxidation states possible for these actinoid elements. Actinoid elements are radioactive. Many of the actinoid elements have been made only in nanogram quantities or less by nuclear reactions and their chemistry is not fully studied. The elements coming after uranium are called **transuranium** elements.

Example 1

The elements Z=117 and 120 have not yet been discovered. In which family / group would you place these elements and also give the electronic configuration in each case.

Solution

We see from the periodic table that element with Z=117, would belong to the halogen family (group 17) and the electronic configuration

would be. [Rn] $4f^{14} 5d^{10} 7s^2 7p^5$. the element with Z=120, will be placed in group 2 (alkaline earth metals), and will have the electronic configuration $[Uuo]8s^2$.

In addition to displaying the classification of elements into s-, p-, d-, and f-blocks, the periodic table shows another broad classification of elements based on their properties. The elements can be divided into **Metals** and **Non-metals**. Metals comprise more than 75% of all known elements and appear on the left side of the Periodic Table. Metals are usually solids at room temperature (Mercury is an exception); they have high melting and boiling points. They are good conductors of heat and electricity. They are malleable (can be flattened into thin sheets by hammering) and ductile (can be drawn into wires). In contrast non-metals are located at the top right hand side of the Periodic Table. Non-metals are usually solids or gases at room temperature with low melting and boiling points. They are poor conductors of heat and electricity. Most non-metallic solids are brittle and are neither malleable nor ductile. The elements become more metallic as we go down a group; the non-metallic character increases as one goes from left to right across the Periodic Table. The change form metallic to non-metallic character is not abrupt as shown by the thick zig-zag line in the periodic table. The elements (e.g. germanium, silicon, arsenic, antimony and tellurium) bordering this line and running diagonally across the Periodic Table show properties that are characteristic of both metals and non-metals. These elements are called **Semi Metals** or **Metalloids**.

Example 2

Arrange the following elements in the increasing order of metallic character: Si, Be, Mg, Na, P.

Solution

Metallic character increases down a group and decreases along a period as we move from left to right. Hence the order of increasing metallic character is, P<Si<Be<Mg<Na.

4.4 Periodicity of properties

Repetition of properties of elements at regular intervals is called periodicity in properties. The periodicity is due to similar electronic

configuration of outer-most shells. Some of the properties are discussed below.

(i) Atomic and ionic radii

The size of an atom can be visualized from its atomic radius. The term atomic or ionic radius is generally defined as the distance between the centers of the nucleus and the outermost shell of electrons in an atom or ion. For example, the atomic radius of hydrogen atom is equal to 74/2 pm = 37 (bond distance in hydrogen molecule (H_2) is 74pm).

Atomic and ionic radii both decrease from left to right across a period in the periodic table when we consider only normal elements, e.g. in the elements of 2nd period the covalent radii decrease as we move from Li to F as shown below:

Elements of 2nd period :

Li Be B   C   N   O   F

Covalent radii _____ Values decreasing ➤
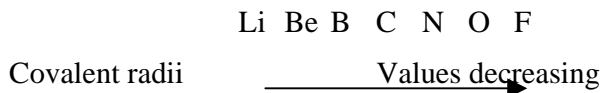
Thus in any period the alkali metals (that are present at the extreme left of the periodic table) have the largest size while the halogens (that are present at the extreme right, excluding the zero group elements) have the smallest size.

Explanations

We know that as we proceed from left to right in a period, the electrons are added to the orbitals of the same main energy level. Addition of different electrons to the same main energy level puts the electrons, on the average, no farther from the nucleus and hence the size can not be increased. But with the addition of each electron, the nuclear charge (i.e. atomic number) increases by one. The increased nuclear charge attracts the electrons more strongly close to the nucleus and thus decreases the size of the atoms.

Table 4.5 Atomic Radii / pm Across the periods

Atom	Atomic radius	Atom	Atomic radius
Li	152	Na	186
Be	111	Mg	160
B	88	Al	143
C	77	Si	117
N	70	P	110
O	74	S	104
F	72	Cl	99
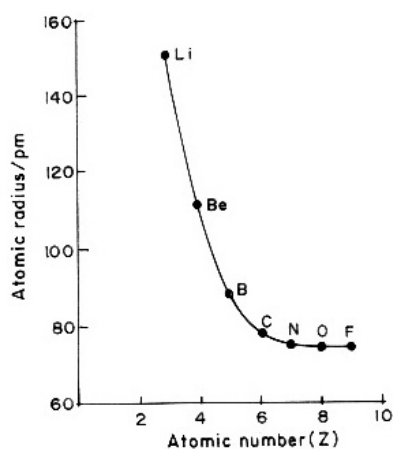
Fig. 4.1 Variation of atomic radius with atomic number across the second period

(b) **In a group**

On moving down a group of regular elements both atomic and ionic radii increase with increasing atomic number, e.g. in the elements of IA Group both covalent and ionic radii of M^+ ions increase when we pass from Li to Cs

Elements of IA Group : Li Na K Rb Cs
Covalent radii/Ionic radii   Values increasing

Explanation

On proceeding downwards in a group the electrons are added to higher main energy levels, which are, on the average, farther from the nucleus. This effect decreases the electrostatic attraction between the nucleus and the valence-shell electrons and this decreased electrostatic attraction increases the atomic and ionic radii.

Table 4.6 Atomic Radii / pm Down the Group Across a Family

Atom	Atomic radius	Atom	Atomic radius
Li	152	F	72
Na	186	Cl	99
K	231	Br	114
Rb	244	I	133
Cs	262	At	140
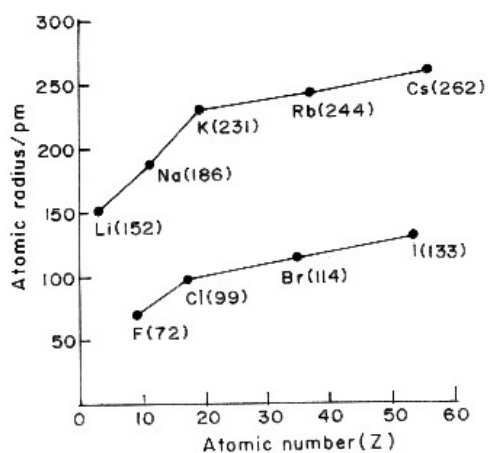
Fig. 4.2 Variation of atomic radius with atomic number for alkali metals and halogens

When we find some atoms and ions, which contain the same number of electrons, we call them **isoelectronic**. For example, O^{2-}, F^-, Na^+ and Mg^{2+} have the same number of electrons (10). Their radii would be different because of their different nuclear charges. The cation with the greater positive charge will have a smaller radius because of the greater attraction of the electrons to the nucleus. Anions with the greater negative charge will have the larger radius. In this case, the net repulsion of the electrons will outweigh the nuclear charge and the ion will expand in size.

Example

Which of the following species will have the largest and the smallest size Mg, Mg^{2+}, Al, Al^{3+}?.

Solution

Atomic radii decrease across a period. Cations are smaller than their parent atoms. Among isoelectronic ions, the one with the large positive nuclear charge will have a smaller radius.

Hence the largest species is Mg; the smallest one is Al^{3+}

The size of an anion greater while that of the cation is smaller than that of its parent atom, e.g. F^- (=1.36 Å)>F(=0.72 Å); Cl^-(=1.81 Å)>Cl(=0.99Å); Na^+(=0.95Å)<Na(=1.90Å); Ca^{2+}(=0.99 Å)<Ca(=1.97Å).

Explanation

Let us consider the radii of Na, Na^+, Cl and Cl^-. The reason of the fact that Na^+ ion is smaller than Na atom is that Na^+ ion has 10 electrons ($Na^+ \rightarrow 1s^2, 2s^2p^6$) while Na atom has 11electrons (Na $\rightarrow 1s^2, 2s^2p^6, 3s^1$). The nuclear charge (charge on the nucleus) in each case is the same, i.e. equal to +11 (atomic number of Na). This nuclear charge of +11 can pull 10 electrons of Na^+ ion inward more effectively than it can pull a greater number of 11 electrons of Na atom. Thus Na^+ ion is smaller than Na atom.

The reason why Cl^- ion is bigger than Cl atom can also be explained on a similar basis. The Cl^- ion has 18 electrons ($Cl^- \rightarrow 1s^2, 2s^2p^6, 3s^2p^6$) while Cl atom has only 17 electrons ($Cl \rightarrow 1s^2, 2s^2p^6, 3s^2p^5$). The nuclear charge in each case is +17, which cannot pull 18 electrons of Cl^- ion as effectively as it can pull 17 electrons of Cl atom inward. Thus Cl^- ion is bigger than Cl atom.

(ii) Ionization Energy: (Ionization Potential**)**

In modern terminology, ionization energy is known as **ionization enthalpy**. The energy required to remove an electron from an atom is known as ionization enthalpy (IE). The first ionization enthalpy may be defined as the amount of energy required to remove the most loosely bound electron from the isolated gaseous atom.

$$\text{Atom (g)} + \text{Energy} \rightarrow \text{Positive ion (g)} + \text{Electron}$$

For example,

$$\text{Li (g)} + 520 \text{ kJ mol}^{-1} \rightarrow \text{Li}^{+} \text{(g)} + e^{-}$$
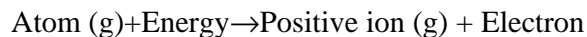
Ionization enthalpy is also called *ionization potential* because it is measured as the amount of potential required to remove the most loosely held electron from the gaseous atom. It is expressed in terms of either kJ/mol or electron Volts/atom.

If a second electron is to be removed from the same element the energy required will be higher than that required for removal of the first electron because it is more difficult to remove an electron from a positively charged species than from a neutral atom.

$$\text{Li}^{+} \text{(g)} + 7297 \text{ kJ mol}^{-1} \rightarrow \text{Li}^{2+} + e^{-}$$
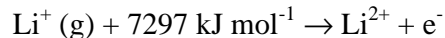
Similarly the third ionization enthalpy will be higher than the second and so on. Fig. 4.3 shows a plot of first ionization enthalpy of some elements.
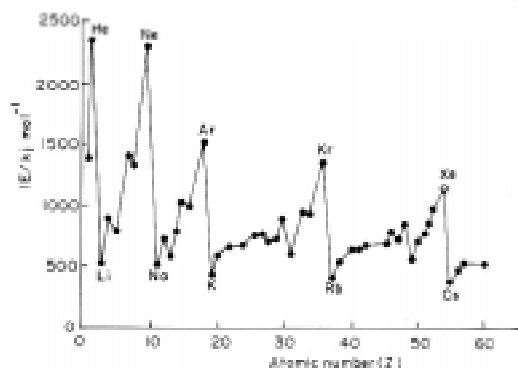
Fig. 4.3 Variation of first ionization analysis with atomic number for elements with Z = 1 to 60

Variation of Ionization Energy in the periodic Table

It is seen from the Fig. 4.4 that the ionization enthalpy of an element depends on its electronic configuration. Ionization potentials of noble gases are found to be maximum and those of alkali metals are found to minimum. The high values of noble gases are due to completely filled electronic configurations in their outermost shells and the low values of alkali metals are due to their large size and a single electron in the outermost shell.

The ionization potentials increases from left to right in a period. This trend can be explained in terms of increase in nuclear charge and decrease in size from left to right in a period. Generally the first ionization enthalpy decreases down a group in the periodic table. As we move down the group, the outer electrons, which are to be removed, are farther from the nucleus and there is an increasing screening of the nuclear charge by the electrons in the inner shells. Consequently the removal of electrons becomes easier down the group.
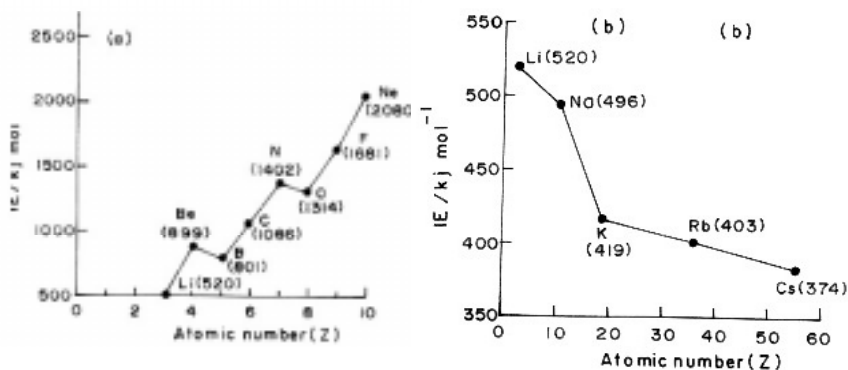
Fig. 4.4 (a) First ionization enthalpies of elements of the second period as a function of atomic number (b) First ionization enthalpies of alkali metals as a function of atomic number

Factors Influencing Ionization Enthalpy

The ionization enthalpy of an atom depends on the following factors.

(i) Size of the atom

As the distance between the electron and the nucleus increases, i.e., as the size of the atom increases, the outermost electrons are less tightly

held by the nucleus. Thus, it becomes easier to remove an outermost electron. Thus ionization enthalpy decreases with increases in atomic size.

(ii) Charge on the nucleus

Ionization enthalpy increases with increase in nuclear charge because of the increase in the attractive force between the nucleus and the electron.

(iii) Screening effect of inner electrons

Ionization enthalpy decreases when the shielding effect of inner electrons increases. This is because when the inner electron shells increases, the attraction between the nucleus and the outermost electron decreases.

(iv) Penetration effect of electrons

The penetration power of the electrons in various orbitals decreases in a given shell (same value of n) in the order: s>p>d>f. Since the penetration power of s-electron towards the nucleus is more, it will be closer to the nucleus and will be held firmly. Thus, for the same shell, the ionization enthalpy would be more to remove the s-electrons in comparison with the p-electron which in turn would be more than that for d-electron and so on.

(v) Effect of half-filled and completely filled sub-levels

If an atom has half-filled or completely filled sub-levels, its ionization enthalpy is higher than that expected normally from its position in the periodic table. This is because such atom, have extra stability and hence it is difficult to remove electrons from these stable configurations.

(iii) Electron affinity

In modern terminology, electron affinity is known as the electron gain enthalpy. Electron gain enthalpy is the amount of energy released when an isolated gaseous atom accepts an electron to form a monovalent gaseous anion.

Atom (g) + Electron → Anion (g) + energy
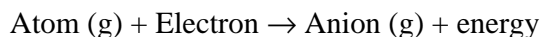
Example, Cl (g) + e$^-$ → Cl$^-$ (g) + EA

If an atom has high tendency to accept an electron, large energy will be released. Consequently, electron gain enthalpy will be high. On the other hand if an atom has less tendency to accept the electron small amount of energy will be released, leading to small value of electron gain enthalpy. The values of electron gain enthalpy are expressed either in electron volt per atom or kilo joules per mole of atoms. For example, electron gain enthalpy of

F = 322 kJ mol^{-1}
Cl = 349 kJ mol^{-1}
Br = 324 kJ mol^{-1} and
I = 295 kJ mol^{-1}

Halogens (elements of group 17) can take up an electron to acquire the stable noble gas configuration. Their values for electron gain enthalpy are thus very high. Electron gain enthalpy values for the halogens are as in Fig. 4.5.

Electron gain enthalpies generally decrease on moving down the group. This is expected on account of the increase in size of atoms, the effective nuclear attraction for electrons decreases. As a result, there is less tendency to attract additional electrons with an increase in atomic number down the group.
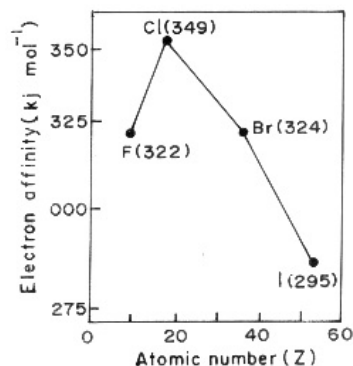
Fig. 4.5 Electron affinity enthalpies of halogens

From the electron gain enthalpy data of halogens it is clear that, contrary to expectation, the electron gain enthalpy of fluorine is lower than that of chlorine. This is because the fluorine atom has a very compact electronic shell due to its small size. The compactness of the fluorine shell results in electron repulsion whenever an electron is introduced into its 2p-orbital. This is why its electron gain enthalpy is less than the expected value. In Cl atom, 3p-orbitals are not as compact as the 2p-orbitals in fluorine atom. The incoming electron is more readily accepted by the chlorine atom because of weaker electron-electron repulsion. The electron gain enthalpy of chlorine is, therefore, higher than that of fluorine.

In the case of noble gases, the outer s-and p-orbitals are completely filled. No more electrons can be accommodated in these orbitals. *Noble gases, therefore, show no tendency to accept electrons.* Their electron gain enthalpies are zero.

Electron gain enthalpies generally increase as we move across a period from left to right. This is due to the increase in the nuclear charge, which results in greater attraction for electrons.

The second electron gain enthalpy refers to a process in which the electron is added to a negative ion. For example:

$$O^- (g) + e^- \rightarrow O^{2-} (g)$$
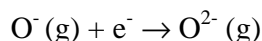
Since a negative ion O^- and an electron repel each other, energy is required and not released by the process. Therefore the second electron gain enthalpy is negative in this case.

Factors influencing the magnitude of electron affinity

The magnitude of EA is influenced by a number of factors such as (i) *Atomic size*; (ii) *Effective nuclear charge*; and (iii) *Screening effect by inner electrons*.

Example

Which of the following will have the most negative electron gain enthalpy and which has the least negative?   P, S, Cl, F.

Explain your answer.

Solution

Electron gain enthalpy generally becomes more negative across a period as we move from left to right. Within a group, electron gain enthalpy becomes less negative down a group. However, adding an electron to the 2p orbital leads to greater repulsion than adding an electron to the larger 3p orbital. Hence the element with most negative electron gain enthalpy is chlorine; the one with the least negative electron gain enthalpy is phosphorus.

(iv) Electronegativity

Electronegativity may be defined as the tendency of an atom in a molecule to attract towards itself the shared pair of electrons. The main factors, which the electronegativity depends, are effective nuclear charge and atomic radius. Greater the effective nuclear charge greater is the electronegativity. Smaller the atomic radius greater is the electronegativity.

In a period electronegativity increases in moving from left to right. This is due to the reason that the nuclear charge increases whereas atomic radius decreases as we move from left to right in a period. Halogens have the highest value of electronegativity in their respective periods.

In a group electronegativity decreases on moving down the group. This is due to the effect of the increased atomic radius. Among halogens fluorine has the highest electronegativity. In fact fluorine is the most electronegative element and is given a value of 4.0 (Pauling's scale) whereas cesium is the least electronegative element (E.N. = 0.7) because of its largest size and maximum screening effect. In other words, cesium is the most electropositive element and hence is the most metallic element in the periodic table.

The main differences between Electron gain enthalpy (electro affinity) and electronegativity are given below :

Electron gain Enthalpy	Electronegativity
It is the tendency of an isolated gaseous atom to attract an electron.	It is the tendency of an atom in a molecule to attract the shared pair of electrons.
It is measured in electron volts/atom or kcal/mole or kj/mole.	It is a number and has no units.
It is the property of an isolated atom.	It is property of a bonded atom.
An atom has an absolute value of electron gain enthalpy.	An atom has a relative value of electronegativity depending upon its bonding state. For example, sp-hybridized carbon is more electronegative than sp^2-hybridized carbon which, in turn, is more electronegative than sp3-hybridized carbon.
It does not change regularly in a period or group.	It changes regularly in a period or a group.

Electronegativity of an element is important in determining the bond character. If two atoms have the same electronegativities the bond between the two will be covalent, while a large difference in electronegativity leads to ionic bond. Between the extremes the purely covalent bond and purely ionic, the bonds will have different degrees of ionic character. As a rough estimate it is seen that a difference of 1.7 in electronegativities, the bond has 50% ionic character. If the difference is less than 1.7, the bond is considered covalent, and greater than 1.7 it is considered ionic.

Table 4.7 Pauling's Electronegativity coefficients (for the most common oxidation states of the elements)

					H
					2.1
Li	Be	B	C	N	O
	F				
1.0	1.5	2.0	2.5	3.0	3.5
	4.0				
Na					Cl
0.9					
3.0					
K					
Br					
0.8					
2.8					
Rb					I
0.8					
2.5					
Cs					
0.7					

4.5 Anomalous periodic properties in terms of screening constant, stability etc.

According to Hund's rule atoms having half-filled or completely filled orbitals are comparatively more stable and hence more energy is needed to remove an electron from such atoms. The ionization potentials of such atoms are, therefore, relatively higher than expected normally from their position in the periodic table.

Example

A few irregularities that are seen in the increasing values of ionization potential along a period can be explained on the basis of the concept of half-filled and completely filled orbitals, e.g., Be and N in the second period and Mg and P in the third period have slightly higher values of ionization potentials than those normally expected. This is explained on the basis of extra stability of the completely-filled 2s-orbital

in Be(Be$\rightarrow$2s^2) and 3s-orbital in Mg (Mg$\rightarrow$3s^2) and of half-filled 2p-orbital in N (N$\rightarrow$2s^{2}p^6) and 3p-orbital in P (P$\rightarrow$3s^{2}p^3).

Another example for irregularity in Ionization potential is observed in the case of B and Be.

Ionization energy of boron (B $\rightarrow$2s^{2}2p^1) is lower than that of beryllium (Be $\rightarrow$ 2s^2) [B = 8.3 eV, Be = 9.3 eV], since in case of boron we have to remove a 2p^1 electron to get B$^+$[B (2s^{2}p^1) $\rightarrow$ B$^+$(2S^2) + e$^-$] while in case of Be we have to remove a 2s^1 electron of the same main energy level to have Be$^+$ ion. [Be (2s^2) $\rightarrow$ Be$^+$(2s^1) +e$^-$].

There is an exception to the vertical trend of ionization potential. This exception occurs in the case of those elements whose atomic numbers are greater than 72. Thus the ionization potentials of the elements from Ta$_{73}$ to Pb $_{82}$ are greater than those of the elements of the same sub-group above them as shown below : (First ionization potential values are given in electron volts, eV).

Table 4.8

V B	VI B	VII B	VIII			I B	II B	III A	IV A
Nb$_{41}$	Mo$_{42}$	Tc$_{43}$	Ru$_{44}$	Rh$_{45}$	Pd$_{46}$	Ag$_{47}$	Cd$_{48}$	In$_{49}$	Sn$_{50}$
6.8	7.1	7.2	7.3	7.4	8.3	7.5	8.9	5.7	7.3
Ta$_{73}$	W$_{74}$	Re$_{75}$	Os$_{76}$	Ir$_{77}$	Pt$_{78}$	Au$_{79}$	Hg$_{80}$	Tl$_{81}$	Pb$_{82}$
7.7	7.8	7.8	8.7	9.2	9.0	9.2	10.4	6.1	7.4

The reason for the abnormal behaviour (i.e. an increase in the value of I$_1$ from Nb $\rightarrow$ Ta, Mo $\rightarrow$ W, ...,Sn $\rightarrow$ Pb) shown by the elements from Ta$_{73}$ to Pb$_{82}$ is due to the lanthanide contraction as a result of which there occurs an increase in the nuclear charge without a corresponding increase in size through the rare earths. In fact, the size actually decreases in this region.

Periodic Variations

Similarly in moving down a group electron affinity values generally decrease, e.g. E$_{Cl}$>E$_{Br}$>E$_I$. This is due to the steady increase in the atomic radius of the elements.

Exceptions

There are, however, some exceptions to this general rule as is evident from the following examples:

It is known that $E_F < E_{Cl}$ (E_F = 322 kJ mol^{-1} , E_{Cl} = 349 kJ mol^{-1}). The lower value of E for F is probably due to the electron-electron repulsion in relatively compact $2p$-orbital of F-atom.

In period, electron affinity values generally increase on moving from left to right in a period in the periodic table.

Exceptions

There are, however, exceptions also to this general rule; e.g.

Be and Mg have their EA values equal to zero. Since Be and Mg have completely filled s-orbitals (Be $\rightarrow 2s^2$, Mg $\rightarrow 3s^2$), the additional electron will be entering the $2p$-orbital in case of Be and $3p$-orbital in case of Mg which are of considerably higher energy than the $2s$-and 3s orbitals respectively.

Questions

A. Choose the Best Answer

1. The elements with atomic numbers 31 belongs to :
   (a) d-block   (b) f-block
   (c) p-block   (d) s-block

2. Representative elements are those which belong to :
   (a) s and d-blocks   (b) s and p-blocks   (c) p and d-blocks
   (d) d and f-blocks

3. The most electronegative element of the periodic table is :
   (a) Iodine (b) Flourine (c) Chlorine (d) Oxygen

4. Which of the following forms stable gaseous negative ion.
   (a) F   (b) Cl   (c) Br   (d) I

5. The elements having highest ionization energies within their periods are called :
   (a) Halogens (b) Noble gases (c) Alkali metals
   (d) Transition elements

6. A property which progressively increases down a group in the periods table is : (a) Ionization enthalpy (b) Electronegativity (c) Electron gain enthalpy (d) Strength as a reducing agent.

7. Elements whose atoms have their s and p-sub-levels complete are the: (a) Normal elements (b) Transition elements (c) Halogens (d) Inert gases.

8. The law of triad is applicable to : (a) Chlorine, bromine and iodine (b) Hydrogen, oxygen and nitrogen (c) Sodium, neon and calcium (d) All of the above

9. The law of octaves was stated by : (a) Dobereiner (b) Mendeleev (c) Moseley (d) Newland

10. Which of the following property decreases down a group : (a) Ionization enthalpy (b) Atomic radii (c) Valency (d) All the above properties

11. Which of the following has the lowest melting point ?
(a) CsCl (b) RbCl (c) KCl (d) NaCl (e) LiCl.

12. Which of the following hydroxide is most basic ?
(a) $Mg(OH)_2$ (b) $Ba(OH)_2$ (c) $Ca(OH)_2$ (d) $Be(OH)_2$

13. Excluding hydrogen and helium, the smallest element in the periodic table is : (a) lithium (b) Oxygen (c) Fluorine (d) Chlorine

14. Which one among the following species has the largest atomic radius:
(a) Na (b) Mg (c) Al (d) Si

15. Which of the following is the lightest metal ?
(a) Calcium (b) Lithium (c) Magnesium (d) Sodium

16. Which of the following has highest ionization potential?
(a) Sodium (b) Magnesium (c) Carbon (d) Fluorine

17. With respect to chlorine, hydrogen will be

(a) Electropositive   (b) Electronegative
(c) Neutral   (d) None of these.

18. Which element has the greatest tendency to lose electrons?

(a) Chlorine (b) Sulphur (c) Francium (d) Berylium.

19. Halogens belong to the : (a) s-block (b) p-block (c) d-block
(d) f- block (e) Zero group of the periodic table.

20. Compared to first ionization enthalpy of an atom, the second is :
(a) Greater (b) Less (c) Same (d) Negligible

21. Which arrangement of the following set of atoms is in order of increasing atomic radius: Na, Rb, K and Mg ;

    (a) Na, Mg, K, Rb (b) Na, K, Mg, Rb (c) Mg, Na, K, Rb
    (d) Na, Mg, Rb, K

22. The first attempt to classify the elements was made by :

    (a) Mendeleev   (b) Newland (c) Lother Meyer
    (d) Dobereiner

23. Characteristic of transition elements is incomplete in : (a) d-orbitals
(b)f-orbitals (c) p-orbitals (d) s-orbitals

24. Which of the following will have lowest first ionization enthalpy ?

    (a) Na (b) Al (c) Mg (d) Si

25. Which of the following atoms is likely to give off more energy on gaining an electron ? (a) Na (b) Mg (c) Al (d) Cl

26. Transition metals have the electronic configuration :

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

    (d) $ns^2 np^6(n-1)d^{1-10}$

27. In the first transition series the incoming electron enters the :

    (a) 4d-orbital (b) 3d-orbital (c) 5d-orbital (d) 6d-orbital

B. Fill in the Blanks

1. Mendeleev's periodic law states that the properties of the elements are the periodic functions of the ………………

2. The Modern periodic law states that the physical and chemical properties of the elements are periodic functions of their ………….

3. The long form of the periodic table is constructed on the basis of repeating electronic …………….. of the atoms when they are arranged in the order of increasing atomic numbers.

4. The first three periods containing 2, 8 and 8 elements respectively are called ……………

5. The valency of representative elements is given by the number of electrons in the outermost orbital and/or equal to …………. Minus the number of outermost electrons.

C. Write in one or two sentence

1. Arrange F, Cl, Br and I in the order of increasing electronic gain enthalpy.

2. Write electronic configurations for the elements of atomic numbers 6 and 14 and from this find out of which group in the periodic table each elements belongs.

3. Which of the following electronic configurations has the lowest ionization enthalpy ? (a) $1s^2, 2s^2, 2p^6$; (b) $1s^2, 2s^2, sp^6$; (c) $1s^2, 2s^2, 2p^6 , 3s^2$.

4. State Modern Periodic Law.

5. Why Noble gases have zero electron gain enthalpy?

6. Which of the following pairs of elements would you expect to have lower first ionization enthalpy ? (a) Cl or F ; (b) Cl or S ; (c) K or Ar ; (d)Kr or Xe.

7. Why do elements in the same group have generally similar properties?

8. Name any two transition elements and any two inner transition elements.

9. Arrange the order of increasing atomic volumes in : (a) Li, Na and K; (b) C, N and O ; (c) Ca, Sr and Ba.

10. Name the different blocks of elements in periodic table. Give the general electronic configuration of each block.

11. To which block does the element with configuration $3d^{10}4s^2$ belongs

12. Why nitrogen has higher I.E. value than oxygen?

13. Out of fluorine and chlorine, which has greater electron gain enthalpy?

14. Why are d-block elements called transition elements?

15. What property did Mendeleev use to classify elements in his periodic table?

16. Among the elements Li, K, Ca, S and Kr which one has the lowest first ionization enthalpy? Which has the highest first ionization enthalpy?

D. Explain briefly the following

1. Why does the first ionization enthalpy would have higher electron gain enthalpy?

2. Which of the following pairs of elements would have higher electron gain enthalpy? (a) N or O ; (b) F or Cl . Explain.

3. Lanthanides and actinides are placed in separate rows at the bottom of the periodic table. Explain the reason for this arrangement ?

4. What do you mean by representative elements? Name the groups of the periodic table, which contain representative elements.

5. Define transition elements. Name the different transition series.

6. Which element of the following pairs have smaller ionization enthalpy? (a) Ca or Be ; (b) Ca or K ; (c) Cl or I. Justify your answer.

7. Why is Na atom bigger than the atoms of both lithium and magnesium ?

8. What do you mean by the term electron gain enthalpy? How does electron gain enthalpy change along a period and in a group?

9. Explain how the elements are arranged in the form of the periodic table.

10. What are normal, transition and inner- transition elements?

11. What are the differences between normal and transition elements?

12. Explain why radii of positive ions are always smaller than the radii of corresponding neutral atoms and why negative ions have larger radii than the corresponding neutral atom.

13. Explain the size of group $Cl^- > Na^+$.

14. What is electron gain enthalpy? On what factors does it depend?

15. Give the general variation of electron gain enthalpies in the periodic table.
16. Define the term ionic radius. Justify that the radius of anion is larger than the parent atom.
17. What do you mean by ionization enthalpy? How does it vary across a period and down a group?
18. What is meant by electronegativity? On what factors does it depend?
19. What are the essential features of the periodic table of Mendeleev? Discuss how his table has been modified subsequently.

SUMMARY

In this Chapter, Historical Survey and review of Periodic Classifications are presented. Starting from Dobereiner law of triads, Newlands law of octaves, Mendelev's periodic law and table are reviewed. Modern Periodic table is explained in detail. Correlating electronic configuration of elements justifies their positions in the modern periodic table. Latest IUPAC nomenclature of elements is also explained for elements having atomic number greater than 100 is explained.

Periodicity of properties like Atomic and ionic radii, ionization energy, electron affinity, and electronegativity is discussed. Their trends along the period and down the group are explained with suitable examples. Anamolous periodic properties in terms of screening effect and stability are discussed.

REFERENCE

Concise. Inorganic Chemistry J.D.Lee, 3rd Edition, 1977.

s - BLOCK ELEMENTS

	1	2	d	
① 1				H
② 2	Li	Be	d	
③ 3	Na	Mg	3	
④ 4	K	Ca		
⑤ 5	Rb	Sr		
⑥ 6	Cs	Ba		
⑦ 7	Fr	Ra		
	ns^1	ns^2		

ns^{1-2}

1 ⟶ Alkali metals

2 ⟶ Alkaline earth metals

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5. GROUP 1 *s* - BLOCK ELEMENTS

OBJECTIVES

- *Know about the occurrence and isotopes of hydrogen.*
- *Understand the nature and application of different isotopes of hydrogen.*
- *Differentiate ortho and para forms of hydrogen.*
- *Gain knowledge about the application of heavy water.*
- *Know about the preparation, properties and uses of hydrogen peroxide.*
- *Understand the special feature of liquid hydrogen used as a fuel - hydrogen economy.*
- *Analyse general properties of alkali metals.*
- *Know about the basic nature of oxides and hydroxides.*
- *Learn the extraction of alkali metal - lithium and sodium.*
- *Recognise the properties and understands the uses of lithium and sodium.*

Hydrogen is the first element in the periodic table. It has the simplest electronic configuration $1s^1$. It contains one proton in the nucleus and one electron.

Isotopes:- Atoms of the same element having same atomic number but different mass number are called isotopes.

There are three isotopes for hydrogen with mass numbers 1, 2 and 3, each possessing an atomic number of one.

Table 5.1 Isotopes of hydrogen

S. No	Name	Symbol	Atomic number	Mass number	Number of Protons	Number of Neutrons	Percentage abundance
1.	Protium or hydrogen	$_1H^1$	1	1	1	0	99.984
2.	Deuterium or heavy hydrogen	$_1H^2$	1	2	1	1	0.016
3.	Tritium	$_1H^3$	1	3	1	2	10^{-15}

The structure of the three isotopes of hydrogen are

Protium   Deuterium   Tritium
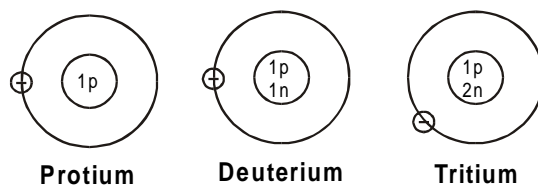
1. **Protium or ordinary hydrogen:** It is the common form of hydrogen. It consists of one proton in its nucleus and one electron revolving around it. It constitutes 99.984% of total hydrogen available in nature. Its mass number is one.

2. **Deuterium or heavy hydrogen:** $_1H^2$ or $_1D^2$. It occurs naturally in very small traces. The proportion present in naturally occurring hydrogen is in the approximate ratio: D: H~ 1:6000. It's nucleus consists of a proton and a neutron. However only a solitary electron is revolving around the nucleus. Its chemical properties are similar to those of protium but their reaction rates are different.

3. **Tritium, $_1H^3$ or $_1T^3$:** It occurs in the upper atmosphere only where it is continuously formed by nuclear reactions induced by cosmic rays. Unlike deuterium, it is radioactive, with a half-life of ~ 12.3 years. It's nucleus consists of one proton and two neutrons.

They will have same similar chemical properties, however, their reaction rates will be different and their physical properties differ appreciably.

Methods of Preparation of deuterium

1. **By Diffusion Process:** It is possible to obtain deuterium directly from hydrogen gas by taking advantage of different rates of diffusion of the two isotopes. The lighter hydrogen diffuses more quickly than deuterium through a porous partition under reduced pressure. Lower the pressure, higher is the efficiency of the process.

The process of diffusion has been carried out in various diffusion chambers called Hertz diffusion units. Each diffusion units consists of a porous membrane.

When the mixture is led into the diffusion units under reduced pressure

by the help of mercury diffusion pumps, the heavier deuterium diffuses less readily while lighter hydrogen diffuses at faster rates. This process is repeated several times till hydrogen gets collected on the left while deuterium on the right. The efficiency of this process could be increased by increasing the number of diffusion units.

2. By fractional distillation of liquid hydrogen: By fractional distillation of liquid hydrogen, it is possible to result in enrichment of the last fraction in deuterium because deuterium boils at 23.5K while hydrogen boils at lower temperature of 20.2K.

3. By electrolysis of heavy water: As water contains about one part of heavy water in 6000 parts, at first, the concentration of heavy water is increased by fractional electrolysis of water containing an alkali between nickel electrodes. For example 1 ml of heavy water is obtained from about 20 litres by this method.

From heavy water, it is possible to get deuterium by decomposing it with sodium, red hot iron or tungsten or by its electrolysis containing sodium carbonate.

$$2D_2O \xrightarrow{\text{Electrolysis}} 2\,D_2 + O_2$$
$$\text{Deuterium}$$
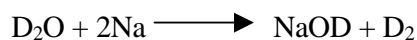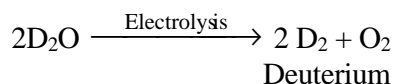
$$D_2O + 2Na \longrightarrow NaOD + D_2$$
$$\text{Sodium deuteroxide.}$$

Deuterium obtained can be further obtained in purified state by the diffusion process.

Physical properties

Like hydrogen, deuterium is a colourless, odourless and tasteless gas which is insoluble in water and bad conductor of heat and electricity. The values of boiling point, melting point, vapour pressure, dissociation energy and latent heat of fusion are found to be lower for protium than deuterium.

Chemical properties

By virtue of its larger mass, deuterium reacts slower than hydrogen.

1. **Burning in oxygen:** Like hydrogen, it is combustible and burns in oxygen or air to give deuterium oxide which is also known as heavy water.

$$2 D_2 + O_2 \longrightarrow 2D_2O.$$
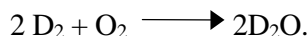
2. **Reaction with halogens:** Like hydrogen, it combines with halogens under suitable conditions to form their deuterides.

$$D_2 + Cl_2 \xrightarrow{\text{in light}} 2 \ DCl$$
Deuterium chloride

$$D_2 + F_2 \xrightarrow{\text{in dark}} D_2 F_2$$
Deuterium fluoride
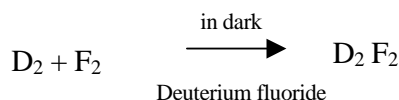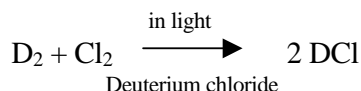
3. **Reaction with nitrogen:** Like hydrogen, it combines with nitrogen in the presence of a catalyst to form nitrogen deuteride which are also known as heavy ammonia or deutero ammonia.

$$3D_2 + N_2 \longrightarrow 2ND_3$$
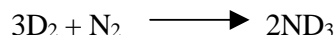
4. **Reaction with metals:** Like hydrogen, it reacts with alkali metals at high temperatures (633K) to form deuterides

$$2 \ Na + D_2 \longrightarrow 2 \ NaD$$

5. **Addition reactions:** Like hydrogen, it gives addition reactions with unsaturated compounds. For example, a mixture of deuterium and ethylene when passed over heated nickel, gives Ethylene deuteride which is saturated hydrocarbon like ethane.

$$C_2H_4 + D_2 \xrightarrow[\text{535 K}]{\text{Ni}} CH_2D \text{ -}CH_2D$$
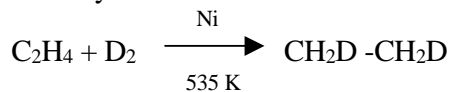
6. **Exchange reactions:** Deuterium and hydrogen atoms undergo ready exchange with H_2, NH_3, H_2O and CH_4 deuterium slowly exchanges their hydrogens partially or completely at high temperatures.

$$H_2 + D_2 \rightleftharpoons 2 \ HD$$

$$2NH_3 + 3D_2 \rightleftharpoons 2ND_3 + 3H_2$$

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$H_2O + D_2 \rightleftharpoons D_2O + H_2$

$CH_4 + 2D_2 \rightleftharpoons CD_4 + 2H_2$

$C_2H_6 + 3D_2 \rightleftharpoons C_2D_6 + 3H_2$
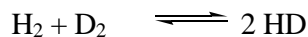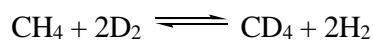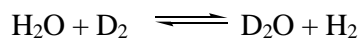
Uses of deuterium

1. It is used as tracers in the study of mechanism of chemical reactions.

2. High speed deuterons are used in artificial radioactivity.

3. Its oxide known as heavy water (D_2O) which is employed as moderator in nuclear reactor to slow down the speed of fast moving neutrons.

Tritium $_1H^3$: It is a rare isotope of hydrogen. Its traces are found in nature due to nuclear reactions induced by cosmic rays.

Tritium is prepared by

i) By bombarding lithium with slow neutrons

$$_3Li^6 + {_0n^1} \longrightarrow {_1T^3} + {_2He^4}$$

ii) By bombarding beryllium with deuterons

$$_4Be^9 + {_1D^2} \longrightarrow {_1T^3} + {_4Be^8}$$

$$_4Be^9 + {_1D^2} \longrightarrow {_1T^3} + 2\,{_2He^4}$$
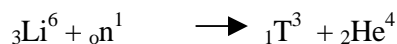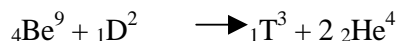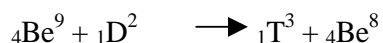
Properties : It is radioactive with a half-life of 12.4 years. It decays into helium -3 with the emission of beta radiation.

$$_1T^3 \longrightarrow {_2He^3} + {_{-1}e^o}$$
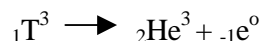
Uses

(i) It is used as a radioactive tracer in chemical research.

(ii) It is used in nuclear fusion reactions.

5.1 Ortho and Para hydrogen

The nucleus of the hydrogen atom spins about an axis like a top. When two hydrogen atoms combine, they form molecular hydrogen.

Thus depending on the direction of the two protons in the nucleus the

following two types of hydrogen molecules are known. Hydrogen molecule in which both the protons in the nuclei of both H-atoms are known to spin in same direction is termed as ortho hydrogen. If the protons in the nuclei of both H-atoms spin in opposite direction, it is termed as parahydrogen.

Orthohydrogen   **Parahydrogen**
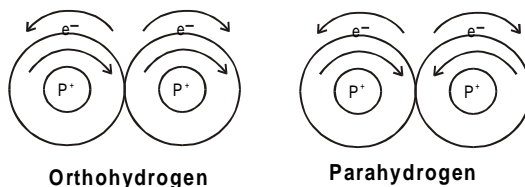
At room temperature ordinary hydrogen consists of about 75% ortho and 25% para form. As the temperature is lowered, the equilibrium shifts in favour of para hydrogen. At 25K. There is 99% para and 1% ortho hydrogen. The change in the proportion of the two forms of hydrogen requires a catalyst such as platinum or atomic hydrogen or silent electric discharge.

The para form was originally prepared by absorbing ordinary hydrogen in activated charcoal in a quartz vessel kept at a temperature of 20K. The charcoal absorbs almost pure para hydrogen. By this method, pure para hydrogen can be isolated.

Conversion of para into ortho hydrogen

Ortho hydrogen is more stable than para hydrogen. The para form is transformed into ortho form by the following methods.

i.   By treatment with catalysts like platinum or iron
ii. By passing an electric discharge
iii. By heating to $800^{o}C$ or more.
iv. By mixing with paramagnetic molecules like O_2, NO, NO_2.
v.   By mixing with nascent hydrogen or atomic hydrogen.

Properties: Ortho and para hydrogen are similar in chemical properties but differ in some of the physical properties.

(i) Melting point of para hydrogen is 13.83K while that of ordinary hydrogen is 13.95 K.

(ii) Boiling point of para hydrogen 20.26K while that of ordinary hydrogen is 20.39K.

(iii)The vapour pressure of liquid para hydrogen is higher than that of ordinary liquid hydrogen.

(iv)The magnetic moment of para hydrogen is zero since the spins neutralise each other while in the case of ortho , it is twice than that of a proton.

(v) Para hydrogen possesses a lower internal molecular energy than ortho form.

5.2 Heavy water

It is also called as deuterium oxide. The oxide of heavy hydrogen (deuterium) is called heavy water. Heavy water was discovered by Urey in 1932. By experimental data he showed that `ordinary water', H_2O contains small proportion of heavy water, D_2O (about 1 part in 5000).

Preparation: The main source of heavy water is the ordinary water from which it is isolated. Generally it is prepared by exhaustive electolysis.

Principle: The heavy water is isolated either by prolonged electrolysis or by fractional distillation of water containing alkali. Taylor, Eyring and First in 1933 formulated the electrolysis of water in seven stages using N/2-NaOH solution and strip nickel electrodes.
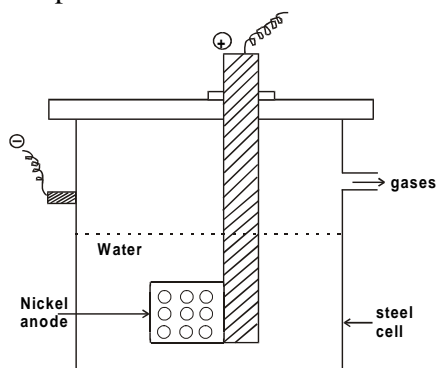
The cell consists of a steel cell 18 inches long and 4 inches in diameter. The cell itself serves as the cathode while the anode consists of a cylindrical sheet of nickel with a number of holes punched in it. A large number of

such cells are used for electrolysis of water in several stages. The gases obtained from each stage are separately burnt and the water thus formed is returned to the previous stage. The heavy water gradually concentrates in the residue left behind. The process usually consists of five stages.

A partial separation of heavy water from ordinary water can be affected by fractional distillation. This method utilises the small difference in boiling points of protium oxide (H_2O) and deuterium oxide (D_2O).

Comparison of water and heavy water

Property	H_2O	D_2O
Density at 20^oC	0.998	1.017
Freezing point	0^oC	3.82^oC
Boiling point	100^oC	101.42^oC
Maximum density	1.000 (4^oC)	1.1073 (11.6^oC)
Specific heat at 20^oC	1.00	1.01
Surface tension at 20^oC	72.8 dynes/cm	67.8 dynes/cm
Dielectric constant	82.0	80.5
Viscosity at 20^oC	10.09 millipoises	12.6 millipoises

The solubilities of substances in heavy water also differ from those in ordinary water. Thus sodium chloride is about 15% less soluble in heavy water than in ordinary water.

Physical Properties

Heavy water is a colourless, odourless and tasteless mobile liquid. Higher viscosity of heavy water is responsible for lower solubility of ionic solids like NaCl and smaller mobilities of ions.

Chemical Properties

The difference in chemical behaviour between H_2O and D_2O is very slight. However, the reaction velocity in general is slightly less in case of D_2O reactions.

Important reactions of heavy water

1. With metals

    D_2O reacts slowly with alkali and alkaline earth metals liberating heavy

hydrogen.

$$2\,Na + 2\,D_2O \longrightarrow 2\,NaOD + D_2$$
Sodium deuteroxide

$$Ca + 2\,D_2O \longrightarrow Ca\,(OD)_2 + D_2$$
Calcium deuteroxide
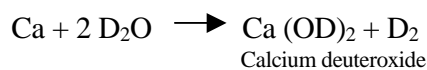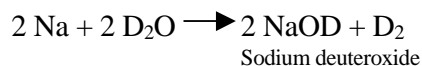
2. With metallic oxides

Metals like sodium and calcium dissolve in D_2O and form heavy alkalies.

$$Na_2O + D_2O \rightarrow 2\,NaOD$$
$$CaO + D_2O \rightarrow Ca(OD)_2$$
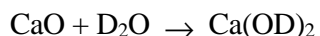
3. With acid anhydrides

D_2O forms corresponding acids containing heavy hydrogen.

$$SO_3 + D_2O \rightarrow D_2\,SO_4$$
Deutero sulphuric acid

$$P_2O_5 + 3D_2O \rightarrow 2D_3\,PO_4$$
Deuterophosphoric acid
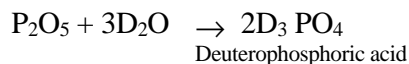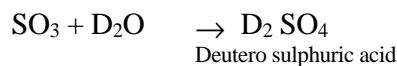
4. Upon electrolysis, heavy water containing dissolved P_2O_5, decomposes into deuterium and oxygen which are liberated at the cathode and anode respectively.

$$2D_2O \longrightarrow 2D_2 + O_2$$

5. With salt and other compounds they form deuterates.

$$Cu\,SO_4.\,5\,D_2O,\ Na_2\,SO_4.\,10D_2O,\ NiCl_2.6D_2O$$

7. Exchange reactions

When compounds containing hydrogen are treated with D_2O, hydrogen undergoes an exchange for deuterium.

$$NaOH + D_2O \longrightarrow NaOD + HOD$$

$$NH_4\,Cl + 4D_2O \longrightarrow ND_4\,Cl + 4HOD$$

Biological Properties

In general heavy water, retards the growth of living organisms like plants and animals. The tobacco seeds do not grow in heavy water. Also, pure heavy water kills small fish, tadpoles and mice when fed upon it. Certain moulds have been found to develop better in heavy water.

Uses of heavy water

1. As a neutron moderator, in nuclear reactors.
2. It is used as a tracer compound in the study of reactions occurring in living organisms.
3. It is used for the preparation of deuterium.

5.3 Hydrogen peroxide

Hydrogen peroxide was first prepared by L.J.Thenard, in 1813 by the action of dilute acid on barium peroxide. Traces of H_2O_2 are found in atmosphere and in certain plants.

Laboratory preparation of hydrogen peroxide

1. By the action of dilute sulphuric acid on sodium peroxide. Calculated quantity of Na_2O_2 is added in small proportions to a 20% ice cold solution of sulphuric acid.

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$
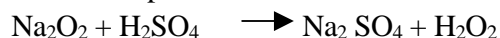
30% solution of H_2O_2 is obtained by this process.

2. Pure H_2O_2 is obtained by reacting BaO_2 with an acid

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

$$3BaO_2 + 2H_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 3H_2O_2$$
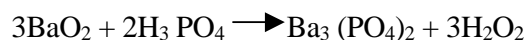
3. H_2O_2 is manufactured by the electrolysis of 50% sulphuric acid followed by vacuum distillation. The distillate is 30% solution of pure H_2O_2.

Reactions

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

$$2HSO_4^- \rightleftharpoons H_2S_2O_8 + 2e^- \text{ (At anode)}$$

$$H_2S_2O_8 + H_2O \rightleftharpoons H_2SO_4 + H_2SO_5$$

$$H_2SO_5 + H_2O \rightleftharpoons H_2SO_4 + H_2O_2$$

$$2H^+ + 2e^- \rightleftharpoons H_2 \text{ (At cathode)}$$
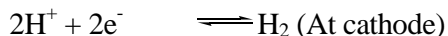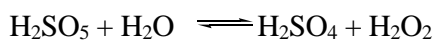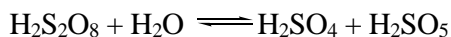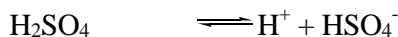
Concentration of hydrogenperoxide solution

The impurities like organic material or metallic ions, may catalyse its explosive decomposition.

i) By careful evaporation of the solution obtained above on a water bath preferably under reduced pressure using fractionating column.

ii) By distillation under reduced pressure at temperatures below 330K, the concentration up to 90% solution is used till crystallisation formed.

Strength of Hydrogenperoxide

The strength of a sample of hydrogen peroxide solution is expressed in terms of the volumes of oxygen at S.T.P that one volume of H_2O_2 gives on heating.

Properties

Physical

H_2O_2 is a colourless, odourless, syrupy liquid in the anhydrous state. It is miscible with water, alcohol, and ether in all proportions.

Chemical

Pure H_2O_2 is unstable and decomposes on standing. On heating when water and oxygen are formed.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Oxidizing Properties

H_2O_2 is a powerful oxidizing agent. It functions as an electron acceptor.

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2 H_2O$$
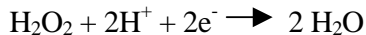
(In acidic solution)

$$H_2O_2^- + 2e^- \longrightarrow 2OH^-$$

(In alkaline solution)

i) It oxidises PbS to $PbSO_4$

$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$

ii) It oxidizes ferrous salts into ferric salts .

$$2Fe^{2+} + 2H^+ + H_2O_2 \longrightarrow 2\ Fe^{3+} + 2H_2O$$

Due to its oxidizing property, it is a valuable bleaching agent, powerful but harmless disinfectant and germicide. Delicate materials like silk, wool, hair which will be destroyed by chlorine, are bleached with H_2O_2.

Reducing Properties

With powerful oxidizing agents, H_2O_2 acts as a reducing agent. Moist silver oxide, acidified $KMnO_4$, ozone, chlorine and alkaline solutions of ferricyanides are reduced.

$$Ag_2O + H_2O_2 \longrightarrow 2\ Ag + H_2O + O_2$$

Uses

i) It destroys bacteria and hence it is used as an antiseptic and germicide for washing wounds, teeth and ears.

ii) It destroys the colour of some organic compounds and is used in bleaching delicate things like hair, wool, silk ivory and feathers.

iii) It is used as an oxidizing agent.

iv) It is also used as a propellant in rockets.

5.4 Liquid hydrogen as a fuel

The hydrogen atom has become a model for the structure of atom. Hydrogen as a substance however, has an equally important place in chemistry. Hydrogen is normally a colourless, odourless gas composed of H_2 molecules. Approximately 40% of the hydrogen produced commercially is used to manufacture ammonia and about the same amount is used in petroleum refining. But the future holds an even greater role for hydrogen as a fuel.

Liquid hydrogen, H_2, is a favourable rocket fuel. On burning, it produces more heat per gram than any other fuel. In its gaseous form, hydrogen may become the favourite fuel of the twenty first century. When hydrogen burns in air, the product is simply water. Therefore, the burning of hydrogen rather than fossil fuels (natural gas, petroleum, and coal) has important advantages.

The burning of fossil fuels is a source of environmental pollutants. They become the source of acid rain and discharge a large amount of toxic gases like SO_2 and CO_2.

Controlling carbondioxide emissions into the atmosphere is a difficult

challenge, but the answer might lie in the conversion to a hydrogen economy, hydrogen would become a major energy barrier. Automobiles, for example may be modified to burn hydrogen. At present, in USA they use car using a modified piston engine and has a hydrogen storage unit in the tank. This proves that it is possible to develop hydrogen-burning cars.

Hydrogen in not a primary energy source. But it is a convenient and non-polluting fuel, but it would have to be obtained from other energy sources.

1) It is produced by heating propane and steam at high temperature and pressure in presence of the catalyst nickel.

$$C_3 H_{8(g)} + 3H_2O_{(g)} \xrightarrow{\text{Ni}} 3 CO_{(g)} + 7H_{2(g)}$$
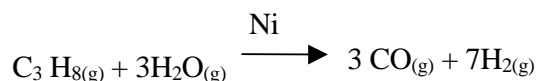
2) Pure hydrogen may be produced by reacting carbonmonoxide with steam in the presence of a catalyst to fix CO_2 and H_2. The CO_2 is removed by dissolving it in a basic aqueous solution.

3) Hydrogen can be obtained directly from water that is decomposed by some form of energy. For example, electricity from solar photovoltic collectors can be used as a source of energy to decompose water by electrolysis. Researchers use solar energy to convert water directly to hydrogen and oxygen.

5.5 Alkali Metals

Position of alkali metals in the periodic table

Alkali metals occupy the group I of the periodic table. Elements lithium, sodium, potassium, rubiduim, caesium and francium constitute alkali metals. They are named so from the Arabic word `Alquili' meaning `plant ashes'. Ashes of plants are composed mainly of sodium and potassium carbonates.

General characteristics

1. The alkali metals are shiny white and soft.

2. They can be readily cut with a knife.

3. They are extremely reactive metals and form strong alkaline oxides

and hydroxides.

4. The last metal of this group, francium is radioactive.

5. Since the alkali metals are extremely reactive they occur only as compounds in nature.

6. All the alkali metals exhibit an oxidation state of +1. This is because the metals can easily lose their single outermost electron.

7. The alkali metals give characteristic colour in bunsen flame. The colours given by Li, Na and K are crimson red, yellow, lilac respectively. This is because when the alkali metal or any of its compounds are heated in a bunsen flame, the ns' electron gets excited to higher energy levels and while returning to their ground state the excitation energy absorbed by them is released as light in the visible region.

Table 5.2 Electronic configuration of alkalimetals

Element	Symbol	Atomic number	Electronic configuration
Lithium	Li	3	[Helium] $2s^1$
Sodium	Na	11	[Neon] $3s^1$
Potassium	K	19	[Argon]$4s^1$
Rubidium	Rb	37	[Krypton]$5s^1$
Caesium	Cs	55	[Xenon]$6s^1$
Francium	Fr	87	[Radon]$7s^1$

Gradation in Physical Properties

1. Density: In general, these elements have high density due to the close packing of atoms in their metallic crystals. Lithium has low density due to the low atomic weight of the atom. Density of the elements increases on moving down the group due to the increase in the mass of the atoms with increasing atomic number. However, K is lighter than Na probably due to an unusual increase in atomic size.

2. Atomic volume: Atomic volume increases on moving down the group from Li to Cs. Hence there is an increase in atomic and ionic radii in the same order.

3. Melting and boiling points : All alkali metals have low melting and boiling point due to the weak bonding in the crystal lattice. The weak interatomic bonds are attributed to their large atonic radii and to the presence of one valence electron. With the increase in the size of the metal atoms, the repulsion of the non-bonding electron gets increased and therefore melting and boiling points decreases on moving down the group from Li to Cs.

4. Ionization energy : The first ionization energies of alkali metals are relatively low and decreases on moving down from Li to Cs.

$$M_{(g)} \rightarrow M^+_{(g)} + 1e^-$$

As the atomic radius gets increased on moving down the group, the outer electron gets farther and farther away from the nucleus and therefore ionization energy decreases.

The second ionization energies of alkali metals are fairly high. This implies that the loss of the second electron is quite difficult, because it has to be pulled out from the noble gas core.

5. Electropositive character : As alkali metals have low ionization energies, they have a great tendency to lose electrons forming unipositive ions. Therefore they

$$M \rightarrow M^+ + 1e^-$$

have strong electropositive character. Electropositive character increases as we go down the group. The alkali metals are so highly electropositive that they emit electrons when irradiated with light. This effect is known as photoelectric effect. Due to this property, Cs and K are used in photoelectric cells.

6. Oxidation state: All the alkali metals have only one electron in their outermost valence shall. As the penultimate shell being complete, these elements lose one electron to get the stable configuration of the nearest inert gas. Thus, they are monovalent elements showing an oxidation state of +1.

7. Reducing properties : As alkali metals have low ionization energy, they lose their valence electrons readily and thus bring about reduction reaction. Therefore these elements behave as good reducing agents.

5.6 Extraction of Lithium and Sodium

Extraction of Lithium - Electrolysis of Lithium chloride.

Lithium metal is obtained by the electrolysis of moisture free lithium chloride in a crucible of thick porcelain using gas-coke splinter anode and iron wire cathode. For the preparation of the metal on a large scale, a fused mixture of equal parts of lithium and potassium chloride is used, as it melts at a lower temperature of 720 K.

Lithium is also obtained by the electrolysis of a concentrated solution of lithium chloride in pyridine or acetone.

Properties of Lithium

Physical : Lithium is a silvery white metal and it is the lightest of all solid elements. It's vapours impart calamine red colour to the flame. It is a good conductor of heat and electricity. It gives alloys with number of metals and forms amalgam.

Chemical

1) With air: Lithium is not affected by dry air but in moist air it is readily oxidized. When heated in air above 450K, it burns to give lithium monoxide and lithium nitride

$$4\,Li + O_2 \longrightarrow 2\,Li_2O$$

$$6\,Li + N_2 \longrightarrow 2\,Li_3N$$
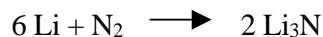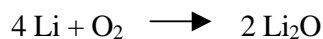
2) It decomposes cold water forming lithium hydroxide and hydrogen

$$2\,Li + 2\,H_2O \longrightarrow 2\,LiOH + H_2$$
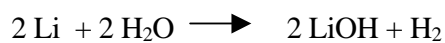
3) Lithium is a strongly electropositive metal and displaces hydrogen from acid with the formation of corresponding lithium salts. Dilute and concentrated hydrochloric and dilute sulphuric acid react readily while concentrated sulphuric acid reacts slowly. With nitric acid, the action is violent and metal melts and catches fire.

Uses

1) For the manufacture of alloys.

2) As a deoxidizer in the preparation of copper and nickel.

3) Lithium citrate and salicylate are used in the treatment of gout.

4) LiAlH$_4$ is used as an reducing agent.

5) Its compounds are used in glass and pottery manufacture.

Extraction of Sodium

Down's process : It is now manufactured by electrolysis of fused sodium chloride.

Down's electrolytic cell, consists of an iron box through the bottom of which rises a circular carbon anode. The anode is surrounded by a ring shaped iron cathode enclosed in a wire gauze shell which also acts as a partition and separates the two electrodes.

On electrolysis, chlorine is liberated at the anode and let out through an exit at the top. Sodium is liberated at the cathode and remains in the wire-gauze shell. Level of molten sodium rises and it overflows into a receiver.

$$2 \text{ NaCl} \longrightarrow 2\text{Na} + \text{Cl}_2$$

DOWN PROCESS
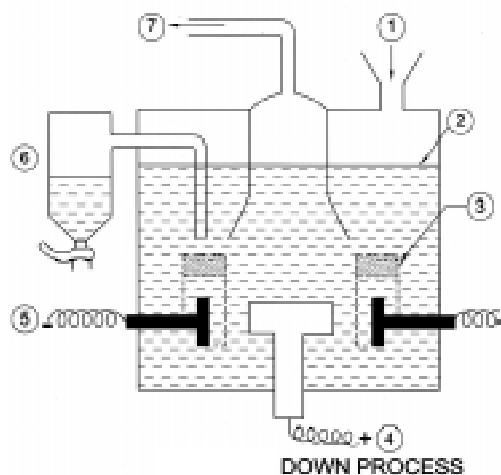
1	NaCl
2	FUSED NaCl
3	WIRE GAUZE SHELL
4	GRAPHITE ANODE
5	IRON CATHODE RING-SHAPED
6	SODIUM
7	CHLORINE

Physical properties

1) It is a silvery white metal when freshly cut but is rapidly tarnished in air. It forms tetragonal crystals.

2) It is a soft metal.

3) It is a good conductor of electricity.

4) It dissolves in liquid ammonia forming an intense blue solution.

Chemical

1) **Action of air :** In moist air a layer of sodium oxide, hydroxide and carbonate is formed on its surface which loses its lustre.

$$4Na + O_2 \xrightarrow{\hspace{1cm}} 2\,Na_2O \xrightarrow{\;2H_2O\;} 4NaOH \xrightarrow{\;2CO_2\;} Na_2CO_3 + 2H_2O$$
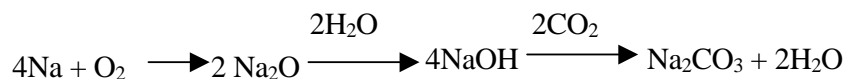
When heated in air, it burns violently to form the monoxide and the peroxide.

$$4\,Na + O_2 \longrightarrow 2Na_2O$$

$$2\,Na + O_2 \longrightarrow Na_2O_2$$
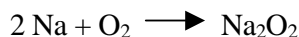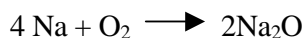
2) **Action of water :** It decomposes water vigorously, liberating hydrogen and forming sodium hydroxide.

$$2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2$$
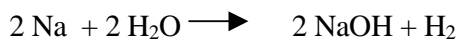
3) **Action of ammonia:** Sodium gives sodamide with ammonia liberating hydrogen.

$$2\,Na + 2NH_3 \xrightarrow{\;570\text{-}670K\;} 2\,Na\,NH_2 + H_2.$$
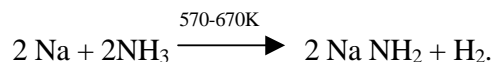
Sodium dissolved in liquid ammonia is used as a reducing agent in organic chemistry.

4) **Action of acids:** It displaces hydrogen from acids

$$2\,HCl + 2\,Na \longrightarrow 2\,NaCl + H_2.$$
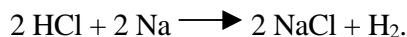
5) **Reducing action:** Reduces many compounds when heated with them in the absence of air

$$Al_2O_3 + 6\,Na \longrightarrow 2\,Al + 3\,Na_2O$$

$$SiO_2 + 4Na \longrightarrow Si + 2\,Na_2O.$$

Reduces carbondioxide when heated forming carbon and sodium carbonate.

$$4 Na + 3 CO_2 \longrightarrow 2 Na_2CO_3 + C.$$
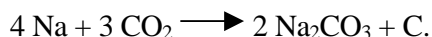
6) With Mercury : When heated with mercury, sodium forms an amalgam of varying composition Na_2Hg, Na_3Hg, $NaHg$ etc.

Uses

1) For the preparation of sodium peroxide, sodamide and sodium cyanide, tetraethyl lead etc.

2) Sodium amalgam is employed as a reducing agent.

3) As a deoxidizing agent in the preparation of light alloys and some rare earth metals from their oxides.

4) It acts as a catalyst in the polymerisation of isoprene (C_5H_3) into artificial rubber.

5) As a reagent in organic chemistry.

Questions

A. Choose the best answer

1. Atoms of the same element having same atomic number but different mass number are called
   (a) isotopes   (b) isobars   (c) isotones   (d) isomerism

2. Deuterium nucleus consists of
   (a) 2 protons only   (b) one neutron
   (c) one proton and one neutron (d) 2 protons and one neutron

3. Deuterium with oxygen gives
   (a) oxydeuterium   (b) water   (c) heavy water (d) all the above

4. Tritium is prepared by bombarding lithium with
   (a) deutrons   (b) mesons (c) slow neutrons   (d) all helium nucleus

5. At room temperature ordinary hydrogen consists of about
   (a) 25% para and 75% ortho   (b) 75% para and 25% ortho
   (c) 99% para and 1% ortho   (d) 1% para and 99% ortho

6. D_2O reacts with P_2O_5 and gives
   (a) DPO_4 (b) D_2PO_4 (c) D_3PO_3 (d) D_3PO_4

7. _____ is used for the preparation of deuterium
   (a) deuterium oxide   (b) heavy water
   (c) both a and b   (d) deuterium peroxide

8. H_2O_2 is a powerful _____ agent
   (a) dehydrating   (b) oxidising   (c) reducing   (d) desulphurising
9. _____ is used as a propellant in nucleus
   (a) H_2O_2 (b) D_2O (c) ND_3 (d) $CH_2 = CH_2$
10. The oxidation state of alkali metals is
   (a) +2   (b) 0   (c) +1   (d) +3
11. When heated in bunsen flame, lithium gives _____ colour
   (a) yellow   (b) blue   (c) lilac   (d) crimson red
12. On moving down the group, density of the alkali metals
   (a) increases   (b) decreases
   (c) increases and then decreases   (d) decreases and then increases
13. If the element can lose an electron readily, they are said to be
   (a) electronegative   (b) electropositive
   (c) electronative   (d) electrovalent

B. Fill in the blanks

1. The first element in the periodic table is _____.
2. _____ is the common formd of hydrogen.
3. The half-life of tritium is _____.
4. Deuterium reacts with ammonia to form _____.
5. The rare isotope of hydrogen is _____.
6. _____ is employed in nuclear reactor to slow down the speed of fast moving neutrons.
7. The magnetic moment of para hydrogen is _____.
8. Deuterium with salt and other compounds forms _____.
9. Hydrogen peroxide was first prepared by _____ in _____.
10. Pure H_2O_2 is _____.
11. The Arabic word `Alquili' means _____.
12. The electronic configuration of potassium is _____.
13. All alkali metals have _____ melting and boiling points.
14. On moving down the group of alkali metals, ionization energy _____.
15. _____ is the lightest of all solid elements.

C. Write in one or two sentences

1. What are isotopes? Mention the isotopes of hydrogen.
2. Write a short note on tritium.
3. How does deuterium react with nitrogen?
4. How does deuterium react with metals?
5. Mention the uses of deuterium.

6. How is tritium prepared?
7. How do you convert para hydrogen to ortho hydrogen?
8. How does heavy water react with metals?
9. How is hydrogen peroxide prepared in the laboratory?
10. How is hydrogen peroxide solution concentrated?
11. Write about the reducing property of hydrogen peroxide.
12. Mention two important uses of H_2O_2.
13. Why alkali metals have low melting and boiling points?
14. Why alkali metals have strong electropositive character?

D. Explain briefly on the following

1. How is deuterium obtained by diffusion process?
2. Write about the exchange reactions of deuterium.
3. What are ortho and para hydrogen? Explain.
4. Differentiate between ortho and para hydrogen.
5. Explain the preparation of heavy water.
6. Compare water and heavy water.
7. Explain the oxidizing property of hydrogen peroxide.
8. Explain how liquid hydrogen can be used as a fuel.
9. How is lithium extracted from its ore?

Problem

An element occupies group number 1 and period number 3. This element heated in air gives compound A. With water it gives compound B - a strong base. With ammonia gives compound C, which is used as a reducing agent in organic chemistry. Identify the element A,B and C.

Solution

(i) As per the position in the periodic table this element occupying group number 1 and period number 3 is sodium.

(ii) When heated in air, it forms sodium peroxide (A)

$$4Na + O_2 \longrightarrow 2Na_2O_2$$
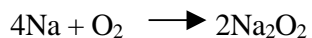
(iii) With water, sodium gives sodium hydroxide (B)

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$
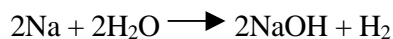
(iv) With ammonia, sodium gives sodamide (I)

$$2Na + 2NH_3 \xrightarrow{\text{570-670 K}} 2NaNH_2 + H_2$$
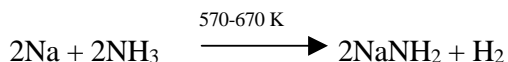
The element is sodium.
The compound A is sodium peroxide.
The compound B is sodium hydroxide.
The compound C is sodamide.

Problems

1. An isotope of hydrogen reacts with oxygen to give compound (A), which is used as a moderator in nuclear reactor. Like hydrogen, this isotope also undergoes addition reaction. It reacts with ethylene to give compound B, which is a saturated hydrocarbon. Identify the element A and B. A is radioactive.

2. An isotope of hydrogen is prepared by bombarding beryllium with deuterons. It decays to an element A, with the emission of beta radiation. Identify the isotope and the element A.

3. A deuterium compound (A) which is used as a moderator in nuclear reactor reacts with Ca to form compound B. A reacts with SO_2 to give compound C. Upon electrolysis compound A gives deuterium molecule. Identify A, B and C.

4. An element occupies group number 1 and period number 2. This element burns with air and forms compound A. With water, it gives compound B, with hydrogen it forms an ionic compound C. Identify the elements, A, B and C.

SUMMARY

Hydrogen is the first element in the periodic table. It exists in 3 isotopes. Protium, deuterium and tritium. The preparation properties of deuterium are dealt in detail.

Depending on the spins of the nucleus of hydrogen atom in a molecule, two types ortho and para hydrogen are known. It can be converted from one to another form.

One of the important compound of deuterium is heavy water, which is isolated from ordinary water. It reacts with metals, metallic oxides, acid anhydrides etc. It also undergo exchange reaction.

In 1813, L.J. Thenard prepared hydrogen peroxide by the action of dilute acid on barium peroxide. Traces of it are found in atmosphere. Pure H_2O_2 is unstable. It acts as a powerful oxidizing agent.

The use of liquid hydrogen as a fuel is explained in this chapter.

Group 1 elements are known as alkalimetals. There is mostly regular gradation in properties like density, atomic volume, melting and boiling point, ionization energy etc. along the group.

The extraction of lithium and sodium and its properties are explained in detail.

REFERENCES

1. General Chemistry - John Russell
   McGraw Hill International Editions 3rd Edition.

2. Inorganic Chemistry, P.L. Soni.

6. GROUP 2 *s* - BLOCK ELEMENTS

OBJECTIVES

- *Understands the general characteristics of alkaline earth metals*
- *Know the comparison of alkali and alkaline earth metals.*
- *Understand the extraction of magnesium by electrolytic process, its properties and uses.*
- *Recognise the different compounds of alkaline earth metals.*
- *Understand and learn in detail about the preparation, properties and uses of CaO, plaster of paris and MgSO₄.*

6.1 The second group of the periodic table contains Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra). These elements are also a known as "Alkaline Earth Metals". The word earth was applied in old days to a metallic oxide and because the oxides of calcium, strontium and barium produced alkaline solutions in water and, therefore these metals are called the alkaline earth metals. Radium corresponds to all the alkaline earth metals in its chemical properties but being radioactive, it is studied along with other radioactive elements.

Like the alkali metals, they are very reactive and hence never occur in nature in free form and react readily with many non metals.

Electronic configuration

Element	At No.	Electronic	Configuration of Valence Shell
Beryllium	4	$1s^2 2s^2$	$2s^2$
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$	$3s^2$
Calcium	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$4s^2$
Strontium	38	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^6 5s^2$	$5s^2$
Barium	56	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s_2 4p^6 4d^{10} 5s^2 5p^6 6s^2$	$6s^2$
Radium	88	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 5d^{10} 5f^{14} 6s^2 6p^6 7s^2$	$7s^2$

The electronic configurations show that for each element, the neutral atom has two electron after inert gas core and two electrons are in a

completed s-subshell. Thus, the outer electronic configuration of each element is ns^2 where n is the number of the valence shell. It can be expected that the two electrons can be easily removed to give the inert gas electronic configuration. Hence these elements are all bivalent and tend to form ionic salts. Thus ionic salts are less basic than group 1. Due to their alike electronic structure, these elements resemble closely in physical and chemical properties.

The variation in physical properties are not as regular as for the alkalimetals because the elements of this group do not crystallise with the same type of metallic lattice.

These elements have been sufficiently soft yet less than the alkalimetals as metallic bonding in these elements has been stronger than in first group alkali elements.

Beryllium is unfamiliar, partly because it is not very abundant and partly because it is difficult to extract. Magnesium and calcium are abundant and among the eight most common elements in the earth's curst. Strontium and barium are less abundant but are well known, while radium is extremely scarce and its radioactivity is more important than its chemistry.

Metallic properties

The alkaline earth metals are harder than the alkali metals. Hardness decreases, with increase in atomic number. They show good metallic lustre and high electrical as well as thermal conductivity because the two s-electrons can easily move through the crystal lattice.

Melting and Boiling Points

Both melting and boiling points do not show regular trends because atoms adopt different crystal structures. They possess low melting and boiling points. These are, however, higher than those of alkali metals because the number of bonding electrons in these elements is twice as great as group 1 elements.

Atomic radius

The atoms of these elements are somewhat smaller than the atoms of the corresponding alkali metals in the same period. This is due to higher

nuclear charge of these atoms which tends to draw the orbital electrons inwards. Due to the smaller atomic radius, the elements, are harder, have higher melting points and higher densities than the elements of group 1. Atomic radius is seen to increase on moving down the group on account of the presence of an extra shell of electron at each step.

Ionic radius

The ions are also large but smaller than those of the elements in group 1. This is due to the fact that the removal of two orbital electrons in the formation of bivalent cations M^{2+}, (Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, etc) increases the effective nuclear charge which pulls the electrons inwards and thus reduces the size of the ions. The ionic radius is seen to increase on moving down the group 2.

Atomic volume

Due to the addition of an extra shell of electrons to each element from Be to Ra, the atomic volume increases from Be to Ra.

Ionisation Energy

As the alkaline earth metals are having smaller size and greater nuclear charge than the alkali metals, the electrons are more tightly held and hence the first ionisation energy would be greater than that of the alkali metal.

The second ionisation energy has been to be nearly double than that of the first ionisation energy.

It is interesting to observe that although the IE_2 of the alkaline earth metals is much higher than the IE_1 they are able to form, M^{2+} ions. This is due to their high heat of hydration in aqueous solution and high lattice energy in the solid state. As the atomic size gets increased from Be to Ba, the values of IE_1 and IE_2 of these elements would decrease on going down the group, ie, Be to Ba.

As among second group elements beryllium has the highest ionisation energy. It has the least tendency to form Be^{2+} ion.

Thus its compounds with nitrogen, oxygen, sulphur and halogens are covalent whereas the corresponding compounds of Mg, Ca, Sr and Ba are ionic.

The total energy required to produce gaseous divalent ion for second group elements is over four times greater than the amount needed to ionise alkali metals. This very high energy requirement is more than offset by the hydration energy or the lattice energy being more than four times greater.

Oxidation states

Because of the presence of two s-electrons in the outermost orbital, being high heat of hydration of the dipositive ions and comparatively low value of IE_2, the alkaline earth metals have been bivalent. The divalent ion is having no unpaired electron, hence their compounds are diamagnetic and colourless, provided their anions have been also colourless.

Flame colouration

These elements and their compounds impart characteristic colours to flame. Thus, barium - apple green, calcium - brick red, strontium - crimson red, radium - crimson red.

The reason for imparting the colour to flame is that when elements or their compounds are put into flame, the electrons get energy and excite to higher energy levels. When they return to the ground state they emit the absorbed energy in the form of radiations having particular wavelength.

Beryllium and magnesium atoms are smaller and their electrons being strongly bound to the nucleus are not excited to higher energy levels. Therefore they do not give the flame test.

Diagonal relationship between Beryllium and Aluminium

In case of beryllium, a member of second period of the periodic table, which resembles more with Aluminium group (13 group) than the member of its own group (2nd). The anamolous behaviour of beryllium is mainly ascribed to its very small size and partly due to its high electronegativity. These two factors tend to increase the polarising power of Be^{2+} tends to form ions to such extent that it is significantly equal to the polarising power of Al^{3+} ions. Thus the two elements resemble very much.

6.2 Magnesium

The magnesium comes from the name of the mineral magnesite, which in turn is believed to stem from the name Magnesia. The British chemist Humphry Davy discovered the pure element magnesium in 1808.

Due to its low density, it is considered to be a structural unit.

Important Ores

Magnesium does not occur in the native state. In the combined state it occurs very abundantly in the earth crust.

Magnesite, $MgCO_3$ Dolomite, $MgCO_3$, $CaCO_3$

Epsomsalt, $MgSO_4$, $7H_2O$ Carnallite $MgCl_2$ $KCl.6H_2O$

However magnesium ion Mg^{2+}, is the third most abundant dissolved ion in the oceans, after Cl^- and Na^+. The oceans are the best sources for magnesium. It is widely distributed in the vegetable kingdom being present in chlorophyll, the green colouring matter of the leaves.

Metallurgy

Magnesium is prepared on a large scale by the electrolysis of either fused magnesium chloride or magnesia.

1. Electrolysis of fused magnesium chloride

The purified carnallite ore is the principal source for this process. A mixture of equal quantities of carnallite and NaCl is fused to a clear liquid at 973K. The alkali chloride prevents hydrolysis of magnesium chloride and increases the conductivity of the fused mass.
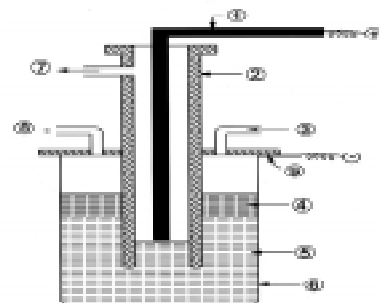
ELECTROLYTIC REDUCTION OF MAGNESIUM CHLORIDE

1. GRAPHITE ANODE
2. PORCELAIN HOOD
3. INERT GAS LIKE COAL GAS
4. MAGNESIUM
5. ELECTROLYTE (MOLTEN)
6. IRON CELL
7. CHLORINE
8. INERT GAS
9. IRON CATHODE

The electrolysis of the fused mass is carried out in an atmosphere of coal gas in air tight iron cell which can hold 6-7 tonnes of the electrolyte. The temperature of the elctrolyte bath is maintained at 970K. The iron cell itself acts as a cathode unlike the anode consists of a carbon or graphite rod surrounded by a porcelain tube through which the liberated chlorine escapes. Molten magnesium being lighter than the electrolyte, rises to the surface and is periodically removed with perforated ladle. The electrolysis is carried out in an atmosphere of coal gas so as to avoid the oxidation of molten magnesium. The metal thus obtained is 99.9% pure. It may be further purified by remelting with a flux of anhydrous magnesium chloride and sodium chloride.

Physical

Pure magnesium metal is a relatively active silvery white metal. At slightly below its melting point, it is malleable and ductile and can be drawn into wire or rolled into ribbon in which form it is generally sold. It is a very light metal.

Chemical Properties

1. **Action of Air :** It does not tarnish in dry air but a layer of white oxide is formed on its surface in moist air.

2. **With air on burning :** It burns in air or oxygen with a dazzling light rich in ultraviolet rays, forming magnesium oxide and magnesium nitride.

$$2Mg + O_2 \rightarrow 2Mg\,O$$

$$3Mg + N_2 \rightarrow Mg_3N_2$$
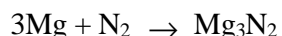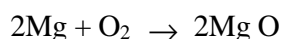
3. **With CO_2**

   It continues to burn in CO_2,

   $$2\,Mg + CO_2 \rightarrow 2\,MgO + C$$
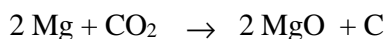
4. **Action of Water**

   When heated with steam it burns brilliantly producing magnesium oxide and hydrogen.

$$Mg + H_2O \rightarrow MgO + H_2$$
$$\text{steam}$$
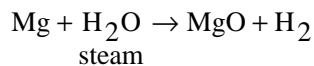
5. Action of Acids

Dilute HCl or H_2SO_4 gives hydrogen with magnesium. With dilute HNO_3, part of the hydrogen liberated is oxidised by nitric acid, which itself is reduced to a variety of products depending upon the concentration. With concentrated HNO_3, it gives ammonium nitrate.

$$4Mg + 10HNO_3 \rightarrow 4\,Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$$
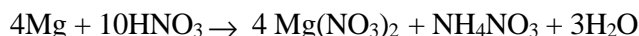
6. Displacement of Metals

It is a strongly electropositive metal and hence Mg displaces nearly all the metals from the solutions of their salts eg.

$$Mg + 2AgNO_3 \rightarrow Mg(NO_3)_2 + 2Ag$$
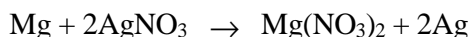
7. Reducing Action

Mg has great affinity for oxygen and it liberates sodium, potassium, boron and silicon from their oxides at high temperatures.

$$K_2O + Mg \rightarrow MgO + 2K$$
$$B_2O_3 + 3Mg \rightarrow 3MgO + 2B$$
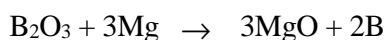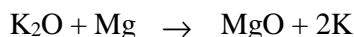
Uses of Magnesium

1. In flashlight photography, pyrotechnics and in fireworks.

2. As a reducing agent in the preparation of boron and silicon and deoxidiser in metallurgy.

6.3 Compounds of alkaline earth metals

Magnesium sulphate, epsom slat, $MgSO_4. 7H_2O$

It is prepared by dissolving magnesium oxide or carbonate in dilute sulphuric acid.

$$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$$
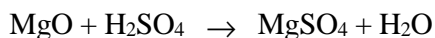
Uses

1) As a purgative
2) In dyeing and tanning processes and in dressing cotton goods.
3) Platinised $MgSO_4$ is used as a catalyst.

Calcium oxide, CaO, quicklime

It is prepared by burning limestone in specially designed kilns.

$$CaCO_3 \xrightarrow{1070K} CaO + CO_2$$
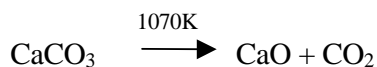
Properties

1. Lime is a white porous solid

2. On adding water it gives a hissing sound and becomes very hot. The fine powder obtained is known as slaked lime and consists of calcium hydroxide $Ca(OH)_2$. This process is called slaking of lime.

$$CaO + H_2O \rightarrow Ca(OH)_2$$
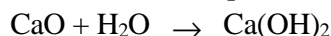
The paste of lime in water is called milk of lime whereas the filtered and clear solution is known as lime water.

3. With chlorine it gives bleaching powder $CaOCl_2 . H_2O$

4. With carbondioxide, it forms calcium carbonate while with sulphurdioxide, calcium sulphite is obtained.

5. Moist hydrochloric acid gas reacts with it to give calcium chloride but there is no action with the dry gas.

$$CaO + 2\,HCl \rightarrow CaCl_2 + H_2O$$
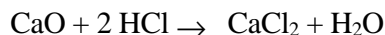
Uses

1 For the manufacture of calcium chloride, cement, mortar and glass.

2. For drying gases and alcohol.

3. As milk of lime, used in refining sugar and white washing.

4. As lime water, used as a reagent in laboratory and in medicine.

Calcium sulphate, CaSO₄

It occurs as Anhydrite, $CaSO_4$ and Gypsum $CaSO_4. 2H_2O$. It may be prepared by adding dilute sulphuric acid to the solution of a calcium salt.

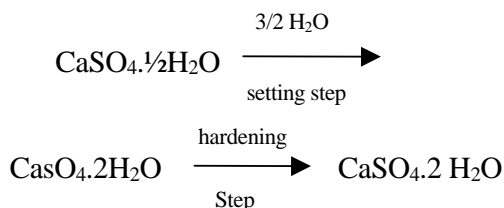$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$
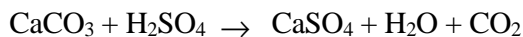
Uses of Gypsum

It is used
1. For preparing plasters
2. As a retardant for the setting of cement

Plaster of Paris

When Gypsum is heated to about 393K it loses 1½ molecules of water and forms plaster of paris with the formula $CaSO_4$ ½H_2O, Calcium Sulphate hemihydrate. The substance is known as plaster of paris because the large deposits of Gypsum used for the manufacture of plaster are at Montmeite (Paris).

When plaster of paris is wetted with, it forms a plastic mass which sets in from 5 to 15 minutes to a white porous hard mass. A slight expansion occurs during the setting so that it will take sharp impression of a mould. The process of setting takes place in two steps, the setting step and the hardening step. The final product of setting is gypsum.

$$CaSO_4.½H_2O \xrightarrow[\text{setting step}]{3/2\ H_2O}$$

$$CasO_4.2H_2O \xrightarrow[\text{Step}]{\text{hardening}} CaSO_4.2\ H_2O$$

The setting step may be catalysed by NaCl while it is retarded by borax or alum.

Uses : It is used

1. In surgery for plastering the fractured bones.

2. In making moulds for statues, in dentistry etc.

3. In making false ceilings.

Questions

A. Choose the best Answer

1. Among the following, which is known as `alkaline earth metal'.
    (a) Sodium   (b) Calcium   (c) Lithium   (d) Potassium

2. Alkaline earth metals are
    (a) monovalent   (b) trivalent   (c) divalent   (d) zerovalent

3. Among alkaline earth metals ————— is having the highest ionization energy.
    (a) Beryllium (b) magnesium   (c) Calcium   (d) Barium

4. The colour given by barium in flame is
   (a) Brick red   (b) Apple Green   (c) Red   (d) Blue
5. The third most abundant dissolved ion in the ocean is
   (a) Beryllium (b) Barium   (c) Calcium   (d) Magnesium
6. Quick lime is
   (a) Calcium oxide   (b) Calcium hydroxide
   (c) Calcium nitrate   (d) Calcium sulphate
7. The formula of bleaching powder is
   (a) $CaCl_2. H_2O$ (b) $CaOCl_2. H_2O$
   (c) $CaSO_4. 2H_2O$ (d) $CaSO_4. ½H_2O$
8. Plaster of paris is
   (a) $CaSO_4. 2H_2O$ (b) $CaCl_2$
   (c) $CaSO_4$ (d) $CaSO_4. 2H_2O$
9. The compound used in making moulds for statues is
   (a) Epsom salt   (b) Calcium sulphide
   (c) Plaster of paris   (d) Gypsum
10. The element used in pyrotechnics is
   (a) Magnesium   (b) Barium   (c) Calcium   (d) Beryllium

B. Fill in the Blanks

1. The general electronic configuration of alkaline earth metals is _____.
2. The ionic radius _____ on moving down the group 2.
3. In flame, calcium gives_____ colour.
4. Beryllium resembles more with an element in 13th group _____.
5. Magnesium comes from the name of the mineral —————·
6. ————————— is present chlorophyll.
7. Magnesium is prepared by the electrolysis of fused —————·
8. With air, Magnesium forms ————— and —————·
9. The formula of epsom salt is —————·
10. Epsom salt is used as _____.

C. Match the following

1. Magnetite $CaSO_4 . 2H_2O$
2. Dolamite $Mg\ Cl_2 . KCl . 6H_2O$
3. Epsom salt $MgCO_3$
4. Carnallite $MgCO_3 . CaCO_3$
5. Gypsum $MgSO_4 . 7H_2O$

Problem

An element occupies group number 2 and period number 3. This element reacts with oxygen and nitrogen to form compound A and B. It is a strong electropositive metal so it displaces Ag from $AgNO_3$ solution. With concentrated nitric acid, it forms compound C. Identify the element, compound A, B and C.

D. Write in one or two sentence

1. Why the oxides of Group 2 metals have high melting points?
2. Why there is increase in the ionisation potential for forming M^{3+} ion for group 2 metals?
3. Why the ionization potential of M^{2+} is not very much greater than M^+?
4. Why a precipitate of $Mg(OH)_2$ is not formed when aqueous ammonia, NH_4OH is added to a solution of $MgCl_2$?
5. List the carbonates and hydroxide of alkaline earth metals in order of their increasing stability and their solution.
6. Why do beryllium halides fume in air?
7. Why group 2 elements are harder than alkali metals?
8. Beryllium halides are covalent whereas magnesium halides are ionic. Why?
9. Why are monoxides of alkaline earth metals are very stable?
10. The basic strength of the oxides of group 2 elements increases from Be to Ba. Why?

D. Explain briefly on the following

1. What are alkaline earth metals? Why are they called so?
2. In what respects Be and Mg differ from all the other metals of group 2.

3. How can you explain the anomalous behaviour of beryllium.
4. How does magnesium occur in nature? How is the metal extracted from its Ore?
5. In the light of metallic bonding account for the following properties of group 2 elements.
   a. These are harder than alkali metals
   b. These are good conductors of heat and electricity.
6. Why the first ionization energy of alkaline earth metals higher than that of Ist group.
7. Mention the uses of plaster of Paris.
8. How is plaster of paris prepared?
9. How is $MgSO_4$ prepared?
10. Mention the uses of Magnesium?

SUMMARY

The second group of periodic table is known as alkaline earth metals. Like alkali metals they are reactive. The physical properties and chemical of these elements are explained.

The metallurgy of Mg, its physical and chemical properties are explained in detail. Some compounds of alkaline earth metals such as Epsom salt, calcium sulphate, quick lime, gypsum and plaster of paris are dealt.

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p - BLOCK ELEMENTS

ns^2 np$^{1-5}$

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

13 ⟶ Boron group

14 ⟶ Carbon group

15 ⟶ Nitrogen group

16 ⟶ Oxygen group

7. *p*-BLOCK ELEMENTS

OBJECTIVES

After studying this unit, you will be able to

*   *Understand the nature and properties of p-block elements.*
*   *Know the important ores of boron.*
*   *Understand the isolation of boron from its ores.*
*   *Understand the preparation, properties and uses of boron compounds.*
*   *Learn about the allotropes of carbon.*
*   *Understand the structure of graphite and diamond and the difference between them.*
*   *Acquire knowledge about oxides, carbides, halides and sulphides of carbon group.*
*   *Learn about fixation of nitrogen.*
*   *Understand the preparation, properties and structure of nitric acid.*
*   *Recognise the uses of nitrogen and its compounds.*
*   *Know the importance of molecular oxygen and the differences between nascent oxygen and molecular oxygen.*
*   *Realise the importance of ozone to life.*

7.1 General Characteristics

The elements belonging to the group 13 to 18 of the periodic table, in which p-orbitals are progressively filled are collectively known as p-block elements.

In all these elements while s-orbitals are completely filled, their p-orbitals are incomplete. These are progressively filled by the addition of one electron as we move from group 13 (ns^2np^1) to group 17 (ns^2np^5). In group 18 (ns^2np^6) both s and p-orbitals are completely filled.

p-block elements show a variety of oxidation state both positive and negative. As we go down the group, two electrons present in the valence `s' orbital become inert and the electrons in the `p' orbital are involved in chemical combination. This is known as `inert pair effect'.

The inert pair effect is really a name, not an explanation. A full explanation involves the decreasing strength of the M-X bond going down the group (for covalent compounds) or the decreasing lattice energies of compounds containing the M^{4+} ion (for ionic compounds). In this way the energy input needed to form compounds of the formula MX_4 are less likely to be balanced by the energy released when the four M-X bonds are formed, so the equilibrium favours the left hand side.

$$MX_2 + X_2 \rightarrow MX_4$$
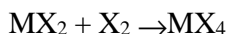
The existence of a positive oxidation state corresponding to the group number and of another state two units lower is an illustration of the inert pair effect, the term referring to the valence `s' electrons, used in bonding in the higher oxidation state but not in the lower.

With the increase in atomic mass, the ionic character of bonds of the compounds of the group 13 (IIIA) elements increases, and some of the heavier metal ions do exist in the +3 oxidation state in aqueous solution. The stability of such compounds with the +3 oxidation state is, however, lower than those with the +1 oxidation state in the case of heavier members of this group. Thus thallium in +1 oxidation state is more stable than in +3 state. This is because, the s electrons in the ns sub-shell do not prefer to form bonds.

This inertness is found only, i) when the `s' electrons are in the fifth or higher principal quantum number ii) when their loss does not afford a species with a noble gas configuration. This property of stabilising the lower oxidation state keeping the paired electron in the ns orbital is referred to as the `inert pair effect'. This effect is also observed in the elements of groups 12 (IIB), 14(IVA) and 15(VA) where the heavier elements exhibit 0, +2 and +3 oxidation states respectively.

Nature of oxides

Oxides of p-block elements may be basic (in case of metallic elements), amphoteric (in case of metalloids) or acidic (in case of non-metals). Non-metals also form a number of oxyacids. In all the groups, the acidic character of the oxide decreases as we move down the group while it increases in the same period from left to right.

For example

Basic oxide	-	Bi_2O_3
Amphoteric oxide	-	SnO, SnO_2, PbO, Pb_2O_3
Acidic oxides	-	SO_3, Cl_2O_7
Oxyacids	-	HNO_3, H_2SO_4.

Basic character increases down the group

| CO_2 | SiO_2 | GeO_2 | SnO | PbO |
| acidic | less acidic | amphoteric | basic | most basic |

Acidic character increases across a period

| Al_2O_3 | SiO_2 | P_4O_{10} | SO_2 | Cl_2O_7 |
| amphoteric | acidic | | | most acidic |

Nature of hydrides

Many of the p-block elements form hydrides. The hydrides of non-metals are more stable. Thus in any group the stability of the hydride decreases from top to bottom; its strength as an acid also increases in this order. Thus among all the hydrides, hydrogen iodide forms the strongest acid solution in water. In group 15, nitrogen forms the stablest hydride of all. Thus the order of stability of these hydrides is

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

Nature of halides

Out of the p-block elements, the non-metals form covalent halides. Metallic halides show a gradation from an ionic character to covalent character. As we move from left to right across the period, ionic character of the halides decreases and covalent character increases. For example, $SbCl_2$ is partially ionic whereas $TeCl_4$ is covalent.

In case metals forms halides in more than one oxidation states, halides in lower oxidation state are largely ionic and those in higher oxidation state are largely covalent.

Polarizability of a halide ion depends on its size. Iodides and bromides are more covalent while fluorides are more ionic.

7.2 Group 13 - Boron Group (B, Al, Ga, In, Tl)

Boron does not occur in the free state in nature. In the combined state, it occurs mainly in the form of the salts of boric acid.

### 7.2.1 Ores of Boron

i) Boric acid H_3BO_3
ii) Borax $Na_2B_4O_7.10H_2O$

7.2.2 Extraction

On a large scale, boron is extracted from its minerals, borax $Na_2B_4O_7$ or colemanite $Ca_2B_6O_{11}$. The latter is first converted to borax by boiling with a solution of sodium carbonate in the requisite proportion.
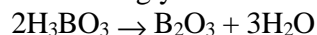
$$2Ca_2B_6O_{11} + 3Na_2CO_3 + H_2O \rightarrow 3Na_2B_4O_7 + 3CaCO_3 + Ca(OH)_2$$
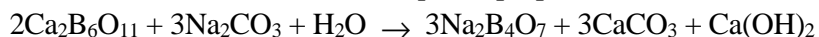
The insoluble calcium carbonate settles down and borax is crystallized from the mother liquor. Boron is isolated from borax in the following two steps.

a) Preparation of boron trioxide:- Borax is treated with hot concentrated hydrochloric acid, when the sparingly soluble boric acid slowly separates out.

$$Na_2B_4O_7 + 2HCl \rightarrow 2NaCl + H_2B_4O_7$$
$$H_2B_4O_7 + 5H_2O \rightarrow 4H_3BO_3$$
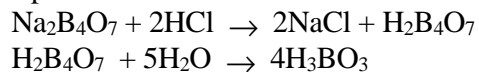
Boric acid is strongly heated when borontrioxide is obtained

$$2H_3BO_3 \rightarrow B_2O_3 + 3H_2O$$

b) Reduction of borontrioxide:- A mixture of borontrioxide with sodium, potassium or magnesium pieces is heated in a crucible to bright redness. The residual boron is broken up and boiled with concentrated HCl to dissolve out magnesium oxide and excess of boric acid when a dark brown powder of amorphous boron is obtained as a residue: It is washed with water and dried.

$$B_2O_3 + 3Mg \rightarrow 2B + 3MgO.$$
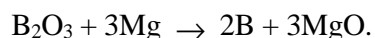
Pure boron is obtained in the crystalline form by passing a mixture of boron tribromide vapours and hydrogen over electrically heated filament of tungsten at 1470K. It may also be prepared by submitting a mixture of borontrichloride vapour and hydrogen to the action of a high tension electric arc, when boron is obtained on cooling as a hard black amorphous mass.

Physical properties

Boron exists in two allotropic forms amorphous and crystalline boron. Boron is a non-metallic element and is a non-conductor of electricity.

Chemical properties

1) **Action of air:-** It is unaffected by air at ordinary temperature but when heated in air to about 975K, it burns forming boron trioxide and a little boron nitride, BN

$$4B + 3O_2 \rightarrow 2B_2O_3$$

$$2B + N_2 \rightarrow 2BN$$
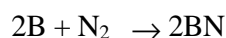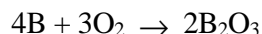
2) **With acids: -** Amorphous boron dissolves in hot concentrated sulphuric and in nitric acid to form boric acid.

$$B + 3HNO_3 \rightarrow H_3BO_3 + 3NO_2$$

$$2B + 3H_2SO_4 \rightarrow 2H_3BO_3 + 3SO_2.$$
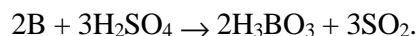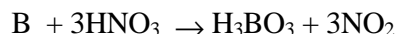
3) **With caustic alkali:-** It dissolves in fused caustic alkali and forms boric acid.

4) **As a reducing agent:-** Boron is a powerful reducing agent and can even replace carbon from carbon dioxide and silicon from silica.

$$3CO_2 + 4B \rightarrow 2B_2O_3 + 3C$$

$$3SiO_2 + 4B \rightarrow 2B_2O_3 + 3Si$$
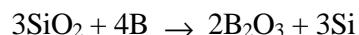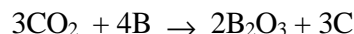
5) **With metals:-** It combines with metals (except Cu, Ag and Au) at high temperature in the electric furnace to form borides.

6) **With non-metals:-** Boron combines with nitrogen, chlorine, bromine and carbon at higher temperature forming boron nitride, BN, boron trichloride, BCl_3, boron tribromide, BBr_3 and boron carbide, B_4C respectively. Boron carbide is probably the hardest substance known.

7.2.3 Compounds of Boron

Borax (or) Sodium tetraborate, $Na_2B_4O_7$ - Tincal, a crude form of borax, contains 55% of it and is found in the land dried up lakes of Tibet.

Borax can be prepared

i) **From colemanite:-** It is boiled with concentrated solution of sodium carbonate.

$Ca_2B_6O_{11} + 2Na_2CO_3 \rightarrow 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$.

On filtration and concentration, crystals of borax separate. A current of CO_2 is passed through the mother liquor to convert the metaborate into borax.

$4NaBO_2 + CO_2 \rightarrow Na_2CO_3 + Na_2B_4O_7$
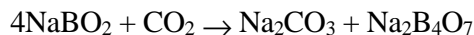
The residual sodium carbonate is used again for the treatment of a fresh quantity of colemanite.

ii) **From Tincal -** Naturally occurring crude borax (Tincal) is dissolved in water, filtered, concentrated and crystallized when pure borax is obtained.

Properties

1. When borax is heated above its melting point until all the water of crystallization is expelled, it forms a colourless glassy substance known as borax glass. It then decomposes to give sodium meta borate and boron (III) oxide.

$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O$

$Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$
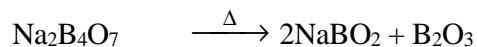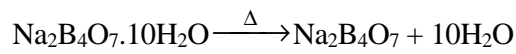
When this mixture is fused with metallic oxide it forms characteristic coloured beads. With the help of the colour, the metal ions can be identified. For example

$$CuO + B_2O_3 \rightarrow Cu(BO_2)_2.$$
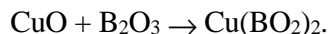
Uses: Borax is used

1) to identify the metallic radicals in the qualitative analysis
2) as a flux in welding metals
3) in the manufacture of glass, soap and porcelin
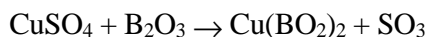4) as cleaning and dyeing agent in tanneries
5) as a food preservative.

Borax bead test

A pinch of borax is heated in a platinum loop, it melts to give a colourless glassy bead. It is then dipped in a coloured metallic salt solution and again heated. Characteristic coloured beads are formed. From the
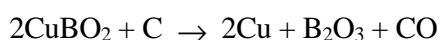
colour of the beads, the basic radicals are identified. Due to the formation of metallic metaborate, the characteristic colours are formed.

Example: Copper salts give blue beads

In an oxidising flame

$CuSO_4 + B_2O_3 \rightarrow Cu(BO_2)_2 + SO_3$

In a reducing flame

$2Cu(BO_2)_2 + C \rightarrow 2CuBO_2 + B_2O_3 + CO$

$2CuBO_2 + C \rightarrow 2Cu + B_2O_3 + CO$

Borax bead test is used to identify the coloured salts.

Metallic compounds	Colour in oxidising flame	Colour in reducing flame
Copper	Blue	Red
Iron	Yellow	Bottle green
Manganese	Pinkish violet	Colourless
Cobalt	Blue	Blue
Chromium	Green	Green
Nickel	Brown	Grey

7.3 Carbon group elements

The elements carbon, silicon, germanium, tin and lead constitute the 14th group of the periodic table. These are p-block elements having the configuration ns^2np^2.

Element	At.No.	Electronic structure
Carbon	6	[He] $2s^2\ 2p^2$
Silicon	14	[Ne] $3s^2\ 3p^2$
Germanium	32	[Ar] $3d^{10}\ 4s^2\ 4p^2$
Tin	50	[Kr] $4d^{10}\ 5s^2\ 5p^2$
Lead	82	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$

7.3.1 Allotropic forms of carbon

Carbon exhibits allotropy and occurs as

i)   Diamond, a beautiful crystalline substance

ii) Graphite, a soft greyish black crystalline substance

iii) Amorphous carbon, black residue left when carbon compounds are heated.

Different amorphous varieties of carbon are (i) Coal, (ii) Coke, (iii) Charcoal, (iv) Bone black or animal charcoal, (v) lampblack, (vi) carbon black, (viii) Gas carbon and (ix) petroleum coke.

7.3.2 Structure of diamond

In diamond every atom is bonded with the other by covalent links resulting in the formation of giant molecule. Each carbon atom is linked with four neighbouring carbon atoms held at the corners of a regular tetrahedron by covalent bonds. The C-C bonds are very strong. The crystal of diamond is very hard and has high melting and boiling points.
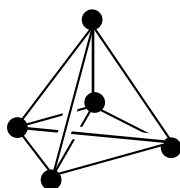
A tetrahedral arrangement of carbon atoms is repeated to give the structure of diamond.
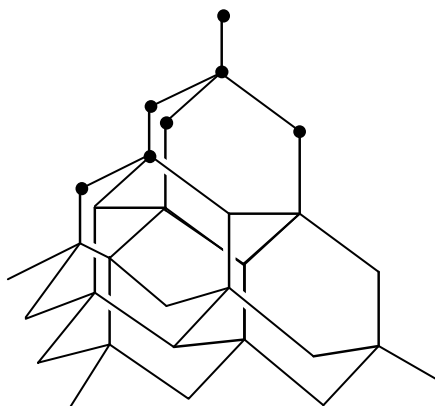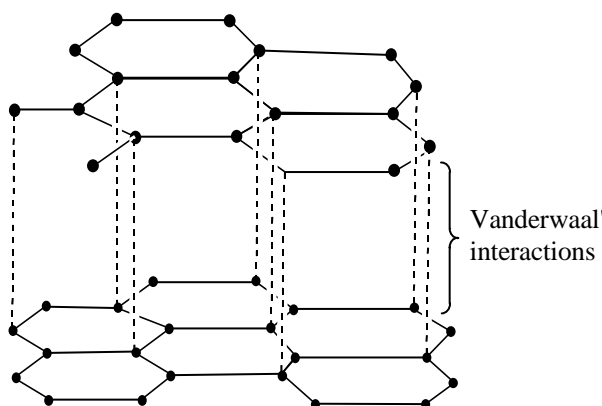

Structure 7.3 :

The combined strength of the many carbon-carbon bonds within the structure of diamond give it both great hardness and a lack of chemical reactivity.

Structure of graphite

It consists of separate layers. The carbon atoms are arranged in regular hexagons in flat parallel layers. There is no strong bonding between different layers, which are, therefore, easily separable from each other. Since there are no covalent linkages between the adjacent planes, graphite can be easily cleaves along the lines of the planes. Whilst the bonds within the layers are strong, those between the layers are not and so they slide over each other easily This accounts for the softness and lubricating power of graphite.

Structure 7.4 : The structure of graphite.

Structure of Buckminster fullerenes

Fullerenes

In 1985, a new allotrope of carbon was discovered by Richard Smalley and Robert Curl of Rice University, Texas, working with Harry Kroto of Sussex University. The first to be identified and the most symmetrical of the family, with 60 atoms and 32 sides (20 hexagons and 12 pentagons), was nick named `buckyball' and was then named buck minister fullerene, because it resembles the geodesic domes developed by an American inventor called R.Buckminister fuller. The group of spherical carbon molecules is called fullerenes. These compounds have superconducting properties and its potential for opening new areas of chemistry have made

study of the `buckyball' as one of the most rapidly expanding areas of chemical research.

Fullerene

Amorphous form of carbon

Amorphous carbon is the most reactive form of carbon. It burns relatively easily in air, thereby serving as a fuel, and is attacked by strong oxidising agents. This form has structural features of graphite, such as sheets and layers. It's atomic structure is much more irregular.

General properties

7.3.4. Metallic character

Carbon and silicon are non-metals, germanium is a metalloid while tin and lead are metals. Thus metallic character increases on descending the group since ionization energy decreases on descending the group.

Hydrides

All of these elements form covalent hydrides though the number of hydrides and the ease with which these are formed decreases from carbon to lead. Carbon gives a vast number of hydrides (alkanes), silicon and germanium (silanes and germanes) whereas stannane (SnH_4) and plumbane (PbH_4) are the only hydrides of tin and lead are known.

Unlike alkanes, silanes are strong reducing agents, explode in chlorine and are readily hydrolysed by alkaline solutions. The difference is probably due to the difference in electronegativity between C and Si resulting in difference between C-H and Si-H linkages.

Halides

All these elements give tetrahalides. Tetrachlorides are usually fuming liquids at ordinary temperature. Carbon tetrahalide resists hydrolysis. This is because due to the absence of d-orbitals. Maximum covalency of carbon is only four and there is no possibility of formation of coordinate linkages with H_2O, which could lead to hydrolysis.

Tetrahalides of rest of the elements undergo hydrolysis. For example

$SiX_4 + 2H_2O \rightarrow SiO_2 + 4HX$
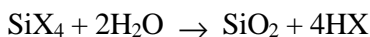
Carbon, silicon and germanium form trihalides of the type MHX_3. Lead and tin do not form trihalides. Silicon, germanium, tin and lead form dihalides.

Chlorides

1. The chlorides are all simple molecular substances with tetrahedral molecules.

2. The stability of the chlorides decreases down the group and the +2 oxidation state becomes more stable than the +4 state. Only tin and lead form chlorides in which their oxidation state is +2, the other chlorides existing solely in the +4 state. Tin(II) chloride is a solid that is soluble in water, giving a solution which conducts electricity. It is also soluble in organic solvents. Its melting point is 246°C. Lead(II) chloride is also a solid. It is sparingly soluble in water. The chlorides of the group 14 elements in their +4 oxidation state illustrate further the change in character of the elements from non-metal to metal down the group and giving a solution which conducts electricity, and melts at 501°C. These observations suggest that tin(II) chloride has both covalent and ionic character, while lead(II) chloride is predominantly ionic.

3. All the chlorides with +4 oxidation state are readily hydrolysed by water, except tetrachloromethane (CCl_4).

Carbides

Compounds of carbon with less electronegative elements (eg. metals, Be, B, Si etc.) are called carbides. These are of three main types.

i) Ionic or salt-like eg. acetylides, methanides, allylides
ii) Interstitial or metallic eg. WC and
iii) Covalent eg. B_4C, SiC.

All the three types of carbides are prepared by heating the element or its oxide with carbon or a hydrocarbon to a high temperature.

$$2Be + C \quad \rightarrow \quad Be_2C$$
$$CaO + 3C \rightarrow \quad CaC_2 + CO$$
$$SiO_2 + 3C \rightarrow \quad SiC + 2CO$$
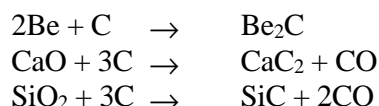
Oxides

1. The oxides show a marked trend in structure from the molecules of carbondioxide to giant structures intermediate between ionic and covalent lower down the group.

2. The +2 oxidation state is the more stable state in the case of leadoxide, and lead (IV) oxide decomposes on heating giving lead(II) oxide, a solid that melts at 886°C. The structure of lead(II) oxide is predominantly ionic.

3. The oxides at the top of the group (CO_2 and SiO_2) have an acidic nature, the carbonate ion CO_3^{2-} being produced easily in dilute aqueous solutions. The ease of formation of oxoanions (SiO_3^{2-}, GeO_3^{2-} etc.) decreases down the group as the acidic character decreases. The oxides of germanium, tin and lead are amphoteric, reacting to form simple salts with acids.

Uses of carbon and its compounds

1. Carbon and its compounds play an enormous role in the global economy, eg. Fossil fuels.

2. Halogenated carbon compounds are used as refrigerants, aerosol propellants, fire extinguisher and solvents.

3. CS_2 is used in the manufacture of viscose rayon (artificial silk) and cellophane.

7.4 Nitrogen Group

The elements nitrogen, phosphorus, arsenic, antimony and bismuth constitute 15th group of the periodic table. This group is called nitrogen group. These elements have the general electronic configuration ns^2np^3. All

these elements have five electrons in their outermost orbitals. The `s' orbital contains two electrons and p orbital contains three electrons. These three electrons are equally distributed in three p-orbitals as px^1 py^1 pz^1 which correspond to half-filled configuration.

As we go down the group, the two electrons present in the valence `s' orbital become inert and only the three electrons present in the outermost p-orbitals are involved in chemical combinations. This is known as inert pair effect. As we move from nitrogen to bismuth, the pentavalency becomes less pronounced while trivalency becomes more pronounced.

Nitrogen was discovered in 1772 by Daniel Rutherford, a Scottish physician and chemist. Elementary nitrogen constitutes three-fourths of air by weight. It is also abundant in the combined state as saltpetre (KNO_3), sodium nitrate (chile saltpetre) and ammonium salts. Nitrogen is an essential constituent of all vegetable and animal proteins.

Fixation of nitrogen

The nitrogen present in the atmosphere is free or elementary nitrogen whereas nitrogen present in various nitrogenous compounds is called combined or fixed nitrogen. The conversion of free atmospheric nitrogen to a nitrogen compound is called fixation of nitrogen.

Method employed for fixation or bringing atmospheric nitrogen into combination:

Manufacture of ammonia (Haber's process) :

A mixture of nitrogen and hydrogen in the ratio 1:3 under pressure (200-900 atm) is passed over a catalyst finely divided iron and molybdenum as promoter, heated to about 770K.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
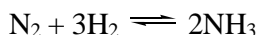
The ammonia so manufactured can be oxidised to nitric oxide by passing a mixture of ammonia and air over heated platinum gauze at 1070K. Nitric oxide combines with more of oxygen to give nitrogen dioxide which when absorbed in water in the presence of excess of air, gives nitric acid (Ostwald's process).

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$
$$2NO + O_2 \rightarrow 2NO_2$$
$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3.$$
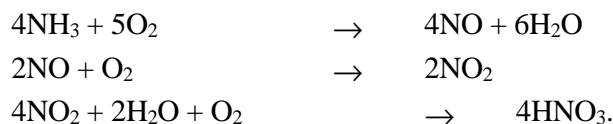
Ammonia and nitric acid manufactured above may be converted into ammonium salts and nitrates suitable as fertilizers. Thus these methods of nitrogen fixation are of vital importance to the agriculturists.

Nitrogen fixation in nature

Due to electrical disturbances atmospheric nitrogen and oxygen combine to give nitric oxide which gets further oxidised to nitrogen dioxide. This reacts with rain water in the presence of excess of oxygen to produce nitric acid and is washed down to earth. Here it reacts with bases of the soil to give nitrates.

In addition to this, certain bacteria living in the nodules on roots of leguminous plants e.g. pea, beans etc., convert nitrogen into nitrogenous compounds which can be directly assimilated by the plant.

Nitrogen cycle

There is a continual turnover of nitrogen between the atmosphere, the soil, the sea and living organisms. The nitrogen passes from atmosphere to plants and animals, converted into useful products like ammonia, nitric acid etc. and still its percentage in the atmosphere remains practically unchanged. This is due to the fact that combined nitrogen is constantly passing back to the atmosphere. This cycle of changes involved is known as nitrogen cycle.
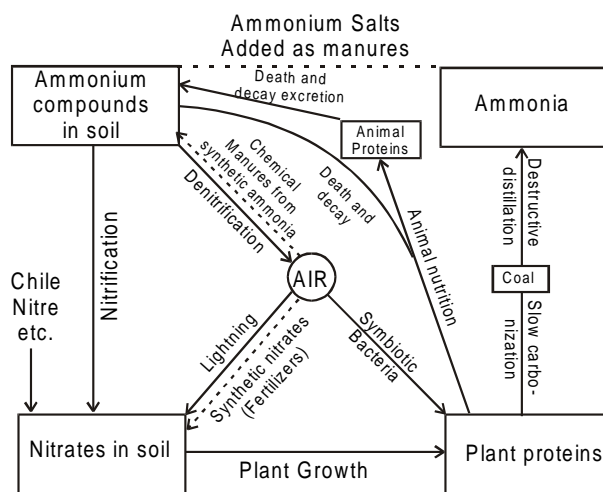
Uses of nitrogen compounds

1. Liquid ammonia is used as solvent.

2. Ammonia is used as a refrigerant in ice-plants.

3. Ammonia is used in the manufacture of artificial silk, urea, manures, washing soda etc.

4. Nitrous oxide mixed with oxygen is used as anaesthetic for minor operations in dentistry and surgery.

5. Nitrous acid is used in the manufacture of azo-dyes.

6. Nitric acid is used in the manufacture of fertilizers, explosives like TNT, GTN, etc.

7. Nitric acid is used in the purification of gold and silver.

8. Nitric acid is used in pickling of stainless steel.

9. Nitric acid is used in the manufacture of perfumes, artificial silk, medicines etc.

10. Liquid nitrogen is used as a refrigerant.

7.4.2 Nitric acid

Nitric acid is an important oxyacid of nitrogen. It was called as `aqua tortis' by alchemists. It means strong water. It was first prepared by Glauber (1650). Later Cavendish (1784) stated that nitric acid may be formed by passing electric sparks through the mixture of nitrogen and moist oxygen. Traces of nitric acid occur in air where it is formed by electric sparks through the mixture of nitrogen and moist oxygen. Traces of nitric acid occur in air where it is formed by electric discharges and is washed down by rain.

Preparation

1. Laboratory preparation

Nitric acid is prepared in the laboratory by heating a nitrate salt with concentrated sulphuric acid.

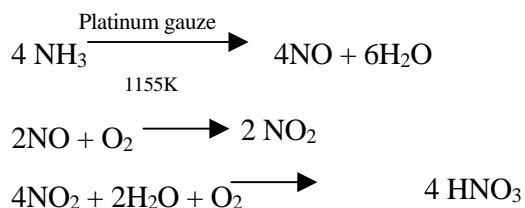$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$
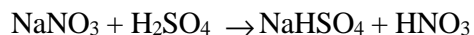
Vapours of nitric acid are condensed to a brown liquid in a receiver cooled under cold water. Dissolved oxides of nitrogen are removed by redistillation or blowing a current of carbondioxide or dry air through the warm acid.

2. Manufacture of nitric acid

1. Nitric acid is manufactured by blowing air into an electric arc struck between two water cooled copper electrodes and spread into a disc with the help of a magnetic field at right angle. The serious disadvantage of the method is now obsolete.

2. Ostwald's process

Large quantities of ammonia manufactured by Haber's process are converted into nitric acid by Ostwald's process.

$$4\,NH_3 \xrightarrow[\text{1155K}]{\text{Platinum gauze}} 4NO + 6H_2O$$

$$2NO + O_2 \longrightarrow 2\,NO_2$$

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4\,HNO_3$$

Dilute nitric acid may be concentrated by distillation until a constant boiling point mixture is obtained (98%). Fuming nitric acid is obtained by distilling this acid with concentrated sulphuric acid. Crystals of pure nitric acid may be obtained by cooling 98% acid in a freezing mixture.

Properties

Physical properties

1. It is a colourless fuming liquid when pure, but may be coloured yellow by its dissociation products mainly nitrogen dioxide.

2. It has extremely corrosive action on the skin and causes painful sores.

3. Pure acid has a specific gravity of 1.54. It boils at 359K and freezes to a white solid (m.p. 231K).

7.5 Oxygen group - group 16

The elements oxygen, sulphur, selenium, tellurium and polonium constitute 16th group of the periodic table. The first four elements are non

metals. Collectively they are called the 'chalcogens' or ore -forming elements. This is because a large number of metals are oxides or sulphides.

Oxygen is a very important element in inorganic chemistry, since it reacts with almost all the other elements. Oxygen is the most abundant of all elements. It exists in the free form as dioxygen or molecular oxygen and makes up 20.9% by volume and 23% by weight of the atmosphere.
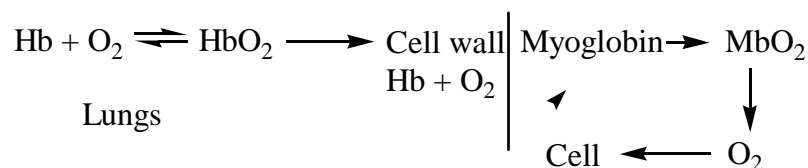
7.6 Importance of molecular oxygen

Haemoglobin is an iron containing coordination compound in red blood cells responsible for the transport of oxygen from the lungs to various parts of the body. Myoglobin is a similar substance in muscle tissue, acting as a reservoir for the storage of oxygen and as a transport of oxygen within muscle cells.

Haemoglobin consists of heme, a complex of Fe(II) bonded to a porphyrin ligand and globin protein. The sixth position is vacant in free hemoglobin but is occupied by oxygen in oxyhaemoglobin. Hemoglobin (Hb) and O_2 are in equilibrium with oxyhaemoglobin.

$$Hb + O_2 \rightleftharpoons HbO_2$$
$$\text{Oxyhaemoglobin}$$
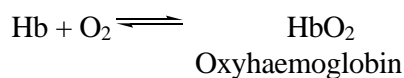
oxyhaemoglobin is formed in the lungs and carried to the cells, where it gives up its oxygen.

Haemoglobin then binds with HCO_3^- which is formed by the reaction of CO_2 (released by the cell) with water. After reaching the lungs, due to hydrolysis CO_2 is released.

$$Hb + O_2 \rightleftharpoons HbO_2 \longrightarrow \text{Cell wall} \mid \text{Myoglobin} \rightarrow MbO_2$$
$$\text{Hb} + O_2$$
$$\text{Lungs} \qquad\qquad \text{Cell} \longleftarrow O_2$$

Most of the O_2 has been produced by photosynthesis. The dioxygen (or) molecular oxygen is prepared by the green plants. The chlorophyll in the green parts of the plants uses the solar energy to make carbohydrate and molecular oxygen. Oxygen makes up 46.6% by weight of the earth's crust, where it is the major constituent of silicate minerals.

Practically all the elements react with dioxygen either at room temperature (or) on heating except Pt, Au, W and Noble gases. Eventhough the bond energy of oxygen is high (493 kJ mol^{-1}), the reactions are generally strongly exothermic and once started often continue spontaneously.

Dioxygen is also called as molecular oxygen. The molecular oxygen is essential for respiration (for the release of energy in the body) by both animals and plants. It is therefore essential for life. Hence molecular oxygen acts as a cell fuel.

The complex formed between dioxygen and haemoglobin (the red pigment in blood) is of vital importance. Since it is the method by which higher animals transport dioxygen around the body to the cells.

7.6.1 Nascent oxygen and molecular oxygen

Oxygen molecule is very stable. It dissociates only to a small extent when heated to a very high temperature. This reaction is endothermic

$$O_2 \rightarrow 2[O] \quad \Delta H = +116.8 \text{ kcal}$$

However, when an electric discharge is passed through oxygen at a very low pressure, it dissociates to the extent of about 20%.

For example when oxygen is passed at about 1 mm pressure through a discharge tube, the resulting gas is found to be chemically more reactive. Its line spectrum shows that it consists of the free atoms. Hence atomic oxygen is formed according the following endothermic reactions.

$$O_2 \rightarrow O + O : \Delta H = 489.6 \text{ kJ}$$

Reactions

1. Formation of molecular oxygen

When a thin platinum wire is placed in atomic oxygen, it quickly gets heated up and begins to glow due to the recombination of oxygen atoms with liberation of heat energy. The rise of temperature of platinum wire under standardised conditions is a measure of the concentration of the atomic oxygen in the gas.

2. Formation of ozone

Atomic oxygen combines with molecular oxygen to give ozone which may be condensed by means of liquid air
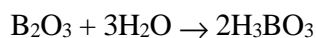
$$O_2 + [O] \longrightarrow O_3$$
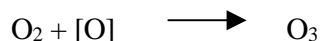
3. Oxidation

Atomic oxygen is an extremely powerful oxidizing agent and oxidises aliphatic and aromatic hydrocarbons and methyl alcohol with emission of heat and light. With nitric oxide, a characteristic greenish - white luminescence is produced. H_2S and CS_2 react with it and burst into greyish blue coloured flame.

7.6.2 Oxides

Generally all the elements react with dioxygen to form oxides. Oxides are binary compounds of oxygen. Oxides may be classified depending on their structure (or) their chemical properties.

i) Acidic oxides

The oxides of non-metals are usually covalent and acidic. They have low melting and boiling points, though some B_2O_3 and SiO_2 form infinite "giant molecules" and have high melting points. They are all acidic. Some oxides dissolve in water and thus forming acids. Hence they are called as acid anhydrides

$$B_2O_3 + 3H_2O \rightarrow 2H_3BO_3$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

others which do not react with water such as SiO_2 reacts with NaOH and shows acidic properties.

ii) Basic oxides

Metallic oxides are generally basic. Most metal oxides are ionic and contain the O^{2-} ion. Some oxides dissolve in water and form alkaline solution.

$Na_2O + H_2O \rightarrow 2NaOH$

$BaO + H_2O \rightarrow Ba(OH)_2$
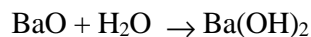
Many metal oxides with formula M_2O_3 and MO_2, though ionic, do not react with water.

Examples : Tl_2O_3, Bi_2O_3 and ThO_2.

These oxides react with water to form salts and hence they are bases.

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$
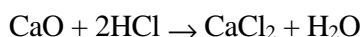
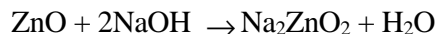If a metal exists in more than one oxidation state and they form more than one oxide

eg. CrO, Cr_2O_3, CrO_3, PbO, PbO_2

iii) Amphoteric oxides

The oxides which react with both strong acids and strong bases are called as amphoteric oxides.

$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$

Sodium zincate

$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$
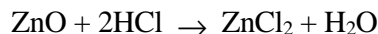
iv) Peroxides

These oxides contain more oxygen than would be expelled from the oxidation number of M. Some are ionic and contains the peroxide ion O_2^{2-}. The metal belonging to the group I and II (Na_2O_2, BaO_2) contain O_2^{2-} ion. Others are covalently bound and contain -O-O- in the structure.

Oxides such as PbO_2 react with acids liberate Cl_2

$PbO_2 + 4HCl \rightarrow PbCl_2 + 2H_2O + Cl_2$

v) Compound oxides

Some oxides behave as if they are compounds of the two oxides.

Ex. Ferrous-ferric oxide (Fe_3O_4). This is considered to be the mixture of FeO and Fe_2O_3.

They react with acids and forms a mixture of ferrous and ferric salts.

$Fe_3O_4 + 8HCl \rightarrow FeCl_2 + 2FeCl_3 + 4H_2O$

vi) Neutral oxides

A few covalent oxides have no acidic (or) basic properties (N_2O, NO, CO).

vii) Dioxides

They also contain higher proportion of O_2 than expected. But they do not liberate H_2O_2 with acid.

Ex. NO_2, SO_2

7.7 Ozone

Ozone is an allotropic form of oxygen and its molecular formula is O_3. It is an unstable dark blue diamagnetic gas. The presence of ozone in extremely small quantities has been observed in the atmosphere in places near the seaside (or) big lakes. It is present in sufficient quantities in the atmosphere at attitudes of 12 to 15 miles above the earth's surface. Ozone is particularly important since there is a layer of ozone in the upper atmosphere which absorbs harmful UV radiations from the sun and protect the people and other living organisms on the earth.

Laboratory preparation

Ozone is prepared in the laboratory by passing silent electrical discharges through dry oxygen in an apparatus known as the ozoniser. The commonly used ozoniser is Siemen's ozoniser

(i) Siemen's ozoniser

It consists of two concentric metal tubes sealed together at one end. The inner side of the inner tube and the outer side of the outer tube are coated with tin foil and connected to one terminal each of an induction coil. A current of pure dry oxygen at low temperature is passed through annular space between the two tubes and by the silent action of electric discharge, the oxygen is partially converted into ozone. The sample of gas escaping from ozoniser is called ozonised oxygen and contains about 12% ozone.
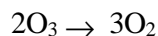

TIN FOIL

Dry O_2

Induction Coil
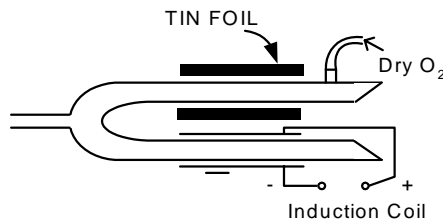
Properties

(i) Physical properties

It is a light blue gas which condense at 160.6 K into a dark blue liquid. This liquid freezes at 23.3 K.

Chemical properties

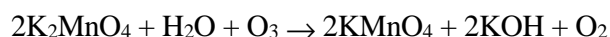1) Decomposition : Pure ozone decomposes with an explosive violence.

$$2O_3 \rightarrow 3O_2$$

2) Oxidising action : Since it can liberate an atom of nascent oxygen easily ($O_3 \rightarrow O_2 + O$) it acts as a powerful oxidising agent.

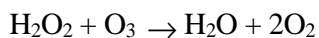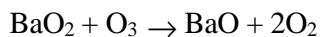i) Lead sulphide is oxidised to lead sulphate

$$PbS + 4O_3 \rightarrow PbSO_4 + 4O_2$$
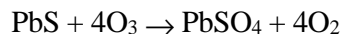
ii) Potassium manganate is oxidised to potassium permanganate

$$2K_2MnO_4 + H_2O + O_3 \rightarrow 2KMnO_4 + 2KOH + O_2$$

3) Ozone reacts with peroxides and reduces it to oxides with the liberation of oxygen.

$$BaO_2 + O_3 \rightarrow BaO + 2O_2$$
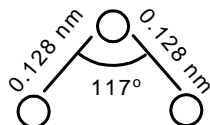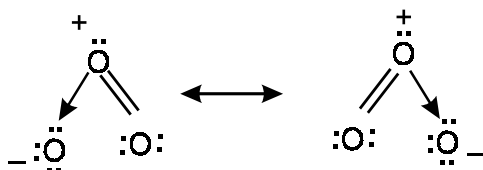
$$H_2O_2 + O_3 \rightarrow H_2O + 2O_2$$

Uses of ozone

1) It is used as germicide and disinfectant.

2) It is used for bleaching oils, ivory, flour, starch, etc.

3) Used in the manufacture of artificial silk and synthetic camphor.

Ozone structure

The ozone molecule consists of three oxygen atoms having a bent structure

Each O atom contributes six valence electrons and so the total 3x6=18 electrons.


Ozone molecule is said to be resonance hybrid of the two contributing forms I & II.

Ozone layer

Ozone is produced in the upper atmosphere through absorption of a photon, hυ of ultraviolet light by an O_2 molecule.

$$O_{2(g)} + h\upsilon \rightarrow 2O_{(g)}$$

$$O_{(g)} + O_{2(g)} \rightarrow O_{3(g)}$$
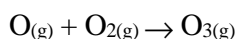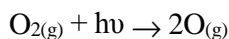
The ozone molecule formed has an excess of energy and dissociates back to O_2 and O and it reacts with another molecule (M) such as CO_2, N_2 or O_2, which causes the excess energy thus stabilizes the ozone molecule

$$O^*_{3(g)} + M_{(g)} \rightarrow O_{3(g)} + M^*_{(g)}$$
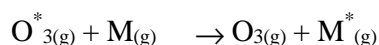
Factors affecting ozone layer

The ozone in the upper atmosphere is important in shielding us from the intense ultraviolet radiation coming from the sun. The so-called ozone shield is a shell about 30 km altitude which contains enough ozone to absorb short wavelength UV radiation (less than 300 nm). Hence ozone is considered to be 'earth's protective umbrella'. The absorption causes dissociation of O_3 to reform O_2.

$$O_{3(g)} + h\upsilon \rightarrow O_{2(g)} + O_{(g)}$$
$$2O_{(g)} \rightarrow O^{\bullet}_{2(g)}$$
$$O^{\bullet}_{2(g)} + M_{(g)} \rightarrow O_{2(g)} + M^{\bullet}_{(g)}$$
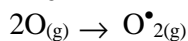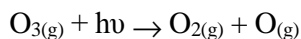
Existence of ozone shield owes to the life on the earth, since living tissues are very sensitive to wavelengths of ultraviolet absorbed by ozone. In recent years, the shield is damaged mainly by supersonic aircraft and

chlorofluorocarbon products in the jet exhaust reduce ozone, and decreases its concentration in the shield.

Chlorofluorocarbons react with O_3 and causes a hole in the ozone layer. CFC's are used as refrigerants and as propellants in some "aerosol sprays". The lifetime of CFCs are so long that in another decades, the extent of ozone depletion in the upper atmosphere will be tremendous. It is reported that the holes caused in the ozone layer over the Antarctic and Arctic ocean are due to the use of CFCs in aerosols and refrigerators. It is feared that this will allow an excessive amount of UV light to reach the earth which will cause skin cancer (melanoma) in human.

$$CFC \xrightarrow{UV} Cl_{(g)}$$

$$Cl_{(g)} + O_{3(g)} \rightarrow ClO_{(g)} + O_{2(g)}$$

$$ClO + O_{(g)} \rightarrow Cl_{(g)} + O_{2(g)}$$

$$O_{3(g)} + O_{(g)} \rightarrow 2O_{2(g)}$$
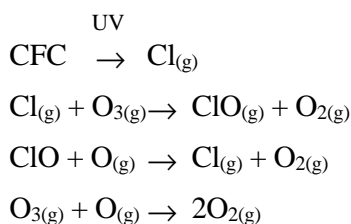
It is also seen that the oxides of nitrogen (from car exhausts) and the halogen can damage the ozone layer. Therefore the protecting shield of the earth must be protected by taking immediate steps over the control of pollution.

Questions

A. Choose the best answer

1) The elements of group 13 to 18 of the periodic table are known as

    a) s - block elements   b) p - block elements
    c) d - block elements   d) f - block elements

2) The general electronic configuration of group 18 elements is

    a) ns^2 b) $ns^2\,np^1$ c) $ns^2\,np^{1-5}$ d) $ns^2\,np^6$

3) The basic oxide among the following

    a) Bi_2O_3 b) SnO_2 c) HNO_3 d) SO_3

4) The most stable hydride of the following

    a) NH_3 b) PH_3 c) ASH_3 d) BiH_3

5) The formula of Borax is

    a) $NaBO_2$ b) $Na_2B_4O_7$ c) H_3BO_3 d) None of the above

6) The general electronic configuration of carbon group elements is
   a) ns^2np^6 b) ns^2 c) ns^2np^1 d) ns^2np^2
7) The process used for the manufacture of ammonia is
   a) Contact process   b) Ostwald process
   c) Haber's process   d) Linde's process
8. The oxides of non-metals are usually
   a) ionic   b) coordinate   c) covalent   d) none of the above
9. Metallic oxides are generally
   a) acidic   b) basic   c) amphoteric   d) neutral
10. Fixation of nitrogen is a source for
    a) Various oxygen compounds b) Various phosphorus compounds
    c) Various nitrogen compounds d) Various sulphur compounds
11. The oxyacid of nitrogen which is used in the manufacture of azo dyes.
    a) Nitrous acid   b) Nitric acid   c) Hyponitrous acid d) Pernitric acid
12. The hydride of V group element which is used in the manufacture of artificial silk
    a) ammonia   b) stibine   c) phosphine   d) bismuthine
13. Anaesthetic used for minor operation dentistry
    a) nitrous oxide   b) nitric oxide
    c) nitrous oxide + oxygen d) nitrogen dioxide
14. An allotrope of carbon discovered by Richard Smalley *et al.*
    a) graphite   b) diamond   c) fullerene   d) carbon black

B. Fill in the blanks
1. The general electronic configuration of Boron group elements is___.
2. Boron combines with nitrogen to form _____.
3. _____ is used to identify the metallic radicals in the qualitative analysis.
4. _____ is known as `inorganic benzene'.
5. In diamond, every carbon atom is bonded with the other by _____ bond.
6. C_{60} Buckminister fullerene was nicknamed as _____.
7. Carbon tetrachloride _____ hydrolysis.
8. Nitrogen was discovered by _____.
9. Nitric acid means _____.
10. Oxidising power of nitric acid _____ with dilution.
11. Dioxygen is also called as _____.

12. Atomic oxygen combines with molecular oxygen to give _____.
13. The ozoniser commonly used in the preparation of ozone are ___ and _____.
14. Ozone can liberate a _____ oxygen easily.
15. _____ is used in the manufacture of synthetic camphor.

C. Match the following

a.

1. Borax	a.	Allotrope of carbon
2. Graphite	b.	$Na_2B_4O_7$
3. ZnO	c.	Ozone
4. CFCs	d.	Neutral oxide
5. NH_3	e.	Fertilizer
	f.	Fixation of nitrogen

b.

1. Inert pair effect	a.	Nitric acid
2. Oxyacid	b.	Cell fuel
3. Liquid nitrogen	c.	Stabilisation of lower oxidation state
4. Ostwald process	d.	Ozone
5. Molecular oxygen	e.	Platinum gauze
	f.	Refrigerant

c. Borax bead test

1. Copper	a.	Blue
2. Iron	b.	Grey
3. Manganese	c.	Red
4. Cobalt	d.	Bottlegreen
5. Chromium	e.	Colorless
	f.	Green

D. Write in one or two sentence

1. Mention the reasons for the stabilisation of lower oxidation state of p-block element.
2. Show the electron accepting property of boron trifluoride by giving an example.
3. Give an example of monovalent and trivalent element in group III.
4. Why diamond is hard compared with graphite?
5. Why Boron family has a tendency to form hydrides?

6. Boron does not form B^{3+} ion. Why?
7. Why NH_3 has high boiling point than PH_3?
8. NH_3 is soluble in water whereas other hydrides of group 15 elements are insoluble in water. Why?
9. Which is considered to be "earth's protective umbrella"?
10. Mention any 3 uses of ozone.
11. What are CFC's? Mention its environmental action.
12. What are compound oxides? Give an example.
13. Mention the metal ions present in haemoglobin and myoglobin and state its function.
14. What happens when ozone reacts with
    a) lead sulphide   b) potassium manganate

E. Explain briefly on the following
1. Explain inert pair effect with suitable example.
2. Give an account of nature of hydrides of 15th group elements.
3. How is boron extracted from borax?
4. What happens when boron reacts with
    a) conc.H_2SO_4 b) conc.HNO_3 c) SiO_2
5. How is borax prepared from colemanite?
6. How borax bead test is helpful in identifying basic radicals in qualitative analysis?
7. Discuss the structural difference between diamond and graphite.
8. Write a short note on fixation of nitrogen.
9. How nitric acid is prepared by ostwald process.
10. Why silicon carbide is used as an abrasive?
11. How molecular oxygen is important for all oxygenated animals?
12. How ozone reacts with the following (a) PbS (b) $KmnO_4$

Problem

An element occupies group no.13 and period number 2 is an representative element of that group reacts with carbondioxide and forms an oxide (A). (A) reacts with $CuSO_4$ give blue beads (B). Identify the element compound (A) and (B). Write the reaction.

Solution

As per the position in the periodic table this element which occupies group number 13 and period number 2 is boron and it reacts with CO_2 to form boric oxide

1) $3CO_2 + 4B \rightarrow 2B_2O_3 + 3C$

∴ the compound A is B_2O_3

2) B_2O_3 reacts with $CuSO_4$ to form $(CuBO_2)_2$

$CuSO_4 + B_2O_3 \rightarrow Cu(BO_2)_2 + SO_3^{(Red)}$
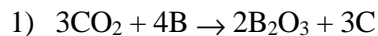
∴ the compound B is copper bead. $Cu(BO_2)_2$
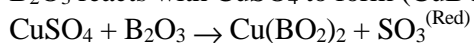
Attempt the following problem.

Problems for practice

1. BF_3 reacts with LiH and forms a compound A. The compound A reacts with water to give the compound B. A reacts with ammonia at 390 K and form C. Identify (A), (B) and (C).

2. An element occupies group number 15 and period number 2 reacts with hydrogen under high pressure and in the presence of a catalyst it terms a hydride (A). In presence of excess of air and in the presence of platinum it forms an oxyacid (B). Identify the element, A and B.

3. An element occupies group No.16 and period number 2. This element on passing through silence electric discharge forms (A). (A) also reacts with lead sulphide and forms (B). (A) also reacts with BaO_2 and forms (C). It reacts with H_2O_2 and forms (D). Identify the dement (A), (B), (C) and (D).

4. An element occupies group No.14 and period number 2 exists in different allotropic forms. One form of this element has lubricating property (A). Another form is the hardest substance (B). New allotrope of this element is named as `Buckyball' (C) and it is superconducting. Identify the element, (A) (B) and (C).

SUMMARY

Groups 13 to 18 of the periodic table are known as p-block elements. The lower oxidation states of these elements are stabilised by inert pair effect.

Group 13 is known as Boron group. The element boron is extracted from its ore borax and colemanite. It reacts to give many compounds. Most

important of them is borax, which is used to identify the metallic radicals in the qualitative analysis.

Group 14 is known as carbon group. Carbon exists in different allotropic forms such as diamond, graphite, fullerenes and other amorphous form. The elements of this group form various hydrides, oxides, halides and carbides.

Group 15 is known as nitrogen group. The element nitrogen is essential for plant life. It plays a vital role in fixation of nitrogen and the importance can be studied by the nitrogen cycle.

Nitric acid is the important oxyacid of nitrogen. It is prepared by Ostwald process. It oxidises metals, non-metals, compounds, etc.

Group 16 is known as oxygen group. Oxygen is the essential element for life. Dioxygen or molecular oxygen plays an important role in functioning of haemoglobin and myoglobin. The study about ozone and the depletion of ozone layer in the upper atmosphere is very essential. The causes of ozone depletion must be considered seriously and steps should be taken to stop the depletion.

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PHYSICAL CHEMISTRY
8. THE SOLID STATE - I

OBJECTIVES

- *Definition of a crystalline solid.*
- *Difference between crystalline and an amorphous materials.*
- *Definition of a unit cell.*
- *Study of Sodium Chloride and Cesium Chloride unit cells.*
- *Definition of Miller Indices.*
- *Learn to identify the important planes in a cubic system in terms of Miller indices.*
- *To recognizes different types of cubic crystal system.*

8.1 Crystalline solids

Some solids, like sodium chloride, sulphur and sugar, besides being incompressible and rigid, have also characteristic geometrical forms. In these solids the atoms or molecules are arranged in a very regular and orderly fashion in a three dimensional pattern. Such substances are called **crystalline solid.**

The X-ray diffraction studies reveal that their ultimate particles (viz., molecules, atoms or ions) are arranged in a definite pattern throughout the entire three-dimensional net-work of a crystal. This definite and ordered arrangement of molecules, atoms or ions (as the case may be) extends over a large distance. This is termed as **long-range order.**

The outstanding characteristics of a crystalline solid are its sharp melting point. Crystalline solids are **anisotropic** since they exhibit different physical properties in all directions e.g., the electrical and thermal conductivities are different in different directions.

Amorphous solids

There is another category of solids such as glass, rubber and plastics, which possess properties of incompressibility and rigidity to a certain extent but do not have definite geometrical forms. Such substances are called **amorphous solids**

Amorphous solids (from the Greek words for 'with out form') neither have ordered arrangement nor sharp melting point like crystals but when heated, they become pliable until they assume the properties usually related to liquids. These solids lack well-defined faces and shapes. Many amorphous solids are mixture of molecules that do not stick together well. Most others are composed of large complicated molecules. Amorphous solids are therefore regarded as super cooled liquids with high material becomes rigid but there the forces of attraction holding the molecules together are so great that the material becomes rigid but there is no regularity of structure. Thus, amorphous solids do not melt at specific temperatures. Instead they soften over a temperature range as intermolecular forces of various strengths are overcome.

Amorphous solids are **isotropic** as they exhibit same physical properties in all the directions.

Difference between Crystalline and Amorphous Solids. Crystalline and amorphous solids differ from one another in the following respects

1. Characteristic geometry

A crystalline solid has a definite and regular geometry due to definite and orderly arrangement of molecules or atoms in three-dimensional space. An amorphous solid, on the other hand, does not have any pattern of arrangement of molecules or atoms and, therefore, does not have any define geometrical shape. It has been found that even if some orderly arrangement of molecules or atoms exists in a few amorphous solids, it does not extend more than a few Angstrom units. Thus unlike crystalline solids, amorphous solids do not have a long range order.

2. Melting points

As a solid is heated, it's molecular vibrations increase and ultimately becomes so great that molecules break away from their fixed positions. They now begin to move more freely and have rotational motion as well. The solid now changes into liquid state. The temperature at which this occurs is known as the melting point.

A crystalline substance has a sharp melting point, i.e., it changes abruptly into liquid state. An amorphous substance, on the contrary, does not have a sharp melting point. For example, if glass is heated gradually, it softens and starts to flow without undergoing a definite and abrupt

change into liquid state. The amorphous solids are, therefore, regarded as liquids at all temperatures. There is some justification for this view because it is known form X-ray examination that amorphous substance do not have well-ordered molecular or atomic arrangements. Strictly speaking, solid state refers to crystalline state, i.e., only a crystalline material can be considered to be a true solid.

3. Isotropy and Anisotropy

Amorphous substances differ from crystalline solids and resemble liquids in another important respect. The properties such as electrical conductivity thermal conductivity, mechanical strength and refractive index are the same in all directions. Amorphous substances are, therefore, said to be isotropic. Liquids and gases are also isotropic. Crystalline solids, on the other hand, are anisotropic, *i.e., their physical properties are different in different directions.* For example, the velocity of light passing through a crystal varies with the direction in which it is measured. Thus, a ray of light entering such a crystal may split up into two components each following a different path and travelling with a different velocity. This phenomenon is known as **double refraction**. Thus, anisotropy in itself is a strong evidence for the existence of ordered molecular arrangements in such materials. This can be shown on reference to Fig. 8.1 in which a simple two-dimensional arrangement of only two different kinds of atoms is depicted.
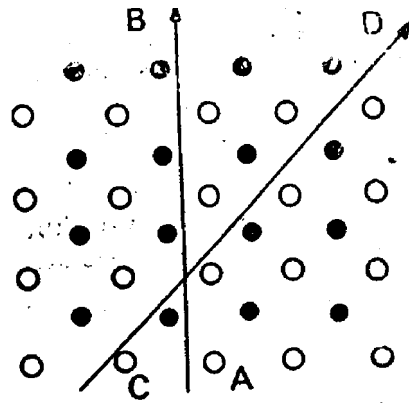
Fig. 8.1 Anisotropic behaviour of crystals

If the properties are measured along the direction indicated by the slanting line CD, they will be different from those measured in the direction indicated by the vertical line AB. The reason is that while in the first case, each row is made up of alternate type of atoms, in the second case, each row is made up of one type of atoms only. In amorphous solids as well as in liquids and gases, atoms or molecules are arranged at random and in a disorderly manner and, therefore, all directions are identical and all properties are alike in all directions.

Size and shape of crystals

Several naturally occurring solids have definite crystalline shapes, which can be recognized easily. There are many other solid materials, which occur as powders or agglomerates of fine particles and appear to be amorphous. But when an individual particle is examined under a microscope, it is also seen to have a definite crystalline shape. Such solids, in which the crystals are so small that can be recognized only under a powerful microscope, are said to be **microcrystalline**. The size of a crystal depends on the rate at which it is formed: the slower the rate the bigger the crystal. This is because time is needed by the atoms or molecules to find their proper positions in the crystal structure. Thus, large transparent crystals of sodium chloride, silver chloride, lithium chloride, etc., can be prepared by melting these salts and allowing them to cool very slowly at a uniform rate. It is for this reason that crystals of most of the minerals formed by geological processes are often very large.

Crystal possess the following characteristic feature:

i). Faces: Crystals are bound by plane faces. The surfaces usually plannar and arranged on a definite plane (as a result of internal geometry), which bind crystals are called faces.

Faces are of two types:

Like: A crystal having all faces alike e.g. Fluorspar.

Unlike: A crystal having all faces not alike e.g. Galena.

ii) Form: All the faces corresponding to a crystal are said to constitute a form.

iii) Edges: The intersection of two adjacent faces gives rise to the formation of edge.

iv) Interfacial Angle: The angle between the normals to the two intersecting faces is called interfacial angle.

Although the size of the faces or even faces of the crystals of the same substance may vary widely with conditions of formation, etc., yet the interfacial angles for any two corresponding faces of the crystals remain invariably the same throughout.

Although the external shape is different yet the interfacial angles are same. The measurement of interfacial angles in crystals is, therefore, important in the study of crystals. The subject is known as **crystallography.**
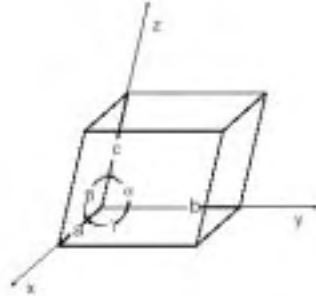
8.2 Unit Cell

Crystals are built up of a regular arrangement of atoms or ions in three dimensions. *The smallest structure of which the crystalline solid (or crystal) is built by its repetition in three dimensions is called as unit cell.* A unit cell may be considered as the brick of a wall depends upon the shape of brick, the shape of crystal also depends upon the shape of unit cell. Therefore, a unit cell is the fundamental elementary pattern of a crystalline solid. The characterization of the crystal involves the identification of its unit cell.

· Unit cell: the repeating unit
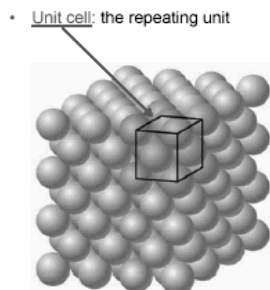
Characteristic parameters of unit cell
1. Crystallographic axes: The lines drawn parallel to the lines of intersection of any three faces of the unit cell which do not lie in the same plane are called crystallographic axes.
2. Interfacial angles: The angles between the three crystallographic axes are known as interfacial angles.
3. Primitives: The three sides a, b and c (as shown in figure) of a unit cell are known as primitives or characteristic intercepts.

Crystallographic axes : OX, OY, OZ

Interfacial angles   : α, β, γ

Primitives (distances) : a, b, c

The unit cell is characterized by the distances a, b and c and angles α, β & γ.

The size (edge length) of a unit cell depends on the size of the atoms or ions and their arrangement. Because a unit cell is representative of the entire structure, the ratio of ions in the unit cell is the same as the ratio in the overall structure.

There are seven classes of unit cells. *1. Cubic , 2. Triclinic, 3. Monoclinic, 4. Orthorhombic, 5. Tetragonal, 6. Hexagonal and 7. Rhombohedral.*

Packing arrangement variations exist in each of the classes, yet here we will only explore the cubic system because it is the simplest.

Cubic unit cells

Three types of cubic unit cells are discussed in this chapter. Each unit cell is defined by one type of atom. Consequently, whichever atom you choose when defining that unit cell is the ***only*** atom used in defining the unit cell. (Ignore all other types.)

Simple cubic

The most simple unit cell is known as a simple cubic unit cell. This is where one atom occupies each of the eight corners of a cube. The distance from atom to atom along the lattice is the same in every direction, and the angle between each of axes is 90°.

Body-centred cubic

The next unit cell is known as the body-centred cubic. In this form of crystal, there is an atom at each corner of the unit cell and also there is an additional atom in the center of the cube. This packing can fit more atoms into less space than the simple cubic unit cell.

Face-centred cubic

A slightly more tightly packed unit cell is the face-centred cubic unit cell. In this form of crystal, there is an atom at each corner of the unit cell. And there is an atom at the center of each of the six faces of the cubic unit cell. This crystal packing form has an even higher density than the body-centred cubic unit cell.

Atoms or ions are shared between adjacent unit cells. The lattice position of the atom or ion determines the number of unit cells involved in the share. There are four different lattice positions an atom or ion can occupy.

Body: Not shared

Face: Shared by two unit cells

Edge: Shared by four unit cells

Corner: Shared by eight unit cells.

Sodium chloride crystal

Space lattice of sodium chloride is known to consist of a face-centered cubic lattice of Na^+ ions interlocked with a similar lattice of Cl^- ions. A unit cell of this combined lattice is shown in figure. This unit cell repeats itself in three dimensions throughout the entire crystal. The yellow spheres indicate chloride ions and red spheres represent sodium ions. The lattices are constituted entirely by ions are known as **ionic lattices**. All electrovalent compounds show such lattices.
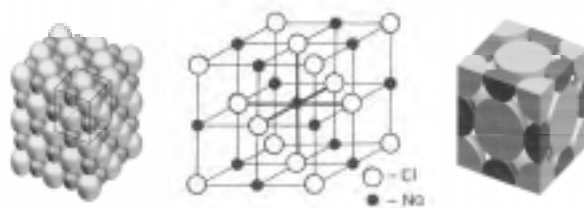
There are four units of NaCl in each unit cube with atoms in the positions

Cl: 0 0 0;   ½ ½ 0;   ½ 0 ½;   0½ ½ ;
Na: ½ ½ ½;   0 0 ½;   0 ½ 0;   ½ 0 0;
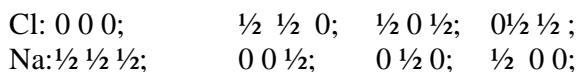
As will be seen figure, the unit cell of sodium chloride consists of 14 chloride ions and 13 sodium ions. Each chloride ion is surrounded by 6 sodium ions and similarly, each sodium ion is surrounded by 6 chloride ions.

Notice that the particles at corners, edges and faces do not lie wholly within the unit cell. Instead these particles are shared by other unit cells. A particle at a corner is shared by eight unit cells, one at the centre of face is shared by two and one at the edge is shared by four. The unit cell of sodium chloride has 4 sodium ions and 4 chloride ions as shown below;

No. of Sodium ions

$$= \quad 12 \text{ (At edge centers) x (1/4)} + 1 \text{ (At body center) x 1}$$

$$= \quad \frac{N_{ec}}{4} + \frac{N_b}{1} + \frac{N_F}{2} + \frac{N_C}{8}$$

$$= \quad 12 \text{ x ¼} + 1\text{x } 1 = \mathbf{3 + 1 = 4}$$

No. of Chloride ions

$$= \quad 8 \text{ (At corners) x (1/8)} + 6 \text{ (At face centre) x (1/2)}$$

$$= \quad 8 \text{ x (1/8)} + 6 \text{ x (1/2)} = \mathbf{1 + 3 = 4}$$

Thus, number of NaCl units per unit cell is 4.

The sodium chloride structure is also called rock-salt structure.

Representative crystals having the NaCl arrangements includes: LiH, NaI, KCl, RbF, RbI, PbS etc.

Cesium Chloride structure

The cesium chloride, CsCl, structure has body-centred cubic system and is shown in figure. The body-centred cubic arrangement of atoms is not a close packed structure. There is one molecule per primitive cell, with atoms at the corners (000) and body-centred positions 1/2 1/2 1/2 of the simple cubic space lattice.
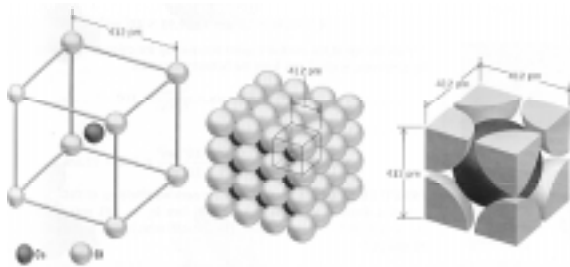
1. The Cl⁻ ions are at the corners of a cube where as Cs^+ ion is at the centre of the cube or vice versa

2. Each Cs^+ ion is connected eight Cl⁻ ions and each Cl⁻ ion is connected eight Cs^+ ions i.e., 8:8 coordination. Thus each atom is at the center of a cube of atoms of the opposite kind, so that the coordination number is eight.

The unit cell of cesium chloride has one Cs^+ ion and one Cl⁻ ion as shown below

No. of Cl⁻ ions

   = 8(At corners) x 1/8 (common to eight unit cell)

   = 8 x 1/8 = **1**

No. of Cs^+ ion = 1 (At the body center) x 1

           = 1 x 1 = **1**

Thus number of CsCl units per unit cell is 1.

Representative crystals having the CsCl arrangements include: CsBr, CsI, TlBr, TlI, NH_4Cl etc.

8.3 Miller Indices

The geometry of a crystal may be completely defined with the help of coordinate axes all meeting at a point (origin). The number and inclination of these crystal intercept them at definite distances from the origin or are parallel to some of the axes, i.e., intercepting at infinity. The law of rational indices or intercepts states that it is possible to choose along the three coordinate axes unit distances (a, b, c) not necessarily of the same length such that the ratio of the intercepts of any plane in the crystal is given by (la : mb : nc) where l, m and n are simple integers like 1, 2, 3 or fractions of whole numbers.

For example consider plane LMN in the crystal shown in Fig. 8.2.
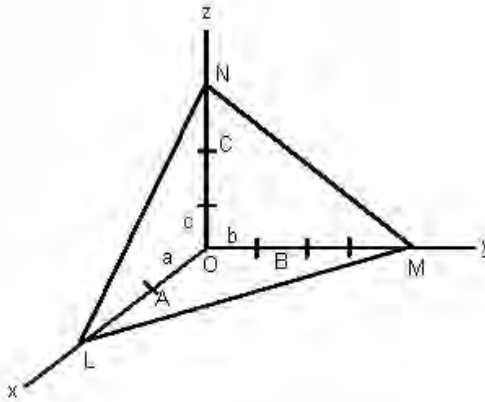
Fig. 8.2   The intercepts of a crystallographic plane

This plane has intercepts OL, OM and ON along the x-, y- and z-axes at distances 2a, 4b and 3c respectively, when OA = a, OB = b and OC = c are the chosen unit distances along the three coordinates. These intercepts are in the ratio of 2a : 4b : 3c wherein 2, 4, 3 are simple integral whole numbers.

The coefficients of a, b and c (2, 4 and 3 in this case) are known as the Weiss indices of a plane. It may be borne in mind that the Weiss indices are not always simple integral whole numbers as in this case. They may have fractional values as well as infinity (an indefinite quantity). Weiss indices are, therefore, rather awkward in use and have consequently been replaced by miller indices. Taking the reciprocals of Weiss indices and multiplying throughout by the smallest number in order to make all reciprocals as integers obtain the **Miller indices** of a plane. The Miller indices for a particular family of planes are usually written (**h, k, l**) where h, k and l are positive or negative integers or zero.

Consider a plane which in Weiss notation is given by 2 a: 4b: 3c. Taking reciprocals of coefficients of a, b and c, we get the ratio 1/2, 1/4, 1/3. Multiplying by 12 in order to convert them into whole numbers, we get 6, 3, 4. These numbers are called the Miller indices of the plane, and the plane is designated as the (634) plane. In (634) plane, h = 6, k = 3 and l = 4.

Similarly the Miller's indices for the plane which the Weiss notation is given by ∞ a : 2b : c. Taking reciprocals of coefficients of a, b and c, we get the ratio $1/\infty$, 1/2, 1/1, i.e., 0, 1/2, 1. Multiplying by 2 in order to convert them into whole numbers, we get 0, 1, 2. The plane is designated as the (012) plane in which , h = 0, k = 1 and l = 2.

The distances between parallel planes in a crystal are designated as d_{hkl}. For different cubic lattices these interplanar spacings are given by the general formula

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Where **a** is the length of the cube side while h, k and l are the Miller indices of the plane.

Definition of Miller Indices in three dimensions
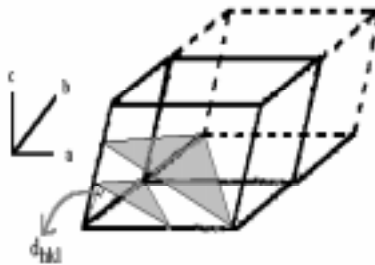
A pair of planes with Miller indices (213)

The **Miller indices** of a face of a crystal are inversely proportional to the intercepts of that face on the various axes.

The **Miller indices** of this particular family of planes are given by the reciprocals of the fractional intercepts along each of the cell directions. E.g. 1/2 x a, 1x b, 1/3 x c.

The procedure for determining the miller indices for a plane is as follows:

1. Prepare a three-column table with the unit cell axes at the tops of the columns.

2. Enter in each column the intercept (expressed as a multiple of a, b or c) of the plane with these axes.

3. Invert all numbers.

4. Clear fractions to obtain h, k and l.

(364) Plane
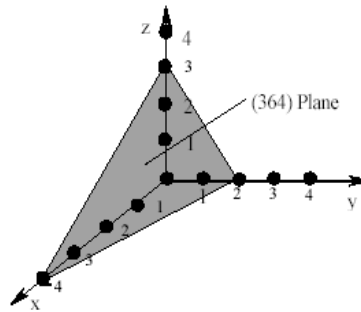
Consider the x-, y-, z- axes in the above figure with the dots representing atoms in a single crystal lattice. To determine the Miller indices, one finds the intercepts on the three axis. The intercepts are: x = 4, y = 2 and z = 3. Then the reciprocals are taken, ie., ¼, ½, 1/3 and finally these fractions are reduced to the smallest integers, ie., 3, 6, 4 by 12. These are the Miller indices represented as (364).

Miller Indices: Example

*   Normalized intercepts:
    *   1,2,3
*   Reciprocals:
    *   1, 1/2, 1/3
*   Multiplier is 6
*   Miller indices for this plane:
    *   (6,3,2)
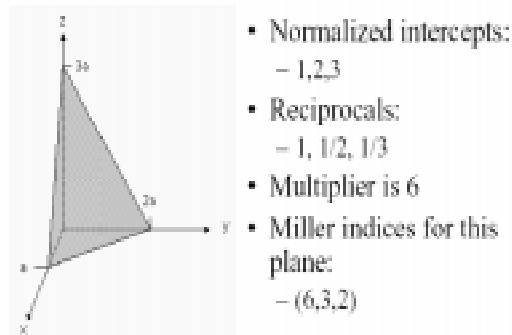
Let us look at the most common planes in a cube, shown below in figure. As an example the front crystal face shown here intersects the x-axis but does not intersect the y- or z -axes but parallel to y and z axis. The front crystal face intersects only one of the crystallographic axes(x-axes). So the miller indices for the plane is (100). The side plane has intercepts

x = ∞, y = 1, z = ∞ because the plane is parallel to the x- and z-axes, forming the Miller indices gives (010). The top plane has intercepts x = ∞, y = ∞ , z = 1 because the plane is parallel to the x- and y- axes , forming the Miller indices gives (001).

The (110) plane intercepts x=1, y=1 and z= ∞ which is parallel to z-axis. Similarly the other two planes are (101) and (011). The (111) plane intercepts all the three axes x=1, y=1 and z=1.

| (100) | (010) | (001) |

| (110) | (101) | (011) |

(111)
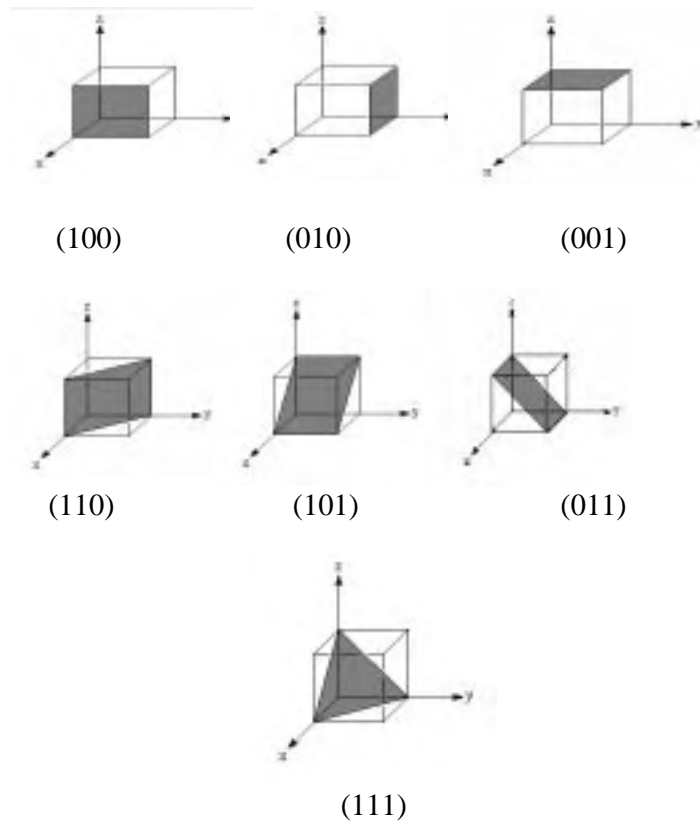
Example 1: Calculate the Miller indices of crystal planes which cut through the crystal axes at (i) (2a, 3b, c) (ii) (a, b, c) (iii) (6a, 3b, 3c) and (iv) (2a, -3b, -3c).

Solution : following the procedure given above, we prepare the tables as follows:

(i) a   b   c

2	3	1	intercepts
½	1/3	1	reciprocals
3	2	6	clear fractions

Hence, the Miller indices are (326).

(ii) a   b   c

1	1	1	intercepts
1	1	1	reciprocals
1	1	1	clear fractions

Hence, the Miller indices are (111).

(iii) a   b   c

6	3	3	intercepts
1/6	1/3	1/3	reciprocals
1	2	2	clear fractions

Hence, the Miller indices are (122).

(iv) a   b   c

2	-3	-3	intercepts
½	-1/3	-1/3	reciprocals
3	-2	-2	clear fractions

Hence, the Miller indices are (322).

Note: The negative sign in the Miller indices is indicated by placing a bar on the integer. The Miller indices are enclosed within parentheses.

Example 2: How do the spacings of the three planes (100), (110) and (111) of cubic lattice vary?

Applying the formula

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$d_{(100)} = \frac{a}{\sqrt{1^2 + 0 + 0}} = a$$

$$d_{(110)} = \frac{a}{\sqrt{1^2 + 1^2 + 0}} = \frac{a}{\sqrt{2}}$$

$$d_{(111)} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

Thus $d_{(100)} : d_{(110)} : d_{(111)}$ = 1: $1/\sqrt{2}$: $1/\sqrt{3}$

= 1: 0.707 : 0.577

Example 3: A metallic element exists as a cubic lattice. Each edge of the unit cell is 2.88Å. The density of the metal is 7.20 g cm^{-3}. How many unit cells there will be in 100g of the metal?

Solution: Volume of unit cell = $(2.88Å)^3$ = 23.9 x 10^{-24} cm^3

Volume of 100 g of the metal = $\dfrac{m}{\rho}$

= 100 = 13.9 cm^3

Number of unit cells in this volume

= $\dfrac{13.9 \text{ cm}^3}{23.9 \text{ x } 10^{-24} \text{ cm}^3}$ = 5.82 x 10^{23}

Example 4: Calculate the number(n) of atoms contained within (i) a primitive cubic unit cell (ii) a body –centred cubic unit cell and (iii) a face-centred cubic (f.c.c) unit cell

Solution: (i) The primitive unit cell consists of one atom at each of the 8 corners; each atom is thus shared by 8 unit cells. Hence n = 8 x (1/8) = 1

(ii) The b.c.c unit cell consists of 8 atoms at the 8 corners and one atom at the centre. At each corner only 1/8th of the atom is within the unit cell. Thus the contribution of the 8 corners is 8 x (1/8) = 1 while that of the body-centred atom is 1. Hence, n = 1+1 =2

(iii) The 8 atoms at the corners contribute 8 x (1/8) = 1 atom. There is one atom each of the 6 faces, which is shared by 2 unit cells each. Therefore, the contribution face-centred atoms = 6x (1/2) = 3 Hence, n = 1+3 = 4.

Example 5 : At room temperature, pollonium crystallizes in a primitive cubic unit cell. If a = 3.36Å, calculate the theoretical density of pollonium; its atomic mass is 209 g mol^{-1}.

Solution: A primitive cubic unit cell contains atoms only at the 8 corners with each corner contributing $1/8^{th}$ of an atom. Hence $n = 8 \times (1/8) = 1$.

Volume $V = a^3 = (3.36\text{Å})^3$

From Eq. 1 $\quad \rho = \dfrac{nMm}{N_0V}$

$$= \dfrac{(1)\ 209\ \text{g mol}^{-1})}{(6.022 \times 10^{23}\ \text{mol}^{-1})\ (3.36 \times 10^{-8}\ \text{cm})^3}$$

$= 9.15\ \text{g cm}^{-3}$

Questions

A. Choose the best answer

1. The structure of sodium chloride crystal is:
   (a) body centred cubic lattice
   (b) face centred cubic lattice
   (c) octahedral
   (d) square planar

2. The number of atoms in a face centred cubic unit cell is:
   (a) 4   (b) 3   (c) 2   (d) 1

3. The 8:8 type of packing is present in:
   (a) CsCl   (b) KCl   (c) NaCl   (d) MgF_2

4. In a simple cubic cell, each point on a corner is shared by
   (a) 2 unit cells (b) 1 unit cells (c) 8 unit cells (d) 4 unit cells

5. An amorphous solid is :
   (a) NaCl   (b) CaF_2 (c) glass   (d) CsCl

6. Each unit cell of NaCl consists of 4 chlorine ions and:
   (a) 13 Na atoms   (b) 4 Na atoms
   (c) 6 Na atoms   (d) 8 Na atoms

7. In a body centred cubic cell, an atom at the body of centre is shared by:
   (a) 1 unit cell   (b) 2 unit cells (c) 3 unit cells (d) 4 unit cells

8. In the sodium chloride structure, formula per unit cell is equal to
   (a) 2   (b) 8   (c) 3   (d) 4

9. In a face centred cubic cell, an atom at the face centre is shared by:
   (a) 4 unit cell   (b) 2 unit cells   (c) 1 unit cells(d) 6 unit cells

Answers:

1) b   2) a   3) a   4) c   5) c   6) b   7) a   8)d   9) b

B. Fill in the Blanks :

1. In NaCl ionic crystal each Na^+ ion is surrounded by -------- Cl^- ions and each Cl^- ion is surrounded by -------- Na^+ ions.

2. The coordination number of Cs^+ in CsCl crystal is -----------

3. ---------- solids do not possess sharp melting points and can be considered as ------ liquids.

4. A body centred unit cell has an atom at the each vertex and at --------- of the unit cell.

5. The three types of cubic unit cells are --------, ------------ and -------

6. A crystal may have a number of planes or axes of symmetry but it possesses only one ----- of symmetry.

7. Amorphous solids that exhibit same physical properties in all the directions are called ---------.

8. Crystalline solids that exhibit different physical properties in all directions are called ---------.

9. The number of atoms in a single unit cell of cubic close packed sphere is ---------

10. In a bcc, an atom of the body centre is shared by ----------- unit cell.

11. The Weiss indices of a plane are 1/2, 1/2, 1/2. Its miller indices will be -----and the plane is designated as ---------.

12. A plane is parallel to x & z axes and makes unit intercepts along y-axis. Its Weiss indices are --------. Its Miller indices are --------. The plane is designated as -------.

Answers :

(1) 6, 6   (2)8   (3) Amorphous, supercooled (4) Centre

(5) simple cubic,bcc, fcc   (6)   Centre   (7) isotropic

(8) Anisotropic   (9) 4   (10)   1   (11) 2, 2, 2; (222) plane

(12) ∞, 1, ∞ ;   0, 1, 0 ; (010) plane

C. Write in one or two sentence :

1. What governs the packing of particles in crystals?
2. What is meant by 'unit cell' in crystallography?
3. How many types of cubic unit cell exits?
4. What are Miller Indices?
5. Mention the number of sodium and chloride ions in each unit cell of NaCl
6. Mention the number of cesium and chloride ions in each unit cell of CsCl

D. Explain briefly on the following :

1. Define and explain the following terms
   a) Crystalline solids b) Amorphous solids c) Unit cell
2. Give the distinguishing features of crystalline solids and amorphous solids.
3. Explain the terms Isotropy and Anisotropy.
4. What is the difference between body centred cubic and face centred cubic?
5. Draw a neat diagram for sodium chloride structure and describe it accordingly.
6. Draw a neat diagram for Cesium chloride structure and describe it accordingly.

Problems

1. How many atoms are there per unit cell in (i) simple cubic arrangement of atoms, (ii) body centred cubicarrangement of atoms, and (iii) face-centred cubic arrangement of atoms?
   Ans: (i) : 1,   (ii) : 2 and (iii) :   4
2. How do the spacings of the three planes (100), (101) and (111) of simple cubic lattice vary?
   Ans: 1: $1/\sqrt{2}$: $1/\sqrt{3}$
3. How do the spacings of the three planes (001), (011) and (111) of bcc lattice vary?
   Ans: $1/2$: $1/\sqrt{2}$: $1/2\sqrt{3}$
4. How do the spacings of the three planes (010), (110) and (111) of fcc lattice vary?
   Ans: $1/2$: $1/2\sqrt{2}$: $1/\sqrt{3}$

SUMMARY

Solids form an important part of the world around us, providing materials with a definite shape and predictable properties.

Crystalline solids are made of ordered arrays of atoms, ions or molecules.

Amorphous solids have no long-range ordering in their structures.

The unit cell is the basic repeating unit of the arrangement of atoms, ions or molecules in a crystalline solid.

Lattice refers to the three dimensional array of particles in a crystalline solid. Each particle occupies a lattice point in the array.

A simple cubic unit cell has lattice points only at the eight corners of a cube.

A body-centred cubic unit cell has lattice points at the eight corners of a cube and at the centre of the cube.

A face-centred cubic unit cell has the same kind of particles (lattice paints) at the eight corners of a cube and at the centre of each face.

The geometry of the crystal may be completely defined with the help of coordinate axes meeting at a point.

The miller indices of a face of a crystal are inversely proportional to the intercepts of that face on the various axes.

The study of crystal is known as crystallography.

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9. GASEOUS STATE

OBJECTIVES

- *To recognise the measurable properties of gases like P,V,T and mass.*
- *To learn various gas laws and ideal gas equation*
- *To learn different units of gas constant `R'.*
- *To understand the Dalton's law of partial pressures & Graham's law of diffusion.*
- *To analyse the deviation of ideal behaviour and to know Vanderwaal's equation of state.*
- *To understand and deduce the relationship between critical phenomena and vanderwaal's constants.*
- *To understand Joule - Thomson effect and the role of inversion temperature.*
- *To know methods of liquefaction of gases and adiabatic demagnetisation.*

9.1 Properties of gases

Matter is known to exist in three states - solid, liquid and gas. A substance may be made to exist in any one of the three states by varying the temperature or pressure or both. Dynamic motion of molecules therefore is an inherent property in gaseous and liquid states of matter. The energy of motion known as kinetic energy is present in the gaseous molecules. Therefore the basic theory which explains the behaviour of gases is called as kinetic theory of gases.

A gaseous state can be described in terms of four parameters which are known as **measurable properties** such as the volume, V; Pressure, P; Temperature, T and Number of moles, n of the gas in the container.

Pressure effect

A gas may be considered to consist of a large number of molecules moving haphazardly all around in a vessel. Due to their constant motion, the molecules may not collide against one another very frequently, but can strike against the walls of the containing vessel. The molecular collisions are regarded as ideal (ie) perfectly elastic, so that there is no loss of energy in these collisions. **Pressure is defined as force per unit area.** This

depends upon the number of molecules that strike per unit area of the walls of the container in one second. The greater the number of molecules striking per unit area of the walls in one second, the greater would be the pressure exerted by the gas. Thus for example, when we pump air into a bicycle tube, the number of molecules within the tube increases and hence the number of collisions of the molecules with the walls per second increases and the pressure goes up.

Temperature effect

The kinetic energy of molecules is given by $1/2\ mv^2$ where m is the mass of the molecule and v is the velocity of its motion. When a gas is heated, its temperature increases. Although the mass of the molecule remains constant, its velocity increases. This causes an increase in kinetic energy. Therefore the molecules strike the wall of the containing vessel more frequently. In this case there is no change in the number of molecules, but the number of collisions against the walls of the container in a given time increases. Therefore the pressure of the gas increases with rise in temperature when the amount and its volume remain constant.

Volume effect

The volume of the container is considered as the volume of the gas sample. This is considered from the postulates of kinetic theory of gases. That is, the volume of gas molecules themselves are negligible compared to the container volume. Volume of gas is determined by its pressure, temperature and number of moles at any instant.

Number of moles (n) effect

Effects of pressure and volume of a gas bear a direct proportionality with number of moles. When `n' increases the number of molecules colliding against the wall of container increases. This effect increases the pressure of the gas. When the amount of gas increases the volume occupied by themselves also, increases.

9.2 The gas laws

Boyle's law

Robert Boyle in 1662, studied the effect of change of pressure on the volume of a given mass of gas at constant temperature. According to

Boyle's law, for given mass of a gas at constant temperature, the pressure (P) is inversely proportional to its volume (V).

$$P \propto \frac{1}{V} \quad \text{(at constant temperature)}$$

(or)

PV = constant.

Thus if V_1 is the volume occupied by a given mass of a gas at pressure P_1 and V_2 is the volume when pressure changes to P_2, then as the temperature remains constant, according to Boyle's law

$$P_1 V_1 = P_2 V_2 = \text{Constant}$$

Charle's Law

The variation in the volume of a gas with temperature at constant pressure is given by charle's law. The law may be stated as,

For a given mass of gas, at constant pressure, its volume (V) varies directly as its absolute temperature (T).

$$V \propto T \quad \text{(or)} \quad \frac{V}{T} = \text{Constant}$$

Based on charle's law, the pressure - temperature relation is deduced as, for a given quantity of a gas, at constant volume, the pressure (P) varies directly as its absolute temperature (T)

$$P \propto T \quad \text{(or)} \quad \frac{P}{T} = \text{Constant}$$

where T is temperature in kelvin.

The equation of state for an ideal gas

Gases which obey Boyle's law and Charle's law are known as ideal gases. By combining these two laws, an equation of state of an ideal gas can be derived.

According to Boyle's law at constant temperature,

$$P \alpha \frac{1}{V}$$

From Charle's law

$$P \alpha T \text{ (at constant volume)}$$

By combining these proportionalities,

$$P \alpha \frac{T}{V} \quad \text{(or)} \quad PV \alpha T$$

$$\therefore PV = RT$$

where `R' is a proportionality constant, commonly called as the **gas constant.** Generally, the ideal gas equation is written as

$$PV = n\,RT$$

where `n' is the number of moles of the gas.

$$\text{No. of moles} = \frac{\text{Mass of the gas in gram}}{\text{Molecular mass of the gas in gmol}^{-1}} = \frac{m}{M} = mol$$

$$PV = \frac{m}{M}\,RT$$

m = mass of the gas.

The ideal gas equation can be written for a constant mass of a gas as,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Standard temperature and Pressure (S.T.P)

The conditions of a gas system present at standard temperature and standard pressure are its temperature at 273K and its pressure being at normal atmospheric pressure namely 1.013×10^5 Nm^{-2} (1 atm). Value of R (Gas constant) depends on the different units of pressure and volume.

9.3 Numerical values of gas constant (R)

The numerical value of the gas constant `R' depends upon the units in which pressure and volume are expressed,

$$R = \frac{PV}{T} \text{ (assuming one mole of gas)}$$

$$\therefore R = \frac{\text{Pressure x Volume}}{\text{Temperature}}$$

$$= \frac{\text{Force}}{\text{Area}} \text{ x } \frac{\text{Volume}}{\text{Temperature}}$$

Since Volume = Area x length

$$\therefore R = \frac{\text{Force x Length}}{\text{Temperature}}$$

$$= \frac{\text{Work}}{\text{Temperature}}$$
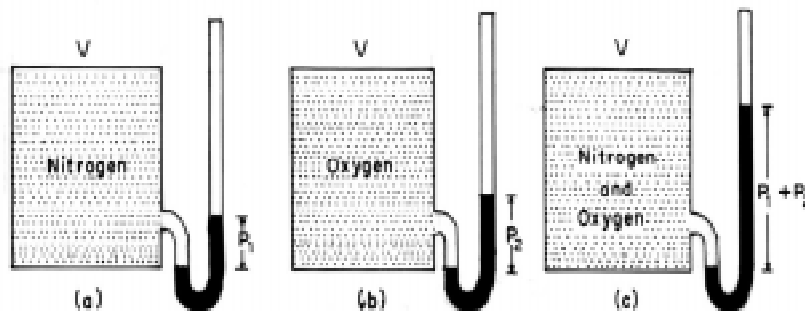
The dimensions of R are thus energy per degree per mole.

a. In litre - atmosphere

One mole of gas at S.T.P occupies a volume of 22.4 litre and thus

At STP

P = 1 atm   R = PV/T (for 1 mole)

V =   22.4 litre R = (1 x 22.4)/273

Fig. 9.1 Total pressure equals the sum of partial pressures of

T = 273 K   R = 0.0821 litre atm $K^{-1}mol^{-1}$

$= 0.0821$ dm^3.atm $K^{-1}mol^{-1}$

($\because$ 1 litre $= 1$ dm^3)

b. In C.G.S. System

At STP 1 mole of gas has

P = 1 atm = 1 x 76 x 13.6 x 980 dyne cm^{-2}

$= 1.013$ x 10^6 dyne cm^{-2}

V $= 22400$ cm^3; T $= 273$ K

$$\therefore R = \frac{PV}{T} = \frac{1.013 \times 10^6 \times 22400}{273}$$

R $= 8.314$ x 10^7 erg K^{-1} mol^{-1}

c. In M.K.S. System

In MKS or SI units, the unit of R is joule

Since 10^7 erg $=$ 1 Joule

199

$\therefore$ R = 8.314 Joule K^{-1} mol^{-1}

1 calorie = 4.184 Joule

$\therefore$ R = 1.987 cals deg^{-1} mol^{-1}

9.4 Dalton's law of partial Pressures

When two or more gases, which do not react chemically, are mixed together in a vessel, the total pressure of the mixture is given by Dalton's law of partial pressures which states that,

"At constant temperature, the total pressure exerted by the gaseous mixture is equal to the sum of the individual pressures which each gas would exert if it occupies the same volume of mixture fully by itself. Partial pressure is the measure of the pressure of an individual gas in a mixture of same volume and temperature.

Thus, if p_1, p_2, p_3 .... are the partial pressures of the various gases present in a mixture, then the total pressure P of the gaseous mixture is given by

P = $p_1 + p_2 + p_3$ ..., provided the volume and temperature of mixture and that of the individual gases are the same.

Equation of state of a Gaseous mixture

Let a gaseous mixture consists of n_A, n_B and n_C moles of three ideal gases A, B and C respectively, subjected to constant T and V, then, according to ideal gas equation.

$$p_A = \frac{n_A RT}{V}; \quad p_B = \frac{n_B RT}{V}$$

and

$$p_c = \frac{n_c RT}{V}$$

where p_A, p_B, p_C are the partial pressures of A,B,C gases respectively. Hence the total pressure of the mixture is given as

P = $p_A + p_B + p_c$

$$P = \frac{n_A RT}{V} + \frac{n_B RT}{V} + \frac{n_C RT}{V}$$

$$\therefore \ PV = (n_A + n_B + n_C) \ RT$$

This equation is known as **equation of state of gaseous mixture.**

Calculation of Partial Pressure

In order to calculate the pressure (p_A) of the individual component say A, in a mixture (A and B), which is equal to the partial pressure of A, according to the equation of state of gaseous mixture it is seen that,

P = Total pressure of the mixture

$$P = (n_A + n_B) \ \frac{RT}{V}$$

But $p_A = \dfrac{n_A}{V} RT$ and $p_B = \dfrac{n_B}{V} RT$

The ratio is given by

$$\frac{p_A}{P} = \frac{n_A}{(n_A + n_B)} \cdot \frac{V}{RT} \cdot \frac{RT}{V}$$

$$= x_A = \text{mole fraction of A.}$$

Or $\boxed{p_A = X_A P}$

i.e:- Partial pressure, p_A = mole fraction of A x total pressure. Similarly;

$$\boxed{p_B = X_B P}$$

Thus, the partial pressure of the individual component in the mixture can be calculated by the product of its mole fraction and total pressure.

Problem 1

Calculate the partial pressures N_2 and H_2 in a mixture of two moles of N_2 and two moles of H_2 at STP.

$$p_{N_2} = \frac{\text{number of moles of } N_2}{V} \quad x \quad RT$$

$$p_{H_2} = \frac{\text{number of moles of } H_2}{V} \quad x \quad RT$$

Mole fraction of $N_2 = X_{N_2} \quad = \quad \frac{2}{2+2}$

$$= \quad \frac{2}{4} \quad = \quad 0.5$$

$\therefore \quad X_{H_2} \quad = \quad 0.5 \quad (X_{N_2} + X_{H_2} = 1.0)$

But $P = \dfrac{RT}{V}$. For 1 mole, V = 22.4 litres

For 4 moles V = 4 x 22.4 litres and
$$R \quad = \quad 0.0821 \text{ lit - atm } K^{-1}mol^{-1}$$

$$P \quad = \quad \frac{0.0821 \times 273}{4 \times 22.4} \quad = \quad 0.2501 \text{ atm.}$$

$p_{N_2} = 0.2501 \times 0.5 \quad = \quad 0.1251 \text{ atm}$

$p_{H_2} = 0.2501 \times 0.5 \quad = \quad 0.1251 \text{ atm}$

Self Test

Calculate the partial pressures of O_2 and H_2 in a mixture of 3 moles of O_2 and 1 mole of H_2 at S.T.P.

[Ans: $p_{O_2} = 0.1876$ atm; $p_{H_2} = 0.0625$ atm]

9.5 Graham's Law of Diffusion

When two gases are placed in contact, they mix spontaneously. This is due to the movement of molecule of one gas into the other gas. This process of mixing of gases by random motion of the molecules is called as **diffusion.**

In 1829, Graham formulated what is now known as Graham's law of diffusion. It states that,

"Under the same conditions of temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square roots of their molecular masses". Mathematically the law can be expressed as

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

where r_1 and r_2 are the rates of diffusion of gases 1 and 2, while M_1 and M_2 are their molecular masses respectively.

When a gas escapes through a pin-hole into a region of low pressure or vacuum, the process is called **Effusion**. The rate of diffusion of a gas also depends on the molecular mass of the gas. Dalton's law when applied to effusion of a gas is called the Dalton's law of Effusion. It may be expressed mathematically as

$$\frac{\text{Effusion rate of Gas 1}}{\text{Effusion rate of Gas 2}} = \sqrt{\frac{M_2}{M_1}}$$

The determination of rate of effusion is much easier compared to the rate of diffusion. Therefore Dalton's law of effusion is often used to find the molecular mass of a given gas.

Problem 2

If a gas diffuses at the rate of one-half as fast as O_2, find the molecular mass of the gas.

Solution

Applying Graham's law of diffusion.

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \; ; \qquad \frac{1/2}{1} = \sqrt{\frac{32}{M_1}}$$

Squaring both sides of the equation

$$\left(\frac{1}{2}\right)^2 = \frac{32}{M_1} \; (or) \frac{1}{4} = \frac{32}{M_1}$$

$$M_1 = 128$$

Thus the molecular mass of the unknown gas is 128.

Self Test

If a gas diffuses at the rate of one quarter as fast as N_2. Find the molecular mass.

[Ans = 448]

Problem 3

50ml of gas A effuse through a pin - hole in 146 seconds. The same volume of CO_2 under identical conditions effuse in 115 seconds. Calculate the molecular mass of A.

$$\frac{\text{Effusion rate of } CO_2}{\text{Effusion rate of } A} = \sqrt{\frac{M_A}{M_{CO_2}}}$$

$$\frac{50/115}{50/146} = \sqrt{\frac{M_A}{44}} \; ; \quad (1.27)^2 = \frac{M_A}{44}$$

$M_A = 71 \quad \therefore$ Molecular mass of A is 71.

Self Test

75ml of gas A effuses through a pin hole in 73 seconds. The same volume of SO_2 under identical conditions effuses in 75 seconds. Calculate the molecular mass of A.

(Ans = 60.6)

9.6 Causes for deviation of real gas from ideal behaviour

The perfect gas equation of state is given by

$$PV = nRT$$

The gases which obey this equation exactly are referred as ideal gases or perfect gases. Real gases do not obey the perfect gas equation exactly. Real gases show deviation because of intermolecular interaction of the gaseous molecules. Repulsive forces between the molecules cause expansion, and attractive forces cause reduction in volume. Under the conditions of low pressure and high temperature the inter-molecular interactions of the gaseous molecules are lower and tend to behave ideally under these conditions. At other conditions of pressure and volume, deviations are seen.

Volume deviation

Based on one of the postulates of the kinetic theory of the gases it is assumed that the volume occupied by the gaseous molecules themselves is negligibly small compared to the total volume of the gas. This postulate holds good for ideal gases and only under normal conditions of temperature and pressure for real gases. When temperature is lowered considerably, the total volume of the real gas decreases tremendously and becomes comparable with the actual volume of gaseous molecules. In such cases, the volume occupied by the gaseous molecules cannot be neglected in comparison with total volume of the gas.
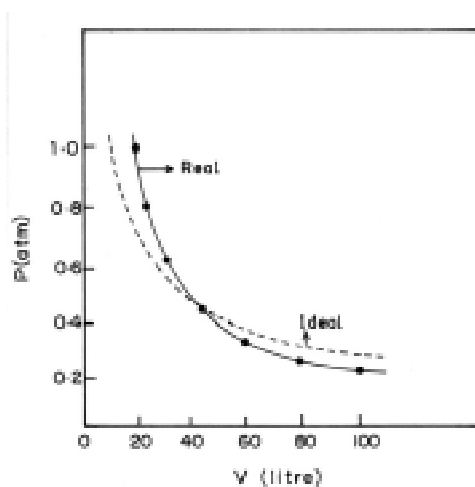

Fig. 9.2   Pressure - volume dependence of ideal and real gases

Thus, the volume deviations created at high pressure and low temperature make the real gas to deviate from the ideal behaviour.

Pressure deviation

For an ideal gas the forces of attraction between the gaseous molecule are considered to be nil at all temperature and pressure.

For a real gas this assumption is valid only at low pressure or at high temperature. Under these conditions, the volume of the gas is high and the molecules lie far apart from one another. Therefore the intermolecular forces of attraction becomes negligible.

But at high pressure (or) at low temperature, the volume of the gas is small and molecules lie closer to one another. The intermolecular forces of attraction becomes appreciable and cannot be neglected. Therefore it is necessary to apply suitable corrections to the pressure of the real gas in the equation of state.

9.7 Vanderwaal's Equation of state

For an ideal gas PV = nRT, is considered as the equation of state. By including the correction terms in the ideal gas equation to account for (i) volume of the gaseous molecules themselves in V and (ii) the intermolecular forces of attraction in pressure, P, the equation of state for the real gas is arrived, J.O Vanderwaal's deduced the equation of state of real gases.

i) Volume correction of real gas

The volume of a gas is the free space in the container in which molecules move about. Volume V of an ideal gas is the same as the volume of the container. The volume of a real gas is, therefore, ideal volume minus the volume occupied by the gas molecules themselves. If V_m is the volume of the single molecule then, the excluded volume which is termed as "b" is determined as follows.
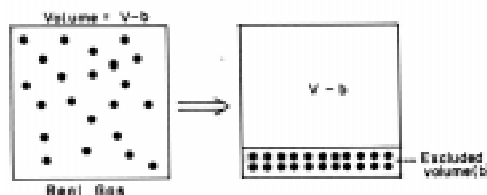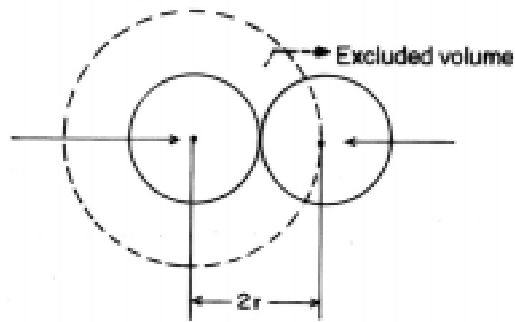

Fig. 9.3   Free volume and excluded volume of a real gas

Fig. 9.4   Collision diameter (2r) and excluded volume of real gas molecules

Let us consider two colliding molecules with radius `r'. The space indicated by dotted sphere of radius 2r will not be available for other molecules to freely move about. (i.e) the dotted spherical volume is known as **excluded volume** per pair of the molecules.

Thus,

$$\text{excluded volume for two molecules} = \frac{4}{3} \pi (2r)^3$$

$$= 8 \left(\frac{4}{3} \pi r^3 \right)$$

Excluded volume per molecule

$$V_C = \frac{1}{2} \times 8 \quad \frac{4}{3} \pi r^3$$

$$= 4 V_m$$

where V_m is the actual volume of a single molecule.

∴   The excluded volume for n molecules, 'b' = 4n V_m, where 4 V_m is the excluded volume of a molecule.

∴ The corrected volume of the real gas is = (V-b) = free space for molecular movement.

ii) Pressure Correction

In a real gas the pressure deviation is caused by the intermolecular forces of attraction. According to kinetic theory, the pressure of the gas is directly proportional to forces of bombardment of the molecules on the walls of the container. Consider a molecule placed in the interior of the container. It is surrounded equally by other gas molecules in all directions such that the forces of attraction in any direction is cancelled (or) nullified by similar force operating in the opposite direction. However a molecule near the wall of the container which is about to strike is surrounded unequally by other gaseous molecules as shown in Fig 9.5.
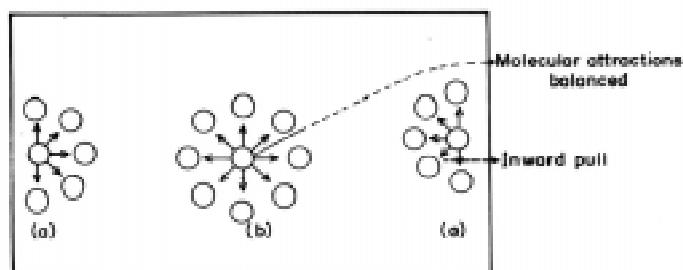
Fig. 9.5   Intermolecular forces of attraction and pressure deviation in real gas molecules

The molecule near the wall experiences attractive forces only such that it will strike the wall with a lower force which will exert a lower pressure than if such attractive forces are not operating on it. Therefore it is necessary to add the pressure correction term to the pressure of the gas to get the ideal pressure. The corrected pressure should be P + p' where p' is the pressure correction factor.

The force of attraction experienced by a molecule near the wall depends upon the number of molecules per unit volume of the bulk of the gas. It is found experimentally that, p' is directly proportional to the square of the density of the gas (ρ) which is a measure of the intermolecular attraction of the molecules.

(i.e) $\qquad P' \, \alpha \, \rho^2 \qquad \left(\text{where } \rho \; = \; \dfrac{n}{V} \right)$

Density is inversely related to the volume `V' which is the volume occupied by one mole of the gas. Therefore P′ of one mole of the gas is given by

$$P' \; \alpha \; \frac{1}{V^2} \; ; \quad \text{(or)} \quad \left(P' \; = \; \frac{a}{V^2} \right)$$

where `a' is a proportionality constant that depends upon the nature of the gas.

$\therefore$ corrected pressure $\; = \; P + P'$

$$= \left(P + \frac{a}{V^2} \right)$$

Replacing the term for corrected volume and the corrected pressure in the ideal gas equation for one mole, the equation of state of the real gas is

$$\left(P \; + \; \frac{a}{V^2} \right) \; (V\text{-}b) \; = \; RT$$

where `a' and `b' are known as vanderwaal's constants.

This equation is also known as Vanderwaal's equation of state.

If there are `n' moles of the real gas then the vanderwall's equation becomes

$$\boxed{\left(P \; + \; \frac{n^2 a}{V^2} \right) \; (V\text{-}nb) = nRT}$$

Units for vanderwaal's constant

The dimensions of the vanderwaal's constant a and b depend upon the units of P and V respectively.

$$a = \frac{Pressure \cdot (Volume)^2}{mole^2}$$

$$a = atm \cdot dm^6 \, mol^{-2} \quad (\_ 1 \, litre = 1 \, dm^3)$$

Thus a is expressed as $atm.dm^6 \, mol^{-2}$ units. If volume is expressed in dm^3 then b is expressed as

$$\frac{Vol}{n} = \frac{dm^3}{mol}$$

$$\frac{V}{n} = dm^3 \, mol^{-1}$$

$$Unit \ of \ b = dm^3 \, mol^{-1}$$

Significance of Vanderwaal's constant (a) and (b)

1. The term a/V^2 is the measure of the attractive forces of the molecules. It is also called as the cohesion pressure (or) internal pressure.

2. The inversion temperature of a gas can be expressed in terms of `a' and `b'

$$T_i = \frac{2a}{Rb}$$

3. The vanderwaal constants `a' and `b' enable the calculation of critical constants of a gas.

Problem 4

One mole of carbon-dioxide was found to occupy a volume of 1.32 litre at 48°C and at a pressure of 16.4 atm. Calculate the pressure of the gas that would have been expected to behave ideally and non-ideally.

$[a = 3.59 \text{ atm dm}^6 \text{ mol}^{-2}]$;

$[b = 4.27 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$ and

$R = 0.082 \text{ dm}^3 \text{ atm deg}^{-1}.\text{mol}^{-1}]$

$V = 1.32$ lit

$T = 48 + 273 = 321$ K

$R = 0.082 \text{ dm}^3.\text{atm K}^{-1}.\text{mol}^{-1}$

(n = 1 mole)

For ideal behaviour,

$$PV = RT$$

$$P = \frac{RT}{V} = \frac{0.082 \times 321}{1.32}$$

$$P_{ideal} = 19.94 \text{ atm}$$

For real behaviour,

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (n = 1 \text{ mole})$$

$$P = \left(\frac{0.082 \times 321}{1.32 - 0.0427} \right) - \left(\frac{3.59}{(1.32)^2} \right)$$

$$= 20.6 - 2.06$$

$$P_{real} = 18.54 \text{ atm}$$

Limitations of Vanderwaal's equation

1. It could not explain the quantitative aspect of deviation satisfactorily as it could explain the qualitative aspects of P and V deviations.

2. The values of `a' and `b' are also found to vary with P and T, and such variations are not considered in the derivation of Vanderwaal equation.

3. Critical constants calculated from Vanderwaal's equation deviate from the original values determined by other experiments.

9.8 Critical phenomena

The essential condition for the liquefaction of the gas is described by the study of critical temperature, critical pressure and critical volume and their inter relationships.

When a gaseous system is transformed to its liquid state, there is a tremendous decrease in the volume. This decrease in volume can be effectively brought about by lowering of temperature, or by increasing pressure (or) by both. In both these effects the gaseous molecules come closer to each other and experience an increase in force of attraction which results in liquefaction of gases. At any constant temperature when pressure is increased volume is decreased and vice versa. Such P-V curves at constant temperature are known as isotherms. A typical isotherm can be considered similar to Fig.9.2.

The figure 9.2 shows the continuous decrease in pressure with increase in volume for both ideal and real gases. There is a definite deviation exhibited by the real gas from ideal gas behaviour at high pressure and low volumes.

Critical temperature (T_c)

It is defined as the characteristic temperature of a gas at which increase in pressure brings in liquefaction of gas above which no liquefaction occurs although the pressure may be increased many fold. For instance T_c of CO_2 is 31.1°C. This means that it is not possible to liquefy CO_2 by applying pressure when its temperature is above 31.1°C.

Critical pressure (P_c)

It is defined as the minimum pressure required to liquefy 1 mole of a gas present at its critical temperature.

Critical volume (V_c)

The volume occupied by 1 mole of a gas at its critical pressure and at critical temperature is the critical volume (V_c) of the gas.

A gas is said to be at its **critical state** when its pressure, volume and temperature are P_c, V_c and T_c.

9.8.1 Andrews isotherms of carbondioxide

The importance of critical temperature of a gas was first discovered by Andrews in his experiments on pressure - volume isotherms of carbon dioxide gas at a series of temperature. The isotherm of carbondioxide determined by him at different temperatures are shown in Fig.9.6.
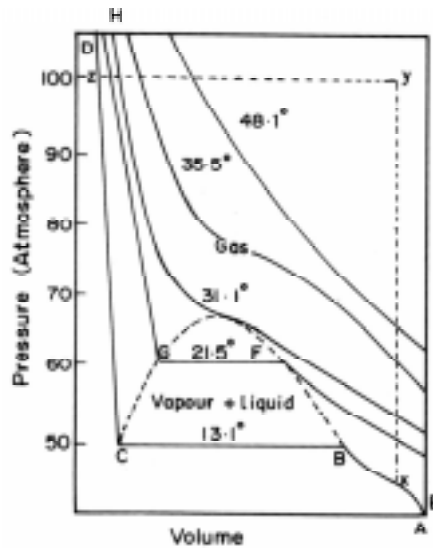
Fig. 9.6   Andrews isotherms of carbondioxide

Consider first the isotherm at the temperature 13.1°C. The point A represents carbondioxide in the gaseous state occupying a certain volume under a certain pressure. On increasing the pressure its volume diminishes as is indicated by the curve AB. At B, liquefaction of gas commences and thereafter a rapid decrease in the volume takes place at the same pressure, since more and more of the gas is converted into the liquid state. At C, the gas becomes completely liquefied. After `C' the increase of pressure produces only a very small decrease in volume. This is shown by a steep line CD which is almost vertical. Thus, along the curve AB, carbon dioxide exist as gas. Along BC, it exists in equilibrium between gaseous and liquid state. Along CD it exists entirely as a liquid. The isotherm at 21.5°C shows that the decrease in volume becomes smaller because higher the temperature greater is the volume. Therefore more pressure is applied to

decrease the volume. This effect makes liquefaction to commence at higher pressure compared to the previous isotherm at 13.1°C.

At still higher temperature, the horizontal portion of the curve becomes shorter and shorter until at 31.1°C it reduces to a point. The temperature 31.1°C is regarded as the critical temperature of CO_2. At this temperature, the gas passes into liquid imperceptibly. Above 31.1°C the isotherm is continuous. CO_2 cannot be liquefied above 31.1°C no matter how high the pressure may be. The portion of area covered by curve H with zyx portion always represents the gaseous state of CO_2.

9.8.2   Continuity of state

Thomson's experiment

Thomson (1871) studied the isotherm of CO_2 drawn by Andrews. He suggested that there should be no sharp points in the isotherms below the critical temperature. These isotherms should really exhibit a complete continuity of state from gas to liquid. This, he showed as a theoretical wavy curve. The curve MLB in Fig.9.7 represents a gas compressed in a way that it would remain stable. The curve MNC represents a superheated liquid because compression above T_c, leads to heating effects. This type of continuity of state is predicted by Vanderwaal's equation of state which is algebraically a cubic equation. The Vanderwaal's equation may be written as
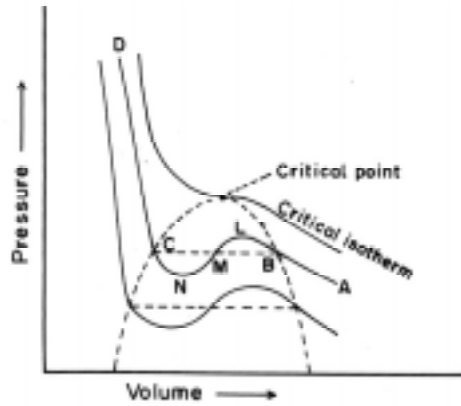
$$\left(P + \frac{a}{V^2} \right) (V-b) = RT$$

expanding the expression,

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} - RT = 0$$

Multiplying by V^2

$$PV^3 - (RT + Pb) V^2 + aV - ab = 0$$

Fig. 9.7   Thomson's isotherms of CO_2

Thus, for any given values of P and T there should be three values of V. These values are indicated by points B,M and C of the wavy curve. The three values of V become closer as the horizontal part of the isotherm rises. At the critical point the three roots of Vanderwaal 'V' become identical and there is no longer any distinction between the gas and liquid states. Here, the gas is said to be in critical state. This effect enables the calculation of T_c, P_c and V_c in terms of Vanderwaal's constants.

9.8.3   Derivation of critical constants from Vanderwaal's constants

Let us derive the values of critical constants T_c (critical temperature), V_c (critical volume) and P_c (critical pressure) in terms of the Vanderwaal's constants `a' and `b'. The Vanderwaal's equation is given by

$$\left(P + \frac{a}{V^2} \right) (V-b) = RT \quad (1)$$

Expanding this equation

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} - RT = 0 \quad (2)$$

Multiplying by $\dfrac{V^2}{P}$

$$\dfrac{V^2}{P}\left(PV + \dfrac{a}{V} - Pb - \dfrac{ab}{V^2} - RT\right) = 0$$

$$\therefore V^3 + \dfrac{aV}{P} - bV^2 - \dfrac{ab}{p} - \dfrac{RTV^2}{p} = 0 \qquad (3)$$

Rearranging this equation in the powers of V

$$V^3 - \left(\dfrac{RT}{P} + b\right)V^2 + \dfrac{aV}{P} - \dfrac{ab}{P} = 0 \qquad (4)$$

For this cubic equation of V, three roots (values of V) are possible. At the critical point, the three values of V become identical and is equal to the critical volume (V_c).

Therefore $V = V_c$ at T_c

$$\therefore (V - V_c) = 0 \qquad (5)$$

$$\therefore (V - V_c)^3 = 0 \qquad (6)$$

upon expanding this equation

$$V^3 - 3V_cV^2 + 3V_c^2 V - V_c^3 = 0 \qquad (7)$$

This equation is identical with the cubic equation derived from Vanderwaal's equation if we substitute T by T_c and P by P_c.

$$V^3 - \left(\dfrac{RT_c}{P_c} + b\right)V^2 + \dfrac{aV}{P_c} - \dfrac{ab}{P_c} = 0$$

$$\qquad (8)$$

Equating the powers of V from equation

$$-3\,V_c\,V^2 \;=\; -\left(\dfrac{RT_c}{P_c} + b\right)V^2$$

$$3\,V_c \;=\; b \;+\; \dfrac{RT_c}{P_c} \qquad\qquad (9)$$

$$3\,V_c^2 \;=\; \dfrac{a}{P_c} \qquad\qquad (10)$$

$$V_c^3 \;=\; \dfrac{ab}{P_c} \qquad\qquad (11)$$

$$\dfrac{V_c^3}{3V_c^2} \;=\; \dfrac{ab}{P_c}\;\cdot\;\dfrac{P_c}{a}$$

$$\dfrac{V_c}{3} \;=\; b$$

or $\boxed{V_c \;=\; 3b}$ $\qquad\qquad (12)$

substituting $V_c = 3b$ in equation (11)

$$(3b)^3 \;=\; \dfrac{ab}{P_c}$$

$$27b^3 \;=\; \dfrac{ab}{P_c}$$

$$\boxed{P_c = \dfrac{a}{27b^2}} \qquad\qquad (13)$$

substituting the value of V_c and P_c in equation (9)

$$3 \times 3b = b + \frac{RT_c}{a} \times 27b^2$$

$$9b-b = \frac{RT_c}{a} 27b^2$$

$$8b = \frac{RT_c \, 27b^2}{a}$$

$$\boxed{T_c = \frac{8a}{27Rb}} \qquad (14)$$

Hence the critical constants can be calculated using the values of Vanderwaal's constants of a gas and vice versa. Since P_c and T_c can often be determined experimentally, these values may be employed to calculate the constants a and b.

$$a = 3V_c^2 P_c$$

$$b = \frac{V_c}{3}$$

Based on the critical temperature values, gases are categorised as "permanent" and "temporary" gases. H_2, N_2, He, ... gases having very low critical temperature belong to the permanent type. Gases like NH_3, CO_2, SO_2, HCl etc. having critical temperature in the ordinary range of temperatures belong to the temporary gases type.

Problem 5

Vanderwaal's constants for hydrogen chloride gas are $a = 3.67$ atm lit^{-2} and $b = 40.8$ ml mol^{-1}. Find the critical temperature and critical pressure of the gas.

Solution

$$T_c = \frac{8a}{27Rb}$$

$$= \frac{8 \times 3.67}{27 \times 0.0821 \times 0.0408} = 324.7 \text{ K}$$

$$= 51.7°C$$

$$P_c = \frac{a}{27b^2} = \frac{3.67}{27 \times (0.0408)^2}$$

$$= 81.6 \text{ atm}$$

Problem 6

The critical temperature of hydrogen gas is 33.2°C and its critical pressure is 12.4 atm. Find out the values of `a' and `b' for the gas.

Solution : We know

$$T_c = \frac{8a}{27Rb} \quad ... \text{(i)}; \quad P_c = \frac{a}{27b^2} \quad .... \text{(ii)}$$

Dividing (i) by (ii) we get

$$\frac{T_c}{P_c} = \frac{8a}{27Rb} \times \frac{27b^2}{a} = \frac{8b}{R} \quad ...\text{(iii)}$$

Given $T_c = 33.2°C = 33.2 + 273 = 306.2K$ and $P_c = 12.4$ atm; $R = 0.082$ atm. litre $K^{-1}mol^{-1}$. Substituting the values in equation (iii), we get

$$\frac{306.2}{12.4} = \frac{8 \times b}{0.082}$$

$$b = \frac{306.2 \times 0.082}{12.4 \times 8}$$

$$= 0.253 \text{ litre mol}^{-1}.$$

Now, substituting the value of `b' in equation (i) we have

$$T_c = \frac{8a}{27Rb} \text{ (or) } 306.2 = \frac{8 \times a}{27 \times 0.082 \times 0.253}$$

(or) $a = 21.439 \text{ atm litre}^2 \text{ mol}^{-1}$

9.9 Joule-Thomson Effect

Joule-Thomson showed that when a compressed gas is forced through a porous plug into a region of low pressure, there is appreciable cooling.

The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure, is known as Joule - Thomson effect.

When the gas is allowed to escape into a region of low pressure the molecules move apart rapidly against the intermolecular attractive forces. In this case work is done by the gas molecules at the expense of internal energy of the gas. Therefore cooling occurs as the gas expands. This reduction in the temperature is generally referred as Joule-Thomson effect and is used in the liquefaction of gases.

9.10   Inversion temperature (Ti)

The Joule-Thomson effect is obeyed by a gaseous system only when its temperature is below a characteristic value. The characteristic temperature below which a gas expands adiabatically into a region of low pressure through a porous plug with a fall in temperature is called as inversion temperature (Ti).

Ti is characteristic of a gas and it is related to the Vanderwaal's constant `a' and `b',

$$\boxed{Ti = \frac{2a}{Rb}}$$

At the inversion temperature there is no Joule Thomson effect (ie) there is neither fall nor rise in temperature. Only when the temperature of the gas is below the inversion temperature there is a fall in temperature during adiabatic expansion. If the temperature of the gas is above Ti there is a small rise in temperature. For gases like H_2 and He whose Ti values are very low -80°C and -240°C respectively, these gases get warmed up instead of getting cooled during the Joule-Thomson experiment. These gases will obey Joule-Thomson effect only when they are cooled to a temperature below these Ti values.

9.11   Conditions of liquefaction of gases

Many industrial processes require large quantities of liquid air, liquid ammonia, liquid carbondioxide etc. The production of liquids from various gases is therefore an important commercial operation.

There are different methods of liquefaction of gases, such as (i) based on the concept of critical temperature followed by the compression (ii) based on Joule-Thomson effect (iii) Adiabatic demagnetisation.

In the case of gases like NH_3, Cl_2, SO_2 and CO_2 whose T_c values are near and below the ordinary temperatures, they can be liquefied easily by increasing the pressure alone at their respective Tc values.

Gases like H_2, O_2, N_2 and He have very low T_c values and hence Joule Thomson effect may be applied to bring in effective cooling.

Helium is cooled by Joule-Thomson effect to a lower temperature and further cooling for its liquefaction, is carried out by the method of adiabatic demagnetisation.

Linde's Method

This method makes use of Joule Thomson effect and is used to liquify air or any other gas. Pure air or any gas is first compressed to about 200 atmospheres and is allowed to enter the innertube of the concentric pipes as shown in Fig.10.8. The valve v of jet J is then opened and the gas is allowed to expand suddenly into the wider chamber C.
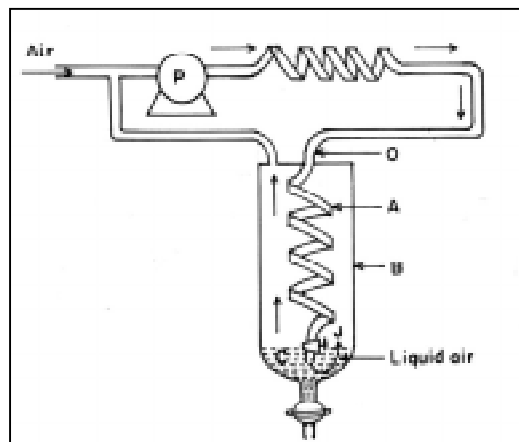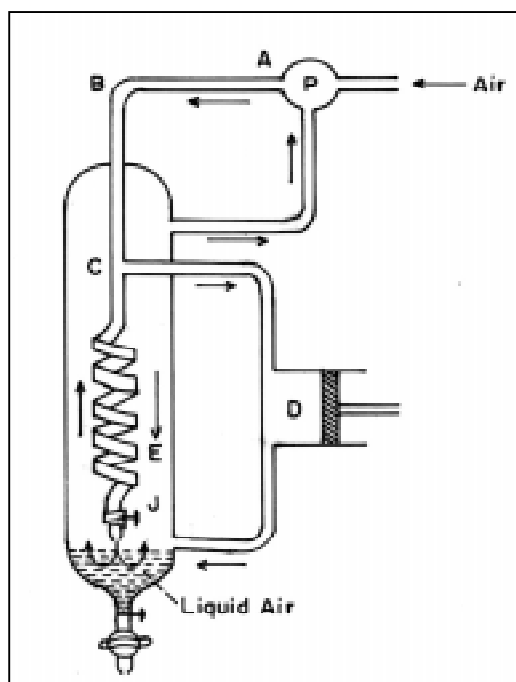
Fig. 9.8   Linde's apparatus for liquefaction of gas

The gas gets cooled due to expansion and its pressure is reduced to about 50 atm. The gas is now allowed to pass through the outer tube `O'. At this stage the incoming gas is initially cooled by the outgoing gas. Further cooling of the incoming gas occurs during expansion in the chamber C. The cooled gas is again compressed and is circulated in. By repeating the process of cooling and compression followed by expansion, the gas is liquefied and finally the liquid air drops out from the jet into the bottom of chamber C.

Claude's process

In this method compressed air is allowed to do mechanical work of expansion. This work is done at the expense of the kinetic energy of the gas and hence a fall of temperature is noted. This principle is combined with Joule-Thomson effect and utilised in Claude's process of liquefaction of air. Air is compressed to about 200 atmospheres and is passed through the pipe ABC (Fig.9.9). At C, a part of the air goes down the spiral towards the jet nozzle J and a part of the air is led into the cylinder D provided with an air tight piston. Here the air moves the piston outwards and expands in volume as a result of which considerable cooling is produced. The cooled air passes up the liquefying chamber during which process it cools the portion of the incoming compressed air. The precooled incoming compressed air then experiences Joule-Thomson expansion when passed through Jet nozzle J

and gets cooled further. The above process takes place repeatedly till the air is liquefied.

Fig. 9.9 Claude's apparatus for liquefaction of air

Adiabatic demagnetisation

Generally, the method used to reach the very low temperature of about 10^{-4} K is adiabatic demagnetisation. In this method the paramagnetic samples such as Gadolinium sulphate is placed surrounding the gas sample and cooled to about 1K along with the gas in any one of the cooling methods. The paramagnetic sample used in this method is suddenly magnetised by the application of strong magnetic field. This magnetisation (ordering of molecular magnets) occurs while the sample surrounds the cooled gas and has thermal contact with the walls of the container. When the magnetic field is suddenly removed, demagnetisation occurs which brings in a disordered state of the molecular magnets. To reach this state

thermal energy is taken away from the cooled air such that its temperature gets further lowered. By this technique, as low as zero kelvin can be reached.

Questions

A. Choose the correct answer :

1. A curve drawn at constant temperature is called an isotherm. This shows relationship between
   (a) P and $\dfrac{1}{V}$ (b) PV and V
   (c) P and V   (d) V and $\dfrac{1}{P}$

3. The critical temperature of a gas is that temperature
   (a) Above which it can no longer remain in the gaseous state
   (b) Above which it can not be liquified by pressure
   (c) At which it solidifies
   (d) At which volume of gas becomes zero.

4. If a gas expands at constant temperature.
   (a) Number of molecules of the gas decreases
   (b) The kinetic energy of the molecules decreases
   (c) The kinetic energy of the molecules decreases
   (d) The kinetic energy of the molecules increases

5. The molecules of a gas A travel four times faster than the molecules of gas B at the same temperature. The ratio of molecular weight (M_A/M_B) will be
   (a) $\dfrac{1}{16}$ (b) 4   (c) $\dfrac{1}{4}$ (d) 16

B. Fill in the blanks

6. The correction term for pressure deviation is ……in the Vanderwaal equation of state.

7. The relation between inversion temperature and Vanderwaal's constants `a' and `b' is ____

8. To liquefy Helium _____ method is exclusively used.

9. The adiabatic expansion of a real gas results in _____

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10. The rate of diffusion of gas is _____ to square root of both ____ _____ and molecular mass.

C. Match the following

A	B
11. Ideal gas behaviour	(a) Critical temperature
12. Adiabatic demagnetization	(b) Liquid oxygen
13. CO_2 at 31.1^{o}C	(c) Mole fraction of the gas
14. Joule Thomson Experiment	(d) Number of moles of the gas
15. Ratio of the partial pressure to the total pressure	(e) Low pressure and high temperature
	(f) Liquid Helium

D. Write in one or two sentence

16. Write the mathematical expression for Boyle's law.

17. Compare the partial pressures of gases A and B when 3 moles of A and 5 moles of B mixed in constant volume, and 25°C and 1 atm pressure.

18. Give the correction factors for the volume and pressure deviation for a Vanderwaal's gas.

19. A sample of an ideal gas escapes into an evacuated container, there is no change in the kinetic energy of the gas. Why?

20. What is the change in temperature when a compressed real gas is allowed to expand adiabatically through a porous plug.

21. Define Boyle's law and Charle's law.

22. What are measurable properties of gases?

23. What is the molar volume of nitrogen at 500K and 600 atm according to ideal gas law?

24. Define Graham's law of diffusion.

25. Give the values of R-gas constant in calories and Joules.

26. What are the units of Vanderwaals constants `a' and `b' ?

27. Write the significance of Vanderwaal's constants.

28. Write the limitations of vanderwaal equation of state.

29. Define Joule-Thomson effect.

30. What is meant by inversion temperature ?

E. Explain briefly on the following

31 At 27°C, H_2 is leaked through a tiny hole into a vessel for 20 minutes.

Another unknown gas at the same T and P as that of H_2 is leaked through the same hole for 20 minutes. After effusion of the gas, the mixture exerts a pressure of 6 atm. The H_2 content of the mixture is 0.7 moles. If volume of the container is 3 litres what is the molecular weight of unknown gas ?

32 Calculate the pressure exerted by 5 moles of CO_2 in one litre vessel at 47^oC using Vanderwaal's equation. Also report the pressure of gas if it behaves ideally in nature. Given that a=3.592 atm lit^2 mol^{-2}. b = 0.0427 lit mol^{-1}

$$\left(\begin{array}{lll} \text{Ans.:} & P_{real} & = & 77.2 \text{ atm} \\ & P_{ideal} & = & 131.36 \text{ atm} \end{array}\right.$$

33. Calculate the total pressure in a 10 L cylinder which contains 0.4 g of helium, 1.6 g of oxygen and 1.4 g of nitrogen at 27^oC. Also calculate the
partial pressures of He gas in the cylinder. Assume Ideal behaviour for gases.
R = 0.082 L atm k^{-1} mol^{-1}

$$\left(\begin{array}{ll} \text{Ans.} & P_{total} = 0.4926 \text{ atm} \\ & p_{He} = 0.2463 \text{ atm.} \\ & P_{O2} = 0.1231 \text{ atm,} \\ & p_{N2} = 0.123 \text{ atm} \end{array}\right.$$

34. The critical constants for water are 374^oC, 218 atm and 0.0566 litre mol^{-1}. Calculate `a' and `b' of water.

$$\left(\begin{array}{lll} \text{Ans.} & a & = & 2.095 \text{ } lit^2 \text{ atm } mol^{-} \\ & b & = & 0.0189 \text{ lit } mol^{-1} \end{array}\right.$$

35. Vanderwaal's constant in litre atmosphere per mole for carbon dioxide are a = 3.6 and b = 4.28 x 10^{-2}. Calculate the critical temperature and critical volume of the gas. R = 0.0820 lit atm K^{-1}. mol^{-1}

36. Explain the causes for deviation for real gases from ideal behaviour.

36. Deduce the relationship between critical constants and Vanderwaal's constants.

38. Describe Linde's process of liquefaction of gases with neat diagram.

39. Describe Claude's process of liquefaction of gases with neat diagram.

40. What is meant by adiabatic demagnetisation? Explain its use in liquefaction of gases.

SUMMARY

- P,V,T and mass are the measurable properties of gas. They obey Boyle's and Charle's law. The equation of state for an ideal gas in PV = nRT.

- For constant mass of a gas,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

- Different units of R :0.0821 it atm $K^{-1} mol^{-1}$;

$$8.314 \times 10^7 \ erg \ K^{-1} \ mol^{-1};$$

$$8.314 \ joule \ K^{-1} \ mol^{-1};$$

$$1.987 \ cal \ K^{-1} \ mol^{-1}.$$

- Equation of state of gaseous mixture is $PV = (n_A + n_B + n_C) \ RT$.

- By Graham's law, (diffusion $rate_1$/diffusion $rate_2$) = $(M_2/M_1)^{1/2}$ (or) (effusion $rate_1$/ effusion $rate_2$) = $(M_2/M_1)^{1/2}$

- Real gases deviate from V_{ideal} and P_{ideal}. The equation of state of real gas = Vanderwaal equation.

$$\left[P + \frac{a}{V^2} \right] (V-b) = RT \ for \ n = 1.$$

- Critical temperature, critical pressure, critical volume represent the critical state of the gas. Andrew's isotherm describes critical temperature of carbondioxide. Thomson's experiment describes continuity of state.

  P_c, V_c, T_c are related to Vanderwaal's constants a and b as $V_c = 3b$;

$$P_c = \frac{a}{27b^2}; \quad T_c = \frac{8a}{27Rb}$$

- Joule Thomson effect predicts adiabatic expansion of a compressed gas through an orifice to cause a fall in temperature. Inversion temperature = 2a/Rb is the temperature below which Joule Thomson effect is obeyed.

- Liquefaction of gases is carried out by Linde's and Claude's processes adopting Joule-Thomson effect. Liquefaction of Helium and zero kelvin are achieved by adopting adiabatic demagnetisation.

REFERENCES :

Text book of physical chemistry, Lewis and Glasstone.

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