A Textbook of CHEMISTRY XI

Balochistan Textbook Board, Quetta

Reasons درخشوں سے لیکھ گوزیم طرا للکا یہ

بسم اللہ الرحمن الرحیم

(In the name of ALLAH the most beneficent and the most merciful)

Chemistry XI

Taleem 360° تعلیم

Published by:
New College Publications, Quetta

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- New College Publications, Quetta

Printer
- New College Publications, Quetta

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CONTENTS

Chapter 1: Stoichiometry 7

Introduction: 7

1.1 Mole and Avogadro's Number: 8
1.2 Mole Calculations: 11
1.3 Percentage Composition: 20
1.4 Excess and Limiting Reagents: 21
1.5 Percentage Yield: 25

Chapter 2: Atomic Structure 34

Introduction: 35

2.1 Discharge Tube Experiments: 35
2.2 Discovery of Nucleus and Rutherford's Atomic Model: 45
2.3 Planck's Quantum Theory: 47
2.4 Bohr's Atomic Model: 49
2.5 X-Rays: 61
2.6 Quantum Numbers and Orbitals: 64
2.7 Electronic Configuration: 72

Chapter 3: Theories of Covalent Bonding and Shapes of molecules 84

Introduction: 84

3.1 Shapes of molecules: 86
3.2 Resonance: 92
3.3 Theories of covalent bonding: 94
3.4 Bond Characteristics: 113
3.5 Effect of Bonding on Physical and Chemical Properties: 125

Chapter 4: States of Matter I: Gases 134

Introduction: 135

4.1 Kinetic Molecular Theory of Gases: 136
4.2 Boyle's Law: 141
4.3 Charles's Law: 143
4.4 Avogadro's Law: 146
4.5 Ideal Gas Equation: 149
4.6 Deviation From Ideal Gas Behavior: 155
4.7 Van der Waals Equation: 157
4.8 Dalton's Law of Partial Pressure: 159
4.9 Graham's Law of Diffusion and Effusion: 164
4.10 Liquefaction of Gases: 167
4.11 Fourth State of Matter: Plasma: 170

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Chapter 5: States of Matter II: Liquids 180
Introduction: 181
5.1 Kinetic Molecular Interpretation of Liquids: 181
5.2 Intermolecular Forces (Vander Waal's Forces): 182
5.3 Physical properties of Liquids: 191
5.4 Energetics of Phase Changes: 204
5.5 Liquid Crystals: 207

Chapter 6: States of Matter III: Solids 216
Introduction: 217
6.1 Kinetic Molecular Interpretation of Solids: 217
6.2 Types of Solids: 218
6.3 Properties of Crystalline Solids: 220
6.4 Crystal Lattice and the Unit Cell: 224
6.5 Types of Crystalline Solids: 230

Chapter 7: Chemical Equilibrium 243
Introduction: 244
7.1 Reversible Reactions and Dynamic Equilibrium: 245
7.2 Factors Affecting Equilibrium (Le-Chatelier's Principle): 259
7.3 Industrial Application of Le-Chatelier's Principle: 264
7.4 Solubility Product and Precipitation Reactions: 266
7.5 Common Ion Effect: 270

Chapter 8: Acids, Bases and Salts 278
Introduction: 279
8.1 Acidic, Basic and Amphoteric Substances: 280
8.2 Bronsted-Lowery Definitions of Acids and Bases: 281
8.3 Relative strength of Acids and Bases: 283
8.4 Expressing the Strength of Acids and Bases: 285
8.5 Lewis Definitions of Acids and Bases: 298
8.6 Buffer Solutions and their Applications: 299
8.7 Salt Hydrolysis: 301

Chapter 9: Chemical Kinetics 311
9.1 Introduction to Chemical Kinetics: 312
9.2 Rates of Reactions: 313
9.3 Collision Theory, Transition State and Activation Energy: 324
9.4 Catalysis: 327

Chapter 10: Solutions and Colloids 338
Introduction: 339
10.1 General Properties of Solutions: 340
10.2 Concentration Units: 349
10.3 Raoult's Law: 359

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10.4 Colligative Properties of dilute Solutions: 364
10.5 Colloids: 375

Chapter 11: Thermochemistry 385
Introduction: 386
11.1 Energy in Chemical Reactions: 387
11.2 Thermodynamics: 388
11.3 Internal Energy: 390
11.4 First Law of Thermodynamics: 391
11.5 Standard State and Standard Enthalpy Changes: 395
11.6 Heat Capacity: 398
11.7 Calorimeter: 399
11.8 Hess's Law of Constant Heat Summation: 402
11.9 Born-Haber Cycle: 403

Chapter 12: Electrochemistry 411
Introduction: 412
12.1 Oxidation-Reduction Concepts: 412
12.2 Electrode: 422
12.3 Electrochemical Cells: 423
12.4 Standard Cell Potential and standard Electrode Potential: 427
12.5 Modern Batteries: 433
12.6 Corrosion: 438

Answers to the Selected Practice Exercises 446
Answers to the Selected Problems 446
Index 446
Appendix 453
Glossary 458
PeriodicTable 469

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Chapter # 01

Stoichiometry

Major Concepts

1.1. Mole and Avogadro's number
1.2. Mole Calculations
1.3. Percentage Composition
1.4. Excess and Limiting Reagents
1.5. Percentage Yield

Learning Outcomes

The students will be able to:

- Interpret a balanced chemical equation in terms of interacting moles, representative particles, masses and volumes of gases at STP. (Analyzing)
- Construct mole ratios from balanced equations for use as conversion factors in stoichiometric problems. (Applying)
- Perform stoichiometric calculations with balanced equations using moles, representative particles, masses and volumes of gases at STP. (Analyzing)
- Identify the limiting reagent in a reaction. (Analyzing)
- Knowing the limiting reagent in a reaction calculate the maximum amount of product(s) produced and the amount of any unreacted excess reagent. (Analyzing)
- Given information from which any two of the following may be determined, calculate the theoretical yield, actual yield and percentage yield. (Understanding)
- Calculate the theoretical yield and the percent yield when given the balanced equation, the amounts of reactants and the actual yield. (Applying)

Introduction:

Stoichiometry (pronounced as stoy-key-om-eh-tree) is the branch of Chemistry in which we study the relationship between the amounts of reactants and products in a balanced chemical equation.

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Stoichiometry (Greek stoicheion, "element" and metron, "measure") means quantitative measure (of reactants and products). Such knowledge plays an important role when calculating the amount of products such as masses, moles, volumes and percentage yield etc. with the help of balanced chemical equation.

Keep in Mind

A balanced chemical equation has the same number of atoms of each type on both sides of the equation. While writing chemical equations, use the correct formulas for reactants and products and never change the subscripts in the formulas. If you change the subscripts, you change the identity of substances, so we have to balance the equation by changing the number of molecules of each type that appear in the equation.

Balanced chemical equations have definite ratios of reactants and products just as compounds have definite ratios of elements. Those ratios are used to calculate the mass (or moles) of other substances in a reaction from the mass (or moles) of any one of the substances. It tells you that how to calculate the quantities of substances involved in a reaction. It covers the calculation of the percentage yield of a product from the actual yield and the theoretical yield, based on the amounts of reactants.

1.1 Mole and Avogadro`s Number:

You buy quantity of items in several ways like eggs in dozen (12 numbers), Shoes in pairs (2 numbers), cans in case (24 cans), playing cards in pack (52 numbers), papers in ream (500 sheets), and pencils in gross (144 numbers). Bulk foods, like rice, wheat, sugar, and peanuts are usually purchased by mass, because it is very difficult to count them. All these methods are used by chemists to determine the quantity of matter (counting and weighing).

The most convenient unit of matter for counting and weighing is mole. It connects the macroscale world (so large that can be weighed or count) to the nanoscale world (so small that is inconvenient to weigh or count them).

1.1.1 The Mole:

Mole is a Latin word; it means a 'huge mass'. Its symbol is **mol** and is represented by **n**. One mole is the amount of substance that has as many particles (atom, molecules, ions or formula units) as the number of atoms in exactly 12 g of carbon-12. The mass of one mole of a substance(element or compound) depends on what that substance

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is, and is equal to the formula mass of that substance in grams. We, therefore, say that the atomic mass, molecular mass, ionic mass or formula mass of a substance when expressed in grams is equal to one mole. Examples are:

One mole of carbon atoms = 12g

One mole of CO_2 molecules = 44g

One mole of NaCl formula units = 58.5g

One mole of SO_4^{2-} ions = 96g

1.1.2 The Avogadro's Number:

The number of particles (atom, molecules, ions or formula units) present in one mole of a substance is called Avogadro's number. It is represent by N_A. The number of particles in one mole of a substance is 6.0221421×10^{23}, which we will usually round to 6.02×10^{23}. Scientists call this value Avogadro's number in the honour of the Italian scientist Amedeo Avogadro (1776-1856). The unit of Avogadro's number is read as either "per mole" or "inverse of mole". Examples are:

Interesting Information

If we were able to count atoms at the rate of 5 million per second, it would take about 4 billion years to count the atoms in one mole.

One mole of carbon-12 contains 6.02×10^{23} atoms of carbon-12.

One mole of H_2O contains 6.02×10^{23} molecules of H_2O.

One mole of CaO contains 6.02×10^{23} formula units of CaO.

One mole of CO_3^{2-} contains 6.02×10^{23} ions of CO_3^{2-}.

Table 1.1: The Formula Masses, Molar Masses and Number of Particles of Some Substances

Name of Substance	Formula	Formula Mass (amu)	Mass of one Mole (g/mol)	Number of Particles in one Mole
Oxygen atom	O	16	16	6.02×10^{23} atoms
Oxygen molecule	O_2	32	32	6.02×10^{23} molecules
Water	H_2O	18	18	6.02×10^{23} molecules
Potassium nitrate	KNO_3	101	101	6.02×10^{23} formula units
Carbonate ion	CO_3^{-2}	60	60	6.02×10^{23} ions

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Molar Mass and Volume

The volume of one mole of an ideal gas at STP (standard temperature and pressure) is called molar volume.

Its value is equal to $22.414 dm^3$. It is denoted by V_m.

Table 1.2: The Molar Volumes, Molar Masses and Number of Molecules of Some Gases at STP (0°C and 1atm)

Symbol Name	Hydrogen	Methane	Ammonia	Carbon dioxide
Molar mass (g/mol)	2	16	17	44
Number of moles	1 mole	1 mole	1 mole	1 mole
Volume of gas (in dm^3)	22.414	22.414	22.414	22.414
Number of molecules	6.02×10^{23} molecules	6.02×10^{23} molecules	6.02×10^{23} molecules	6.02×10^{23} molecules

The equal volume of all gases at STP has equal number of molecules but they have different masses.

The mass of one mole of a substance in grams is called molar mass.

The unit of molar mass is g/mol.

To determine molar mass, we change the units from atomic mass units to grams of a substance. The substance may be an element or a compound.

For an element, the molar mass in grams per mole is numerically equal to the atomic mass of that element in atomic mass units. For example:

i) Hydrogen atom has an atomic mass of 1.008 amu, so the molar mass of hydrogen atom is 1.008 g/mol and contains 6.02×10^{23} atoms of hydrogen.

ii) Oxygen atom has an atomic mass of 16 amu, so the molar mass of oxygen is 16 g/mol and contains 6.02×10^{23} atoms of oxygen.

If we know the atomic mass of an element, we also know its molar mass.

For a compound, the molar mass in grams per mole is numerically equal to the formula mass of that compound in atomic mass units. For example:

i) Ammonia (NH_3) has a formula mass of 17 amu, so the molar mass of ammonia is 17g/mol and contains 6.02×10^{23} molecules of ammonia.

ii) Potassium nitrate (KNO_3) has a formula mass of 101 amu, so the molar mass of potassium nitrate is 101g/mol and contains 6.02×10^{23} formula units of potassium nitrate.

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Example 1.1

Calculate the molar mass of Benzene (C_6H_6).

Solution:

Each mole of C_6H_6 contains six moles of carbon atoms and six moles of hydrogen atoms in the formula.

The molar mass of benzene can be calculated as:

6 moles of carbon × 12g / mol = 72g

6 moles of hydrogen × 1g / mol = 6g

The molar mass of Benzene(C_6H_6) = 78g

Practice Exercise 1:

Calculate the molar mass of $KMnO_4$.

1.2 Mole Calculations

1.2.1 Calculation of Number of Moles of a Substance

i) If we know the mass of a substance, we can calculate the number of moles by dividing the mass of a substance by molar mass.

$$\text{No. of moles of a substance} = \frac{\text{Given mass of a substance}}{\text{Molar mass of a substance}}$$

Example 1.2

How many moles are present in 20g of NaOH?

Solution:

Mass of NaOH = 20g

Moles of NaOH = ?

$$\text{Moles of NaOH} = \frac{\text{Mass of NaOH}}{\text{Molar mass of NaOH}}$$

$$\text{Moles of NaOH} = \frac{20\text{g}}{40\text{gmol}^{-1}} = 0.5\text{mol}$$

Practice Exercise 2:

The given mass of $KClO_3$ is 12.25g. Calculate the number of moles of potassium chlorate.

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ii) If we know the number of moles of a substance, we can calculate the mass by multiplying number of moles with molar mass.

Mass of a substance = Number of moles of a substance × Molar Mass

Example 1.3

Calculate mass of 0.25 moles of H_2SO_4.

Solution:

Moles of H_2SO_4 = 0.25mol

Mass of H_2SO_4 = ?

Mass of H_2SO_4 = Moles of H_2SO_4 × Molar mass of H_2SO_4

= 0.25mol × 98gmol^{-1}

= 24.5g

Practice Exercise 3:

What is the mass of 1.50 moles of $Ca(OH)_2$?

iii) If we know about the number of particles of a substance, we can calculate the number of moles by dividing the number of particles by Avogadro's number.

$$\text{No. of moles of a substance} = \frac{\text{No. of particles of a substance}}{\text{Avogadro's Number}}$$

Example 1.4

Sucrose, table sugar, contains 3.76×10^{24} molecules of $C_{12}H_{22}O_{11}$. What is the number of moles of sucrose?

Solution:

$$\text{Number of moles of sucrose} = \frac{\text{No. of particles of sucrose}}{\text{Avogadro's Number}}$$

$$\text{Number of moles of sucrose} = \frac{3.76 \times 10^{24}\ \text{molecules}}{6.02 \times 10^{23}\ \text{molecules mol}^{-1}}$$

= 6.25 moles

Practice Exercise 4:

An aluminum wire contains 5.5×10^{25} atoms of aluminum. Calculate the number of moles of aluminum.

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1.2.2 Calculation of Number of Particles

i) If we know the moles of a substance, we can calculate the number of particles by multiplying number of moles with Avogadro's number.

No. of particles of substance = No. of moles of substance × Avogadro's Number (N_A)

Example 1.5

How many atoms are there in a sodium metal that contains 2.5 moles?

Solution:

Number of moles of sodium = 2.5 mol

Number of atoms of sodium = ?

Number of atoms of sodium = Number of moles of sodium × N_A

$= 2.5 \text{ mol} \times 6.02 \times 10^{23} \text{ atoms mol}^{-1}$

$= 15.05 \times 10^{23} \text{ atoms}$

$= 1.505 \times 10^{24} \text{ atoms}$

Practice Exercise 5:

How many molecules are present in 2.50 moles of H_2O_2?

ii) If we know the mass of a substance, we can calculate the number of particles by dividing mass of substance by molar mass and the answer is multiplied by Avogadro's number.

$$\text{No. of particles of substance} = \frac{\text{Given mass of substance (m)}}{\text{Molar mass of substance (M)}} \times \text{Avogadro's Number}(N_A)$$

Example 1.6

How many atoms are present in 50 g of gold ring?

Solution:

Mass of gold = 50g

Molar mass of gold = 197g/mol

Number of atoms of gold = ?

$$\text{Number of atoms of gold} = \frac{\text{Mass of gold}}{\text{Molar mass of gold}} \times \text{Avogadro's Number}$$

$$= \frac{50\text{g}}{197\text{gmol}^{-1}} \times 6.02 \times 10^{23} \text{ atoms mol}^{-1}$$

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$$= 0.254 \times 6.02 \times 10^{23} \text{ atoms}$$
$$= 1.529 \times 10^{23} \text{ atoms}$$

Practice Exercise 6:

Calculate number of water molecules in one cup of water having mass equal to 200g.

1.2.3 Calculation of Volume of a Gas

i) If we know the number of moles of a gas, we can calculate the volume of a gas at STP by multiplying number of moles of a gas by molar volume.

Volume of a gas = Moles of a gas × Molar volume

Example 1.7

What is the volume in dm^3 of 4.75mol of ethane gas?

Solution:

Number of moles of ethane = 4.75 mol

Volume of ethane in dm^3 = ?

Volume of ethane in dm^3 = Moles of ethane × Molar volume

$= 4.75 \text{ mol} \times 22.414 dm^3 mol^{-1}$

$= 106.47 dm^3$

Practice Exercise 7:

Calculate the volume in decimeter cube of 2.25 moles of laughing gas (N_2O).

ii) If we know the mass of a gas, we can calculate the volume of a gas at STP by dividing the mass of a gas by molar mass and the answer is multiplied by molar volume?

$$\text{Volume of a gas} = \frac{\text{Mass of a gas}}{\text{Molar mass of a gas}} \times \text{Molar volume}$$

Example 1.8

Argon is placed in a light bulb to minimize the rate of evaporation of the tungsten filament. What is the volume in cm^3 of 3.99g of argon?

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Solution:

Mass of argon = 3.99g

Volume in cm^3 of argon = ?

$$\text{Volume of argon} = \frac{\text{Mass of argon}}{\text{Molar mass of argon}} \times \text{Molar volume}$$

$$= \frac{3.99g}{39.9gmol^{-1}} \times 22.414dm^3mol^{-1}$$

$$= 0.1 \times 22.414dm^3$$

$$= 2.214\,dm^3$$

$$\text{Volume of argon in } cm^3 = 2.214dm^3 \times 1000cm^3dm^{-3}$$

$$= 2214cm^3$$

Practice Exercise 8:

Calculate the volume in decimeter cube of 50 g of propane (C_3H_8) gas.

1.2.4 Stoichiometric Calculations

A chemist needs to know how much product is obtained from certain amounts of reactants or a chemist needs to know how much reactants are used to get certain amounts of products. Chemists use stoichiometric calculations to answer these questions.

Principles of Stoichiometric Calculations

Stoichiometric calculations are based on the following principles:

i) Reactants are completely converted into products.

ii) No side reaction occurs.

iii) While doing calculations, the law of conservation of mass and the law of definite proportions are obeyed.

Law of Conservation of Mass

According to law of conservation of mass, matter (mass) can neither be created nor destroyed.

Law of conservation of mass states that the total mass of reactants is equal to the total mass of products in a balanced chemical equation.

Law of Definite Proportions

According to law of definite proportions, a pure compound always contains the same element combined in the same ratio by mass.

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(e.g.) Water has 88.89% oxygen and 11.11% hydrogen by mass, no matter what is its source.

Stoichiometric Relationship

The following types of relationship can be studied with the help of balanced chemical equations.

i) Mass-Mass Relationship

The mass of one substance can be calculated from the given mass of another substance and vice versa.

ii) Mole-Mole Relationship

The moles of one substance can be calculated from the given moles of another substance and vice versa.

iii) Volume-Volume Relationship

The volume of one substance can be calculated from the given volume of another substance and vice versa.

iv) Mole-Mass Relationship

The mass of one substance can be calculated from the given moles of another substance and vice versa.

v) Mass-Volume Relationship

The volume of one substance can be calculated from the given mass of another substance and vice versa.

How to Solve a Stoichiometry Problem

Step 1: Write all the given data with relevant units.

Step 2: Write a balanced chemical equation for the reaction under consideration.

Step 3: Convert the given mass of all the reactants to number of moles.

Step 4: Use the chemical equation to determine the mole ratio of the unknown quantity to the known quantity. The mole ratio can be determined by dividing the coefficient of the unknown by the coefficient of the known.

$$\frac{\text{Moles of unknown}}{\text{Moles of known}}$$

This mole ratio can be used to convert the number of moles of known quantity to a number of moles of unknown. The mole ratio is multiplied with the moles of known calculated in the third step.

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$$\frac{\text{Moles of unknown}}{\text{Moles of known}} \times \text{Moles of known} = \text{Moles of unknown}$$

Step 5: Convert moles back to mass by multiplying with molar mass of unknown substance to get answer in grams, if necessary.

Example 1.9 (Mass-Mass Conversion)

Calculate the mass of quicklime (calcium oxide) that is produced by the thermal decomposition of 200g of limestone (calcium carbonate). The equation for this reaction is:

$$CaCO_{3(s)} \xrightarrow{\Delta} CaO_{(s)} + CO_{2(g)}$$

Solution:

Step 1: Write all the given data with relevant units.

Mass of CaO = ?

Mass of $CaCO_3$ = 200g

Molar mass of CaO = $56gmol^{-1}$

Molar mass of $CaCO_3$ = $100gmol^{-1}$

Step 2: Write a balanced chemical equation for the reaction.

$$\underset{1mol(100g)}{CaCO_{3(s)}} \xrightarrow{\Delta} CaO_{(s)} + \underset{1mol(56g)}{CO_{2(g)}}$$

Step 3: Use the chemical equation to determine the mass ratio of the unknown quantity to the known quantity.

100g of $CaCO_3$ produces CaO = 56g

$$1g \text{ of } CaCO_3 \text{ produces CaO} = \frac{56g}{100g}$$

$$200g \text{ of } CaCO_3 \text{ produces CaO} = \frac{56g}{100g} \times 200g$$

$$= 112g$$

So, the mass of quicklime produced is 112g.

Practice Exercise 9:

How much HCl can be produced when 5g of hydrogen reacts with an excess amount of chlorine? The equation for this reaction is:

$$H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$$

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Example 1.10 (Mole-Mole Conversion)

When 2.5 mol of nitrogen reacts with hydrogen to form ammonia, how many moles of hydrogen are consumed in the process? The equation for this reaction is:

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

Solution:

Step 1: Write all the given data with relevant units.

Number of moles of N_2 = 2.5mol

Number of moles of H_2 = ?

Step 2: Write a balanced chemical equation for the reaction.

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

Step 3: Use the chemical equation to determine the mole ratio of the unknown quantity to the known quantity.

1 mole of N_2 needs H_2 to produce NH_3 $= \frac{3}{1} = 3$mol

2.5 moles of N_2 needs H_2 to produce $NH_3 = 3 \times 2.5 = 7.5$mol

So, the moles of hydrogen used in the process are 7.5 moles.

Practice Exercise 10:

How many moles of carbon dioxide are produced when 1.25 moles of glucose are used by a person? The oxygen is in excess. The equation for the reaction is:

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(l)}$$

Example 1.11 (Mole-Mass Conversion)

What mass of hydrogen can be produced by the decomposition of 4.3 moles of water? The balanced chemical equation for the reaction is:

$$2H_2O_{(l)} \longrightarrow 2H_{2(g)} + O_{2(g)}$$

Step 1: Write all the given data with relevant units.

Mass of hydrogen = ?

Moles of water = 4.3mol

Molar Mass of H_2 = 2g mol^{-1}

Step 2: Write a balanced chemical equation for the reaction.

$$2H_2O_{(l)} \longrightarrow 2H_{2(g)} + O_{2(g)}$$

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Step 3: Use the chemical equation to determine the mole ratio of the unknown quantity to the known quantity.

2 moles of H_2O produces H_2 = 2mol

1 mol of H_2O produces H_2 = $\frac{2}{2}$ = 1mol

4.3 moles of H_2O produces H_2 = $1 \times 4.3 = 4.3$mol

Step 4: Convert moles back to mass of the unknown.

Mass of H_2 = Moles of H_2 × Molar mass of H_2

= $4.3\text{mol} \times 2\text{g mol}^{-1}$

= 8.6g

So, the mass of hydrogen produced by the decomposition of water is 8.6g.

Practice Exercise 11:

Calculate the mass of sodium hypochlorite (NaOCl), household bleach, produced by the reaction of 1.75 moles of chlorine with excess sodium hydroxide. The balanced equation is:

$$2\,NaOH_{(aq)} + Cl_{2(g)} \longrightarrow NaOCl_{(aq)} + NaCl_{(aq)} + H_2O_{(\ell)}$$

Example 1.12 (Mass-Volume Conversion)

Nitrogen peroxide (NO_2) is a reddish brown gas and is used in the manufacture of nitric acid. It can be prepared by the oxidation of nitric oxide (NO):

$$2\,NO_{(g)} + O_{2(g)} \longrightarrow 2\,NO_{2(g)}$$

Determine the volume (in litre) of NO_2 produced by 12 g of NO.

Solution:

Step 1: Write all the given data with relevant units.

Volume of NO_2 = ?

Mass of NO = 12g

Molar mass of NO = 30gmol^{-1}

Step 2: Write a balanced chemical equation for the reaction.

$$2\,NO_{(g)} + O_{2(g)} \longrightarrow 2\,NO_{2(g)}$$

Step 3: Convert the given mass of the reactant to moles.

$$\text{Moles of NO} = \frac{\text{Mass of NO}}{\text{Molar mass of NO}} = \frac{12\text{g}}{30\text{g mol}^{-1}} = 0.4\text{ mol}$$

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Step 4: Use the chemical equation to determine the mole ratio of the unknown quantity to the known quantity.

2 mole of NO produces NO_2 = 2mol

1 mole of NO produces NO_2 = $\frac{2}{2}$ = 1mol

0.4 mole of NO produces NO_2 = $1 \times 0.4 = 0.4$mol

Step 5: Convert moles to volume of the unknown.

Volume of NO_2 = Mole of NO_2 × Molar volume of NO_2

= $0.4\text{mol} \times 22.414\text{L mol}^{-1}$

= 8.97L

So, the volume of NO_2 produced by the oxidation of NO is 8.97 L.

Practice Exercise 12:

Methane gas is used as a domestic fuel in the form of natural gas and in the manufacture of urea fertilizer on commercial scale. On combustion, methane gas produces CO_2 and H_2O. Write balanced chemical equation for the reaction. What volume of CO_2 gas is produced when 0.5Kg of methane is burnt in excess oxygen?

1.3 Percentage Composition

The percentage composition is the number of parts by mass of an element in to 100 parts by mass of a compound. Each symbol in the formula of a compound represents the mass of one mole of atoms of the elements. The formula shows mass of one mole of the compound. The chemical formula provides information about the composition of a compound in terms of moles. For example, 1 mole of sodium carbonate, Na_2CO_3 contains 2 moles of sodium, 1 mole of carbon and 3 moles of oxygen atoms. The percentage composition of sodium carbonate tells us the relative masses of Na, C, and O atoms that are present in the compound.

A two-step process is required to calculate the percentage composition of the compound:

i) Calculate the molar mass of a compound.

ii) Divide the total mass of each element in one mole of the compound by the molar mass of the compound and the answer is multiplied by 100.

Mathematically,

$$\text{Percentage composition of an element} = \frac{x\,(\text{Molar mass of an element})}{\text{Molar mass of a compound}} \times 100$$

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Where, x is the number of moles of the element present in one mole of the compound.

Example 1.13

What is the percentage composition of each element in sodium carbonate?

Solution:

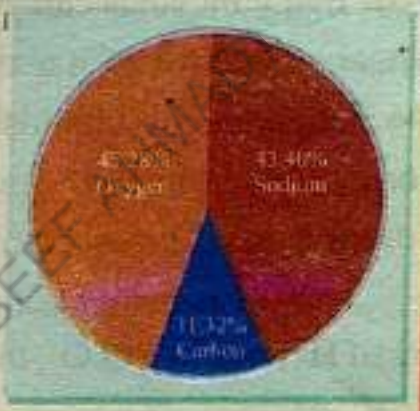
The chemical formula of sodium carbonate is Na_2CO_3. It contains 2 moles of sodium, 1 mole of carbon, and 3 moles of oxygen.

Molar mass of $Na_2CO_3 = 23\times2+1\times12+16\times3 = 106 gmol^{-1}$

$$\%\text{ age of Na} = \frac{2(23gmol^{-1})Na}{106gmol^{-1}} \times 100 = 43.40\%$$

$$\%\text{ age of C} = \frac{1(12gmol^{-1})C}{106gmol^{-1}} \times 100 = 11.32\%$$

$$\%\text{ age of O} = \frac{3(16gmol^{-1})O}{106gmol^{-1}} \times 100 = 45.28\%$$



Remember:

The sum of percentages of all the elements present in the formula should be equal to $100\% \pm 0.02\%$.

Practice Exercise 13:

Calculate the percentage of nitrogen in ammonia (NH_3) and nitric acid (HNO_3).

1.4 Excess and Limiting Reagents

In many chemical processes, the quantities of the reactants used are usually not present in the proportions indicated by the balanced chemical equation. Because the main objective of the reaction is:

i) To produce maximum amount of product, frequently a large amount of inexpensive reactant is supplied to ensure that whole of the mass of expensive reactant is completely converted to the desired product.

ii) To increase the rate of reaction.

At the end of the reaction only one of the reactants may be consumed completely while the other reactants will remain unreacted. The reactant that is completely consumed at the completion of reaction is called limiting reagent (or limiting reactant). The maximum amount of product formed depends upon the

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amount of limiting reactant in the reaction mixture. When this reactant is consumed completely, the reaction stops and no further products are formed. The reactants which are in larger amounts and remain unreacted at the end of the reaction are called "excess reagents" (or excess reactants). The concept of the limiting reagent is analogous to the relationship between the numbers of frames and wheels to make bicycles. Suppose you want to make some bicycles. Each is made from one bicycle frame and two bicycle wheels. You have 70 bicycle frames and 100 bicycle wheels. How many bicycles can you make? The answer is 50. When you run out of bicycle wheels you must stop making bicycles. Cycle wheels are the "limiting reagent" in the language of chemistry, because they limit the number of bicycles. The component (wheels) which produces the fewer number of bicycles is the limiting component while the component (frames) left behind is the excess component.

Now consider a chemical reaction between hydrogen and oxygen. If we react 6g of H_2 with 32g of O_2, then we will get 36g of water as:

$$\underset{6g}{2H_2} + \underset{32g}{O_2} \longrightarrow \underset{36g}{2H_2O}$$

When the reaction between hydrogen and oxygen proceeds to completion, 32g of oxygen consumes completely and the reaction stops and no more products are formed. In this reaction, formation of water is limited by oxygen (O_2) and hydrogen (H_2) is in excess. Out of 6g of hydrogen, 2g remains unreacted. Here H_2 is an excess reactant and O_2 is limiting reactant.

Identification of Limiting Reagent

You can determine the limiting reagent with the help of the following steps:

i) Write the balanced chemical equation.

ii) Convert the given mass of all the reactants to moles.

iii) Calculate the amount of product (in moles or grams, as required) from each reactant with the help of balanced chemical equation.

iv) The reactant that gives the least amount of product is the limiting reagent.

v) Calculate the amount of product formed by limiting reactant.

vi) The reactant that is left over after the completion of reaction is excess reagent.

vii) If you want to find the amount of excess reagent, then subtract the amount used from the starting quantity of the reactant.

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Example 1.14

Natural gas consists primarily of methane (CH_4). The complete combustion of methane (CH_4) gives carbon dioxide (CO_2) and water.

$$CH_{4(g)} + 2O_{2(g)} \xrightarrow{\text{Ignition}} CO_{2(g)} + 2H_2O_{(g)}$$

a) How many grams of CO_2 can be produced when 30g of CH_4 and 50g of O_2 are allowed to combine?

b) How many grams of excess reagent are left unreacted after the completion of reaction?

Solution (a):

Mass of methane (CH_4) = 30g

Mass of oxygen (O_2) = 50g

Mass of CO_2 in grams = ?

Mass of excess reactant left behind in grams = ?

Step 1: Write balanced chemical equation:

$$CH_{4(g)} + 2O_{2(g)} \xrightarrow{\text{Ignition}} CO_{2(g)} + 2H_2O_{(g)}$$

Step 2: Convert the given mass of both the reactants in to their moles:

$$\text{Moles of } CH_4 = \frac{\text{given mass of } CH_4}{\text{molar mass of } CH_4} = \frac{30g}{16gmol^{-1}} = 1.875 \text{ mol}$$

$$\text{Moles of } O_2 = \frac{\text{given mass of } O_2}{\text{molar mass of } O_2} = \frac{50g}{32gmol^{-1}} = 1.563 \text{ mol}$$

Step 3: Calculate the number of moles of product from each reactant:

- Compare the number of moles of CH_4 with those of CO_2

From the balanced chemical equation we know:

1 mole of methane produces CO_2 = 1mol

1.875 mole of methane produces CO_2 = 1×1.875 mol

= 1.875 mol of CO_2

- Compare the number of moles of O_2 with those of CO_2

From the balanced chemical equation we know:

2 moles of oxygen produces CO_2 = 1 mol

1 moles of oxygen produces $CO_2 = \frac{1mol}{2mol}$

1.563 moles of oxygen produces $CO_2 = 0.5 \times 1.563$mol

= 0.7815 moles of CO_2

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- From the above calculation, it is clear that the limiting reactant is O_2 because it produces fewer amounts (moles) of product (CO_2) than CH_4.
- Notice that the limiting reactant is not necessarily the reactant which is present in small amount.

Step 4: Now multiply the moles of CO_2 with its molar mass to get amount of carbon dioxide produced at the end of the reaction.

Mass of CO_2 in grams = Moles of CO_2 × Molar mass of CO_2

$= 0.7815 \text{ moles} \times 44 \text{ g mol}^{-1}$

$= 34.39 \text{ g}$

(b)

Step 5: The quantity of limiting reactant can also be used to calculate the quantity of excess reactant used:

2 moles of O_2 reacts with moles of CH_4 $= 1 \text{ mol}$

1 mole of O_2 reacts with moles of CH_4 $= \frac{1}{2} \text{ mol}$

1.563 moles of O_2 reacts with moles of $CH_4 = \frac{1}{2} \times 1.563 \text{mol}$

$= 0.7815 \text{ mol}$

Step 6: The mass of methane (excess reagent) is equal to the starting quantity minus the amount used during the reaction.

Number of moles of CH_4 = Starting quantity − Quantity use

$= 1.875 \text{mol} - 0.7815 \text{mol}$

$= 1.0935 \text{ mol}$

Mass of CH_4 (excess reagent) = Moles of CH_4 × Molar mass

$= 1.0935 \text{ mol} \times 16 \text{ g mol}^{-1}$

$= 17.5 \text{g}$

Practice Exercise 14:

Which of the following reaction mixtures could produce the greatest amount of product when they combine according to the reaction given below?

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

a) 1 mole of N_2 and 3 moles of H_2

b) 2 mole of N_2 and 3 moles of H_2

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c) 1 mole of N_2 and 5 moles of H_2
d) 3 mole of N_2 and 3 moles of H_2
e) Each produce the same amount of product

Society, Technology and Science

Chemistry is a Quantitative Science

- Stoichiometry is very important in medical sciences and is used to:
  - Determine the glucose level in the blood of diabetics.
  - Determine the steroid and other stimulants in the urine of athletes. Athletes use steroids and other stimulants to enhance performance and increase strength.
  - Determine the cholesterol level in the blood of patients. Cholesterol is a form of fat that's not all bad. But cholesterol can have harmful effects.
- It is helpful in determining the amount of drugs to give a patient. The medicine has no effect when given in small amounts and can cause toxic state or death when given in large amounts. For example, paracetamol is used as a pain killer and to decrease fever. An overdose may result a blood thinning, organ damage and severe liver damage.
- It is the stoichiometry that enables the pilots to determine the distance that a plane will travel before needing to be refueled.

1.5 Percentage Yield

The amount of product either calculated from balanced chemical equation or actually obtained from a reaction is called yield or chemical yield.

The amount of product calculated from balanced chemical equation is called theoretical yield or expected yield while the amount of product actually obtained from a chemical reaction is called actual yield or practical yield. If the actual yield is very low, the final cost can be very high.

In most chemical reactions, the amount of product obtained (actual yield) is always less than theoretical yield due to following reasons:

i) In some reactions the products formed may react further among themselves or with the reactants (Side reactions take place) that give products (by-products) other than the main product.

ii) Many reactions are reversible. They do not go to completion. In these reactions the products formed react to produce the original reactants.

iii) Impurities in the reactants. Suppose you want to prepare chlorine gas from 10g of NaCl that contains some impurities (the substances other than sodium chloride). So you do not know exactly how much pure sodium chloride you have. If you calculate the amount of product from equation, it should be greater than the amount

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of product actually obtained from a reaction. It means that there is not 10g of pur NaCl in the sample.

iv) Moreover, many reactions simply are not complete; some amount of reactan remains unreacted at the end of the reaction.

v) Loss of product during separation, filtration, washing, drying, distillation crystallization etc.

For these and other reasons, it is useful to point out a difference between the theoretical and the actual yields of a chemical reaction and to calculate the percentage yield. Actual yield divided by theoretical yield and the answer multiplied by 100 is called percent yield.

$$\text{Percentage Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100$$

Significance of % age yield:

i) Percentage yield shows efficiency of reaction.

ii) Greater the % age yield, higher will be the efficiency of reaction and vice versa

Example 1.15

Lithium on heating with nitrogen produces lithium nitride:

$$6Li + N_2 \longrightarrow 2Li_3N$$

When 30g of lithium reacts with an excess of nitrogen then how much lithium nitride is produced? If the actual yield of lithium nitride is 38g, what is the percent yield of the reaction?

Solution:

Given mass of Lithium = 30g

Actual yield of Li_3N = 38 g

Mass of lithium nitride produced = ?

Percent yield of the reaction = ?

Before going to calculate percent yield we must know about theoretical yield and actual yield.

i) Theoretical yield:

Equation:

$$\underset{\text{6 moles}}{6Li} + \underset{\text{Excess}}{N_2} \longrightarrow \underset{\text{2 moles}}{2Li_3N}$$

or $\quad 42g \qquad\qquad 70g$

According to the above balanced chemical equation:

42g of lithium produces lithium nitride = 70g

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1g of lithium produces lithium nitride $= \frac{70g}{42g}$

30g of lithium produces lithium nitride $= \frac{70g}{42g} \times 30g$

$= 50g$

So,

Theoretical yield of lithium nitride is 50g.

ii) Actual yield of lithium nitride

Actual yield of lithium nitride is 38g.

iii) Percent yield of lithium nitride

$$\%\text{ yield of lithium nitride} = \frac{\text{Actual yield of lithium nitride}}{\text{Theoretical yield of lithium nitride}} \times 100$$

$$\%\text{ yield of lithium nitride} = \frac{38g}{50g} \times 100$$

$$= 76\%$$

Practice Exercise 15:

Iron sulphide is produced by heating iron with sulphur:

$$Fe_{(s)} + S_{(s)} \longrightarrow FeS_{(s)}$$

When 28kg of iron is combined with excess of sulphur, 40 kg of iron sulphide (FeS) is formed. Calculate the percentage yield of the FeS.

Summary of Facts and Concepts

- The study of quantities of materials consumed and produced in chemical reactions is called Stoichiometry.
- Calculations using balanced equations are called stoichiometric calculations.
- When you know the quantity of one substance in a reaction, you can calculate the quantity of any other substance consumed or created in a reaction.
- The amount of substance that has as many particles as the number of atoms in exactly 12 g of carbon-12 is called mole. Therefore, 12 g of carbon contains 6.02×10^{23} carbon atoms.
- One mole of atoms of any element contains 6.02×10^{23} atoms, regardless of the type of element.
- The number of particles in one mole of a substance is called Avogadro's number. Its value is equal to 6.02×10^{23}.

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- The volume occupied by one mole of an ideal gas at STP is called molar volume and this amount is equal to 22.414 dm^3.
- The limiting reactant is the reactant that is consumed first in a chemical reaction and produces the smallest yield. When this reactant is consumed completely, the reaction stops and no further products are formed. The reactant that is left after the reaction has stopped is known as excess reagent.
- The amount of product which is calculated using the balanced equation is called theoretical yield. The amount of product obtained when the reaction takes place is called actual yield. The ratio of actual yield to theoretical yield is called percent yield. Percent yields may range from a fraction of 1 percent to 100 percent.

Questions and Problems

Q.1: Four answers are given for each question. Select the correct answer.

i) The branch of Chemistry which describes the relationship between the amounts of reactants and products in a balanced chemical equation is called:

(a) Physical chemistry (b) Biochemistry
(c) Stoichiometry (d) Organic chemistry

ii) What are the number of covalent bonds in 68g of H_2S gas?

(a) 3.01×10^{23} (b) 6.02×10^{23}
(c) 2.41×10^{24} (d) 24.1×0^{24}

iii) The mass of O_2 required to burn 0.1 mole of C_2H_5OH is:

(a) 32g (b) 3.2g
(c) 5.6g (d) 9.6g

Equation: $C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$

iv) The volume occupied by 1.4g of N_2 at STP is:

(a) $2.24dm^3$ (b) $22.4dm^3$
(c) $1.12dm^3$ (d) $112dm^3$

v) A beaker contains 9 g of water. The number of hydrogen atoms is:

(a) 6.02×10^{23} (b) 3.01×10^{23}
(c) 6.02×10^{24} (d) 3.01×10^{24}

vi) One mole of diamond chain and one mole of gold ring have same number of:

(a) neutrons (b) protons
(c) electrons (d) atoms

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vii) The largest number of molecules are present in:

(a) 4.8g of C_2H_5OH (b) 3.6g of H_2O

(c) 2.8g of CO (d) 5.4g of N_2O_5

viii) Limiting reactant is that:

(a) Which remains unreacted

(b) Which gives maximum amount of product

(c) Which gives minimum amount of product

(d) Which has low-price

ix) The amount of product obtained practically is called:

(a) Expected yield (b) Theoretical yield

(c) Actual yield (d) fractional yield

x) The reactant which is in larger amount and remains unreacted is called:

(a) Limiting reactant (b) Excess reactant

(c) Expensive reactant (d) Restricting reactant

Q.2: Fill in the blanks with suitable words given in the brackets:

i) A balanced chemical equation has the _____ number of atoms of each element on both sides of the equation. (same / different)

ii) There are _____ molecules in two moles of CH_3OH. (6.02×10^{23} / 12.04×10^{23})

iii) The number of atoms in one mole of neon is _____. (6.02×10^{23} / 12.04×10^{23})

iv) The mass of _____ moles of N_2 is 56g. (one / two)

v) The space occupied by 0.50 moles of Cl_2 at STP is _____. ($11.207dm^3$ / $22.414dm^3$)

vi) The equal volume of all gases at STP has _____ number of molecules but they have _____ masses. (equal / different)

vii) The percentage of nitrogen in N_2O_4 is _____. (30.43% / 69.57%)

viii) 1 mole of Cu_2O has _____ atoms of copper and _____ atoms of oxygen. (6.02×10^{23} / 12.04×10^{23})

ix) Limiting reactant gives _____ amount of product. (Minimum / Maximum)

x) Actual yield is always _____ than theoretical yield. (less / more)

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Q.3: Label the following statements as True or False.

i) Stoichiometry tells you that how to calculate the quantities of substances involved in a reaction.

ii) The stoichiometric calculations can be performed only when Avogadro's law is obeyed.

iii) One atom of Mg is twice in mass as compared to one carbon atom.

iv) The reactants are on the right side of arrow in a chemical equation.

v) Avogadro's number is represented by N_A.

vi) The number of hydrogen atoms in 1.5 moles of H_2S is equal to the number of hydrogen atoms in 1.5 moles of HI.

vii) The molar mass of PO_4^{-3} ion is $95 g mol^{-1}$.

viii) Ionic compounds consist of molecules.

ix) The amount of product calculated from balanced chemical equation is called actual yield.

x) Greater is the percentage yield; higher will be the efficiency of reaction.

Q.4: What is stoichiometry? Why is stoichiometry important? Give some examples.

Q.5: Give the principles and relationships of stoichiometric calculations.

Q.6: How can you solve a Stoichiometry Problem?

Q.7: a) Define and explain mole and Avogadro's number with examples.

b) Define and explain molar mass and molar volume with examples. How can we calculate the molar mass of a substance?

c) What does the mole have in common with the pair, the dozen and the gross?

Q.8: Explain the following:

a) What is the mass, in grams, of one mole of C^{12}? 12g

b) How many carbon atoms are present in a mole of C^{12}? 6.6×10^{23}

c) What is Avogadro's number, and how is it related to the mole?

d) Avogadro's number of atoms of different elements has different masses.

e) Why chemists use mole as a unit? These particles are very small that why they use a unit

f) Which would have a higher mass: a mole of Na atoms or a mole of C atoms?

g) Which would contain more atoms: a mole of Na atoms or a mole of C atoms? they are same

h) How many atoms are present in 1 molar mass of sulphuric acid?

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Q.9. What is percentage composition? How can you calculate the percentage composition of a compound?

Q.10: a) What are limiting and excess reagents? How will you determine them?

b) Can there be a limiting reagent if only one reactant is present?

c) We use expensive reactants in small amounts and inexpensive in large amounts, why?

Q.11: Give an everyday example that illustrates the limiting reagent concept.

Q.12: Define theoretical, actual yield and percentage yield. How do we calculate the percentage yield of a chemical reaction?

Q.13: Actual yield of a reaction is always smaller than that of theoretical yield, why?

Q.14: How much iron is required to produce 162.3g of $FeCl_3$ when chlorine is in excess?

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$

Q.15: Calcium metal reacts with oxygen to form calcium oxide, CaO.

a) Write a balanced equation for the reaction.

b) How many grams of oxygen are required to react with 35g of Ca?

c) How many grams of CaO will be produced?

Q.16: Urea, a fertilizer, can be prepared in the laboratory by the combination of ammonia and carbon dioxide according to the following balanced equation:

$$2NH_{3(g)} + CO_{2(g)} \longrightarrow (NH_2)_2CO_{(aq)} + H_2O_{(l)}$$

(a) Calculate the number of moles of urea formed by the combination of 2.75 moles of ammonia.

(b) Calculate the number of moles of carbon dioxide needed to combine with 2.75 moles of ammonia.

Q.17: Oxygen gas can be prepared by the thermal decomposition of potassium chlorate ($KClO_3$) in the laboratory:

$$2KClO_{3(s)} \longrightarrow 2KCl_{(s)} + 3O_{2(g)}$$

How many grams of oxygen can be prepared from 5 moles of $KClO_3$?

Q.18: Acetylene gas (C_2H_2) is used for welding and for the artificial ripening of fruits. Acetylene gas reacts with hydrogen gas to form ethane gas (C_2H_6). The balanced chemical equation for the reaction is:

$$C_2H_{2(g)} + 2H_{2(g)} \longrightarrow C_2H_{6(g)}$$

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If 10 grams of hydrogen gas reacts with excess acetylene, how many litres of ethane gas can be produced?

Q.19: Octane (C_8H_{18}) is a component of gasoline that burns according to the equation:

$$2C_8H_8 + 20O_2 \longrightarrow 16CO_2 + 8H_2O$$

How many moles of O_2 are needed to burn 2.5mol of C_8H_{18}?

Q.20: Calculate how many moles of oxygen are required to make 270g of aluminum oxide. The balanced equation is:

$$4Al_{(s)} + 3O_{2(g)} \longrightarrow 2Al_2O_{3(s)}$$

Q.21: What are the Molar Masses of the following Compounds?

i) NH_3 ii) H_2O
iii) H_2SO_4 iv) C_2H_5OH
v) NH_4Br

Q.22: How many moles are in each of the following samples?

i) 10g of Ca ii) 100g of Hg
iii) 30g of NaOH iv) 94.5g of HNO_3
v) 402g of $HClO_4$

Q.23: How many grams are in a mole of each of the following substances?

i) N_2 ii) I_2
iii) CaO iv) Kbr
v) $CoCl_2.6H_2O$

Q.24: How many moles are in 25g of each of the following substances?

i) F_2 ii) Ni
iii) CS_2 iv) $C_2F_2Cl_2$
v) $FeSO_4$

Q.25: How many particles are present in 2.5 moles of carbonate ion, CO_3^{2-} in 2×10^3 moles of aspirin ($C_9H_8O_4$)?

Q.26: What is the volume of 1.25 moles of SO_2 and 0.50 moles of argon gas?

Q.27: Butane gas is a fuel and used in pocket lighters. Its molecular formula is C_4H_{10}. Calculate its percentage composition.

Q.28: Calculate the percentage of oxygen in each of the following:

i) SO_2 ii) SiO_2
iii) $(NH_2)_2CO$ iv) SO_4^{2-}
v) $C_6H_{12}O_6$

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Q.29: Hydrogen and bromine react to produce hydrobromic acid:

$H_2 + Br_2 \longrightarrow 2HBr$

How many grams of HBr are formed from reaction of 4.50g of H_2 with 15.75g of Br_2? Which reactant is limiting?

Q.30: How much water can be made from 50g of hydrogen and 50g of oxygen by the reaction?

$2H_2 + O_2 \longrightarrow 2H_2O$

Q.31: When 30g of silica reacts with 12g of carbon, silicon carbide is produced; this is an important ceramic material.

$SiO_2 + 3C \longrightarrow SiC + 2CO$

(Silicon carbide)

Calculate which reactant is limiting and how much silicon carbide is produced.

Q.32: When 227g of NH_4NO_3 decomposes, how much N_2O and H_2O are formed?

$NH_4NO_3 \longrightarrow N_2O + 2H_2O$

Q.33: 4.64g of iron reacts completely with an excess of $CuSO_4$ and gives 5g of copper.

$Fe + CuSO_4 \longrightarrow FeSO_4 + Cu$

a) What is the theoretical yield of the reaction?

b) What is the percentage yield of the reaction?

Q.34: Hydrazine is used as fuel in rockets and can be prepared by the following reaction:

$ClNH_2 + 2NH_3 \longrightarrow N_2H_4 + NH_4Cl$

Hydrazine

145g of hydrazine is produced by the combination of 280g of $ClNH_2$ with an excess of NH_3. Calculate the percentage yield of this reaction.

29

Ans:- Data is given mass of H_2 = 4.5g

given mass of Br_2 = 15.75 g

Molar mass of H_2 = 2 g mol^{-1}

Molar mass of Br_2 = 160 g mol^{-1}

Mass of HBr = ?

limiting reactant = ?

No of moles of H_2 = $\frac{4.5}{2}$ = 2.25 mole

No of moles of Br_2 = $\frac{\text{given mass}}{\text{Molar mass}}$

= $\frac{15.75}{160}$

= 0.084 moles

$1H_2 + 1Br_2 \rightarrow 2HBr$

$\frac{\text{moles of unknown}}{\text{moles of known}} \times$ given moles

$\frac{2}{1} \times 2.25$

2×2.25 = 4.5 moles HBr.

$\frac{\text{moles of unknown}}{\text{moles of known}} \times$ given m

$\frac{2}{1} \times 0.084$

2×0.084

0.168 HBr

Mass of HBr = No of moles of HBr × Molar mass of HBr

= 0.168 × 81 = 15.9 g of HBr

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Chapter # 02

Atomic Structure

Major Concepts

2.1 Discharge Tube Experiment
2.2 Planck's Quantum Theory
2.3 Bohr's Atomic Model
2.4 X-Rays
2.5 Quantum Numbers and Orbitals
2.6 Electronic Configurations

Learing out comes

The students will be able to:

- Summarize Bohr's atomic theory. (Applying)
- Use Bohr's model for calculating radii of orbits. (Understanding)
- Use Bohr's atomic model for calculating energy of electron in a given orbit of hydrogen atom.
- Relate energy equation (for electron) to frequency, wave length, and wave number of radiation emitted or absorbed by electron.
- Explain production, properties, types and uses of X-rays.(Understanding)
- Define photon as a unit of radiation energy.(Remembering)
- Describe the concept of orbitals. (Understanding)
- Explain the significance of quantized energies of electrons.(Applying)
- Distinguish among principal energy levels, energy sub levels, and atomic orbitals. (Understanding)
- Describe the general shapes of s, p, and d-orbitals.(Understanding)
- Relate the discrete line spectrum of hydrogen to energy levels of electrons in the hydrogen atom. (Applying)
- Describe the hydrogen atom using the Quantum theory.(Understanding)
- Use the Auf bau Principle, Pauli Exclusion Principle and Hund's Rule to write the electronic configuration of the elements.(Applying)
- Describes the orbitals of hydrogen atom in order of increasing energy. (Understanding)
- Explain the sequence of filling of electrons in many electron atoms.(Applying)
- Write electronic configuration of atoms.(Applying)

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Introduction

We know that universe is made of matter. All the matter is composed of atoms. It means that everything before you is composed of very small particles which cannot be seen by you. The water we drink, the food we eat, the cloths we wear, the air we breathe, the chair you are sitting on, the trees swaying in the invisible breeze, the rivers, the high mountains you are climbing on, the seashores you are enjoying a lot, the flowers that give you a lot of fragrance, the daily life items we use, the shining stars, even you and I are composed of these tiny particles. The idea that matter is made up of fundamental particles called atoms is known as the atomic theory of matter.

The History of Atomic Theory

The theory of the atom has had a long history. The Greek philosopher Democritus was among the first who described the material world as made up of tiny indivisible particles which he called atoms, derived from the Greek word atomos, meaning "uncutable" or "indivisible". This hypothesis was not based on scientific observations. The idea of Democritus was not accepted by Plato and Aristotle, the Scientist of the same time.

John Dalton
(1766-1844)

In 1803, John Dalton, an English school teacher, chemist, meteorologist, and physicist proposed the first modern theory of the atom which was experimental based. He is best known for his pioneering work in the development of modern atomic theory, and his research into color blindness. He postulated that all matter is made of extremely small particles, called atoms, and that all atoms of a given element are identical, but they are different from atoms of all other elements.

On the basis of Dalton's atomic theory, the atom can be defined as the basic unit of an element that can enter into chemical reaction. In this regard, he is recognized as the father of the atomic theory. However, this theory raised more questions and a series of investigations, in the late 19th century, began to suggest that atoms are made up of even smaller particles which are called subatomic particles. These particles include electron, proton, neutron, positron, neutrino etc. The arrangement of these particles within an atom determines its physical and chemical properties as well as its structure.

2.1 Discharge Tube Experiment

William Crookes, a British physicist, and other scientists designed the discharge tubes which were called the Crookes discharges tubes or cathode rays

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tubes. This discharge tube was later slightly modified by J. J. Thomson. The Crooks tube was used by Crookes in a number of experiments and was later used in experiments leading to the discovery of protons by Gold Stein (1886), X-rays by W. C. Roentgen (1895) and of the electron by J. J. Thomson (1897).

William Crookes
(1832 - 1919)

Construction of Discharge tube

Discharge tube (cathode rays tube) is a thick walled glass tube from which most of the air has been evacuated. It has two met electrodes (negatively charged electrode, cathode and positively charged electrod anode). It is also connected to a vacuum pump to reduce pressure inside the tube. It filled with a gas, air or vapours of a substance under low pressure (10 torr). Th electrodes of this tube are attached to a high voltage battery (5000-10000 V).

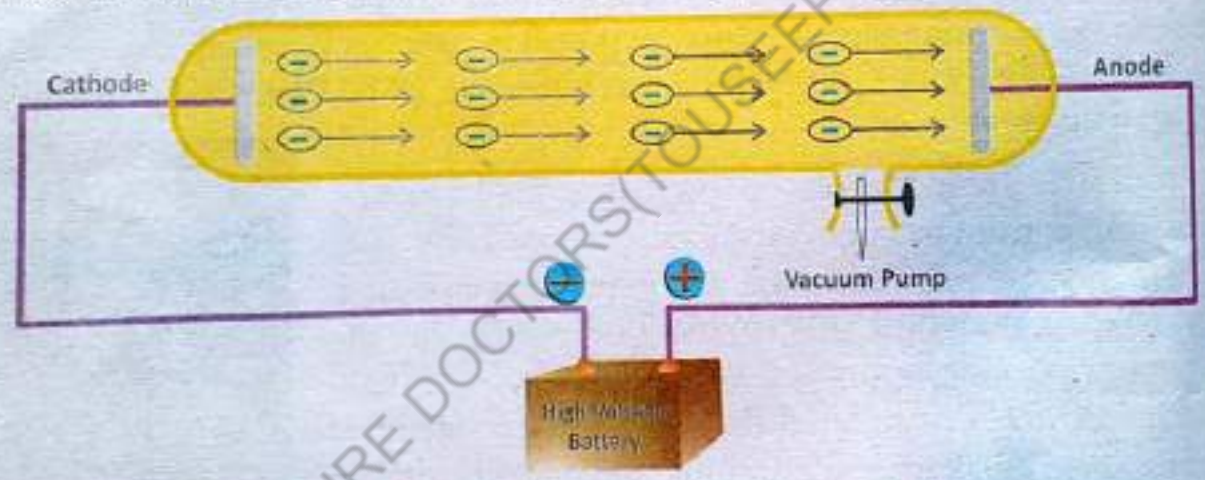

Figure 2.1: Discharge tube (cathode rays tube)

2.1.1 Cathodes rays-Discovery of the Electron

The electric current cannot pass through gases at ordinary pressure. When press inside the tube is reduced and high voltage is applied, then the gas begins to cond electric current by producing a uniform glow inside the tube. The colour of gl depends on the nature of gas and also depends on the material of glass tube. In discharge tube, the helium gas glows with pink colour while neon glows with orange red colour. When pressure is further reduced to 0.01 torr, glow disappe and some invisible rays are produced in the tube, traveling from the negativ charged electrode (the cathode) to the positively charged electrode (the anod They produce glow on the zinc sulphide (a substance that produces a visible li when struck by a charged particle) coated glass wall of tube opposite to the catho These rays are emitted from cathode, hence called cathode rays.

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Crookes and many other scientists conducted numerous experiments with discharge tubes to study the passage of electric discharge through gases during 1870s. From experiments, Crookes concluded that cathode rays were actually some sort of particles which possess momentum and kinetic energy, but other researches belived cathode rays were form of light.

In 1891, George Stoney, an Irish scientist, proposed that electricity was made of negatively charged particles called electrons.

Electrons were first discovered by a British scientist, Joseph John Thomson (J.J. Thomson) in 1897, who was more interested in electricity than atomic structure. He modified Crookes tube and calculated the charge-to-mass ratio for the electron by studying the degree of deflections of cathode rays in different strengths of electric and magnetic fields. He concluded that electrons are much smaller and lighter than atoms. He found that the mass of one of these particles was almost 2,000 times lighter than a hydrogen atom. Thomson suggested that atoms were divisible, and that the electrons were the basic constituent of matter.

Joseph John Thomson (1856-1940)

J. J. Thomson got Nobel Prize in 1906 in physics for discovery of electron and for his work on the conduction of electricity in gases.

Properties of Cathode Rays

i) In 1869, Hittorf observed that cathode rays produce shadow, when an opaque object is placed in their way. This proves that they travel in straight line in the absence of electrical and magnetic field.

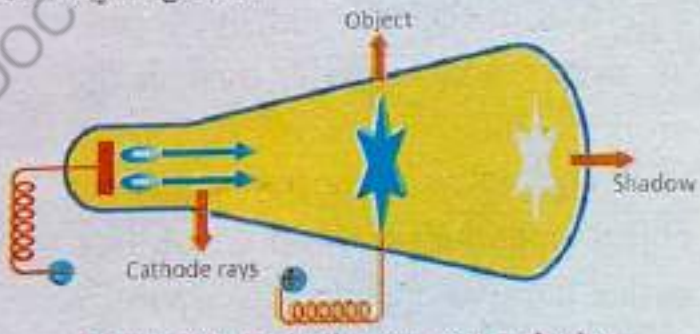

Figure 2.2: Cathode rays cast a shadow

ii) In 1870, William Crookes demonstrated that cathode rays can rotate a small thin mica paddle wheel placed in their way. It proves that cathode rays consist of particles having definite mass, velocity and momentum.

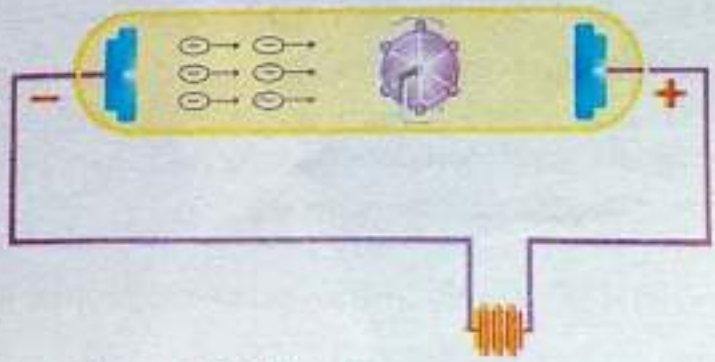

Figure 2.3: Cathode rays rotate a small paddle wheel

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iii) In 1895, J. Perrin demonstrated that cathode rays bend towards positive plate of electric field. This shows that, they are negatively charged.

iv) In 1895, Wilhelm Roentgen demonstrated that cathode rays produce x-rays on striking with heavy metals anode like tungsten.

v) In 1897, J. J. Thomson demonstrated that if they are passed through magnetic field, the magnet neither attracts nor repels the particles but causes them to move in curved path perpendicular to the line drawn between the poles of the magnet.

vi) Thomson also determined e/m ratio of electrons. He found that the e/m value of electrons remained same, no matter which gas is used in the discharge tube.

vii) They increase the temperature of object (platinum foil) on which they strike. It proves that they have particle nature.

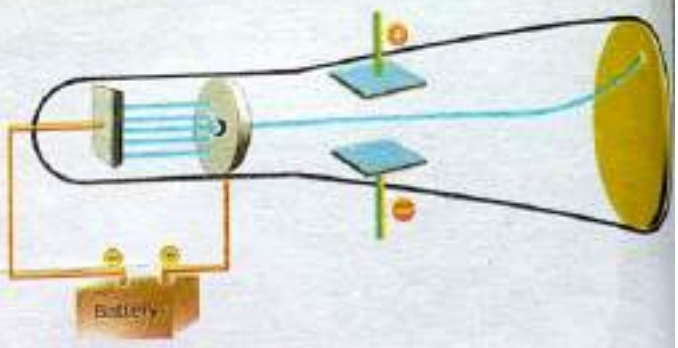

Figure 2.4: Deflection of cathode rays in the presence of electric field

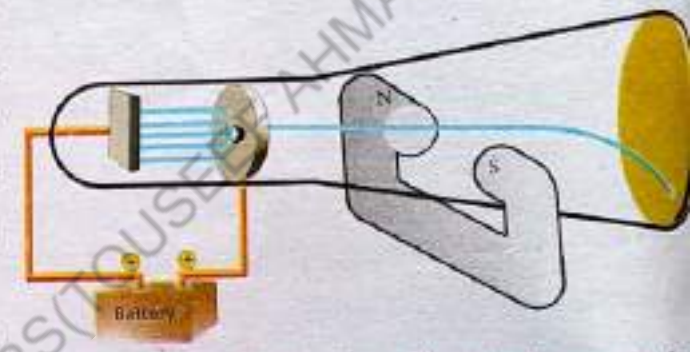

Figure 2.5: Deflection of cathode rays in the presence of magnetic field

Interesting Information

Nowadays cathode rays are used as advertisement neon signs. Television picture tube and monitors of computer are also cathode rays tube. The television and monitor pictures result due to fluorescence on the television and monitor screens coated with certain fluorescent materials.

viii) They produce glow when ZnS is placed in their way.

ix) They can ionize a gas.

x) They can pass through a very thin sheet of metal.

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xi) They produce fogging effect on photographic plates.

xii) They can cause a chemical change because of their reducing power.

Measurement of e/m Ratio of Electron

In 1897, J. J. Thomson measured e/m ratio of electron. A discharge tube used for this purpose is shown here.

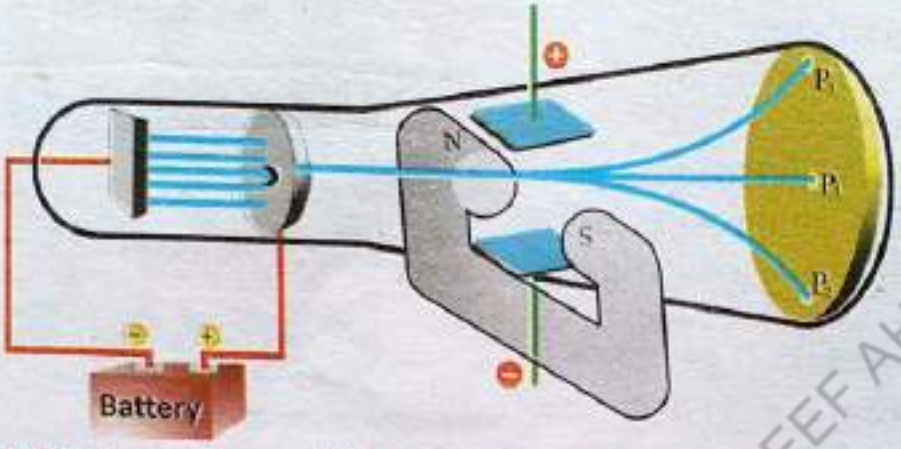
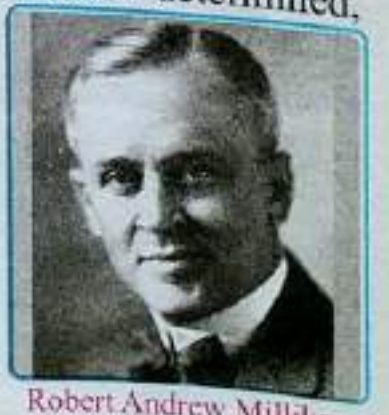


Figure 2.6: Discharge tube used for measurement of charge/mass ratio of an electron

In this experiment, a beam of cathode rays is passed through slits of anode. Then cathode rays (electrons) are allowed to pass through electric and magnetic fields. In the absence of any field, the beam of electrons gives bright luminous spot at P_1. When only magnetic field is applied, the beam of rays (electrons) strikes at point P_2. When only electric field is applied, the electrons strike at point P_3. When both the fields are applied simultaneously, then electrons again strike at point P_1. Hence by comparing the strengths of both the fields and with the help of mathematical calculations, J. J. Thomson determined the e/m ratio of electrons. Its calculated value is equal to 1.7588×10^{11} coulomb kg^{-1}, this means that 1kg of electrons have 1.7588×10^{11} coulombs charges.

After the charge-to-mass ratio for the electron had been determined, additional experiments were necessary to determine the value of its charge so that the mass should be calculated.



Robert Andrew Millikan (1868-1953)

Measurement of Charge on Electron (Millikan's Oil Drop Experiments)

In 1909, Robert Millikan working at the University of Chicago, determined the charge on electrons by oil drop experiment.

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Construction

The apparatus consists of:

i) A metallic chamber having two parts:

(a) The upper part: It has an oil atomizer (sprayer).

(b) The lower part: It has two electrodes A and B. These electrodes are used to produce electric field in the space between the electrodes.

ii) There is a telescope in lower part to observe oil droplets.

iii) X-rays are used in the lower part of chamber for ionization of gas.

iv) An arc lamp is used to illuminate the space between the electrodes.

v) A **vacuum pump:** It is used to adjust the pressure inside the chamber.

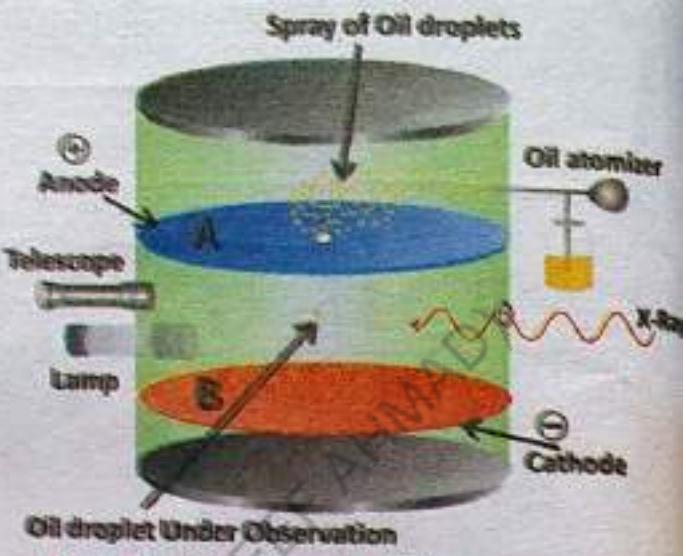

Figure 2.7: Millikan's oil drop experiment to measure the charge of an electron

Working

A fine spray of oil droplets is produced by atomizer in the space above the two plates (electrodes). A few droplets enter the space between the two electrodes through the small hole. The hole is closed at once; the arc lamp is turned on to illuminate the space between the electrodes. Without applying electric field, the droplet falls under the force of gravity. The velocity of fall of the droplet is measured. The velocity of droplet is directly proportional to its weight.

$$V_1 \propto mg \quad \ldots\ldots\ldots\ldots \text{(i)}$$

Now the air present in the chamber is ionized by a beam of x-rays. In this process, electrons are produced. The oil droplets take up electrons and become charged. The electrodes A and B are then connected to a battery. In this way an electric field is produced. Now droplet is under two forces (force of gravity and electric force). The charged droplets move up wards against the force of gravity with velocity V_2, when electric force is greater than that of gravitational force.

$$V_2 \propto H.e - mg \quad \ldots\ldots\ldots\ldots \text{(ii)}$$

By dividing eq. (i) by (ii), we have:

$$\frac{V_1}{V_2} = \frac{mg}{H.e - mg} \quad \ldots\ldots\ldots\ldots \text{(iii)}$$

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By re-arranging eq. (iii), we have:

$$e = \frac{V_2 \times mg + mg}{V_1 \times H} \quad \text{.....(iv)}$$

By putting the values of velocities (V_1 and V_2), force of gravity (g), mass of droplet (m) and electric strength (H), the charge (e) on oil droplet is calculated.

By changing the strength of electric field (H), Millikan and his coworkers found that the charge on each droplet is different. The smallest charge which they found was 1.59×10^{-19} coulomb. This was the charge of one electron. This value is very close to the recent value of 1.602176×10^{-19} coulomb. With this value and the charge-to-mass ratio determined by Thomson, Millikan was able to calculate the mass of the electron as 9.11×10^{-31} kg.

Keep in Mind:

Millikan and his coworker measured hundreds of droplets and found that the charge on them was always a simple multiple of a basic unit, 1.59×10^{-19} coulomb. From this they concluded that the charge on an electron was numerically 1.59×10^{-19} coulomb.

Calculation of Mass of Electron

The mass of an electron can be calculated from the values of charge-to-mass ratio (e/m) and charge on electron (e).

e/m value of electron $= 1.758820 \times 10^{11}$ coulomb kg^{-1}

Charge of electron $= 1.602176 \times 10^{-19}$ coulomb / electron

Mass of an electron $= ?$

Mass of an electron $= \frac{e}{e/m}$

By putting the values, we have:

$$\text{Mass of electron} = \frac{1.602176 \times 10^{-19} C / \text{electron}}{1.758820 \times 10^{11} C/kg}$$

$$= 9.10938 \times 10^{-31} kg/\text{electron}$$

$$= 9.10938 \times 10^{-28} g/\text{electron}$$

2.1.2 Discovery of Proton

In 1886, Eugen Goldstein took a discharge tube in which cathode was perforated. He observed that another type of rays was also travelling from anode to cathode along with cathode rays in the discharge tube. He observed a glow behind the cathode. This was due to striking of rays on the glass wall after passing through the canals or holes of cathode. Hence these rays were passing through the canals of

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cathode; therefore, they were called canal rays. Later on these rays were called positive rays.

These rays do not emit from anode. They are positive ions which are formed due to striking of fast moving cathode rays (electrons) with gas molecules in the discharge tube. As a result of this, they eject electrons from the atoms of gas molecules.

Eugen Goldstein
(1850-1930)

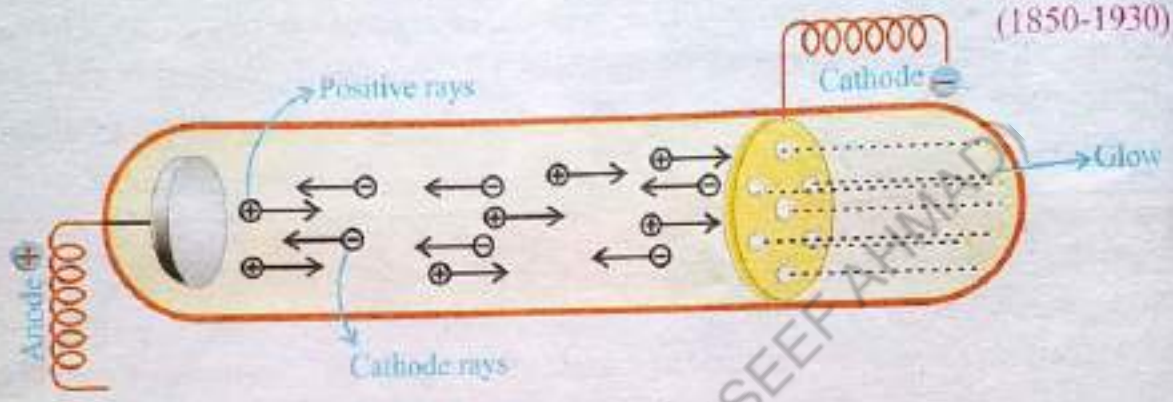

Figure 2.8: Canal rays

Properties of Canal Rays

Properties of canal rays are:

i) They move in straight line towards cathode.

ii) The behaviour of these particles in the magnetic or electrical field is opposite to that observed for electron or cathode rays.

iii) Charge to mass (e/m) ratio is much smaller than that of electron. Charge to mass ratio depends upon the nature of gas present in the cathode rays tube. Heavier the gas, smaller the e/m ratio.

iv) The lightest and simplest positive ions (canal rays) were produced from hydrogen gas and were called protons. The name proton was given by Rutherford.

v) The mass of canal rays is never less than that of proton.

vi) Mass of proton (positive particle) is 1.00727amu or 1.6727×10^{-27} Kg.

vii) Charge of proton is 1.6022×10^{-19} coulombs.

Interesting Information:

The elements can be identified by the number of protons (atomic number) in their atoms. The atoms which have same number of protons are the atoms of the same element and the atoms which have different number of protons are the atoms of different elements.

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2.1.3 Discovery of Neutron

In 1920, Rutherford predicted that some neutral particles having mass equal to proton must present in the nucleus of an atom. Because he observed that hydrogen atom has only one proton and that the helium atom has two protons. Therefore the mass of helium must be two times greater than that of hydrogen atom (electrons are much lighter than protons, their masses can be ignored). In reality, it was four times the mass of hydrogen atom. The added mass was due to another subatomic particle found in the nucleus, the neutron. But he failed to discover this sub atomic particle.

In 1932, a British scientist, Sir James Chadwick discovered neutron by artificial radioactivity and was awarded noble prize in Physics in 1935.

Sir James Chadwick
(1891-1974)

Chadwick bombarded a thin sheet of Beryllium by α-particles. He found that some highly penetrating radiations which have mass slightly greater than that of protons were produced. These radiations were called neutrons because the charge detector showed them to be neutral. Their nuclear reaction is:

$$^{4}_{2}He + ^{9}_{4}Be \longrightarrow ^{12}_{6}C + ^{1}_{0}n$$

Keep in mind:

- The neutron has about the same mass as the proton, but it has no electric charge. Any object that has no net electric charge is said to be electrically neutral, and that is where the neutron got its name.
- In a neutral atom the number of electrons is equal to the number of protons but the number of neutrons in a nucleus is not directly related to the numbers of protons and electrons.

Properties of Neutrons

Properties of neutrons are:

i) They are neutral particles.
ii) They cannot ionize gases.
iii) They are highly penetrating particles.
iv) They can knock protons out from paraffin, water, paper etc.
v) The mass of neutron is nearly equal to proton i.e. 1.00867 amu.
vi) Free neutron decays into a proton, electron and neutrino.

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$$^{1}_{0}n \longrightarrow {}^{1}_{+1}P + {}^{0}_{-1}e + {}^{0}_{0}n$$

vii) When neutrons travel with energy 1-20 MeV, they are called fast neutrons. When they travel with kinetic energy 1-10 eV, then they are called slow neutrons. Slow neutrons are more effective than fast neutrons.

viii) When they are used as a projectile, they can carry out nuclear reactions. For example:

a) $^{1}_{0}n + {}^{14}_{7}N \longrightarrow {}^{11}_{5}B + {}^{4}_{2}He$

b) $^{1}_{0}n + {}^{65}_{29}Cu \longrightarrow {}^{66}_{29}Cu + h\nu$

$$^{66}_{29}Cu \longrightarrow {}^{66}_{30}Zn + {}^{0}_{-1}e$$

Uses:

They are used in the treatment of cancer, in nuclear fission and to produce radioactive elements.

Keep in mind:

The number of neutrons in the nuclei of atoms of the same element can be different. If two atoms have the same number of protons and different numbers of neutrons, they are atoms of the same element. However, they have different masses because of the different numbers of neutrons. Such atoms are said to be isotopes of each other. Each isotope of an element is usually identified by its mass number (A), which is defined as the sum of the number of protons and the number of neutrons in the nucleus of an atom.

Table 2.1: Properties of Three Fundamental Particles

Particle	Symbol	Charge in Coulomb	Mass in amu	Mass in grams	Relative Charge	Mass Relative to Electron
Electron	$^{0}_{0}e^{-}$	-1.6022×10^{-19}	0.00054	9.10938×10^{-28}	−1	----
Proton	$^{1}_{1}P^{+}$	$+1.6022\times10^{-19}$	1.00727	1.67262×10^{-24}	+1	1836
Neutron	$^{1}_{0}n^{0}$	0	1.00867	1.67493×10^{-24}	0	1842

Example 2.1

How can you calculate the mass of proton relative to electron?

Solution:

Mass of proton $= 1.67262\times10^{-24}$ g

Mass of electron $= 9.10938\times10^{-28}$ g

Mass of proton relative to electron = ?

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$$\text{Mass of proton relative to electron} = \frac{\text{Mass of proton}}{\text{Mass of electron}}$$
$$= \frac{1.67262 \times 10^{-24}\text{g}}{9.10938 \times 10^{-28}\text{g}}$$
$$= 1836$$

Practice Exercise 1:
How can you calculate the mass of neutron relative to electron?

2.2 Discovery of Nucleus and Rutherford's Atomic Model

2.2.1 Discovery of Nucleus

Rutherford
(1871 - 1937)

In 1911, the New Zealand physicist Lord Ernest Rutherford in England performed an experiment. He bombarded α-particles on thin gold foil of 0.00004cm. The α-particles were emitted from a radioactive metal (polonium or radium). During experiment, he observed that, most of the α-particles (more than 99%) passed through the metal foil directly without any deflection, but less than 1% (about 1 of every 20,000) was deflected at different angles. Some of these were deflected backward. They were detected by photographic plate coated by ZnS.

Results of this experiment were put forward by Rutherford in the form of Rutherford's Atomic Model.

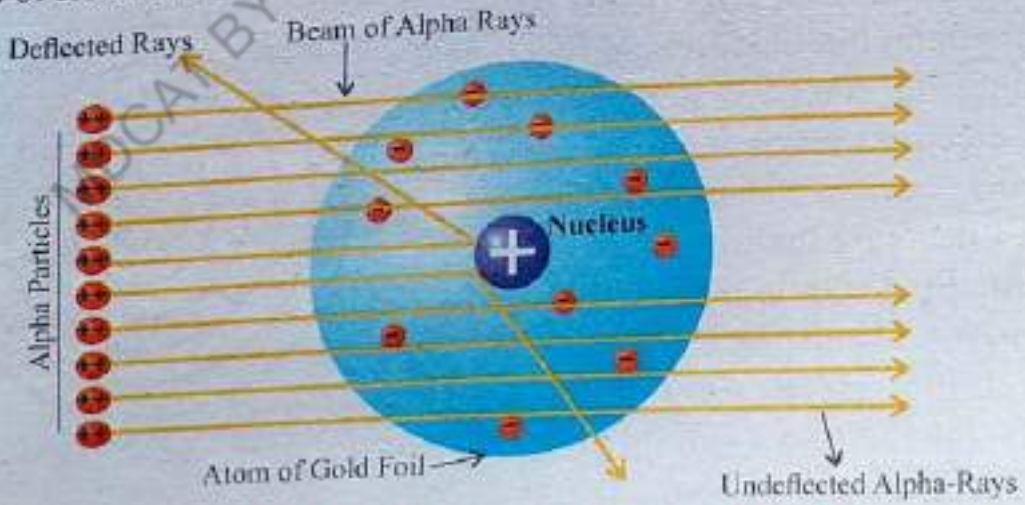

Figure 2.9: Few Alpha Rays are deflected which shows the presence of small positively charged nucleus

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2.2.2. Rutherford's Atomic Model

Main points of Rutherford's atomic model are as follows:

i) Most of the volume of an atom is empty space in which electrons move around the nucleus.

ii) Nearly all the mass of an atom is present in the central part, called 'nucleus'.

iii) The size of nucleus is very small as compared to the size of atom.

iv) Nucleus of an atom has positive charge. This is indicated by wide range deflection of few-particles.

v) Positive charge on nucleus is equal the number of protons in the nucleus.

vi) The nucleus is surrounded by a number of negatively charged particles, called electrons.

vii) The number of electrons (negatively charged particles) is equal to number of protons (positively charged particles) in an atom. Therefore, atom as a whole is neutral.

viii) The electrons are in constant motion around the nucleus at large distances with very high velocities like plants around the sun in their orbits.

ix) Protons and neutrons are present in the nucleus and they are called nucleons.

x) There is electrostatic force of attraction between protons and electrons.

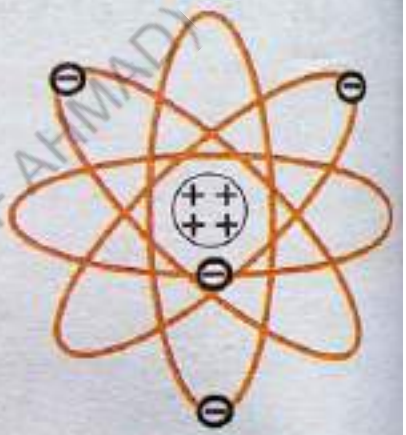

Figure 2.10:
Rutherford's Atomic Model

Defects in Rutherford's Model

Rutherford's atomic model was similar to our solar system. It has following defects

i) Rutherford's atomic model was based on the laws of gravitation and motion which could applied to the neutral bodies like plants but not to the charged particles like electrons and protons.

ii) According to Maxwell's theory, charge particles i.e. electrons revolving in an orbit must radiate (emit) energy. Therefore energy of electron must decrease and it will go into spiral motion. So finally it should fall into the nucleus. Thus the atom would collapse.

iii) If revolving electrons release energy continuously, then they should produce a continuous spectrum but in actual practice, line spectrum in produced by an atom.

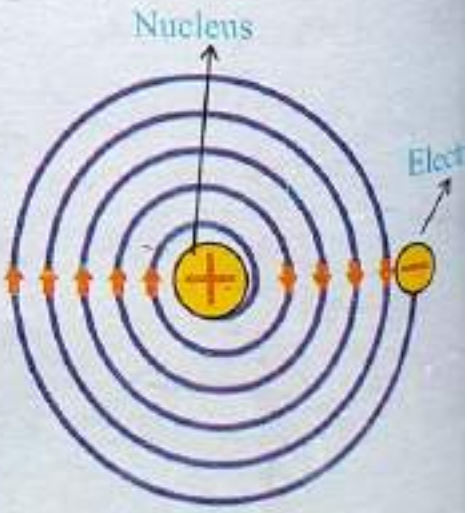

Figure 2.11:
Spiral Motion of Electron

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2.3 Planck's Quantum Theory

Max Planck
(1858–1947)

In 1900, a German physicist Max Planck gave quantum theory of radiation. He studied the emission and absorption of radiations which are obtained from hot objects at different temperatures. Planck said that atoms and molecules could emit or absorb energy only in discrete quantities (small bundles). Planck gave the name quantum (meaning "fixed amount") to the smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiations.

Main points of this theory are:

i) Energy is not emitted or absorbed continuously in radiation form.

ii) Energy is emitted or absorbed in packets. Each packet is called quantum. In case of light, the wave packets are often called photon.

iii) Energy of each quantum is directly proportional to the frequency of radiation.

$E \propto \nu$ or

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

Where, E is Energy of quantum, ν (nu) is Frequency and h is Planck's constant. Its value is 6.6262×10^{-34} J. sec.

iv) An atom or molecule can emit or absorb either quantum of energy ($h\nu$) or any integral multiple of a quantum ($nh\nu$)

$E = nh\nu$ ..... (ii)

Where, $n = 1, 2, 3, 4, \ldots \infty$

The energy can be emitted as $h\nu$, $2h\nu$, $3h\nu$ and so forth but never as $1.5h\nu$, $2.6h\nu$, $4.3h\nu$ or any other fractional value of $h\nu$.

In 1918 Planck was awarded the Nobel Prize in Physics for his work on the quantum theory.

Frequency

The number of waves passing through a point in one second is called frequency. It is shown by ν. Its units are hertz or cycles/sec. It is measured by spectrometer.

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

Where c is velocity of light that is 3×10^8 m/sec and λ (Lambda) is wavelength.

Note that ν is directly proportional to c and inversely proportional to λ.

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Wavelength

The distance between two adjacent crests or troughs of wave is called wavelength. It is shown by λ (Lambda). Its units are m, nm or A°.

Table 2.2: Units of Wavelength for Electromagnetic Radiations

Unit	Symbol	Wavelength(m)	Radiation Type
Meter	M	1	Radio waves
Centimeter	cm	10^{-2}	Microwave
Millimeter	mm	10^{-3}	Infrared
Micrometer	μm	10^{-6}	Infrared
Nanometer	nm	10^{-9}	Ultraviolet, Visible
Angstrom	A°	10^{-10}	X-ray
Picometer	pm	10^{-12}	Gamma ray, Cosmic ray

Amplitude

The vertical distance from the midline of a wave to the crest or trough is called amplitude.

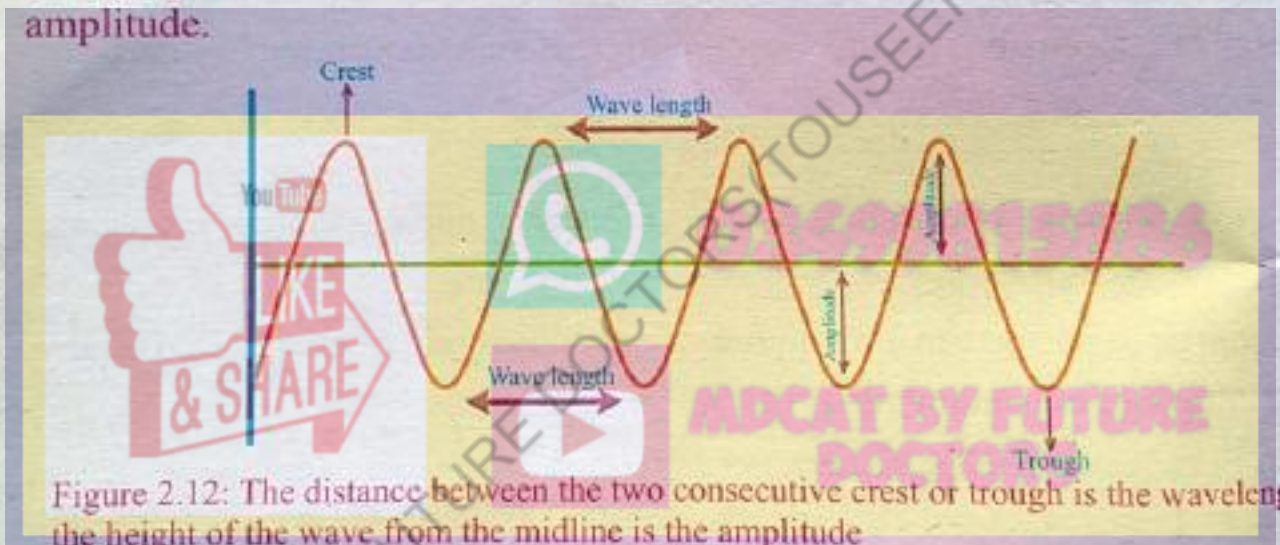

Figure 2.12: The distance between the two consecutive crest or trough is the wavelength and the height of the wave from the midline is the amplitude

Wavenumber

The number of waves present in one centimeter distance is called wave number. It is the inverse of wave length. It is shown by $\bar{\nu}$ (nu bar).

As,

$$\nu = c\bar{\nu}$$

Hence,

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

Its unit is cm^{-1}. Its SI unit is m^{-1}.

Atomic Number

The number of protons in an atom is called atomic number. It is also called proton number. It is shown by Z. Atoms are neutral because they have the same number

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electrons and protons. The number of electrons in a neutral atom is also equal to the atomic number.

Relation between Frequency and Wavelength

The frequency is related to the wavelength of the photon as:

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

By putting the value of ν in equation (i), we get

$$E = h \cdot \frac{c}{\lambda} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (iii)$$

So, energy of photon is directly proportional to velocity of light and inversely proportional to wavelength.

Relation between Wavelength and Wavenumber

Wave number ($\bar{\nu}$) is the inverse of wavelength.

$$\bar{\nu} = \frac{1}{\lambda} \quad \text{or}$$

$$E = hc\bar{\nu} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (iv)$$

So, energy of photon is directly proportional to wave number.

2.4 Bohr's Atomic Model

In 1913, the Danish scientist Neil Henrik David Bohr explained spectrum of hydrogen atom. He received the Noble Prize in Physics in 1922 for this work. Bohr's theory was based on Planck's quantum theory.

Neil Henrik David Bohr
(1885–1962)

The main points of this theory are:

i) Electrons revolve around the nucleus in the circular path called orbits or energy levels or shells. Electrons in each orbit have a definite amount of energy and are at a fixed distance from the nucleus.

ii) Electron does not radiate (emit or absorb) energy as long as it is revolving in its orbit.

iii) The electron absorbs energy when it jumps from lower orbit to higher orbit and it loses energy of one photon when it jumps from higher to lower orbit.

iv) When an electron jumps from one orbit to another orbit, there will be a change in energy. For example when an electron jumps from first orbit (E_1) to second orbit (E_2), then the energy change is given by Planck's equation,

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$E_2 - E_1 = h\nu$ or

$\Delta E = E_2 - E_1 = h\nu$

Where,

ΔE is change in energy, 'h' is Planck's constant and 'ν' is frequency

The angular momentum (mvr) of an electron revolving around the nucleus is quantized. It is an integral multiple of Planck's constant (nh) divided by 2π.

$$\text{Angular momentum (mvr)} = \frac{nh}{2\pi}$$

Where,

n = 1, 2, 3, 4, ... ∞. It represents number of orbits.

'm' is mass of electron, 'v' is velocity of electron and 'r' is radius of orbit.

By putting the values 1, 2, 3, etc. of n, we have:

$$\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{3\pi}, \text{ etc.}$$

There is no fractional value for $\frac{nh}{2\pi}$.

An atom has only a limited number of permitted energy levels, and an electron is bound to remain in one of these energy levels (orbits) and not in between them. This is analogous to steps on a staircase. Where you are on a staircase is bound to stand on any one of the steps and you cannot stand between two adjacent steps.

2.4.1 Derivation of Radius, Energy, Frequency, Wavelength, and Wavenumber:

Calculation of Radius of Orbit

Consider an electron of charge *e* and mass *m* is revolving around the nucleus with velocity v at a distance r. Nucleus has total charge Ze^+, where Z is the proton number and e^+ is the charge on proton. There are two forces acting on electron:

i) The attractive or centripetal force

ii) The repulsive or centrifugal force.

The centrifugal force which takes electron away from nucleus is:

$$F = \frac{mv^2}{r} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

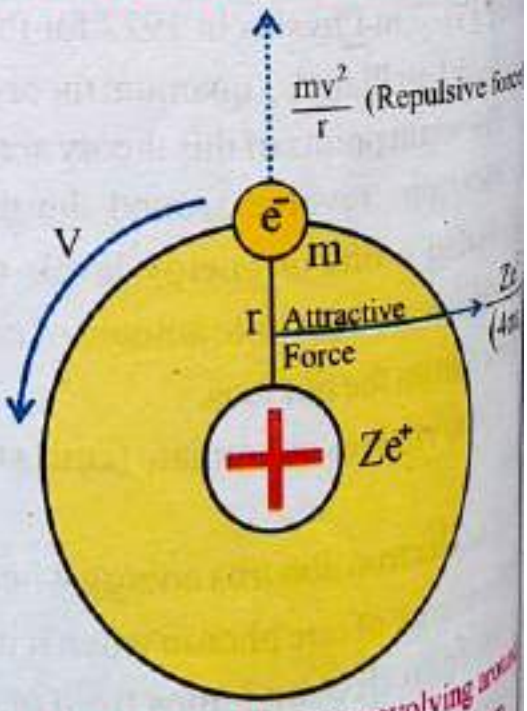

Figure 2.13: Electron revolving around the nucleus in the hydrogen atom

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The electrostatic force of attraction (centripetal force) between electron and nucleus is:

$$F \propto \frac{Ze.e}{r^2} \quad \text{or}$$

$$F \propto \frac{Ze^2}{r^2} \quad \text{or}$$

$$F = \frac{Ze^2}{(4\pi\varepsilon_o)r^2} \quad \ldots\ldots\ldots\ldots\ldots \text{(ii)}$$

Where, $4\pi\varepsilon_o$ is proportionality constant. ε_o (Epsilon not) is vacuum permittivity. Its value is equal to $8.8545\times10^{-12}\ C^2J^{-1}m^{-1}$.

In order to keep the electron in its orbit, the centrifugal force must be equal to centripetal force.

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\varepsilon_o r^2}$$

$$v^2 = \frac{Ze^2r}{4\pi\varepsilon_o r^2 m}$$

$$v^2 = \frac{Ze^2}{4\pi\varepsilon_o rm} \quad \ldots\ldots\ldots\ldots\ldots \text{(iii)}$$

According to Bohr's atomic model, the angular momentum of an electron is:

$$mvr = \frac{nh}{2\pi} \quad \text{or}$$

$$v = \frac{nh}{2\pi mr}$$

By taking the square, we have:

$$v^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \quad \ldots\ldots\ldots\ldots\ldots \text{(iv)}$$

By putting the value of v^2 from eq. (iv) in eq. (iii), we get

$$\frac{Ze^2}{4\pi\varepsilon_o r\, m} = \frac{n^2h^2}{4\pi^2m^2r^2}$$

Now, we can calculate the value of r,

$$\frac{r^2}{r} = \frac{n^2h^2}{4\pi^2m^2} \times \frac{4\pi\varepsilon_o m}{Ze^2}$$

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$$r = \frac{n^2 h^2 \varepsilon_o}{\pi m Z e^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (v)$$

Equation (v) can be written as,

$$r = \frac{h^2 \varepsilon_o}{\pi m e^2} \times \frac{n^2}{Z}$$

This equation tells us that, the radius, r of an atom is directly proportional to the square of number of orbit (n). So higher orbit has larger radius. In the eq. (v), the factor $\frac{h^2 \varepsilon_o}{\pi m e^2}$ is constant. Its value is $0.529 A^\circ$ (52.9pm or 5.29×10^{-10} m). It is denoted by a_o (Bohr's radius).

Hence,

$$a_o = \frac{h^2 \varepsilon_o}{\pi m e^2}$$

Therefore,

$$r = \frac{n^2}{Z} \times a^\circ \quad \text{or} \quad r \propto \frac{n^2}{Z}$$

The above relationship shows that,

i) The radius of an atom is directly proportional to the square of number of orbits.

ii) The radius (r) of an atom is inversely proportional to the atomic numb (number of proton) Z.

Example 2.2

Calculate the radius of first four orbits of electron of hydrogen atom.

Solution:

The equation to calculate the radius of an orbit is:

$$r = \frac{n^2}{Z} \times a_o$$

The atomic number (Z) of hydrogen atom = 1

Bohr's radius (Value of a_o) $= 0.529 A^\circ$

By putting the values of n as 1, 2, 3, 4 in the equation we get:

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Radius of first orbit of hydrogen atom $(r_1) = \frac{(1)^2}{1} \times 0.529\text{Å} = 0.529\text{Å}$

Radius of second orbit of hydrogen atom $(r_2) = \frac{(2)^2}{1} \times 0.529\text{Å} = 2.11\text{Å}$

Radius of third orbit of hydrogen atom $(r_3) = \frac{(3)^2}{1} \times 0.529\text{Å} = 4.75\text{Å}$

Radius of fourth orbit of hydrogen atom $(r_4) = \frac{(4)^2}{1} \times 0.529\text{Å} = 8.46\text{Å}$

It is cleared from the above data that distance between orbits goes on increasing from lower to higher orbits. Hence,

$$r_2 - r_1 < r_3 - r_2 < r_4 - r_3 < \ldots$$

i) The second orbit is four times away from the nucleus than that of first orbit.

ii) The third orbit is nine times away and fourth orbit is sixteen times away from the nucleus.

Calculation of Energy of an Electron (in H-atom)

Total energy of an electron revolving around the nucleus is the sum of its kinetic and potential energies.

$$E = K.E + P.E \quad \ldots\ldots\ldots\ldots \quad (vi)$$

$$K.E = \frac{1}{2} mv^2 \quad \ldots\ldots\ldots\ldots \quad (vii)$$

Potential energy is the amount of total work done for bringing the electron from infinity to distance r.

$$P.E = -\frac{Ze^2}{4\pi\varepsilon_o r} \quad \ldots\ldots\ldots\ldots \quad (viii)$$

In equation (viii) minus sign shows that the energy is released (or decreased) due to attraction between electron and nucleus.

By putting the values of equation (vii) and (viii) in equation (vi), we have

$$E = \left(\frac{1}{2} mv^2\right) + \left(-\frac{Ze^2}{4\pi\varepsilon_o r}\right)$$

$$E = \frac{1}{2} mv^2 - \frac{Ze^2}{4\pi\varepsilon_o r} \quad \ldots\ldots\ldots\ldots \quad (ix)$$

By putting the value of v^2 from equation (iii) in equation (ix), we have

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$$E = \frac{1}{2} m.\frac{Ze^2}{4\pi\varepsilon_o r m} - \frac{Ze^2}{4\pi\varepsilon_o r} \quad \text{or}$$

$$E = \frac{Ze^2}{8\pi\varepsilon_o r} - \frac{Ze^2}{4\pi\varepsilon_o r}$$

$\because v^2 = \frac{Ze^2}{4\pi\varepsilon_o m}$

By taking LCM we have,

$$E = \frac{Ze^2 - 2Ze^2}{8\pi\varepsilon_o r}$$

$$E = -\frac{Ze^2}{8\pi\varepsilon_o r} \quad \text{.....(x)}$$

By putting the value of r in equation (x), we have

$$E = -\frac{Ze^2}{8\pi\varepsilon_o \frac{n^2h^2\varepsilon_o}{\pi mZe^2}} \quad \text{or}$$

$\because r = \frac{n^2h^2\varepsilon_o}{\pi mZe^2}$

$$E = -\frac{Ze^2}{8\pi\varepsilon_o} \times \frac{\pi mZe^2}{n^2h^2\varepsilon_o} \quad \text{or}$$

$$E = -\frac{Z^2e^4m}{8\varepsilon_o^2 n^2h^2} \quad \text{or}$$

$$E = -\frac{e^4m}{8\varepsilon_o^2h^2} \times \frac{Z^2}{n^2} \quad \text{.....(xi)}$$

In the above equation when constants (8, e, m, ε_o, h) are replaced by constant K, the equation (xi) will become:

$$E = -K \times \frac{Z^2}{n^2}$$

$\because \frac{e^4m}{8\varepsilon_o^2h^2} = K$

Energy of electron in the nth orbit is:

$$E_n = -K \times \frac{Z^2}{n^2}$$

The value of K is 2.18×10^{-18} J, hence the equation can be written as:

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

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Where,

E_n = energy of the electron in the nth orbit.

Z = Atomic number of the element.

n = Principal quantum number. It shows number of shells.

In the above equation:

i) The negative sign shows that the electron is bound to the nucleus in the orbit by the electrostatic force of attraction.

ii) As the value of *n* increases, the value of *E* should decrease but due to presence of negative sign in the formula, the actual value of energy will increase.

Example 2.3

Calculate the energies of electron of first four shells (orbits) of hydrogen atom.

Solution:

The equation to calculate the energy of electron in a shell is:

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

Atomic number of Hydrogen = Z = 1

Energy of electron in the 1st orbit (n = 1) = E_1 = $-2.18\times10^{-18}\ J \times \frac{(1)^2}{(1)^2}$

= $-2.18\times10^{-18}J$

Energy of electron in the 2nd orbit (n = 2) = E_2 = $-2.18\times10^{-18}J \times \frac{(1)^2}{(2)^2}$

= $-0.54\times10^{-18}J$

Energy of electron in the 3rd orbit (n = 3) = E_3 = $-2.18\times10^{-18}J \times \frac{(1)^2}{(3)^2}$

= $-0.24\times10^{-18}J$

Energy of electron in the 4th orbit (n = 4) = E_4 = $-2.18\times10^{-18}J \times \frac{(1)^2}{(4)^2}$

= $-0.14\times10^{-18}J$

We can see that energy of the electron increases when number of orbits increases.

$$E_1 < E_2 < E_3 < E_4$$

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Calculation of Energy Difference (ΔE):

ΔE is the amount of energy released or absorbed when an electron jumps from one orbit to another orbit.

$$\Delta E = E_2 - E_1 \quad \ldots\ldots\ldots\ldots\ldots \text{(xiii)}$$

According to Bohr's equation, the energy of electron in an orbit is:

$$E_n = -K \times \frac{Z^2}{n^2}$$

The energy of electron in any lower orbit (n_1) is:

$$E_1 = -K \times \frac{Z^2}{n_1^2}$$

The energy of electron in any higher orbit (n_2) is:

$$E_2 = -K \times \frac{Z^2}{n_2^2}$$

By putting the values of E_1 and E_2 in equation (xiii) we have:

$$\Delta E = \left(-K \times \frac{Z^2}{n_2^2}\right) - \left(-K \times \frac{Z^2}{n_1^2}\right) \quad \text{or}$$

$$\Delta E = \left(-K \times \frac{Z^2}{n_2^2} + K \times \frac{Z^2}{n_1^2}\right) \quad \text{or}$$

$$\Delta E = K \times \frac{Z^2}{n_1^2} - K \times \frac{Z^2}{n_2^2} \quad \text{or}$$

$$\Delta E = KZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \ldots\ldots\ldots\ldots\ldots \text{(xiv)}$$

For Hydrogen atom $Z = 1$, hence,

$$\Delta E = K\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

We know that the value of $K = 2.8 \times 10^{-18}$ J, therefore,

$$\Delta E = 2.18 \times 10^{-18}\ \text{J}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Example 2.4

Calculate the amount of energy needed when an electron jumps from second orbit ($n = 2$) to fourth orbit ($n = 4$) of hydrogen atom.

Solution:

Amount of energy needed = ΔE = ?

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The value of constant $K = 2.18 \times 10^{-18} J$

The equation to calculate the ΔE is:

$$\Delta E = 2.18 \times 10^{-18} J[\frac{1}{n_1^2} - \frac{1}{n_2^2}]$$

By putting the values we have,

$$\Delta E = 2.18 \times 10^{-18} J[\frac{1}{(2)^2} - \frac{1}{(4)^2}]$$

$$= 2.18 \times 10^{-18} J[\frac{1}{4} - \frac{1}{16}]$$

$$= 2.18 \times 10^{-18} J[\frac{4-1}{16}]$$

$$= 2.18 \times 10^{-18} J[\frac{3}{16}]$$

$$= 2.18 \times 10^{-18} J \times 0.1875$$

$$= 4.087 \times 10^{-19} J$$

Calculation of Frequency

According to Planck's theory, the energy change (ΔE) is directly proportional to the frequency of radiation.

$$\Delta E = h\nu$$

We know that,

$$\Delta E = KZ^2[\frac{1}{n_1^2} - \frac{1}{n_2^2}]$$

Therefore,

$$h\nu = KZ^2[\frac{1}{n_1^2} - \frac{1}{n_2^2}] \quad \text{or}$$

$$\nu = \frac{KZ^2}{h}[\frac{1}{n_1^2} - \frac{1}{n_2^2}] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (xv)$$

Unit of frequency is cycles per second or Hertz.

Calculation of Wave number

We know from Planck's theory that,

$$\nu = c\bar{\nu}$$

We also know that,

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$$\nu = \frac{KZ^2}{h}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

By putting the value of ν in the above equation, we get,

$$c\bar{\nu} = \frac{KZ^2}{h}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\bar{\nu} = \frac{KZ^2}{hc}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \text{or}$$

$$\bar{\nu} = \frac{K}{hc} \cdot Z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

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The constants $\frac{K}{hc}$ can be replaced by constant R_∞ (Rydberg's constant) a

$$\bar{\nu} = R_\infty Z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

For hydrogen atom Z=1, therefore,

$$\bar{\nu} = R_\infty\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Unit of wave number is m^{-1}.

The value of R_∞ is $1.09678 \times 10^7 m^{-1}$.

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Usefulness of Bohr's Atomic Model

i) It is useful to calculate the radius of an orbit.
ii) It is useful to calculate the energy of an electron.
iii) It helped to calculate the ΔE, frequency and wavenumber.
iv) It explained the spectra of hydrogen and hydrogen like atoms (ions) such He^{1+}, Li^{2+} and Be^{3+}.
v) It explained the stability of atoms and their ionization energy.
vi) It shows the orbits in hydrogen atom.

2.4.2 Spectrum of Hydrogen Atom

Hydrogen spectrum is an important example of atomic spectrum. When hydro gas is filled in discharge tube at very low pressure and then high voltage is appli bluish light is emitted from discharge tube. If this light is passed thro

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spectrometer, several sharp lines of different wavelengths are produced. They are called spectral lines. These spectral lines are classified into five groups called spectral series. These series were named after their discoverers.

i) Lyman Series
ii) Balmer Series
iii) Paschen Series
iv) Bracket Series
v) Pfund Series

The first four series were discovered before Bohr's atomic model.

Origin of Hydrogen Spectrum

We know that, there is one electron in hydrogen atom which is present in first orbit at room temperature. This is the lowest energy state or ground state of this electron. When hydrogen gas is heated, its electron jumps from lower energy state i.e. $n_1 = 1$ to higher energy state or excited state i.e. $n_2 = 2, 3, 4, 5, 6, 7$ etc. depending upon the amount of energy absorbed. Now the electron will become unstable. When it comes back from higher energy levels i.e. $n_2 = 2, 3, 4, 5, 6, 7$ etc. to lower energy level i.e. $n_1 = 1$, the same amount of energy is released in the form of spectral lines (bright lines). The series of spectral lines are as follows:

Lyman Series

When an electron jumps from a higher energy level n_2 (i.e. 2, 3, 4, 5, 6 etc.) to lower energy level n_1 (i.e. 1), a series of spectral lines are produced. This series of lines appears in the UV region of the spectrum.

Balmer Series:

When an electron jumps from a higher energy level n_2 (i.e. 3, 4, 5, 6 etc.) to a lower energy level n_1 (i.e. 2), a series of spectral lines are produced. This series appears in the visible region.

Paschen Series:

When an electron jumps from a higher energy level n_2 (i.e. 4, 5, 6, etc.) to a lower energy level n_1 (i.e. 3), a series of spectral lines are produced. This series appears in the infra-red region.

Bracket Series:

When an electron jumps from a higher energy level n_2 (i.e. 5, 6, etc.) to a lower energy level n_1 (i.e. 4), a series of spectral lines are produced. This series appears in infra-red region.

Pfund Series:

When an electron jumps from a higher energy level n_2 (i.e. 6, 7, etc.) to a lower

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energy level n_1 (i.e. 5), a series of spectral lines are produced, called pfund se
This series appears in infra-red region.

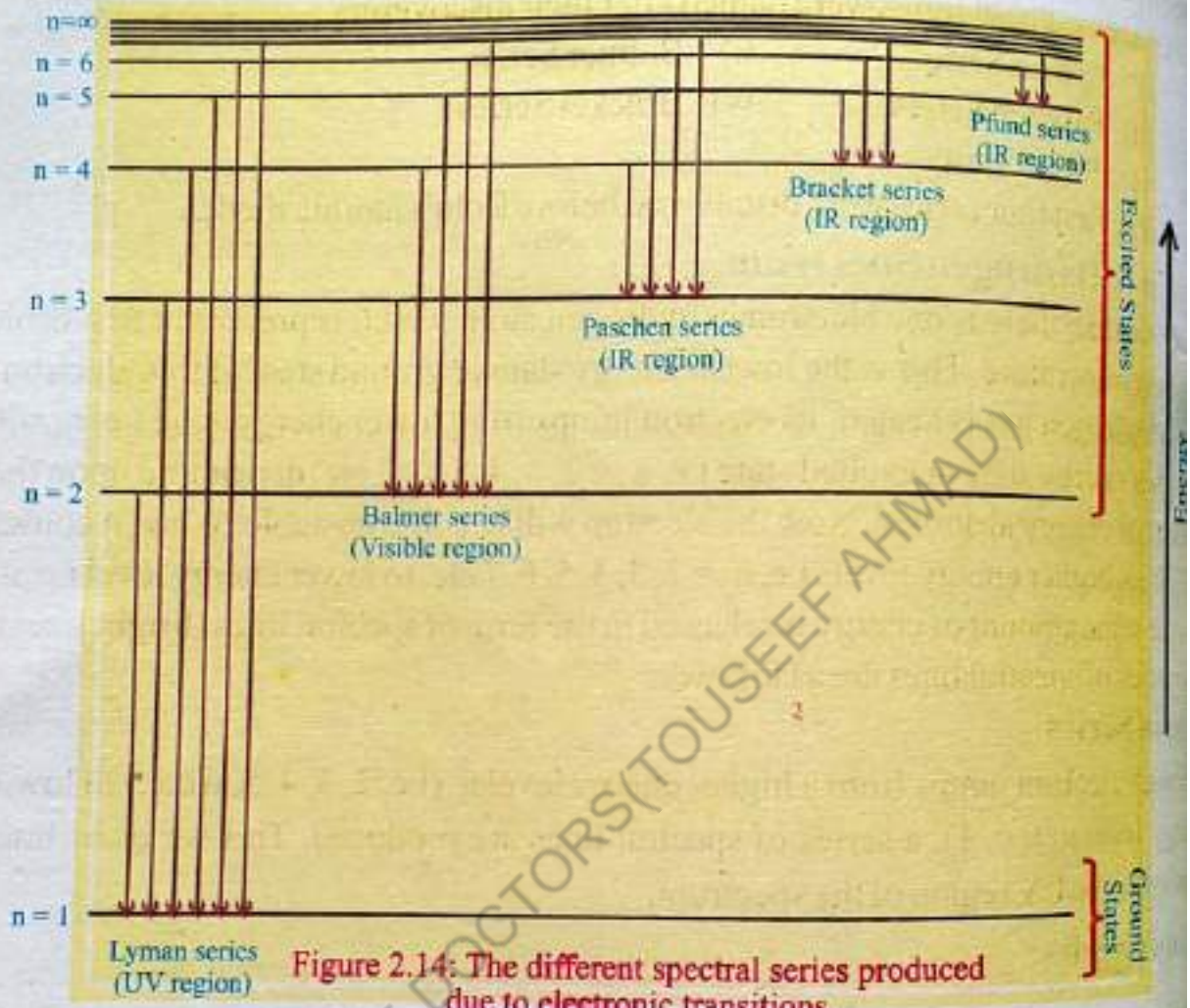

Figure 2.14: The different spectral series produced due to electronic transitions

Table 2.3: The Series of Spectral Lines

Series of Spectral Lines	Jumping of Electrons		Region	Wavelength (A°)
	n_2	n_1		
Lyman	2, 3, 4, 5 ... ∞	1	Ultraviolet	920 – 1200
Balmer	3, 4, 5, 6 ... ∞	2	Visible	400 – 6500
Paschen	4, 5, 6, 7 ... ∞	3	Infra-red	9500 – 18750
Bracket	5, 6, 7, 8 ... ∞	4	Infra-red	19450 – 40500
Pfund	6, 7, 8, 9 ... ∞	5	Infra-red	38000 – 75000

2.4.3 Defects of Bohr's Atomic Model

It failed to explain:

i) The spectrum of more complicated (multi electron) atoms.
ii) The objections raised on Rutherford's atomic model.
iii) Zeeman Effect (splitting of spectral lines into still thinner and closely spa

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lines in the presence of magnetic field) and Stark effect (splitting of spectral lines into still thinner and closely spaced lines in the presence of electric field).

iv) Motion of electrons in three dimensional spaces. It explains motion of electrons in circular orbits.

Reason of Zeeman and Stark Effects

When a strong electric and magnetic field is applied, the spectral line of sodium atom splits up into further thinner closely spaced lines. The number of closely spaced lines is corresponding to the number of values of magnetic quantum number. Hence each line represents an orbital.

Society, Technology and Science

Firework Displays:

Firework is a device containing explosives and combustible chemicals that generate coloured lights, smoke and noise and are used for display and celebrations. There is a lot of chemistry involved in fireworks. The colours that appear in fireworks are due to the presence of different metal compounds. The metal compounds emit characteristic colours when heated. When an element is heated, its electron jumps from lower energy state (ground state) to higher energy state (excited state). Now the electron will become unstable. When it comes back from higher energy state to lower energy state, the energy is released as light of specific colours. The colour of light depends on the element (metal) to be heated. For example, lithium compounds ($LiCO_3$) create **red** colours; sodium compounds (NaCl) create **yellow** colours, barium compounds ($BaCl_2$) create **green** colours, copper compounds ($CuCl_2$) create **blue-green** colours, potassium compounds (KNO_3) create **violet-pink** colours, rubidium compounds ($RbNO_3$) create **violet-red** colours, and aluminum, beryllium or magnesium powders create bright white colours in fireworks.

2.5 X-Rays

2.5.1 Production, Properties and Uses

Production of X-Rays

In 1895, a German Scientist Wilhelm Conrad Roentgen discovered that when fast moving electrons collide with heavy metal anode in the discharge tube, some unknown very high energy rays are produced. They were called X-rays. X-rays are electromagnetic radiations. They are not visible and are of higher frequency and shorter

Wilhelm Conrad Roentgen (1845-1923)

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wavelength than visible light. Roentgen was awarded the Nobel Prize in 190

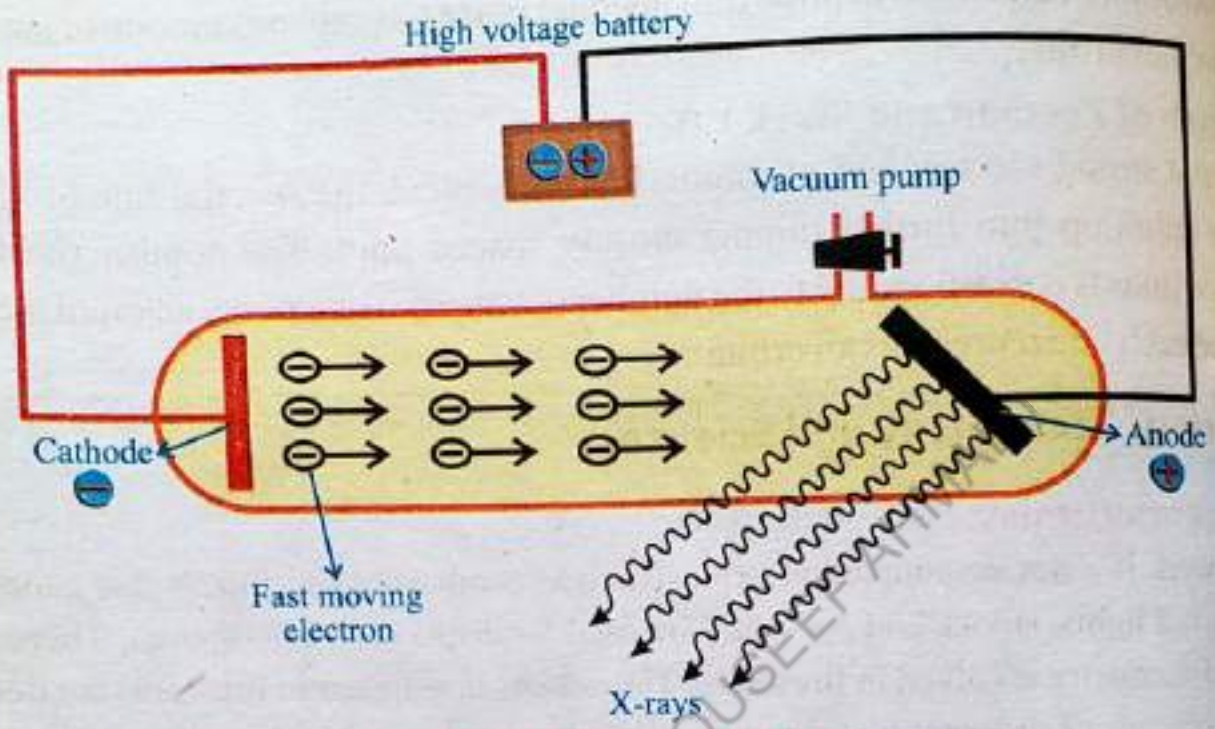

Figure 2.15: Production of X-rays

Properties of X-Rays

i) They are electromagnetic radiations and cannot be deflected by electric a magnetic fields. Thus, travel in straight lines.

ii) They are invisible to the eyes but can affect the photographic plate.

iii) They have very high penetrating power through matter. This is because th rays are used to study the interior of the objects.

iv) They can damage genes, chromosomes and other cell components wh passing through living tissues.

v) They are highly energetic rays. Therefore, they ionize gases.

vi) They have high frequency. Their frequency depends upon the materia anode. Due to this reason, different elements produce X-rays of differ wavelengths.

vii) The frequency of X-rays increases with atomic number of the element used anode in the X-rays tube.

viii) Frequency of X-rays ranges from 3×10^{16} to 3×10^{19} Hz.

ix) The wavelength of X-rays range from 0.01 to 10nm.

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Keep in Mind:

- Electromagnetic radiation is a form of energy that travels through space at a constant speed of $3\times10^{8} ms^{-1}$ and can exhibit wavelike or particle-like properties.
- The wavelength of electromagnetic radiation determines the amount of energy carried by one of its photons. The shorter the wavelength, the greater the energy of each photon.
- The frequency and energy of electromagnetic radiations are inversely proportional to its wavelength.

Uses of X-Rays

i) X-rays diffraction techniques are used in the study of crystal structure because X-ray wave lengths are comparable to the atomic separation distances in solids (about 0.1nm).

ii) X-rays are used as a diagnostic tool in medicine and as a treatment for certain forms of cancer.

iii) X-ray images are used for the detection of dental cavities, bone fractures and to differentiate between hard tissues (bone) and soft tissues (blood and muscles). X-rays pass through soft body tissue but are stopped by harder tissue.

v) When high energy X-ray photons are passed through gases, they increase the temperature of atoms and molecules and electrons are ejected. These free electrons may ionize additional neutral species. Through this process, reactive ions and free radicals are formed, leading to further chemical reactions.

) X-rays are used for quick examination to check the luggage of passengers at rports.

i) In industry, X-ray images are used to detect flaws (i.e. cracks) non-estructively in metal castings that are invisible.

ii) X-ray microscopes are capable of magnifying X-ray absorption images so as resolve features on scales as small as about 40nm.

iii) The presence of coatings and varnishes, and the compositions of glasses, rcelain, and enamels are revealed through X-ray analysis.

) X-rays are used to study chemical reactions on surfaces, the electronic ructures of semiconductors and magnetic materials, and the structure and function proteins and biological macromolecules.

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2.5.2 Types of X-Rays

When an electron in the cathode rays collides with metal anode (target), it can knock an electron from an inner shell (K-shell) of the atom. The knocked electron will have to leave the atom because there is no vacancy in the higher energy levels. This produces a vacancy (hole) in the inner shell. The electron from higher energy levels (i.e. L-shell or M-shell) then drops down to fill the vacancy, emitting a high energy photon of X-rays. L-shell to K-shell jump produces a K_α X-ray. M-shell to K-shell jump produces a K_β X-ray. The energy of the K_β transitions is higher than that of the K_α transitions.

Figure 2.16: Types of X-rays

2.6 Quantum Numbers and Orbitals

After the failure of Bohr's atomic model, in 1926, an Austrian Physicist Erwin Schrodinger, an expert on the theory of vibrations and standing waves, set up a wave equation for hydrogen atom. This is called Quantum Mechanical Model of an atom. Schrodinger was awarded noble prize in Physics in 1933 for setting up this equation. The main problem before Schrodinger was where we would find the electron if we were to look for it. According to Schrodinger:

Erwin Schrodinger (1887–1961)

Although the position of an electron cannot be found exactly, the probability of finding the electron at a particular position in space can be found.

The concept of electron density gives the probability that an electron will be found in a particular region of an atom. The most likely place to find an electron is where the density is greatest. An atomic orbital is the wave function of an electron in an atom. The wave function and its square, ψ^2 (Psi) have values for locations about a nucleus. Keep in mind that the electron density is large near the nucleus for hydrogen atom, indicating that the electron is most likely to be found in this region. The electron density decreases rapidly as the distance from the nucleus increases.

An atomic orbital, therefore, has a characteristic energy, as well as

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characteristic distribution of electron density (characteristic shape). The Schrodinger equation works nicely for the simple hydrogen. The Schrodinger equation cannot be solved exactly for a multi-electron atom.

The numbers which completely describe the behavior (energy, size, shape, position and orientation or arrangement) of orbitals are called quantum numbers.

These numbers are derived from the mathematical solution of the Schrödinger equation for the hydrogen atom. They are called the principal quantum number, the azimuthal quantum number, and the magnetic quantum number. These quantum numbers are used to describe the energy level of the orbital and the three dimensional shape of the region in space occupied by a given electron. A fourth quantum number–the spin quantum number refers to a magnetic property of electrons called spin.

2.6.1 Principal Quantum Number

Number which determines the distance of electron from the nucleus (size) and its energy is called principal quantum number. It is shown by n. Its values are non-zero, positive integers up to infinity.

$n = 1, 2, 3, 4, 5, 6, 7, \ldots \infty$.

The values of 'n' can also be shown by letters K, L, M, N, O, P and Q respectively.

Table 2.4: Total Number of Orbitals and Electrons in a Shell.

Value of n	1	2	3	4	5	6	7
Letter used	K	L	M	N	O	P	Q
Total number of orbitals	1	4	9	16	25	36	49
Maximum number of electrons	2	8	18	32	50	72	98

Keep in Mind:

- Total number of orbitals in the given shell can be calculated by taking square of principal quantum number (n^2) of that shell.
- The maximum number of electrons in a shell can be calculated by $2n^2$ formula.
- Greater the value of 'n' greater will be the distance of electron from the nucleus and greater will be the size of an atom and vice versa.
- Greater the value of 'n' greater will be the energy of electron and vice versa.
- In the case of the hydrogen atom or single-electron atomic ions, such as He^{1+} and Li^{2+}, n is the only quantum number determining the energy. For other atoms, the energy also depends to a slight extent on the azimuthal quantum number.

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2.6.2 Azimuthal Quantum Number

Numbers which determine the shape of an orbital and the energy of an electron, to to lesser extent than 'n' is called azimuthal quantum number. It is shown by *l*. Its values are always positive and in small whole numbers. Its values range from 0, 1, 2 and 3 ------- up to n – 1. If

n = 1 then *l* = (1 – 1) = 0	It shows 1s	Subshell
n = 2 then *l* = (2 – 1) = 0,1	It shows 2s, 2p	Subshells
n = 3 then *l* = (3 – 1) = 0,1,2	It shows 3s, 3p,3d	Subshells
n = 4 then *l* = (4 – 1) = 0,1,2,3	It shows 4s, 4p,4d,4f	Subshells

The co-efficient of subshells 1,2,3,4 show the number of shells to which the subshells belong.

Table 2.5: Total Number of Orbitals and Electrons in a subshell

Value of *l*	0	1	2	3	4	5
Letter used	s	p	d	f	g	h
Total number of orbitals	1	3	5	7	9	11
Total number of electrons	2	6	10	14	18	22

Total number of orbitals in a subshell can be determined by the formula, 2*l*+ and the total number of electrons in a subshell can be calculated by the formula $2(2l+1)$.

Each shell consists of one or more subshells or sub-levels. The number of subshells in a shell is equal to the value of n. For example in the first shell (n = 1) there is only one subshell which corresponds to *l* = 0. There are two subshells (*l* = 0, 1) in the second shell (n = 2), three (*l* = 0, 1, 2) in third shell (n = 3) and so on. Each subshell is assigned an azimuthal quantum number (*l*).

Different subshells are usually represented by letter rather than by numbers following the order s, p, d, f and g. (Historically, the letters s, p, d, and f originate from the use of the words sharp, principal, diffuse and fundamental which have definite meanings in spectroscopy.) After f, successive subshells are designated alphabetically: g, h and so on. The values of azimuthal quantum number also tell about shape of orbitals (s-orbital has spherical shape, p has dumbbell shape, d has sausage and f has complicated shape).

2.6.3 Magnetic Quantum Number

Number which explains the orientation (arrangement) of the orbital in space is called magnetic or orientation quantum number. It also shows magnetic properties

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of electrons. It is shown by m. Its values are changing from positive to negative through zero. Within a subshell, the value of m depends on the value of the angular momentum quantum number, l. For a certain value of l, there are (2l + 1) integral values of m, as follows:

$+l, (+l-1), \ldots 0 \ldots (-l+1), -l$ or

$m = 0, \pm 1, \pm 2, \ldots$ or

$m = +2, +1, 0, -1, -2$

For s subshell, $l = 0$, then $m = 0$

There is only one orbital in the s-subshell. This orbital has same orientation along x, y and z-axis.

For p subshell, $l = 1$, then $m = [(2 \times 1) + 1]$ or three values of m, namely, +1, 0, -1.

It means there are three different orbitals (px, py and pz) in the p subshell. The orbitals have the same shape but different orientations in space. In addition, all orbitals of a given subshell have the same energy.

For d subshell, $l = 2$, then $m = [(2 \times 2) + 1]$ or five values of m, namely, +2, +1, 0, -1, -2. It means there are five different orbitals (dxy, dyz, dxz, dx^2-y^2 and dz^2) in the d subshell. All of these orbitals have same energy.

2.6.4 Spin quantum number

An electron spins around its own axis, much in a similar way as earth spins around its own axis while revolving around the sun. Number which shows the direction of spin of an electron around its own axis is called spin quantum number. It is also called spin magnetic quantum number. It is denoted by m_s where, the subscript s stands for spin. It has two values +1/2 and −1/2. The spins are also designated as ↑ or ↓. The upward arrow and the value +1/2 show that the electron spins in anticlockwise direction. The downward arrow and the value −1/2 show that the electron spins in clockwise direction.

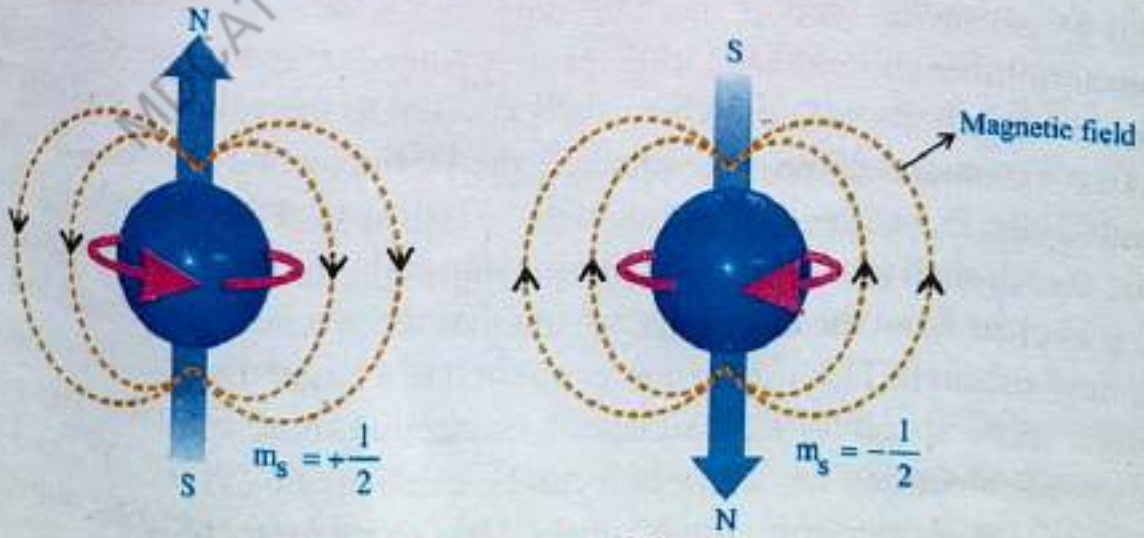

Figure 2.17: Spinning of electrons

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Table 2.6: Relationship Between Shells, Subshells and Orbitals

Principal Quantum Number (n)	Azimuthal Quantum Number (*l*)	Subshell Designation	Magnetic Quantum Number (m)	Number of Orbitals in the subshell	Total Number of Orbitals in the Shell	Total Number of Electrons in a Shell
1	0	1s	0	1	1	2
2	0	2s	0	1	4	8
	1	2p	1,0, –1	3		
3	0	3s	0	1	9	18
	1	3p	1,0, –1	3		
	2	3d	2,1,0, –1, –2	5		
4	0	4s	0	1	16	32
	1	4p	1,0, –1	3		
	2	4d	2,1,0,–1,–2	5		
	3	4f	3,2,1,0,–1,–2,–3	7		

Shells, Subshells and Orbitals

A group of subshells with the same value of principal quantum number (n) is known as a shell. It is also recognized as orbit or energy level. The shells are designated by the letters K, L, M, N, O, P, and Q, counting from the nucleus outwards. The principal quantum numbers (n) are 1,2,3,4,5,6,7, ... respectively. The larger the value of 'n' the higher is the energy of the shell and vice versa. The number of electrons in a shell is calculated by $2n^2$ formula. First shell (n = 1) has 2, second shell (n = 2) has 8 and third shell (n = 3) has 18 electrons.

Each principal energy level (shell) is divided into sub-levels. They are also known as subshells. One or more orbitals which have same values of principal quantum number (n) and azimuthal quantum number (*l*) are called subshells. The number of subshells within a given shell is equal to the value of n. Thus, the first shell (n = 1) consists of only one subshell, the 1s; the second shell (n = 2) consists of two subshells, 2s and 2p; the third shell (n = 3) consists of three subshells, 3s, 3p and 3d; the fourth shell (n = 4) consists of four subshells, 4s, 4p, 4d and 4f, and so forth. Now it is clear from the above discussion that when a new shell is added, we also add a new subshell. This is because; each shell to a larger distance from the nucleus provides more space for new subshells containing more orbitals. The maximum number of electrons in a subshell can be calculated by $2(2l + 1)$. The s-subshell has room for 2 electrons, the p-subshell has room for 6 electrons, the d-subshell

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has room for 10 electrons, and the f-subshell has room for 14 electrons and so on. These may be shown as s^2, p^6, d^{10}, and f^{14}. A convenient way to designate such a configuration is to write the shell and subshell designation and add a superscript to denote the number of electrons occupying that subshell. For example, the electronic configuration of the calcium atom is written as follows:

$$_{20}Ca = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$$

Each subshell has specific number of orbitals. The number of orbitals per subshell depends on the type of subshell, but not on the value of n. The number of orbitals in a subshell is calculated by the formula $2l + 1$. Thus each s-subshell ($l = 0$) contains one orbital; each p-subshell ($l = 1$) contains three orbital; each d-subshell ($l=2$) contains five orbital, and so on. The orbitals of the same subshell in a shell have same energies and are called degenerate orbitals.

If two electrons in an atom have the same principal quantum number, the same angular momentum quantum number, and the same magnetic quantum number, the electrons are said to be in the same orbital.

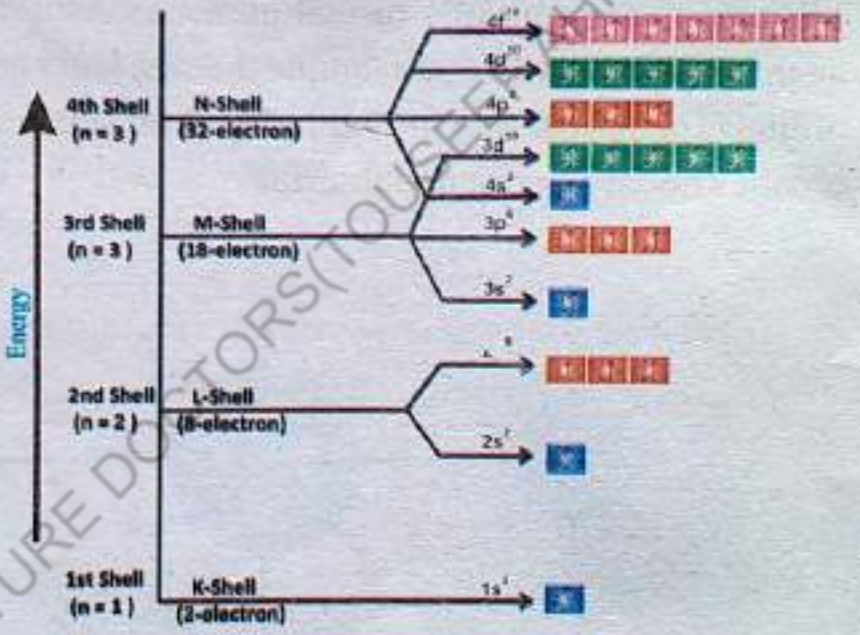

Figure 2.18: The arrangement of shells, subshells and orbitals in an atom

2.6.5 Shapes of s, p, and d-Orbitals

The shapes of orbitals have no physical existence. These are the regions in space where probability of finding an electron is very high. But these regions have no definite boundaries. Let us look the shapes of the most important orbitals that are actually occupied in known elements. Their shapes help us visualize how the electron density is distributed around the nucleus.

Shape of s-orbitals

Recall that the azimuthal quantum number for s-subshells is 0; hence, it must have magnetic quantum number 0. Thus there is only one *s* orbital in each shell. All s-orbitals have spherical shapes and are shown by circles. The probability of finding

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an s electron at a given distance from the nucleus does not depend on direction. I depends only on the distance from the nucleus. The electron density is high near the nucleus for an s orbital. It decreases sharply as distance from the nucleus increases it never goes to zero, even at a large distance. If you ask someone where the electron is, he or she could not show the exact position of electron. This means that an atom does not have a definite boundary and definite shape. However, we usually draw a line around the outer edge enclosing the volume where an electron spends most (say, 95%) of its time. The space where the probability of finding the electron is maximum is called an orbital. The 1s orbital represented in this manner is merely a sphere. All s orbitals (2s, 3s, 4s, and so forth) are spherical in shape but differ in size. The size and energy of s-orbital increases with increase in the value of principal quantum number (n). For example the size and energy of 2s orbital is larger than 1s orbital. The probability of finding electron between two orbitals is zero. This plane is called nodal plane or nodal surface.

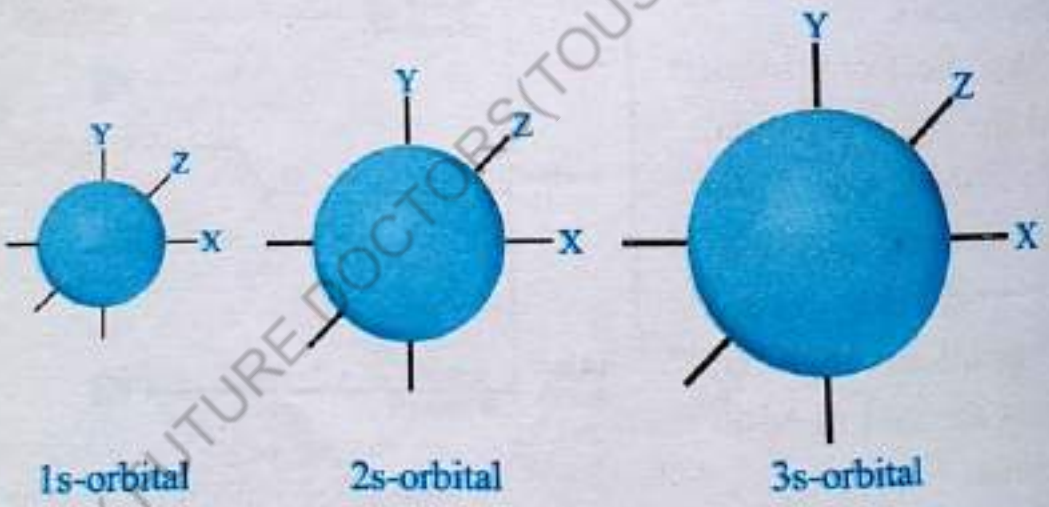

Figure 2.19: Representation of the three s-orbials of the lowest energy

Shapes of p-orbitals

As we know that the p-orbitals start with the principal quantum number n Beginning with the n=2 shell, the value of azimuthal quantum number for subshell is 1; therefore, the possible values of magnetic quantum number for subshell are +1, 0 and –1. The three values of magnetic quantum number show the p-orbitals have three orientations in space i.e. along x, y and z-axis. We therefore have three 2p orbitals: $2p_x$, $2p_y$ and $2p_z$, which are oriented in space at 90° angles to one another along the three coordinate axes x, y, and z. These three p-orbitals are identical in size, shape, and energy; they differ from one another only in orientation

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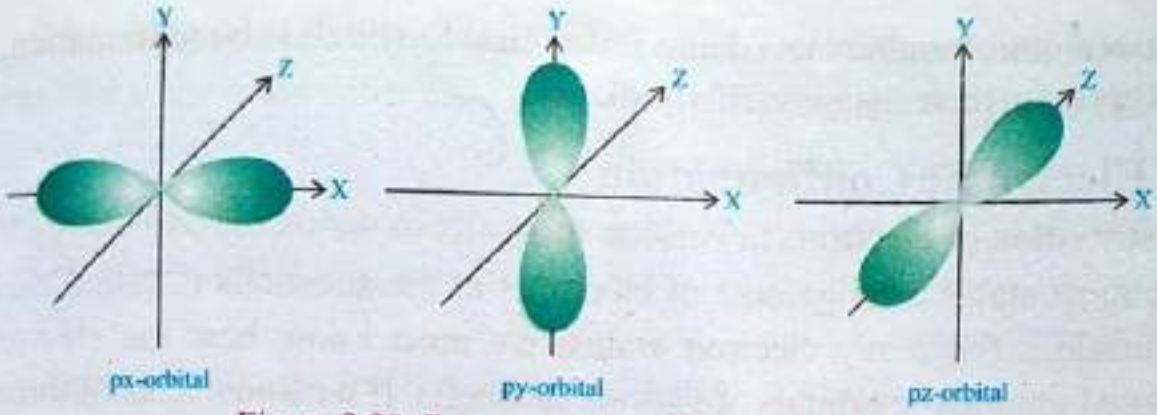

Figure 2.20: Representation of three p-orbitals

Shapes of d-orbitals

As you know that the d orbitals start with the principal quantum number $n=3$. When $n=3$ and, $l=2$, then $m=+2, +1, 0, -1, -2$. As there are five values of m for d-subshell. The d-orbitals are, therefore, of five types (d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2}). Each d-orbital has clover leaf shape except d_{z^2} which has dumb-bell shape. The orbital d_{z^2} has two egg shaped lobes and an extra doughnut shape (ring shape) in the center, while other four orbitals have four egg shaped lobes. The probability of electron density is zero on the plane where the lobes touch each other. The d-orbitals of the same shell (3d orbitals) in an atom have same energy. The d-orbitals of 4th and higher shells have shapes similar to 3d orbital, but differ in energy and size. They are shown as:

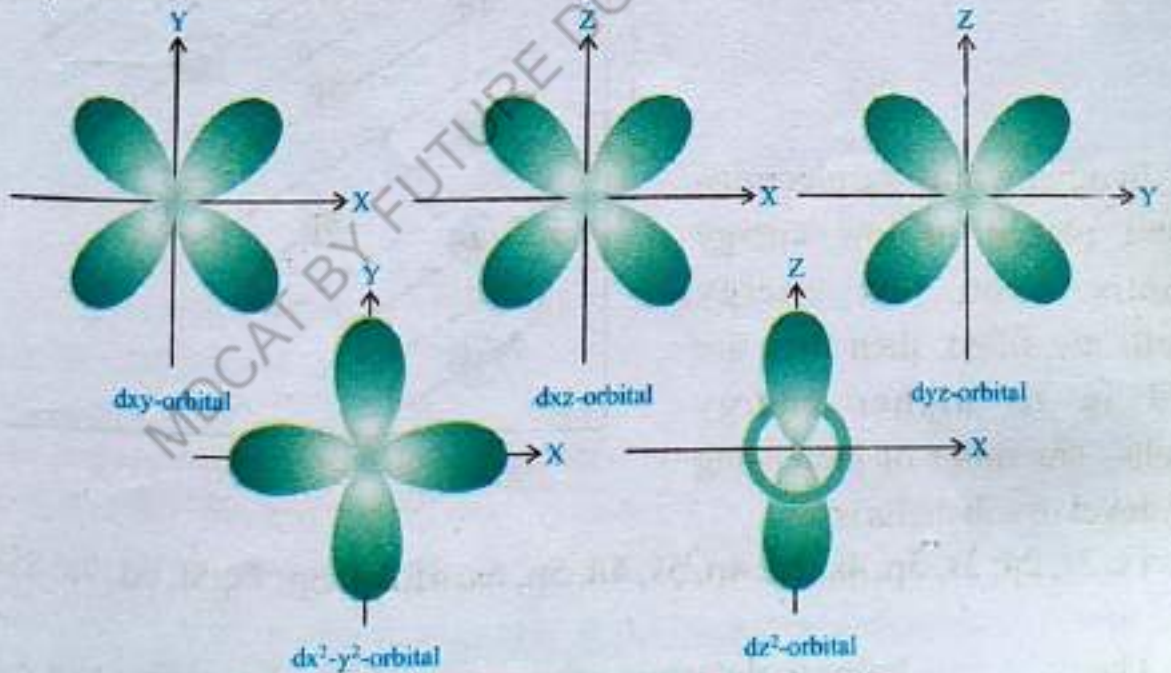

Figure 2.21: Representation of five d-orbitals

The fourth shell (n = 4) contains four subshells specified by s, p, d and f. There are seven equivalent f-orbitals. Each orbital has eight lobes. The shapes of the f-orbitals are even more complicated than those of the d-orbitals. Most of the

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elements (atomic numbers less than 57) don't use f-orbitals in bond formation, so we do not represent their shapes in this book.

2.7 Electronic Configuration

The distribution of electrons in various subshells in the increasing energy level get the most stable arrangement of electrons in the subshells is called electron configuration. For many electron atoms, we must know how the electrons are distributed among the orbitals of various subshells. If we know a set of three rules then we will be able to predict for each element which orbitals are occupied by electrons. The rules for distribution of electrons are as follows:

2.7.1 Aufbau Principle

The aufbau principle helps us to assign the electronic configuration to the atoms of different elements. Aufbau is a German word that means "building up". Because of this it is also known as Building up Principle. This principle states that, "The electrons are added to subshells in the order of increasing energy level".

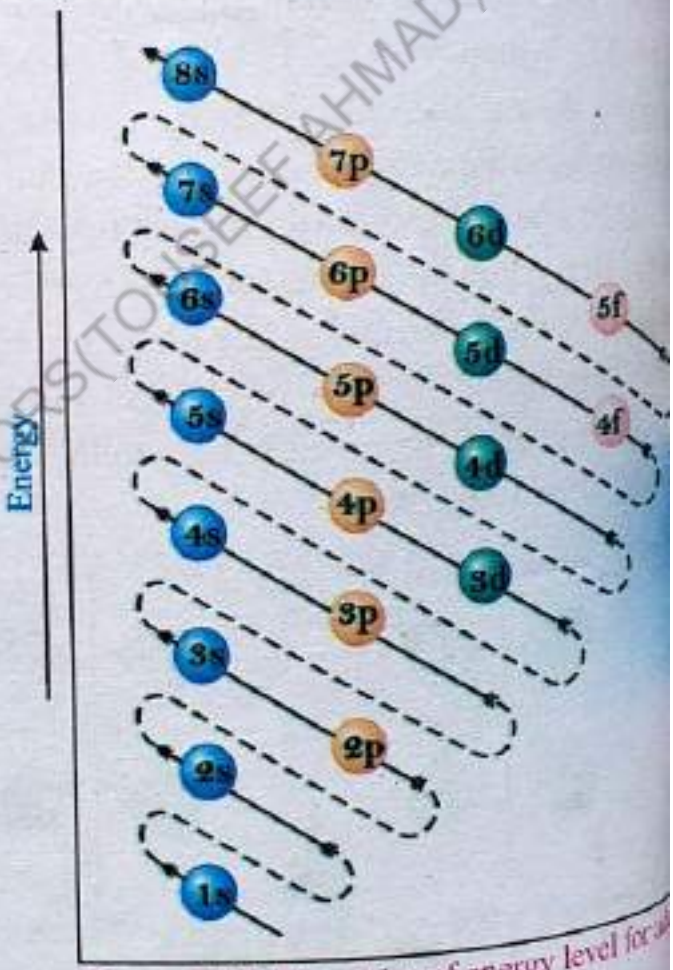

Figure 2.22: The order of energy level for ... of electrons into subshell

In other words the electrons are first placed in low energy subshells when low energy subshells are filled, then they are placed in to higher energy subshells. The order of increasing energy level of subshells is:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, 8s and on.

The n + l rule helps to determine the energy order. According to n + l ... the electron will first enter into that subshell which has lower value of n + l. If ... values for two or more subshells are same, then electron will enter into that sub... which has lower value of n.

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Table 2.7: n + l values for some subshells

Subshell	n + l value	Subshell	n + l value
1s	1 + 0 = 1	3d	3 + 2 = 5
2s	2 + 0 = 2	4s	4 + 0 = 4
2p	2 + 1 = 3	4p	4 + 1 = 5
3s	3 + 0 = 3	4d	4 + 2 = 6
3p	3 + 1 = 4	4f	4 + 3 = 7

2.7.2 Pauli Exclusion Principle

Wolfgang Pauli (1900-1958)

In 1926, an Austrian scientist Wolfgang Pauli gave the exclusion principle. According to this principle, no two electrons in the same orbital of an atom can have the same values of four quantum numbers. It means an orbital can hold at the most two electrons which have the same value of three quantum numbers n, *l* and m, but must have the different values of spin quantum number i.e. opposite spins (↑↓). For example, Helium atom has two electrons in 1s orbital. The spin of these electrons should be in opposite direction (↑↓). The parallel spin (↑↑ or ↓↓) of electrons is not possible. The values of four quantum numbers for both electrons of helium are given in the table.

Table 2.8: Values of four Quantum Numbers for two Electrons of same orbital

Principle Quantum Number (n)	Azimuthal Quantum Number (*l*)	Magnetic Quantum Number (m)	Spin Quantum Number(m_s)	
1	0	0	+1/2	For first electron
1	0	0	− 1/2	For second electron

2.7.3 Hund's Rule

Friedrich Hund (1896-1997)

In 1927, the German physicist Friedrich Hund found a rule for the determination of the lowest energy arrangement of electrons in a subshell. Hund's rule states that, "When two or more degenerate orbitals (same energy orbitals) are available, then the electrons should be placed in separate orbitals with same spin rather than to put them in same orbital with opposite spin".

As we know p-subshell has three, d-subshell has five and f-subshell has seven orbitals. The pairing of electrons begins in the p-orbitals only when the fourth electron enters into p-orbitals. In case of d and f-orbitals the pairing of electrons begins with the entry of sixth and eighth electron respectively. Hund's rule results from the fact that electrons repel one

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another and therefore remain as far apart as possible. They can be lower in energy if they are in different orbitals. The electronic configuration in the orbitals of same element is given in table 2.9.

Applications of Rules

i) These rules are used to write electronic configuration of elements.

ii) These rules are used to predict valency.

iii) These rules show number and type of half-filled orbitals.

iv) These rules show orbitals involved in bond formation.

2.7.4 Writing the Electronic Configuration of Elements

Before we assign the electronic configurations to atoms of the different elements, we have to know the methods of representing these configurations. There are two different ways (methods) for writing the electronic configuration of an atom.

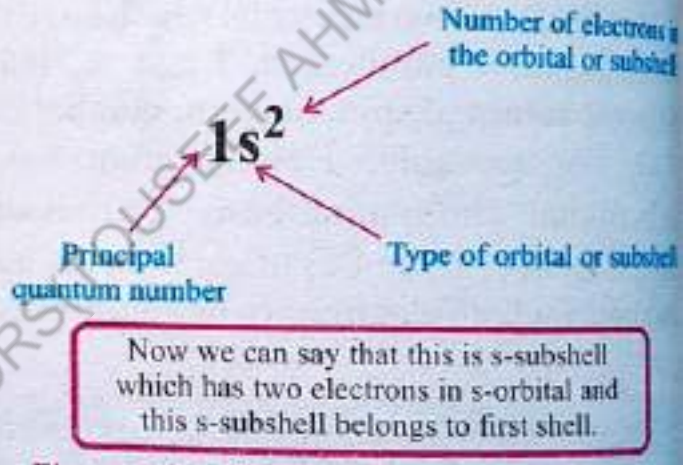

Figure 2.23: Method of writing the electronic configuration

i) In this method, we write the symbol for the occupied subshell and add a superscript to indicate the number of electrons in that subshell and then we write the principal quantum number before the particular subshells. The electronic configuration of Helium atom is shown in figure 2.23. The electronic configuration of nitrogen atom can be written as $1s^2\ 2s^2 2p^3$.

ii) In this method, each orbital of the sub-shell is represented by a box and the electron is shown by an arrow (↑). The arrow points up when electron spins anticlockwise and down when electron spins clockwise. If an orbital contains only one electron, an arrow pointing upward (↑) is placed in the box. If an orbital contains two electrons, the second arrow pointing downward (↓) is placed in the box. The two electrons in orbital which have opposite spins are said to be paired. The single electron in an orbital which has no partner of opposite spin is said to be unpaired electron. The priority is given to this method over the first because it represents all the four quantum numbers.

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Table 2.9: Electronic Configurations and Orbital Diagrams for First 18 Elements

Element	Atomic Number	Electronic Configuration	Orbital 1s	2s	2p	3s	3p
H	1	$1s^1$	↑				
He	2	$1s^2$	↑↓				
Li	3	$1s^2\ 2s^1$	↑↓	↑			
Be	4	$1s^2\ 2s^2$	↑↓	↑↓			
B	5	$1s^2\ 2s^2\ 2p^1$	↑↓	↑↓	↑		
C	6	$1s^2\ 2s^2\ 2p^2$	↑↓	↑↓	↑ ↑		
N	7	$1s^2\ 2s^2\ 2p^3$	↑↓	↑↓	↑ ↑ ↑		
O	8	$1s^2\ 2s^2\ 2p^4$	↑↓	↑↓	↑↓ ↑ ↑		
F	9	$1s^2\ 2s^2\ 2p^5$	↑↓	↑↓	↑↓ ↑↓ ↑		
Ne	10	$1s^2\ 2s^2\ 2p^6$	↑↓	↑↓	↑↓ ↑↓ ↑↓		
Na	11	$1s^2\ 2s^2\ 2p^6\ 3s^1$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	
Mg	12	$1s^2\ 2s^2\ 2p^6\ 3s^2$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	
Al	13	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑
Si	14	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑ ↑
P	15	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑ ↑ ↑
S	16	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑ ↑
Cl	17	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑
Ar	18	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓

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Instead of writing out the whole electronic configuration of an element, we write the condensed electronic configuration by writing the electronic

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configuration of the previous noble gas. The electronic configuration of the n gas is represented by its chemical symbol in brackets. For example, the electro configuration of silicon is written as $[Ne]3s^2 3p^2$.

Where, [Ne] denotes the "neon core." Similarly we can write the electro configuration of calcium as $[Ar]4s^2$.

Table 2.10: The Condensed form of Electronic Configurations from Potassium (Z = 19) to Krypton (Z = 36)

Element	Symbol	Atomic Number	Electronic Configuration
Potassium	K	19	$[Ar]4s^1$
Calcium	Ca	20	$[Ar]4s^2$
Scandium	Sc	21	$[Ar]4s^2 3d^1$
Titanium	Ti	22	$[Ar]4s^2 3d^2$
Vanadium	V	23	$[Ar]4s^2 3d^3$
Chromium	Cr	24	$[Ar]4s^1 3d^5$
Manganese	Mn	25	$[Ar]4s^2 3d^5$
Iron	Fe	26	$[Ar]4s^2 3d^6$
Cobalt	Co	27	$[Ar]4s^2 3d^7$
Nickel	Ni	28	$[Ar]4s^2 3d^8$
Copper	Cu	29	$[Ar]4s^1 3d^{10}$
Zinc	Zn	30	$[Ar]4s^2 3d^{10}$
Gallium	Ga	31	$[Ar]4s^2 3d^{10} 4p^1$
Germanium	Ge	32	$[Ar]4s^2 3d^{10} 4p^2$
Arsenic	As	33	$[Ar]4s^2 3d^{10} 4p^3$
Selenium	Se	34	$[Ar]4s^2 3d^{10} 4p^4$
Bromine	Br	35	$[Ar]4s^2 3d^{10} 4p^5$
Krypton	Kr	36	$[Ar]4s^2 3d^{10} 4p^6$

The electron configuration of chromium (Z = 24) is $[Ar]\ 4s^1 3d^5$ instead of $4s^2 3d^4$, as we might expect. Similarly the electronic configuration of copper (Z= is $[Ar]\ 4s^1 3d^{10}$ rather than $[Ar]\ 4s^2 3d^9$. This is because the half-filled ($3d^5$) completely filled ($3d^{10}$) subshells are more stable than partially filled subshells.

Summary of Facts and Concepts

- Atoms are the basic building blocks of matter. They are the smallest unit an element which chemically react. An atom consists of a very small, den and positively charged central nucleus and a diffused region of negat charge around nucleus. Atoms are composed of three fundamental partic

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the electron, the proton, and the neutron.

- The number of protons in the nucleus of an atom of an element is called atomic number (Z). Atomic number is the identity of an atom of an element. All atoms of a given element have the same atomic number, which differs from the atomic numbers of other elements. The number of electrons is always equal to the number of protons in an atom.
- The mass number (A) is the sum of the number of protons and the number of neutrons in the nucleus of an atom. Isotopes are atoms of the same element that have the same number of protons but different mass numbers because they have different numbers of neutrons. An isotope is identified by the symbol of the element, with the mass number as a superscript to the left. Isotopes have chemical behavior identical to that of any other isotope of the same element.
- Max Planck, in 1900, gave quantum theory of radiations.
- Neil Bohr, in 1913, successfully explained spectrum of hydrogen and hydrogen like atoms. He proposed that the electron revolves around the nucleus in the circular path with a definite amount of energy. He called these paths orbits or shells.
- Spectrum is the bands of different colours which are produced by passing light through prism. Rainbow is the best example of spectrum.
- X-rays are produced when fast moving electrons collide with heavy metals anode in the discharge tube. These rays were discovered by a German scientist W.C. Roentgen in 1895.
- After the failure of Bohr's atomic model, Erwin Schrodinger, in 1926, proposed an equation called Schrödinger equation to describe the electron distributions in space and the allowed energy levels in atoms.
- In a hydrogen atom and hydrogen like atoms, which contains only one electron, the energy of an orbital depends only on n. In a multi-electron atom, the energy of an orbital depends on both n and l. The lower the value of $(n+l)$ for an orbital, the lower is its energy. If two orbitals have the same $(n+l)$ values, the orbital with lower value of n has the lower energy. In addition; the spin quantum number determines the electron spin as either clock wise or anti-clock wise.
- According to Aufbau principle, the electrons are added to energy subshells in the order of increasing energy level.
- Pauli Exclusion Principle states that no two electrons in the same orbital of an atom can have the same values of four quantum numbers.
- Hund's rule states that the pairing of electrons in the degenerate orbitals (same energy orbitals) does not take place until each degenerate orbital has got one electron each.

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Questions and Problems

Q.1. Four answers are given for each question. Select the correct one.

i) The fundamental particles of an atom are:

(a) Electron, positron, neutron (b) Electron, proton, neutron

(c) Electron, neutrino, proton (d) Electron, positron, meson

ii) Proton was discovered by:

(a) Gold Stein (b) Chadwick

(c) Thomson (d) W. Crooks

iii) The colour of the glow inside the discharge tube depends upon:

(a) Nature of discharge tube (b) Nature of the gas

(c) Nature of cathode (d) Nature of anode

iv) The mass of electron is almost equal to:

(a) Hydrogen atom (b) Proton

(c) Neutron (d) Positron

v) How many times the second orbit of hydrogen atom is away from th nucleus:

(a) Four (b) Six

(c) Nine (d) Sixteen

vi) Which one of the following elements is **NOT** radioactive:

(a) Uranium (b) Polonium

(c) Radium (d) Germanium

vii) The properties of elements are determines by:

(a) Atomic mass (b) Mass number

(c) Atomic number (d) All of these

viii) When 6s orbital is complete, the entering electron goes into:

(a) 7s (b) 6p

(c) 5d (d) 4f

ix) If n is equal to 4, then l is equal to:

(a) 0 (b) 0, 1

(c) 0,1,2 (d) 0,1,2,3

x) How many electrons an orbital can accommodate:

(a) 14 (b) 10

(c) 6 (d) 2

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Q.2. Fill in the blanks with suitable words given in the brackets:

i) Cathode rays produce _____ on striking with heavy metals anode. (canal rays/X-rays)

ii) Mass of proton in amu is _____. (1.00727/1.00867)

iii) Pfund series of lines appear in _____ region of spectrum. (UV/IR)

iv) Mathematical value for Bohr's radius constant (a_o) is _____. (5.29 A°/0.529 A°)

v) Cathode rays bent toward _____ of electric field. (positive plate/negative plate)

vi) Energy is _____ when electron jumps from lower to a higher orbit. (absorbed/released)

vii) Greater the value of principle quantum number, _____ will be the size of an atom. (lesser/greater)

viii) The subshell p has _____ shape. (spherical/dumbbell)

ix) The wavelength of X-rays is _____ than microwaves. (greater/lesser)

x) Wavelength of large sized particles is very _____. (small/large).

Q.3. Label the following statements as True or False:

i) Neutrino is the fundamental particle of an atom.

ii) The electric current cannot pass through gases in the discharge tube at 760 torr.

iii) The mass of electron in kg is 9.11×10^{-31}.

iv) The charge to mass ratio of canal rays depends upon the nature of gas in the tube.

v) Planck's equation is $E = mc^2$.

vi) The electronic configuration of H^- is $1s^2$.

vii) If $n = 4$, then l is equal to 0, 1, 2.

viii) Orbit gives the idea of plane motion of electrons.

ix) Monitor of computer is anode rays tube.

x) The space where probability of finding the electron between two orbitals is zero is called nodal plane.

Q.4. What is discharge tube? Describe the experiment which led to the discovery of electron.

Q.5. Give the characteristic properties of cathode rays.

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Q.6. Answer the questions given below:

i) The cathode rays are produced when pressure inside the discharge tube is reduced and high voltage is applied.

ii) The charge-to-mass ratio of cathode rays remains same, no matter which gas is used in the discharge tube.

iii) The charge-to-mass ratio of cathode rays is equal to that of electron.

iv) The evidence that cathode rays consist of negatively charged particles.

v) Electrons are the elementary particles of all the matter.

Q.7. What are canal rays? Give reason for the production of canal rays.

Q.8. What are the properties of canal rays?

Q.9. Explain the following with reasons:

i) The positive rays are also called canal rays.

ii) The canal rays depend upon the nature of gas.

iii) The e/m values of canal rays for different gases are different.

iv) The e/m value of cathode rays is 1836 times greater than positive rays that are obtained from hydrogen gas.

Q.10. How were neutrons discovered? Describe the properties of neutrons.

Q.11. Slow neutrons are more effective than fast neutrons, how?

Q.12. Explain J. J. Thomson experiment for determining the e/m ratio of electron.

Q.13. Compare the properties of fundamental particles of atom.

Q.14. Which two types of subatomic particles must be present in equal number for an atom to be neutral?

Q.15. What is the atomic number of an atom that has 17 protons, 17 electrons and 18 neutrons? Also calculate its mass number.

Q.16. An atom with mass number of 36 contains four more neutrons than protons. What is the atomic number and name of this atom?

Q.17. Discuss Rutherford's experiment for the discovery of nucleus.

Q.18. Write main points of Rutherford's atomic model. What are the defects of this model.

Q.19. What are the most important points of Planck's quantum theory? Explain what a quantum is?

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Q.20. What is the relationship between?

a) Frequency and wavelength

b) Wavelength and wavenumber

Q.21. Define the terms given below:

(a) Frequency (b) Wavelength

(c) Wavenumber (d) Atomic number

(e) Amplitude

Q.22. What are the postulates of Bohr's atomic model? What are the merits and demerits of this concept?

Q.23. Derive an expression for the radius of nth orbit of hydrogen atom with the help of Bohr's model.

Q.24. Derive an expression for calculating the energy of an electron in the n^{th} orbit of hydrogen atom with the help of Bohr's model.

Q.25. Derive the formulas for calculating the energy difference (ΔE), frequency of photon and wavenumber of photon.

Q.26. Answer the following questions:

a) The distance between different orbits goes on increasing when we move from lower to higher orbits.

b) Energy of electron is inversely proportional to the square of number of orbits (n^2).

c) The energy of higher orbits is greater than lower orbits.

d) The energy of electron at an infinite distance from the nucleus is zero.

e) The radius of cation is smaller than its parent atomic radius.

f) Velocities of electrons in higher orbits are less than those in the lower orbits of hydrogen atom.

g) Why the size of helium ion (He^+) is smaller than hydrogen atom as both have same number of electrons in the first shell?

Q.27. What do you know about Zeeman Effect and Stark Effect?

Q.28. What is spectrum? Explain the spectrum of hydrogen atom.

Q.29. What are X-rays? How are they produced? Describe the properties and uses of X-rays.

Q.30. Explain the role of Mosley's law in determining the atomic numbers of different elements.

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Q.31. Define energy level. What is the difference between ground state and excited state?

Q.32. How can you define orbit and orbital? Explain the difference between orbit and orbital.

Q.33. What are quantum numbers? State the significance of each quantum number.

Q.34. What values of quantum numbers are assigned to the following orbitals?

(a) 2s-orbital (b) 3p-orbital (c) 4d-orbital (d) 5f-orbital

Q.35. Describe the shapes of s, p, and d-orbitals. How are these orbitals related to azimuthal and magnetic quantum numbers?

Q.36. What do you know about shells, subshells and orbitals? Describe in detail.

Q.37. What is Aufbau principle? Arrange the subshells according to this principle. Get the ground state electronic configuration of first 18 elements by using this principle.

Q.38. Discuss the following:

a) Pauli's Exclusion Principle.

b) Hund's Rule

Q.39. What is electronic configuration? Describe the basic rules and method of writing electronic configuration for the atoms of different elements.

Q.40. Answer the following question:

a) What are the total number of subshells and orbitals in an atom whose principle quantum number, $n = 4$?

b) What is the maximum number of electrons in first, second, third and fourth shells?

c) How many orbitals are in the 2p and 3p subshells?

d) Calculate the number of orbitals in $l = 4$ subshell.

e) Give the values of the quantum numbers associated with 2s, 3p and 4d orbitals.

f) What are the similarities and dissimilarities between 2p and 3p orbitals?

g) Discuss the difference between $2p_x$ and $2p_y$ orbitals.

h) Which of the following orbitals do not exist: 1s, 1p, 2p, 2d, 3f and 4g?

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i) Which subshell in each of the following pairs is higher in energy?

(i) 4p or 5s (ii) 5s or 6p (iii) 6s or 4f

j) What is the meaning of $3p^4$?

k) How many unpaired electrons are present in oxygen and silicon atoms in the ground state?

Q.41. Calculate the energy of one photon of blue light having wavelength of 490nm.

Q.42. Calculate the frequency, energy and wavenumber of a yellow light emitted from a sodium lamp which has a wavelength of 570nm.

Q.43. Explain Millikan's oil drop experiment for measurement of charge of electron.

Q.44. Calculate the ΔE when electron jumps from lower orbit (n_1) to higher orbit (n_2).

Q.45. Calculate the frequency (Hz) and wavelength (nm) of the light absorbed by hydrogen atom when an electron jumps from the $n = 2$ to then $= 3$ level.

Q.46. Explain why the subshell is not full in oxygen atom and full in neon atom?

Q.47. Calculate mass of electron from e/m ratio and mass.

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Chapter # 03

Chemical Bonding

Major Concepts

3.1 Shapes of Molecules
3.2 Resonance
3.3 Theories of Covalent Bonding
3.4 Bonding Characteristics
3.5 Effects of Bonding on Physical and Chemical Properties

Learning Outcomes

The students will be able to:

- Use VSEPR and VBT theories to describe the shapes of simple covalent molecule *(Applying)*
- Describe the features of sigma and pi bonds. *(Understanding)*
- Describe the shapes of simple molecules using orbital hybridization. *(Applying)*
- Determine the shapes of some molecules from the number of bonded pairs and lo pairs of electrons around the central atom. *(Analyzing)*
- Define bond energies and explain how they can be used to compare bond streng of different chemical bonds. *(Analyzing)*
- Predict the molecular polarity from the shapes of molecules. *(Applying)*
- Describe how knowledge of molecular polarity can be used to explain so physical and chemical properties of molecules. *(Analyzing)*
- Describe the change in bond lengths of hetero-nuclear molecules due to differe in electronegativity values of bonded atoms. *(Understanding)*
- Describe the difference among molecular network and metallic sol *(Understanding)*
- Explain what is meant by the term ionic character of a covalent bo *(Understanding)*

Introduction

Why do two oxygen atoms combine and give an O_2 molecule while two neon a stay apart from each other and do not give a Ne_2 molecule? Why do some a combine while certain others do not? Certainly there must be some force holds two oxygen atoms together. forces of attraction which holds

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elements (atoms or ions) together in different chemical compounds are called chemical bonds.

It is the natural tendency of an element to be stabilized. If there are two or eight electrons in the outermost shell of an atom then this is called a stable one. Stable elements do not form chemical bonds e.g. Noble gases are the most stable elements and have a little tendency to form chemical bonds. The elements with incomplete outermost shells are tried to gain, lose or share their electrons with other elements to complete their valence (outermost) shells. In this way chemical reactions are occurred and chemical bonds are formed.

Chemical bonds between atoms are usually classified as either ionic or covalent.

Ionic bonds are formed between oppositely charged ions (cations and anions) by the transfer of electrons from one element to another e.g. the bonds in NaCl, KBr, and CaO are ionic. They generally result when a metal reacts with a non-metal. It is non-directional. The electronegativity (E.N) difference should be more than 1.7.

Covalent bonds are formed by the mutual sharing of electrons between two different or similar atoms. The bonds in N_2, H_2O, and CO_2 are covalent. The E.N difference for covalent bond should be less than 1.7. They generally occur between non-metal atoms. They are directional and are shown by signs (–, =, ≡).

If you know the type of bonds in a compound, you can predict many of its physical properties.

In this chapter we will discuss the geometries of molecules and we will also explore two theories of chemical bonding: valence bond theory and molecular orbital theory.

Society, Technology and Science

Straight and Curly Hair

Hairs are mainly made up of protein, called keratin. Keratin is also present in nails and skin. Keratin is composed of long chain of sulphur containing amino acids called cysteine. The cysteine of one keratin molecule forms a disulphide bond (a covalent bond formed between the sulphur atoms of two thiol groups) with the cysteine of the neighbouring keratin molecule. The greater the number of disulphide

Straight Hair Curly Hair Wavy Hair

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bonds, the curlier the hair. The fewer the number of disulphide bonds, the straighter the hair. It depends upon the number of disulphide bonds between cysteine molecules of keratin whether your hair is curly, wavy or straight. A disulphide bonds imbalance causes the hair to appear straight in certain areas and curly in other areas. People with straight hair can change their hair to force it into curly state by using chemicals. They are chemically forcing the making of strong disulphide bonds. The waves do not stay for all time, because the new hair grows in, which is straight, and only the ends curly.

3.1 Shapes of Molecules

Why do molecules possess definite shapes? Why is the shape of CO_2 linear? Why is the shape of water angular? The answers of these and many more questions can be found in the VSEPR theory. Chemists are interested in the shapes of molecules. The bond angle and molecular shape are very important concepts in chemistry. The physical and chemical properties of substances such as melting point, boiling point, bond energy and density etc. are strongly influenced by the geometry (3-D arrangement of atoms in space). The shapes of molecules can be best explained with the help of "ball-and-stick" models. The ball represents the atom and the stick represents the bond pair.

3.1.1 Valence Shell Electron Pair Repulsion (VSEPR) Theory

In 1940, the Sidgwick and Powel pointed out that the shapes of molecules can be explained by the arrangement of electron pairs in the valence shell (outer most shell) of central atom. The atom in the center which is not present at the terminal in the polyatomic molecule is called central atom.

In 1957, Gillespie and Nylholm proposed VSEPR (pronounced as "vesper") theory. It explains shapes and bond angles of molecules and ions in terms of the electrostatic repulsion between electron pairs. The repulsion between the negative charges of electron pairs around the central atom determines the geometry of the molecule but we name the shape of molecules by the position of the atoms.

Keep in mind

The shared pair of electrons is called *bond pair* while the unshared pair of electrons is called *lone pair*. We can say that the electrons that are involved in making bonds are called bond pairs and the electrons that are not involved in making bonds are called lone pairs.

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Main Features (Postulates)

The main points of VSEPR theory are as follows:

i) Electron pair geometry of molecules depends upon the number of electron pairs (both bond pairs and lone pairs) present in the outermost shell of central atom.

ii) Geometry (shape) of molecules depends upon the number of bond pairs present in the outermost shell of central atom.

iii) The electron pairs in the valence shell repel one another because they are negatively charged.

iv) Electron pairs around central atom are located at maximum distances where repulsion is the minimum.

v) A lone pair (*l*p) occupies more space than a bond pair (bp).

vi) Repulsion between electron pairs in valence shell decreases in the following order:

$$lp - lp >> lp - bp > bp - bp$$

The repulsion between electron pairs in the valence shell may be called Van der Waals repulsion or exchange repulsion.

vii) A multiple bond (double or triple bond) occupies more space than a single bond. However these behave as a single electron pair bond for the purpose of VSEPR theory.

viii) The shape of molecule will be regular, if a molecule has only bond pairs.

ix) The shape of molecule will be irregular, if a molecule has some lone pairs of electrons.

x) The geometry around an atom is described by the general formula:

$$AB_mE_n$$

Where A is central atom, B is a bonded atom, E is a lone pair, m is the number of B atoms around the central atom A and n is the number of lone pairs around central atom.

Table 3.1: Shapes of Molecules according to VSEPR Theory

Number of Electron Pairs	Number of Bond Pairs	Number of Lone Pairs	Electron Pair Geometry	Formula	Molecular Geometry	Example	Ball and Stick Model
1	1	0	Linear	AB	Linear	HF	
2	2	0	Linear	AB_2	Linear	CS_2	
3	3	0	Trigonal planar	AB_3	Trigonal planar	BF_3	

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Number of Electron Pairs	Number of Bond Pairs	Number of Lone Pairs	Electron Pair Geometry	Formula	Molecular Geometry	Example	Ball and Stick Model
3	2	1	Trigonal planar	AB_2E	Bent	SO_2	
4	4	0	Tetrahedral	AB_4	Tetrahedral	CH_4	
4	3	1	Tetrahedral	AB_3E	Trigonal pyramidal	NH_3	
4	2	2	Tetrahedral	AB_2E_2	Bent	H_2O	
5	5	0	Trigonal bipyramidal	AB_5	Trigonal bipyramidal	PCl_5	
6	6	0	Octahedral	AB_6	Octahedral	SF_6	

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Applications of VSEPR Theory

The shapes of regular and irregular molecules are discussed below:

1) Shape of Molecules having one Electron Pair (AB type)

A diatomic molecule has only one bond pair and no bond angle. Because the geometric shape determined by two points is a straight line, all diatomic molecules are linear in shape. Examples are: HCl, CO, F_2, and N_2.

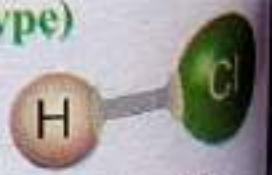

Figure 3.1: Linear Geometry

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2) Shape of Molecules having two Electron Pairs (AB_2 type)

Molecules having two bond pairs and no lone pair give linear geometry. Their bond angle would be of 180°. Examples are: $BeCl_2$, $CdCl_2$, CO_2, CS_2, $HgCl_2$.

Figure 3.2: Linear Geometry

$MgCl_2$ has two bond pairs and minimize it's repulsion by arranging bond pairs at an angle of 180°and thus assume linear geometry.

3) Shape of Molecules having Three Electron Pairs

Such molecules are further divided into two types:

i) Molecules having three bond pairs and no lone pair (AB_3 type) give planar triangular geometry. Their bond angles are of 120°.

Examples are: BCl_3, $AlCl_3$, SO_3, hydrides of group IIIA.

The molecular shape of BF_3 is triangular planar because the triangle of boron atom and the fluorine atoms all lie in the same plane.

Figure 3.3: Planar Triangular Shape

ii) Molecules having two bond pairs and one lone pair (AB_2E type) give distorted triangular shapes. Their bond angles are less than 120°. Examples are: $SnCl_2$, $PbCl_2$, SO_2.

As we know that the lone pair occupies more space than a bond pair, hence it pushes the bond pair closer to each other and cause compression of angle between two bond pairs.

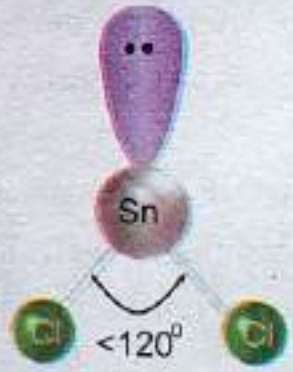

Figure 3.4: Distorted Triangular Shape

Conceptual Check Point:

The molecules which have two bond pairs but no lone pair show linear shapes while those which have two bond pairs and one lone pair show distorted triangular shapes. What will be your answer?

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4) Shape of Molecules having Four Electron Pairs:

Such molecules are further divided into three types:

i) Molecules having four bond pairs and no lone pair(AB_4 type) give tetrahedral geometry with an angle of 109.5°. Examples are: SiH_4, CCl_4, CH_4.

The methane molecule has four bond pairs which are directed from the center towards the corners of a regular tetrahedron. These four bond pairs should be placed 109.5° apart to give them a tetrahedral geometry. At an angle of 109.5° the distance between bond pairs is the maximum and repulsion is minimum.

Figure 3.5: Tetrahedral Shape

ii) Molecules in which central atom has three bond pairs and one lone pair (AB_3 type) give trigonal pyramidal shapes instead of tetrahedral shapes. Their bond angles are less than 109.5°. Examples are: NH_3 and NF_3.

In ammonia, the lone pair occupies more space than bond pairs. Therefore three N–H bond pairs are pushed closer and the bond angle decreases from 109.5° to 107°.

In NF_3, fluorine is the most electronegative element. So N–F bond is more polar than N–H. Therefore, lone pair exerts more repulsion on bonding pairs in NF_3. Hence, bond angle further reduces to 102°.

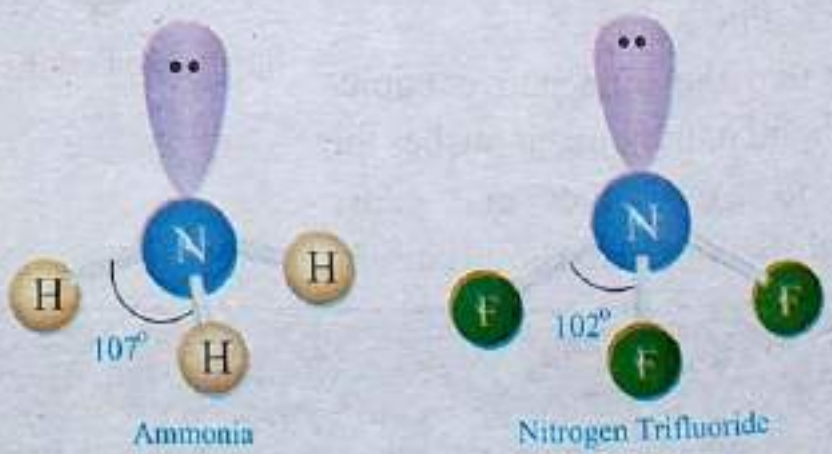

Figure 3.6: Pyramidal Shape

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Other examples are: PCl_3, PH_3, AsH_3.

(ii) The Molecules in which central atoms have two bond pairs and two lone pairs (AB_2E_2 type) give angular or bent shape. Their bond angles are 104.5° instead of 109.5°. Examples are: H_2O, H_2S, SCl_2, $SeCl_2$.

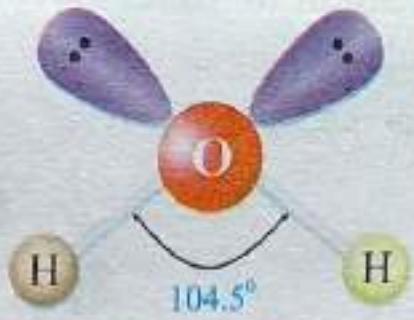

Figure 3.7: Angular Shape

In water molecule, the two lone pairs occupy more space than two bond pairs. As lone pair – lone pair repulsion is greater than lone pair – bond pair which in turn is greater than bond pair – bond pair. Hence, this forces the bond pairs closer together and reduces the bond angles to 104.5°. Therefore, the shape of water molecule is bent or angular or V–shaped.

Conceptual Check Point:

Why the shape of HCN is linear and that of H_2O is angular, although both of the molecules are triatomic?

(5) Shape of Molecules having Five Electron Pairs (AB_5 type)

Molecules having five bond pairs and no lone pair give triangular bipyramidal geometry. The equatorial bond angles are 120° and axial bonds are at right angles (90°) to the plane. Examples are: PF_5, PCl_5, $SbCl_5$, $ScCl_5$.

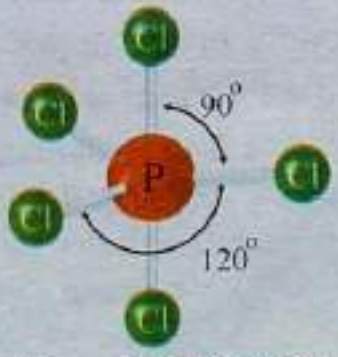

Figure 3.8: Triangular bi-pyramidal Geometry

Keep in mind

The atoms lie at the corner of an equilateral triangle are called equatorial atoms while the atoms above and below the plane of the triangle are called axial atoms. The bonds of equatorial atoms are called equatorial bonds while the bonds of axial atoms are called axial bonds.

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6) Shape of Molecules having Six Electron Pairs (AB_6 Type)

Molecules having six bond pairs give octahedral geometry with bond angle equal to 90°. Examples are: SF_6, TeF_6.

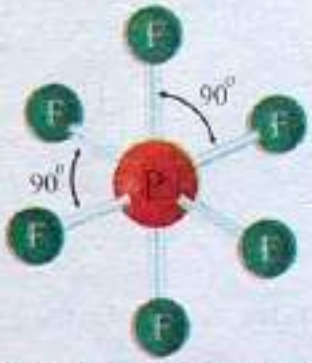

Figure 3.9: Octahedral Geometry

Keep in mind

In octahedral molecule, we can not use the terms 'axial' and 'equatorial' as in trigonal bipyramidal molecule because all the six bonds are equivalent.

Limitations of VSEPR Theory

This theory was failed to explain:

i) The sharing of electrons in the valence shell.
ii) The paramagnetic nature of O_2 molecule.
iii) The shapes of molecules having delocalized π-electrons.

3.2 Resonance

The process in which two or more structures are written for a compound which differs only in the arrangement of electrons is called resonance. The different structures obtained are called resonance structures. Resonance structures are not actual structures. They are hypothetical and exist only on paper. They are, therefore, cannot be prepared or isolated in the laboratory. The real or actual structure is a hybrid of all the resonance structures. The resonance is represented by a double headed arrow (⟷). There are some molecules and polyatomic ions for which no single Lewis structure can be written. Let us take the example of oxygen. It exists in two allotropic forms; the dioxygen, O_2 (oxygen molecule) and the trioxygen, O_3 (ozone). Ozone is present in larger amounts in the upper atmosphere where it shields life on earth from harmful UV radiation from the sun. It is also present in trace amounts in the lower atmosphere where it may damages plants and animal tissues. There are two possible Lewis structures "A" and "B" for Ozone which are

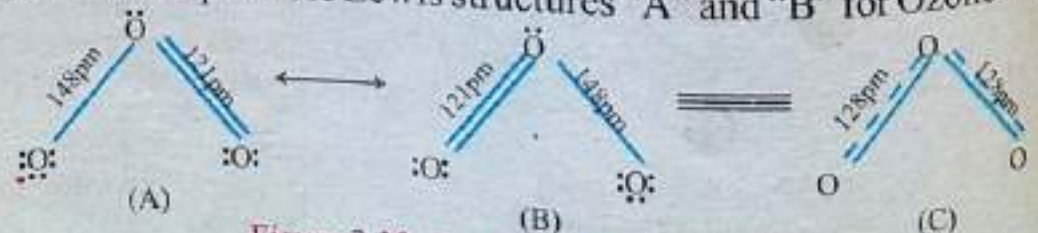

Figure 3.10: Lewis structures for Ozone

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The O – O single bond in O_3 should be longer than the O=O double bond because the double bonds should be shorter than single bonds. But experimental evidence shows that the oxygen-to-oxygen bonds are equal in length (128 pm). This bond length is shorter than the O – O single bond length of 148 pm in hydrogen peroxide, H – O – O – H, but it is longer than the double bond length of 121 pm in diatomic oxygen, O = O. Hence neither of the above structures can be correct. The bond identity cannot be satisfactorily represented by any single structure and it becomes necessary to write more than one Lewis structures. To describe such situations a concept called resonance is used. The bonds in ozone are equivalent and intermediate in strength and length between a double bond and a single bond. The resonance structures of ozone are:

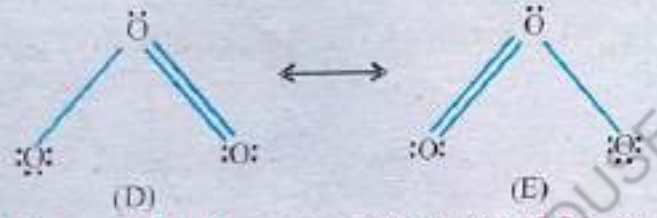

Figure 3.11: Resonance Structures of Ozone

They both are identical. They have same number of electrons (18 electrons) and both have octets around all three oxygen atoms. Which resonance structure is correct? Neither structure accurately represents the structure of ozone. The actual structure is the average (hybrid) of these two Lewis structures. They both have equal contributions to the real structure (hybrid structure) of ozone (structure "C" given above). A common analogy might help to clarify this concept. A horse and a donkey may be crossbred to produce a hybrid, the mule. The mule doesn't look or behave exactly like either parent, yet it has attributes of both. The resonance hybrid of a molecule has properties of each resonance form but is not identical to any one form.

Keep in Mind:

- Resonance structures are not real.
- The real structure is the hybrid of resonance forms.
- Resonance forms are not in equilibrium with each other.
- Resonance forms are not isomers. Resonance forms have different arrangement of electrons while isomers have different arrangement of both electrons and atoms. In witting resonance structures we are allowed to move electrons and not the atoms.

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3.3 Theories of Covalent Bonding

VSEPR theory explains the shapes of simple molecules but it does not explain formation of chemical bond. There are two important quantum mechanical theories which explain the concept of bond formation, bond enthalpies, bond lengths and shapes of molecules. These are valence bond theory (VBT) and molecular orbital theory (MOT). Neither theory completely explains all aspects of chemical bonding. They both help us to understand the observed properties of molecules.

3.3.1 Valence Bond Theory and Hybridization

Valence Bond Theory (VBT)

This theory was first proposed by W. Heitler and Fritz London in 1927 and later developed by Linus Pauling and J.C. Slater in 1931. This theory explains bond formation (sharing of electrons), bond strength, and geometry of molecules.

Main Points

Linus Pauling (1901-1994)

i) Covalent bonds are formed by overlapping of half-filled atomic orbitals.

ii) A single covalent bond is formed by the overlap of two half-filled atomic orbitals.

iii) A multiple bond (double or triple covalent bond) is formed by the overlap of more than two half-filled atomic orbitals. Overlapping means a common region of two orbitals with high electron density.

iv) As a result of overlapping, the electrons with opposite spins paired up and become stable by releasing energy.

v) When they form a bond, the atomic orbitals maintain their identities; only outermost shell electrons lose their identities.

vi) Greater the overlapping, the stronger is the bond.

vii) The direction of bond is determined by the direction of the two overlapping orbitals when other than s-orbital are involved.

Types of Overlapping and Nature of Covalent Bonds:

On the basis of overlapping of orbitals, covalent bonds can be divided into two types i.e. Sigma bond and pi-bond.

i) Sigma bond (σ – bond)

A covalent bond formed by head to head or linear overlap of two atomic orbitals in which electron density is the maximum around the bond axis) is called sigma bond.

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(Sigma is the English word for the Greek letter, which corresponds to the English letter *s*). Overlapping of s – s and s – p orbitals always form σ – bonds but p – p may form sigma bonds. It may also be formed by overlapping of atomic-hybrid and hybrid-hybrid orbitals. All single covalent bonds are sigma bonds.

Types of Overlapping

s – s Overlapping (Formation of H_2)

This type of overlapping takes place between half-filled s-orbitals of two atoms along the bond axis. For example, consider the formation of H_2 molecule from two hydrogen atoms. Each atom has the electronic configuration $1s^1$. The half-filled atomic orbitals ($1s^1$) of both H-atoms overlap to form a sigma bond. The electron density is maximum between the two nuclei.

$H + H \longrightarrow H_2$

Figure 3.12: s-s overlapping

p – p Overlapping (Formation of F_2)

This type of overlap takes place between half-filled p-orbitals of the two atoms when they approach each other. The formation of fluorine, chlorine and bromine are the common examples of this type of overlapping. Consider the bonding between two fluorine atoms. The electronic configuration of each fluorine atom is $1s^2$, $2s^2$, $2p_x^1$, $2p_y^2$, $2p_z^2$. The F – F sigma bond is formed by overlap of half-filled p-p orbitals of two fluorine atoms. The electron density is maximum between two nuclei.

$F + F \longrightarrow F_2$

Figure 3.13: p-p overlapping

s-p Overlapping (Formation of HF)

This type of overlap takes place between half-filled s-orbital of one atom and half-filled p-orbital of another atom.

$H + F \longrightarrow HF$

Figure 3.14: s-p overlapping

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Consider the bonding between a hydrogen atom and a fluorine atom. The electronic configuration of fluorine atom is $1s^1$, $2s^2$, $2p_{x^1}$, $2p_{y^2}$, $2p_{z^2}$. The half-filled p-orbital (2Px) of fluorine atom overlap with 1*s* orbital of one hydrogen atom to form a σ-bond. The other filled 2*s* and 2*p* orbitals of fluorine do not participate in bonding to the hydrogen.

Conceptual Check Point:

How can you explain the bonding in Cl_2 and HCl with respect to VBT?

ii) Pi Bond (π-bond)

The bond formed by sidewise or parallel overlap of two p-orbitals is called Pi bond.

Examples are: O=O, N=N, CH_2=CH_2

This bond is named after the Greek letter π. The overlap of electronic clouds in pi bonds is not as good as in sigma bonds, and they are correspondingly weaker. Pi bonds are often found in molecules with double or triple bonds. In π-bond, two p-orbitals are in one plane. In π-bond, molecular orbital (bonding) has two region of electron density i.e. above and below the bond axis. In almost all cases single bonds are sigma bonds. A double bond consists of one pi bond and one sigma bond, and a triple bond consists of one sigma bond and two pi bonds.

Formation of O_2 Molecule

The electronic configuration of each oxygen atom is $1s^2$, $2s^2$, $2p_{x^1}$, $2p_{y^1}$, $2p_{z^2}$. There are two half-filled p-orbitals on each oxygen atom. Oxygen has one sigma bond which is formed by head to head overlap of $2p_x$ orbitals. It has one π-bond which is formed by side to side overlap of $2p_x$ orbitals. The electron density is maximum above and below the bond axis.

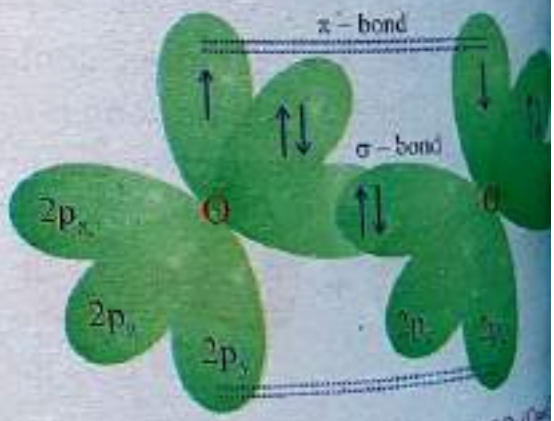

Figure 3.15: Orbital diagram of O_2 ($O=O$)

Formation of N_2 Molecule

The electronic configuration of each nitrogen atom is $1s^2$, $2s^2$, $2p_{x^1}$, $2p_{y^1}$, $2p_{z^1}$. There are three half-filled p orbitals in each nitrogen atom. N_2 molecule has one σ-bond and two π-bonds. σ-bond is formed by linear overlap of $2p_x$ orbitals while π-bonds are formed by parallel overlap of $2p_y$ and $2p_z$ orbitals.

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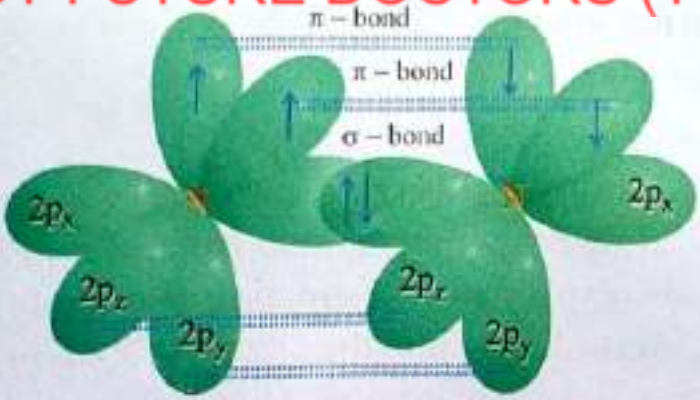

Figure 3.16: Orbital diagram of N_2 (N≡N).

Table 3.2: Difference between Sigma and Pi Bonds

Sigma Bond	Pi Bond
A covalent bond formed by linear overlap of two half-filled atomic or hybrid orbitals is called sigma bond.	A covalent bond formed by parallel overlap of two half-filled atomic orbitals is called pi bond.
It has electron density around the bond axis.	It has electron density above and below the bond axis.
All single covalent bonds are sigma bonds.	In a multiple bond, one is essentially a sigma bond which is formed earlier than pi bond.
It is stronger due to greater overlap of orbitals.	It is weaker due to lesser overlap of orbitals.
It is less reactive than pi bond.	It is more reactive than sigma bond.
Its formation does not depend on pi bond.	It is formed after the formation of sigma bond.
The shape of a molecule is determined only by the orbitals forming sigma bonds	The shape of a molecule is not determined by the orbitals forming pi bonds.
We can easily rotate the atoms around the bond axis of sigma bond.	Rotation about the double bond is not possible. The rotation is restricted because pi bond has two regions of electron density.
Example: In the molecule of NH_3, all bonds between nitrogen and hydrogen are sigma bonds.	Example: N_2 molecule has one sigma and two pi bonds.

Limitations of VBT

It does not explain:

- Bivalency of Be, trivalency of B and tetravalency of C.

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ii) The angle between the bonds.
iii) The paramagnetism of O_2 molecule.

Atomic Orbital Hybridization

In 1931 Linus Pauling introduced the concept of hybridization to explain characteristic geometrical shapes of polyatomic molecules like CH_4, NH_3, $BeCl_2$, $AlCl_3$ and H_2O etc. He also explained the formation of multiple bonds in molecules such as C_2H_2 and C_2H_4. According to him the atomic orbitals of different shapes and energy combine to form a new set of equivalent orbitals called hybrid orbitals and the phenomenon is known as hybridization.

Keep in Mind

- The number of hybrid orbitals formed is always equal to the number of atomic orbitals that are combined.
- The hybridized orbitals are always equivalent in energy and shape.
- Hybridization is the mixing of at least two nonequivalent atomic orbitals, for example, s and p orbitals. Therefore, a hybrid orbital is not a pure atomic orbital.
- The shape of any hybrid orbital is different from the shapes of the original atomic orbitals.
- The geometries are exactly as predicted by VSEPR theory.
- Hybridization takes place in an atom (usually the central atom) before bond formation. The concept of hybridization is not applied to isolated atoms.
- The hybrid orbitals form stable bonds than the pure atomic orbitals.

Types of Hybridization

There are three main types of orbital hybridization i.e. sp^3, sp^2, sp depending on the number and nature of orbitals. They are as follows:

(i) sp^3-Hybridization (ii) sp^2-Hybridization (iii) sp-Hybridization

i) sp^3-Hybridization

The process of mixing of one s and three p-orbitals to give four identical sp^3-hybrid orbitals is called sp^3-hybridization.

Each sp^3-hybridized orbital has 25% s -character and 75% p-character.

Examples are methane, water and ammonia.

Formation of Methane

Consider the example of methane. In methane the ground state electronic configuration of carbon ($1s^2$, $2s^2$, $2p_{x^1}$, $2p_{y^1}$, $2p_{z^0}$) shows that the 2s orbital is filled and two of the p-orbitals are half-filled. But how can carbon form four bonds if two of its valence electrons are already paired and only two unpaired electrons are available for sharing? To account for the four C–H bonds in methane, one of the 2s electrons is promoted from the lower-energy 2s orbital to the empty, higher-energy

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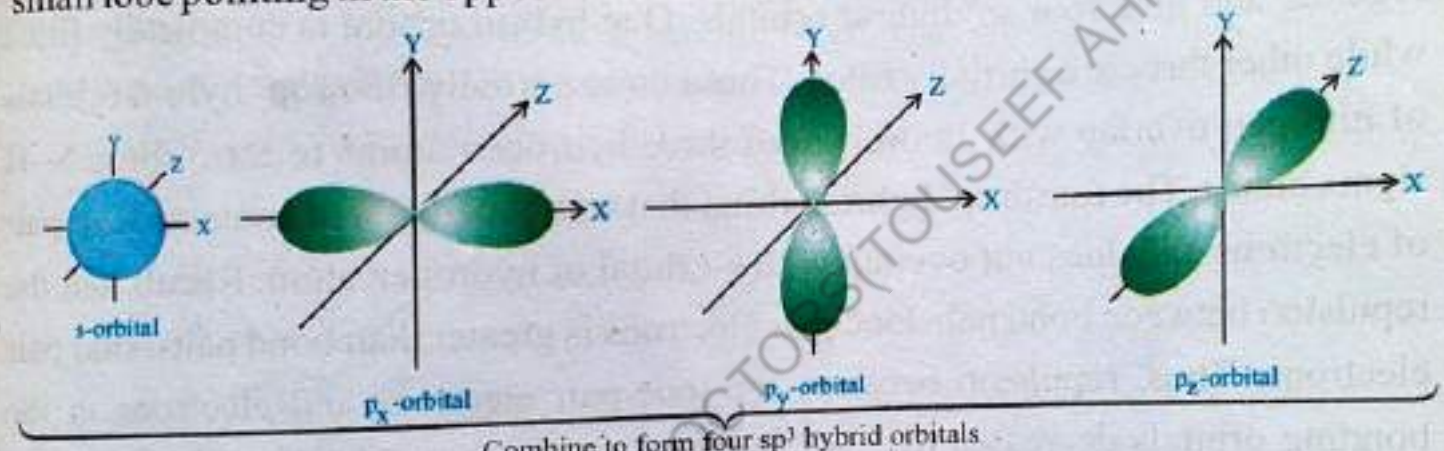
2p orbital, giving an excited-state configuration ($1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$) which has four unpaired electrons. Now we have four orbitals, each of which could overlap with the 1s orbital of hydrogen atom to form a sigma bond. Experiment shows, however, that the four C–H bonds in methane are identical. If excited-state carbon uses two kinds of orbitals for bonding, 2s and 2p, how can it form four equivalent bonds? The p-orbitals are at right angles to each other, so three of the bond angles would be 90°, and the position of the sigma bond formed by overlap with the 2s orbital is unclear. This is where hybridization comes in. For this reason, the four valence orbitals of the carbon atom combine during the bonding process to form four new, but equivalent, hybrid orbitals. In this case, one s-orbital and three p orbitals are mixed to form four identical sp^3 (pronounced as "s-p-three") hybrid orbitals. Each hybrid orbital has one large lobe pointing in one direction and one small lobe pointing in the opposite direction.



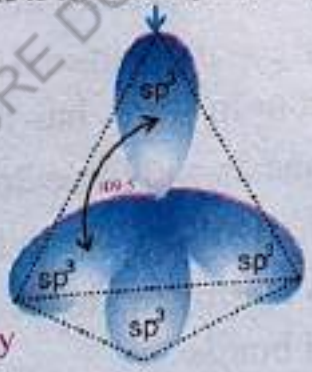


Figure 3.17
Tetrahedral geometry

In methane molecule, these four sp^3-hybrid orbitals of carbon overlap with 1s half-filled orbitals of four H-atoms to give four identical C–H bonds. The four C–H bonds are $s–sp^3$ sigma bonds and formed due to overlap.

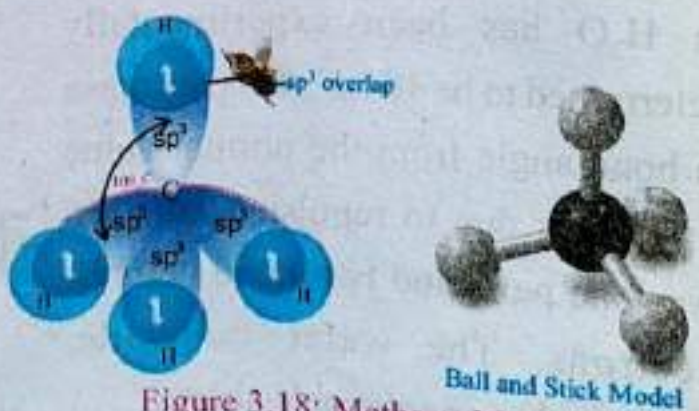


Figure 3.18: Methane Molecule

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Covalent bonds made with sp^3 hybrid orbitals are often strong ones. In fact, the energy released on forming the four strong C–H bonds in CH_4 is greater in amount than the energy required to produce the excited state of carbon. Methane has tetrahedral shape with an angle of 109.5°. The shape of methane is the same as predicted by VSEPR theory.

Formation of Ammonia and Water

The shapes of NH_3 and H_2O molecules can be best explained with the help of sp^3–hybridization. In ammonia, the ground state electronic configuration of nitrogen is $1s^2, 2s^2, 2px^1, 2py^1, 2pz^1$ having one filled 2s-orbital and three half-filled 2p- orbitals. Here one 2s and three 2p orbitals of nitrogen atom are combined together and give four sp^3 hybrid orbitals. One hybrid orbital is completely filled while other three are partially filled. These three partially filled sp^3 hybrid orbitals of nitrogen overlap with 1s orbitals of three hydrogen atoms to form three N–H sigma bonds. The fourth sp^3 hybrid orbital that was already filled contains lone pair of electrons and does not overlap with s-orbital of hydrogen atom. Recall that the repulsion between bond pair-lone pair electrons is greater than bond pair-bond pair electrons. Thus, repulsion between the lone-pair electrons and electrons in the bonding orbitals decreases the HNH bond angles from 109.5° to 107° and the molecule of NH_3 thus gets the trigonal pyramidal shape.

Similarly the oxygen atom in water has four sp^3 hybrid orbitals which are formed by the overlapping of one 2s and three 2p orbitals. Two hybrid orbitals are completely filled and two are half-filled. These two half-filled sp^3 hybrid orbitals overlap with 1s orbitals of two hydrogen atoms and form two O–H sigma bonds. The actual angle between O–H bonds in H_2O has been experimentally determined to be 104.5°. This decrease in bond angle from the normal value (109.5°) is due to repulsion between two lone pairs and two bond pairs of electrons. The water molecule, therefore, has angular or V-shape.

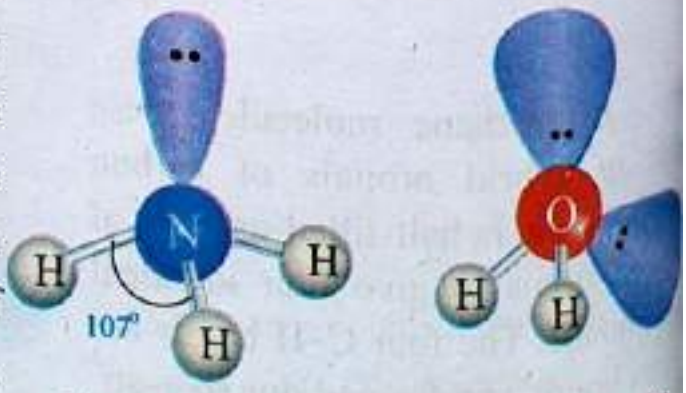

Figure 3.19: Ammonia and Water Molecules

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ii) sp^2-Hybridization

The process of mixing of one s and two p-orbitals to give three identical sp^2-hybrid orbitals is called sp^2-hybridization.

Each sp^2-hybrid orbital has 33% s-character and 67% p-character. Examples are boron tri-fluoride and ethene.

Formation of Boron Tri-fluoride:

In BF_3 molecule, the ground state electronic configuration of central boron atom is $1s^2, 2s^2, 2p_x^1, 2p_y^0, 2p_z^0$. First we promote one of the lower energy 2s electrons to an empty higher energy 2p-orbital giving an excited state electronic configuration $1s^2$, $2s^1, 2p_x^1, 2p_y^1, 2p_z^0$ in which boron has three unpaired electrons. These three orbitals (one 2s and two 2p) having unpaired electrons are mixed together to produce three sp^2 hybrid orbitals of same shape and energy. Note that one of the 2p orbitals of boron remains un-hybridized and is unoccupied by the electrons. This un-hybridized orbital will be important when we will discuss double bonds in the next examples.

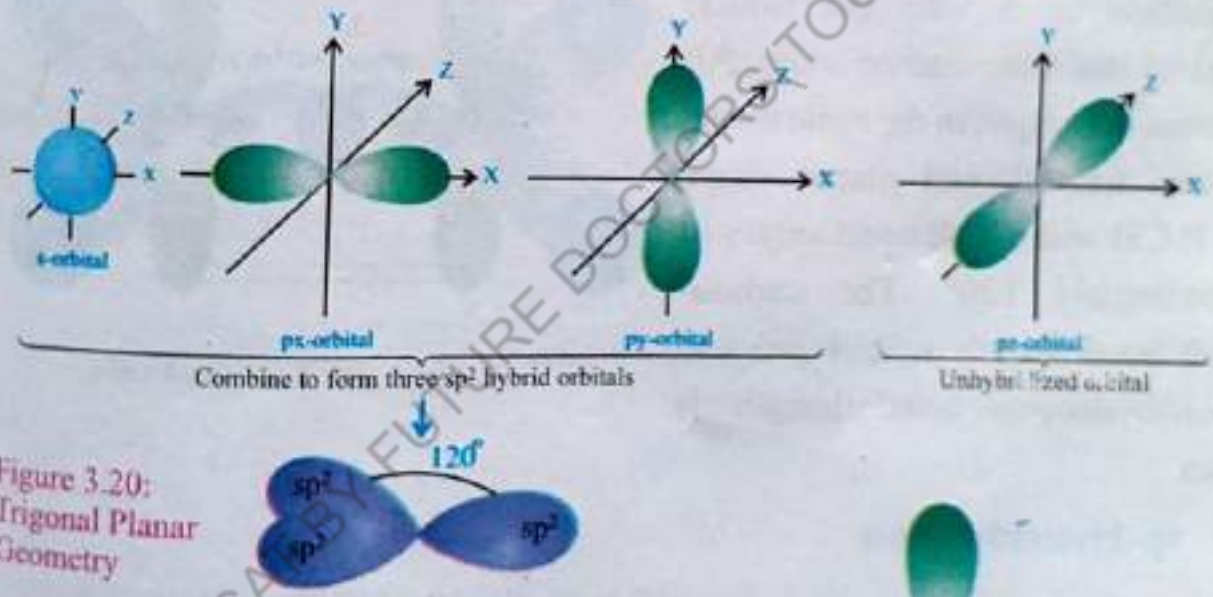

Figure 3.20: Trigonal Planar Geometry

These three sp^2 hybrid orbitals of boron overlap with p-orbitals of three fluorine atoms and form three sigma F–B bonds. The BF_3 molecule is planar with all the $F\hat{B}F$ angles equal to 120°. The geometry of BF_3 is trigonal planar.

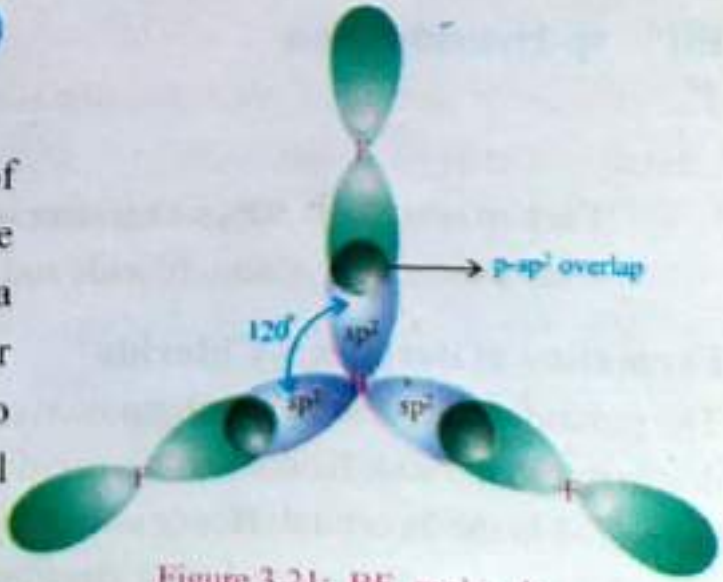

Figure 3.21: BF_3 molecule

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Formation of Ethylene

Consider the example of ethylene molecule, C_2H_4 which has a C=C double bond. In this case, three sp^2 hybrid orbitals are required, because each carbon atom is bonded to three other atoms (one carbon and two hydrogen atoms) and there is no lone pair of electrons. As we know, the excited state electronic configuration of carbon is $1s^2, 2s^1, 2p_{x^1}, 2p_{y^1}, 2p_{z^1}$. In ethylene, one 2s and two 2p orbitals of carbon atom are mixed together to give three sp^2 hybrid orbitals of same shape and energy. The remaining $2p_z$ orbital does not take part in the hybridization. In ethylene, each C–H sigma bond is formed by overlap of sp^2 hybrid orbitals on carbon with the 1s orbitals of each hydrogen atom. There is one sigma bond between two carbon atoms which is formed by the overlap of two sp^2 hybrid orbitals, one on each carbon atom and one π-bond which is formed due to overlap of un-hybridized p-orbital of one carbon atom with the similar orbital of the other carbon atom. All six atoms in C_2H_4 lie in the same plane. Ethylene has trigonal planar shape with $H\hat{C}H$ and $H\hat{C}C$ bond angles of approximately 120°. The carbon-carbon bond length is 134 pm and carbon-hydrogen bond length is 108pm.

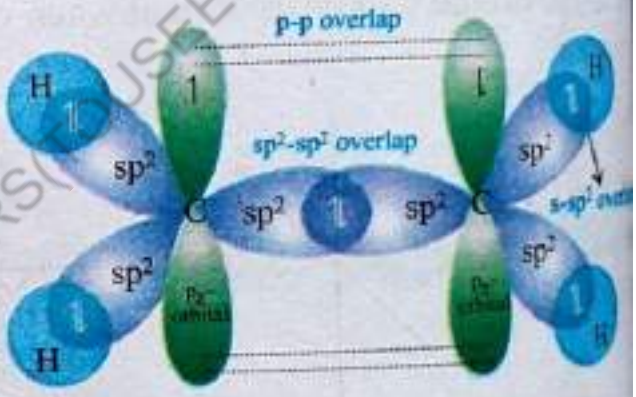

Figure 3.22: C_2H_4 molecule

iii) sp-Hybridization

The process of mixing of one s and one p-orbital to give two identical sp hybrid orbitals is called sp-hybridization.

Each sp orbital has 50% s-character and 50% p-character.

Examples are beryllium chloride and acetylene.

Formation of Beryllium Chloride

The ground state electronic configuration of Be is $1s^2, 2s^2, 2p_{x^0}, 2p_{y^0}, 2p_{z^0}$. We know that in its ground state Be does not form covalent bonds with Cl because its electrons are paired in the 2s orbital. Hence one of the 2s electrons is promoted to vacant orbital. Therefore the excited state electronic configuration of Be is $1s^2, 2s^1, 2$

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$2p_y$, $2p_z$. Now there are two Be orbitals available for bonding, the 2s and 2p. The half-filled (2s and $2p_x$) orbitals of Be are mixed together to give two sp hybrid orbitals. These two new orbitals are identical in shape.

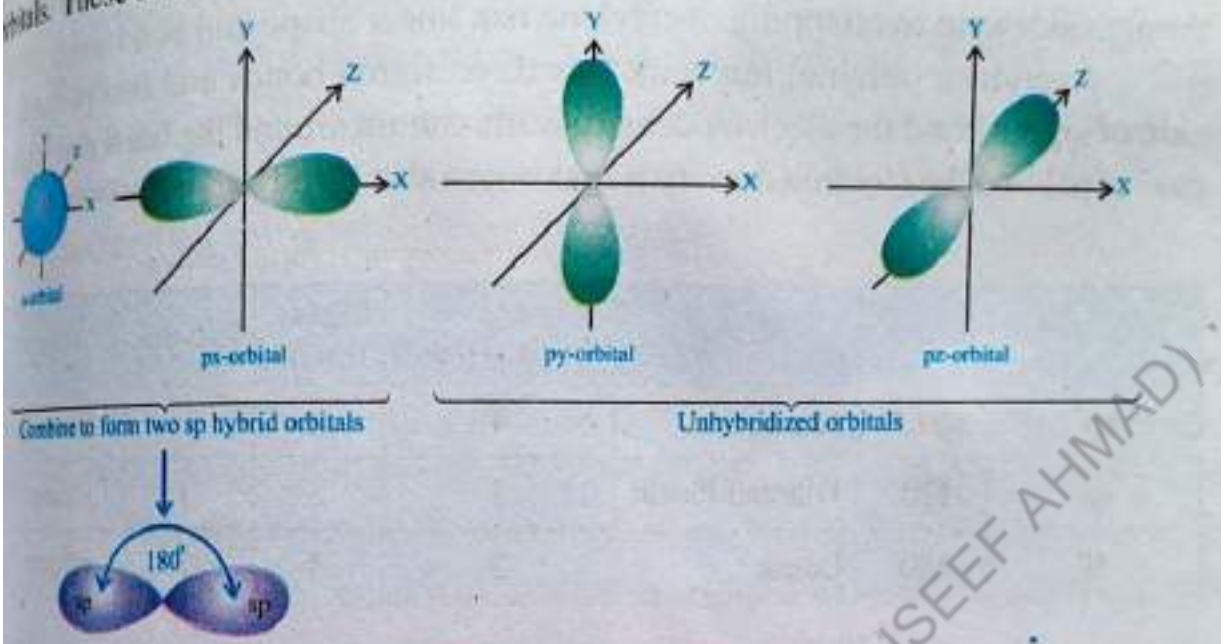

Figure 3.23: Linear Geometry

The remaining vacant $2p_y$ and $2p_z$ orbitals do not take part in hybridization. Two sp-hybrid orbitals of Be overlap with half-filled p orbitals of two chlorine atoms and form two Be–Cl sigma bonds. The bond angle between Cl–Be–Cl is 180°. It has a linear geometry.

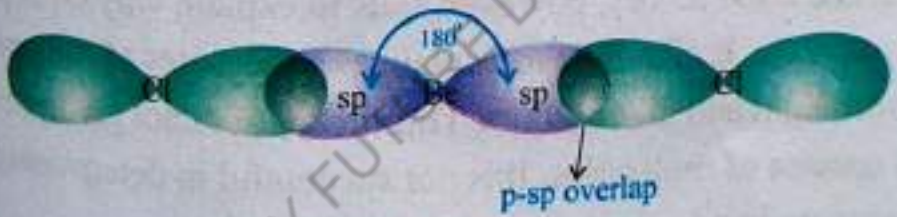

Figure 3.24: $BeCl_2$ molecule

mation of Acetylene

excited state electronic configuration of carbon is $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$, In acetylene, one *s* ($2s^1$) and one p orbitals of carbon get hybridized ve two hybrid sp orbitals. One of two sp hybrid orbitals of each on atom overlaps with 1s half- orbital of hydrogen atom and C–H sigma bonds, while the

Figure 3.25: C_2H_2 molecule

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other sp hybrid orbital of one carbon atom overlaps with sp hybrid orbital of other carbon atom to form C–C sigma bond. The remaining $2p_y$ and $2p_z$ orbitals not take part in hybridization. They form two pi bonds between two carbon atoms through sidewise overlapping. Acetylene has linear shape and bond angle is 180°.

Acetylene (ethyne) molecule has three sigma bonds and two pi bonds. In case of sigma bond the electron density is maximum around the bond axis while in case of pi bond the electron density is maximum above and below the bond axis.

Table 3.3: Nature of Bonds and Shapes of Hybrid Orbitals

Hybridization	Angle	Shape	Number of Hybrid Orbitals	Sigma Bonds	Pi-bond	Example
sp^3	109.5°	Tetrahedral	4	4	0	Methane
sp^2	120°	Trigonal Planar	3	5	1	Ethene
sp	180°	Linear	2	3	2	Ethyne

3.3.2 Molecular Orbital Theory (MOT)

Valence bond theory provides an explanation of bonding in molecules and stabi of the covalent bond in terms of overlapping atomic orbitals. With the help hybridization we can explain molecular geometries predicted by the VSEPR theo It also helps to explain bivalency of beryllium, trivalency of boron and tetravalen of carbon. Valence bond theory, however, fails to explain why O_2 is paramagn and N_2 is diamagnetic. It also fails to explain excited states of molecules that h molecules absorb light and give colours. This theory does not give an explanation the electronic spectra of molecules. It is not successful in determining the locat of unpaired electrons in odd electron molecules like NO.

For this reason, in about 1932, a German physicist Friedrich Hund (19 1996), and American chemist Robert Sanderson Mulliken, gave the concept of molecular orbital theory. The molecular orbital model is more complex than the valence bond model, particularly for larger molecules, but magnetic and other properties of molecules are some times better explained by molecular orbital (MO) theory. Molecular orbital theory concentrates on molecule as a whole rather than concentrating on individual atoms. A wave function whose square gives the probability of finding an electron within a

Robert Sanderson Mulliken (1896-1986)

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given region of space in an atom is called atomic orbital while a wave function whose square gives the probability of finding an electron within a given region of space in a molecule is known as molecular orbital. Like atomic orbitals, molecular orbitals have specific energy levels and specific shapes, and they can be occupied by a maximum of two electrons with opposite spins. The difference between a molecular orbital and an atomic orbital is that an atomic orbital is associated with only one atom while molecular orbitals spread over all the atoms in the molecule. We may say that in an atomic orbital the electron is influenced by one nucleus while in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule.

Main Points of MOT

i) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. For example, two atomic orbitals overlap and give two molecular orbitals. One is bonding molecular orbital and the other is anti-bonding molecular orbital.

ii) The overlapped atomic orbitals do not maintain their identity.

iii) The molecular orbital which has less energy than parent atomic orbital is called bonding molecular orbital e.g. σ, π-orbitals.

iv) The molecular orbital which has greater energy than parent atomic orbitals is called anti-bonding molecular orbitals e.g. σ^*, π^*-orbitals. The asterisk, which you read as "star," tells us that the molecular orbital is anti-bonding.

v) The electron density in bonding molecular orbital is the maximum between the nuclei of the bonded atoms while in case of anti-bonding molecular orbital the electron density is the minimum between the nuclei of the bonded atoms.

vi) The bonding molecular orbital has greater stability than the corresponding anti-bonding molecular orbital because bonding molecular orbital is lower in energy than its corresponding anti-bonding molecular orbital.

Formation of Molecular Orbitals

Two types of molecular orbitals are formed as atoms approach each other and their atomic orbitals overlap.

i) The low energy molecular orbitals (bonding molecular orbitals).

ii) The high energy molecular orbitals (anti-bonding molecular orbitals).

These two types of molecular orbitals are formed due to s-s and p-p overlap.

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s-s Overlap

Two types of molecular orbitals are formed due to s-s overlap, one is a bonding molecular orbital at a lower energy than the original atomic orbitals. The other is an anti-bonding molecular orbital at a higher energy than the original atomic orbitals.

Consider the formation of H_2 molecule. Each hydrogen atom has one electron in 1s orbital. Hence, two $1s^1$ orbitals of two hydrogen atoms overlap to produce two molecular orbitals designated as σ_{1s} and σ^*_{1s}. The subscripts 1s indicate that the molecular orbital is formed from two 1s orbitals. The σ_{1s} orbital is called bonding molecular orbital whereas σ^*_{1s} (read "sigma-star-one-s") orbital is called anti-bonding molecular orbital. The electron density in a bonding molecular orbital is located between the nuclei of the bonded atoms because of which the repulsion between the nuclei is very less while in case of an anti-bonding molecular orbital, most of the electron density is located away from the space between the nuclei. This means that in this molecular orbital, the electrons spend little time between the nuclei. Note that the energy of a bonding molecular orbital is less than that of the separate atomic orbitals, whereas the energy of an anti-bonding orbital is higher. The total energy of two molecular orbitals remains the same as that of two original atomic orbitals.

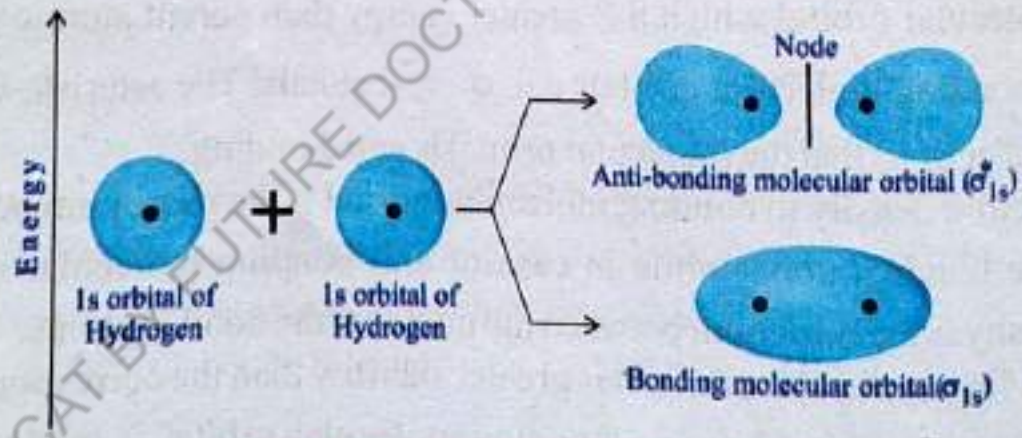

Figure 3.26: Linear overlap of s-s orbitals

It is important to note that 1s orbital of one atom can combine with 1s orbital of another atom but not with 2s orbital because of the higher energy of 2s orbital as compared to 1s orbital. Hence, the overlapping atomic orbitals must have equal or approximately equal energy. It is possible when atoms are different from each other.

p-p Overlap

The situation is more complex when the bonding involves p-orbitals. Two p-orbitals can form either a sigma bond or a pi bond. There are two different ways in which 2p

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atomic orbitals can combine (overlap).

i) Linear overlap ii) Parallel overlap

One set of 2p orbitals (2px atomic orbitals) can overlap along the same axis (x-axis)to give one bonding and one anti-bonding σ-orbital (σ_{2px} and σ^*_{2px}). These orbitals have cylindrical symmetry around the molecular axis.

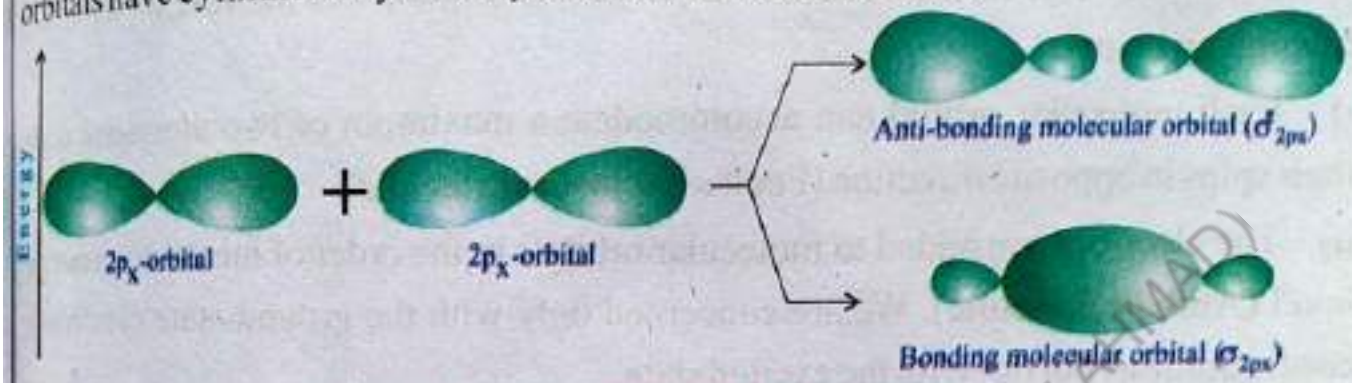

Figure 3.27: Linear overlap of $2p_x$-$2p_x$ orbitals

Keep in Mind

If atomic orbitals do not have the same symmetry then they will not combine. For example, $2p_x$ orbital of one atom can combine with $2p_x$ orbital of the other atom but not with the $2p_y$ or $2p_z$ orbital due to their different symmetries.

The other two sets of 2p orbitals ($2p_y$ and $2p_z$) are perpendicular to the x-axis, and they will overlap sidewise to give two bonding and two anti-bonding π-orbitals. The π molecular orbitals that result from degenerate $2p_y$ and $2p_z$ atomic orbitals are identical and have same energy and are said to be degenerate.

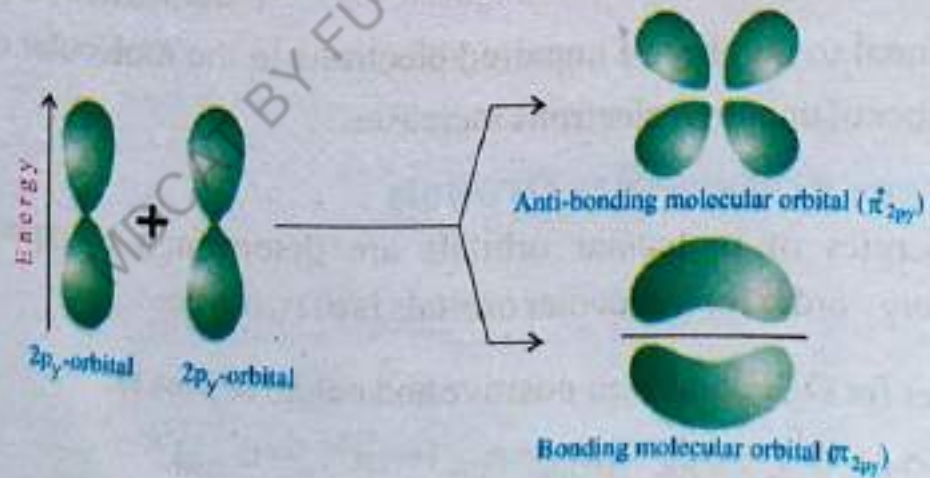

Figure 3.28: Parallel overlap of p_y-p_y orbitals

The overlap of the two p-orbitals is normally greater in a σ– molecular orbital than in a π–molecular orbital. Hence sigma bonds are stronger than pi bonds.

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Molecular Orbital Electronic Configuration

The distribution of electrons among various molecular orbitals is called the molecular orbital configuration. The method for determining the electronic configuration of a molecule is similar to that of the electronic configuration of atoms. To write the molecular orbital electronic configuration, we have to know the rules given below:

i) Each molecular orbital can accommodate a maximum of two electrons with their spins in opposite direction (Pauli's Exclusion Principle).

ii) The electrons are added to molecular orbitals in the order of increasing energy level (Aufbau Principle). We are concerned only with the ground-state electronic configurations but not with the excited state.

iii) If two or more same energy molecular orbitals are available then electrons prefer to occupy each molecular orbital singly before pairing begins (Hund's rule).

iv) The number of electrons in the molecular orbitals is equal to the sum of all the electrons on the bonding atoms.

The molecules are said to be diamagnetic if they have paired electrons in the molecular orbitals (bonding and antibonding molecular orbitals) and they are said to be paramagnetic if they have unpaired electrons in the molecular orbitals. Paramagnetic substances are attracted by a magnetic field whereas diamagnetic substances are slightly repelled by a magnetic field. Paramagnetic character is directly proportional to number of unpaired electrons in the molecular orbitals. It increases as number of unpaired electrons increases.

Relative Energies of Molecular Orbitals

The relative energies of molecular orbitals are determined by spectroscopic methods. The energy order for molecular orbitals is of two types:

i) Energy order for O_2, F_2 and their positive and negative ions is:

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2px} < (\pi_{2py} = \pi_{2pz}) < (\pi^*_{2py} = \pi^*_{2pz}) < \sigma^*_{2px}$$

ii) Energy order for Li_2, Be_2, B_2, C_2 and N_2 is:

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < (\pi_{2py} = \pi_{2pz}) < \sigma_{2px} < (\pi^*_{2py} = \pi^*_{2pz}) < \sigma^*_{2px}$$

Energy level diagrams are shown as:

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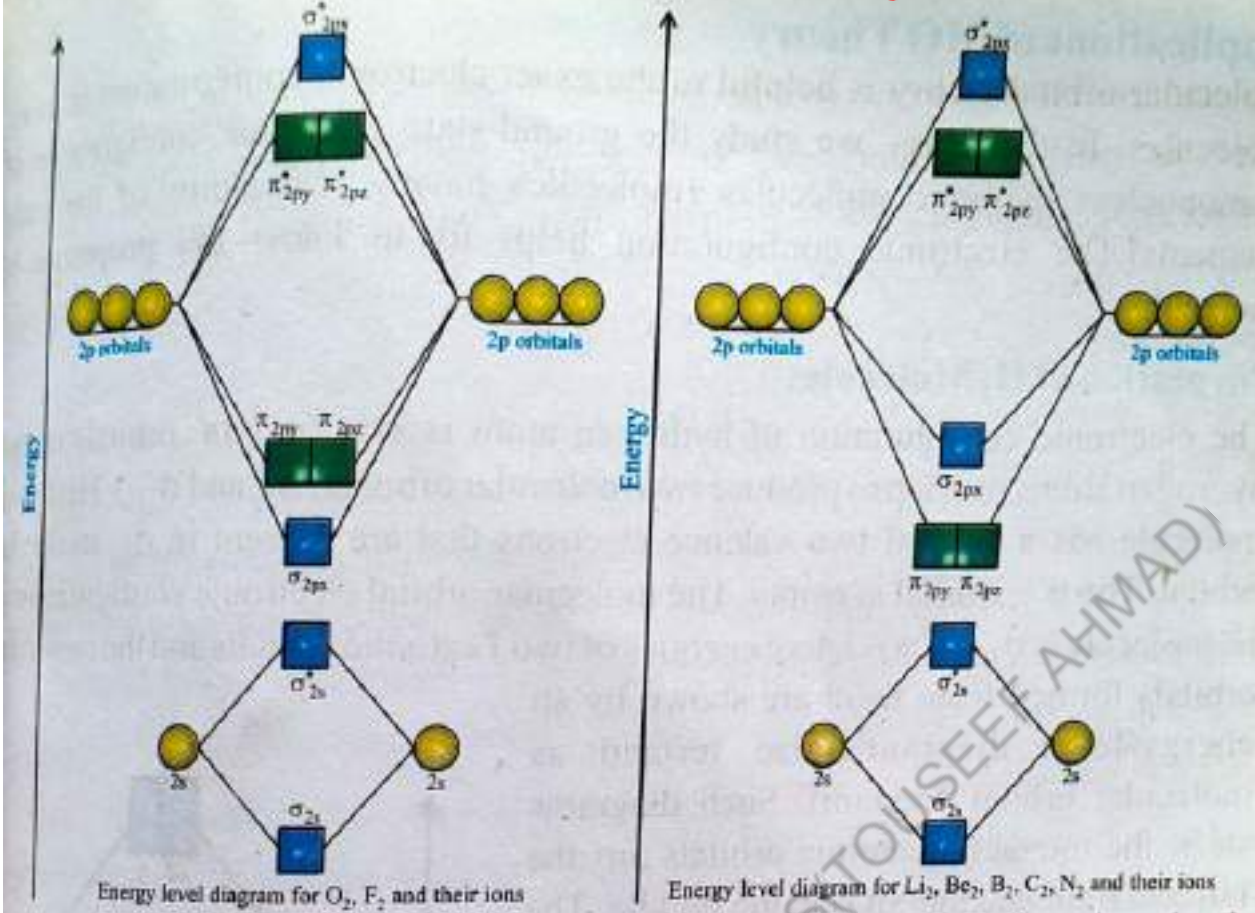

Energy level diagram for O_2, F_2 and their ions

Energy level diagram for Li_2, Be_2, B_2, C_2, N_2 and their ions

gure 3.29: Energy level diagrams for first and second period homo-nuclear diatomic molecules d ions

The overlap of the two 2px atomic orbitals is greater than two 2py or 2pz bitals. Because of this the bonding σ_{2px} molecular orbital has lower energy than e degenerate π_{2py} and π_{2pz} molecular orbitals. While in case of Li_2, Be_2, B_2, C_2 and the bonding σ_{2px} molecular orbital has higher energy than the degenerate π_{2py} and e molecular orbitals. This U-turn is due to the overlap of a 2s orbital on one of the ms with a 2p orbital on the other. Due to overlapping, the energy difference tween σ_{2s} and σ_{2px} molecular orbitals increases, where the energy of σ_{2s} decreases d that of σ_{2px} increases. The energy of σ_{2px} is raised to such an extent that it comes higher in energy than π_{2py} and π_{2pz} molecular orbitals.

nd Order

e number of bonds formed between two atoms by the overlap of atomic orbitals is led bond order.

r diatomic molecules, it can be defined as:

The half of the difference between the number of bonding electrons (n_b) and mber of anti-bonding electrons (n_a) is called bond order.

Mathematically:

$$\text{Bond Order} = \frac{n_b - n_a}{2}$$

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Applications of MO Theory

Molecular orbital theory is helpful to the exact electronic configuration of molecules. In this class, we study the ground-state electronic configuration homonuclear diatomic molecules (molecules having two atoms of the same elements). The electronic configuration helps us to know the properties molecules.

Formation of H_2 Molecule:

The electronic configuration of hydrogen atom is $1s^1$. Two $1s^1$ orbitals of hydrogen atoms overlap to produce two molecular orbitals (σ_{1s} and σ^*_{1s}). Hydrogen molecule has a total of two valence electrons that are present in σ_{1s} molecular orbital. The σ^*_{1s} orbital is empty. The molecular orbital electronic configuration H_2 molecule is σ_{1s}^2. The relative energies of two 1s atomic orbitals and the molecular orbitals formed from them are shown by an energy-level diagram (also termed as molecular orbital diagram). Such diagrams show the interacting atomic orbitals on the left and right and the MOs in the middle. The bond order of H_2 molecule can be calculated as:

$$\text{Bond Order of } H_2 = \frac{n_b - n_a}{2} = \frac{2-0}{2} = 1$$

Hence one single covalent bond is formed in H_2. We, therefore, say that the H_2 molecule is stable and can exist.

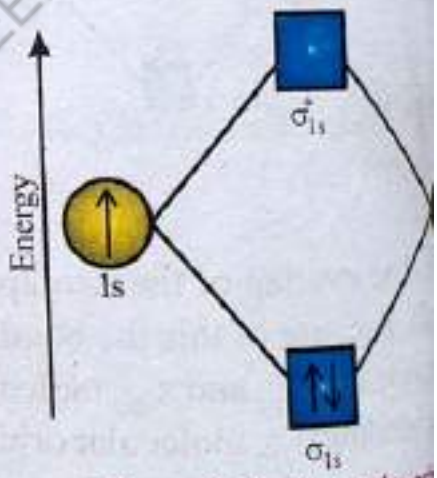

Figure 3.30: Molecular orbital diagram for H_2

Formation of He_2 (Hypothetical)

The electronic configuration of helium is $1s^2$. Two $1s^2$ orbitals of two Helium atoms combine to give one bonding (σ_{1s}) and one anti bonding (σ^*_{1s}) molecular orbital. A hypothetical molecule has four electrons, two in σ_{1s} and two in σ^*_{1s} as shown in the figure 3.31. The molecular orbital electronic configuration of helium is $\sigma_{1s}^2 < \sigma^*_{1s}^2$.

$$\text{Bond Order of } He_2 = \frac{n_b - n_a}{2} = \frac{2-2}{2} = 0$$

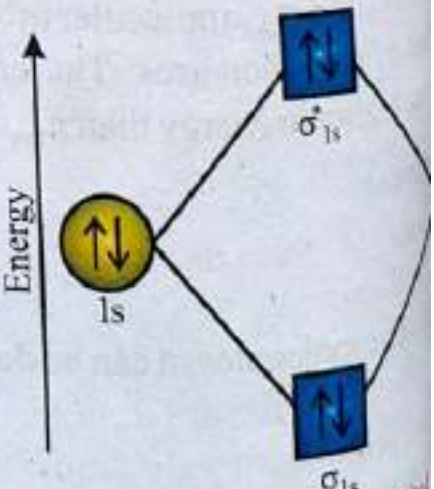

Figure 3.31: Molecular orbital for Hypothetical He_2 Mole

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Zero Value shows that this molecule is unstable and no bond would be formed between two helium atoms. Hence, it is mono-atomic molecule.

Formation of N_2 Molecule

The electronic configuration of nitrogen atom is $1s^2, 2s^2, 2px^1, 2py^1, 2pz^1$. When two nitrogen atoms approach one another to form N_2 molecule, only like orbitals on the two atoms combine. The 1s orbital of one atom combines with 1s orbital of the other atom and the 2s orbital of one atom combines with 2s orbital of the other atom. The 1s orbital of one atom does not combine with the 2s orbital of the other atom, because their energies are quite different. The two 2px orbitals that lie on the same plane (internuclear axis) overlap head on and form σ_{2px} and σ^*_{2px} molecular orbitals. The other two pairs of 2py and 2pz orbitals which are perpendicular to the x-axis overlap sidewise and form two degenerate bonding molecular orbitals (π_{2py} and π_{2pz}) and two degenerate anti-bonding molecular orbitals (π^*_{2py} and π^*_{2pz}).

The molecular orbital diagram of N_2 molecule is shown in figure 3.32. Because of the absence of unpaired electrons in the molecular orbitals, the nitrogen is diamagnetic and is very stable molecule. The molecular orbital electronic configuration of N_2 is:

$$\sigma_{1s^2} < \sigma^*_{1s^2} < \sigma_{2s^2} < \sigma^*_{2s^2} < \pi_{2py^2} = \pi_{2pz^2} < \sigma_{2px^2} < \pi^*_{2py^0} = \pi^*_{2pz^0} < \sigma^*_{2px^0}$$

Since the inner shell electrons (K-shell) have no significant effect on bonding, therefore, the $\sigma_{1s^2} < \sigma^*_{1s^2}$ is frequently condensed as KK. Now the configuration of nitrogen molecule can be written as:

$$KK < \sigma_{2s^2} < \sigma^*_{2s^2} < \pi_{2py^2} = \pi_{2pz^2} < \sigma_{2px^2} < \pi^*_{2py^0} = \pi^*_{2pz^0} < \sigma^*_{2px^0}$$

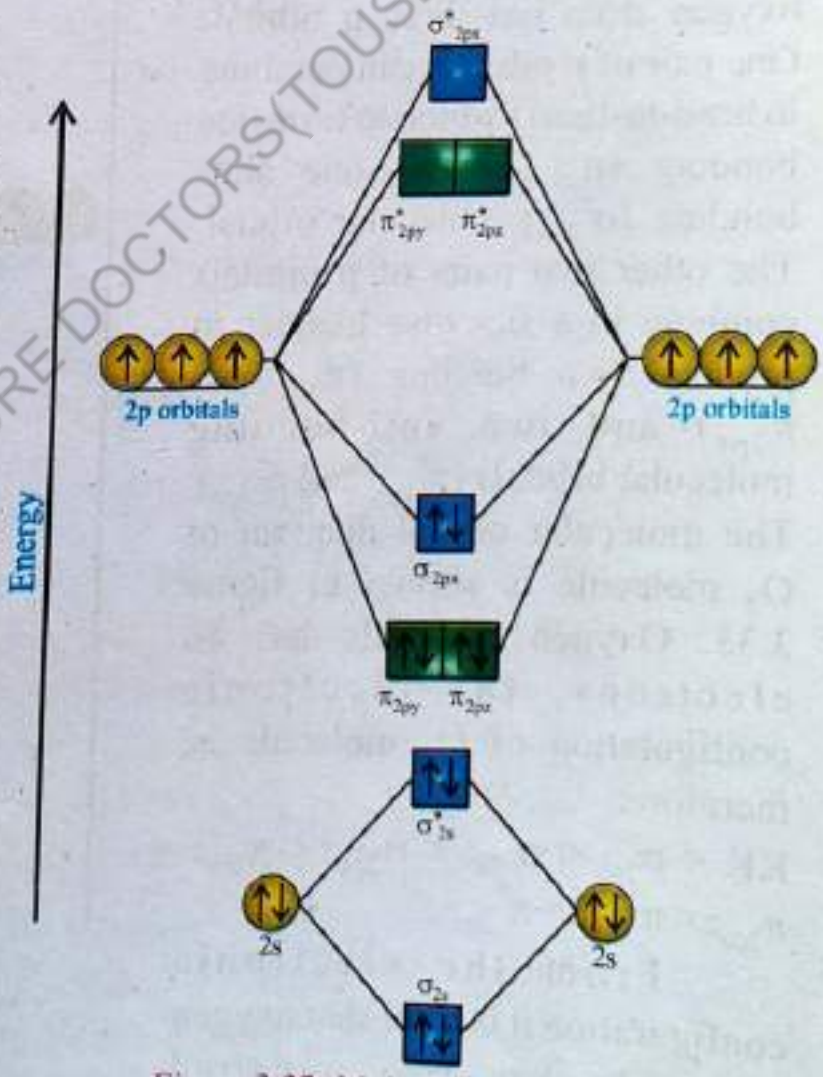

Figure 3.32: Molecular orbital diagram for N_2 molecule

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N_2 molecule has eight bonding electrons and two anti-bonding electrons therefore the bond order of nitrogen is:

$$\text{Bond Order of } N_2 = \frac{n_b - n_a}{2} = \frac{8-2}{2} = 3$$

The bond order of nitrogen molecule is three which shows that it forms triple bond (N≡N), one is sigma and two are pi-bonds.

Formation of O_2 Molecule

The electronic configuration of oxygen atom is $1s^2$, $2s^2$, $2p_{x^1}$, $2p_{y^1}$, $2p_{z^2}$. As $1s^2$ and $2s^2$ orbitals have no significant effect on bonding, therefore we will not discuss the interactions of these orbitals. Each oxygen atom has three p orbital. One pair of *p* orbitals can combine in head-to-head fashion to form one bonding (σ_{2px}) and one anti-bonding (σ^*_{2px}) molecular orbital. The other two pairs of p orbitals combine in a sidewise manner to produce two bonding (π_{2py} and π_{2pz}) and two anti-bonding molecular orbitals (π^*_{2py} and π^*_{2pz}). The molecular orbital diagram of O_2 molecule is shown in figure 3.33. Oxygen molecule has 16 electrons, the electronic configuration of O_2 molecule is, therefore:

$$KK < \sigma_{2s^2} < \sigma^*_{2s^2} < \sigma_{2px^2} < \pi_{2py^2} = \pi_{2pz^2} < \pi^*_{2py^1} = \pi^*_{2pz^1}$$

From the electronic configuration it is clear that oxygen molecule has two unpaired electrons in its two degenerate π^*_{2py}

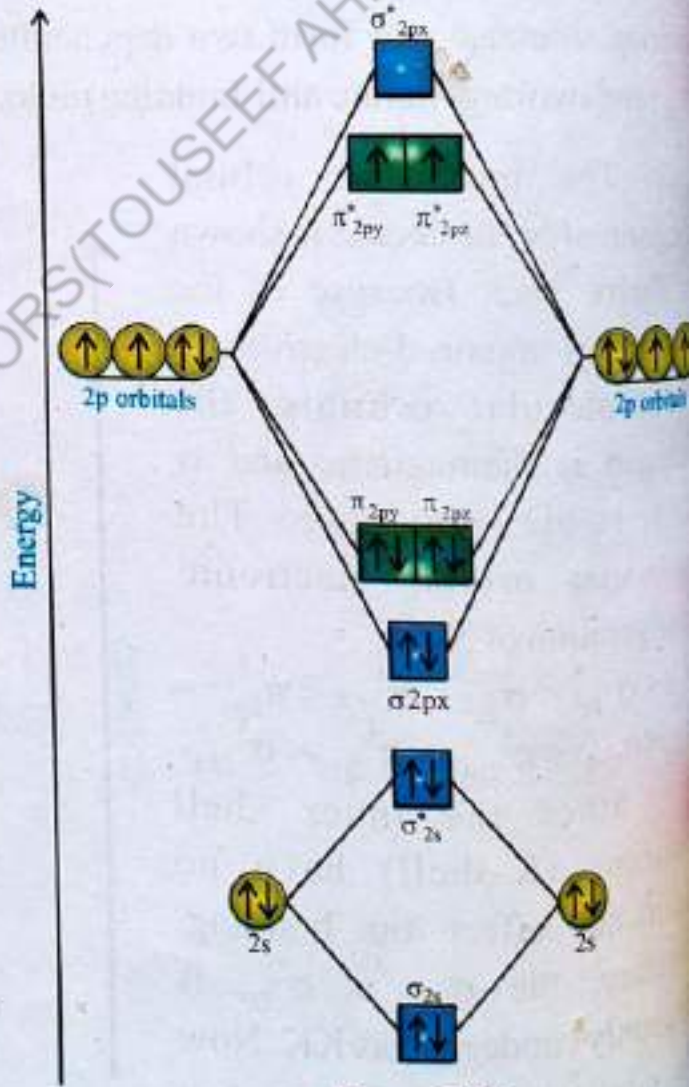

Figure 3.33:
Molecular orbital diagram for O_2 molecule

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and π^*_{2pz} orbitals and is, therefore, paramagnetic. In the molecular orbital diagram, eight electrons occupy bonding orbitals and four electrons anti-bonding molecular orbitals, so the bond order of O_2 molecule is:

$$\text{Bond Order of } O_2 = \frac{n_b - n_a}{2}$$

$$= \frac{8-4}{2} = 2$$

A bond order of two indicates that there is double covalent bond in O_2 molecule. One bond is sigma and other one is π-bond.

3.4 Bond characteristics

3.4.1 Bond Energy

The average amount of energy needed to break all bonds in one mole of a gaseous substance is called bond energy.

It is also called bond enthalpy as it is a measure of enthalpy change (ΔH) at 298K. For example, the bond enthalpy for the bond in H_2 is the enthalpy change when one mole of gaseous H_2 dissociates into hydrogen atoms.

$$H-H \longrightarrow 2H \qquad \Delta H = +436 \text{kJ/mol}$$

This equation tells us that breaking the covalent bonds in 1 mole of gaseous H_2 molecules requires 436kJ of energy.

The bond energy can also be defined as:

The amount of energy released when one mole of bonds are formed from component atoms is called bond energy.

For example, the bond energy for the formation of H_2 molecules is:

$$2H \longrightarrow H-H \qquad \Delta H = -436 \text{kJ/mol}$$

Keep in Mind

- Bond breaking is an endothermic process.
- Bond formation is an exothermic process.
- When the net energy value is positive, the reaction is endothermic.
- When the net energy value is negative, the reaction is exothermic.

The unit of bond energy is kJ/mol or kcal/mol. The bond energy is a measure of the stability of molecule. The stability of a molecule is related to the strengths of covalent bonds. The strength of a covalent bond between two atoms is determined by the energy required to break the bond. The greater the bond energy,

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the stronger the chemical bond and the stable is the molecule. For exam hydrazine (N_2H_4) is highly reactive (unstable) whereas nitrogen (N_2) is a sta molecule. Because nitrogen has a very strong nitrogen-nitrogen triple bond (N≡ while hydrazine has a weak nitrogen-nitrogen single bond (N – N).

Bond energies play an important role in thermochemistry. It helps us explain the heat of chemical reactions. For a chemical reaction, the enthalpy cha can be written as:

$$\Delta H = \Sigma BE \text{ (reactants)} + \Sigma BE \text{ (Products)}$$

Where, Σ shows the sum of terms and *BE* shows the bond energy. The enthalpy of the reaction,(ΔH), is the sum of energies needed to break old bo in the reactants plus the sum of the energies released in the formation of new bo in the products. Consider the reaction between hydrogen and chlorine to form H When one mole of hydrogen gas reacts with one mole of chlorine gas then 2 m of HCl gas is formed.

$$H_2 + Cl_2 \longrightarrow 2HCl \qquad \Delta H = -1432 \text{ kJ/mol}$$

This reaction involves breaking one H–H and one Cl–Cl bond and form two H–Cl bonds. The enthalpy change for this reaction is estimated as:

The amount of energy required to break H–H bond = 436 kJ/mol

The amount of energy required to break Cl–Cl bond = 242 kJ/mol

The sum of bond energies of H–H and Cl–Cl = 436kJ/mol + 242kJ/mol = 678kJ

The amount of energy released when H–Cl bonds are formed = –432 kJ/mol

The energy released when 2 moles of H–Cl bonds are formed = –864 kJ/mol

ΔH for HCl = ΣBE (reactants) + ΣBE (products)

= (+678kJ/mol) + (–864kJ/mol)

= –186kJ/mol

This is an example of an exothermic reaction. In an exothermic reactio energy required to break the bonds is less than the energy released to make th bonds. The excess energy is released as heat. Conversely, in an endoth reaction, the energy required to break the bonds is more than the energy rele make the new bonds. Energy is drawn in from the surroundings to comple reaction.

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Table 3.1: Average Bond Energies (kJ/mol)

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H – H	436	C – Br	276	O – F	190		
H – F	565	C – I	216	O – Cl	203	S – H	347
H – Cl	432			O – Br	234	S – S	266
H – Br	366	N – H	391	O – I	234	S – F	327
H – I	299	N – N	160			S – Cl	271
		N = N	418	Si – H	323	S – Br	218
C – H	413	N ≡ N	941	Si – O	368	S – I	170
C – C	348	N – P	209	Si – Si	226		
C = C	614	N – O	201	Si – S	226	F – F	159
C ≡ C	839	N = O	607	Si – F	565	F – Cl	193
C – Si	301	N ≡ O	631	Si – Cl	381	F – Br	212
C – N	305	N – F	272	Si – Br	310	F – I	263
C = N	615	N – Cl	200	Si – I	234		
C ≡ N	891	N – Br	243			Cl – Cl	243
C – O	358	N – I	159	P – H	320	Cl – Br	215
C = O	745 (799 in CO_2)			P – Si	213	Cl – I	208
C ≡ O	1070	O – H	463	P – P	200		
C – P	264	O – O	204	P – F	490	Br – Br	193
C – S	259	O = O	495	P – Cl	331	Br – I	175
C – F	453	O – P	351	P – Br	272	I – I	151
C – Cl	339	O – S	265	P – I	184		

Factors Affecting Bond Energy

Electronegativity (E.N) Difference

Greater the electronegativity difference of the bonded atoms, greater would be the bond energy. For example, the bond energies for HF, HCl, HBr, and HI are 565, 432, 366 and 299kJ/mol respectively. The bond energies of hydrogen halides decrease in the following order:

$$HF > HCl > HBr > HI$$

The highest value of bond energy of HF is due the greatest E.N difference value and the lowest value of bond energy of HI is due to the smallest E.N difference value.

Multiple Bonds

Bond energies of multiple bonds (= or ≡) are greater than single bond. For example, the bond energy of nitrogen-nitrogen single bond (N–N), double bond (N=N) and

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triple bond (N≡N) is 160, 418, and 941 kJ/mol, respectively. It shows that the triple bond is stronger than the double bond, which in turn is stronger than the single bond.

Bond Length

Shorter the bond length, greater will be the bond energy and vice versa.

As the number of bonds between the carbon atoms increases, the bond length decreases and the bond enthalpy increase. That is, the carbon atoms are held more closely and more tightly together.

Table 3.5: The Relation between Bond Length and Bond Energy

Bond	Average Bond Length (pm)	Average Bond Energy (kJ/mol)
C - C	154	348
C = C	133	614
C ≡ C	120	839

Atomic Size

Greater the size of bonded atoms, greater would be the bond length, hence smaller will be the bond energy and vice versa. For example, the bond energy of I_2(151kJmol^{-1}) is smaller than that of Cl_2(243kJmol^{-1}). This is because the I–I bond length is larger than Cl – Cl bond length.

3.4.2 Bond Length

The distance between the nuclei of two covalently bonded atoms is called bond length. It is also known as bond distance. Bond lengths can experimentally be determined by using the physical techniques such as, electron diffraction, x-ray diffraction, and spectral studies. In many cases, bond lengths for single covalent bonds in compounds can be roughly predicted from covalent radii. Hence, bond length can be estimated as the sum of the covalent radii of the two atoms. For example, because the covalent radius of hydrogen is 37pm (one half the bond length of H – H i.e. $\frac{1}{2} \times 74 = 37$) and that of chlorine is 99pm which is one-half of the bond length (198pm), therefore the H–Cl bond length in hydrochloric acid is approximately 136pm (37pm + 99pm = 136pm). The actual value of bond length in HCl is 127pm. The bond length of triple bond is shorter than double bond which in turn is shorter than single covalent bond. As the number of bonds (bond order) between two atoms increases, the bonds length decreases. For example, the average bond lengths for carbon-carbon single, double and triple bonds are given here in the table 3.6.

Table 3.6: Bond length of single and multiple bonds of carbon

Types of bond	Bond Length
C – C	154pm
C = C	133pm
C ≡ C	120pm

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The values of average bond lengths help us:

i) To provide the clue to the type of bonding present.

ii) To understand resonance structures in molecules like ozone.

Table 3.7: Average Bond Lengths (pm)

Bond	Bond Length	Bond	Bond Length	Bond	Bond Length	Bond	Bond Length
H – H	74	C – O	143	N – P	177	O – F	190
H – F	92	C = O	123	N – O	144	O – Cl	164
H – Cl	127	C ≡ O	113	N = O	120	O – Br	172
H – Br	141	C – P	187	N ≡ O	106	O – I	194
H – I	161	C – S	181	N – F	139		
		C – F	133	N – Cl	191	Si – H	148
C – H	109	C – Cl	177	N – Br	214	Si – O	161
C – C	154	C – Br	194	N – I	222	Si – Si	234
C = C	133	C – I	213			Si – S	210
C ≡ C	120			O – H	96	Si – F	156
C – Si	186	N – H	101	O – O	148	Si – Cl	204
C – N	147	N – N	146	O = O	121	Si – Br	310
C = N	127	N = N	122	O – P	160	Si – I	240
C ≡ N	115	N ≡ N	110	O – S	151		
P – H	142					Cl – Br	214
P – Si	227	S – H	134	F – F	143	Cl – I	243
P – P	221	S – S	204	F – Cl	166		
P – F	156	S – F	158	F – Br	178	Br – Br	228
P – Cl	204	S – Cl	201	F – I	187	Br – I	248
P – Br	222	S – Br	225			I – I	266
P – I	184	S – I	234	Cl – Cl	199		

Factors Affecting Bond Length

Atomic Size

The bond length increases by increasing atomic size and vice versa. For example, bond length of I – I (266 pm) is more than Br – Br (228 pm).

Electronegativity (E.N) Difference

The bond length increases by decreasing the electronegativity difference of two bonded atoms. For example, the HCl bond length is greater than HF bond length.

Heteronuclear Molecules	ΔEN (Electronegativity Difference)	Bond Length (pm)
HF	1.9	92
HCl	0.9	127
HBr	0.7	141
HI	0.4	161

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So order of bond length will be:

$HF < HCl < HBr < HI$

Type of Hybridization

Greater the s-orbital character in the hybrid orbital, shorter will be bond length. F example, the carbon-carbon bond distances in ethane, ethene and ethyne are 1 133 and 120 pm respectively, because ethane, ethene and ethyne have sp^3, sp^2 and hybridization respectively. The bond length also reduces due to the presence of bonds in ethene and ethyne.

3.4.3 Electronegativity (E.N)

The measure of the ability of an atom in a molecule to attract the bonding electr (shared electrons) to itself is called electronegativity.

The electronegativity of elements decreases from top to bottom in a group periodic table due to increase in atomic size. It increases from left to right in a per of periodic table due to decrease in atomic size.

Table 3.8: The Pauling Electronegativity Values

H 2.20																
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.00
K 0.82	Ca 1.00	Sc 1.36	Ti 1.50	V 1.63	Cr 1.60	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.60	Ge 1.80	As 2.18	Se 2.55	Br 2.96
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.60	Mo 2.16	Tc 1.90	Ru 2.20	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.86	Sb 2.03	Te 2.10	I 2.66
Cs 0.79	Ba 0.98	Lu 1.27	Hf 1.30	Ta 1.50	W 2.36	Re 1.90	Os 2.20	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.00	At 2.20
Fr 0.70	Ra 0.89	Lr 1.30	Rf ---	Db ---	Sg ---	Bh ---	Hs ---	Mt ---	Ds ---	Rg ---	Cn ---	Nh ---	Fl ---	Mc ---	Lv ---	Ts ---

La 1.10	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.20	Gd 1.20	Tb 1.20	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25
Ac 1.10	Th 1.30	Pa 1.50	U 1.70	Np 1.36	Pu 1.28	Am 1.30	Cm 1.30	Bk 1.30	Cf 1.30	Es 1.30	Fm 1.30	Md 1.30

The elements with high electronegativity values, such as fluorine, at bonding electrons more strongly than the elements such as sodium that have electronegativity values.

3.4.4 Ionic Character

Unequal distribution of bonding electrons between two atoms is called character or polarity of molecule. The measure of extent of sharing of elec

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(how equally or unequally the electrons are shared) in a covalent bond is known as bond polarity.

A covalent bond involves the sharing of at least one pair of electrons between two atoms. In a molecule like H_2, in which the atoms are identical, the bonding electrons are shared equally. That is, the electrons spend the same amount of time in the vicinity of each atom. We can say that the electron pair is situated exactly between the two identical nuclei. The bond so formed is called non-polar covalent bond or simply non-polar bond. But when the two atoms are of different elements, the bonding electrons are not shared equally. That is, the bonding electrons spend more time near one atom than the other. For example, in the case of the HCl molecule, the bonding electrons spend more time near the chlorine atom than the hydrogen atom. This "unequal sharing" of the bonding electron pair results in a relatively greater electron density near the chlorine atom and a correspondingly lower electron density near hydrogen. The resultant covalent bond is a polar covalent bond (or polar bond).

Keep in Mind

Polar covalent bonds are called polar because the unequal electron sharing creates two poles across the bond. The HCl bond has two poles, just like in battery, one positive and one negative. The symbol (delta) is used to denote a partial charge. The symbols δ^+ and δ^- (delta plus and delta minus) are used to show the distribution of partial charges in a polar covalent bond. These symbols, delta plus and delta minus, represent a partial positive charge and a partial negative charge.

You can consider the polar covalent bond as intermediate between a nonpolar covalent bond (where sharing of electrons is exactly equal), as in H_2, and n ionic bond (where transfer of the electron(s) is nearly complete), as in NaCl. rom this point of view, an ionic bond is simply an extreme example of a polar valent bond. We use a quantity called electronegativity to estimate whether a ven bond is nonpolar covalent, polar covalent, or ionic.

Electronegativity is used to predict nature of bond. But predictions may not ways be correct because there is no clear-cut division between ionic bond and lar covalent bond. The electronegativity difference of two bonded atoms predicts e nature of bond or bond polarity. The greater the difference between the ectronegativity values of the bonding atoms, the greater would be the bond larity and the stronger will be the bond. The electronegativity difference between

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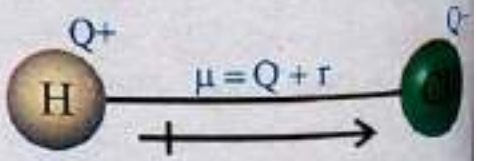
two bonding atoms is often represented by the symbol ΔEN, where EN is a symbol for electronegativity and Δ is the Greek letter delta which means "difference." The electronegativity difference (ΔEN) is determined by subtracting the smaller electronegativity value from the larger. When ΔEN is zero, the bond will be a pure covalent bond (100 % covalent). When the electronegativity difference in a bond is 1.8 or greater, the bond will be ionic. If the ΔEN is from 0.5 to 1.6, the bond will be a polar covalent bond. When the ΔEN is below 0.5, the bond is normally classified as a covalent bond, with little or no polarity. If ΔEN is equal to 1.7 the bond will have 50% covalent character and 50% ionic character.

3.4.5 Dipole Moment

Dipole moment is the measure of polarity of the bond in a covalently bonded molecule. We can say that the polarity of a molecule can be measured experimentally by measuring its permanent dipole moment. The greater the dipole moment, the greater is the polarity of molecule. The molecule is considered as non-polar when its dipole moment is zero. We know that polar covalent bonds form between atoms of different electronegativity. In the HCl molecule, the chlorine atom is more electronegative than hydrogen, and the chlorine atom thus attracts the electrons towards itself. As a consequence, the electrons are displaced toward the more electronegative chlorine atom and it gets partial negative charge (δ^-). On the other hand, the less electronegative hydrogen atom attains partial positive charge (δ^+). The molecule such as HCl which has a partial negative charge at one end and partial positive charge at the other end is said to be polar.



Dipole moment is defined as:

The product of electric charge on either end of a polar bond and the distance between the charges is called dipole moment. It is shown by μ (mu).

Mathematically,

$$\text{Dipole moment} = \text{Charge} \times \text{distance}$$

$$\mu = Q \times r$$

Where Q is charge and r is distance. Q refers only to the magnitude of the charge and not to its sign, so is always positive. Dipole moment is usually measured in debye units (D), (pronounced as duh-bye), named for the Dutch-American chemist and physicist Peter Debye. In SI units, dipole moments are measured in coulomb-meters (C.m).

Peter Debye
(1884 - 1966)

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$1D = 3.34 \times 10^{-30} C.m$

The dipole moment of water is 1.85D and that of ammonia is 1.47D. The larger value for the dipole moment of water means that water is more polar than ammonia. The dipole moment is a vector quantity which has both magnitude and direction. The direction of dipole moment is from positive toward negative. We often represent the dipole using an arrow with a cross at one end ($+\longrightarrow$) to indicate the direction of electron displacement. The point of the arrow represents the negative end of the dipole (δ^-) and the crossed end (which looks like a plus sign) represents the positive end (δ^+). The length of arrow shows magnitude and its head shows direction.

Diatomic molecules containing atoms of different elements (for example, HF, HCl, HBr, HI, CO, and NO) have dipole moments and are called polar molecules. Diatomic molecules containing atoms of the same element (for example, H_2, O_2, N_2, F_2 and Cl_2) do not have dipole moments and are called nonpolar molecules. For a molecule made up of three or more atoms, both the polarity of the bonds and the molecular geometry determine whether there is a dipole moment. Even if polar bonds are present, the molecule will not necessarily have a dipole moment. It is noted that if a molecule is polyatomic and has two or more dipoles, then net dipole moment is the vector sum of individual bond moments. An example is the CO_2 molecule, which is a linear molecule. In this case the opposing bond polarities cancel out, and the carbon dioxide molecule does not have a dipole moment. There are many cases besides that of carbon dioxide where the bond polarities oppose and exactly cancel each other. Some common types of molecules with polar bonds but no dipole moment are CS_2, SO_3, CH_4, SiH_4 and CCl_4.

Example 3.1

Calculate the dipole moment, in Debye unit, of a hypothetical 100 % ionic molecule where unit positive and unit negative charges are at a distance of $1A^\circ$. The charge on the either ends of the molecule is $1.60 \times 10^{-19} C$.

Solution

Distance $= r = 1A^\circ = 1 \times 10^{-10} m = 10^{-10} m$

Charge $= Q = 1.60 \times 10^{-19} C$

Dipole moment $= \mu = ?$

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As we know that,

$\mu = Q \times r$

Therefore,

Dipole moment of the hypothetical molecule $= 1.60 \times 10^{-19}\ C \times 10^{-10}\ m$

$= 1.60 \times 10^{-29}\ C.m$

Since, $1D = 3.34 \times 10^{-30}\ C.m$

Hence, $\mu = \dfrac{1.60 \times 10^{-29}\ C.m}{3.34 \times 10^{-30}\ C.m/D} = 4.79D$

Applications of Dipole Moment

Dipole moment can be used to determine:

i) Percentage ionic character ii) Geometries of molecules.

i) Percentage Ionic Character:

It is defined as:

The observed dipole moment divided by ionic dipole moment and the answer is multiplied by 100 is called %age ionic character.

$$\%age\ ionic\ character = \frac{Observed\ dipole\ moment}{Ionic\ dipole\ moment} \times 100$$

%age ionic character of some molecules is:

HF = 43%, HCl = 17%, HBr = 12%, HI = 5%

It decreases by decreasing dipole moment. If dipole moment is zero, the bond is 100% covalent.

Example 3.2

The observed dipole moment of HCl is 1.03D and the distance between the atoms (bond length) is 127pm. Find the percentage ionic character of the HCl bond?

Solution:

Observed dipole moment of HCl = μ_{obs} = 1.03 D

Distance between H and Cl atoms = r = $127 \times 10^{-12}\ m = 1.27 \times 10^{-10}\ m$

When HCl is 100 ionic, then the charge on each atom (Q) is the electronic charge and it is equal to 1.60×10^{-19} C.

The ionic dipole moment can be calculated as:

Ionic dipole moment = $(1.60 \times 10^{-19}\ C) \times (1.27 \times 10^{-10}\ m) = 2.03 \times 10^{-29}\ C.m$

$$\text{Ionic dipole moment in Debye unit} = \frac{2.03 \times 10^{-29}\ C.m}{3.34 \times 10^{-30}\ C.m/D} = 6.08D$$

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The percentage ionic character of HCl can be calculated by dividing the observed dipole moment with ionic dipole moment and the answer is multiplied by 100:

$$\text{Percentage ionic character of HCl} = \frac{1.03D}{6.08D} \times 100\% = 16.9\%$$

ii) Geometries of Molecules

The dipole moment helps to determine the geometries of molecules.

Geometries of Diatomic Molecules:

The geometry of diatomic molecules is always linear whether they are polar or non-polar.

Table 3.9: Dipole Moments and Geometries of Some Diatomic Molecules

Name of Molecule	Formula	Dipole Moment (D)	Nature of Bond	Geometry of Molecule
Hydrogen fluoride	HF	1.82	Polar	Linear
Hydrogen chloride	HCl	1.03	Polar	Linear
Hydrogen bromide	HBr	0.78	Polar	Linear
Hydrogen iodide	HI	0.38	Polar	Linear
Carbon monoxide	CO	0.12	Polar	Linear
Hydrogen	H_2	0.00	Non-polar	Linear
Nitrogen	N_2	0.00	Non-polar	Linear

The HF molecule has dipole moment because the electronegativity of fluorine (3.98) is greater than that of hydrogen (2.1). Thus fluorine attains partial negative and hydrogen attains partial positive charge and HF molecule becomes polar. On the other hand hydrogen molecule is non-polar and has no dipole moment. This is because the two hydrogen atoms share electrons equally and no bond polarity occurs.

Geometries of Triatomic Molecules

Whether a triatomic molecule has linear or angular geometry, it can be decided with the help of dipole moment. Triatomic linear molecules have no dipole moment, because the bond moments of the two polar bonds are equal and opposite. They cancel the effect of each other. For example,

i) Carbon dioxide is a molecule with polar covalent bonds. The shape of CO_2 molecule is linear. It has two dipoles. They are equal and have opposite directions. So they cancel the effect of each other. Therefore, the dipole moment of

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CO_2 is zero. Although carbon dioxide has relatively strong polar covalent bonds, CO_2 is a nonpolar molecule. On the other hand, if the CO_2 molecule were bent, the two bond moments would partially reinforce each other, so that the molecule would have a dipole moment.

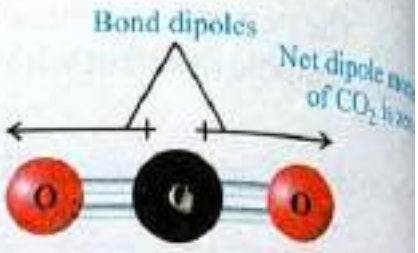

Figure 3.34: Geometry of CO_2 Molecule

Keep in Mind

You can think of two groups (say one group belongs to first year and the other belongs to second year) of students in a tug-of-war. The first year students are at one end of the rope and the second year students are at the other end. Each group pulls the rope towards itself, There is no movement, because each group pulls on the rope with the same force but in the opposite direction. Hence, the net force is zero.

ii) Consider the water molecule which has two polar O–H bonds. The bond dipoles point from the hydrogen atoms toward the more electronegative oxygen. They are equal but do not have opposite directions. So they do not cancel the effect of each other. This is due to non-linear geometry of H_2O. The shape of H_2O is bent or angular. Because of its bent shape, the water molecule as a whole has a negative pole and a positive pole. If the H_2O molecule were linear, the dipole moment would be zero. Similarly, geometries of H_2S and SO_2 are also angular.

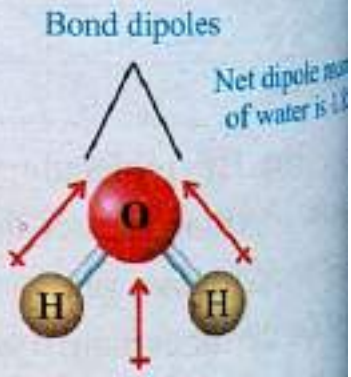

Figure 3.35: Geometry of Water Molecule

Geometries of Symmetrical Molecules

The symmetrical triangular planar molecules (BF_3, $AlCl_3$ and SO_3) and tetrahedral molecules (CH_4, SiH_4 and CCl_4) have zero dipole moments. In these molecules bond moments cancel effect of one another.

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$\mu = 0$
Boron Trifluoride
(Non-polar)

$\mu = 0$
Carbon
Tetrachloride
(Non-polar)

$\mu = 0$
Methane
(Non-polar)

Figure 3.36: Geometries of symmetrical polyatomic molecules

Table 3.10: Dipole Moments and Geometries of Some Polyatomic Molecules

Name of Molecule	Formula	Dipole Moment (D)	Nature of Bond	Geometry of Molecule
Carbon dioxide	CO_2	0.00	Non-polar	Linear
Carbon disulphide	CS_2	0.00	Non-polar	Linear
Hydrogen monoxide	H_2O	1.85	Polar	Angular (or bent)
Hydrogen sulphide	H_2S	0.95	Polar	Angular
Sulphur dioxide	SO_2	1.61	Polar	Angular
Ammonia	NH_3	1.46	Polar	Trigonal pyramidal
Phosphine	PH_3	0.55	Polar	Trigonal pyramidal
Boron fluoride	BF_3	0.00	Non-polar	Trigonal planar
Sulphur trioxide	SO_3	0.00	Non-polar	Trigonal planar
Methane	CH_4	0.00	Non-polar	Tetrahedral
Methyl fluoride	CH_3F	1.81	Polar	Tetrahedral
Methyl chloride	CH_3Cl	1.45	Polar	Tetrahedral
Methyl bromide	CH_3Br	1.85	Polar	Tetrahedral
Methyl iodide	CH_3I	1.35	Polar	Tetrahedral
Methylene chloride	CH_2Cl_2	1.58	Polar	Tetrahedral
Chloroform	$CHCl_3$	1.15	Polar	Tetrahedral
Carbon tetrachloride	CCl_4	0.00	Non-polar	Tetrahedral

3.5 Effects of Bonding on Physical and Chemical Properties

The physical properties such as melting point, boiling point, density, colour, solubility, bond energy, vapour pressure and chemical properties such as reactivity, and rate of reaction etc. of compounds depend on the nature of bond present in them.

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3.5 Solubility of Ionic and Covalent Compounds

Solubility is a measure of the amount of a solute that will dissolve in a solvent at specific temperature. For example, 36g of sodium chloride will dissolve in 100g of water at 20°C. We say then that the solubility of NaCl in water is 36g/100g of H_2O at 20°C. Why some compounds such as sodium chloride and sugar are readily soluble in water while others, such as marble, sand and gold are insoluble in water. Solubility is a complex matter, and it is not always possible to make correct predictions. Solubility involves many factors but we will discuss only one factor in this topic. The saying "like dissolves like" helps in predicting the solubility of a substance in a solvent. What this expression means is that two substances with intermolecular forces of similar type and magnitude are likely to be soluble in each other. For example, both carbon tetrachloride (CCl_4) and benzene (C_6H_6) are non-polar liquids. The only intermolecular forces present in these substances are London dispersion forces. When these two liquids are mixed, they readily dissolve in each other, because the attraction between CCl_4 and C_6H_6 molecules is comparable in magnitude to that between CCl_4 molecules and between C_6H_6 molecules. On the other hand, water molecules are very polar and are attracted to other polar molecules or ions. When NaCl is placed in water, polar water molecules become attracted to the sodium and chloride ions on the crystal surfaces and weaken the attraction between Na^+ and Cl^- ions. The positive end of the water molecule is attracted to the Cl^- ions, and the negative end of the water molecule to the Na^+ ions. The weakened attraction allows the ions to move apart, making room for more water molecules. Thus, the water molecules surround the ions. This process is known as hydration.

Keep in Mind

Most of the covalent compounds are insoluble in water; however, some of them (such as ethyl alcohol and acetic acid.) dissolve in water due to hydrogen bonding.

Conceptual Check Point:

Why sugar is soluble in water and not in benzene?

3.5.2 Reactions of Ionic and Covalent Compounds

The reactions of covalent compounds are much slow, because they involve both breaking and formation of bonds whereas the reactions of ionic compounds are very fast, because their ions are already separated and no energy is needed to break the bonds.

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3.5.3 Directional and Non-directional Nature of Ionic and Covalent Bonds

Ionic bonds are non-directional and they do not show the phenomenon of isomerism while covalent bonds are directional and they show the process of isomerism.

Keep In mind

The compounds having same molecular formula but different structures are called isomers and the phenomenon is called isomerism. The covalent compound butane (C_4H_{10}) has two isomers i.e. n-butane and iso-butane.

Summary of Facts and Concepts

- The VSEPR theory explains shapes (geometries) and bond angles of molecules and ions. It assumes that the valence shell electron pairs (bond pairs and lone pairs) of the central atom of a compound being negatively charged will be arranged in space as far apart from each other as possible to minimize the repulsion between electron pairs. Information about the geometry of a molecule can sometimes be obtained from the presence or absence of a dipole moment.
- According to valence bond theory, the covalent bond is formed by the overlapping of half-filled atomic orbitals. Basically the VB theory discusses bond formation in terms of overlap of orbitals.
- The overlapping is of two types:
  (i) Linear overlapping (ii) Parallel overlapping
- The overlapping of orbitals either form sigma bonds or pi-bonds. Sigma bond is formed by head to head or linear overlap of two atomic orbitals where electron density is maximum around the bond axis. Pi-bond is formed bond by sidewise or parallel overlap of two atomic orbitals (p-orbitals) where electron density is maximum below and above the bond axis.
- Linus Pauling gave the concept of hybridization to explain the bi-valency of beryllium, tri-valency of boron, and tetra-valency of carbon. The geometrical shapes and bond angles are better explained by hybridization.
- The sp^3-hybrid orbitals give tetrahedral geometry, sp^2-hybrid orbitals give trigonal planar geometry, and sp-hybrid orbitals give linear geometry.
- Molecular orbital theory can also be used to explain bonding in molecules.

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This theory is particularly useful for explaining the paramagnetic character of oxygen molecule and other substances.

- The bond order is the half of the difference between the number of electrons in bonding MOs and the number of electrons in antibonding MOs. A bond order of one corresponds to a single bond; two corresponds to a double bond, and so forth. Bond orders can be fractional numbers.
- The distribution of electrons into molecular orbitals takes place according to Aufbau principle, Pauli's exclusion principle, and Hund's rule.
- A covalent bond in which the electron pair is not shared equally by the two bonded atoms is called polar covalent bond whereas a covalent bond in which the electron pair is shared equally by the two atoms is called non-polar covalent bond.
- The bond energy (bond enthalpy) is defined as the average amount of energy needed to make or break all bonds in one mole of a substance. Energy is released when a bond is formed, and energy is absorbed when a bond is broken.
- The distance between the nuclei of two covalently bonded atoms is called bond distance or bond length. Bond length depends on bond order; as the bond order increases, the bond length decreases.
- Electronegativity is a measure of the ability of an atom to attract bond pair of electrons towards itself in a molecule. Fluorine is the most electronegative element whereas the cesium is the least electronegative element in the periodic table. Electronegativity values range from 0.7 for Cs to 4.0 for F. The difference in the electronegativity of bonded atoms can be used to determine the polarity of a bond. The greater the electronegativity difference between two atoms in a chemical bond, the more polar the bond and the more ionic its character.
- The product of electric charge on either ends of a polar bond and the distance between them is called dipole moment. It is a vector quantity and has both magnitude and direction. Dipole moment is the measure of polarity of molecule. Molecules with zero dipole moment are non-polar while those with resultant dipole moment are polar molecules. The shapes of molecules can also be determined by dipole moment.

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Questions and Problems

Q.1. Four answers are given for each question. Select the correct one.

i) Which bond is formed first between two atoms?

(a) Sigma bond (b) Pi-bond
(c) Double bond (d) Triple bond

ii) Molecules having four bond pairs and no lone pair give geometry:

(a) Trigonal (b) Tetrahedral
(c) Octahedral (d) Triangular

iii) Which of the following compounds has linear shape?

(a) CO_2 (b) CS_2 (c) $BeCl_2$ (d) All of them

iv) Which of the following molecules show sp^1 hybridization?

(a) NH_3 (b) $AlCl_3$ (c) $MgCl_2$ (d) BeH_2

v) Which one of the following compounds is polar?

(a) H_2 (b) CH_4
(c) CCl_4 (d) $CHCl_3$

vi) The s-character in each sp^2-hybrid orbital is:

(a) 25% (b) 33% (c) 50% (d) None of these

vii) How many lone pairs of electrons are there in NH_3?

(a) 4 (b) 3 (c) 2 (d) 1

viii) Which one of the following atoms is the second most electronegative atom?

(a) Nitrogen (b) Fluorine
(c) Chlorine (d) Oxygen

ix) Bond length of C=C is:

(a) 120 pm (b) 133pm (c) 154 pm (d) None of these

x) Acetylene molecule has:

(a) One sigma and one pi-bond
(b) One sigma and two pi-bonds
(c) Two sigma and two pi-bonds
(d) Three sigma and two pi-bonds

Q.2. Fill in the blanks with suitable words given in the brackets:

i) Resonance structures are _____ structures. (Real/hypothetical)

ii) The carbon-carbon _____ bond length is shorter than carbon-carbon _____ bond. (Single/double)

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iii) Energy is _____ when two atoms form a bon (Evolved/absorbed)

iv) The sigma bond is _____ than pi-bond. (Weaker/stronger)

v) The bond order of O_2 is _____ and that of N_2 is _____ (Two/three)

vi) Molecular orbital theory is _____ to valence bond theo (Superior/non-superior)

vii) N_2 is _____ whereas O_2 is _____. (Paramagnetic diamagnetic)

viii) Dipole moment of CO_2 is _____ and that of water is _____ (zero/not zero)

ix) H_2S has _____ geometry while CS_2 has _____ geome (Linear/bent)

x) Ionic bonds are _____. (directional/non-directional)

Q.3. Label the following statements as True or False:

i) The formation of a chemical bond always results in decrease energy.

ii) Atomic radius decreases down the group.

iii) A shared pair of electrons is called lone pair.

iv) The electronegativity difference for an ionic bond is greater t 1.7.

v) CCl_4 is a polar molecule.

vi) Bond length of C=C is 120 pm.

vii) The SI unit of dipole moment is Debye.

viii) A molecule with zero dipole moment is non-polar.

ix) KCl has covalent bond in it.

x) Hybridization is exothermic process.

Q.4(a) Discuss the basic features of VSEPR theory. Explain the applicati the theory for predicting the shapes of NH_3 and H_2O.

(b) What is the deference between molecular shape and molecular geome

Q.5. Why the magnitude of repulsion increases in the following order:

Bond pair-bond pair < bond pair-lone pair < lone pair-lone pair

Q.6.(a) The geometry of CH_4 is tetrahedral while that of NH_3 is pyramidal. W As both the molecules have four electron pairs.

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(b) The molecules of BF_3 and $AlCl_3$ have planar triangular geometries while the molecules of NH_3 and PCl_3 have triangular pyramidal geometries, as in all of these molecules, the central atom is bonded with three other atoms. Explain this on the basis of VSEPR theory.

Q.7. Predict the shapes of the following species using the VSEPR theory:
$BeCl_2$, $ZnCl_2$, $AlCl_3$, PCl_3, SiH_4, $CHCl_3$, PH_3 and AsF_5

Q.8. When you have three electron pairs around a central atom, how can you have a distorted triangular geometry?

Q.9. How many atoms are directly bonded to the central atom in a linear molecule, tetrahedral molecule, and octahedral molecule?

Q.10. What do you know about bond pair and lone pair of electrons?

Q.11. Is it possible for hydrogen to form double or triple covalent bonds in a molecule?

Q.12. Define the term resonance. Explain the important aspects of resonance with reference to the ozone molecule.

Q.13. The resonance concept is sometimes described by analogy to a mule, which is a cross between a horse and a donkey, discuss.

Q.14. Describe the salient features of valence bond theory. What are the disadvantages of this theory?

Q.15.(a) Why chemical bonds are formed?

(b) Distinguish between a sigma and a pi bond.

Q.16. Explain the structure of HF and N_2 molecules according to VB theory.

Q.17. What is meant by hybridization of atomic orbitals? Discuss different types of hybridization.

Q.18. Why is it not possible for an isolated atom to exist in the hybridized state?

Q.19. Why is it not possible for s and p orbitals to produce sp^4 hybrid orbitals?

Q.20. What do you know about the rules for hybridization of orbitals?

Q.21. What is the hybridization of nitrogen in N_2 molecule and phosphorus in PCl_3?

Q.22. What is the angle between:

i) sp^3 and sp^3 hybrid orbitals, ii) sp^2 and sp^2 hybrid orbitals

iii) sp and sp hybrid orbitals

Q.23. What are the main points of molecular orbital theory? How does it differ from valence bond theory?

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Q.24. How molecular orbital theory is superior to VSEPR and VB theories?

Q.25. How would you distinguish between bonding and anti-bonding molecular orbitals?

Q.26. What is bond order? Explain the significance of bond order. Calculate the bond order of H_2, O_2, N_2 and N_2^+.

Q.27. Do all the sigma molecular orbitals result from the overlap of s-atomic orbitals?

Q.28. Explain the following with reasons:

(i) The molecule of hydrogen (H_2) is stable and that of helium (He_2) is unstable.

(ii) N_2 is diamagnetic whereas O_2 molecule is paramagnetic.

(iii) The bond energy of N_2 is greater than O_2.

(iv) The bond order of O_2 is less than O_2^+.

(v) According to MOT the Be_2 molecule does not exist.

Q.29. What is the difference between atomic and molecular orbital?

Q.30. Distinguish between diamagnetic and paramagnetic substances.

Q.31. Draw the molecular orbital diagrams of He_2, C_2, F_2 and Ne_2 molecules.

Q.32. Define bond energy. Describe in general how the bond energy of elements changes across a period and down the group.

Q.33. Explain why bond breaking is always endothermic and bond formation always exothermic?

Q.34. Explain how we can use bond energies to estimate the heat of reaction.

Q.35. Estimate the enthalpy change for the combustion of hydrogen gas:

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$$

Q.36. Define bond length. Describe the various factors that affect bond length.

Q.37. What is the relationship between bond order and bond length? Illustrate with an example.

Q.38. What is electronegativity? Discuss general trends of electronegativity in the periodic table.

Q.39. Explain polar and non-polar covalent bonds with suitable examples.

Q.40. Polar covalent bonds are stronger than non-polar covalent bonds. Justify.

Q.41. Classify the following bonds as covalent, polar covalent and ionic. Also justify your answer:

(a) The bond in H_2 (b) The bond in HCl

(c) The bond in NaCl

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Q.42. The electronegativity difference of two bonded atoms helps us to predict the nature of bond, how?

Q.43. With the help of periodic table, predict which atom in each pair has the smaller values of electronegativity:

(a) N, O (b) K, Ca (c) C, Si (d) Na, K

Q.44. Define dipole moment. What are the units and symbol for dipole moment? Explain the relationship between dipole moment and molecular geometry.

Q.45. How can we calculate the %age ionic character with the help of dipole moment?

Q.46. How dipole moment helps us to find the geometry of molecules?

Q.47. Although the bond in beryllium hydride (BeH_2) molecule is polar but the dipole moment of the molecule is zero. Explain.

Q.48. CO_2 and H_2O are triatomic molecules; the shape of CO_2 is linear while that of H_2O is angular. How are their shapes different?

Q.49. Arrange the molecules in order of increasing dipole moment: HF, H_2O, HI, NH_3, CO_2 and H_2S.

Q.50. The dipole moment of HF is 1.82 D and the bond length is 92 pm. Calculate the percent ionic character of the H – F bond. The unit positive or negative charge is 1.60×10^{-19} C. Is HF more ionic or less ionic than HCl?

Q.51. Calculate the dipole moment, in Debye, of HCl molecule. The bond length in the HCl molecule is 127pm and the charge on each atom is 1.60×10^{-19} C.

Q.52. ClF gas is inter-halogen compound (the compound which has bonds between different halogen atoms). The bond length of the molecule is 163pm and the dipole moment of the molecule is 0.88D. Calculate the unit charge on the atom that has partial positive charge.

Q.53. Separate those molecules, from the molecules given below, which have dipole moment equal to zero:

(i) HBr (ii) Cl_2 (iii) SO_2 (iv) C_2H_2 (v) H_2O
(vi) CS_2 (vii) C_6H_6 (viii) $CHCl_3$ (ix) NH_3 (x) SiH_4.

Q.54. What is the meaning of the expression "like dissolves like"? Explain with suitable examples.

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Chapter # 04

States of Matter I: Gases

Major Concepts

4.1 Kinetic Molecular Theory of Gases
4.2 Boyle's Law
4.3 Charles's Law
4.4 Avogadro's Law
4.5 Ideal Gas Equation
4.6 Deviation from Ideal Gas Behavior
4.7 Van der Waal's Equation
4.8 Dalton's Law of Partial Pressure
4.9 Graham's Law of Diffusion and Effusion
4.10 Liquefaction of Gases
4.11 Fourth State of Matter: Plasma

Learning Outcomes

The students will be able to:

- List the postulates of Kinetic Molecular Theory. (Remembering)
- Describe the motion of particles of a gas according to Kinetic Theory. (Applying)
- State the values of standard temperature and pressure (STP). (Remembering)
- Relate temperature to the average kinetic energy of the particles in a substance. (Applying)
- Use Kinetic Theory to explain gas pressure. (Applying)
- Describe the effect of change in pressure on the volume of gas. (Applying)
- Describe the effect of change in temperature on the volume of gas. (Applying)
- Explain the significance of absolute zero, giving its value in degree Celsius and Kelvin. (Understanding)
- State and explain the significance of Avogadro's Law. (Understanding)
- Derive ideal gas equation using Boyle's, Charles', and Avogadro's Laws. (Understanding)
- Explain the significance and different units of ideal gas constant. (Understanding)
- Distinguish between ideal and real gases. (Understanding)
- Explain why real gases deviate from the gas laws. (Analyzing)
- Define and describe the properties of Plasma. (Applying)
- Derive new form of Gas Equation with volume and pressure corrections for real gases. (Understanding)

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- State and use Graham's Law of diffusion. (Understanding)
- State and use Dalton's Law of Partial Pressures. (Understanding)
- Describe some of the implications of the Kinetic Molecular Theory, such as the velocity of molecules and Graham's Law. (Applying)
- Explain Lind's method for the liquefaction of gases. (Understanding)
- Define pressure and give its different units. (Remembering)
- Define and explain plasma formation. (Understanding)

Introduction

What is matter? Matter is anything which has mass and occupies space. Matter is classified by its physical state as solids, liquids, gases and plasma. Under normal conditions, most matter on earth exists in one of three physical states, namely, solid, liquid, or gas. Solids have both definite volume and definite shape. Their particles are close together and fixed into place due to the greatest interaction forces. Liquids have definite volume but have no definite shape. They adopt the shape of container in which they are placed. Their particles are still close together but move freely. Their molecules have greater attractive forces than gases but less than solids. Gases neither have definite volume nor definite shape. They occupy all the available space of the container. Their molecules are neither close together nor fixed in place due to weak attractive forces. The gases occupy about 0.1% (99.9% empty space) whereas liquids and solids occupy about 70% (30% empty space) of the total volume at room temperature and one atmosphere pressure. Our body contains matter in all three physical states: solid (bone, hair, muscles etc.), liquid (blood and body fluids), and gas (the gases we inhale and exhale and the gases that are produced in the intestine). The particular state of a substance is determined by temperature and pressure under which they exist. For example water changes to solid (ice or snow) at/below 0°C and changes to gas (steam) above 100°C. The physical state of a substance usually means its state at room temperature (about 20°C to 25°C) and at

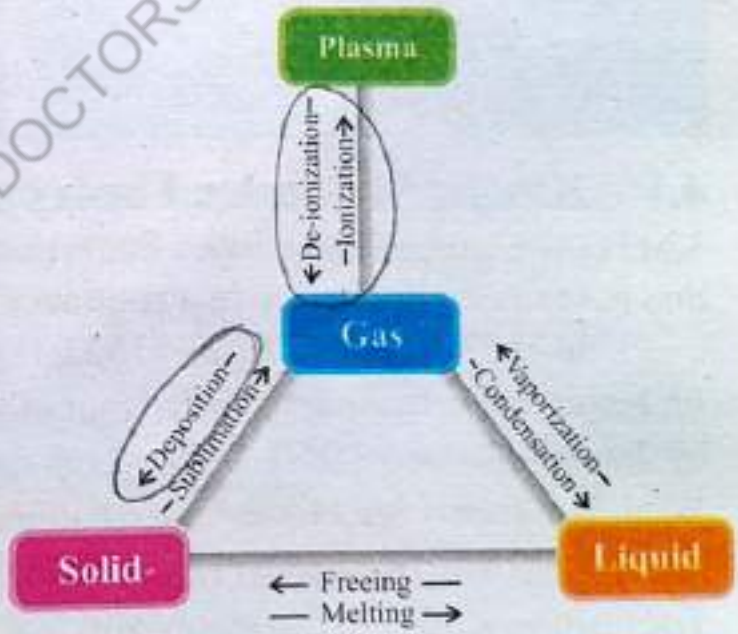

Figure 4.1: Diagram showing possible changes of states of matter

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one atmosphere pressure. At room temperature and one atmosphere pressure, ... physical state of water, milk and vinegar is liquid; salt (NaCl), sugar (sucrose), ... gold is solid; and that of oxygen, carbon dioxide and methane is gas. The simple... form of matter is the gaseous state. The most of the matter around us is in the ... state. The liquid state of any substance exists only with in a relatively narrow ... of temperature and pressure. A fourth state of matter, called plasma, is less fami... Plasma is ionized gas mixture. Stars are made of plasma. Fire is an example ... plasma. Most of the universe is composed of plasma. Plasma, like gases have ... indefinite shape and an indefinite volume.

Out of 118 elements only 11 elements are gases under normal conditions ... they are hydrogen, helium, nitrogen, oxygen, fluorine, neon, chlorine, argo... krypton, xenon and radon.

Table 4.1: Some Compounds Found as Gases at Room Temperature (25°C) and One Atmosp... Pressure

HCl	Hydrogen chloride	CO	Carbon monoxide
HBr	Hydrogen bromide	CO_2	Carbon dioxide
NO	Nitric oxide	NH_3	Ammonia
N_2O	Nitrous oxide	NO_2	Nitrogen dioxide
H_2S	Hydrogen sulphide	SO_2	Sulphur dioxide
HCN	Hydrogen cyanide	SO_3	Sulphur trioxide

4.1 Kinetic Molecular Theory of Gases (KMTG)

KMTG was proposed by Swiss Mathematician Bernoulli. In 1738, he suggested that gaseous molecules are in a continuous state of motion.

In 1857, Rudolf Clausius (1822-1888) postulated 'Kinetic molecular theory' for better understanding the behaviour of gases. This theory was further developed by James Maxwell (1831-1879), Ludwig Boltzmann (1844-1906), and Van ... Waal. This theory sometimes called Billiard ball model.

4.1.1 Postulates of Kinetic Molecular Theory

The main postulates of this theory are:

i) All gases consist of very large number of tiny particles called atoms ... molecules.

ii) The molecules of gases are widely separated from each other. Hence most ... the volume of the gas is empty space (nearly 99.96%). That is why gases can be ... compressed and mixes completely with each other.

iii) The actual volume of gas molecules is negligible (very small) as compared ...

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the volume of the gas or volume of its container.

iv) Gas molecules are in constant random motion in straight lines. Their direction of motion changes only when they collide with one another or with the walls of container. That is why gases quickly and completely fill any container in which they are placed. Pressure exerted by gas is due to collision of molecules with one another or with the walls of container.

v) The collisions of gas molecules are completely elastic. This means that total energy of molecules before and after the collision remains same. In other words, energy can be transferred from one molecule to another as a result of a collision. However, the total energy of all the molecules in a system remains the same. Therefore, the average kinetic energy of gas molecules is not affected by these collisions and remains constant as long as there is no change in temperature.

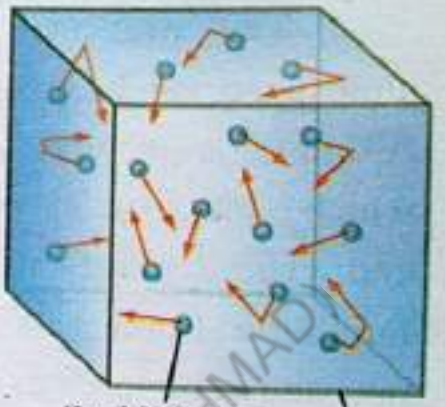

Figure 4.2: Random motion of gas molecules

vi) Due to large intermolecular distance, no attractive or repulsive forces are present among gas molecules. Therefore, they are independent in their behaviour.

vii) Gas molecules have kinetic energy. This is due to constant motion. By increasing temperature, the average kinetic energy of gas molecules increases. Any two gases at the same temperature will have the same average kinetic energy. Gas particles move faster as the temperature increases, hitting the walls of the container with more force and producing higher pressures.

Interesting Information:

In hot summer days, oxygen gas molecules move faster than a jet airplane at an average speed of about 1660 Km per hour. But those oxygen gas molecules are unable to cross the room very fast because each molecule of gas has about 5 to 6 billion collisions with other molecules in one second.

4.1.2 Pressure and its Units

One of the most important properties of any gas is its pressure. Gas pressure is a result of the force exerted by the collision of particles with the walls of the container.

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The force exerted by gas molecules per unit area per second is called gas pressure or simply pressure.

$$\text{Pressure}(P) = \frac{\text{Force } (F)}{\text{Area } (A)}$$

The pressure exerted by Earth's atmosphere can be measured with a barometer. A simple barometer is one meter long glass tube which is closed at one end and open at the other end. The barometer is probably the most familiar instrument for measuring atmospheric pressure (The force exerted by atmosphere on unit area is called atmospheric pressure). How atmospheric pressure is measured?

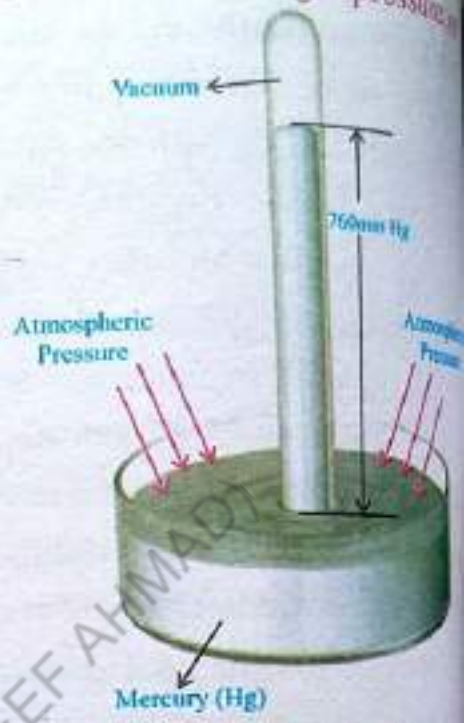

Figure 4.3: The height of mercury column in the barometer

Barometer is constructed by filling a glass tube with liquid mercury (Hg), and then inverting it into a mercury containing dish. The mercury in the tube on inverting, flow out in to the container, creating a vacuum the top (closed end) of the tube due to the force of gravity. This fall becomes equal the force exerted by the atmosphere which balances the gravitational force is called atmospheric pressure.

The length of tube (column) measures atmospheric pressure. Atmospheric pressure varies from place to place and with changing weather conditions. Therefore some standard pressure must be taken. The standard atmospheric (1 atm) pressure is the force exerted by 760 mm of mercury on an area of $1cm^2$ at 0°C. It is the average atmospheric pressure at sea level.

Units

A number of different units are used to measure pressure. The common unit of pressure is millimeters of mercury, symbolized mmHg. The pressure of millimeter of mercury (mmHg) is also called the torr in the honor of Evangelista Torricelli (1608-1647), the Italian mathematician and physicist who invented the barometer in 1643. Thus we have the following relation:

1 atm = 760 mmHg = 760 torr

The SI unit of pressure is the *Pascal (Pa)*, named in honor of

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mathematician and physicist Blaise Pascal (1623-1662). He was the first to propose that atmospheric pressure decreases with increasing altitude. One Pascal (Pa) is defined as the pressure exerted by a force of one Newton (1N) acting on an area of one square meter (m^2).

The commonly used units of pressure other than Pascal are as follows:

(i) mmHg (ii) cm Hg (iii) torr
(iv) atmosphere (v) psi (vi) bar

- 1 atm = 760 mmHg = 760torr = 76 cmHg
- 1 atm = 101325 P_a or Nm^{-2} = 101.325 kP_a
- 1 atm = 1.01325bar = 1013.25 mbar (millibar)
- 1 atm = 14.7psi (pounds per square inch)
- 1 atm = 29.92 inches of Hg

Torr is often used for low pressure. In the English or British system, pressure is measured in terms of pounds per square inch.

Keep in Mind

Barometer can be used only to measure atmospheric pressure and vapour pressure of a liquids. It cannot measure air pressure inside a tire and in a closed container like cylinder of gas or football. The pressure of the air inside an inflated tire or a football is measured by a tire-pressure gauge. The blood pressure is measured by sphygmomanometer.

Example 4.1

The air pressure inside the tire of a small car is 35psi. What is the equivalent pressure in (a) atm, (b) Pascal, (c) kPa, (d) bar and (e) torr?

Solution:

a) We know that, $1\text{atm} = 14.7\text{psi}$

Hence, $14.7\text{psi} = 1\text{atm}$

$$1\text{psi} = \frac{1\text{atm}}{14.7\text{psi}}$$

$$35\text{psi} = \frac{1\text{atm}}{14.7\text{psi}} \times 35\text{psi}$$

$$= 2.38\text{atm}$$

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b) We know that, $14.7\ \text{psi} = 1\ \text{atm} = 101325\text{Pa}$

Hence, $14.7\ \text{psi} = 101325\ \text{Pa}$

$$1\ \text{psi} = \frac{101325\text{Pa}}{14.7\text{psi}}$$

$$35\ \text{psi} = \frac{101325\text{Pa}}{14.7\text{psi}} \times 35\text{psi}$$

$$= 241250\text{Pa}$$

c) We know that, $14.7\ \text{psi} = 1\ \text{atm} = 101.325\text{kPa}$

Hence, $14.7\ \text{psi} = 101.325\text{kPa}$

$$1\ \text{psi} = \frac{101.325\text{kPa}}{14.7\text{psi}}$$

$$35\ \text{psi} = \frac{101.325\text{kPa}}{14.7\text{psi}} \times 35\text{psi}$$

$$= 241.250\text{kPa}$$

d) We know that, $14.7\ \text{psi} = 1\ \text{atm} = 1.01325\ \text{bar}$

Hence, $14.7\ \text{psi} = 1.01325\ \text{bar}$

$$1\ \text{psi} = \frac{1.01325\text{bar}}{14.7\text{psi}}$$

$$35\ \text{psi} = \frac{1.01325\ \text{bar}}{14.7\text{psi}} \times 35\text{psi}$$

$$= 2.41250\ \text{bar}$$

e) We know that, $14.7\ \text{psi} = 1\ \text{atm} = 760\ \text{torr}$

Hence, $14.7\ \text{psi} = 760\ \text{torr}$

$$1\ \text{psi} = \frac{760\text{torr}}{14.7\text{psi}}$$

$$35\ \text{psi} = \frac{760\ \text{torr}}{14.7\text{psi}} \times 35\text{psi}$$

$$= 1809.52\text{torr}$$

Practice Exercise 1:

The pressure of atmosphere on the top of Mt. Everest is 270 torr. Represent this pressure in **(a)** atm, **(b)** mbar, and **(c)** psi.

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4.2 Boyle's Law(Pressure-Volume Relationship)

In 1662, the pioneering English scientist Robert Boyle and his assistant Robert Hooke (1635 - 1703) used a J-shaped glass tube closed at one end to measure the volume of gas at different pressures. They kept temperature constant. They observed an inverse relationship between volume and pressure-an increase in one results in a decrease in the other.

Robert Boyle
(1627-1691)

This law can be stated in two ways:

i) The volume of a fixed amount of gas is inversely proportional to pressure at constant temperature.

If the gas pressure is doubled, the volume is halved; if the pressure is halved, the gas volume doubles.

$$V \propto \frac{1}{P} \quad \text{(at Constant Temperature)}$$

$$V = K\frac{1}{P}$$ Where K is proportionality Constant

or

$$PV = K$$

With the help of this equation, the Boyle's law can be defined as:

ii) At constant temperature, the product of pressure and volume is constant for the given mass of gas.

Mathematically,

$$P_1V_1 = P_2V_2 = P_3V_3 = K$$

It means that, P_1 is the initial pressure and V_1 is the initial volume. If we increase pressure to P_2 the volume will reduce to V_2 and if we again increase pressure to P_3, the volume will reduce to V_3 and so on.

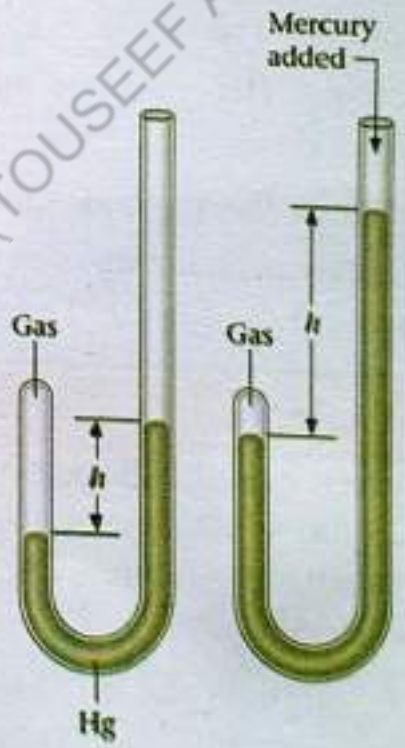

Figure 4.4:
Verification of Boyle's Law

Conceptual Check Point:

What happens when you squeeze a hydrogen-filled balloon?

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Point of Interest:

When a student of your class fills helium gas inside the balloon, it inflates, until the pressure of gas inside the balloon becomes equal to external pressure. Because the mass of same volume of helium is less than the mass of same volume of air (i.e. helium is less dense than air) at constant temperature and pressure. Because of this, it rises up. The balloon carry on travelling until the pressure inside and outside becomes equal. Then it stops rising and remains in one place in the atmosphere.

Graphical Representation of Boyle's Law

i) If a graph is plotted between pressure on the x-axis (abscissa) and volume on the y-axis (ordinate), then a curve is obtained, which shows that, pressure is inversely proportional to volume. This curve is called isotherm or hyperbola. (Iso means same; therm means heat).

ii) The process in which the temperature of the system remains constant is called isothermal process.

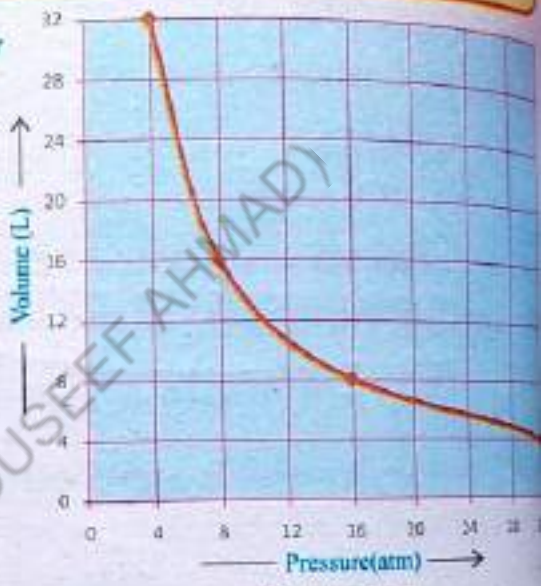

Figure 4.5:
Graphical representation of Boyle's la

Example 4.2

A green colour balloon occupies a volume of 25dm^3 when the gas pressure is 1.25atm. What will be its volume if the pressure is increased to 2.50atm at constant temperature?

Solution:

Initial volume $= V_1 = 25\ dm^3$

Initial pressure $= P_1 = 1.20\ atm$

Final volume $= V_1 = ?$

Final pressure $= P_1 = 2.50\ atm$

According to Boyle's law:

$$P_1V_1 = P_2V_2 \quad \text{or} \quad V_2 = \frac{P_1V_1}{P_2}$$

By putting the values we get,

$$V_2 = \frac{(1.25\ atm)(25\ dm^3)}{2.50\ atm}$$

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$V_2 = 12.5\,dm^3$

By increasing pressure volume of gas decreases, hence final volume is less than initial volume.

Practice Exercise 2:

Methane gas found in Sui Gas (Natural gas) contains a volume of $70dm^3$ at a pressure of 75atm. What volume would the gas occupy if the pressure is increased by four times? The temperature of gas remained unchanged.

4.3 Charles's Law (Temperature-Volume Relationship)

In 1787, a French physicist Jacques Charles, who was the first person to fill a balloon with hydrogen gas and who made the first solo balloon flight, found a relationship between volume and temperature of a gas (volume increases as temperature increases and decreases as temperature decreases). This relation is called Charles law. In 1848, a Scottish physicist William Thomson (1824-1907), whose title was Lord Kelvin, proposed an absolute-temperature scale, now known as the Kelvin scale. He identified −273.15°C as absolute zero, theoretically the lowest attainable temperature. In terms of the Kelvin scale, Charles's law states: Volume of a fixed amount of gas is directly proportional to absolute temperature at constant pressure.

Jacques Charles (1746-1823)

Mathematically,

$V \propto T$ (At constant pressure)

$V = K.T$

Where K is proportionality constant

$\frac{V}{T} = K$

If temperature is changed from T_1 to T_2 and volume changes from V_1 to V_2,

$\frac{V_1}{T_1} = K$ and $\frac{V_2}{T_2} = K$

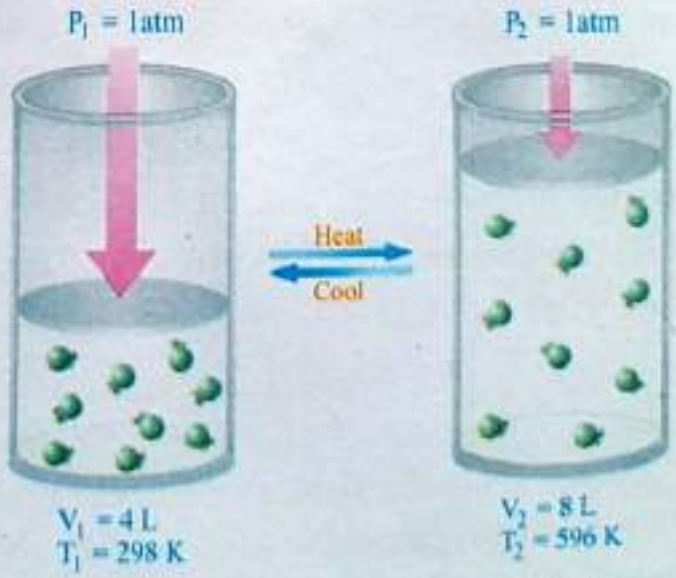

Figure 4.6: Verification of Charles's Law

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So,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = K$$

The law can also be stated as:

For the given mass of a gas, the ratio of volume and temperature remains constant at constant pressure.

Keep in Mind

The word *degree* and the symbol for degrees (°) are not used with the Kelvin scale. The Kelvin (absolute) scale must be used in all gas law problems involving temperature.

Conceptual Check Point:

- What happens if someone put hot carbon dioxide filled-balloon into a freezer?
- We can put more gas during the cold winter days in the CNG cylinder of car as compared to hot summer days, why?
- Have you ever noticed that the same amount of gas exerts more pressure inside the LPG cylinder at Sibi and less pressure at Ziarat?

Graphical Explanation of Absolute Zero:

When a graph is plotted between temperature on x-axis and volume on y-axis for the sample of a gas, a straight line is obtained which intersects the temperature axis at –273.15°C. This shows that if the sample of gas is cooled to –273.15°C, the volume of the gas will become zero. Any volume less than zero are not possible. The temperature at zero volume is –273.15°C (0K), no matter what kind of gas is used. This hypothetical temperature (–273.15°C) at which volume of a gas is considered as zero is called absolute zero or zero of Kelvin or absolute scale. This lowest possible temperature could be achieved only if the substance remains in gaseous state. Since all real gases are converted into liquid state before this temperature, therefore, this is not possible for real gases. This is against the Law of Conservation of Mass.

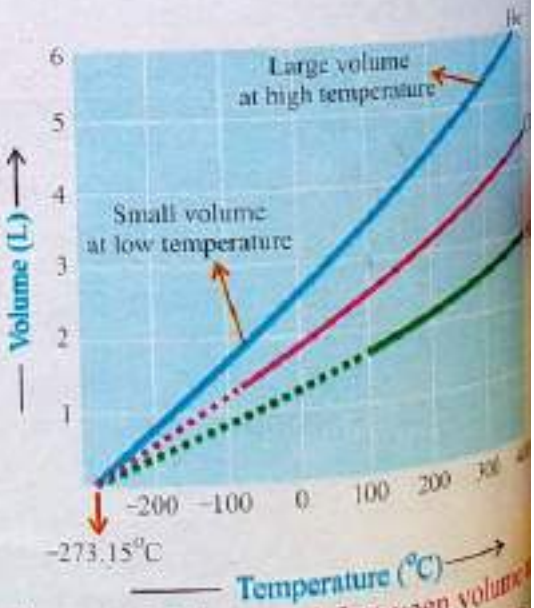

Figure 4.7: The graph between volume and temperature for three different gases

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Keep in Mind

- Kelvin and a degree Celsius have the same magnitude. Thus, while we add 273.15 to the temperature in °C to get the temperature in Kelvin, a change in temperature in Celsius is equal to the change in temperature in Kelvin. A temperature of 25°C is the same as 298.15K. A change in temperature of 25°C, however, is the same as a change in temperature of 25 K.
- In most calculations we will use 273 instead of 273.15 as the term relating K and °C. By convention, we use **T** to denote absolute (Kelvin) temperature and **t** to denote Celsius temperature.

Absolute zero can also be defined as: the temperature at which the molecular motion ceases (stops) and a substance would have zero kinetic energy. At this temperature, none of the particles would be moving at all. Their speed and their kinetic energy would both be zero. The absolute zero is difficult to attain. Anyhow, recently the temperature as below as 10^{-6} K (0.000001K) has been attained which is greater than absolute zero. Charles law is not obeyed when temperature is in degree Celsius (°C). The temperature on Celsius scale has negative values (below 273.15 Kelvin). If we put negative values of temperature in to the equation, we get negative volumes. The negative volume for matter (gas) is not possible. In order to ensure that only values of V= 0 occur, we have to use an absolute temperature scale where T=0. The standard absolute scale is the Kelvin (K) scale.

Greater the mass (no. of moles) of a gas taken, greater would be the slope of the straight line. This is because, greater the number of mole of a gas, greater would be the volume of a gas.

Keep in Mind

The Scientists prefer the Kelvin scale to the Celsius, and certainly to the Fahrenheit scales. If the Kelvin temperature of a gas is doubled, its volume has doubled as well. The same cannot be said if the temperature were doubled from, say, 25°C to 50°C, or from 77°F to 122°F, since neither the Celsius nor the Fahrenheit scale can be used to calculate the volume of gas.

Example 4.3

A balloon is inflated to a volume of 1.5 dm^3 at room temperature (25°C). What would be the new volume of the balloon when it is placed in a hot water (temperature 60°C)? The pressure stays constant.

Solution:

Initial volume $= V_1 = 1.5 dm^3$

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Initial temperature $= T_1 = 25^{\circ}C + 273 = 298K$

Final volume $= V_2 = ?$

Final temperature $= T_2 = 60^{\circ}C + 273 = 333K$

Pressure $= P = \text{Constant}$

According to Charles' law,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{or} \quad V_2 = \frac{V_1}{T_1}.T_2$$

By putting the values we have,

$$V_2 = \frac{1.5dm^3}{298K} \times 333K$$

$$V_2 = 1.68dm^3$$

The final volume is greater than initial volume, because, according to Charles' law, volume increases by increasing Kelvin temperature.

Practice Exercise 3:

A child blows a bubble that has a volume of 25 cm^3 at 10°C. As the bubble rises, it comes across the hot air where the temperature is 30°C. What is the volume of the bubble, if the pressure does not change?

4.4 Avogadro's Law (Amount-Volume Relationship)

Amedeo Avogadro (1776-1856)

The Italian scientist Amedeo Avogadro (1776-1856), a professor of higher physics at the University of Turin for many years, observed a relationship between the volume and number of moles of a gas at constant temperature and pressure. This relation is known as Avogadro's law. This law was proposed in 1811 but it was not generally accepted until after 1858, when an Italian chemist, *Stanislao Cannizzaro*, set up a logical system of chemistry based on it. The law is approximately valid for real gases at sufficiently low pressures and high temperatures.

Avogadro's law can be stated in three ways:

i) Equal volumes of different gases contain equal numbers of molecules at the same temperature and pressure.

One dm^3 of hydrogen gas contain the same number of moles (or molecules) as one dm^3 of helium, nitrogen, oxygen or any other gas at fixed temperature and pressure.

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ii) Equal numbers of molecules of different gases occupy equal volumes at the same temperature and pressure.

One mole (6.02×10^{23} molecules) of hydrogen gas occupies the same volume ($22.414dm^3$) as a one mole of oxygen, argon or any other gas at STP.

Table 4.2: Molar Volumes of Some Gases at STP.

Gas	Formula	Molar Mass (g/mol)	Molar Volume (dm^3/mol)	Number of Molecules in one mole
Hydrogen	H_2	2.02	22.428	6.02×10^{23}
Helium	He	4.002	22.426	6.02×10^{23}
Nitrogen	N_2	28.01	22.404	6.02×10^{23}
Oxygen	O_2	32.00	22.394	6.02×10^{23}
Chlorine	Cl_2	70.91	22.063	6.02×10^{23}
Ammonia	NH_3	17.03	22.094	6.02×10^{23}
Carbon dioxide	CO_2	44.01	22.256	6.02×10^{23}
Any ideal gas	------	------	22.414	6.02×10^{23}

We may say that,

The volume occupied by one mole of an ideal gas at STP is called molar volume. It is equal to 22.414 dm^3. It is always constant.

Equal volumes of all ideal gases have equal number of molecules but different masses.

Mass and size of gas molecules do not affect volume of the gas.

Avogadro's law can also be stated as:

The volume of a gas is directly proportional to number of moles at constant perature and pressure.

According to Avogadro's law, the volume of an ideal gas at a constant ure and temperature depends on its molar amount. If the amount of the gas is ed, the gas volume is doubled; when the amount of the gas is tripled, the e is tripled; if the amount is halved, the volume is halved; when the amount of s is zero, the volume is zero.

hematically,

$V = nK$ (at constant temperature and pressure)

here n represents the number of moles and **K** is the proportionality constant.

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$$V = Kn \quad \text{or} \quad \frac{V}{n} = K$$

Have you ever inflated a balloon? If yes, then you experience Avogadro's law. With each exhaled breath, you add more gas particles to the inside of the balloon, increasing its volume. The more air you would put into the balloon, the greater its volume would be, because the volume of the balloon is the volume of the trapped gas. If a hole is poked in the balloon, the gas escapes, decreasing both the amount of gas and the volume.

For two samples of gas at the same temperature and pressure, the relationship between volumes and numbers of moles can be represented as:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} = K$$

Where, V_1 and n_1 are the initial volume and number of moles of the gas and n_2 are the final volume and number of moles.

In calculations, we use Avogadro's law in a manner similar to the other gas laws.

Conceptual Check Point:

- What will be your observation when?
  i) The pressure inside the balloon is greater than external pressure.
  ii) The pressure inside the balloon is less than external pressure.
  iii) The pressure inside the balloon becomes equal to external pressure.
- Why children don't want to inflate the balloon to a maximum extent?

Example 4.4

Nitrogen peroxide gas contains 0.1 moles in 2.24 dm^3 balloon at STP. How many moles of this gas are present when the volume of gas becomes 11.2dm^3 at same temperature and pressure?

Solution:

$n_1 = 0.1$ mol, $V_1 = 2.24\ dm^3$

$n_2 = ?$ $V_2 = 11.2 dm^3$

According to Avogadro's law,

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \quad \text{or} \quad n_2 = \frac{n_1}{V_1} \cdot V_2$$

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By putting the values,

$$n_2 = \frac{0.1\text{mol}}{2.24\text{dm}^3} \times 11.2\text{dm}^3$$

$$n_2 = 0.5\text{mol}$$

Practice Exercise 4:

At constant temperature and pressure 10 moles of ammonia gas occupies a 224000mL volume in a closed container with a moveable piston. What will be the new volume of the gas when 2.5 moles of gas is removed from the container?

1.5 Ideal Gas Equation

Ideal gas equation is a relationship between pressure, volume, temperature and number of moles (amount) of a gas without assuming that any of the parameters is constant.

1.5.1 Derivation of Ideal Gas Equation

Ideal gas equation is derived by combining Boyle's law, Charles law and Avogadro's law.

According to Boyle's law:

$$V \propto \frac{1}{P} \qquad \text{(at constant } n \text{ and } T\text{)} \quad \ldots\ldots \text{(i)}$$

According to Charles law:

$$V \propto T \qquad \text{(at constant } n \text{ and } P\text{)} \quad \ldots\ldots \text{(ii)}$$

According to Avogadro's law,

$$V \propto n \qquad \text{(at constant } T \text{ and } P\text{)} \quad \ldots\ldots \text{(iii)}$$

By combining the above three equations, we have

$$V \propto \frac{nT}{P}$$

This equation indicates that the volume of a gas is directly proportional to the number of moles of gas and to the temperature of the gas, but is inversely proportional to the pressure of the gas. We can replace the proportionality sign with equals sign by incorporating R.

$$V = R\frac{nT}{P}$$

By rearranging the above equation we get,

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$$PV = nRT \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (iv)$$

Where P is pressure, V is volume, n is number of moles, R is general gas constant and T is temperature.

Equation (iv) is called ideal gas equation and R is called general or universal gas constant. This equation is also called general gas equation or perfect gas law. The Ideal gas equation can be used to calculate the value of any one of the four variables P, V, T, and n, when the values of the other three variables are given.

General gas equation can be used to predict what happens when the pressure, volume, and temperature of a gas sample are all changed at once. We find that the value of pressure times volume divided by the Kelvin temperature is the same for the gas sample before and after the change. Hence, for one mole of gas, equation (iv) can be written as,

$$PV = RT \quad \text{or}$$

$$\frac{PV}{T} = R$$

If P, V and T are changed for a gas from P_1, V_1 and T_1 to P_2, V_2 and T_2, the equation will become:

$$\frac{P_1V_1}{T_1} = R$$

$$\frac{P_2V_2}{T_2} = R$$

Therefore,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (v)$$

This is another form of an ideal gas equation. This equation can be solved for any one of the six variables if the other five are known and is useful in dealing with the pressure-volume-temperature relationships of gases.

However, each of the quantities in the ideal gas equation must be expressed in the units within R.

Pressure (P) must be expressed in atmospheres, volume (V) in liters or decimeters cube, amount of gas (n) in moles and temperature (T) in Kelvins.

Conceptual Check Point:

What would have to be done to maintain a constant volume if the temperature increased?

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Applications of Ideal Gas Equation

i) Ideal gas equation is used to calculate the mass of the gas, if P, V, T and molecular mass of the gas is known.

Since, $$n = \frac{\text{Mass of gas(m)}}{\text{Molecular mass of gas(M)}}$$

By putting the value of n in PV = nRT, we have

$$PV = \frac{m}{M}RT \qquad \text{or}$$

$$m = \frac{PVM}{RT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(vi)}$$

ii) Ideal gas equation is used to calculate the molecular mass of the gas.

By re-arranging the equation (vi), we have

$$M = \frac{mRT}{PV}$$

Since, $\frac{M}{V}$ = density

Therefore,

$$M = d\frac{RT}{P} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(vii)}$$

iii) Ideal gas equation can be used to calculate density of the gas.

By re-arranging the equation (vii), we have,

$$d = \frac{PM}{RT}$$

The density of a gas is directly proportional to pressure and molar mass but inversely proportional to temperature. The higher the molar mass and pressure, the denser the gas. The higher the temperature, the less dense the gas. When we have equal molar masses of two gases at the same pressure but different temperatures, the hotter gas is less dense than the cooler one.

Conceptual Check Point:

Have you ever noticed that the tire pressure increases when the car has been recently driven?

4.5.2 Gas Constants and its Units

Ideal gas equation is used to determine the value of R. The value of R for one mole of gas at STP is calculated as:

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$P = 1atm$

$V = 22.414dm^3$

$n = 1mol$

$T = 273.15K$

$R = ?$

Formula used:

$$PV = nRT \quad \text{or} \quad R = \frac{PV}{nT}$$

By putting the values in the equation, we have

$$R = \frac{1atm \times 22.414dm^3}{1mole \times 273.15K}$$

$$= 0.08206atmdm^3mol^{-1}K^{-1}$$

If pressure is expressed in Newton per meter square (Nm^{-2}) and volume in cubic meter (m^3), then we find that,

$P = 101325Nm^{-2}$

$V = 0.0224m^3$

$n = 1mol$

$T = 273.15K$

$R = ?$

Formula used:

$$PV = nRT \quad \text{or} \quad R = \frac{PV}{nT}$$

By putting the values, we have

$$R = \frac{101325Nm^{-2} \times 0.022414m^3}{1mole \times 273.15K}$$

$$= 8.31Nm\,mol^{-1}K^{-1}$$

Since,

$1Nm = 1J$

Therefore,

$$R = 8.31\,J\,mol^{-1}K^{-1}$$

Since,

$1\,cal = 4.184\,J$

Therefore,

$$R = \frac{8.31}{4.184}$$

$$= 1.986cal\,mol^{-1}K^{-1}$$

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Ideal gas equation can also be used to calculate the volume occupied by one mole of an ideal gas at STP.

$P = 1\ atm$

$n = 1\ mole$

$R = 0.08206\ dm^3\ atm\ mol^{-1}K^{-1}$

$T = 273.15\ K$

$V = ?$

Formula used:

$PV = nRT \quad or \quad V = \frac{nRT}{P}$

By putting the values, we have

$$V = \frac{1mole \times 0.08206 dm^3 atm\ mol^{-1}K^{-1} \times 273.15K}{1atm}$$

$$= 22.414\ dm^3$$

Example 4.5

At STP, the volume of carbon monoxide gas is 7.25 litre. What would be the volume of this gas at 29.4 psi and 25°C?

Solution:

Standard temperature $= T_1 = 273K$

Standard pressure $= P_1 = 1atm$

Initial volume of CO gas $= V_1 = 7.25L$

Final volume of CO gas $= V_2 = ?$

Final pressure $= P_2 = \frac{29.4psi}{14.7psi\ atm^{-1}} = 2atm$

Final temperature $= T_2 = 25°C + 273 = 298K$

According to combined gas law,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad or \quad V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}$$

By putting the values,

$$V_2 = \frac{(1atm)(7.25\ L)}{273\ K} \times \frac{298\ K}{2\ atm}$$

$$V_2 = 3.96L$$

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Practice Exercise 5:

A sample of H_2S gas has a volume of $1.7dm^3$ at a temperature of 37°C. If gas has 3 moles, what will be the pressure of the gas?

Example 4.6

What is the molar mass of 134 grams of a gas at −73°C? The pressure of gas is 10 atm and its volume is 5 dm^3.

Solution:

Molar mass = M = ?

Mass of gas = m = 134g

Temperature = T = −73°C + 273 = 200K

Pressure = P = 10atm

Volume = V = $5dm^3$

Formula used: $M = \frac{mRT}{PV}$

By putting the values,

$$M = \frac{(134g)(0.08206atm\ dm^3mol^{-1}K^{-1})(200K)}{(10atm)(5dm^3)}$$

$$M = 44g\ mol^{-1}$$

Practice Exercise 6:

A syringe has 20mL of gas at 47°C and 50.6625kPa pressures. What is the molar mass of the gas in Kilograms? The mass of gas is 1.52 grams.

Example 4.7

Calculate the density of H_2S gas in g/dm^3 at 0°C and 960mmHg pressure.

Solution:

Density of H_2S gas = d = ?

Temperature = T = 0°C + 273 = 273K

Pressure = P = 960mmHg / 760mmHg atm^{-1} = 1.26atm

Molar mass of H_2S gas = M = $34g\ mol^{-1}$

Formula used: $d = \frac{PM}{RT}$

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By putting the values,

$$d = \frac{(1.26\text{atm})(34\text{gmol}^{-1})}{(0.08206\ \text{atm dm}^3\text{mol}^{-1}\text{K}^{-1})(273\text{K})}$$

$$d = 1.91\text{g mol}^{-1}$$

Practice Exercise 7:

What is the density in g/dm^3 of butane (C_4H_{10}) gas at 100°C and one atmosphere pressure?

4.6 Deviation of Real Gases from Ideal Gas Behaviour

The gases which obey gas laws strictly at all conditions of temperatures and pressures are called ideal or perfect gases while those which do not obey gas laws strictly are known as non-ideal or real or actual gases. The behavior of a real gas is often somewhat different from that of an ideal gas. In actual practice no gas is ideal. All known gases are non-ideal. The gases at sufficiently high temperature and low pressure behave ideally.

4.6.1 Graphical Explanation

A useful measure of how much a gas deviates from ideal gas behavior is found in its compressibility factor. The compressibility factor (Z) of a gas is the ratio PV/RT. From the ideal gas equation (for one mole of a gas) we see that for an ideal gas, the ratio PV/RT = Z = 1. The compressibility factor values can be less than or more than one for a real gas. When the pressure is increased for real gas, the volume of one mole of the gas is decreased because of strong intermolecular forces. As a result of this, the value of compressibility factor (Z) becomes less than one (Z < 1). When the pressure is further increased (i.e. at very high pressure), the gas molecules are crowded closely together and the intermolecular repulsions become operative, and by doubling the pressure cannot halve the total volume. As a result, the actual volume of a real gas is larger than expected for an ideal gas, and the value of compressibility factor (Z) becomes greater than one (Z > 1). The ratio PV/RT approaches 1 only at very low pressures (≤ 10 atm.) for real gases.

The extent of deviation depends on the nature of the gas, temperature and pressure under which the behaviour of a real gas is studied. The deviation (departure) from ideal behaviour is most significant at *high pressures* and *low temperatures*, that is, near the conditions under which the gas liquefies.

) Deviation at high pressure

In order to check the ideality of a gas we plot a graph between pressure on X-axis and compressibility factor (Z) on y-axis for four real gases and an ideal gas at a

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given temperature. In case of ideal gas a straight line parallel to x-axis is obtained. But all real gases (H_2, He, N_2 and NH_3) has been found to show marked deviation from ideal behaviour.

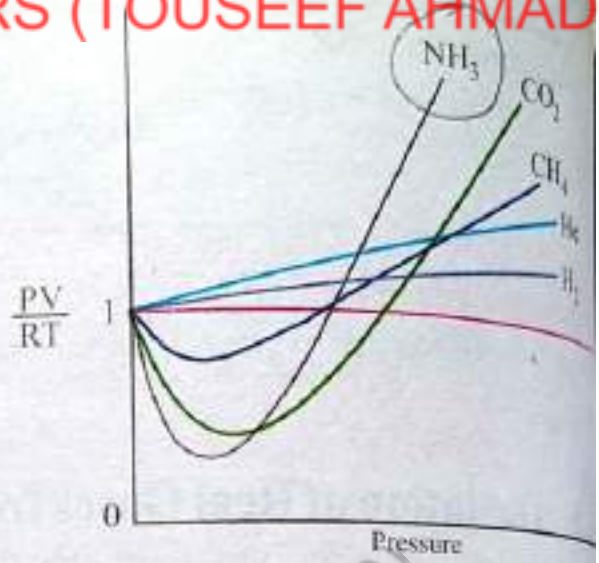

Figure 4.8: It is clear from the graph that deviation of gases from the ideal behaviour is greater at high pressure. This is due to more attractive forces at room temperature.

At one atmospheric pressure (and room temperature), most gases behave nearly like an ideal gas, because

i) The molecules are moving so rapidly and are so far apart that the attractions between them are very weak or negligible.

ii) The space between the molecules is so large that the volume occupied by the molecules themselves is insignificant (negligible).

At high pressure, the gas volume decreases and the empty spaces among molecules decrease. As a result of this, the volume of actual gas molecules becomes significant (does not remain very small as compared to the volume of container total volume of the gas) and hence cannot be neglected.

Different gases deviate differently from ideal behaviour. The deviation real gases from ideal behaviour is higher for polar gases and lower for non-polar gases. For gases such as hydrogen, helium, nitrogen, neon, or oxygen, deviation from the ideal gas behaviour are less than 0.1 percent at room temperature and atmosphere pressure. Other gases, such as CO_2, SO_2, NH_3, or H_2O, have strong intermolecular forces and hence show greater deviation from ideal behaviour.

ii) Deviation at Low Temperature

As the temperature of gas molecules decreases, the kinetic energy and velocity gas molecules decreases. As a result of this, the number of collisions decreases the gas molecules come close to each other. thus forces of attractions among molecules become effective. Hence at very low temperature, near the temperature under which the gas liquefies, the gases deviate from ideal behaviour.

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4.6.2 Causes for Deviation

The deviation is due to two faulty assumptions:

i) The actual volume of the gas is very small as compared to the volume of the gas or the volume of the container.

ii) There is no force of attraction among gas molecules.

The postulate (i) is responsible for the deviation at very high pressure and postulate (ii) is responsible for the deviation at very low temperature..

4.7 Van der Waal's Equation

Johannes Van der Waals
(1837-1923)

The Dutch physicist Johannes Van der Waals, in 1873, at the University of Amsterdam modified the general gas equation in order to calculate the volume and pressure of a real gas. He recognized that the ideal-gas equation could be corrected by performing the volume correction and pressure correction. He got a Nobel Prize in 1910 for his work.

i) Volume Correction

When an actual gas is compressed, the molecules come close to each other and a stage comes when it is not possible to compress it any more. At this stage, they produce force of repulsion, because gas molecules have definite volume. The actual volume of gas molecules is very small but it cannot be neglected. If the effective volume of the molecules per mole of a gas is b, then the available (free) volume to gas molecules is the volume of the container minus the volume of gas molecules.

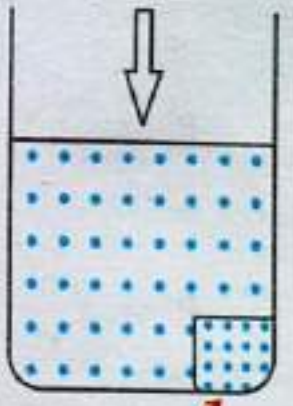

Figure 4.9

$$V_{free} = V_{container} - V_{molecules}$$

or $$V_{free} = V_{container} - b$$

This equation can be written as:

$$V_{real} = V_{ideal} - nb \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

Where, 'n' is the number of moles and 'b' is effective or excluded volume of gas. The volume occupied by one mole of a gas in highly compressed state is called effective volume. It is four times of the actual volume of the gas molecules.

$$b = 4\,V_m$$

Where, V_m is the actual volume of one mole of a gas.

> P' will be proportional to the number of molecules per unit volume colliding with the walls of container and also to the number of molecules per unit volume dragging them.

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ii) Pressure Correction

Consider a molecule in the interior of a gas is attracted by other molecules from all sides and there is no net attraction on the molecule. When such molecules strike with the walls of container, it cannot exert full pressure due to backward pull of gas molecules. So these molecules do not collide with a force with which it should collide. Hence less pressure is exerted on the wall than actual pressure (ideal pressure).

$$P_{obs} = P_i - P'$$

or $$P_i = P_{obs} + P' \quad \ldots\ldots\ldots\ldots\ldots \text{(ii)}$$

Where,

P_{obs} is observed pressure, P_i is ideal gas pressure and P' is decrease in ideal pressure

The P' will decrease as the volume will increase due to decrease in forces of attractions. Mathematically,

$$P' \propto \frac{n}{V} \times \frac{n}{V}$$

or

$$P' \propto \frac{n^2}{V^2}$$

or

$$P' = a\frac{n^2}{V^2}$$

Where, "**a**" is proportionality constant.

By putting the value of P' in equation (ii), we have

$$P_i = P_{obs} + \frac{an^2}{V^2} \quad \ldots\ldots\ldots\ldots\ldots \text{(iii)}$$

By putting the value of equation (i) and equation (iii) in the general equation (PV = RT), we have

$$\left(P_{obs} + \frac{a\,n^2}{V^2}\right)(V - n\,b) = n\,RT$$

This is Vander Waal's equation where *'a'* and *'b'* are experimentally determined constants called Vander Waal's constants. When 'a' and 'b' are both

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the van der Waal's equation reduces to the ideal gas equation. In this equation, P, V, T, and n represent the measured values of pressure, volume, temperature, and number of moles, respectively, just as in the ideal gas equation.

The values of constants 'a' and 'b' for real gases are given in the table.

Table 4.3: Van der Waal's Constants for Some Real Gases:

Name	Formula	a (atm $dm^6 mol^{-2}$)	b ($dm^3 mol^{-1}$)
Hydrogen	H_2	0.244	0.0266
Helium	He	0.034	0.0237
Nitrogen	N_2	1.390	0.0391
Oxygen	O_2	1.360	0.0318
Argon	Ar	1.345	0.0322
Krypton	Kr	2.318	0.0398
Methane	CH_4	2.253.	0.0428
Ammonia	NH_3	4.170	0.0371
Water	H_2O	5.464	0.0305
Carbon dioxide	CO_2	3.592	0.0427
Hydrogen chloride	HCl	3.667	0.0408

It is clear from the above table that polar gases have greater values of 'a' than non-polar gases. This is due to the presence of strong intermolecular forces in polar gases as compared to non-polar gases.

4.8 Dalton's Law of Partial Pressure

The English scientist John Dalton (1766-1844), in 1803, made an important contribution to the study of gaseous mixtures. Dalton's law of partial pressures states that the total pressure exerted by a mixture of non-reacting gases is equal to the sum of the partial pressures of all the gases present in the mixture.

Suppose in a system three gases A, B, and C are present. The partial pressures of these gases are:

P_A = Partial pressure of gas A

P_B = Partial pressure of gas B

P_C = Partial pressure of gas C

Then Dalton's law may be mathematically written as:

$$P_T = P_A + P_B + P_C + \ldots$$

Where, P_T is the total pressure of mixture of gases.

The air we breathe is a mixture of about 78.084% nitrogen, 20.948% oxygen,

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0.934% argon and, 0.033% carbon dioxide and other gases (Hydrogen, helium, methane, krypton, carbon monoxide, xenon, ozone, ammonia, nitrogen dioxide, suphur dioxide and water vapours) in trace amounts. Due to the force of gravity, molecules making up the atmosphere are most concentrated near Earth's surface. In dry air, total pressure is the sum of partial pressure of N_2, O_2, Ar, CO_2 and other gases.

Interesting information:

The composition of air does not change appreciably with altitude, but the total pressure decreases rapidly. The partial pressure of oxygen in air therefore decreases with increasing altitude, and it is this change that leads to difficulty in breathing at high elevations.

Mathematically, it can be expressed as,

$$P_{atm} = P_{N_2} + P_{O_2} + P_{Ar} + P_{CO_2} + P_{other\ gases}$$

Suppose the partial pressure of nitrogen, oxygen, argon, carbon dioxide, and other gases in the air is 593 torr, 159.5 torr, 7.14 torr, 0.23 torr, and 0.13 torr respectively. So the total pressure of the gases in the air will be:

$$P_{atm} = 593 + 159.5 + 7.14 + 0.23 + 0.13$$

$$P_{atm} = 760 torr$$

A partial pressure is the pressure of an individual gas in the mixture of gases. This law says that the pressure of a gas remains same whether gas is alone or mixed with other gases at constant temperature and pressure.

Put another way, pressure of a gas is due to collision of molecules. It depends upon number of molecules or moles of a gas present in the mixture. Greater the number of moles (molecules) in a mixture, greater would be the pressure. It means

$$P \propto n$$

So, pressure of a gas is directly proportional to the number of moles of a gas. For instance, if we have 1000 gaseous molecules at 50°C in a container and they exert a pressure of 0.1atm, then adding another 1000 gaseous molecules of the substance at the same temperature to the container would increase the pressure to 0.2atm.

Conceptual Check Point:

Imagine what would happen if someone starts filling the air in the tyre of a bike and cannot stop this process?

Expressions for Calculation of Partial Pressure of a Gas

i) From general gas equation

In a mixture of gases, the partial pressures of gases can be calculated from the general gas equation when number of moles and total pressure of each gas is given at constant temperature and volume.

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Suppose two gases A and B are present in the gas cylinder having partial pressures P_A and P_B respectively. The number of moles of gases A and B are n_A and n_B. The general gas equation is $PV = nRT$. Since R, T and V are same for gases A and B, hence the partial pressures of these gases are:

$$P_A = n_A \frac{RT}{V} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

Similarly,

$$P_B = n_B \frac{RT}{V} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(ii)}$$

For a mixture of two gases A and B, the total pressure is given by the expression:

$$P_{Total} = P_A + P_B = (n_A + n_B) \frac{RT}{V}$$

or $$P_{Total} = n_{Total} \cdot \frac{RT}{V} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(iii)}$$

Conceptual Check Point:

Suppose we have 2 separate tanks, one filled with nitrogen gas (N_2) at 450 mmHg and the other with oxygen at 250 mmHg. When both of the gases are transferred to a single tank with the same volume and temperature, then, what would be the total pressure of the gas mixture in this tank?

By dividing equation (i) by (iii) we get,

$$\frac{P_A}{P_T} = \frac{n_A \frac{RT}{V}}{n_T \frac{RT}{V}}$$

$$\frac{P_A}{P_T} = \frac{n_A}{n_T}$$

$$P_A = \frac{n_A}{n_T} \cdot P_T \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(iv)}$$

here,

P_A is partial pressure of gas A, n_A is number of moles of gas A, n_T is total nber of moles of gases and P_T is total pressure of gases

nilarly,

$$P_B = \frac{n_B}{n_T} P_T$$

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ii) From Mole Fraction of Gases

The number of moles of a particular gas divided by total number of moles of gas present in the mixture is called mole fraction and is represented by X. therefore,

$$\frac{n_A}{n_T} = X_A \qquad (n_T = n_A + n_B)$$

By putting the value of n_A / n_T in equation (iv) we have,

$$P_A = X_A . P_T$$

Where, X_A is mole fraction of gas A. This equation tells us that the pressure of a gas in a mixture of gases is the product of its mole fraction and the total pressure of the mixture. You can determine the partial pressure of gas A (P_A) by multiplying its mole fraction with the total pressure (P_T).

Similarly

$$P_B = X_B . P_T$$

Where, X_B is mole fraction of gas B.

For example, the mole fraction of oxygen in air is 0.21; hence its partial pressure is 0.21atm or 159.5 torr at standard temperature and pressure.

Applications of Dalton's Law

i) Determining the pressure of pure and dry gases

Some gases like H_2, N_2 and O_2 are collected by downward displacement of water. Due to evaporation, some water molecules are mixed with gas and gas becomes moist. The partial pressure of such gases can easily be determined by using the equation of Dalton's law of partial pressure:

$$P_{gas} = P_T - P_{water vapours}$$

$$P_{H_2} = P_T - P_{water\ vapours}$$

The partial pressure of water vapours in gases is called aqueous tension or vapour pressure of water.

Table 4.4: Vapour Pressure of Water at Various Temperatures:

Temperature (°C)	Vapour Pressure (mmHg)	Temperature (°C)	Vapour Pressure (mmHg)
0	4.6	60	149.4
10	9.2	70	233.7
20	17.5	80	355.1
30	31.8	90	525.8
40	55.3	100	760.0
50	92.5		

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Process of Respiration

(ii) Respiration is due to difference in partial pressure of O_2 in air (159 torr) and lungs (116 torr). Oxygen flows from a region of higher partial pressure to a region of lower partial pressure. The partial pressure of CO_2 inside the body is greater than in atmosphere. So CO_2 comes out from the lungs.

At higher Altitude

(iii) At higher altitude, pilot feels uncomfortable where pressure is around 150 torr which is less than 159 torr (at which we feel comfortable). So pilot uses pressurized cabins. On top of the highest mountain, Mt. Everest, the total atmospheric pressure is 270 torr, so the partial pressure of oxygen is only 57 torr, or about one-third of normal. That is why a human cannot survive for long at such a low pressure of oxygen. At that altitude, the mountaineers use an oxygen tank and mask, which give an increased partial pressure of oxygen to the lungs.

Deep Sea Divers

(iv) The partial pressure of air (O_2) increases at the depth below the surface of water. Partial pressure of oxygen increases five times at the depth of 40 meters. Ordinary air cannot be used there. So, deep sea divers use a mixture of helium (96%) and oxygen (4%) called ***heliox*** that contains a lower percentage of O_2 than air. Helium gas does not dissolve well in blood, and thus it is safer for a diver to inhale this oxygen-helium mixture. At the same time, the oxygen exerts the same pressure that it would normally at one atmosphere pressure.

Conceptual check point:

- Explain why the pressure goes up when gas molecules are added to a sample of gas in a fixed-volume container at constant temperature?
- What happens to the partial pressure of each gas in a mixture when the volume is decreased by (a) lowering the temperature or (b) increasing the total pressure?

Example 4.8

A tube light which has a volume of 500 mL contains 10 grams of argon and 0.5 grams of neon at room temperature (25°C). Calculate the total pressure of the mixture of gases in mmHg.

Solution:

$$\text{Volume of gases} = V = \frac{500\text{mL}}{1000\text{mL/L}} = 0.5\text{L}$$

$$\text{Mass of argon} = 10\text{g}$$

$$\text{Mass of neon} = 0.5\text{g}$$

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Temperature = $T = 25^{\circ}C + 273 = 298K$

Total pressure = $P_T = ?$

Before going to calculate total pressure,

We should know about moles of gases,

$$\text{Moles of argon} = n_{Ar} = \frac{10g}{39.948 g mol^{-1}} = 0.250 mol$$

$$\text{Moles of neon} = n_{Ne} = \frac{0.50g}{20.179 g mol^{-1}} = 0.025 mol$$

According to Dalton's law,

$$P_T = (n_{Ar} + n_{Ne})\frac{RT}{V}$$

By putting the values,

$$P_T = (0.250\ mol + 0.025 mol)\frac{(0.08206 atm\ dm^3 mol^{-1}K^{-1})(298K)}{(0.50K)}$$

$$P_T = 13.45 atm$$

The total pressure of gases in mmHg can be calculated as,

$$P_T = 13.45\ atm \times 760\ mmHg atm^{-1} = 10222\ mmHg$$

Practice Exercise 8:

What is the total pressure of 3.50 grams of oxygen and 9.25 grams of nitrogen gases at 9°C? Both of the gases are present in 100 mL perfume bottle.

4.9 Graham's Law of Diffusion and Effusion

Diffusion is the spontaneous mixing of gas molecules by random motion where molecular collision occurs. When a perfume bottle is opened at the front of a classroom, it takes some time before everyone in the room can smell it, because time is required for the perfume molecules to mix with the air. Lighter molecules diffuse more quickly than heavier ones, so the first molecules you would smell from a perfume mixture are the lighter ones. The rate of diffusion is the rate of the mixing of gases. Effusion is the escape of gas molecules through a

Figure 4:10(a) Diffu

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tiny (small) hole into a vacuum without molecular collision. Lighter molecules effuse more quickly than heavier ones. The rate of effusion is inversely proportional to molar mass of the gas. If we have two balloons in which one has helium and the other has carbon dioxide gas. A helium filled balloon deflates rapidly as compared to carbon dioxide filled balloon because the rate of effusion through the tiny holes of the balloon is faster for the lighter helium atoms than the heavier carbon dioxide molecules.

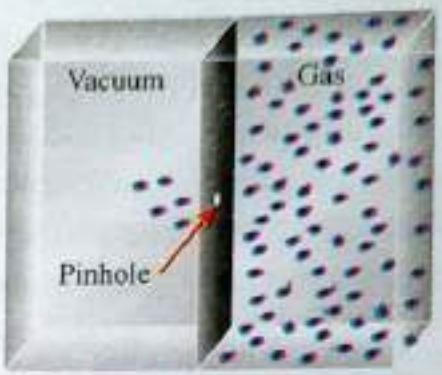

Figure 4.10(b): Effusion

The rates at which both of these processes occur depend on the speeds of gas molecules; the faster the molecules move, the more rapidly diffusion and effusion occur. In 1846, Thomas Graham, a Scottish chemist, studied the rates of diffusion and effusion of gases. He recognized that the rate of diffusion and effusion of a gas is related to their molar masses or densities.

This relation is known as Graham's Law of diffusion and effusion, which is stated as,

"The rate of diffusion or effusion of two gases is inversely proportional to the square roots of their densities or molar masses at constant temperature and pressure".

Thomas Graham
(1805-1869)

Graham's law is usually used to compare the rates of diffusion and effusion of different gases, so the proportionality constant can be eliminated and an equation can be formed by writing the ratio of diffusion and effusion rates:

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

or

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

Where,

r_1 is rate of diffusion or effusion of gas 1, r_2 is rate of diffusion or effusion of gas 2, d_1 is density of gas 1, d_2 is density of gas 2, M_1 is Molecular mass of gas 1 and

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M_2 is Molecular mass of gas 2.

Gases with low molar masses diffuse (and effuse) more rapidly than gases with high molar masses. Thus, H_2 with a molar mass of 2 will diffuse more rapidly than ammonia, NH_3, with a molar mass of 17.

The rate of effusion of molecules from a container depends on three factors:

i) The cross-sectional area of the hole (the larger the hole, the more likely the gas molecules are to pass through the hole);

ii) The number of molecules per unit volume (the more congested the molecules are, the more likely they are to come across the hole); and

iii) The average molecular speed (the faster the gas molecules are moving, the more likely the gas molecules are to escape).

Demonstration of Graham's Law

Take 100 cm long glass tube open at both ends. Put two cotton plugs soaked in HCl and NH_3 solutions at each end of the tube simultaneously. The vapours of NH_3 and HCl escape from their respective ends and producing a white ring of NH_4Cl when they meet several minutes later. The distance travelled by ammonia is 59.5 cm and by HCl gas is 40.5 cm.

$$NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$$

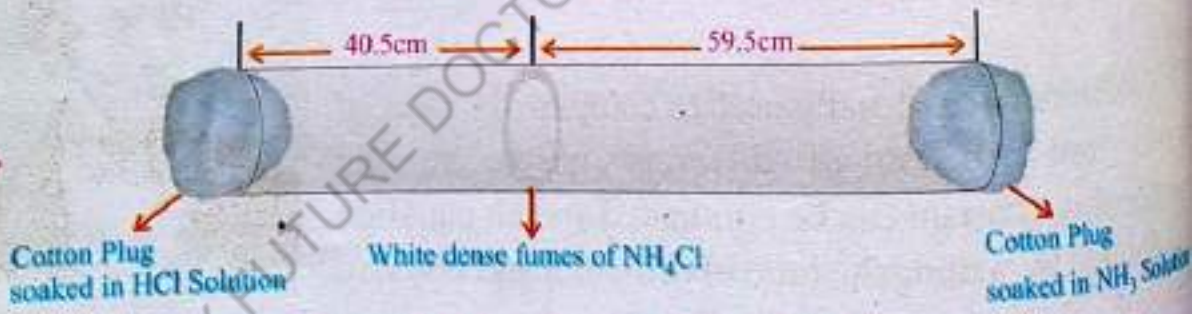

Figure 4.11: Verification of Graham's Law

The ratio of velocities (rates) of two gases depends on their distance traveled by the different gases at the same time.

$$\frac{\text{The rate of diffusion of } NH_3}{\text{The rate of diffusion of HCl}} = \frac{\text{Distance traveled by } NH_3}{\text{Distance traveled by HCl}} = \frac{59.5\text{cm}}{40.5\text{cm}} = 1.$$

This means that the rate of diffusion of NH_3 gas is 1.46 times greater than HCl gas, because NH_3 gas is lighter than HCl.

Conceptual Check Point:

Why does the hydrogen leak out from the balloon at a higher rate than the nitrogen?

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Example 4.9

An unknown gas (hydrocarbon) diffuses two times as fast as SO_2 gas at constant temperature. Calculate the molar mass of unknown gas and suggest what this gas might be?

Solution:

Molar mass of SO_2 gas $= M_{SO_2} = 64 gmol^{-1}$

Molar mass of unknown gas $= M_x = ?$

Rate of diffusion of SO_2 gas $= r_{SO_2} = 1$

Rate of diffusion of unknown gas $= r_x = 2$

According to Graham's law,

$$\frac{r_x}{r_{SO_2}} = \sqrt{\frac{M_{SO_2}}{M_x}}$$

By putting the values,

$$\frac{2}{1} = \sqrt{\frac{64 gmol^{-1}}{M_x}}$$

By taking square on both sides,

$$\frac{4}{1} = \frac{64 gmol^{-1}}{M_x} \quad \text{or}$$

$$M_x = \frac{64 gmol^{-1}}{4} = 16 g\,mol^{-1}$$

The unknown gas is methane, because it has hydrogen and carbon atoms and has molar mass $16 gmol^{-1}$.

Practice Exercise 9:

Calculate the rate of diffusion of equal volumes of NH_3 and HCl at constant temperature.

4.10 Liquefaction of Gases

The conversion of gases into liquids is called liquefaction of gases. The conversion of gas into liquid needs high pressure and low temperature.

At high pressure, molecules of a gas come close to each other and at low temperature, attractive forces among gas molecules increase.

Keep in mind, the gaseous substance is capable of being liquefied by

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compressing when it has a temperature below its critical temperature. Critical temperature is the temperature above which a gas cannot be liquefied no matter how much pressure is applied. It is denoted by T_C. If room temperature is *below* critical *temperature*, the gas can be liquefied by applying sufficient pressure. If room temperature is above critical temperature, then the gas can only be liquefied at the cost of added pressure and a lowering of temperature to a value below critical temperature. For example, carbon dioxide is a gas at room temperature (approximately 25°C). This is below its critical temperature of 31.1°C. If the CO_2 is gradually compressed, a pressure will eventually be reached that will cause the CO_2 to liquefy. Gases such as O_2 and N_2, which have critical temperatures far below 0°C, can never be liquefied at room temperature. When they are compressed, they simply become high pressure gases. To make liquid N_2 or O_2, the gases must be made very cold as well as be compressed to high pressures.

The intermolecular attraction is a finite quantity for any given substance. Below T_C, this force is sufficiently strong to hold the molecules together (under some appropriate pressure) in a liquid. Above T_C, molecular motion becomes so energetic that the molecules can always break away from this attraction. Critical temperature depends upon size and shape of gas molecules and the strength of intermolecular forces. The pressure required to liquefy the gas at its critical temperature is called critical pressure. It is denoted by P_C. The volume occupied by one mole of a gas at critical temperature and critical pressure is called critical volume. It is denoted by V_C.

Table 4.5: Critical Temperature, Pressure and Volume of Some Gases

Substance	Formula	T_c(°C)	P_c(atm)	V_c(cm^3 mol^{-1})
Helium	He	−267.9	2.26	62
Hydrogen	H_2	−239.9	12.8	70
Nitrogen	N_2	−147.1	33.5	90
Carbon monoxide	CO	−138.8	35.0	90
Argon	Ar	−122.2	48.0	78.5
Oxygen	O_2	−118.8	49.0	74
Methane	CH_4	−83.1	45.6	99
Carbon dioxide	CO_2	31.1	73.0	94
Ammonia	NH_3	132.5	111.5	72
Chlorine	Cl_2	133.9	76.1	123.8
Sulphur dioxide	SO_2	157.1	77.7	122
Methyl alcohol	CH_3OH	239.9	78.5	118
Water	H_2O	374.0	217.7	56

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The gases can be liquified by Joule-Thomson effect. According to Joule Thomson effect "When highly compressed gases are suddenly allowed to expand, they produce cooling and the temperature of gas falls to such an extent that it changes into liquid state."

The process is called Joule-Thomson or Joule-Kelvin effect.

The molecules of the compressed gas are very close to each other and have appreciable attractive forces. When this gas is allowed to expand suddenly through the nozzle of jet, then the molecules move apart from each other. For expansion, some amount of energy is required to break intermolecular forces. This energy is taken from the gas itself, therefore the temperature of gas falls and cooling is produced.

Lind's Method

In 1895, Lind used the principle of Joule-Thomson effect for the liquefaction of air (O_2 and N_2). Lind's Method is used for liquefaction of all gases except H_2 (T_C=33.3 K) and He (T_C = 5.3 K) which have critical temperature values very close to absolute zero. The apparatus used for this process is: (i) Compressor (ii) Cooler (iii) Expansion Chamber (iv) Spiral pipe

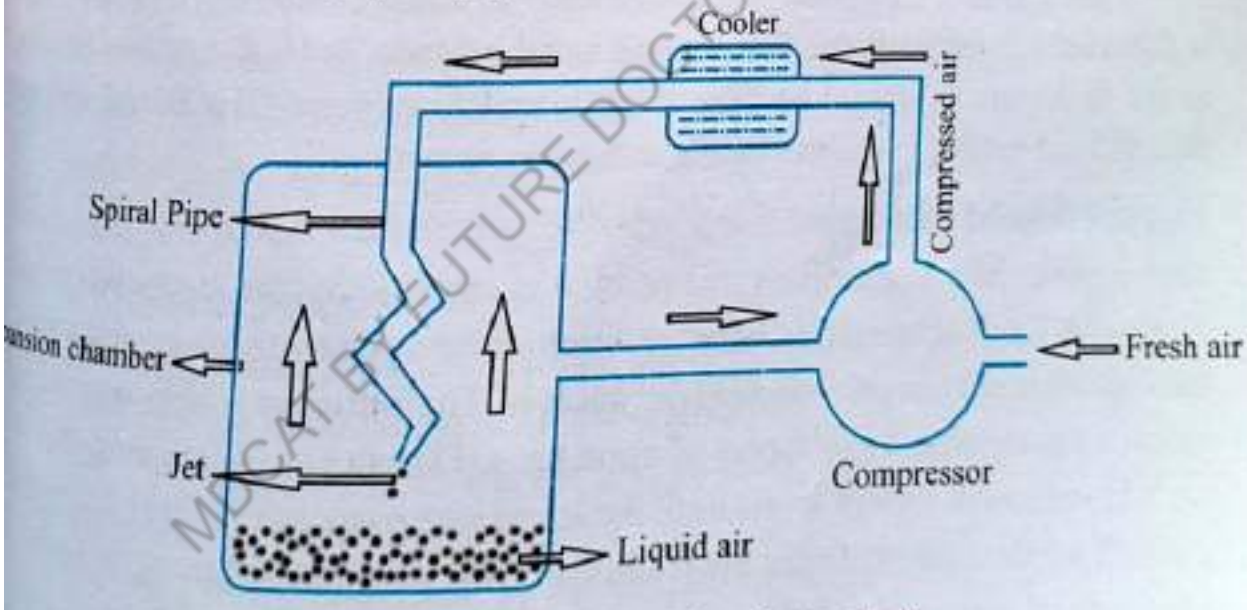

Figure 4.12: Lind's method for liquefaction of air

For the liquefaction of air, pure dry air is compressed to about 200 atm by a pressor. Some heat is produced due to compression. This heat is removed by ing gas through water cooled pipe or cooler. Compressed air is then passed ugh a spiral pipe having a jet at the end. When the air comes out suddenly from et, the expansion takes place from 200 atm to 1atm. In this way, the temperature

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of gas falls and it is cooled. This cooled air goes up and cools the incoming compressed air and then returns to the compressor. This process is repeated again and again till the air is completely liquefied.

Keep in Mind

Liquefied natural gas (LNG) and liquefied petroleum gas (LPG) are among the examples of liquefied gas in daily use. In both cases, the volume of the liquefied gas is far less than it would be if the gas were in a vaporized state, thus enabling ease and economy of transport. Liquefied gases have a lot of applications. They are used for heating purposes at homes and as a fuel for cars, boats etc. Liquefied hydrogen and oxygen gases are used as a fuel in rocket engines; and liquefied oxygen and petroleum is used in welding.

4.11 The Fourth State of Matter: Plasma

The fourth very high-temperature physical state of matter which has an ionized gas mixture of ions, electrons and neutral atoms, is called plasma state.

It was first identified in a Crooks tube by British English chemist and physicist, Sir William Crooke in 1879 and he called this state a "radiant matter". The word "PLASMA" was first applied to ionized gas by Dr. Irving Langmuir (1881-1957) an American chemist and physicist, in 1929.

Plasma is often called the "fourth state of matter", assuming that solid, liquid and gas are respectively the first, second and third state. But is should be considered as the first state of matter because it has been known since "Big Bang" and more than 99% of matter in the universe is in the plasma state.

Formation of Plasma

Matter on Earth has electrons that revolve in orbit around the nucleus in an atom. There is a force of attraction between electrons and positively charged nucleus, so the electrons stay in orbit around the nucleus. The sufficient energy is provided to atoms to overcome these forces of attractions. Plasma comes into existence when we add sufficient energy to gas until the atoms lose some or all of their electrons. As a result of this, atoms break apart into positive ions and electrons, or sometimes even into atomic nuclei and free electrons. This state is known as plasma. Atoms are at least partially ionized. The degree of ionization does not have to be too large for the size of the plasma formation is big enough. Even a partially ionized gas in which as little as 1% of the particles are ionized can have the characteristics of plasma (i.e. response to magnetic fields and high electrical conductivity). The energy provided to change gas into plasma can be of various origins: thermal, electrical, or

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(ultraviolet light or intense visible light from a laser).

Properties of Plasma

Plasmas have their own unique qualities just as solids, liquids and gases do.

i) Plasma state is overall neutral because it has equal number of electrons and positive ions.

ii) Plasmas are good conductors of electricity and are affected by magnetic fields because they are composed of ions (negatively charged electrons and positively charged nuclei).

iii) Plasmas neither have definite shape nor definite volume like gases because the particles can move past one another.

iv) Plasmas are easily compressible because their particles are far apart from each other.

v) The free electrons in a metal are considered as plasma.

Comparison of Plasma and Gas Phases

The characteristics of plasmas are significantly different from those of ordinary neutral gases so that plasmas are considered a distinct "fourth state of matter."
It differs from gases in number of ways:

i) Plasma is different from a gas, because it is made up of groups of positively and negatively charged particles and are strongly influenced by electric and magnetic fields while neutral gases are not.

ii) Gases are excellent insulators due to absence of charged particles while plasmas are good conductors of electricity due to presence of charged particles.

Applications of Plasma

Plasmas occur naturally but also can be easily produced in a laboratory and in industry. Numerous technologies make use of plasma.

i) They light up our offices and homes, make our computers and electronic equipment work.

ii) They drive lasers, help clean up the environment, and make tools corrosion-resistant.

iii) It is found in fluorescent lamps to produce light. When electric current is passed through a tube containing neon gas at low pressure, the neon atoms absorb the energy and use it to excite electron from the (filled) second shell to a less stable empty shell lying much farther from the nucleus. The electron doesn't stay in the far shell for long. When it comes back from the higher energy empty shells to the proper

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lower energy shell, it releases the extra energy as visible light of various colours. The predominant colour of the light emitted by neon is orange-red. "Neon" lights having other colours use a different gas or colored glass. In particular, argon, krypton, and xenon are also used in some "neon" lights. Hydrogen gas glows with green colour, helium glows with pink colour, nitrogen glows with purple colour whereas argon glows with a blue colour. HG, HeP. NP. AB

iv) It can be used for cleaning and sterilization of food and operation theaters.

v) Plasma can be used to destroy bacteria, viruses, fungi and spores.

vi) Our computers and electronic devices work on the basis of plasma. You are well aware of plasma TV and cell phones which are manufactured using plasma.

vii) Most of the synthetic fibers used in clothing, and advanced packaging materials are plasma treated.

viii) It is used in automobile industry in painting the bumpers and other parts made up of plastic.

ix) Plasma is used for the treatment of exhaust gases and also for the treatment of burns, ulcers and other skin diseases.

x) Plasma torches are used in industry to cut metals.

Plasma is expected to soon be widely used in surgery, decontamination and sterilization of surfaces and devices, and air and water streams, as well as in direct treatment of skin diseases.

Summary of Facts and Concepts

- There are four main states of matter. Solids, liquids, gases, and plasmas. They are all different states of matter. Each of these states is also known as a phase. Substances can be changed from one phase to another by increasing or decreasing temperature.
- Gases exert pressure, which is the force per unit area. The SI unit of pressure is Pascal (Pa).
- The behavior of gas is described in terms of its pressure, temperature, volume and amount (number of moles).Equations relating these four parameters are called the gas laws.
- Boyle's law states that the volume of a sample of gas is inversely proportional to pressure at constant temperature.

$$V \propto \frac{1}{P} \qquad \text{(at constant temperature)}$$

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- Charles's law states that the volume of a sample of gas is directly proportional to its absolute temperature at constant pressure.

  $V \propto T$ (at constant pressure)

- Avogadro's law states that the volume of a sample of gas is directly proportional to the number of moles at constant temperature and pressure.

  $V \propto n$ (at constant temperature and pressure)

- The general gas equation ($PV = nRT$) is obtained by combining the laws of Boyle, Charles, and Avogadro and relates pressure, volume, temperature, and number of moles without assuming that any of the parameters is constant.
- The temperature 0°C and 1 atm pressure is known as standard temperature and pressure (STP).
- Dalton's law of partial pressures states that the total pressure exerted by a mixture of non-reacting gases is the sum of the partial pressures of the components.

  $P_T = P_A + P_B + P_C + \ldots$

  This law is used to calculate the partial pressure of gases.
- The kinetic molecular theory of gases is a model that accounts for ideal gas behavior. The behavior of most gases is nearly ideal except at very high pressures and low temperatures.
- Diffusion is the mixing of two or more gases whereas effusion is the escape of gas molecules from a container through a small hole into an empty chamber.
- The departure of a real gas from ideal gas behavior is called deviation. Deviation from ideal gas behavior increase in magnitude as pressure increases and as temperature decreases.
- Van der Waal's equation is a modified equation which is used to calculate the pressure and volume of real gases.
- Gases can be liquefied by applying pressure at critical temperature or below it. Gases can't be liquefied above critical temperature.
- Plasma is considered as the fourth state of matter. It consists of ions, electrons and neutral particles. About 99% of the visible universe is made up of plasma.

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Questions and Problems

Q.1. Four answers are given for each question. Select the correct one:

i) Matter exists in the number of states:

(a) Two (b) three (c) four (d) five

ii) The SI unit of pressure is:

(a) Atmosphere (b) Pascal

(c) Newton (d) Torr

iii) The value of general gas constant, R in SI system is:

(a) $8.31 NmK^{-1}mol^{-1}$ (b) $8.31 atm\ dm^3 mol^{-1}K^{-1}$

(c) $0.0821 Nm^{-1}mol^{-1}$ (d) $0.0821 atm\ dm^3 mol^{-1}K^{-1}$

iv) The instrument that is used to measure the atmosphere pressure is:

(a) Thermometer (b) Manometer

(c) Barometer (d) Voltmeter

v) When the Kelvin temperature of a gas is doubled, the volume will:

(a) Remain same (b) be doubled

(c) reduce to one half (d) increase four times

vi) When the Kelvin temperature of the gas is doubled and the pressure is reduced to one-half, then the volume of the gas will:

(a) Remain same (b) be doubled

(c) reduce to one-fourth (d) increase four times

vii) Which one of the following gases diffuse more rapidly:

(a) N_2 (b) CH_4 (c) O_2 (d) CO_2

viii) All the gases can be liquefied by Lind's method except:

(a) H_2 and NH_3 (b) H_2 and N_2

(c) H_2 and He (d) N_2 and O_2

ix) What is the rate of effusion of an unknown gas of molar mass 80 compared to hydrogen gas, H_2?

(a) Same (b) five times

(c) 1/5 times (d) 1.5 times

x) The molar volume of CO_2 is maximum at:

(a) STP (b) 127°C and 1 atm

(c) 0°C and 2 atm (d) 273°C and 2 atm

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Q.2. Fill in the blanks with suitable words given in the brackets:

i) The variable that stays constant when using the Charle's law is _____. (Pressure / Temperature)

ii) When the number of moles of a gas is _____, the volume will be doubled. (doubled/tripled)

iii) Partial pressure of oxygen in the _____ at one atm is 159 torr. (lungs/air)

iv) Gases have _____ shape and indefinite volume. (definite/indefinite)

v) Mathematical expression for Boyle's law is _____. ($PV=K/V\propto T$)

vi) Plasma is a _____ of electricity. (conductor/ non-conductor)

vii) The _____ has no relationship with plasma. (moon/aurora)

viii) The number of molecules of hydrogen and oxygen is _____ in one dm^3 of both gases at same temperature and pressure separately. (same/different)

ix) Charles' law established a relationship between volume and _____ in 1787. (pressure/temperature)

x) A gas can be liquefied by applying pressure when the temperature is _____ its critical temperature. (above/below)

Q.3. Label the following statements as True or False.

i) Gases contract on heating and expand on cooling.

ii) The collisions of ideal gas molecules are perfectly elastic.

iii) High temperature and low pressure make the gases non-ideal.

iv) The value of general gas constant at STP is 0.08206 atm $dm^3 mol^{-1} K^{-1}$.

v) The rate of diffusion varies directly to the square root of its molar mass.

vi) At constant temperature and pressure one mole each of N_2 and O_2 gases have same kinetic energy.

vii) Lighter gases can diffuse more quickly than heavier one.

viii) Ideal gas is the one which does not obey gas laws strictly at all conditions of temperature and pressure.

ix) Van der Waal's equation is used to calculate the pressure and volume of real gases.

x) The scale at which boiling point of water is taken is 212°F is known as Celsius scale.

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Q.4: Define pressure and give the common units for pressure.

Q.5: What is barometer? How does it measure theatmospheric pressure?

Q.6: Name four elements and four compounds that exist as gases at room temperature.

Q.7: What are the basic assumptions of the kinetic–molecular theory of gases? Which assumption is incorrect at very high pressures? Which one is incorrect at low temperatures?

Q.8: Describe Boyle's law of gases? Give the mathematical expression and graphical representation of this law.

Q.9: Describe Charles' law of gases? Give the mathematical expression of this law.

Q.10: Explain absolute temperature scale on the basis of Charles Law.

Q.11: What is Avogadro's law of gases? Describe an experiment to demonstrate it.

Q.12: Derive ideal gas equation. Describe the applications of ideal gas equation.

Q.13: Calculate the numerical value of ideal gas constant R at STP for one mole of a gas:

(a) When the pressure is in atmosphere and volume is in dm^3.

(b) When the pressure is in Pascal and volume is in m^3.

Q.14: Define the molar volume, how will you calculate it?

Q.15: What is compressibility factor? The compressibility factor values can be less than or more than one for a real gas. Justify your answer.

Q.16: Describe the difference between an ideal gas and a real gas. Under what conditions does a real gas behave most like an ideal gas?

Q.17: (a) Why gases show non-ideal behaviour at low temperature and high pressure?

(b) Why helium and hydrogen are ideal whereas ammonia and sulphur dioxide are non-ideal at room temperature and one atmosphere pressure?

Q.18: Define Van der Waal's equation and derive it for real gases.

Q.19: What is meant by the partial pressure of a gas? Explain Dalton's law of partial pressure and describe its important applications.

Q.20: Define mole fraction. Does mole fraction have units?

Q.21: (a) What is the difference between effusion and diffusion?

(b) What are the factors on which the rate of effusion depends?

Q.22: Define and explain Graham's law of diffusion and effusion and describe experiment to demonstrate it.

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Q.23: What is critical temperature? What is its importance for liquefaction of gases? Why a gas can't be liquefied above its critical temperature?

Q.24: What is meant by liquefaction of gases? Discuss the Lind's method of liquefaction of gases. What are the examples of liquefied gas in daily use?

Q.25: Define plasma and describe some of its properties. How can you differentiate between plasma and gas?

Q.26: Where in the universe are plasmas commonly found? Where can plasmas are found on Earth? What are the applications of plasma?

Q.27: Answer the following questions.

a) Why is mercury a more suitable substance to use in a barometer than water?

b) What is meant by standard temperature and pressure (STP)?

c) Why the Scientists prefer the Kelvin scale to the Celsius, and to the Fahrenheit, scales?

d) Why hydrogen and oxygen gases move with different velocities at the same temperature although their kinetic energies are same?

e) Explain why -273.15°C is the lowest possible temperature.

f) Explain why pressure increases as a gas is compressed into a smaller volume.

g) Why does a helium-filled balloon lose pressure faster than an air-filled balloon?

h) Explain why a helium filled weather rubber balloon expands as it rises in the air. Assume that the temperature does not change.

i) Two identical balloons have same volume of gases at STP. One balloon has nitrogen gas and the other has carbon dioxide gas. Which balloon has more molecules?

j) Why do deep-sea divers breathe a mixture of helium and oxygen?

k) When a gas is collected by the downward displacement of water, is a pure gas? If yes, then why, if not, then why not?

l) Explain why the second story of a double-story building is often warmer than a ground story during hot summer days?

(m) Which gas will a student smell first, the ammonia, NH_3, and hydrogen sulphide, H_2S? When both are released together across a class room?

(n) Why are the rates of diffusion and effusion of CO & N_2 the same?

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(o) Which gas has stronger intermolecular forces, argon (T_c=-122.3 °C) or methane (T_c=-81.9°C) and why?

(p) The temperature of a highly compressed real gas that is allowed to expand into a vacuum usually falls. Why?

(q) We often experience pain in our ears because of rapid changes in altitude, why?

(r) Would it be easier to drink apple juice with a straw on top of Mt. Everest or at the base? Explain

Q.28: The pressure of helium gas in the neon sign is 7.6cmHg. What is the pressure of this gas in the neon sign in psi and mbar?

Q.29: At what pressure would neon gas occupy 2.85 dm^3 if it occupies 142.4 dm^3 at a pressure of 2.22 atm? (The temperature does not change).

Q.30: A Freon gas (used in the refrigeration systems) has a volume of 2.5dm^3 at a pressure of 76 mmHg. What is the pressure of this gas when it is expanded until its volume is 12.5dm^3? Assume the temperature of gas does not change.

Q.31: A sample of gas at 10°C and 760mmHg contains a volume of 8.45 cm^3. What is the volume of this gas at 43°C and one atmosphere pressure?

Q.32: The volume of a bubble is 2.5mL. If its temperature increases from 30 to 70°C, what is its final volume?

Q.33: The volume of argon gas at 120°C is 380mL. The gas is heated to a volume of 560mL. What will be the new temperature of gas if the pressure is held constant?

Q.34: What is the effect on the volume of a gas if you simultaneously:

a) Halve its pressure and double its Kelvin temperature?

b) Halve its pressure and halve its Kelvin temperature?

c) Double its pressure and double its Kelvin temperature?

Q.35: The weather balloon is inflated to a volume of 605dm^3 at STP. The balloon is heated to 35°C. What would be its volume at 76cmHg?

Q.36: A 0.75 moles of hydrogen gas contains a volume of 16.8dm^3. What is the volume of 1.25 moles of this gas at constant temperature and pressure?

Q.37: What is the volume occupied by 2.75 moles N_2 gas at STP?

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Q.38: The helium filled balloons are used to record temperature, pressure, relative humidity, and wind velocity in the upper atmosphere. Supposed a balloon is launched at a room temperature (25°C) and 760mmHg. Its volume is $3.5m^3$ at ground level. What will be its volume at height of 30 miles where pressure is 40mmHg and temperature is –40°C.

Q.39: The volume of laughing gas (N_2O) at 480mmHg and 100°C is 800mL. The gas is cooled to a volume of 300mL at 760mmHg. What is its new temperature?

Q.40: The volume of nitrogen gas in an automobile air bag is 25 litre at –20°C and 1.50 atm. Calculate the number of moles of nitrogen gas in the air bag.

Q.41: A motor cycle tube contains 10.2 grams of gas and has a volume of 3×10^3mL Calculate the molar mass of the gas at 32°C and 506625 Nm^{-2}.

Q.42: What is the molar mass of a gas that has a density of 5.75 g/L at STP?

Q.43: What are the densities of N_2 and He at STP?

Q.44: What is the total pressure in a cylinder filled with air if the pressure of the oxygen is 250mmHg and the pressure of nitrogen is 510mmHg?

Q.45: A CNG cylinder contains a mixture of methane and ethane gases. The total pressure of the gases is 6.5 psi. What is the partial pressure of methane gas, if the partial pressure of ethane gas is 2.5 psi?

Q.46: Calculate the partial pressures of 2.5g Hydrogen, 5g Neon, and 15g Krypton at STP.

Q.47: Calculate the ratio of effusion rates of helium and nitrogen gases at same temperature and pressure.

Q.48: Oxygen gas effuses 1.173 times as swift as at the rate of an unknown gas through a balloon. Calculate the molar mass of unknown gas and identify it. This gas is produced during the combustion of hydrocarbons like methane.

Q.49: H_2 effused 2.82 times faster than an unknown gas. What was the molar mass of the unknown gas?

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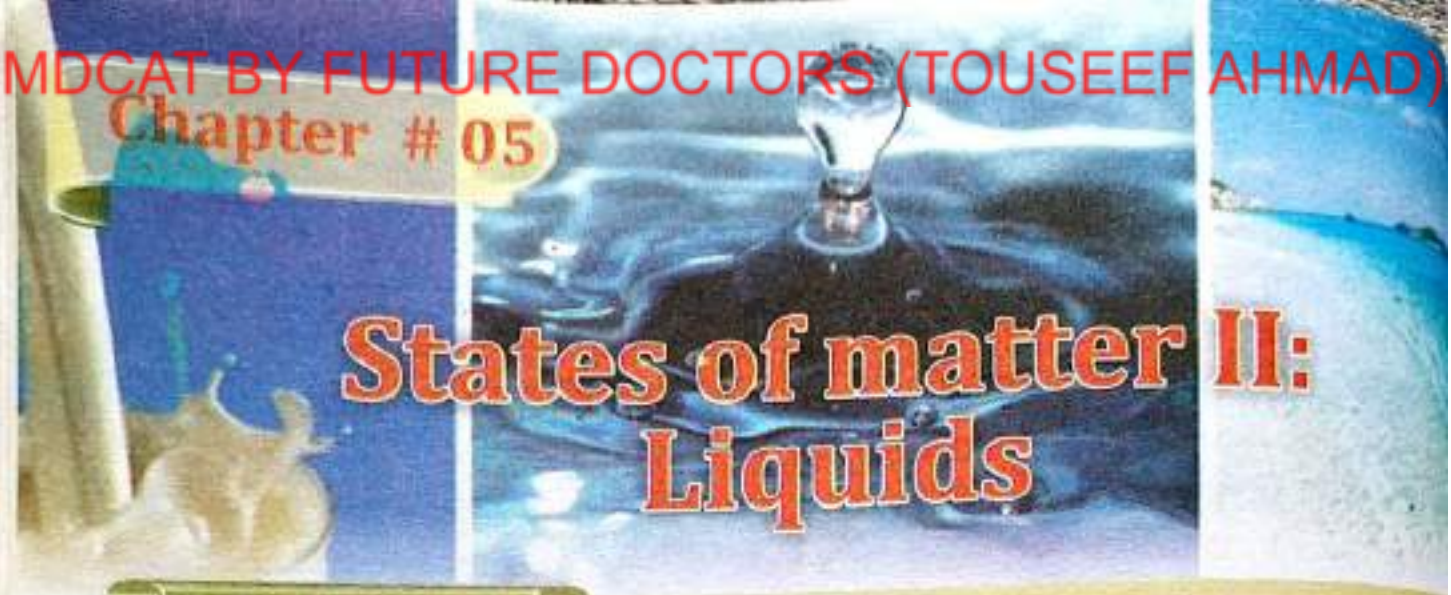
Chapter # 05



States of matter II: Liquids

Major Concepts

5.1 Kinetic Molecular interpretation of Liquids
5.2 Intermolecular forces (Van der Wall's forces)
5.3 Physical properties of Liquids
5.4 Energetics of Phase Changes
5.5 Liquid Crystals

Learning Outcomes

The student will be able to:

- Describe simple properties of liquids e.g., diffusion, compression, expansion, motion of molecules, spaces between them, intermolecular forces and kinetic energy based on kinetic molecular theory. (Understanding)
- Explain applications of dipole-dipole forces, hydrogen bonding, and London forces. (Applying)
- Explain physical properties of liquids such as evaporation, vapor pressure, boiling point, viscosity and surface tension. (Understanding)
- Use the concept of hydrogen bonding to explain the following properties of water: high surface tension, high specific heat, low vapour pressure, high heat of vaporization, and high boiling point. And anomalous behavior of water when its density shows maximum at 4°C. (Applying)
- Define molar heat of fusion and molar heat of vaporization. (Remembering)
- Describe how heat of fusion and heat of vaporization affect the particles that make up matter. (Understanding)
- Relate energy changes with changes in intermolecular forces. (Applying)
- Define dynamic equilibrium between two physical states. (Remembering)
- Describe liquid crystals and give their uses in daily life. (Applying)
- Differentiate liquid crystals from pure liquids and crystalline solids. (Applying)

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Introduction

Do you know, what is liquid? The water you use for drinking, washing, swimming, and as a solvent, the blood running in the veins and arteries of your body, the milk you use for drinking and making tea, the mercury in thermometer which is used to measure the temperature, the petrol and diesel used as motor fuels, the oils used in engines, gear boxes, in the hydraulic brakes and other hydraulic systems and the vegetable oil used for cooking are all liquids. Out of 118 elements only two elements (bromine and mercury) are liquid at room temperature and normal pressure. There are four more elements which have melting points slightly above room temperature, these elements are, gallium, rubidium, cesium and francium. Liquids have definite volume but they do not have definite shape. In this chapter we focus on the properties of liquids and the forces of attractions that exist between them.

5.1 Kinetic Molecular Interpretation of Liquids

The key points of kinetic molecular theory are given below:

i) Liquids consist of atoms or molecules.

ii) The molecules of liquid are so close together that there is very little empty space. For that reason, liquids are much denser and are much more difficult to compress as compared to gases. The spaces between liquid molecules are greater than solids and smaller than gases.

iii) Liquids do not show an appreciable increase in volume, when they are heated.

iv) The intermolecular forces in liquids are stronger than gases but weaker than solids. Because of this, liquids have lower melting and boiling points than solids and higher melting and boiling points than gases.

v) The liquid molecules have high kinetic energy than solids and low kinetic energy than gases. Their kinetic energy decreases by decreasing temperature and increase by increasing temperature. They are converted into solids by decreasing kinetic energy (on cooling) and are converted into vapours by increasing kinetic energy (on heating).

vi) The liquid molecules are in state of constant motion that are why their molecules slip and slide over one another. That are, therefore, able to flow and are poured in the container. Hence, it has no definite shape and adopts the shape of container in which they are placed.

vii) Liquids diffuse into other liquids with which they are miscible. The diffusion is due to movement of liquid molecules. The diffusion in liquids occur slowly because the molecules of one liquid slowly past the molecules of other liquid.

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5.2 Intermolecular Forces (Van der Waal's Forces)

To know the properties of liquid, we have to know the types of attractive forces present in them. There are two types of attractive forces which are associated with a liquid; that is, intramolecular forces and the Intermolecular forces. The forces of attraction exist between atoms within each molecule are called intramolecular forces whereas the forces of attractions exist between molecules of a substance are called intermolecular forces. Intramolecular forces are chemical bonds (discussed in 2nd chapter). Physical properties of a substance such as boiling point, vapour pressure, surface tension, viscosity, heat of vaporization, heat of fusion, heat of sublimation etc. depend upon intermolecular forces. The stronger the intermolecular forces in a substance, the more difficult it is to separate molecules. The chemical properties, shapes of molecules and bond energies depend upon intramolecular forces. Intramolecular forces are much stronger than intermolecular forces.

Consider the example of water; it exists in liquid state at room temperature and one atmospheric pressure. Water molecule has two hydrogen atoms and one oxygen atom which are linked through strong covalent bonds. It is important to note that the conversion of liquid into vapours to overcome intermolecular forces needs little energy as compared to decompose the molecules into their component atoms to overcome the covalent bonds. Consider the following conversions:

$$H_2O_{(l)} \xrightarrow{\text{Vaporization}} H_2O_{(g)} \qquad \Delta H = +40.67 kJmol^{-1}$$

$$H_2O_{(g)} \xrightarrow{\text{Decomposition}} 2H_{(g)} + O_{(g)} \qquad \Delta H = +934 kJmol^{-1}$$

From the above conversions, it is noted that 40.67kJ/mol energy is required to vaporize one mole of liquid water and 934kJ/mole energy is required for the dissociation of one mole of gaseous water molecules into hydrogen and oxygen atoms. Now it is clear that the intramolecular forces are stronger than intermolecular forces because the strong attractive forces need much energy to break.

Keep In Mind

The intermolecular forces are broken during the process of evaporation of water molecules whereas the intramolecular forces are broken during the decomposition of water molecules.

Types of Intermolecular Forces

Intermolecular forces as a whole are usually known as Van der Waals forces after the Dutch scientist Johannes Van der Waals (1837-1923) who suggest the importance

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intermolecular forces and studied the non-ideal behavior of real gases. There are three major types of intermolecular forces; that are,

Dipole-dipole interactions, hydrogen bonding and London forces

5.2.1 Dipole-dipole Interactions

The attractive forces between the positive ends of one molecule with the negative end of other molecule are called dipole-dipole interactions or dipole-dipole forces.

These forces are present in polar molecules of the same or a different type. A polar molecule is sometimes described as dipole. The diatomic molecules which have elements of different electronegativities like HCl, has an unequal distribution of electron density and therefore has partial positive charge at one end and partial negative charge at the other end. In HCl molecule, chlorine is more electronegative than hydrogen atom. Due to this chlorine gains partial negative charge whereas hydrogen gains partial positive charge. When the molecules come close to each other, the positive end of one HCl molecule attracts the negative end of other HCl molecule, called dipole-dipole interaction.

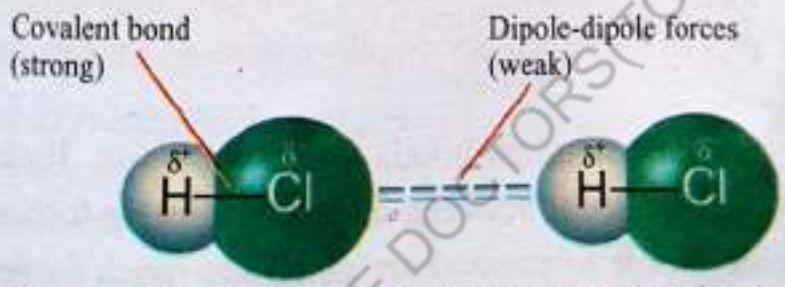

Figure 5.1: Dipole-dipole Forces between HCl Molecules

The repulsions can also occur when negative ends or positive ends of two molecules come close to each other. In liquids, the molecules which are attracting with other spend more time near each other than other molecules that are repelling with other. The overall effect is a net attraction strong enough to keep the molecules of liquid from moving apart to form a gas. Dipole-dipole forces are only about 1-4% as strong as a covalent or ionic bonds. These forces are very weak in gases but strong in liquids. The compounds having these forces generally have high melting points, boiling points, heat of vaporization (ΔH_{vap}) and heat of sublimation (ΔH_{sub}). The strength of dipole-dipole forces depends upon the distance between the molecules and electronegativity difference. Greater the electronegativity difference (ΔEN) of two bonded atoms in a molecule, greater will be its polarity. The greater the polarity of a substance, the greater will be the strength of dipole-dipole forces

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and higher will be the boiling point of the substance. For example, propane and acetaldehyde both have same molar masses ($44 gmol^{-1}$) but different strengths of dipole-dipole forces. The boiling point of polar acetaldehyde (20.85°C) is higher than that of non-polar propane (-42.15°C). This is because polar molecules have stronger intermolecular attractions than non-polar molecules. The electrons in polar molecules can form instantaneous dipoles, so all polar molecules also show London forces.

Intermolecular forces also have an effect on solubility. As you know, like dissolves like, the polar molecules dissolve (mix) in polar solvents and non-polar molecules dissolve in non-polar solvents. The polar molecules are not dissolving in non-polar solvents. Water, for instance, is a polar liquid and can mix with other polar liquids such as ethanol, acetic acid etc. and can't mix with non-polar liquids like gasoline, oil etc. therefore the oily stains on cloth cannot be washed away with water and it can be washed away with gasoline a non-polar solvent.

5.2.2 Hydrogen Bonding

The force of attraction between partial positive hydrogen atom of one molecule and lone pair of highly electronegative atom of another molecule is called hydrogen bonding.

These are not real chemical bonds in formal sense. Hydrogen bonds are intermolecular forces that occur between molecules. These forces are special type of very strong dipole-dipole forces and are generally much weaker than chemical bonds. Hydrogen bond is about five to ten times stronger than other dipole-dipole forces. Hydrogen bond is formed between those two same or different molecules which have the following characteristics:

i) One molecule has a hydrogen atom covalently bonded to a small, highly electronegative atom such as fluorine, oxygen, nitrogen and rarely chlorine.

ii) The other molecule has a small, highly electronegative atom such as fluorine, oxygen, nitrogen and rarely chlorine

For example, the molecules like HF, NH_3 and H_2O, experience hydrogen bonding. In a molecule such as HF, the fluorine atom pulls the electrons away from the hydrogen atom which has no inner electrons, and as a result of this the hydrogen atom acquires a significant positive charge and the nucleus of hydrogen atom unshielded. This unshielded positive hydrogen is strongly attracted to the lone pair of highly electronegative fluorine atom of a nearby HF molecule. The hydrogen

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atom is small in size and can approach a highly electronegative atom very closely and thus results in an extra strong dipole-dipole attraction. This unusual strong attraction between polar molecules is called hydrogen bonding. The strength of hydrogen bonds depends upon the polarity of the bond and the distance between the molecules.

The amount of energy needed to break hydrogen bond is 15–40kJmol^{-1} whereas the amount of energy needed to break covalent bonds between hydrogen and oxygen atoms is 150 –1100kJmol^{-1}. Hydrogen bonds are shown by dotted lines (...) and covalent bonds are shown by solid lines (—). Some examples of hydrogen bonds are given in figure 5.2.

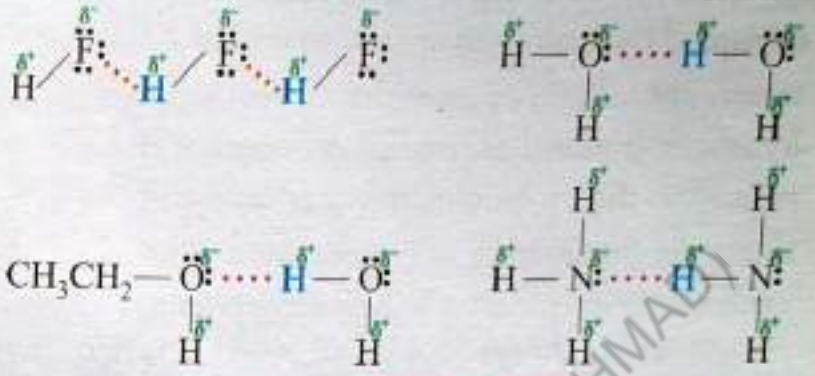

Figure 5.2: Hydrogen Bonding

Hydrogen bonding acts as a bridge between two electronegative atoms. Hence, it is also called bridge bonding. Due to Hydrogen bonding, molecules are joined with each other in a zigzag manner.

Applications of Hydrogen Bonding

Hydrogen bonds play an important role in our life. It helps in explaining the properties of some substances.

) Physical Properties

Hydrogen bonding affects thermodynamic properties like melting point, boiling point and heat of vaporization of compounds. The molecules that form hydrogen bonds have much higher heat of vaporization, melting and boiling points. For example, the hydrides of group IVA(14) have low boiling points than group VA(15), VIA(16) and VIIA(17) hydrides. This is due to lack of hydrogen bonds among hydrides of less electronegative elements of group IVA.

Table 5.1: The Boiling Points of Group IVA, VA, VIA, and VIIA Hydrides

Hydrides of Group IVA	Boiling Points (°C)	Hydrides of Group VA	Boiling Points (°C)	Hydrides of Group VIA	Boiling Points (°C)	Hydrides of Group VIIA	Boiling Points (°C)
CH_4	-164	NH_3	-33.3	H_2O	100	HF	19.9
SiH_4	-112	PH_3	-88	H_2S	-60.3	HCl	-85
GeH_4	-88	AsH_3	-55	H_2Se	-41.2	HBr	-67
SnH_4	-52	SbH_3	-17	H_2Te	-2	HI	-36

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ii) Hydrogen Bonding and Structure of Ice

Water molecules have tetrahedral structures. Two lone pairs of electrons on oxygen atom occupy two corners of the tetrahedron and other two corners are occupied by hydrogen atoms. In the liquid state, the water molecules experience hydrogen bonds that continually break and reform as the molecules move around and thus, the molecules are associated with each other irregularly. When temperature is decreased, the molecules of water arrange themselves in a regular hexagonal pattern in such a way that empty spaces are created in the structure of ice and it expands. Hence, ice occupies 10% more space and its density decreases. The result is that, the ice cubes and icebergs float on water. Hence, ice is an insulator of heat and it prevents the underneath water from freezing.

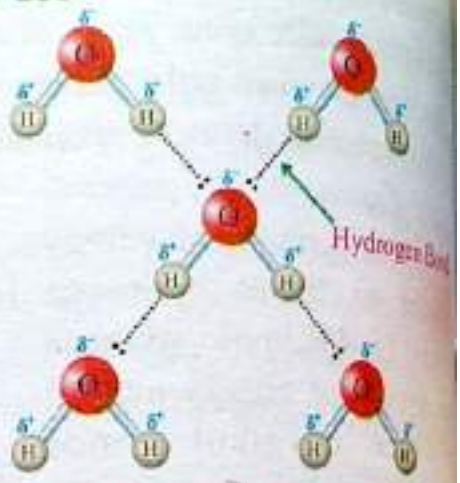

Figure 5.3: Hydrogen Bonding in Water

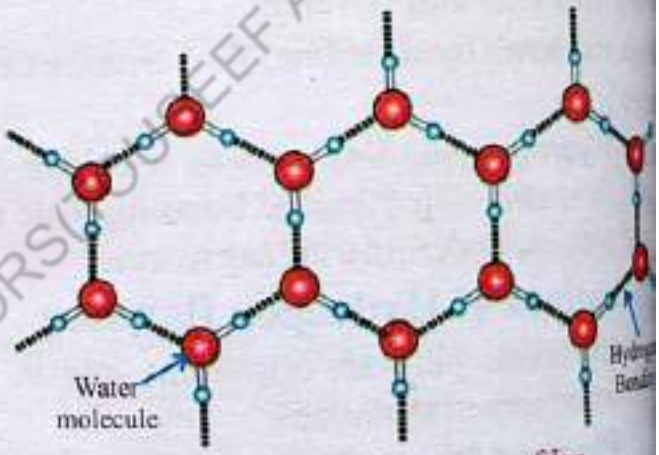

Figure 5.4: Structure of Ice

Therefore, fish and other aquatic life (animals and plants) can survive without being frozen under this layer of ice in the winter season. If ice were a typical solid, it would have high density than liquid water. Then the lakes and oceans would freeze from bottom to top. This would have harmful effects for aquatic life.

The expansion of water upon freezing shows adverse effects too. In cold winter nights, it causes water pipes to burst and cracks the radiators of car. To prevent this we use antifreeze in the radiators of car. In cold weather cities, it breaks up streets and produces potholes in it. The ice formation is also responsible for splitting of rocks where water leaks through cracks of rocks.

iii) Biological Significance

Biological molecules such as proteins and Deoxyribonucleic acid (DNA) play important roles in biochemistry. The typical structures of proteins and DNA which are required for their functions are due to hydrogen bonding. Proteins are made up of long chain of amino acids. The long chains of amino acids are coiled around each other into a spiral, called helix. Helix may either be right handed or left handed.

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the right handed helix the –NH– groups of one spiral form hydrogen bonds with C=O of other spiral. On the other hand DNA has two spiral chains. These two long molecular chains (strands) of DNA coiled around each other are also held together by hydrogen bonds. Life would be impossible without hydrogen bond.

Interesting information:

Proteins are the major components of skin, hair, and muscle and are essential for the contraction of muscles, digestion of food, and clotting of blood. DNA, present in the cells of organisms, carries genetic information from one generation to other.

b) Extraordinary High Specific Heat Capacity of Water

The strong hydrogen bonding is responsible for the extraordinary high specific heat of water. Specific heat is the amount of energy required to raise the temperature of one gram of a substance by one degree Celsius. Due to high values of specific heat, the water in swimming pools, lakes and oceans takes time in gaining the energy from the sun in the daytime to become warm. Once it has warmed up, it does not cool down rapidly. Because of this property, water has an enormous effect on weather and moderates the temperature at the surface of earth. If there were no water on the surface of earth, the temperature would shoot up in the daytime and would fall steeply at night because the rocks have much lower specific heat and has little capacity to gain energy in the daytime from the sun and release that energy at night. It is water that absorbs much heat from the sun during the daytime and released this stored heat at night and helps to keep up the temperature of the air of coastal cities such as Karachi and Gwadar.

Table 5.2: Specific Heats of Some Substances

Substance	Specific Heat ($J/g^{\circ}C$)	Substance	Specific Heat ($J/g^{\circ}C$)
Iron (Fe)	0.45	Wood	1.76
Cement (concrete)	0.84	Ethanol ($CH_3CH_2OH_{(l)}$)	2.46
	0.88	Water ($H_2O_{(l)}$)	4.18

Interesting information:

The air temperatures near large mass of water such as in Karachi are usually lower in the summer and higher in the winter than those areas which are far away from large bodies of water (sea) such as Sibi.

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v) Solubility of Hydrogen Bonded Molecules

Compounds which contain hydrogen bonds are soluble in each other. For example ethanol and acetic acid are soluble in water due to presence of hydrogen bonds whereas methane and benzene are insoluble in water due to absence of hydrogen bonding.

vi) Cleaning Action

Cleaning action of detergents and soaps is because of hydrogen bonding. We use soaps and detergents for washing our bodies, clothes, dishes and so on. The one end of soaps and detergents is polar and the other is non-polar. The polar ends form hydrogen bonds with water and are soluble in water. The non-polar end attracts oil and grease that are present at the surface of dishes and cloths.

vii) Hydrogen Bonding in Food Materials

The food materials (carbohydrates) also form hydrogen bond due to presence of OH groups in their structures.

viii) Hydrogen Bonding in Paints and Dyes

The adhesive properties of paints and dyes are because of hydrogen bonding. The stickiness of honey and glycerin is also due to hydrogen bonding.

ix) Surface Tension and Viscosity

Water has high surface tension and viscosity as compared to many other liquids due to presence of hydrogen bonding. This is because the presence of hydrogen bonds make it more difficult for molecules to escape from the liquid state; additional energy is required to overcome the hydrogen bonds.

Conceptual Check Point:

- Which has the higher boiling point, H_2O or H_2S? Why?
- What bonds are broken when water boils?
- Why the boiling point of water is higher than that of hydrogen fluoride and ammonia?

5.2.3 London Forces

The weakest types of intermolecular forces which occur between all atoms or molecules (polar or non-polar) and produced due to temporary dipoles are called London forces. These forces of attraction are also known as London dispersion forces or instantaneous dipole-induced dipole forces.

In 1930, Fritz London a German physicist, recognized these weak forces of attraction between non-polar molecules and for this reason these forces of attraction are known as London forces. He found that the non-polar gases can be liquefied

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under the right conditions of pressure and temperature, therefore the non-polar molecules must show intermolecular forces that are different from other intermolecular forces because they originate from motion of electrons in an atom or molecule and produce an instantaneous dipole. These forces are present in halogens, noble gases, and non-polar molecules such as H_2, N_2, CH_4, CO_2, SO_2, SiH_4 and CCl_4 and so on. In the absence of London forces, such substances could not condense to form liquids or solidify to form solids. Condensation of some substances occurs only at very low temperatures and/or high pressures.

Fritz London
(1900-1954)

Let us consider the example of neon to understand how non-polar atoms and molecules attract each other. The distribution of electron density in a non-polar atoms and molecules like neon atom is uniform and symmetrical. When atoms of neon come close to each other, then the electrons of one atom repel the electrons of other atom. In this way, symmetry or equality of electronic cloud is disturbed. Therefore, electronic cloud bends towards one side and nucleus (positive portion) towards other side. This is called instantaneous dipole. This instantaneous dipole disturbs the electronic cloud of the other nearby atom. So a dipole is induced (induced) in second atom. This is called induced dipole. As a result of this, weak attractive forces are generated, called London forces or London dispersion forces. This process occurs with other nearby atoms and, thus, throughout the sample. These forces disappear when the electrons again become symmetrical around nucleus.

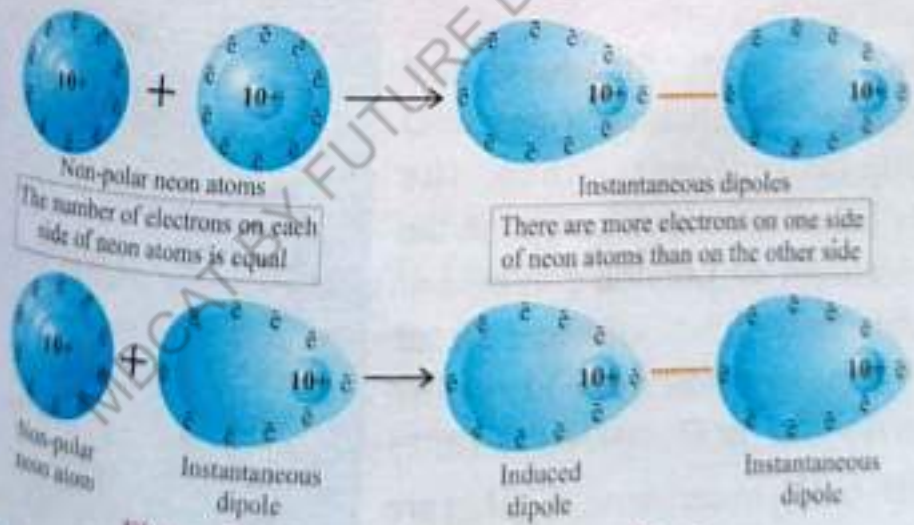

Figure 5.5: London Forces between Neon

...ors Affecting London Forces

...se forces depend upon the following factors:

...tomic or molecular sizes

...ape of molecules

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i) Atomic or Molecular Sizes

The strength of London forces depend upon the size of atoms and molecules. The larger atoms and molecules, with greater number of electrons and heavy mass, polarize more easily as compared to small atoms and molecules. We may say that the strength of London forces is directly proportional to the polarizability of the atom or molecule. For example, in VIIA group (Halogens), the fluorine and chlorine are gases, bromine is liquid, and iodine is solid at room temperature and one atmosphere pressure. The big difference in the physical states of halogens indicates that the polarizability of the halogens increases down the group because of which the strength of attractive forces (London forces) increases down the group. The boiling points of both polar and non-polar molecules increase when the sizes and molar masses of molecules increase. For example, the boiling points of halogens and noble gases increase from top to bottom in a group of periodic table due to increase in atomic size and molar masses.

When the molar masses and molecular sizes of alkanes (saturated hydrocarbons) increase, then the polarizability increases which results in the increase of strength of London forces. For example, the first four alkanes (from methane to butane) are gases due to smaller molecular size, the next sixteen alkanes (from pentane, C_5H_{12} to eicosane, $C_{20}H_{42}$) are liquids due to relatively higher molar masses and molecular sizes and the higher alkanes (from heneicosane, $C_{21}H_{44}$ on ward) are solids because of greater molar masses and molecular sizes.

Keep In mind

Polarizability is the extent to which the electronic cloud of a substance is distorted or polarized.

The polarizability increases as the number of electrons in an atom or molecule increases. The greater the polarizability, the more easily the electron cloud can be distorted (polarized). Hence, more polarizable atoms and molecules have stronger London forces.

Table 5.3: The Boiling Points of Halogens and Noble Gases

Halogen	Molar Mass(g/mol)	Boiling Point(°C)
Fluorine (F_2)	38.0	-188.0
Chlorine (Cl_2)	70.9	-34.6
Bromine (Br_2)	159.8	58.8
Iodine (I_2)	253.8	184.3
Noble Gases	**Molar Mass(g/mol)**	**Boiling Point(°C)**
Helium (He)	4.0	-268.9
Neon (Ne)	20.2	-245.9
Argon (Ar)	39.9	-185.7
Krypton (Kr)	83.8	-153.2
Xenon (Xe)	131.3	-107.1
Radon (Rn)	222.0	-61.8

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Greater the polarizability of a molecule, stronger would be the London forces. Hence molecules have strong forces of attractions. For example, three compounds with same molecular formula, C_5H_{12}, boil at different temperatures, n-pentane boils at 36°C, iso-pentane boils at 28°C and neo-pentane boils at 9.5°C.

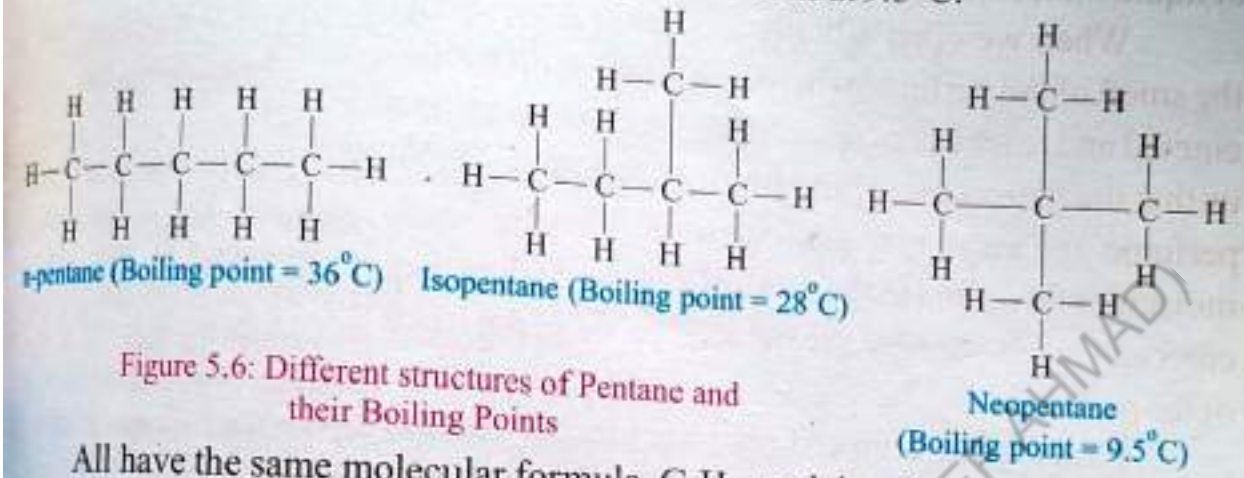

Figure 5.6: Different structures of Pentane and their Boiling Points

All have the same molecular formula, C_5H_{12} and thus the same molar mass, but they differ in the arrangement of the atoms. Boiling points increase as the forces of attraction between molecules increase.

The valence electrons in the carbon-carbon bonds of n-pentane and iso-pentane are closer to the surface of the molecules while in neo-pentane the valence electrons in the carbon-carbon bonds are well inside the molecule. Hence London forces in n-pentane and iso-pentane are stronger than those in neo-pentane.

Keep In Mind

London forces are present among both the polar and non-polar molecules because electrons are in constant motion in all molecules whereas dipole-dipole forces are present only among polar molecules.

3 Physical Properties of Liquids

The properties of liquids depend on the nature and strength of intermolecular forces. In this section we consider five such properties which are associated with liquids in general: evaporation, vapour pressure, boiling point, viscosity and surface tension.

3.1 Evaporation

The spontaneous conversion of liquid molecules into vapours in an open container at a given temperature is called evaporation. In this process, molecules escape from the liquid surface and change into vapours spontaneously.

Consider the example of a liquid which is present in the beaker. At a given temperature, all the liquid molecules do not have same kinetic energies in the

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beaker. Molecules having low kinetic energy move slowly while the molecules having high kinetic energy move faster. If one of the higher speed molecules approaches the surface, then it may escape and overcome the attractions of the neighboring molecules and leaves the bulk of the liquid. This spontaneous change of liquid molecules into vapours is called evaporation.

When we open a bottle of perfume, we detect the smell of the perfume when their gaseous molecules entered and reached our nose. Here our experience tells us that the molecules escape from the liquid surface of perfume and enter into gaseous state. These gaseous molecules travelling in the upward direction when they enter and reach our nose, we become aware of the smell of the perfume.

Evaporation is an endothermic process because energy is required to overcome the intermolecular forces of attraction holding the molecules together.

Keep in mind

Vaporization is the process by which liquid or solid changes to a gas while evaporation is the process by which molecules escape from the surface of a non-boiling liquid and enter the gas phase. Evaporation is a type of vaporization.

Interesting Information:

It is interesting to know that your body regulates its temperature through evaporation in the warm weather or when you exercise. During hot summer days your body passes water to the surface of your skin by means of sweat glands. As the water on the surface of your body evaporates, it removes high energy molecules from your body and low energy molecules are left behind. In this way the temperature of your body falls and your body becomes cool down.

Factors Affecting Evaporation

Temperature

Evaporation occurs at all temperatures. Rate of evaporation increases with increase in temperature and decreases with the decrease in temperature. By increasing temperature, the kinetic energy of molecules increases which results in the rise of rate of evaporation. If you warm the glass of water, it evaporates quickly because the greater the temperature, the greater is the kinetic energy and the greater is the evaporation.

Conceptual Check Point:

Why wet laundry hung on a clothes-line dries faster in the hot days of summer than cold days of winter?

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Surface Area

Evaporation is the surface phenomenon. It occurs on the surface of the liquid. Greater the surface area, greater will be the evaporation and vice versa. The greater surface area provides a greater chance for molecules to come to the surface of the liquid and changes into the gas phase.

Conceptual Check Point:

Which water dries faster, the water present in the bottle or the water sprinkled on the ground? The water in both the cases has the same volume.

Intermolecular Forces

Different liquids have different rates of evaporation at the same temperature. This is due to the different nature and strength of intermolecular forces. Stronger the intermolecular forces, lower will be the rate of evaporation and vice versa. For example, Gasoline evaporates more quickly than water. Because the intermolecular forces between the gasoline molecules are weaker than the intermolecular forces between water molecules.

Conceptual Check Point:

- Which liquid evaporates more quickly: gasoline or gas oil?

5.3.2 Vapour Pressure

The pressure exerted by liquid vapours in equilibrium with its pure liquid at a given temperature is called vapour pressure.

Keep in mind

- The term vapour is usually used for the gas phase of a substance that is found as liquid or solid at normal temperature and pressure.
- The processes of vaporization and condensation are examples of *phase changes*.

Consider we have a liquid in an evacuated closed container. Its vapours are formed because of evaporation which begins together above the surface of liquid. These molecules move freely colliding with each other, with the walls of container and also with the surface of liquid. Condensation (the conversion of vapours into liquid) occurs because a molecule striking the liquid surface becomes captured by intermolecular forces in the liquid. In the beginning, the traffic is only one way: Molecules are moving from the liquid to the empty space and rate of evaporation is greater than rate of condensation. By the passage of time, the pressure of vapours above the liquid increases as the number of vapours molecule increases. But after some times, the rate of evaporation and condensation becomes equal, as shown in figure 5.7(c). At this stage, number of molecules leaving liquid

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surface is equal to number of molecules going back to liquid. This state is called equilibrium state. Thus, at this stage, there is no net change in the masses of the two phases.

$$\text{Liquid} \underset{\text{Condensation}}{\overset{\text{Evaporation}}{\rightleftharpoons}} \text{Vapours}$$

The pressure of the vapours of a substance in equilibrium with its pure liquid is called its equilibrium vapour pressure (or just the *vapour pressure*). It is important to note that the value of the vapour pressure of liquid is maximum at equilibrium state at a given temperature and that it is constant at constant temperature. At equilibrium the volume of the liquid does not change.

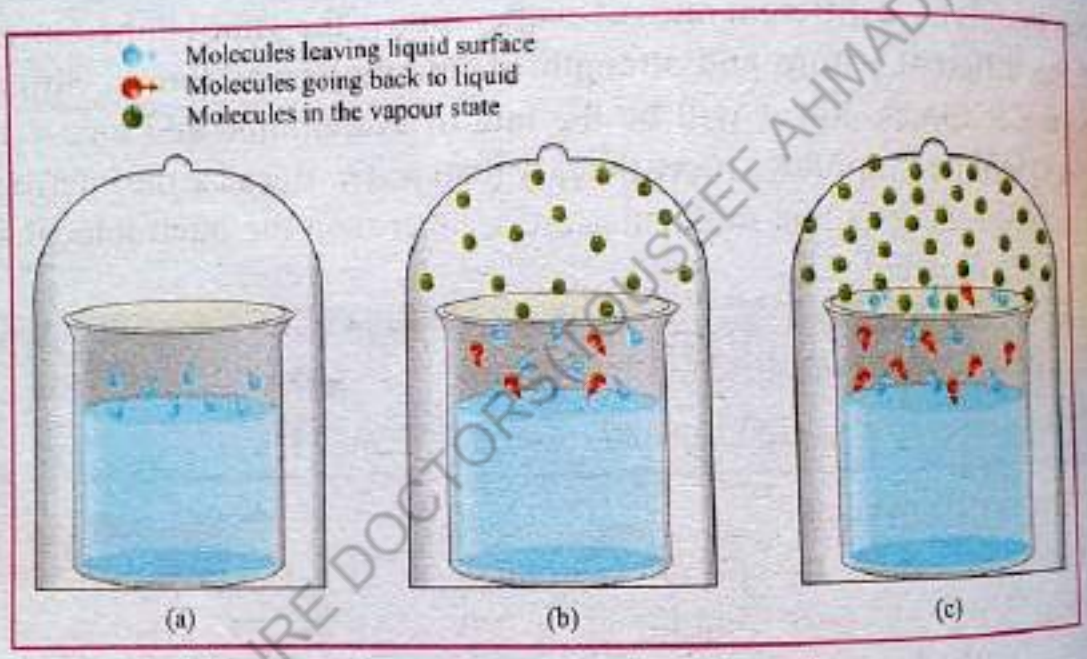

Figure: 5.7: A liquid is allowed to evaporate in a closed vessel.
(a) initially only evaporation occurs,
(b) condensation begins but the rate of evaporation is greater than rate of condensation
(c) dynamic equilibrium is established, now the rate of evaporation is equal to the rate of condensation

Equilibrium in which evaporation and condensation are going on is called dynamic equilibrium.

Factors Affecting Vapour Pressure

The vapour pressure of a liquid depends on the magnitude of the intermolecular forces present in them and on the temperature. Vapour pressure does not depend upon amount of liquid. It also does not depend on the surface area of liquid because an increase in surface area at equilibrium equally affects the rate of evaporation and the rate of condensation.

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Intermolecular Forces

Vapour pressure is inversely related to intermolecular attractions. Weaker the intermolecular forces, greater will be the vapour pressure. For example the vapour pressure of water (18 mmHg) is lower than chloroform (170mmHg). The lower vapour pressure of water is due to the presence of strong hydrogen bonds which are absent in chloroform. Chloroform has weak London forces. In general, the liquids with large molecular sizes or greater molar masses have relatively low vapour pressure due to strong dispersion forces. For example, the vapour pressures of liquid alkanes (saturated hydrocarbons) decrease with increase in the molecular size. The larger the molecular size of a liquid is, the more polarizable it is, and the greater the dispersion forces are.

Keep In Mind

The liquids which evaporate easily and have high vapour pressures are said to be volatile, while those that do not vaporize easily and have low vapour pressures are said to be nonvolatile. Volatile liquids such as nail polish remover evaporate readily while non-volatile liquids such as motor oil evaporate slowly if not heated.

Temperature

Vapour pressure increases with increase in temperature. For example, the vapour pressure of water at 25°C is 24 mmHg and at 100°C its value is 760 mmHg. This is because with the rise in temperature the average kinetic energy of the liquid molecules increases which is high enough for molecule to escape from the liquid surface. It results in the increase of the number of vapours, thus the vapour pressure of the liquid increases.

Measurement of Vapour Pressure

A simple mercury barometer can be used to measure the vapour pressure of a liquid. A drop of liquid whose vapour pressure is to be determined is place under the barometer tube filled with Hg, with the help of a bent tube or dropper. The liquid drop will rise above mercury column, because most of the liquids are less dense than mercury and on reaching above the surface of mercury, a part of liquid will evaporates. The vapours will now push the Hg column downwards. As a result of this, the length of Hg column decreases. This change in length of mercury level from its initial position to its final position is equal to the vapour pressure of liquid.

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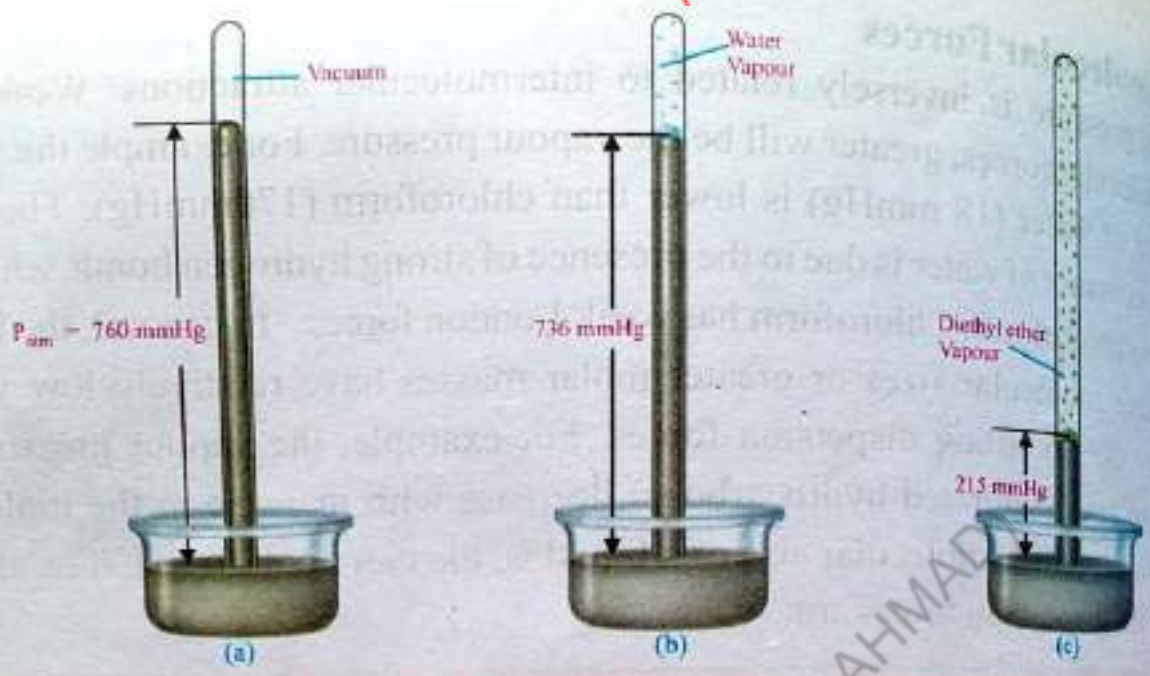

Figure 5.8: Measurement of Vapour Pressures of Water and Diethyl Ether

The vapour pressure of water and diethyl ether at 25°C and 760 mm Hg is 24 mm Hg and 545 mm Hg respectively.

Vapour pressure of liquids can be measured at various temperatures.

Table 5.4: Vapour Pressure of Water at Various Temperatures

Temperature (°C)	Pressure (mmHg)	Temperature (°C)	Pressure (mmHg)	Temperature (°C)	Pressure (mmHg)
0.0	4.6	50.0	92.5	90.0	525.8
10.0	9.2	60.0	149.4	100.0	760.0
20.0	17.5	70.0	233.7	110.0	1074.6
30.0	31.8	80.0	355.1	120.0	1489.1
40.0	55.3				

5.3.3 Boiling Point

The temperature at which vapour pressure of a liquid becomes equal to atmospheric pressure or external pressure is called boiling point of liquid.

When liquid is heated, its average kinetic energy is increased. As a result of this, more molecules escape from liquid surface, hence vapour pressure increases. It goes on increasing till it becomes equal to atmospheric pressure or external pressure. Then the liquid starts boiling. Small bubbles of vapours produced spontaneously below the surface of liquid and they start rising. The bubbles formed consist of vapourized molecules of the liquid, not of air. Temperature at this point is called boiling point.

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Table 5.5: Boiling Points of Some Common Liquids at One Atmosphere Pressure

Liquid	Boiling Point (°C)	Liquid	Boiling Point (°C)
Acetic acid	118.5	Carbon tetrachloride	76.5
Acetone	56.0	Ethyl alcohol	78.3
Ammonia	-33.3	Ethylene glycol	197
Benzene	80.5	Mercury	356.6
n-Butyl alcohol	117	Phenol	181.8
Carbon disulphide	46.3	Water	100.0

Temperature of a liquid remains constant during boiling, why? When a liquid is heated, the average kinetic energy of its molecules increased, so the temperature of the liquid also increased. At boiling, the kinetic energy of molecules is the maximum. Now the heat supplied is only used to break the intermolecular forces and convert the liquid into vapours. Any more heat supplied will not increase the temperature of liquid. In this way, the temperature of the liquid molecules remains constant.

Factors Affecting the Boiling Point

The boiling points of the liquid are affected by the factors given below:

Intermolecular Forces

The boiling point of a pure liquid is directly related to the strength of intermolecular forces. The stronger the intermolecular forces, the higher are the boiling points of the liquids and vice versa. For example, the boiling point of water (100°C) is higher than ethyl alcohol (78.26°C). This is due to stronger intermolecular forces among water molecules as compared to ethyl alcohol.

Keep in mind

Each liquid has its own particular boiling point. The boiling points of liquids do not depend upon amount of liquid.

External (Atmospheric) Pressure

Boiling points depend upon external pressure. It increases with increase in external pressure and decreases with decrease in external pressure. For example, the boiling point of water at one atmosphere (760mmHg) is 100°C. At high altitude, atmospheric pressure is less than 760mmHg; hence water boils at temperature lower than 100°C. So the boiling point of water at Murree hills where atmospheric pressure is 0.921atm (700mmHg) is about 98°C and at the top of Mount Everest where atmospheric pressure is 0.316atm (240mmHg) is about 71°C. On the other

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hand the boiling point increases when the external pressure increases. For example, the boiling point of water at 1.414atm (1074.6mmHg) is 110°C.

Keep In Mind

The boiling point depends on the pressure of the atmosphere because the bubbles of vapour cannot even form until the temperature of the liquid raises to a point at which the vapour pressure of the liquid becomes equal the atmospheric pressure.

Applications

The change of boiling point of a liquid with external pressure has very important applications in chemistry as well as in our daily life.

Boiling Point and External Pressure (Pressure Cooker)

Boiling point of a liquid increases with increase in external pressure. This property is used in pressure cooker e.g. When a liquid is heated in a closed vessel i.e. pressure cooker, more and more vapours are gathered over the liquid surface. These vapours cannot go out from cooker, hence pressure is developed. It increases with increase in temperature. Due to high external pressure, boiling point of a liquid i.e. water is increased. A commercial pressure cooker reaches an internal temperature of 140°C.An increase in temperature of only 10°C will cause food to cook in approximately half the normal time. Therefore food cooks more quickly in cooker. It saves time and greater energy costs. In the hospitals, the same principle is used for the sterilization of instruments and laundries in autoclaves where temperature is high enough to destroy bacteria. Autoclave produces steam at 2atm because of high pressure, temperature of steam is increased and it destroys bacteria at such a high temperature and pressure efficiently.

Conceptual Check Point:

How does the pressure cooker balance the effects of the lower atmospheric pressure on the boiling of liquid at higher altitude?

Vacuum Distillation (Reduced Pressure Distillation)

Distillation at low pressure is called vacuum distillation. Boiling point of a liquid decreases with decrease in external pressure. This process is used to purify those liquids which decompose at their boiling points. In order to boil (distil) them at lower temperature, distillation is carried out under reduced pressure e.g. Glycerol boils and decomposes at 290°C at 760torr (1atm) but on lowering pressure to 90 it can be boiled at 120°C without decomposition.

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Conceptual Check Point:

Is it possible to condense steam and recover the water as a liquid? If yes, then how?

5.3.4 Viscosity

Some liquids such as honey and glycerin flow very slowly while others such as gasoline and water flow speedily. The internal resistance to flow of a liquid is called viscosity. It is denoted by eta (η). The greater the viscosity of the liquid, the more slowly it flows. Consider the example of oil which is flowing through a pipeline in the form of layers. Each layer experiences resistance to the flow of other layer due to internal friction. The internal friction is produced because of cohesive force (forces of attraction among liquid molecule) that reduces the rate of flow of oil.

Keep in mind

The liquids which flow slowly are called viscous liquids. They show greater internal resistance to flow because of strong cohesive forces.

Figure shows the internal resistance to flow of a liquid. The velocity of flow of a liquid nearer to the sides of tube is less than the velocity of flow in the center of tube

The rate of flow of the oil close to the margins of pipeline is not as much as the rate of flow in the middle of the pipeline.

Table 5.6: Viscosity of Some Common Liquids at 20°C

Liquid	Formula	Viscosity ($Kgm^{-1}s^{-1}$)
Acetone	C_3H_6O	3.16×10^{-4}
Benzene	C_6H_6	6.25×10^{-4}
Blood	-----	4.00×10^{-3}
Carbon tetrachloride	CCl_4	9.69×10^{-4}
Diethyl ether	$CH_3CH_2O\,CH_2CH_3$	2.33×10^{-4}
Ethyl alcohol	CH_3CH_2OH	1.20×10^{-3}
Ethylene glycol	$HOCH_2CH_2OH$	26×10^{-3}
Glycerine	$C_3H_8O_3$	1.49
Mercury	Hg	1.55×10^{-3}
Water	H_2O	1.01×10^{-3}

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Conceptual Check Point:

Which liquid takes much time, the olive oil or water, when they are pouring in the cups?

Factors Affecting Viscosity

The viscosity of a liquid is related to its intermolecular forces, temperature, molecular size and molecular shape.

Intermolecular Forces

The stronger the intermolecular forces, the greater the viscosity of liquids because liquid molecules cannot move around each other freely so the resistance to flow increases. In general, the liquids with small non-polar molecules such as benzene have relatively low viscosities due to weak intermolecular forces and the liquids with polar molecules such as ethyl alcohol have higher viscosities due to stronger intermolecular forces. On the other hand, the liquids which have ability to form hydrogen bonds have higher viscosities than those which are unable to form hydrogen bonds. For example, the viscosity of water is higher than methyl alcohol because of strong hydrogen bonding in water. It is interesting to know that, the glycerine has higher viscosity than that of all other liquids. It is more viscous than water because its molecule has more sites for making hydrogen bonds as compared to water. Each water molecule has only one –OH group and glycerine has three -OH groups for making hydrogen bonds.

Conceptual Check Point:

Why water, H_2O is more viscous than hydrogen fluoride, HF?

Temperature

Viscosity generally decreases with increasing temperature and increases with decreasing temperature. Because at high temperature molecules have high kinetic energy and can overcome some of the intermolecular attractive forces to slip past one another between the layers. For example, the viscosity of honey and cooking oil decreases as their temperature rises.

Molecular size

The viscosity of a liquid increases by increasing molecular sizes or molar masses and decreases by decreasing molecular sizes or molar masses. For example, diesel is more viscous than petrol, because the larger size molecules (diesel molecules) with higher molar masses are difficult to slip past one another.

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Conceptual Check Point:

Give reason which substance is more viscous, gasoline or kerosene oil?

Molecular Shape

Viscosity also depends on the shape of molecules. The viscosity of irregular shaped molecules such as glycerine is greater than regular shaped molecules such as ether. The molecules of viscous liquid become entangled rather than to slip past one another as the molecules of less viscous liquids do.

Measurement of Viscosity

It is difficult to measure the absolute value of viscosity; therefore relative viscosity of liquids is measured. The relative viscosity is the ratio of viscosity of a liquid to the viscosity of water taken as standard. The Ostwald viscometer is used to measure the viscosity of liquid. It has two bulbs, one at each limb. Definite amount of liquid is taken in bulb B and is sucked from bulb B to mark X. The liquid is, then, allowed to flow from mark X to Y. The time of flow of liquid is noted. The viscometer is now cleaned and the same process is repeated with the same amount of water at same temperature. The densities of both the water and given liquid are measured by specific gravity bottle at the same temperature. Relative viscosity of the liquid is calculated from the equation given below:

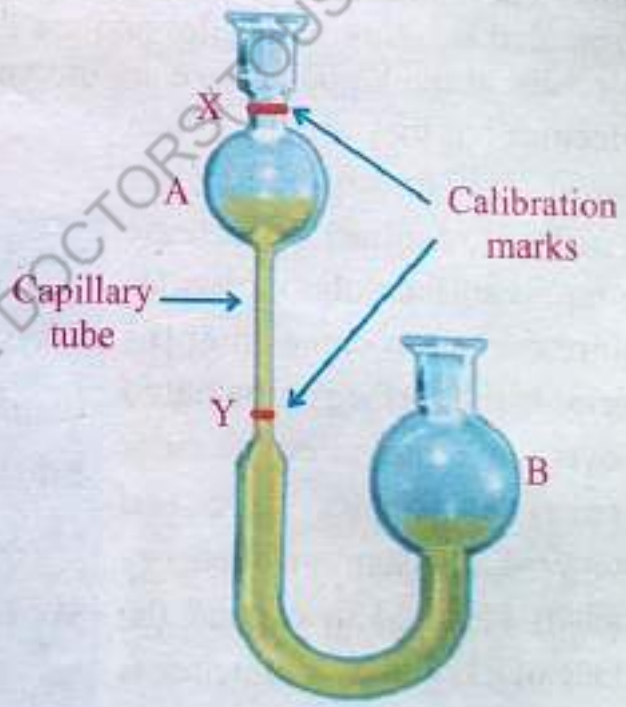

Figure 5.9: Ostwald's Viscometer

$$\frac{\eta_l}{\eta_w} = \frac{d_l t_l}{d_w t_w}$$ or

$$\eta_l = \frac{d_l t_l}{d_w t_w} \times \eta_w$$

Where, η_l is the viscosity of liquid, η_w is the viscosity of water, d_l is the

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density of liquid, d_w is the density of water, t_l is the time of flow of liquid and t_w is the time of flow of water.

The unit of viscosity is poise (1 poise = 100 centipoise). The SI unit of viscosity is Newton-second per meter square, Nsm^{-2} (one Nsm^{-2} is equal to one kilogram per meter per second, $Kgm^{-1}s^{-1}$).

1 poise = $10^{-1} Kgm^{-1}s^{-1}$.

5.3.5 Surface Tension

A property common to all liquid is surface tension; it is defined as the amount of energy required to increase the surface of a liquid by a unit area. It is denoted by Greek letter γ (gamma). The unit of surface tension is erg per centimeter square (erg/cm^2) or dynes per centimeter (dynes/cm). Its SI unit is Newton per meter square (N/m^2) or joule per meter square (J/m^2).

The surface tension is due to variation of attractive forces at the surface of a liquid. The molecules present inside the body of the liquid are completely surrounded by other molecules and are drawn equally in all directions while the molecules at the liquid surface are drawn downward and from the sides by the molecules but they are not drawn upward. This inward pull causes the surface to contract. To increase the liquid surface, the molecules require energy to come from the interior to the surface of the liquid to overcome the intermolecular attractive forces directed downward. This amount of energy which is required to expand the surface of a liquid by a unit area is called surface tension.

Table 5.7: Surface Tension of Some Common Substances at 20°C

Substance	Formula	Surface Tension (J/m²)
Ethyl alcohol	CH_3CH_2OH	2.23×10^{-2}
Benzene	C_6H_6	2.89×10^{-2}
Ethylene glycol	$HOCH_2CH_2OH$	4.8×10^{-2}
Glycerine	$C_3H_8O_3$	6.34×10^{-2}
Water	H_2O	7.29×10^{-2}
Mercury	Hg	4.60×10^{-1}

Due to surface tension the water surface behave like a stretched piece of rubber. A razor blade if kept carefully on the surface of the water can be made to float although it is made of steel.

Factors Affecting the Surface Tension

The magnitude of the surface tension of the liquid depends upon the following factors:

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Intermolecular Forces

The liquids with strong intermolecular forces have higher surface tension than liquids with weak intermolecular forces. Water, for instance, has higher surface tension than many other liquids such as ethyl alcohol, benzene, and ether. This is due to the presence of strong hydrogen bonds in water molecules. Rain drops or the drops on the waxy surface of an apple or leaves are nearly spherical in shape. In a spherical drop, nearly all the attraction at the surface is inward, thus the sphere has the less surface area per unit volume than any other shape. Substances such as soaps and detergents which are used for washing are known as surfactants. They can be added to water to reduce the surface tension of water by the breakage of hydrogen bonds. This increases the interaction of water with grease and dirt and it becomes easier to remove grease and dust particles from the fabrics.

Interesting information:

Because of high surface tension, some animals such as spider can stand, walk or run on water without breaking the surface.

Temperature

The surface tension of the liquid decreases as the temperature is raised. By raising the temperature the kinetic energy of liquid molecules increases and hence, the strength of intermolecular forces decreases which results in the decrease of surface tension.

Measurement of Surface Tension

Surface tension of liquid can be measured by Stalagmometer method. It is also called drop method. Stalagmometer consists of glass bulb between tubes *A* and *C* as shown in the figure 5.9.

Water is filled in the dry clean Stalagmometer up to mark *X* and then it is allowed to flow down slowly from mark *X* to *Y* in the form of drops. The number of drops formed with water is counted. The Stalagmometer is now cleaned and the same process is repeated with the same volume of the given liquid at same temperature. The densities of both the water and given liquid are measured by specific gravity bottle at the same temperature. Surface tension of the liquid is calculated by the relation given below:

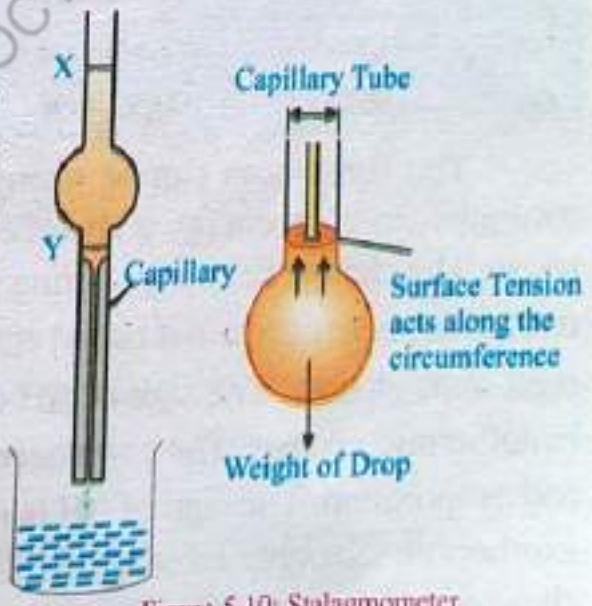

Figure 5.10: Stalagmometer

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$$\frac{\gamma_l}{\gamma_w} = \frac{n_w d_l}{n_l d_w} \quad \text{or}$$

$$\gamma_l = \frac{n_w d_l}{n_l d_w} \times \gamma_w$$

Where, γ_l is the surface tension of the liquid, γ_w is the surface tension of water, n_l is the number of drops formed with liquid, n_w is the number of drops formed with water, d_l is the density of liquid, and d_w is the density of water.

5.4 Energetics of Phase Changes

The process in which a substance is transformed from one physical state to another physical state is called phase change (state change). Phase change is an example of physical change. Six possible phase changes takes place among the states of matter.

Table 5.8:Possible Changes of States

Change of State	Process	Example
Solid ⟶ Liquid	Melting or fusion	Ice ⟶ Water
Solid ⟶ Gas	Sublimation	Iodine ⟶ Iodine vapours
Liquid ⟶ Solid	Freezing	Water ⟶ Ice
Liquid ⟶ Gas	Vaporization	Water ⟶ Steam
Gas ⟶ Liquid	Condensation	Steam ⟶ Water
Gas ⟶ Solid	Deposition	Iodine vapours ⟶ Iodine

The substances can be changed from one state to another by heating or cooling them. Heat energy is absorbed or evolved, when a phase changes to another phase. The change in energy during physical or chemical change of a substance at one atmosphere pressure is called enthalpy change. It is denoted by ΔH. The symbol Δ represents change. The sign of ΔH is positive, if energy is absorbed and is called endothermic change. The endothermic changes of state are melting, sublimation and evaporation. The sign of ΔH is negative, if heat energy is evolved and is called exothermic change. Exothermic changes are the reverse of the endothermic changes and they are freezing, condensation, and deposition.

5.4.1 Molar Heat of Fusion, Molar Heat of Vaporization, and Heat of Sublimation

The majority of substances experience two types of changes of state on heating. A solid changes to a liquid at its melting point, and a liquid changes

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at its boiling point. But we also experience, the change of solid into gas directly such as conversion of ice into vapours below 0°C. Therefore, we are going to discuss the enthalpy change of fusion, vaporization and sublimation.

Molar Heat of Fusion

The amount of heat required to convert one mole of solid into liquid state at its melting point is called molar heat of fusion (or molar enthalpy of fusion). It is denoted by ΔH_{fus}. The molar heat of fusion for ice is 6.02 KJ/mol.

$$\underset{\text{Ice}}{H_2O_{(s)}} \longrightarrow \underset{\text{Water}}{H_2O_{(l)}} \qquad \Delta H_{fus} = 6.02 kJ/mol$$

Table 5.9: Molar Heat of Fusion and Melting Point of Some Substances

Substance	Formula	Melting Point (°C)	ΔH_{fus} (kJ/mol)
Water	H_2O	0.0	6.02
Carbon tetrachloride	CCl_4	–23	2.51
Isopropyl alcohol (rubbing alcohol)	$(CH_3)_2CHOH$	–89.5	5.4
Dimethyl ketone (acetone)	CH_3COCH_3	–94.8	5.7
Diethyl ether	$CH_3CH_2OCH_2CH_3$	–116.3	7.3

Freezing is the reverse of fusion (melting). The amount of heat released in ezing a substance is equal to the amount of energy required to melt that substance lid), but the sign is negative.

$$\underset{\text{Water}}{H_2O_{(l)}} \longrightarrow \underset{\text{Ice}}{H_2O_{(s)}} \qquad \Delta H_{fus} = -6.02 kJ/mol$$

olar Heat of Vaporization

e amount of heat required to convert one mole of a liquid into vapours at its ling point is called molar heat of vaporization (or molar enthalpy of orization). It is denoted by ΔH_{vap}. Molar heat of vaporization of water is 67kJ/mol.

$$\underset{\text{Water}}{H_2O_{(l)}} \longrightarrow \underset{\text{Steam}}{H_2O_{(g)}} \qquad \Delta H_{vap} = 40.67 kJ/mol$$

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Table 5.10: Molar Heat of Vaporization and Boiling Point of Some Liquids

Substance	Formula	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
Water	H_2O	100.0	40.7
Benzene	C_6H_6	80.1	31.0
Ethyl alcohol	CH_3CH_2OH	78.3	39.3
Carbon tetrachloride	CCl_4	76.8	32.8
Diethyl ether	$CH_3CH_2OCH_2CH_3$	34.6	26.0

Condensation is the reverse of vaporization. The amount of heat released in condensing a substance is equal to the amount of heat required to vaporize the substance (liquid), but the sign is negative.

$$\underset{\text{Steam}}{H_2O_{(g)}} \longrightarrow \underset{\text{Water}}{H_2O_{(l)}} \qquad \Delta H_{vap} = -40.67 \text{kJ/mol}$$

Molar Heat of Sublimation

The amount of heat required to convert one mole of a solid into vapours directly is called molar heat of sublimation (or molar enthalpy of sublimation). It is denoted by ΔH_{sub}. Molar heat of sublimation for iodine is 62.2 kJ/ mol.

$$\underset{\text{Solid Iodine}}{I_{2(s)}} \longrightarrow \underset{\text{Iodine vapours}}{I_{2(g)}} \qquad \Delta H_{sub} = 62.2 \text{kJ/mol}$$

The reverse of sublimation is called deposition. The amount of heat released in deposition of a substance is equal to the amount of heat required to sublime the substance (solid), but the sign is negative.

$$\underset{\text{Iodine vapours}}{I_{2(g)}} \longrightarrow \underset{\text{Solid Iodine}}{I_{2(s)}} \qquad \Delta H_{sub} = -62.2 \text{kJ/mol}$$

The molar heat of sublimation is equal to the sum of the molar heats of fusion and vaporization:

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

Dry ice (solid carbon dioxide) and iodine sublime at ordinary temperature. The process of sublimation is used for the purification of iodine. This process is used in frost-free refrigerators to remove frost from the inner cold surface by increasing the temperature of freezer at regular intervals. The formation of frost on the cold surface is the example of deposition.

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5.4.2 Energy Change and Intermolecular Forces

The substance that generally have stronger intermolecular attractive forces need greater amount of energy to change their physical states from solid to liquid or liquid to vapours. For example, the liquids having hydrogen bonds among their molecules such as water, ethylene glycol, and ethyl alcohol have high values of heats of vaporization. These liquids have stronger intermolecular attractive forces, hence need high amount of energy to separate their molecules from each other.

Heats of vaporization are generally much higher than heats of fusion. For fusion (to move around the particles freely) of a substance less amount of energy is provided because the small change occurs in the intermolecular distances during the melting process. On the other hand, large amount of heat is required for liquids to break the intermolecular attractive forces completely to separate their molecules from each other during vaporization.

5.4.3 Change of State and Dynamic Equilibrium

The process of conversion of liquid to vapours is called evaporation while the reverse process (conversion of vapours to liquid) is called condensation. The situation in which a forward process (evaporation) and a reverse process (condensation) are occurring simultaneously and at the same rate is called dynamic equilibrium. Dynamic equilibrium is established between liquid and vapours in a closed container. For a dynamic equilibrium to occur, the rates of two opposing change must be equal so that no net change occurs in the volume or amount of components (liquid or vapours) of the system because the two opposite processes counterbalance each other. The term dynamic equilibrium is not limited to evaporation and condensation processes. You will encounter it, in many of the systems, in chemistry. It indicates the equality in rate between two opposing process of any type (i.e. for all the reversible chemical reactions and all the physical changes). For example ice exists in dynamic equilibrium with water when the temperature is kept constant at 0°C.

$$\text{Ice} \underset{}{\overset{0^\circ C}{\rightleftharpoons}} \text{Water}$$

5.5 Liquid Crystals

5.5.1 Brief Description

The intermediate state between solids and liquids in which substances have arrangement of particles like solids but freedom of motion like liquids is called liquid crystals.

$$\text{Solid} \rightleftharpoons \text{Liquid Crystals} \rightleftharpoons \text{Liquid}$$

The crystalline solid have specific melting points. The temperature of solids

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remains constant at melting point until all the solid melts. However, there are some solids which change into turbid liquid before changing into clear liquid. These turbid liquids have the properties of solids such as optical activity and that of liquids such as fluidity, viscosity, and surface tension and are called liquid crystals. A crystalline solid may be isotropic or anisotropic while liquid crystals are always isotropic.

Liquid crystals were first discovered by an Austrian Botanist and chemist Frederick Reinitzer (1857 - 1927) in 1888. He was studying an organic compound cholesteryl benzoate. He found that this compound has an interesting and unusual property. This solid compound melts at 145.5°C and is transformed into viscous milky liquid and becomes a clear liquid at 178.5°C. By cooling, the reverse process occurs, the clear liquid first changes to viscous milky liquid at 178.5°C and then solidifies at 145.5°C. He concluded that he had discovered a new state of matter that has a place between the crystalline solid and liquid states: the liquid crystalline state.

Figure 5.11: The liquid and liquid crystalline phase of cholesteryl benzoate

5.5.2 Applications (uses) of Liquid Crystals

This special kind of material has many applications in our daily life. Liquid crystals are not only used for your wrist watch and packet calculator, these materials are now used in the many fields of science and engineering and have been applied to many products in our society. Some uses of liquid crystals are:

i) They are used as temperature sensors to detect the faulty connections in microelectronic circuit boards.

ii) They are used in thermometers to measure the body temperature of infants.

iii) They are used to detect blockage of veins, arteries and infected areas like tumors. Special liquid crystal devices can be attached to the skin to show a "map" of temperatures. This is useful because of the physical problems, such as tumors, show a different temperature than the surrounding tissue.

iv) They are used as a solvent in chromatographic separations.

v) The most common application of liquid crystal technology is liquid crystal displays (LCDs.). They are used in display of electrical devices such as digital wristwatches, clocks, flat-panel televisions, computers, laptop screens, cell phones

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pH-meters and many other electronic devices. The devices, in which liquid crystals are used, are known as LCD devices.

vi) Some of the liquid crystals are used in hydraulic break due to their high viscosity values.

Summary of Facts and Concepts

- Liquid is the physical state of matter which has definite volume but no definite shape and adopts the shape of container in which they are poured. They are not easily compressed. They have high densities than gases.
- The forces of attractions among atoms present within a molecule are called intramolecular forces. These are true chemical bonds and large amount of energy is required to break these forces.
- The forces of attractions which act to hold molecules together in liquids and solids are called intermolecular forces. These are weak forces of attractions and a small amount of energy is required to break these forces. These forces are collectively known as van der Waal's forces. There are three principal types of intermolecular forces in liquids and they are dipole-dipole forces, hydrogen bonding, and London forces.
- Dipole-dipole forces are present in polar molecules. These forces of attraction are due to unequal sharing of electrons between two atoms in a molecule.
- Hydrogen bonding is the special type of dipole-dipole forces. These forces are present among those polar molecules which contain hydrogen bonded to a highly electronegative atom such as fluorine, oxygen, nitrogen, and rarely chlorine. Hydrogen bonds are generally stronger than dipole-dipole forces and London dispersion forces. The unusual high boiling points of some substance is due to hydrogen bonding. The extraordinary qualities of water are due to hydrogen bonding.
- London forces are short lived weak attractive forces and are produced by instantaneous dipoles in atoms or molecules. These forces increase in strength with molar masses. These forces are not only present in non-polar molecules but also present in polar molecules. These forces are more noteworthy in polar molecules.
- The change in which composition of a substance alters is called chemical change such as burning of wood and rusting of iron while the change in which

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composition of a substance does not alter is called physical change such as melting and evaporation.

- Evaporation is the process of conversion of liquid in vapours while condensation is the reverse of vaporization (the conversion of vapours into liquid). The direct evaporation of solid is known as sublimation. Evaporation is an endothermic process while condensation is an exothermic process. The evaporation and condensation both play key roles in moderating the temperature of climates. Evaporation is a cooling process and occurs at a great rate in the hot summer days to absorb heat and prevent the temperature increase while condensation is the reverse process and it occurs at night to prevent further temperature drop.
- The pressure exerted by vapours in dynamic equilibrium with its pure liquid at a given temperature in a closed system is called vapour pressure. It shows the evaporating tendency of the liquid.
- The temperature at which vapour pressure of the liquid becomes equal to external pressure or atmospheric pressure is called boiling point of the liquid. The temperature at which the vapour pressure of a liquid becomes equal to one atmosphere pressure is called normal boiling point.
- Liquids show properties such as viscosity (the resistance to flow of a liquid) and surface tension (a measure of how difficult it is to stretch or break the surface of liquid) that depend on the attractive forces among the particles of liquid. The viscosity and surface tension of a liquid increase as the strength of intermolecular forces increase and they decrease as temperature increase.
- The transformation of a substance from one physical state to another physical state is called phase change. The changes of states are the physical changes. They are not chemical changes. The matter can be changed from one physical state to another physical state by cooling, heating and changing pressure.
- The amount of energy required to vaporize one mole of the liquid at its boiling point is called molar heat of vaporization whereas the energy required to melt one mole of the solid at its melting point is called molar heat of fusion.
- The intermediate state of substance that displays properties of both of a liquid and a solid is called liquid crystal. Liquid crystals flow like a viscous liquid and it particles exist in highly ordered patterns as in a crystalline solid.

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Questions and Problems

Q.1. Four answers are given for each question. Select the correct one:

i) Greater the strength of intermolecular forces, greater will be:
(a) Heat of fusion (b) boiling point
(c) viscosity (d) all of these

ii) Which hydride of group VIIA has higher boiling point:
(a) HF (b) HCl
(c) HBr (d) HI

iii) Which liquid has weak intermolecular forces:
(a) Gas oil (b) water
(c) ethyl alcohol (d) gasoline

iv) The conversion of vapours into liquid is called:
(a) Condensation (b) fusion
(c) evaporation (d) sublimation

v) The vapour pressure of water at 100°C is:
(a) 260 mmHg (b) 760 mmHg
(c) 1074 mmHg (d) 1489 mmHg

vi) The boiling point of glycerine at 50 mmHg is:
(a) 100°C (b) 120°C
(c) 240°C (d) 360°C

vii) Food cooks more rapidly at:
(a) Karachi (b) Quetta
(c) Murree (d) Mt. Everest

viii) Surface tension is measured by:
(a) Stalagmometer (b) thermometer
(c) viscometer (d) manometer

ix) Viscosity of liquid increases with decrease in:
(a) molecular mass (b) intermolecular forces
(c) temperature (d) atmospheric presure

x) Which one of the following is more volatile?
(a) Water (b) methyl alcohol
(c) gasoline (d) diethyl ether

Q.2. Fill in the blanks with suitable words given in the brackets:

i) The intramolecular attractive forces are _____ stronger than intermolecular attractive forces. (less/more)

ii) Hydrocarbons are insoluble in water due to absence of

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_____.(ionic bond/ hydrogen bond)

iii) Internal resistance to flow of liquid is called _____ of liquid (fluidity / viscosity).

iv) Vapour pressure increases with increase in _____ of liquid. (surface area / temperature)

v) Substances which have both the properties of _____ are called liquid crystals. (solids and liquids/liquids and gases)

vi) Molar heat of vaporization is _____ than molar heat of fusion. (lesser/greater)

vii) Water is liquid while H_2S is gas at room temperature because of the presence of _____ in water molecules. (covalent bonds / hydrogen bonds)

viii) Ice occupies 10% _____ space than water. (more/less)

ix) The element _____ is found in the liquid state while the element _____ is found in the gaseous state. (chlorine / bromine)

x) The surface tension is denoted by Greek letter _____ (gamma, γ / eta, η)

Q.3. Label the following statements as True or False.

i) Liquids and gases both have definite volume.

ii) The thermal expansion for a liquid is generally less than that of the corresponding gas.

iii) The density of a liquid is nearly the same as that of the corresponding gas.

iv) The intermolecular forces between particles of a liquid are called cohesive forces (or cohesion) while the forces of attraction between particles of liquid and another surface are called adhesive forces (or adhesion).

v) The intermolecular forces and temperature are the two factors which affect the vapour pressure of a substance.

vi) London dispersion forces are the weak intermolecular forces that are absent in all of the molecules of liquids and solids.

vii) Viscosity is the inverse of the fluidity of liquid.

viii) Surface tension, viscosity, and vapour pressure are all temperature independent.

ix) Liquid crystal is a turbid liquid that displays some degree of order below the melting point of solid.

x) Specific heat is the amount of heat required to raise the temperature of 1g of a substance by 1°C.

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Q4. Describe the properties of liquids on the basis of kinetic molecular theory of gases.

Q5. What are intramolecular and intermolecular attractive forces? Why intramolecular attractive forces are stronger than intermolecular attractive forces? Name the various types of intermolecular forces.

Q6. Why are the intermolecular forces stronger in liquids as compared to gases?

Q7. What are dipole-dipole forces? Explain dipole-dipole force with the help of an example. What factors determine the strength of dipole-dipole forces between molecules?

Q8. What is hydrogen bonding? What conditions are necessary for the formation of hydrogen bonding?

Q9. What are London dispersion forces? How are they affected by?

(a) The sizes of atoms or molecules;

(b) The shapes of molecules; and

(c) The polarizability of atoms or molecules.

Q10. Which one of the following molecules displays strong hydrogen bonding?

(a) HF (b) HCl (c) H_2O (d) NH_3 (e) CH_3CH_2OH

Q11. What type of intermolecular forces must be overcome when each of the following liquids are converted to vapours?

(a) CH_3OH (b) petrol (c) $CHCl_3$ (d) CCl_4 (e) bromine

Q12. Which substance in each of the following pair has the stronger London forces?

(a) H_2O or H_2S (b) F_2 or Cl_2 (c) CO_2 or CO

(d) argon or krypton (e) CH_4 or C_2H_6

Q13. Why does ice float on the surface of water and all other solids sink in their liquid phase? Give reason.

Q14. Explain why the water pipes are drained or insulated and the antifreeze is added to the radiators of cars in the cold climate areas such as Quetta, Ziarat and Murree in winter?

Q15. Explain why London forces are weaker than other intermolecular attractive forces?

Q16. What is the difference between dipole-dipole forces and London forces?

Q17. Why the boiling point and heat of vaporization of H_2O is higher than HF although their molar masses are nearly the same and hydrogen bonding between HF molecules is stronger than H_2O molecules?

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Q.18. Define and explain evaporation. Explain the factors that affect evaporation.

Q.19. Why the rate of evaporation of liquid increase by increasing temperature?

Q.20. The evaporation is the cooling process and occurs at all temperature, how?

Q.21. Why the wet clothes hanged outdoors dry rapidly on a hot summer day than a cold winter day? Explain.

Q.22. How does perspiration cool the skin of your body in hot weather?

Q.23. Earthen ware such as pitcher keep water cool while those made of metal plastic or glass such as jerrycan and glass bottle are unable to keep water cool, why?

Q.24. What is the equilibrium vapour pressure of the liquid? Discuss the factors that affect vapour pressure. How is it measured?

Q.25. What is meant by dynamic equilibrium? Explain it between two physical states.

Q.26. The change in the surface area of a liquid does not cause the change in the equilibrium vapour pressure of liquid, how?

Q.27. Explain why we feel sense of cooling on the bank of lake after bath?

Q.28. Why autoclaves are considered as the efficient sterilization instrument?

Q.29. How would you change a substance from liquid state to gaseous state without increasing the temperature of the liquid?

Q.30. Define and explain the boiling point of liquid. What are the factors affecting boiling point of liquid? How does the boiling point of a liquid depend on external pressure?

Q.31. The bubbles are formed when water starts boiling. What is present inside the bubbles that form?

Q.32. Why does the boiling point of water is much higher than that of H_2S?

Q.33. Why the boiling point of water in pressure cooker is higher than in ordinary saucepan?

Q.34. Explain why the egg takes a longer time to cook it in boiling water at high altitude than does at lower altitude?

Q.35. Explain why each liquid has its own boiling point?

Q.36. Why the temperature of boiling liquid remains constant even though heat is being added continuously?

Q.37. Explain why the steam at 100°C burns your skin much more severely than liquid water at 100°C?

Q.38. Why the sprinkling of the boiling diethyl ether does not burn as severely as the sprinkling of boiling water on your skin? Explain.

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Q.39. What is a phase change? Name all possible changes that can occur among the vapour, liquid, and solid phases of a substance.

Q.40. Define the terms molar heat of vaporization and molar heat of fusion. Give their units. Why the molar heat of vaporization is greater than that of molar heat of fusion?

Q.41. Which process is exothermic, the fusion or condensation?

Q.42. Why do the droplets appear on the outside of the glass full of ice cold water in the summer time?

Q.43. What is the viscosity of a liquid? How does viscosity change with increasing temperature? What is the effect of intermolecular forces on the viscosity of liquid? How is it measured experimentally?

Q.44. Why does gas oil flow at a higher speed through a pipe when the temperature of oil increases?

Q.45. The drivers are suggested to use the lower viscosity motor oils in the winter and higher viscosity motor oils in the summer, why?

Q.46. What is the surface tension of the liquid? Why are the molecules at the surface of the liquid act differently from those situated inside? What factors affects the surface tension of a liquid? How can it measured experimentally?

Q.47. A razor blade if kept carefully on the surface of water can be made to float although it is made of steel and is much denser than water, how?

Q.48. Explain why a small drop of water assumes nearly a spherical shape on the surface of waxy bonnet of car?

Q.49. What are surfactants? What is the role of surfactants?

Q.50. How does viscosity and surface tension change with temperature? Discuss the relation of intermolecular forces with these properties.

Q.51. What are liquid crystals? Give their applications in daily life.

Q.52. What is the difference between a liquid crystal and a typical solid crystal like that of NH_4Cl?

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Chapter # 06

States of matter III: Solids

Major Concepts

6.1 Kinetic Molecular interpretation of Solids
6.2 Types of solids
6.3 Properties of Crystalline solids
6.4 Crystal Lattice
6.5 Types of Crystalline Solids

Learning Outcomes

The students will be able to:

- Describe simple properties of solids e.g., diffusion, compression, expansion, motion of molecules, space between them, intermolecular forces and kinetic energy based on kinetic molecular theory. (Understanding)
- Differentiate between amorphous and crystalline solids. (Understanding)
- Describe properties of crystalline solids like geometrical shape, melting point, cleavage planes, habit of crystal, crystal growth, anisotropy, symmetry, isomorphism, polymorphism, allotropy, and transition temperature. (Understanding)
- Use oxygen and sulphur to define allotropes. (Understanding)
- Explain the significance of the unit cell to the shape of the crystal using NaCl as example. (Applying)
- Name three types of packing arrangements and draw or construct models of them. (Applying)
- Name three factors that affect the shape of an ionic crystal. (Understanding)
- Define lattice energy. (Remembering)
- Differentiate between ionic, covalent, molecular and metallic crystalline solids. (Applying)
- Explain the low density and high heat of fusion of ice. (Understanding)
- Define and explain molecular and metallic solids. (Understanding)

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Introduction

Solid is the physical state of matter which has definite shape and volume and is rigid and hard. If we look around us we will find lot of substances in the solid state rather than in liquid and gaseous state. The clothes we wear, the paper we write on, the books we read, the television we watch, the radio we listen, the gold used in jewelry, the plastic used in making water bottles, utensils, water pipes, rain coats, surgical gloves, toys and purses, the refrigerator used to preserve foods, the cars and buses we travel in, the trees that bear fruits are all important solids. The solid state of mater is the growing area of chemistry because it relates to the development of interesting new materials. In this chapter we will discuss the properties, structures and types of solids.

6.1 Kinetic Molecular Interpretation of Solids

The key points of kinetic molecular theory are given below:

i) The particles (atom, ions or molecules) of solids are very close to each other and they are tightly packed and more ordered than liquids and are much more ordered than gases. For that reason, solids are slightly denser than liquids and much denser than gases. However, water is an exception to this rule i.e. the ice, the solid form of water, has lower density than liquid water. The spaces between solid particles are smaller than both of the liquids and gases.

ii) The solids are generally less compressible than liquids and are considered as incompressible. The solids such as foam, wood and cork give the impression of being compressible but they are actually not. They have spaces filled with airs. By applying pressure, the spaces are compressed but not the solid matter in the foam, wood or cork.

iii) The temperature or pressure change has a very little influence on the volume of solids.

iv) The attractive forces in solids are much more effective than gases and liquids. Because of this, solids have lower melting and boiling points than gases and liquids.

v) The solid particles have low kinetic energy than liquids and gases. Kinetic energy is directly proportional to the temperature of solids. Their kinetic energy decreases by decreasing temperature and increases by increasing temperature. All the substances are converted into solids if cooled sufficiently.

vi) The solid particles are locked in place that are why their molecules can't slip and slide over one another. They are, therefore, unable to flow (i.e. they are rigid), and hence retain their shapes and volume without a vessel. Solid particles usually

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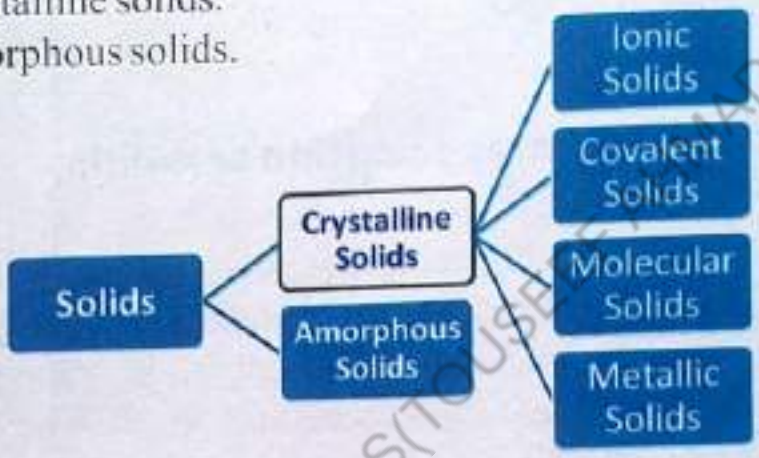
have only vibrational motions.

vii) Solids particles do not diffuse into other solids readily. The diffusion in solids occurs but extremely slowly. If a lead plate and a gold plate are placed in close contact for a several months, a few atoms of lead will diffuse into gold and vice versa. This observation is evidence that diffusion does occur in solids but at a very slow rate.

6.2 Types of Solids

There are two types of solids on the basis of arrangement of particles.

i) Crystalline solids.
ii) Amorphous solids.



6.2.1 Crystalline Solids

The solids which have repetitive three dimensional arrangements of particles are called crystalline solids. They are also called true solids. A crystalline solid is composed of one or more crystals that are fused together. Each particle occupies a fixed position in the crystal. Because of ordered arrangement of particles, crystalline solids usually have flat faces which construct specific angles with one another. The regular arrangement of particles in crystals also produces highly regular shaped beautiful crystals. The beautiful crystals of diamond, quartz (SiO_2), sucrose and table salt are the examples of crystalline solids. Other examples of crystalline solids are alum, urea, KNO_3 and $CuSO_4$.

6.2.2 Amorphous or Non-crystalline Solids

The solids which have non-repetitive three dimensional arrangements of particles are called amorphous solids or pseudo solids. The term *amorphous* is a Greek word which means *shapeless*. These solids do not have the orderly arrangement of particles like that in crystalline solids. The structures of these solids are similar to the structures of liquids but their particles do not have freedom of motion like liquids. The elasticity of rubber and twisting of plastic reveals that the particles in amorphous solids do not have fixed positions as in crystalline solids. From structural point of view, the amorphous solids are considered as the intermediate

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between the liquid and solid states. Therefore, amorphous solids are sometimes called super-cooled liquids. The well-known examples of amorphous solids are glass, rubber, plastic, cement, ceramics and concrete.

Many crystalline solid can be changed into amorphous solids by melting them and then cooling the molten mass rapidly. In this way particles do not find time for orderly arrangement. Amorphous solids are hard and elastic like crystalline solids. They do not have definite melting points. These amorphous solids may have orderly arrangement of particles in small regions. These solids which are partly crystalline and partly amorphous are called crystallites.

Table 6.1: Difference between Crystalline and Amorphous Solids

Crystalline Solids	Amorphous Solids
They have definite geometrical shapes.	They do not have definite geometrical shapes.
The fragments of shattered crystalline solids have definite geometrical shapes.	The fragments of shattered amorphous solids cannot have definite geometrical shapes.
They have regular intermolecular forces throughout.	They have irregular intermolecular forces throughout.
They have sharp and distinct melting points.	They do not have sharp and distinct melting points.
These solids are formed due to slow cooling of liquid.	These solids are formed due to sudden cooling of liquid.
They are anisotropic i.e. they have different physical properties such as electrical conductivity, in different directions.	They are isotropic i.e. they have same physical properties in different directions.
These solids are symmetrical i.e. their appearance do not change when they are rotated by 360° along its axis.	These solids are not symmetrical.
Examples are: NaCl, copper sulphate ($CuSO_4$), sugar, diamond etc.	Examples are: Glass, Plastic, Rubber, coke etc.

Society, Technology and Science

Specific Uses of Solids in our Daily Life:

Both kinds of solids (crystalline and amorphous) play an important role and have specific uses in our daily life. **Table salt** (NaCl), the crystalline solid, is used to flavour foods; **diamond**, the crystalline solid, is used to engrave stones and metals; **NaF**, a crystalline solid, is added to tooth pastes to prevent tooth decay; **silver and gold** are

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precious crystalline solids and are used in ornaments and jewelry; **iron**, a crystalline solid, is used as structural material and is an essential ingredient in our diet. On the other hand the rubber, an amorphous solid, is used in tires and rubber balls. **plastic**, an amorphous solid, has many industrial and commercial uses and is used in the manufacture of CDs, DVDs, footwear and fluid containers such as milk or oil; and **glass**, an amorphous solid, is used to make tumbler, mirrors, dishes, eye glasses, windows and for laboratory equipment such as beaker, test tube, reagent bottle. Amorphous semiconductors are used in solar cells, laser printers, flat-panel television and monitor screens.

6.3 Properties of Crystalline Solids

6.3.1 Symmetry

The concept of symmetry is very useful in describing the shapes of crystals. We easily recognize an object if we know the symmetry of that object. A crystal has a number of surfaces (faces), edges, and the interfacial angles (the angles between the faces). When a crystal is rotated along its axis by 360°, the faces, angles and edges are repeated consistently. The repetition of faces, angles and edges, when a crystal is rotated by 360° along its axis is called symmetry. Various types of symmetrical elements are:

i) Centre of symmetry
ii) Plane of symmetry
iii) Axis of symmetry

6.3.2 Geometric Shape

Crystalline solids have definite geometrical shapes. This is due to the orderly arrangement of their atoms, ions or molecules. The orderly arrangement of atoms, molecules or ions is due to strong attractive forces between their particles. Their interfacial angles and distances are same in spite of the method or conditions of preparation. Even the fragments of finely divided crystalline solid have definite geometric shapes that display their internal structure.

6.3.3 Melting point

The temperature at which the change from solid to liquid occurs is known as the melting point of solid. At melting point, the particles of liquid and solid have same average kinetic energies. Crystalline solids have definite melting points. At melting point, the temperature is reached at which the kinetic energies of the particles of the crystalline solids are enough to overcome the attractive forces holding them together and the particles get free of their fixed positions in the solid. The crystalline solids can be identified from their definite melting points. On the other hand, the amorphous solids have no definite melting points. Because the amorphous solids

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not have orderly arrangement of particles and the particles are not constantly changing their positions. These solids have the ability to flow over a range of temperature. For example, when a glass is heated, first it softens and then starts flowing without undergoing abrupt or sharp change from solid to liquid. Hence amorphous solids are regarded as super cooled liquids.

6.3.4 Cleavage Plane

The breaking of bigger crystals into smaller identical crystals by applying pressure is called cleavage. Crystalline solids are broken down through particular planes (directions or sides). These planes are called cleavage planes. A crystal can easily be broken in one direction and not in any other direction. For example, a mica crystal contains infinite layers of SiO_4^{4-} sheets. The sheets have weak attractive forces and are easily separated parallel to the layers only.

6.3.5 Habit of Crystal

A shape in which a crystal usually grows (prepares) is called habit of crystal. For example, NaCl has cubic habit, white tin has tetragonal habit, and graphite has hexagonal habit.

6.3.6 Crystal Growth

Crystals are usually grown (prepared) by slow cooling of liquid or saturated solution under certain conditions. Outer appearance (shape) of crystals depends upon the method of preparation and conditions (temperature, pressure, concentration) under which it is prepared. For example, NaCl always crystallizes in cubic shape, if conditions are not changed. Different crystals of the same substance may sometimes appear to be different from outside due to different rate of growth by different faces but their interfacial angles are always the same. The change in appearance is because of the presence of impurity in the solution or due to change in conditions. For example, the habit of NaCl is cubic but in the presence of 10% urea as impurity, its habit is octahedral. It is called change of habit.

6.3.7 Anisotropy

The physical properties of crystals depend upon directions. They can vary from direction to direction. These properties are called anisotropic properties and the process is called anisotropy. A substance which has this property is called anisotrope. The physical properties such as thermal expansion, electrical conductivity, cleavage, and refractive index are anisotropic properties. For example, graphite is an isotrope, the conduction of heat and electricity, in graphite, is different in different directions. It conducts electricity parallel to the plane of layers but is a poor conductor perpendicular to the layers.

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6.3.8 Isomorphism

The process in which two or more different elements or compounds exist in same crystalline shape is called isomorphism and compounds are known as isomorphs of each other. The isomorphs have following properties:

i) They have same ratio of atoms.
ii) Their physical and chemical properties are different.

Table 6.2: Isomorphs and their crystalline forms with atomic ratios

Isomorphs	Crystalline Form	Atomic Ratio
NaCl, MgO	Cubic	1:1
$NaNO_3$, $CaCO_3$	Trigonal	1:1:3
$ZnSO_4$, $NiSO_4$	Orthorhombic	1:1:4
Ag_2SO_4, Na_2SO_4	Hexagonal	2:1:4
Diamond, iron	Cubic	1:1
Graphite, zinc	Hexagonal	1:1

In table 6.2, NaCl and MgO are two different compounds and have same shape i.e. cubic shape, hence called isomorphs.

6.3.9 Polymorphism

The process in which same compound is present in more than one crystalline forms is called polymorphism and different crystalline forms of same compound are called polymorphs. The polymorphs have following properties:

i) They have same chemical properties but different physical properties. The difference in physical properties is due to different structural arrangement of particles in space.
ii) They belong to same compound.

In table 6.3, calcium carbonate, the same compound is present in two crystalline forms i.e. trigonal and orthorhombic forms. These crystalline forms of same compound are called polymorphs.

Table 6.3: Polymorphs and their crystalline forms

Polymorphs	Crystalline Forms
$AgNO_3$	Trigonal, Orthorhombic
$CaCO_3$	Trigonal (calcite) Orthorhombic (aragonite)
KNO_3	Trigonal, Orthorhombic

6.3.10 Allotropy

The process in which an element is present in more than one crystalline forms is called allotropy and different forms of the element are called allotropes or allotropic

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forms. Allotropes have same chemical properties but different physical properties due to different arrangement of atoms. The common elements that show allotropy are: carbon, tin, sulphur, and oxygen. Their allotropic forms are given in the table.

In table 6.4, carbon has two different crystalline forms (cubic and hexagonal). These different crystalline forms of the same element (carbon) are called allotropic forms.

Table 6.4: Allotropes and their Crystalline Forms

Allotropes	Crystalline Forms
Carbon	Diamond (cubic) Graphite (hexagonal)
Tin	Grey tin (cubic) White tin (tetragonal) Rhombic tin (orthorhombic)
Suphur	Rhombic sulphur Monoclinic sulphur Plastic sulphur (amorphous form)
Oxygen	Dioxygen (O_2) Ozone (O_3)

Keep in Mind

The allotropy is for elements and the polymorphism is for compounds.

6.11 Transition Temperature

The arrangement of particles of a substance can also be changed with the change of temperature and a new allotrope of an element or a new polymorph of a compound is formed.

The temperature at which two crystalline forms of same substance exist in equilibrium with each other is called transition temperature.

Above and below this temperature only one crystalline form of a substance exists. For example, the transition temperature of KNO_3 is 128.5 °C, at which both the forms of this compound exist in equilibrium with each other. Above this temperature (128.5°C) KNO_3 exists in orthorhombic form and below this temperature, it exists in rhombohedral form.

$$KNO_3\ (\text{Rhombohedral}) \xrightleftharpoons{128.5^\circ C} KNO_3\ (\text{Orthorhombic})$$

The transition temperature of sulphure is 95.5 °C. Above transition temperature, suphur exists in monoclinic form and below this temperature, it exists in rhombic form.

$$S_8\ (\text{Rhombic}) \xrightleftharpoons{95.5^\circ C} S_8\ (\text{Monoclinic})$$

Transition temperature is always less than melting point of substance.

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6.4 Crystal Lattice and the Unit Cell

The crystals are regular shaped solid particles with flat shiny faces and have three dimensional ordered arrangements of particles. The ordered structure of a crystal is described in terms of a crystal lattice. A crystal lattice is a three dimensional structure of points that designates the positions of particles (atoms, molecules, or ions) in a crystal. Crystal lattice is also known as space lattice. A crystal lattice is not an actual object but it is a structure or pattern. The crystal structure depends on the nature and the size of the particles that are involved. The particles that make up the pattern are different in different type of crystals. A crystal is made up of atoms, ions or molecules. These particles are located at particular positions and are represented by points and these points are joined together by lines. This type of structure is known as crystal lattice.

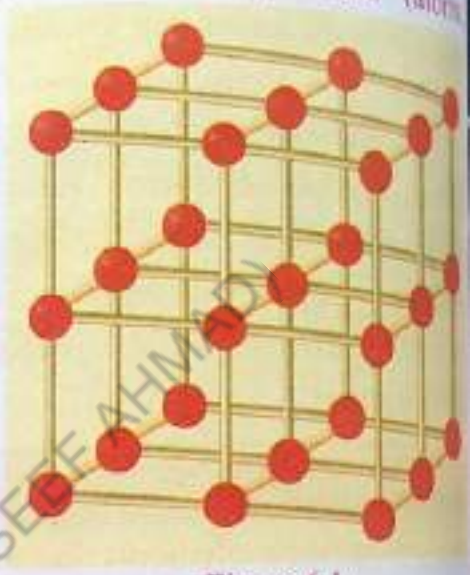

Figure 6.1:
Crystal Lattice Consists of 8 Unit Cells

6.4.1 Unit Cell

The smallest part of crystal lattice showing all the properties of crystal pattern is called unit cell. The crystal lattice is the building block of unit cells. The unit cells repeat in all directions in a perfectly regular way and build up the whole crystal. A unit cell gives complete information about crystal structure. It will be easy to know the exact arrangement of particles in a whole crystal, if we know its arrangement in a unit cell. Unit cell has definite shape and definite number of particles. These particles are arranged in three dimensions.

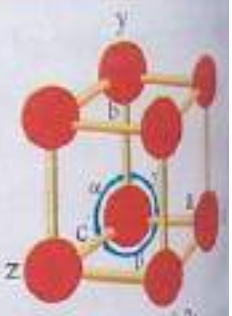

Figure 6.2:
A single unit cell

Representation of a Unit Cell

Shape of unit cell depends upon the length of three sides (a, b, and c) and angles between these sides (α, β and γ). In common practice, side 'a' is along x-axis, side 'b' is along y-axis and side 'c' is along z-axis.

The angle "α" is between sides 'b' and 'c'.

The angle "β" is between sides 'c' and 'a'.

The angle "γ" is between sides 'a' and 'b'.

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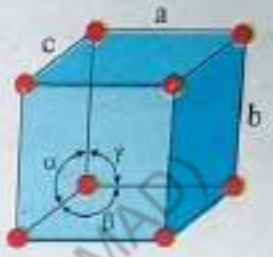
These six parameters of unit cell are called unit cell dimensions or crystallographic elements. Unit cell of CsCl is cubic, in which $a = b = c$ and $\alpha = \beta = \gamma = 90°$.

Seven Crystal Systems OR Crystals and their Classifications

A crystal system can be identified by the dimensions of its unit cell along its three axes a,b,c and three angles α, β and γ. The seven crystal systems are described below:



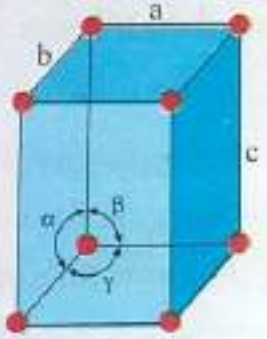
Cubic System

In cubic system, all the three axes are of equal lengths and all angles are of 90°.

$a = b = c$ and $\alpha = \beta = \gamma = 90°$

Example are: NaCl, diamond, iron (Fe), copper (Cu), CsCl

Cubic unit cells are of three types and they are simple cubic, body-centered cubic, or face-centered cubic. They have a total of one, two, or four particles, respectively.

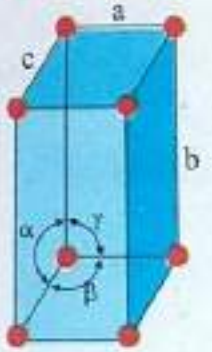


Tetragonal System

In this system, two axes are of equal lengths and the third one is different. It may either be shorter or larger than the other two. All the angles are of 90°.

$a = b \neq c$ and $\alpha = \beta = \gamma = 90°$

Example are: SnO_2, MnO_2, white tin (Sn), NH_4Br



Orthorhombic System

All the lengths are unequal and all the angles are of 90°.

$a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$

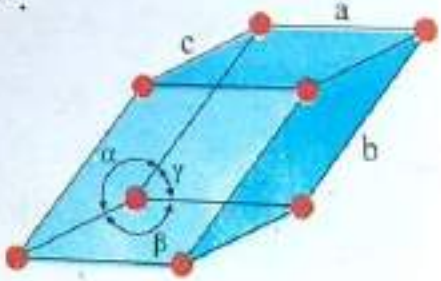
Examples are: $FeSO_4.7H_2O$, $ZnSO_4.7H_2O$, KNO_3, I_2, Rhombic sulfur

Trigonal or Rhombohedral System

All the lengths are equal but none of the angle is of 90°. They lie between 90° and 120°.

$a = b = c$ and $\alpha = \beta = \gamma \neq > 90°$ and $< 120°$

Example are: $NaNO_3$, KNO_3, Bi, Al_2O_3



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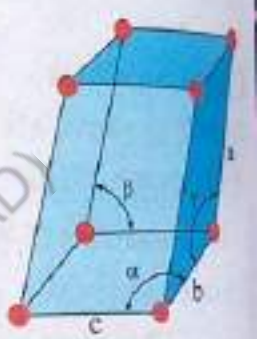
Hexagonal System

Two axes (a and b) are of equal lengths and third (c) is different in length. Two angles are of 90° but third angle is of 120°.

$a = b \neq c$ and $\alpha = \beta = 90°$, $\gamma = 120°$

Examples are: ZnO, CdS, graphite

Monoclinic System

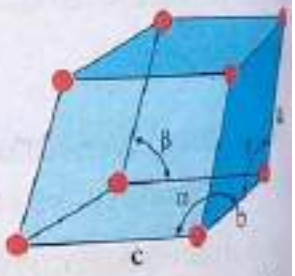


All the lengths are unequal. Two angles of 90° and third one is greater than 90°.

$a \neq b \neq c$ and $\alpha = \beta = 90°$, $\gamma = >90°$

Examples are: $C_{12}H_{22}O_{11}$, $Na_2CO_3.10H_2O$, $Na_2B_4O_7.10H_2O$

Triclinic System



All the lengths and angles are unequal.

$a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90°$

Examples are: $CuSO_4.5H_2O$, $K_2Cr_2O_7$, H_3BO_3 (Boric acid)

The unit cells of the seven different crystal systems are summarized in table 6.5.

Table 6.5: Seven Crystal System

Crystal System	Axes	Angles	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, NaBr, diamond, gold
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	MnO_2, NH_4Br, white tin (Sn)
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	$BaSO_4$, $CaCO_3$ (aragonite), rhombic sulphur, iodine
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90°$, $\gamma \neq 90°$	Sugar, borax, $PbCrO_4$, monoclinic sulphur
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$, $\gamma = 120°$	Ice, $NaNO_3$, CdS, graphite, zinc
Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	$NaNO_3$, $CaCO_3$ (calcite), HgS (cinnabar), bismuth
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7$, $CuSO_4.5H_2O$, H_3BO_3

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6.4.2 Shape of NaCl Crystal

The structure of sodium chloride, is one of the most common ionic crystal lattice. It has face-centered cubic arrangement in the octahedral structure. In the structure, each sodium ion, Na^+, is surrounded by six chloride ions, Cl^-, and each Cl^- ion is surrounded by six Na^+ ions. Hence, the coordination number of each ion is 6. The distance between two adjacent ions of different kinds is 2.815A°.

Chloride ion is bigger in size than sodium ion. The larger chloride ions occupy corners and faces of an octahedron whereas, the smaller sodium ions fit into the cavities (holes) between the adjacent anions. The unit cell of NaCl is repeated in the several directions where we can see six chloride ions around some of the other sodium ions.

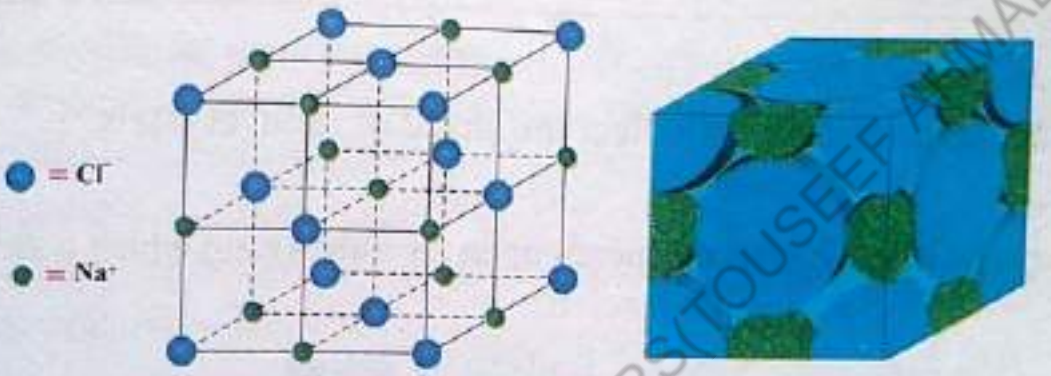

Figure 6.3: Representation of the unit cell of NaCl

The formula of an ionic compound is derived from the unit cell structure. The formula of NaCl is obtained by counting the number of sodium ions and chloride ions present in its unit cell. There are eight chloride ions at each corner of the unit cell. Each Cl^- ion is shared among eight unit cells, hence each contributes one eighth of Cl^- ion to the unit cell. There are six chloride ions in the center of each face. Each Cl^- ion is shared among two unit cells, so each contributes one half of Cl^- ion to the unit cell. The total number of Cl^- ions within the unit cell is calculated as:

$$\frac{1}{8}\ Cl^- \text{ per corner} \times 8 \text{ corners} = 1\ Cl^-$$

$$\frac{1}{2}\ Cl^- \text{ per face} \times 6 \text{ faces} = 3\ Cl^-$$

Total number of Cl^- ions in a unit cell = 4 Cl^- ions

There is one complete Na^+ ion in the center of the unit cell. There are 12 Na^+ ions at the midpoints of edges of the unit cell. Each Na^+ is shared among four unit cells, hence, each contributes one fourth of Na^+ ion to the unit cell. Thus the total number of Na^+ ions within the unit cell is calculated as:

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$\frac{1}{4}$ Na^+ per edge $\times$ 12 edges $= 3Na^+$

1 Na^+ per center $\times$ 1 center $= 1Na^+$

Total number of Na^+ ions in a unit cell $= 4Na^+$ ions

Thus, the unit cell of NaCl has four Na^+ and four Cl^- ions, in the ratio of 1:1 as required by its chemical formula.

Keep in Mind

NaCl crystallizes in face centered cubic shape while CsCl crystallizes in simple cubic shape. The different arrangement of CsCl is due to larger size of cesium ion as compared to sodium ion.

6.4.3 Factors Affecting the Shape of Ionic Crystals

There are three factors that affect the shape of ionic crystals.

(i) Radius Ratio:

The shape of an ionic crystal depends upon the radius ratio which is defined as the ratio of radius of cation to that of anion.

$$\text{Radius Ratio} = \frac{\text{Radius of cation}}{\text{Radius of anion}}$$

The effect of radius ratio in determining the shape of an ionic crystal is known as radius ratio effect. The range of radius ratio may be expressed as limiting radius ratio.

Table 6.6: Limiting Radius Ratio and Shape of Ionic Crystals

Limiting Radius Ratio	Shape	Example
<0.155	Linear	CaF_2
0.155-0.225	Planar triangular	B_2O_3
0.225-0.414	Tetrahedral	ZnS
0.414-0.732	Octahedral	NaCl
0.732-1.000	Body centred cubic	CsCl

The shape of NaCl is Octahedral and that of CsCl is body centred cubic because their radius ratio values are different.

(ii) Electrostatic Forces of Attractions:

Ionic crystals are held together by strong electrostatic forces of attractions between cations and anions. Example: sodium chloride, NaCl. These forces give a well defined geometric shape to ionic crystals.

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(iii) Poor Conductivity:

Ionic crystals do not conduct electricity in solid state because their ions are fixed in positions and are unable to move. Hence, the shape of ionic crystals remains as such. They can only conduct electricity when their ions are free to move i.e. they conduct electricity when dissolved in water or melted.

6.4.4 Lattice Energy

The amount of heat needed to break one mole of ionic crystal into its gaseous ions is called lattice energy.

It has positive value. It is expressed in kJ mol^{-1}.

$$K^+_{(g)} + Cl^-_{(g)} \longrightarrow KCl_{(s)} \qquad \Delta H^\circ = -715 \text{ kJ/mol}$$

Ionic crystals are composed of ions. These ions are located at fixed positions. A definite amount of energy is needed to remove these ions from their fixed positions, called lattice energy. It can also be defined as:

The amount of energy released when gaseous ions of opposite charges are combined to form one mole of crystalline ionic compound is called lattice energy.

It has negative value.

$$KCl_{(s)} \longrightarrow K^+_{(g)} + Cl^-_{(g)} \qquad \Delta H^\circ = +715 \text{ kJ/mol}$$

The magnitude of lattice energy depends on ionic size, ionic charge and arrangement of ions in the solid. The lattice energy decreases by increasing the size of either cation or anion and increases by increasing the ionic charge.

Effect of Ionic Radius

The smaller the ionic radius, the shorter the distance among the ions, and the stronger the attractive forces among ions. As a result of this, the ions come close to each other and their packing become tight. From top to bottom in a group of periodic table, the ionic radius increases, hence, the lattice energies of their compounds decrease.

i) The lattice energies for those compounds, which have same anion but different cations, decrease with the increase in the size of cations.

ii) The lattice energies for those compounds, which have same cation but different anions, decrease with the increase in the size of anions.

Table 6.7: Lattice energies of compounds having same anions

Name	Formulas	Lattice Energies ($kJmol^{-1}$)
Lithium chloride	LiCl	845
Sodium chloride	NaCl	787
Potassium cholride	KCl	715

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The larger the lattice energy, the more stable the ionic compound and the more tightly held the ions. The solid with higher lattice energy has higher melting point than one with smaller lattice energy.

Table 6.8: Lattice Energies of Compounds having same Cations

Name	Formulas	Lattice Energies ($kJmol^{-1}$)
Sodium fluoride	NaF	923
Sodium chloride	NaCl	787
Sodium bromide	NaBr	747
Sodium iodide	NaI	704

Effect of Ionic Charge

The higher the ionic charges, the greater the force of attraction between oppositely charged ions, so the lattice energy has high value for more highly charged ions.

If we compare lithium fluoride with magnesium oxide, then we find that, they have cations (the radius of Li^+ is 76 pm and that of Mg^{2+} is 72 pm) and anions (the radius of F^- is 133 pm and that of O^{2-} is 140 pm) of about equal radii. But lattice energy of MgO ($4050kJmol^{-1}$) is about four times greater than that of LiF ($1050kJmol^{-1}$). This fourfold increase in the lattice energies of CaO is due to the fourfold increase in the product of charges on Mg^{2+} and O^{2-} ions.

Table 6.9: Lattice Energies of Compounds having different Cations or Anions

Name	Formulas	Lattice Energies ($kJmol^{-1}$)
Lithium fluoride	LiF	1050
Magnesium chloride	$MgCl_2$	2527
Magnesium oxide	MgO	405
Calcium oxide	CaO	3424

The lattice energy is directly proportional to the product of charges of cations and anions and inversely proportional to the sum of their radii.

$$\text{Lattice energy } (\Delta H^{\circ}_{\text{lattice}}) \propto \frac{\text{charge of cation} \times \text{charge of anion}}{\text{cation radius} + \text{anion radius}}$$

6.5 Types of Crystalline Solids

The structure and properties of crystalline solids such as melting point, boiling point, hardness, and density depend upon types of particles in the crystalline solids and types of chemical bonding present between their particles. There are four types of crystalline solids on the basis of types of chemical bonding present in them and they are ionic solids, covalent solids, metallic solids and molecular solids.

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Keep In mind

The internal forces of attractions that hold the solid particles together determine many of the properties of solid. For example, copper is a good conductor of electricity while diamond is an isulator although they both are atomic solids. The difference in the properties between these two substances is because of differences in the chemical bonding present in them.

6.5.1 Ionic Solids

The solids in which ions are held together by ionic bonds are called ionic solids. These ions are held together by electrostatic forces of attractions. Examples of such solids are NaCl, KCl, KBr, CsCl, and CaF_2. The ionic solids are generally formed when alkali metals (group IA metals) and alkaline earth metals (group IIA metals) combine with chalcogens (group VIA non-metals), halogens (group VIIA non-metals), and non-metallic polyatomic ions.

Properties

i) The ions in ionic compounds are held together by strong attractive forces; therefore, they are hard and have generally higher melting and boiling points than molecular compounds. They can also have low volatility. The higher the melting and boiling points the stable the ionic compound.

ii) They are highly brittle. For example, the ionic solids are broken into small pieces when we struck them by a hammer, the ions are driven down a layer and the same charge ions come next to each other and because of this the same charge ions repel each other that split the solid.

iii) They have definite geometric shapes; and have high density due to close packing of ions.

iv) They do not conduct electricity in solid state because their ions are fixed in position and are unable to move. When they are melted or dissolved in water, the ions set free and move freely through the solution or liquid, hence the liquid or the solution conducts electricity readily.

v) They are frequently soluble in polar solvents like water. The ions of ionic solids separate from each other when dissolved in water and are surrounded by water molecules. Some ionic compounds are not dissolved in water, because the attractive forces between the ions and water molecules are not enough to overcome the attractions between the ions.

vi) They show the process of isomorphism and polymorphism.

vii) They have formula mass but no molecular mass, because they do not exist in molecular forms.

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Conceptual Check Point:

Ionic crystalline solids are brittle but not malleable, why?

6.5.2 Covalent Solids

The solids in which atoms are held together by covalent bonds are called covalent solids. Examples include diamond, graphite, quartz (SiO_2, found in some kinds of sand) and Silicon carbide (SiC, a common abrasive used in sand paper).

Covalent solids are of two types:

i) When covalent bonds give huge molecule like diamond, SiC, AlN etc.

ii) When atoms combine to give separate layers of atoms like Graphite, Cadmium iodide (CdI_2), Boron nitride (BN) etc.

Properties

i) They are usually very hard and have very high melting and boiling points due to strong attractive forces between covalently bonded atoms.

ii) They are insoluble in polar solvents like water.

iii) They are poor conductors of heat and electricity in either the solid or liquid state. This is due to absence of ions but some of them, such as silicon, are semi-conductors.

iv) Their chemical reactions are very slow.

Conceptual Check Point:

The chemical reactions of ionic solids are faster than covalent solids, why?

6.5.3 Metallic Solids

The solids in which atoms are held together by metallic bonds are called metallic solids. Examples include copper, silver, gold, iron etc.

Many theories have been proposed to explain the metallic bond, but here we will discuss only the electron gas theory.

Electron Gas Theory

According to this theory, the valence electrons in metals are free to move from one part of the crystal to the other. These free electrons do not belong to any particular atom.

These electrons produce negative atmosphere (sea) around metal positive ions. This

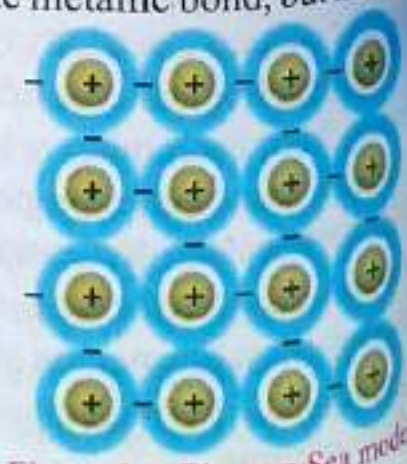

Figure 6.4: Electron Sea model

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atmosphere of electrons is called Electron Sea or pool or gas. The force of attraction which holds metal positive ions and Electron Sea together is called metallic bond. This theory explains the following properties of metallic solids.

Properties of Metallic Solids

i) They are good conductors of heat and electricity because electrons are free to move and carry kinetic energy through the solid.

ii) Most of the metallic solids have lustrous (shining) surface. This is because when light falls on the surface of metals. The electrons are jumped from lower energy level to higher energy level. When the electrons come back from higher energy level to lower energy level, they emit energy in the form of light at the frequency similar to the absorbed frequency. This reflected light is responsible for the lustrous surfaces of metals.

iii) Metallic solids have variable melting points. Some metals have low and the others have very high melting and boiling points. For example, mercury (mp = –38.72°C), gallium (mp = 29.93°C) and francium (mp = 27.00°C) have quite low melting points and on the other hand chromium (mp = 1877.00°C), molybdenum (mp = 2617.00°C), and tungsten (mp = 3427.00°C) have quite high melting points. This is because the charge density of mercury, gallium, and francium is low and they are weakly attracted to the electron sea and the charge density of chromium, molybdenum, and tungsten is high and they are strongly attracted to the electron sea.

iv) They are malleable and ductile. The ability of a substance to be hammered or beaten in thin sheets is called malleability while the ability of a substance to be drawn or pulled into thin wires is called ductility. That is why most of the metallic solids are easy to form into desired shapes.

v) They are insoluble in all common solvents.

Conceptual Check Point:

The metallic solids (metals) usually dent rather than shatter when we struck them by a hammer, why?

Structure of Metals

A pure metal is a crystalline solid in which metal atoms are closely packed in a crystal lattice (metallic lattice). A metal may be regarded as an assembly of positive ions usually considered as spheres, which are packed together to fill space as completely as possible.

To understand the close packing of atoms in metal structures, let us consider the structure of balls. If a number of solid spheres (or metallic balls) are packed in a

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box as shown in figure 6.5, when the box is well shaken, the balls will rearrange as shown in figure 6.6. The rearrangement of balls in figure 6.6 is more stable and more closely packed than figure 6.5.

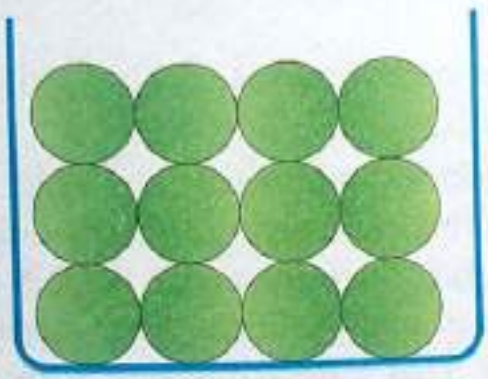

Figure 6.5

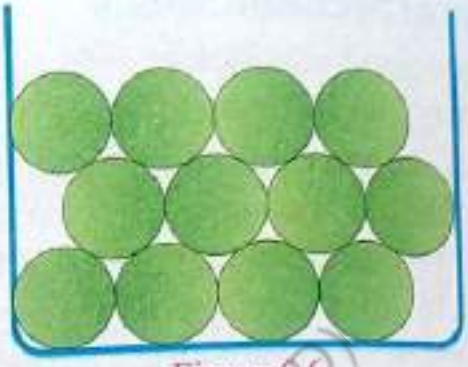

Figure 6.6

Metals have three major types of crystal structures:

i) Face centered cubic structure
ii) Body centered cubic structure.
iii) Hexagonal close packing structure.

I) Face Centered Cubic (FCC) Structure

There are eight atoms at each corner of the unit cell. Each atom is shared by eight unit cells. Hence each atom contributes one eighth to the unit cell. There are six atoms in the center of each face and each atom is shared by two unit cells. So each atom contributes one half to the unit cell. The total number of atoms per unit cell is $\left(\frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 1 + 3 = 4\right)$ four.

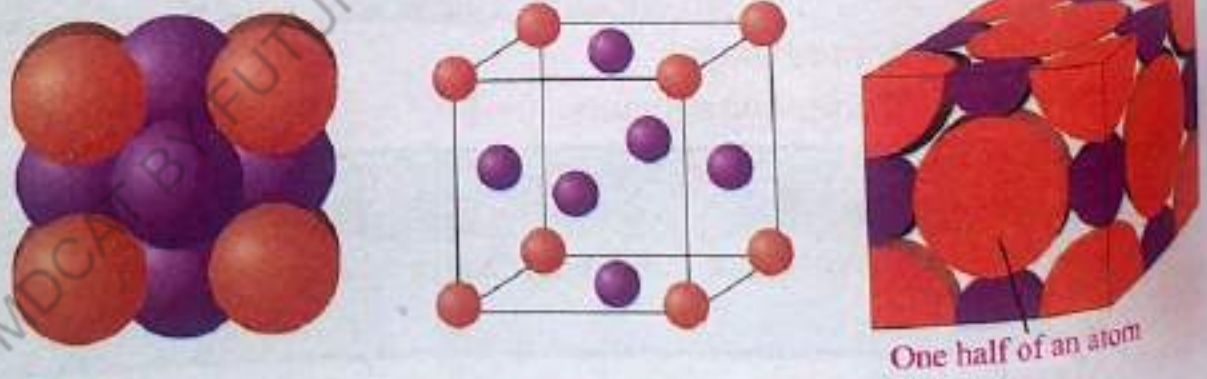

Figure 6.7: Face centered cubic structure

Every atom in the crystal is bonded with twelve neighbours and the coordination number is 12. In this case 74% of the available volume is occupied by the spheres. Examples are Ag, Au, Ca, Co, Cu, and Ni.

ii) Body Centered Cubic (BCC) Structures

In body centered-cubic structures, there is one eighth of an atom at each corner

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the unit cell and only one atom at the center of unit cell. The total number of atoms per unit cell is $(\frac{1}{8} \times 8 + 1 \times 1 = 1 + 1 = 2)$ two.

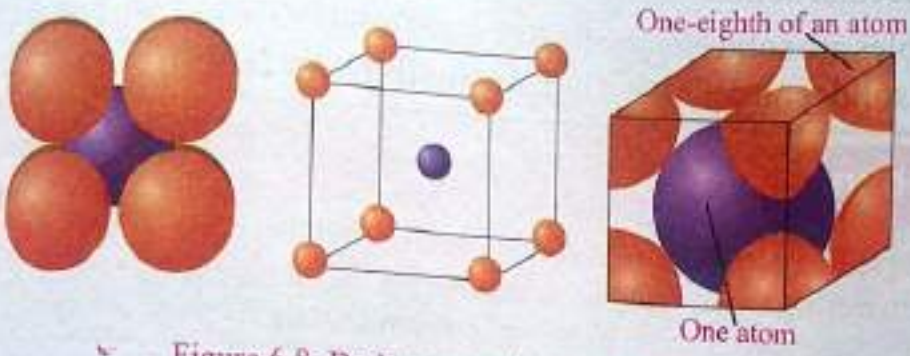

Figure 6.8: Body centered cubic structure

The coordination number is 8. In this case only 68% of the available volume is occupied by the spheres. Examples are Li, Na and K.

(iii) Hexagonal Close Packing Structure (HCP)

Let us consider, the atoms of metals are arranged in the form of layers. In HCP, the top and bottom layers have seven atoms where six atoms arrange themselves in the shape of a hexagon and a seventh atom sit in the middle of the hexagon. The atoms of the top layer (third layer) are exactly above the bottom layer (first layer). The middle layer has three spherical atoms. The spherical atoms of the fourth layer are exactly above the middle (second) layer and so on.

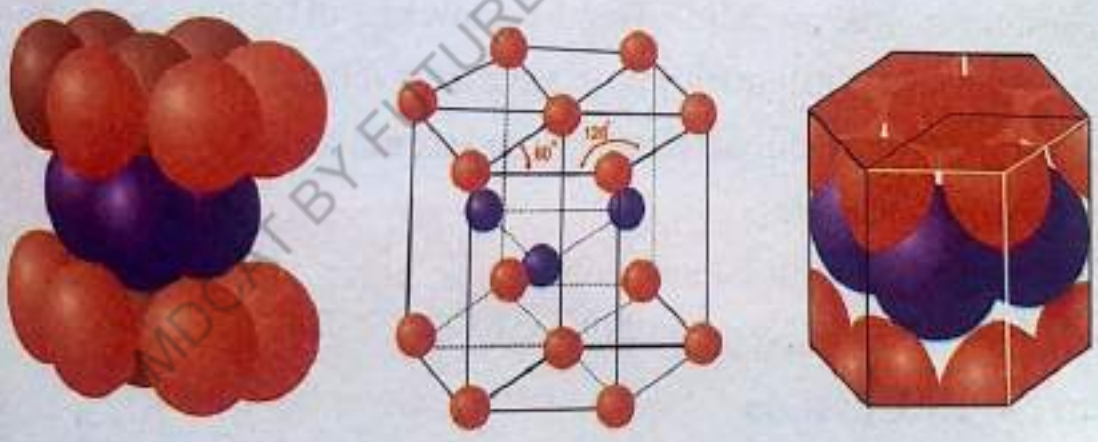

Figure 6.9: Hexagonal close packing structure

The packing efficiency is 74%. Every atom is bonded with twelve neighbours and the coordination number is 12. For example, Ba, Ca, Mg and Zn are crystallizes in HCP.

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6.5.4 Molecular Solids

The solids in which atoms or molecules are held together by intermolecular forces are called molecular solids.

Examples are solid NH_3, solid SO_2, Ice, solid CO_2 (dry ice), I_2 etc.
These solids consist of two types of molecular solids.

Keep In mind

Both covalent solids and molecular solids contain covalent bonds. The covalent bonds are not broken during the melting of molecular solid. The higher the melting points of molecular solids the stronger the intermolecular attractive forces.

i) The molecular solids which have dipole-dipole forces and hydrogen bonding between their molecules are called polar molecular solids. Examples of such solids are ice, sugar, solid HF etc.

ii) The molecular solids in which molecules are held together by London dispersion forces only are called non-polar molecular solids. Examples of such solids are I_2, S_8, P_4, solid CO_2 (dry ice), the solids of group VIIIA(18) elements such as neon etc.

Properties

i) They are soft and can be compressed easily. This is due to weak forces of attractions among the molecules.

ii) They have low to moderately low melting and boiling points. Most of the molecular solids melt below 200°C. They have low heat of fusion.

iii) They are volatile in nature and hence, have relatively high vapour pressure.

iv) They are poor conductors of electricity and are not malleable.

v) They have low densities.

vi) Polar molecular crystals are soluble in polar solvents and non-polar molecular crystals are soluble in non-polar solvents.

Structure of Ice Crystals

The familiar example of molecular solids is ice. The structure of Ice is just like that of diamond. The ice has regular hexagonal rings in which water molecules are held together by hydrogen bonds. The water molecules in the structure of ice arrange themselves in a regular manner in such a way that empty spaces are produced. Hence, ice occupies 10% more space than liquid water and its density decreases. This means that there are fewer molecules, and hence less mass,

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given volume of solid (ice) than in the same volume of liquid water. Water has unusually high heat of fusion due to presence of strong hydrogen bonding among its molecules. The large amount of heat is released in the process of freezing (The conversion of water into ice) which is used to save crops from freezing by spraying them with liquid water. Because of this reason citrus fruit growers spray their trees with water on cold nights to protect the tree from frost damage. When water freezes on the surface of leaves it gives off energy which is enough to save the tree from freezing. The heat of fusion of water is the highest of all molecular solids except ammonia.

Table 6.10: Comparison of the Properties of Ionic, Covalent, Molecular and Metallic Solids

Type of Solid	Force of Attraction	General Properties	Examples
Ionic	Electrostatic Force of attraction	Hard, brittle, high melting point (400 to 3000°C), poor conductor of heat and electricity	NaCl, K_2SO_4, LiF, $CaCO_3$
Covalent	Covalent bond	Very Hard, high melting point (1200 to 4000°C), poor conductor of heat and electricity	Diamond, Silica (SiO_2), Silicon, carbide (SiC)
Molecular	Dipole-dipole forces, Hydrogen bonds, London forces	Soft, low to moderate melting point (-272 to 400°C), poor conductor of heat and electricity	Sucrose, ice, solid CO_2, solid benzene
Metallic	Metallic bond	Variable hardness form soft to very hard, low to high melting point (-39 to 3400°C), good conductor of heat and electricity, malleable and ductile	Gold, iron, copper, sodium etc. All metallic elements.

Interesting Information:

When an apple is kept in the freezer, it freezes; the water within a cell expands and disrupts the cells, the same as water freezing within the pipe bursts the pipe. When the vegetables or foods with high water content like spinach freezes, it will be damaged when you unfreeze it.

Conceptual Check Point:

Why the most of the organisms do not survive freezing?

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Summary of Facts and Concepts

- Solid is the physical state of matter and has definite shape and volume. The particles are closely packed and locked at their position and are unable to move. Their particles have to and fro motions.
- Solids are either crystalline or amorphous. Crystalline solids have orderly arrangement of particles where amorphous solids lack internal order.
- Crystalline solids have high melting and boiling points, low compressibility, very low vapour pressure, and almost no diffusion.
- The particles in crystalline solids are arranged in a three dimensional lattice structure. A crystal lattice consists of a repeating pattern of unit cells.
- Unit cell is the basic repeating structural unit of crystal lattice that displays all the properties of crystal pattern. All of the unit cells in the crystalline solid have alike arrangement of particles.
- Crystalline solids are classified into seven different types of lattice types. X-ray diffraction is one of the most important methods which are used to determine the structures of crystalline solids.
- Crystalline solids can be further divided into four types as ionic, covalent, metallic, and molecular solids depending upon the arrangement of particles and forces of attractions among their particles. For example, ionic solids are hard, covalent solids are very hard, molecular solids are soft and metallic solids have variable hardness. Hardness, melting point, and electrical conductivity are related to the structure of solids.
- Ionic solids are those whose components are ions that are held together by ionic bonds such as NH_4Cl and potash alum.
- Covalent solids are those whose components are atoms that are held together by covalent bonds into giant three dimensional arrays such as diamond and graphite.
- Metallic solids are those whose components are metal atoms that are held together by metallic bonds into large arrays of atoms such as copper and gold.
- Molecular solids are those whose components are simple molecules that are held together by dipole-dipole forces when the molecules are polar such as ice and sucrose (sugar) and by London forces when the molecules are non-polar such as dry ice (solid CO_2) and iodine.
- In a crystalline solid each sphere is surrounded by a certain number of spheres. The numbers of spheres that would found in the vicinity of each sphere is known as coordination number.

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Questions and Problems

Q.1. Four answers are given for each question. Select the correct one.

i) Crystalline solids are also called

(a) True solids (b) pseudo solids

(c) glasses (d) amorphous solids

ii) Which of the following is amorphous solid?

(a) Sucrose (b) NaCl

(c) rubber (d) SiC

iii) Solid is made up of

(a) Atoms (b) ions

(c) molecules (d) all of them

iv) The process in which same compound is present in more than one crystalline forms is called:

(a) Allotropy (b) anisotropy

(c) isomorphism (d) polymorphism

v) Isomorphs have

(a) same physical properties (b) different physical properties

(c) same chemical properties (d) different ratio of atoms

vi) Solids that can be drawn into thin wires are called

(a) Ductile (b) malleable

(c) brittle (d) flexible

vii) Which one of the following has the highest value of lattice energy

(a) NaI (b) NaBr

(c) NaCl (d) NaF

viii) Which one of the following is a polar molecular solid?

(a) Dry ice (b) ice

(c) phosphorus (d) sulphur

ix) In cubic system, the angles

(a) $\alpha \neq \beta \neq \gamma \neq 90°$ (b) $\alpha = \beta = \gamma \neq 90°$

(c) $\alpha = \beta = \gamma = 90°$ (d) $\alpha = \beta = 90°, \gamma \neq 90°$

x) Which of the following is **NOT** the property of solid?

(a) the definite melting point

(b) the high density

(c) the extremely low rate of diffusion

(d) the high expansion on heating

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Q.2. Fill in the blanks with suitable words given in the brackets:

i) The word amorphous means _____. (motionless/shapeless)

ii) Cleavage is an _____ property. (isotropic/anisotropic)

iii) Sugar crystallizes in _____ shape. (cubic/monoclinic)

iv) All the lengths are _____ in rhombohedral system. (equal/unequal)

v) Crystalline solids have ordered _____ dimensional arrangement of particles. (one/three)

vi) The orderly arrangement of particles in crystalline solids is _____ in different direction. (same/different)

vii) The cubic crystals of sodium chloride change to needle like if 10% _____ is added to the solution as impurity. (urea/lime)

viii) In _____ solids, the atoms in the lattice are displaced easily with respect to each other. (ionic/metallic)

ix) In _____ solids, the electrons are localized in the bonds. (metallic/covalent)

x) Wax is the example of _____ solid. (crystalline/amorphous)

Q.3. Label the following statements as True or False:

i) Solids particles have low kinetic energy as compared to liquids.

ii) Heat is absorbed when a liquid is changed to solid.

iii) Plastic is the example of crystalline solid.

iv) Crystalline solids can be divided into seven crystal systems.

v) Six parameters of unit cell are called crystallographic elements.

vi) The branch of science in which we study about crystals is called crystallography.

vii) The particles in solids have translational motion.

viii) Transition temperature is for compounds only.

ix) At melting point the solid and liquid phases exist in equilibrium.

x) The molecular solids are good conductors of electricity in the molten state.

Q.4: What are solids? How kinetic molecular theory explains the behaviour of solids?

Q.5: Define crystalline and amorphous solids. How does a crystalline solid differ from an amorphous solid? Give examples of each.

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Q.6: Explain the following properties of crystalline solids and give examples in each case.

i) Geometrical shape
ii) Melting point
iii) Cleavage planes
iv) Habit of crystal
v) Crystal growth
vi) Anisotropy
vii) Symmetry
viii) Isomorphism
ix) Polymorphism
x) Allotropy
xi) Transition temperature

Q.7: What is the difference between (a) isomorphism and polymorphism, (b)allotropy and polymorphism?

Q.8: What do the terms amorphous, isomorphism and polymorphism mean?

Q.9: What is a unit cell? Explain the significance of the unit cell to the shape of the crystal using NaCl as an example.

Q.10: Describe various types of crystal systems and draw the shapes of the unit cells of various crystal systems?

Q.11: Define and explain lattice energy by giving examples.

Q.12: Give examples of some crystalline and amorphous solids that are used in your community.

Q.13: Discuss the electron sea model. How the electron sea model accounts for the high electrical conductivity, thermal conductivity and lustrous surfaces of metals?

Q.14: What are ionic solids? What types of attractive forces exist among these solids? Discuss their properties. What do you think are they water soluble or not?

Q.15: What are covalent solids? Discuss their properties.

Q.16: What are metallic solids? Give the characteristic properties of metallic solids.

Q.17: What are molecular solids? Give their properties.

Q.18: Explain why ionic solids are generally harder than molecular solids?

Q.19: Why the ceramic bowl breaks and aluminum bowl do not breaks when dropped onto the concrete floor?

Q.20: Explain the density and high heat of fusion of ice.

Q.21: What kind of solid displays each of these sets of properties?

(a) Non-crystalline and melts over a wide range of temperature.
(b) Insoluble in water and conducts electricity in the solid state.

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(c) Do not conduct electricity in solid state but are good conductors in solution form and in molten state.

(d) Soft and melts easily and the solid does not conduct electricity.

Q.22: Outer appearance of both the crystals looks similar but melting point of sucrose (186°C) is many times lower than sodium chloride (801°C), why?

Q.23: What types of attractive forces are there between the particles of?

(a) covalent solids

(b) ionic solids

(c) metallic solids

(d) molecular solids

Q.24: Classify each of the following substances as conductor, semiconductor and non-conductor:

(a) Germanium (b) sulphur (c) silver

Q.25: Define coordination number. What is the coordination number of each atom in face centered cubic structure, body centered cubic structure and hexagonal close packing structure?

Q.26: Explain the following with reasons:

(a) Solids have very low vapour pressure than liquids.

(b) Amorphous solids are termed as "super cooled liquids".

(c) Crystalline solids have sharp and distinct melting points while morphous solids do not.

(d) Cleavage is an anisotropic property.

(e) Metallic solids are good conductors of electricity.

(f) Ionic crystals are shattered when struck by a hammer.

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Chapter # 07

Chemical Equilibrium

Major Concepts

7.1 Reversible Reactions and Dynamic Equilibrium
7.2 Factors Affecting Equilibrium (Le-Chatelier's Principle)
7.3 Industrial Applications of Le-Chatelier's Principle (Haber's Process)
7.4 Solubility Product and Precipitation Reactions
7.5 Common Ion Effect

Learning Outcomes

The students will be able to:

- Define chemical equilibrium in terms of a reversible reaction. (Remembering)
- Write both forward and reverse reactions and describe the macroscopic characteristics of each.(Understanding)
- State the necessary conditions for equilibrium and the ways that equilibrium can be recognized.(Understanding)
- Describe the microscopic events that occur when a chemical system is in equilibrium.(Understanding)
- Write the equilibrium expression for a given chemical reaction.(Understanding)
- Relate the equilibrium expression in terms of concentration, partial pressure, number of moles and mole fraction.
- Write expression for reaction quotient.
- Determine if the equilibrium constant will increase or decrease when temperature is changed, given the equation for the reaction.(Applying)
- Propose microscopic events that account for observed macroscopic changes that take place during a shift in equilibrium.(Applying)
- Determine if the reactants or products are favored in a chemical reaction, given the equilibrium constant.(Analyzing)
- State Le-Chatelier's Principle and be able to apply it to systems in equilibrium with changes in concentration, pressure, temperature, or the addition of catalyst.(Applying)
- Explain industrial applications of Le-Chatelier's Principle using Haber's Process as an example.(Analyzing)
- Define and explain solubility product.(Understanding)
- Define and explain common ion effect giving suitable examples. (Applying)

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Introduction

The digestion of food in our body, the rusting of iron, the spoilage of milk and many other reactions occur in our daily life. A large number of reactions are carried out in different industries which give us a large number of useful products like plastics, fibers, drugs, dyes, soaps and detergents and many other useful products. Some reactions are reversible while others are irreversible.

The reactions which occur only in one direction are called *irreversible reactions*. In these reactions, reactants are completely converted into products and products are not reconverted into reactants. These reactions go to completion. They are shown by putting a single headed arrow (⟶) between the reactants and products. Examples of such reactions are:

i) $2H_2O_{(g)} \xrightarrow{\text{Electric discharge}} 2H_{2(g)} + O_{2(g)}$

ii) $AgNO_{3(aq)} + NaCl_{(aq)} \longrightarrow AgCl_{(s)} + NaNO_{3(aq)}$

iii) Burning of fuel

iv) Digestion of food

A chemical reaction which occurs in forward as well as reverse directions is called reversible reaction. In these reactions, reactants are converted into products and products are reconverted into reactants. These are slow reactions. These reactions never go to completion, hence called incomplete reactions. They are shown by putting the double arrow with double barbs (⟷), pointing in opposite directions, between the reactants and products. The double arrows of equal length also show equilibrium. Examples of some reversible reactions are:

i) $H_{2(g)} + I_{2(g)} \underset{\text{Reverse reaction}}{\overset{\text{Forward reaction}}{\rightleftharpoons}} 2HI_{(g)}$

ii) $N_{2(g)} + 3H_{2(g)} \underset{\text{Reverse reaction}}{\overset{\text{Forward reaction}}{\rightleftharpoons}} 2NH_{3(g)}$

iii) $2SO_{2(g)} + O_{2(g)} \underset{\text{Reverse reaction}}{\overset{\text{Forward reaction}}{\rightleftharpoons}} 2SO_{3(g)}$

iv) $H_2O_{(l)} \underset{\text{Reverse reaction}}{\overset{\text{Forward reaction}}{\rightleftharpoons}} H_2O_{(g)}$

All chemical reactions are considered to be reversible and they reach a state of equilibrium under suitable conditions. A reversible chemical reaction is a dynamic process. The word equilibrium means "a state in which opposing forces are balanced". It may be static (at rest) or dynamic (in constant motion). A person's finger at rest is the example of static equilibrium and the earth that revolves around the sun is the example of dynamic equilibrium.

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7.1 Reversible Reactions and Dynamic Equilibrium

7.1.1 Concept and Explanation

The state in which the rates of forward and reverse reactions are same and the concentrations of the reactants and products remain unchanged with time is called chemical equilibrium. Chemical equilibrium may be physical or chemical. Equilibrium between two phases of the same substance is called physical equilibrium because the changes that take place are physical processes. The conversion of water into vapours in a closed container at a given temperature is an example of physical equilibrium. The rate of evaporation is higher than rate of condensation at the start when water vaporizes within a closed container at constant temperature, but after some times, the rate of evaporation becomes equal to rate of condensation. At this stage liquid and vapours are in the state of dynamic equilibrium i.e. the number of molecules leaving the liquid surface is equal to the number of molecules returning back to the liquid. At equilibrium the pressure exerted by the water molecules at a given temperature remains constant and is called the equilibrium vapour pressure of water.

$$\text{Liquid (water)} \underset{\text{Condensation}}{\overset{\text{Evaporation}}{\rightleftharpoons}} \text{Vapours (steam)}$$

Chemical equilibrium is a *dynamic* state because reactions continue to occur, but because they occur at the same rate, no net change is observed on the macroscopic level.

The study of physical equilibrium gives useful information such as the equilibrium vapour pressure. However, chemists are particularly interested in chemical equilibrium processes because they are involved in many biological, industrial, and environmental processes. Consider the reversible reaction which involves the decomposition of colourless frozen dinitrogen tetraoxide into dark brown nitrogen dioxide.

$$N_2O_{4(g)} \underset{\text{Reverse reaction}}{\overset{\text{Forward reaction}}{\rightleftharpoons}} 2NO_{2(g)}$$

When some amount of pure N_2O_4 is placed in an evacuated flask at room temperature, some brown colour gas appears which shows the formation of NO_2 molecules. The concentration of NO_2 in the flask increases and the brown colour deepens. However, the reverse reaction can also starts. As the reaction proceeds, the concentration of reactant (N_2O_4) goes on decreasing, so the rate of forward reaction also goes on decreasing. On the other hand, the concentration of product (NO_2) goes on increasing, so the rate of reverse reaction also goes on increasing. When the rate

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of forward reaction becomes equal to rate of reverse reaction, the reaction reaches a state of chemical equilibrium and the concentrations of reactants and products become constant. Now the change in colour is stopped. In fact, you see no net change at this stage, although the forward and reverse reactions are going on. The continuing forward and reverse reactions make the equilibrium a *dynamic* process. All chemical equilibriums are dynamic. Once the state of chemical equilibrium is established, it will last forever if conditions are not changed.

Consider a general reaction, in which A reacts with B to produce C and D.

$$\underset{\text{(Reactants)}}{A + B} \underset{\text{Reverse reaction}}{\overset{\text{Forward reaction}}{\rightleftharpoons}} \underset{\text{(Products)}}{C + D}$$

Let us consider initial concentrations of A and B are equal. The concentration of reactants A and B decreases and that of products C and D increases when reaction proceeds in forward direction. Hence, the rate of forward reaction goes on decreasing while that of reverse reaction goes on increasing and a point is reached at which rate of forward reaction becomes equal to rate of reverse reaction. This is called equilibrium point. At equilibrium, product and reactant lines are parallel to each other. The change in concentration of reactants or products is called rate of reaction.

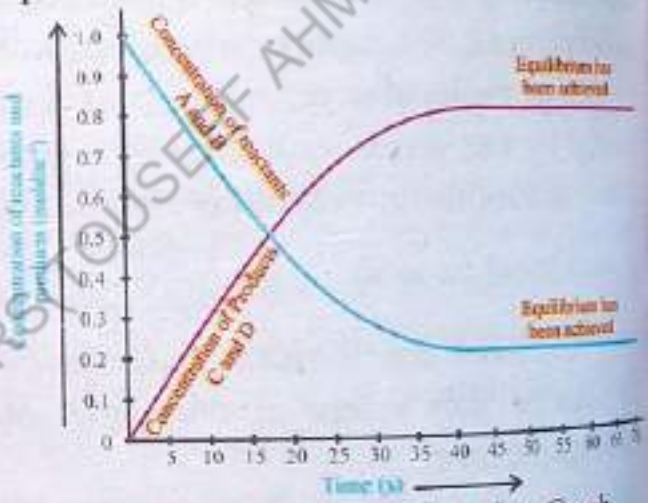

Figure 7.1: Concentration-time Graph

The mixture of reactants and products in the equilibrium state is known as equilibrium mixture and the unvarying amounts of reactants and products are called equilibrium concentrations.

Table 7.1: The Explanation of the Characteristics of Equilibrium State

Characteristics of Equilibrium State	Explanation
Most of the reactions are reversible	The reactions can proceed in both forward and reverse directions.
Equilibrium is dynamic	The reaction has not stopped but the opposing rates are equal (both forward and reverse reactions are still taking place at the equal rate)
The macroscopic properties of a system are constant at equilibrium.	The reaction has not stopped but the opposing rates are equal (both forward and reverse reactions are still taking place at the equal rate)

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Characteristics of Equilibrium State	Explanation
The microscopic processes continue	The forward and reverse reactions are going on but nothing appears to be happening because the forward and reverse reactions occur at the same rates.
Equilibrium is achieved in a closed system	A closed system is a system that does not allow the exchange of matter with the surroundings, so the equilibrium is attained where both reactants and products can react and recombine with each other.
The concentrations of products and reactants remain constant at equilibrium	There is no change in the concentrations of reactants or products in a system of dynamic equilibrium. They are being produced and destroyed at an equal rate. Equilibrium does not mean that concentrations of reactants and products are all equal.
Equilibrium can be approached from either side	The same equilibrium mixture will result under the same conditions, regardless of whether the reaction is started with all reactants, all products or a mixture of both. For example, the proportions of $N_{2(g)}$, $H_{2(g)}$ and $NH_{3(g)}$ are the same at equilibrium no matter whether the reaction is started with $N_{2(g)}$, $H_{2(g)}$ or whether the reaction is stated with $NH_{3(g)}$ or mixture of both. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 3NH_{3(g)}$
Catalysts do not affect equilibrium concentrations	Catalysts speed up the rate of forward and reverse reactions equally. We get the same concentrations of reactants and products at equilibrium, whether the catalyst is present in the reaction mixture or not.

Types of Chemical Equilibriums

There are two types of chemical equilibriums:

Homogeneous Chemical Equilibrium

Chemical equilibrium in which reactants and products are in same physical state is called homogeneous chemical equilibrium. For example,

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

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

Heterogeneous Chemical Equilibrium

Chemical equilibrium in which reactants and products are in different physical states is called heterogeneous chemical equilibrium. For example:

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$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

$$2Fe_{(s)} + 3H_2O_{(g)} \rightleftharpoons Fe_2O_{3(s)} + 3H_{2(g)}$$

7.1.2 Law of Mass Action and Expression for Equilibrium Constant

C. M. Guldberg (1836-1902) Peter Waage (1833-1900)

The law of mass action was postulated by professor of applied mathematics and technology Cato Maximilian Guldberg and professor of chemistry Peter Waage in 1864 at the university of Oslo, Norway. This law states that:

"The rate of reaction is directly proportional to the product of active masses of the reactants".

By active masses we mean molar concentrations of the reactants and products for dilute solution. It is expressed in moles dm^{-3}. Consider a general reversible reaction.

$$\underset{\text{(Reactants)}}{A + B} \underset{\text{Reverse}}{\overset{\text{Forward}}{\rightleftharpoons}} \underset{\text{(Products)}}{C + D}$$

According to law of mass action, the rate of forward reaction is directly proportional to the product of molar concentration of reactants A and B.

$$R_f \propto [A][B] \quad \text{or}$$

$$R_f = K_f[A][B]$$

Where, K_f is the rate constant of forward reaction. Similarly, the rate of reverse reaction is directly proportional to the product of molar concentration of products C and D.

$$R_r \propto [C][D] \quad \text{or}$$

$$R_r = K_r[C][D]$$

Where, K_r is the rate constant of reverse reaction. At equilibrium state, rate of forward reaction is exactly equal to the rate of reverse reaction.

Rate of forward reaction = Rate of reverse reaction

$$R_f = R_r$$

or $$K_f[A][B] = K_r[C][D]$$

or $$\frac{K_f}{K_r} = \frac{[C][D]}{[A][B]}$$

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or $K_c = \frac{[C][D]}{[A][B]}$

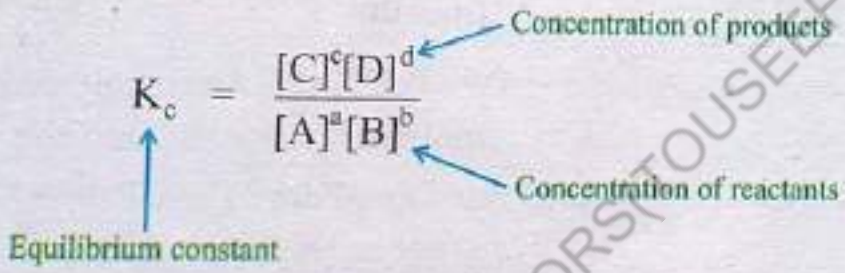
$$\frac{K_f}{K_r} = K_c$$

or $K_c = \frac{\text{Product of molar concentrations of products}}{\text{Product of molar concentrations of reactants}}$

K_c is called equilibrium constant of the reaction. It is defined as: The ratio of concentrations of products to the concentrations of reactants at equilibrium is called equilibrium constant. It has concentration of products in the numerator and concentration of reactants in the denominator. In gaseous equilibriums, concentrations of gases are shown by partial pressure and K_p is used instead of K_c. Consider the more general reversible reaction:

$$aA + bB \rightleftharpoons cC + dD$$

Where a, b, c and d are the coefficients of balanced chemical equation. At equilibrium state,



$K_c = \frac{\text{Product of concentrations of products (raised to power equal to coeffcients)}}{\text{Product of concentrations of reactants (raised to power equal to coeffcients)}}$

The coefficients appear as exponents (powers) of concentrations in the equation of K_c.

Characteristics of Equilibrium Constant

) Equilibrium constant is independent of initial concentrations of reactants and roducts at a given temperature.

) It does not depend upon the direction of reaction. The same equilibrium onstant value is obtained whether the reaction is started from the reactants side or om the products side.

) Its value changes with temperature and is constant at constant temperature.

) Its value depends upon the coefficients of reactants and products in a balanced emical equation.

) The higher value of equilibrium constant is the indication of higher value of oducts as compared to the reactants at equilibrium and vice versa.

) The molar concentrations of pure solids, pure liquids (in heterogeneous

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equilibria), and solvents (in homogeneous equilibria) do not appear in equilibrium constant expressions.

Units of Equilibrium Constant

When the number of moles of reactants and products in balanced chemical equations are equal, then K_c has no unit. For example:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(\text{mol dm}^{-3})(\text{moles dm}^{-3})}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})} = \text{No unit}$$

When the number of moles of reactants and products are unequal, then the K_c has units. For example:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})^3}$$

$$= \frac{(\text{mol}^2\text{dm}^{-6})}{(\text{mol dm}^{-3})(\text{mol}^3\text{dm}^{-9})}$$

$$= \frac{\text{mol}^2\text{dm}^{-6}}{\text{mol}^4\text{dm}^{-12}}$$

$$= \text{mol}^{2-4}\,\text{dm}^{-6+12}$$

$$= \text{mol}^{-2}\,\text{dm}^{+6}$$

But in usual practice, the units of K_c and K_p are not written.

7.1.3 Relationship Between K_c, K_p, K_x and K_n

Relationship Between K_c and K_p

When concentration of reactants and products are taken in moles dm^{-3}, the equilibrium constant is expressed by K_c. Consider the general reversible reaction

$$A + B \rightleftharpoons C + D$$

Hence,

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{or} \quad K_c = \frac{C_C^c \cdot C_D^d}{C_A^a \cdot C_B^b}$$

Square brackets or "C" show molar concentration in moles dm^{-3}.

When all the reactants and products are in gaseous state, then

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concentration of each gas is taken in terms of partial pressure, and the equilibrium constant is expressed by K_p.

$$K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \quad \ldots\ldots\ldots\ldots \quad (i)$$

Where P_A is the partial pressure of gas A and P_B is the partial pressure of gas B.

The value of K_c is generally different from K_p because the partial pressures of reactants and products are not equal to their concentrations expressed in moles per decimeter cube. If we know the value of one, then we can calculate the value of the other by using the general gas equation.

According to combined gas law:

$$PV = nRT \quad \text{or}$$

$$P = \frac{n}{V}(RT)$$

The conventional unit for **n/V** is mol/dm^3 that is equal to Molarity.

Hence, for gaseous reactants A, B and gaseous products C, D the above equation can be written as:

$$P_A = \frac{n_A}{V}(RT) \quad \text{or} \quad P_A = [A](RT)$$

$$P_B = \frac{n_B}{V}(RT) \quad \text{or} \quad P_B = [B](RT)$$

$$P_C = \frac{n_C}{V}(RT) \quad \text{or} \quad P_C = [C](RT)$$

$$P_D = \frac{n_D}{V}(RT) \quad \text{or} \quad P_D = [D](RT)$$

By putting the value of P_A, P_B, P_C, and P_D in equation (i), we get:

$$K_p = \frac{[C]^c(RT)^c \cdot [D]^d(RT)^d}{[A]^a(RT)^a \cdot [B]^b(RT)^b} \quad \text{or}$$

$$K_p = \frac{[C]^c[D]^d(RT)^{c+d}}{[A]^a[B]^b(RT)^{a+b}} \quad \text{or}$$

$$K_p = \frac{[C]^c[D]^d}{[A]^a[B]^b}(RT)^{(c+d)-(a+b)}$$

As, $\frac{[C]^c[D]^d}{[A]^a[B]^b} = K_c$, hence, the above equation can be written as,

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$K_p = K_c(RT)^{\Delta n}$ ..... (ii)

Where, R is general gas constant, T is absolute temperature and Δn is the change in the number of moles between products and reactants of gases. So,

$\Delta n = (c+d)-(a+b)$

Δn = (Sum of moles of gaseous products) – (Sum of moles of gaseous reactants)

When number of moles of reactants and products are equal, then Δn is equal to zero, and $K_p = K_c$.

Example 7.1

Write the equilibrium constant expressions (K_c & K_p) for the two reactions given below:

(a) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

(b) $N_2 + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Solution:

(a) $$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

As we know,

$$K_p = K_c(RT)^{\Delta n}$$

Hence,

$$K_p = \frac{[NO_2]^2}{[N_2O_4]}(RT)$$ Where, $\Delta n = 1$

(b) $$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

As we know,

$$K_p = K_c(RT)^{\Delta n}$$

Hence,

$$K_p = \frac{[NH_3]^2}{[N_2][H_2]^3}(RT)^{-2}$$ Where, $\Delta n = 2-4 = -2$

Practice Exercise 1:

Write the equilibrium constant expressions (K_c & K_p) for the reaction given below:

$$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$$

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Relationship between K_p and K_x

According to Dalton's Law, the partial pressure of a gas is equal to the product of its mole fraction and total pressure.

$$P_i = X_i \cdot P_T$$

Where, P_i is the partial pressure of a gas, X_i is the mole fraction of a gas and P_T is the total pressure of the gases. The values of partial pressures of gases A, B, C, and D are:

$$P_A = X_A \cdot P_T$$

$$P_B = X_B \cdot P_T$$

$$P_C = X_C \cdot P_T$$

$$P_D = X_D \cdot P_T$$

By putting the value of P_A, P_B, P_C and P_D in equation (i), we get

$$K_p = \frac{(X_C P_T)^c (X_D P_T)^d}{(X_A P_T)^a (X_B P_T)^b} \quad \text{or}$$

$$K_p = \frac{(X_C^c)(X_D^d)(P_T)^{c+d}}{(X_A^a)(X_B^b)(P_T)^{a+b}} \quad \text{or}$$

$$K_p = \frac{(X_C^c)(X_D^d)}{(X_A^a)(X_B^b)} (P_T)^{(c+d)-(a+b)}$$

$$\frac{(X_C^c)(X_D^d)}{(X_A^a)(X_B^b)} = K_x$$

Therefore,

$$K_p = K_x (P_T)^{(c+d)-(a+b)} \quad \text{or} \quad K_p = K_x (P_T)^{\Delta n}$$

For one mole of a gas:

$$P_T = \frac{RT}{V}$$

Therefore:

$$K_p = K_x \left(\frac{RT}{V}\right)^{\Delta n} \quad \ldots\ldots\ldots\ldots \text{(iii)}$$

When number of moles of reactants and products are equal, then Δn is equal to zero, and $K_x = K_p$.

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Relationship between K_p and K_n

When concentrations of reactants and products are taken in terms of number of moles, then equilibrium constant is expressed by K_n. According to Dalton's Law, the mole fraction of a gas is equal to number of moles of a particular gas divided by total number of moles of all gases present in the mixture.

$$X_i = \frac{n_i}{n_T}$$

Where, X_i is the mole fraction of a gas, n_i is the number of moles of a gas, and n_T is the total number of moles of gases. We know that,

$$P_i = X_i \cdot P_T$$

Hence, by putting the value of X_i in this equation, we obtain

$$P_i = \frac{n_i}{n_T} \cdot P_T$$

For the reactant gases (A and B) and product gases (C and D), the equation will be:

$$P_A = \frac{n_A}{n_T} \cdot P_T$$

$$P_B = \frac{n_B}{n_T} \cdot P_T$$

$$P_C = \frac{n_C}{n_T} \cdot P_T$$

$$P_D = \frac{n_D}{n_T} \cdot P_T$$

By putting the value of P_A, P_B, P_C, and P_D in equation (i), we get

$$K_p = \frac{(\frac{n_C}{n_T} \cdot P_T)^c (\frac{n_D}{n_T} \cdot P_T)^d}{(\frac{n_A}{n_T} \cdot P_T)^a (\frac{n_B}{n_T} \cdot P_T)^b}$$ or

$$K_p = \frac{(\frac{n_C}{n_T})(\frac{n_D}{n_T})(P_T)^{c+d}}{(\frac{n_A}{n_T})(\frac{n_B}{n_T})(P_T)^{a+b}}$$

As, $$\frac{(\frac{n_C}{n_T})(\frac{n_D}{n_T})}{(\frac{n_A}{n_T})(\frac{n_B}{n_T})} = K_n$$

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Therefore,

$K_p = K_n(P_T)^{(c+d)-(a+b)}$ or $K_p = K_n(P_T)^{\Delta n}$

For one mole of a gas,

$P_T = \frac{RT}{V}$

Therefore,

$K_p = K_n\left(\frac{RT}{V}\right)^{\Delta n}$ ..... (iv)

When number of moles of reactants and products are equal, then Δn is equal zero, and all the equilibrium constants have the same values, hence

$K_c = K_p = K_x = K_n$

7.4 Calculation of Equilibrium Constant

quilibrium constant of chemical reaction is calculated from the values of oncentration or partial pressures at equilibrium. In cases where the equilibrium nstant is known, the concentration or partial pressure values at equilibrium may determined.

Example 7.2

The ammonia, used in the manufacture of fertilizer, is prepared by the reaction of itrogen and hydrogen gases. At equilibrium, the concentrations of nitrogen, ydrogen, and ammonia are 0.030M, 0.037M and 0.016M respectively. alculate the value of K_c at 500°C for the reaction given below:

olution: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Concentration of nitrogen = $[N_2]$ = 0.030M

Concentration of hydrogen = $[H_2]$ = 0.037M

Concentration of ammonia = $[NH_3]$ = 0.016M

Value of K_c for reaction = ?

	$N_{2(g)}$	+	$3H_{2(g)}$	$\rightleftharpoons$	$2NH_{3(g)}$
Equilibrium concentration (M) =	0.030		0.037		0.016

$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$ or

$K_c = \frac{[0.016]^2}{[0.030][0.037]^3} = 168.46$ or 1.68×10^2

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Practice Exercise 2:

Phosgene gas (carbonyl chloride, $COCl_2$) is a highly poisonous gas that was used in the First World War as a chemical weapon. This gas is prepared by the reaction of CO and Cl_2 gases. At equilibrium, the concentrations of CO, Cl_2 and $COCl_2$ are 0.011 M, 0.045M and 0.012M respectively. What is the value of K_c at 100°C for the reaction given below?

$$CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$$

Example 7.3

Calculate the concentration of SO_3 gas, used in the manufacture of H_2SO_4, with the help of the reaction give below:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

The concentration of SO_2 gas is 0.59M and that of O_2 gas is 0.45M. The K_c value of this reaction is 4.32.

Solution:

Concentration of SO_3 $= [SO_3] = ?$

Concentration of SO_2 $= [SO_2] = 0.59M$

Concentration of O_2 $= [O_2] = 0.45M$

Value of K_c $= 4.32$

At equilibrium,

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \quad \text{or}$$

$$[SO_3]^2 = K_c [SO_2]^2[O_2]$$

By putting the values we get,

$$[SO_3]^2 = (4.32)(0.59)^2(0.045)$$

$$[SO_3]^2 = 0.0677$$

By taking under root on both sides we have,

$$[SO_3] = \sqrt{0.0677}$$

$$[So_3] = 0.26M$$

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Practice Exercise 3:

Consider the reaction:

$$2\ NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$$

Suppose NO gas is allowed to reach to equilibrium at 900°C. The measured equilibrium concentrations are 0.021M for N_2, 0.021M for O_2. The value of K_c for the equilibrium system is 76.56. Calculate the concentration of NO.

7.1.5 Importance of Equilibrium Constant

The equilibrium constants of reactions can be used to determine:

i) the direction of reaction.

ii) the extent of reaction.

Determination of Direction of Reaction and the Reaction Quotient

The ratio of concentrations of products to the concentrations of reactants when the reaction is at equilibrium is called equilibrium constant (K_c) whereas, the ratio of concentrations of products to the concentrations of reactants when the reaction is not at equilibrium is called reaction quotient (Q_c).

The ratio $[C]^c[D]^d / [A]^a[B]^b$ at equilibrium is equal to K_c.

The ratio $[C]^c[D]^d / [A]^a[B]^b$ that is not at equilibrium is equal to Q_c.

We say that, the reaction quotient is an expression which has the same form as the equilibrium constant except that the concentrations in reaction quotient are not necessarily those at equilibrium.

The equilibrium quotient is also used to determine whether the reaction is at equilibrium or is not at equilibrium. The reaction is at equilibrium when Q_c is equal to K_c ($Q_c = K_c$) and the reaction is not at equilibrium when Q_c is not equal to K_c ($Q_c \neq K_c$).

The reaction quotient is helpful to determine the direction of reaction. We can determine the direction of chemical reaction by comparing the values of Q_c and K_c. There are three possibilities:

The Q_c may be less than K_c, greater than K_c or equal to K_c.

i) If Q_c is less than K_c ($Q_c < K_c$), then reaction will proceed in forward direction (from left to right) to attain the equilibrium.

$$aA + bB \longrightarrow cC + dD$$

ii) If Q_c is greater than K_c ($Q_c > K_c$), the reaction will proceed in a reverse

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direction (from right to left) to attain the equilibrium.

$$aA + bB \longleftarrow cC + dD$$

iii) If Q_c is equal to K_c ($Q_c = K_c$), then the reaction is at equilibrium. It will not move in any direction.

$$aA + bB \rightleftharpoons cC + dD$$

Determination of Extent of Reaction

Extent of chemical reaction means that how much reactant is converted into product at equilibrium. There are three possibilities:

i) **If K_c is very large:** It means that if K_c value is greater than 10^3 ($K_c > 10^3$), then forward reaction takes place to greater extent and reverse reaction takes place to smaller extent. The forward reaction is almost near to completion. For example:

$$2O_3 \rightleftharpoons 3O_2$$

$$K_c = \frac{[O_2]^3}{[O_3]^2} = 10^{55} \quad \text{at } 25^\circ C$$

The equilibrium constant value for this reaction is very large which shows that the concentration of product is very large as compared to the concentration of reactant at equilibrium. The large value of K_c at equilibrium tells us that the major amount of reactant is changed into product.

ii) **If K_c is very small:** It means that if K_c value is less than 10^{-3} ($K_c < 10^{-3}$), then reverse reaction takes place to greater extent and forward reaction takes place to smaller extent. For example:

$$2HF \rightleftharpoons H_2 + F_2$$

$$K_c = \frac{[H_2][F_2]}{[HF]^2} = 10^{-13} \quad \text{at } 2000^\circ C$$

The equilibrium constant value for this reaction is very small which shows that the concentration of product is very small as compared to the concentration of reactant at equilibrium. The small value of K_c at equilibrium tells us that the major quantity of reactant is changed into products.

iii) **If K_c is neither very large nor very small:** It means that if K_c value is in the range of 10^{-3} to 10^3, then both the forward and reverse reactions take place almost to an equal extent. For example:

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(a) $N_2O_4 \rightleftharpoons 2\,NO_2$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.36 \text{ at } 25^\circ C$$

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

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = 0.1 \text{ at } 2000^\circ C$$

At equilibrium, the molar concentration of products and reactants are almost equal.

7.2 Factors Affecting Equilibrium

The ratio of products to reactants in the equilibrium mixture is known as the position of chemical equilibrium or equilibrium position. The ratio of the reactants and products can be changed by changing the conditions of a reaction at equilibrium. Many useful chemical reactions are reversible in which the reactants are not completely converted into products and the amount of products decreases. The chemists are interested to increase the amount of products by shifting the equilibrium in forward direction. The factors that affect the equilibrium state of a chemical reaction are concentration, pressure and temperature. The effect of such changes on equilibrium state can be best explained with the help of Le Chatelier's Principle.

Le Chatelier's Principle

Henri Louis Le Chatelier was a French chemist specialized in mining engineering and interested in glass and ceramic. He studied the effect of concentration, pressure and temperature on a number of reactions in equilibrium state in 1984. This principle states that, if a system in equilibrium is disturbed by some change, the system will shift so as to counteract the effect of the change.

Henri Louis Le Chatelier (1850-1936)

This principle can be applied to all types of dynamic equilibrium i.e. for physical and chemical systems.

Applications of Le-Chatelier's Principle

Let us explain some of the most common applications of this principle in the following changes.

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7.2.1 The Effect of Concentration Change

Consider a system is in equilibrium:

$$\underset{\text{(Reactants)}}{A + B} \rightleftharpoons \underset{\text{(Products)}}{C + D}$$

i) If we increase the concentration of anyone reactant A or B or both of them, then the reaction moves from left to right in forward direction. The equilibrium is reestablished with a higher concentration of product.

ii) If we increase the concentration of anyone product C or D or both of them, then the reaction moves from right to left in the reverse direction to increase the amount of reactant at time of equilibrium.

iii) If we decrease the concentration of reactant A or B or both of them, then the reaction moves from right to left in reverse direction. This effect is reduced by the decomposition of products to produce reactants.

iv) If we decrease the concentration of product C or D or both of them, then the reaction moves from left to right in forward direction forming more product when equilibrium is reestablished.

In all of the above cases the equilibrium position changes due to change in the concentration of reactants and product. But the equilibrium constant (K_c) value does not change when we change the concentration of reactants and products.

Consider the example of the reaction of equilibrium mixture of N_2, H_2 and NH_3

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

If the concentrations of N_2 or H_2 or both of them are increased, the equilibrium will shift in the forward direction and greater amount of NH_3 is produced when the equilibrium is reestablished. If we remove some amount of N_2 or H_2 or both of them from the equilibrium mixture, then the equilibrium will shift in the reverse direction and NH_3 is decomposed to produce N_2 and H_2. Hence, the increase in the concentration of reactants favours the forward reaction whereas the decrease in the concentration of reactants favours the reverse reaction.

Consider another familiar example of equilibrium mixture of N_2, O_2 and NO

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

If we increase the concentration of NO by adding some amount of it to the equilibrium mixture, then the system will shift in the reverse direction. This effect is reduced by the decomposition of NO to produce N_2 and O_2. If we decrease the concentration of NO by removing some amount of it from the equilibrium mixture, then the system will shift in the forward direction to produce more nitric oxide (NO). Hence, the increase in the concentration of products favours the reverse

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reaction whereas the decrease in the concentration of products favours the forward reaction.

Table 7.2: The Effect of Concentration Change on Equilibrium Position and K_c

Change to System	Change in Direction	Effect on Equilibrium Position	Effect on K_c
Increase in the concentration of reactants	Equilibrium shifts to the product side	Changes	No effect
Decrease in the concentration of reactants	Equilibrium shifts to the reactant side	Changes	No effect
Increase in the concentration of products	Equilibrium shifts to the reactant side	Changes	No effect
Decrease in the concentration of products	Equilibrium shifts to the product side	Changes	No effect

7.2.2 Effect of Pressure or Volume Change

According to Le Chatelier's principle, if the pressure of an equilibrium mixture of gases is increased by decreasing the volume, at constant temperature, the reaction shifts in the direction of fewer moles of gas molecules. If the pressure of an equilibrium mixture of gases is decreased by increasing the volume, at constant temperature, the reaction shifts in the direction of more moles of gas molecules.

Pressure or volume change produces sharp effect in gaseous equilibriums where the total number of moles of reactants on the left side of equation is not equal to the total number of moles of products on the right side of equation. Examples are:

Formation of Ammonia

Consider the reaction,

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

When pressure is increased or volume is decreased at equilibrium, the reaction moves from left to right in the forward direction to increase the amount of product (NH_3). In this case, the equilibrium position shifts to the right (product side) but K_c value remains constant.

Dissociation of PCl_5

Consider the reaction,

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

When pressure is increased at equilibrium; the reaction moves from right to left in the direction of decreased volume to increase the amount of reactant (PCl_5).

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In this case, the equilibrium position shifts to the left (reactant side) but K_c remains constant.

The effect of pressure or volume change is not applicable:

(a) When the system involves solids and liquids. They are not affected by the changes in pressure because they are almost incompressible. Consider the example the water gas (mixture of CO gas and H_2 gas) is produced when steam is passed through red hot coke (carbon).

$$H_2O_{(g)} + C_{(s)} \rightleftharpoons CO_{(g)} + H_{2(g)}$$

When pressure is increased by decreasing volume, the equilibrium will shift from right to left in the direction of fewer moles of gas molecules. In this reaction we ignore the volume or concentration of carbon because it is present in solid state.

(b) When the total number of moles of reactants is equal to the total number of moles of products in gaseous phase homogeneous equilibriums.

Consider the following reaction,

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

When pressure is increased at equilibrium, the rate of both the forward and reverse reactions will increase to the same extent and the equilibrium will not shift in any direction because the total number of moles of reactants is equal to the total number of moles of products in this reaction. In this case, both the equilibrium position and K_c are not changed.

(c) When an inert gas is added to the equilibrium mixture. When a non-reactive gas (inert gas) such as neon which is not part of the equilibrium system(reactants and products) is added, the total pressure of the gases increases in a rigid container but it has no effect on the partial pressures or concentrations of the reactants or products. Thus it cannot affect the equilibrium position (i.e. the relative amounts of reactants and products) of the system. Nitrogen and noble gases are frequently used as inert gases.

Table 7.3: The Effect of Pressure Change on Equilibrium Position and K_c

Change to System	Change in Direction	Effect on Equilibrium Position	Effect on K_c
Increase in pressure or decrease in volume	Equilibrium shifts to the side that has fewer moles of gas molecules	Changes	No effect
Decrease in pressure or increase in volume	Equilibrium shifts to the side that has greater moles of gas molecules	Changes	No effect

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7.2.3 Effect of Temperature Change

Changes in concentration, pressure, or volume alter the equilibrium position without altering the value of the equilibrium constant. The value of equilibrium constant can be altered only when the temperature of the system is changed.

According to Le-Chatelier's Principle, exothermic reactions are favoured by decrease in temperature and endothermic reactions are favoured by increase in temperature. A reaction in which heat is evolved is said to be exothermic whereas a reaction in which heat is absorbed is said to be endothermic. For exothermic reactions heat is regarded as one of the products and for endothermic reactions heat is regarded as one of the reactants.

(a) Consider the example of the formation of nitric oxide:

$$N_{2(g)} + O_{2(g)} \underset{\text{Exothermic}}{\overset{\text{Endothermic}}{\rightleftharpoons}} 2\,NO_{(g)} \qquad \Delta H = +90.25\ \text{Kjmol}^{-1}$$

Here, the forward reaction is endothermic and the reverse reaction is exothermic. In this case the forward reaction is favoured by rise in temperature and the reverse reaction is favoured by fall in temperature. Actually a temperature above 3000°C is used to increase the concentration of product.

(b) Consider the example of the formation of ammonia:

$$N_{2(g)} + 3\,H_{2(g)} \underset{\text{Endothermic}}{\overset{\text{Exothermic}}{\rightleftharpoons}} 2\,NH_{3(g)} \qquad \Delta H = -46.11\,\text{KJmol}^{-1}$$

Here, the forward reaction is exothermic and the reverse reaction is endothermic. In this case, the formation of ammonia is favoured by decrease in temperature. The increase in temperature shifts the equilibrium to the left direction and the ammonia will decompose to produce nitrogen and hydrogen gases. Thus the ammonia should be synthesized at low temperature. But at low temperature, the forward reaction is very slow and takes a long time to reach the equilibrium state. Therefore, a moderate temperature of 450-500°C is used to decrease time of equilibrium and a pressure of 200-300atm is used to prevent the decomposition of ammonia and get the sufficient amount of product (ammonia).

Keep in mind

A reaction which is exothermic in the forward direction will be endothermic in the reverse direction.

The effect of temperature on equilibrium mixture is summarized as, for an endothermic reaction, an increase in temperature shift the equilibrium to the right and increases the amount of product. As a result of this, the value of K_c increases. For an exothermic reaction, an increase in temperature shift the equilibrium to the left and increases the amount of reactant as a result of this the value of K_c decreases.

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Table 7.4: The Effect of Temperature Change on Equilibrium Position and K_c

Change to System	Direction of Change	Effect on Equilibrium Position	Effect on K_c
Increase in temperature for an endothermic reaction	Equilibrium shifts to the product side	Changes	Increases
Decrease in temperature for an endothermic reaction	Equilibrium shifts to the reactant side	Changes	Decreases
Increase in temperature for an exothermic reaction	Equilibrium shifts to the reactant side	Changes	Decreases
Decrease in temperature for an exothermic reaction	Equilibrium shifts to the product side	Changes	Increases

7.3 Industrial Application of Le-Chatelier's Principle (Synthesis of Ammonia by Haber's Process)

Ammonia is unusually valuable compound and is used in the manufacture of fertilizer such as urea, $(NH_2)_2CO$ and diammonium hydrogen phosphate $(NH_4)_2HPO_4$. It is also used in the manufacture of explosives such as TNT (trinitrotoluene), as a refrigerant and as a cleaning agent. It can also be used in the manufacture of polymers such as nylon and rayon. Chemists earlier discovered that the ammonia is produced by passing electric spark through a mixture of hydrogen and nitrogen gases.

$$N_{2(g)} + 3H_{2(g)} \xrightleftharpoons{\text{Electric spark}} 2\,NH_{3(g)}$$

But unluckily they failed to produce the maximum amount of ammonia because the reaction is reversible and its rate of forward reaction is very slow at room temperature. This problem was solved in 1912 by a German chemist Fritz Haber (1868-1934) who developed the process for the synthesis of ammonia. The Haber discovered that the adequate yield of ammonia is obtained by the reaction of hydrogen and nitrogen at about 450-500°C at a pressure of about 200-300 atmospheres in the presence of an iron catalyst. This method is known as Haber's process.

Fritz Haber (1868-1934)

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The experimental conditions must be adjusted to get the maximum yield of ammonia in a suitable time and at a reasonable price.

(i) Reactions occur more rapidly when the reactant concentrations are high. According to Le Chatelier's principle, at equilibrium, an increase in the concentration of any one reactant (N_2 or H_2) shifts the equilibrium to the right and increases the amount of product (NH_3).

(ii) According to Le Chatelier's principle, the high temperature increases the rate of reaction, but for exothermic reactions, it shifts equilibrium to the left and equilibrium constant value decreases.

(iii) The total number of moles of reactants is greater than the total number of moles of products; hence, according to Le Chatelier's principle, the greater amount of product is obtained at higher pressures. The pressure is, therefore, increased on the equilibrium mixture to shift the equilibrium to the right.

(iv) The high temperature does not favour the forward reaction; therefore, the increase in the reaction rate is achieved by the use of catalyst. The use of catalyst enhances the speed of reaction. Hence the synthesis of ammonia is carried out at a moderate temperature of about 450-500°C in the presence of an effective catalyst such as Fe_3O_4 mixed with KOH, SiO_2 and Al_2O_3. The catalyst is not effective below 400°C.

(v) The equilibrium mixture has nearly 35% ammonia by volume. The equilibrium mixture is cooled by refrigeration coils below 0°C (B.P. -33°C) until ammonia liquefies. The liquefied ammonia is then removed from the reaction vessel, which reduces the concentration of the product. The continual removal of ammonia shifts the equilibrium to the product side and increase the yield of ammonia. It also prevents the decomposition of ammonia into reactants.

Haber was awarded a Nobel Prize in chemistry in 1918 for the synthesis of ammonia. After nearly five years Carl Bosch (1874-1940), the engineer, solved the engineering problems and developed the industrial process on a large scale. The Haber process is, therefore, sometimes also called the Haber-Bosch process. The Bosch was awarded the Nobel Prize in 1931 for his work on high pressure reactions. All of the ammonia that is produced worldwide is synthesized by Haber-Bosch process. Industrial plants are usually situated near the reservoirs of natural gas. The natural gas is used to get hydrogen gas which is used in the production of ammonia.

$$CH_{4(g)} + H_2O_{(g)} \longrightarrow CO_{(g)} + 3H_{2(g)}$$

The nitrogen gas is obtained from air which is an endless source of nitrogen.

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7.4 Solubility Product and Precipitation Reactions

The process of solubility is very important. For example, we flavour foods because of the solubility of table salt and sugar in water. X-rays technicians give patients the suspension of barium sulphate to drink before taking X-ray of the large gastrointestinal tract (intestine and stomach). Barium sulphate is a sparingly soluble salt. It is a good absorber of X-rays and is used to improve the clarity of X-rays. The Ba^{2+} ions present in the $BaSO_4$ are toxic. Since it is very slightly soluble, hence it is taken orally without threat. The concept of solubility and solubility product helps doctors to reduce the prevalence of painful kidney stones, and tooth decay. It enables the doctors to make the ingestion of compounds safe. The concept of these reactions helps engineers prevent the formation of deposits in water processing and distribution systems.

Keep in mind

If the solubility of a substance is greater than 1 gram per 100 gram of water it is said to be soluble. If the solubility of a substance is less than 0.1 gram, then the substance is said to be insoluble. If the solubility ranges between these two limits, the substance is said to be sparingly soluble. The insoluble substances are actually very slightly soluble in water.

Some ionic compounds are soluble (NaCl, $NaNO_3$ etc.) and the others are slightly soluble or insoluble in water.

For very slightly soluble salts (AgCl, $PbCl_2$, PbI_2, $BaSO_4$), the dissociation is very small and concentration of salt may be considered as constant. For example when $BaSO_4$, a slightly soluble salt, is placed in water, it dissolves until a saturated solution is obtained, and then equilibrium is established between the ions and solid $BaSO_4$ in the solution.

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

According to law of mass action,

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

Where,

K_c is equilibrium constant and $[Ba^{2+}]$, $[SO_4^{2-}]$, $[BaSO_4]$ are concentrations of Ba^{2+}, SO_4^{2-} and $BaSO_4$ in the solution.

As the salt is slightly soluble, the concentration of undissolved salt, $[BaSO_4]$ remains same.

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Therefore, $[BaSO_4] = K$

Thus,

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

or $$K_c . K = [Ba^{2+}][SO_4^{2-}]$$

or $$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

K_{sp} is the product of two constants K_c and K and is known as solubility product. The product of molar concentrations of positive and negative ions in equilibrium state with solid salt at a given temperature is called solubility product. It is represented by K_{sp}. The value of K_{sp} shows how much salt is soluble in water.

Solubility product is temperature dependent and increases by increase in temperature.

Applications of Solubility Product

Prediction of Precipitation

Many environmental and biological processes involve the precipitation of slightly soluble ionic compounds. The calcium oxalate, a slightly soluble salt, precipitates out in the kidney and forms a kidney stone. A common problem for chemists is to determine the direction in which a reaction proceeds to reach equilibrium. For example, will the precipitation reaction of $BaSO_4$ proceeds in the forward direction or in the reverse direction or the reaction is at equilibrium when we mix the aqueous solutions of $BaCl_2$ and Na_2SO_4? To answer this question we need to calculate ionic product and then compare it with K_{sp}. There are three possible relationships between ionic product and K_{sp} that are as follows:

Keep in mind

Reaction that occurs when cations and anions of two different aqueous solutions combine to form an insoluble solid (precipitate) is called precipitation reaction.

i) If K_{sp} > ionic product, solution is unsaturated and precipitation does not occur. In this case more solid dissolves and increasing the ionic concentration until ionic product = K_{sp}.

ii) If K_{sp} < ionic product, the solution is supersaturated and precipitation occurs, reducing ionic concentrations until ionic product = K_{sp}.

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iii) If K_{sp} = ionic product, solution is saturated and precipitation does not occur because the reaction is at equilibrium.

The solubility and Solubility Product

The solubility and the solubility product of a slightly soluble salt are not the same. Solubility is expressed in g/dm^3. It can also be expressed in mol/dm^3. The solubility product is unit less.

The solubility is temperature dependent. It can be increased for most of the ionic compounds, by increasing temperature. The solubility of ionic compound is determined by experiments, and by the use of solubility data, the value of solubility product is calculated. The values of solubility can also be calculated from solubility product values. Solutes with very low solubility have very small solubility product values.

Table 7.5: Solubility product constant values for some ionic compounds at 25°C

Name	Formula	K_{sp}
Aluminum hydroxide	$Al(OH)_3$	2.0×10^{-32}
Barium sulphate	$BaSO_4$	1.5×10^{-9}
Cadmium sulphide	CdS	8.0×10^{-27}
Calcium carbonate	$CaCO_3$	8.7×10^{-9}
Calcium fluoride	CaF_2	4.0×10^{-11}
Calcium hydroxide	$Ca(OH)_2$	1.3×10^{-6}
Calcium phosphate	$Ca_3(PO_4)_2$	1.3×10^{-32}
Calcium sulphate	$CaSO_4$	6.1×10^{-5}
Iron (II) sulphide	FeS	6.0×10^{-18}
Lead (II) chromate	$PbCrO_4$	2.0×10^{-16}
Silver bromide	$AgBr$	5.0×10^{-13}
Silver chloride	$AgCl$	1.6×10^{-10}
Zinc sulphide	ZnS	3.0×10^{-23}

Example 7.4

The solubility product constant value (K_{sp}) for ZnS is 3.0×10^{-23}. Calculate its solubility at 25°C.

Solution:

The equation for the dissociation of ZnS is:

$$ZnS_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + S^{2-}_{(aq)}$$

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Initial concentrations (M): 0 0
Equilibrium concentrations (M): s s

The expression for the solubility product constant is:

$K_{sp} = [Zn^{2+}][S^{2-}]$

$3.0\times10^{-23} = (s)(s)$

$3.0\times10^{-23} = s^2$

By taking under root on both sides,

$s = \sqrt{3.0\times10^{-23}}$

$s = 5.48\times10^{-12}\,M$

Practice Exercise 4:

Calculate the solubility of $CaCO_3$ at room temperature. The solubility product value of $CaCO_3$ is 8.7×10^{-9}.

Example 7.5

Calculate the solubility product constant, K_{sp} value for $BaSO_4$. The solubility of $BaSO_4$ at room temperature is 1.03×10^{-5} M.

Solution:

Value of K_{sp} for $BaSO_4$ = ?

Solubility of $BaSO_4$ = 1.03×10^{-5} M

The solubility equation for $BaSO_4$ is:

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

Initial concentrations (M): 0 0

Equilibrium concentrations (M): 1.03×10^{-5} 1.03×10^{-5}

The solubility product expression for solubility product constant is:

$K_{sp} = [Ba^{2+}][SO_4^{2-}]$

$K_{sp} = (1.03\times10^{-5})(1.03\times10^{-5})$

$K_{sp} = 1.06\times10^{-10}$

Practice Exercise 5:

The solubility of PbF_2 is 2.25×10^{-3} mol/dm^{-3} at room temperature. What is the value of solubility product constant for PbF_2?

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7.5 Common Ion Effect

The process in which the degree of ionization of a weak electrolyte is decreased by the addition of a strong electrolyte having a common ion is called common ion effect.

This process is used to decrease the solubility of slightly soluble electrolyte (salt) by the addition of strong electrolyte (more soluble electrolyte) having a common ion. For example:

Consider the ionization of less soluble salt:

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}$$

According to law of mass action,

$$K_c = \frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_3]}$$

When $CaCl_2$, a more soluble salt, is added to the solution of $CaCO_3$, Then it will increase the concentration of Ca^{2+} ion (common ion) and it will shift the equilibrium from right to left, hence $CaCO_3$ precipitates out from the solution.

$$CaCl_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$$

$$CaCO_{3(s)} \longleftarrow Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}$$

This is according to Le-Chatelier's Principle.

Consider the ionization of moderately soluble $KClO_4$ in water,

$$KClO_{4(s)} \rightleftharpoons K^{+}_{(aq)} + ClO^{-}_{4(aq)}$$

According to law of mass action,

$$K_c = \frac{[K^+][ClO_4^-]}{[KClO_4]}$$

When more soluble salt of KCl is added to the saturated solution of less soluble $KClO_4$, then as a result of this the concentration of K^+ ion (common ion) increases, it will shift equilibrium from right to left, hence $KClO_4$ precipitates out from the solution.

$$KCl_{(s)} \rightleftharpoons K^{+}_{(aq)} + Cl^{-}_{(aq)}$$

$$KClO_{4(s)} \longleftarrow K^{+}_{(aq)} + ClO^{-}_{4(aq)}$$

This is according to Le-Chatelier's Principle and is known as common ion effect.

Keep in mind

Electrolyte is a compound that conducts electricity either in molten state or in an aqueous solution. Those compounds such as NaCl, KOH, which ionize almost completely in the solution are called strong electrolytes while those compounds such as $CaCO_3$, CH_3COOH, which are ionized partially in the dilute solutions are called weak electrolytes.

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Summary of Facts and Concepts

- Dynamic chemical equilibrium occurs when the rates of forward and reverse reactions are equal and the reactants and products concentrations do not change with time.
- Chemical equilibrium in which all the reactants and products are in the same phase is called homogeneous chemical equilibrium whereas the chemical equilibrium in which all the reactants and products are not in the same phase is called heterogeneous chemical equilibrium.
- According to Law of Mass Action, the rate of forward reaction is directly proportional to the product of active masses of the reactants.
- The ratio of the molar concentrations of the products divided by the molar concentrations of reactants, each raised to powers equal to their coefficients is called equilibrium constant. The equilibrium constants are shown as K_c, K_p, K_n, and K_x. The equilibrium constants of reactions are used to determine the direction and extent of the chemical reaction.
- The reaction quotient, Q_c is defined in the same way as equilibrium constant except that the concentrations in the reaction quotient expression are not necessarily equilibrium concentrations.
- If $Q_c < K_c$, then reaction will proceed in forward direction to attain the equilibrium. If $Q_c > K_c$, then reaction will proceed in reverse direction to attain the equilibrium. If $Q_c = K_c$, then the system is at equilibrium.
- If K_c is very large ($K_c > 10^3$), the equilibrium mixture is mostly products and if K_c is very small ($K_c < 10^{-3}$), the equilibrium mixture is mostly reactants. If K_c is in the range of 10^{-3} to 10^{-3}, then both the forward and reverse reactions take place almost to an equal extent.
- According to Le Chatelier's principle, when a change in concentration, pressure, and temperature is applied to a system at equilibrium, the equilibrium is shifted in the direction that counteracts (minimizes) the effect of the change.
- The value of K_c is temperature dependent. Its value increases for an endothermic reaction and decreases for an exothermic reaction when the temperature increases.
- A catalyst does not affect the equilibrium constant or the equilibrium concentrations. However it increases the rate of chemical reaction by decreasing activation energy at which chemical equilibrium is reached.

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- The product of molar concentrations of positive and negative ions in equilibrium state with solid salt at a given temperature is called solubility product constant. It reflects the solubility of a compound. The greater the solubility products value of a compound, the greater the solubility of compound.
- The process of common ion effect is used for the purification of some compounds like NaCl, in the preparation of buffers and in qualitative analysis.

Questions and Problems

Q.1. Four answers are given for each question. Select the correct one:

i) The reactions that occur only in one direction are known as:

(a) Reversible reaction (b) irreversible reaction
(c) spontaneous reaction (d) non-spontaneous reaction

ii) The reaction will proceed in the reverse direction when

(a) $Q_c < K_c$ (b) $Q_c > K_c$
(c) $Q_c = K_c$ (d) $Q_c = (K_c)^3$

iii) Which of the following change will favour the formation of adequate amount of ammonia at equilibrium in the reaction given below:

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

(a) By decreasing pressure (b) by increasing pressure
(c) by adding ammonia (d) by removing nitrogen

iv) A dynamic equilibrium is disturbed by

(a) Concentration change (b) pressure change
(c) temperature change (d) all of these

v) What is the unit of K_c for the reaction:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

(a) $mol\ dm^{-3}$ (b) $mol^{-1}dm^{-3}$
(c) $mol^{-1}dm^{+3}$ (d) $mol^{2}dm^{-6}$

vi) When the total number of moles of reactants and products are equal then the equilibrium state is **NOT** disturbed by:

(a) Concentration change (b) pressure change
(c) temperature change (d) catalyst

vii) Exothermic reactions are favoured in the forward direction by

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(a) Decrease in temperature (b) increase in temperature
(c) adding a catalyst (d) removal of reactant

viii) When HCl is added to the aqueous solution of NaCl, the ionization of NaCl:

(a) Increases (b) decreases
(c) remains same (d) first decreases and then increases

ix) Precipitation occurs when

(a) K_{sp} < ionic product (b) K_{sp} > ionic product
(c) K_{sp} = ionic product (d) $\sqrt{K_{sp}}$ < ionic product

x) The forward reaction almost near completion if the value of K_c is:

(a) Very small (b) very large
(c) unity (d) zero

Q.2. Fill in the blanks with suitable words given in the brackets:

i) The reactions in which products are reconverted into reactants are called _____. (reversible/irreversible)

ii) All chemical equilibria are _____. (static/dynamic)

iii) Law of mass action was given by _____ in 1864. (Bosch / Guldberg)

iv) For the reaction, $CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$, the increase in pressure favours the _____ of products. (decomposition / formation)

v) If K_{sp} is _____ to / than ionic product, the solution is saturated. (greater / equal)

vi) The removal of the amount of any one reactant from the container at equilibrium will shift the system _____. (to the left/to the right)

vii) Solutes with very high solubility have very _____ solubility product values. (small/high)

viii) For endothermic reactions, the equilibrium constant value _____ by increase in temperature. (increases/decreases)

ix) Catalyst _____ the activation energy of chemical reaction. (decreases/increases)

x) Haber was awarded a Nobel Prize in chemistry in _____. (1931/1918)

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Q.3. Label the following statement as True or False:

i) The concentrations of products and reactants remain constant at equilibrium.

ii) The same equilibrium constant value is obtained whether the reaction is started from the reactants side or from the products side.

iii) The concentrations of reactants are equal to the concentrations of products at equilibrium.

iv) The reaction is at equilibrium when Q_c is equal to K_c ($Q_c = K_c$).

v) When the number of moles of reactants and products are equal in the balanced chemical equation, then $K_c = K_p = K_x = K_n$.

vi) A catalyst does not change the equilibrium constant but it changes the equilibrium position of the reaction.

vii) The NaCl can be purified by passing HCl gas through its saturated solution by common ion effect.

viii) Molar solubility is the number of moles of solute dissolved in one liter of solvent.

ix) As the reaction proceeds in the forward direction, the concentration of product goes on decreasing and that of reactant goes on increasing.

x) Haber solved the engineering problems for the synthesis of ammonia.

Q.4: Write the equilibrium constant expressions for K_c for each of the following processes:

i) $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

ii) $2\,CO_{(g)} + O_{2(g)} \rightleftharpoons 2\,CO_{2(g)}$

iii) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

iv) $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$

v) $CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$

Q.5: What is the value of K_p at 1050°C if K_c value is 2.30×10^{22} for the following reaction?

$2\,CO_{(g)} + O_{2(g)} \rightleftharpoons 2\,CO_{2(g)}$

Q.6: Write the balanced chemical equation corresponding to the equilibrium constant expressions given below:

a) $K_c = \dfrac{[N_2O_5][O_2]}{[N_2O_4][O_3]}$

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b) $K_c = \frac{[NH_4Cl]}{[NH_3][HCl]}$

c) $K_c = \frac{[CH_4]^2[Cl_2]^3}{[CHCl_3]^2[H_2]^3}$

Q.7: How will you predict the direction and extent of a chemical reaction with the help of a chemical equilibrium expression?

Q.8: Define reaction quotient. What is the difference between equilibrium constant and reaction quotient?

Q.9: What does it mean when (a) $Q_c > K_c$ (b) $Q_c < K_c$ (c) $Q_c = K_c$?

Q.10: What is dynamic chemical equilibrium? Explain why the concentrations of reactants and products are not necessarily the same at equilibrium?

Q.11: What are homogeneous and heterogeneous equilibria? Give two examples for each.

Q.12: Explain, what is the law of mass action? Derive the equilibrium constant expression for a general reversible reaction.

Q.13: What is the characteristics of equilibrium constant?

Q.14: How will you relate the equilibrium expression in terms of concentration, partial pressure, number of moles and mole fraction?

Q.15: Explain Le Chatelier's principle. How this principle help chemists to maximize the yield of products. Explain industrial applications of Le-Chatelier's Principle using Haber's Process as an example.

Q.16: Lime, $CaO_{(s)}$ is prepared by heating lime stone, $CaCO_{3(s)}$ to decompose it.

a) Write the balanced chemical equation for the reaction.

b) Predict the sign of enthalpy change for the reaction.

c) Is the reaction favoured by increase in temperature or decrease in temperature.

Q.17: What is the effect of the following changes on the value of equilibrium constant for the exothermic gas phase reaction (a) removal of product (b) addition of product (c) increase in the pressure (d) increase in the volume (e) decrease in the temperature (f) addition of a catalyst?

Q.18: What is the effect of the following changes at equilibrium if we:

a) increase the concentration of reactants in a reaction mixture

b) increase the concentration of products in a reaction mixture

c) decrease the pressure of a reaction mixture if the product side has greater number of moles of gases than reactant side

(d) increase the temperature of an endothermic reaction mixture?

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Q.19: What is the effect of catalyst on:

(a) the rate of chemical reaction

(b) the position of equilibrium in a chemical reaction

(c) the value of equilibrium constant?

Q.20: What is the significance of catalyst in chemistry?

Q.21: Describe the effect of increasing pressure on each of the following reacting systems at equilibrium.

i) $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$

ii) $H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2\,HCl_{(g)}$

iii) $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$

Q.22: Define and explain common ion effect giving suitable examples.

Q.23: What is a solubility product constant? Determine the solubility product expression for slightly soluble AgBr, $Ca(OH)_2$ and $PbCrO_4$.

Q.24: Answer the following questions:

a) There is only one value of the equilibrium constant for a particular system at a particular temperature, how?

b) Why the value of equilibrium constant does not depend on the initial concentrations of reactants and products mixed together?

c) Why the equilibrium vapour pressure of a liquid increases with increasing temperature?

d) Can the equilibrium constant value ever be zero or negative? Explain.

e) How are rates of forward and reverse reactions related in a system at chemical equilibrium?

f) The solubility of $KClO_4$ is decreased by adding KCl to its saturated solution, how?

Q.25: The equilibrium concentrations of hydrogen, iodine, and hydrogen iodide are 0.530M, 0.033M, and 0.934M respectively at 450°C. What is the value of K_c for the following reaction?

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2\,HI_{(g)}$$

Q.26: Calculate the concentration of PCl_5 at 250°C. The equilibrium concentration for both PCl_3 and Cl_2 gases are 0.005M. The value of K_c for the reaction is 1.2×10^{-2}.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

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Q.27: $Ca(OH)_2$ is a slightly soluble base and has a K_{sp} value equal to 1.3×10^{-6}. Calculate its solubility at room temperature.

Q.28: AgCl is a sparingly soluble salt and has a K_{sp} value equal to 1.7×10^{-10}. Calculate its solubility at 25°C.

Q.29: The solubility of PbI_2 at 25°C is 0.55 g/dm^3. What is the solubility product constant value at this temperature?

Q.30: The solubility of CaF_2 at 25°C is 8.60 g/100g of water. What is the solubility product constant value at this temperature?

Q.31: Consider the reaction

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad \Delta H = +92.5 kJ/mol$$

What is the effect on the concentrations of reactants and products if we:

a) Increase the pressure
b) increase the temperature
c) add a catalyst
d) add a neon gas.

Q.32: Consider the gas phase reaction:

$$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)} \qquad \Delta H = -283.0 kJ/mol$$

i) What is the effect of the pressure change on this reaction?
ii) What is the effect of the temperature change on this reaction?
iii) What is the effect of the concentration change on this reaction?

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Chapter # 08

Acids, Bases and Salts

Major Concepts

8.1 Acidic, Basic and Amphoteric Substances.
8.2 Bronsted-lowry Definitions of Acids and Bases
8.3 Relative Strength of Acids and Bases
8.4 Expressing the Strength of Acids and Bases
8.5 Lewis Definitions of Acids and Bases
8.6 Buffers Solutions and their Applications
8.7 Salt Hydrolysis

Learning Outcomes

The students will be able to:

- Define Bronsted and Lowery concepts for acids and bases(Remembering)
- Define salts, conjugate acids and conjugate bases. (Remembering)
- Identify conjugate acid-base pairs of Bronsted-Lowery acid and base(Analyzing)
- Explain ionization constant of water and calculate pH and pOH in aqueous medium using given K_w values. (Applying)
- Use the extent of ionization and the acid dissociation constant, K_a, to distinguish between strong and weak acids. (Applying)
- Use the extent of ionization and the base dissociation constant, K_b, to distinguish between strong and weak bases. (Applying)
- Define a buffer, and show with equations how a buffer system works. (Applying)
- Make a buffered solution and explain how such a solution maintains a constant pH even with the addition of small amounts of strong acid or strong base. (Understanding)
- Use the concept of hydrolysis to explain why aqueous solutions of some salts are acidic or basic. (Applying)
- Use concept of hydrolysis to explain why the solution of a salt is not necessarily neutral. (Understanding)
- Define and explain leveling effect. (Understanding)

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Introduction

Acids, bases and salts are very important and common chemical compounds. They are used in the home and in the chemical industries. For example, vinegar contains acetic acid that is common in many foods and cleaning products. Citrus fruits such as lemons, oranges and tomatoes juices contain citric and ascorbic acids. Apples contain malic acid, and grape juice contains tartaric acid. Dairy products such as sour milk, yogurt and cheese contain lactic acid. Carbonated beverages (soft drinks) contain carbonic acid and may also contain benzoic acid, citric acid and phosphoric acid. Gastric juice contains hydrochloric acid which is essential to digestion and is secreted by the lining of our stomachs in a significant quantity of 1.2-1.5 L/day. The sulphuric acid is used in the lead storage batteries and is also used in the manufacture of fertilizers, explosives, dyes and glues. Bacteria in our mouths yield acids that can dissolve tooth enamel to produce cavities. On the other hand, the sodium hydroxide is a base and is used in the manufacture of soaps, detergents and in the manufacture of other compounds. The ammonia is also a base and is present in many household cleaners. The suspension of magnesium hydroxide also known as milk of magnesia is used as an antacid. Aluminum hydroxide and sodium bicarbonate are also bases and are also used as antacids. The sodium carbonate also known as washing soda is a common example of base and is used for washing purposes.

Keep in mind

Never check the taste of acids in the laboratory because some acids are very corrosive and some are poisonous.

Salts are formed when acids react with bases. Some well-known examples of salts are sodium chloride, sodium nitrate, and potassium iodide. Sodium chloride is not only one of many hundreds of salts that is used for seasoning and preserving foods.

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Preservatives in Food Products and Allergic Reactions in People:

A preservative is a naturally occurring or synthetically produced substance that is added to food or other organic materials to prevent decomposition or fermentation. Preservatives may either be antimicrobial, antioxidants or anti-enzymatic. Antimicrobial preservatives inhibit the growth of bacteria, yeast and molds. Antioxidant preservatives inhibit the oxidation of food constituents. They keep foods from becoming rancid, browning, or developing black spots. Anti-enzymatic preservatives block the enzymatic processes such as ripening of fruits and vegetables occurring in foodstuffs even after harvest. Salt, sugar and vinegar and natural spices are also considered as food preservatives. However, the main concerns of using food preservatives are mostly related to chemical substances and artificial ingredients.

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Some people are sensitive to particular food preservatives and may have reactions like hives, diarrhoea, digestive disorders and respiratory problems such as asthma. Most of the food preservatives are safe.

8.1 Acidic, Basic and Amphoteric Substance

Acids and bases were first recognized by their characteristic properties. The word acid has been taken from Latin word "acidus", which means "sour". Acids are compounds whose water solutions taste sour, turn blue litmus red, and react with bases to form salts. The bases are the compounds that taste bitter, feel slippery, turn red litmus blue and react with acids to form salts. Many theories have been proposed to define an acid and a base. One of the earliest, most significant of these theories was Arrhenius theory of acids and bases. In 1887, Svante Arrhenius (1859-1927), a Swedish chemist, stated that ***acids*** are substances that produce hydrogen ions (H^+ ions) and anions when dissolved in water while ***bases*** are substances that produce hydroxide ions (OH^- ions) and cations when dissolved in water. For example, HCl is an Arrhenius acid because it produces hydrogen ions and anions (Cl^- ions) when dissolved in water.

Svante Arrhenius (1859-1927)

$$HCl_{(g)} \xrightarrow{H_2O} H^+_{(aq)} + Cl^-_{(aq)}$$

The aqueous solution of HCl is called hydrochloric acid.

Keep in Mind

The hydrogen ion is very reactive and cannot exist freely in the aqueous solutions as it combines with solvent water molecule to produce hydronium ion.

$$H^+_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)}$$

The NaOH is an Arrhenius base because it produces hydroxide ions (OH^- ions) and cations (Na^+ ions) when dissolved in water.

$$NaOH_{(s)} \xrightarrow{H_2O} Na^+_{(aq)} + OH^-_{(aq)}$$

The neutralization of an acid by a base produces water and salt. Salt is an ionic compound that is composed of the cation from the base and the anion from the acid.

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

Arrhenius observed that process of neutralization occurs when the H^+ ion from the acid and OH^- ion from the base reacts to produce water.

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$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$$

The substances which have both the properties of acids and bases are called amphoteric substances. An amphoteric substance acts as an acid when combined with strong base and as a base when combined with strong acid. For example, water shows basic properties by reacting with HCl.

$$\underset{\text{Acid}}{HCl_{(aq)}} + \underset{\text{Base}}{H_2O_{(l)}} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$$

Here, H_2O accepts a proton from the HCl molecule in the forward reaction. It also shows acidic properties by reacting with NH_3.

$$\underset{\text{Base}}{NH_{3(aq)}} + \underset{\text{Acid}}{H_2O_{(l)}} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

Here, H_2O donates a proton to NH_3 molecule in the forward reaction. The amphoteric substances may be either molecules or ions. For example, bicarbonate ion of baking soda is amphoteric.

$$\underset{\text{Acid}}{HCO^-_{3(aq)}} + \underset{\text{Base}}{OH^-_{(aq)}} \rightleftharpoons CO^-_{3(aq)} + H_2O_{(l)}$$

Here, the HCO_3^- ion donates a proton to a base and acts as an acid.

$$\underset{\text{Base}}{HCO^-_{3(aq)}} + \underset{\text{Acid}}{H_3O^+_{(aq)}} \rightleftharpoons H_2CO_{3(aq)} + H_2O_{(l)}$$

Here, the HCO_3^- ion accepts a proton from an acid and acts as a base.

The acidic and basic character of amphoteric substance depends on the other substance to which it reacts.

Keep in mind

Soluble bases are known as alkalis. All the alkalis are bases but all the bases are not alkalis. Most bases are water insoluble.

8.2 Bronsted-Lowry Definitions of Acids and Bases

8.2.1 Proton Donors and Acceptors

Although Arrhenius theory is widely used but it failed to answer the question why compounds such as ammonia form a basic solution when dissolved in water although it does not contain hydroxide ion. The Arrhenius definition also does not explain those acid-base reactions which occur in non-aqueous solvents and those which occur in gas phase where no solvent is present. A more general definition of acids and bases was proposed

Bronsted (1879-1947) Thomas Lowry (1874-1936)

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by a Danish chemist Johannes Bronsted and an English chemist Thomas Lowry in 1923. According to the Bronsted-Lowry theory, an acid is a substance that donates a proton (H^+ ion) to another substance, and a base is a substance that accepts the proton from another substance. In short, an acid is proton donor and a base is proton acceptor and acid-base reactions are proton transfer reactions. For example, HCl is a Bronsted-Lowry acid because its molecule donates a proton to water molecule when dissolved in water.

$$HCl_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

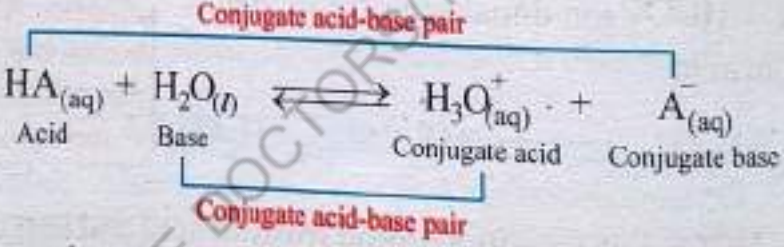
On the other hand, water acts as Bronsted-Lowry base, because its molecule accepts a proton from HCl molecule. Consider the reaction between gaseous HCl and ammonia.

$$HCl_{(g)} + NH_{3(g)} \longrightarrow NH_4^+ + Cl^- \longrightarrow NH_4Cl_{(s)}$$

In the above equation, the HCl donates proton to NH_3 and acts as Bronsted-Lowry acid while NH_3 accepts proton from HCl and acts as the Bronsted-Lowry base. This is gas phase reaction and no solvent is required.

8.2.2 Conjugate Acid-Base Pairs

The dissociation of an acid can best be represented by the general reaction given below:



In the forward reaction, the HA donates protons to water and acts as a Bronsted-Lowry acid and water accepts proton form HA and acts as a Bronsted-Lowry base. In the reverse reaction, the H_3O^+ acts as an acid and A^- acts as a base. An acid and a base such as HA and A^- that differ only by a single proton are called conjugate acid-base pair. Every acid has a conjugate base that is formed by loss of proton from the acid. For example, OH^- is a conjugate base of H_2O and A^- is a conjugate base of HA. Every base has a conjugate acid that is formed by adding the proton to the base. Thus, H_3O^+ is the conjugate acid of H_2O, and HA is the conjugate acid of A^-. We may also say that a conjugate acid is formed by ionization of a base and a conjugate base is formed by the ionization of an acid.

Consider the dissociation of HCl in water:

$$\underset{\text{Acid}}{HCl_{(aq)}} + \underset{\text{Base}}{H_2O_{(l)}} \longrightarrow \underset{\substack{\text{Conjugate}\\\text{Acid}}}{H_3O^+_{(aq)}} + \underset{\substack{\text{Conjugate}\\\text{Base}}}{Cl^-_{(aq)}}$$

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In this reaction HCl acts as an acid because it has donated proton and H_2O acts as a base because it has accepted proton. For any given acid-base pair, the acid always has one more hydrogen atom and one unit fewer negative charges than the base. On the other hand, the base has one fewer hydrogen atom and one unit more negative charge than the acid.

8.3 Relative Strengths of Acids and Bases

The tendency of an acid to give hydrogen ion is called strength of an acid. The tendency of a base to accept hydrogen ion is called strength of a base. Strong acids and bases are strong electrolytes which are assumed to ionize completely in water. Weak acids and bases are weak electrolytes which ionize only to a limited extent in water. For example, HCl is a strong acid and CH_3COOH is a weak acid because HCl is almost 100% ionized and CH_3COOH is about 1% ionized in water. The strength of acids and bases can be determined by passing electricity through their solutions. The aqueous solutions of strong acids and strong bases are good conductors of electricity and the aqueous solutions of weak acids and bases are not the good conductors of electricity.

The strength of conjugate acids and bases are related to the parent acids and bases as:

a) The stronger the acid, the weaker is its conjugate base and vice versa.

b) The weaker the base, the stronger is its conjugate acid and vice versa.

Consider the ionization of HCl in water:

$$\underset{\text{Stronger acid}}{HCl_{(aq)}} + \underset{\text{Weaker base}}{H_2O_{(l)}} \longrightarrow \underset{\text{Stonger acid}}{H_3O^+_{(aq)}} + \underset{\text{Weaker base}}{Cl^-_{(aq)}}$$

HCl is a strong acid that completely donates its protons to water. The chloride ion (the conjugate base of HCl) is an extremely weak base and has very little tendency to gain proton from water. Thus the strongest acids have the weakest conjugate bases.

Consider another example of the ionization of ammonia in water:

$$\underset{\text{Weaker base}}{NH_{3(aq)}} + \underset{\text{Weaker acid}}{H_2O_{(l)}} \longrightarrow \underset{\text{Stronger acid}}{NH^+_{4(aq)}} + \underset{\text{Stronger base}}{OH^-_{(aq)}}$$

Ammonia is a weak base and its conjugate base (NH_4^+ ion) is a strong acid.

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The NH_4^+ ion (the conjugate acid of NH_3) is a strong acid and has greater tendency to donate proton to OH^- ion. Thus the weakest bases have the strongest conjugate acids.

Table 8.1: Relative Strengths of Acids and Bases

	Acid	Name	Base	Name	
Strongest acids	$HClO_4$	Per chloric acid	ClO_4^-	Perchlorate ion	Weakest bases
	HCl	Hydrochloric acid	Cl^-	Chloride ion	
	H_2SO_4	Sulphuric acid	HSO_4^-	Hydrogen sulphate ion	
	HNO_3	Nitric acid	NO_3^-	Nitrate ion	
	H_3O^+	Hydronium ion	H_2O	Water	
	HSO_4^-	Hydrogen suphate ion	SO_4^{2-}	Sulphate ion	
	H_3PO_4	Phosphoric acid	$H_2PO_4^-$	Dihydrogen phosphate ion	
	HNO_2	Nitrous acid	NO_2^-	Nitrite ion	
	HF	Hydrofluoric acid	F^-	Fluoride ion	
	CH_3COOH	Acetic acid	CH_3COO^-	Acetate ion	
	H_2CO_3	Carbonic acid	HCO_3^-	Bicarbonate ion	
	NH_4^+	Ammonium ion	NH_3	Ammonia	
	HCN	Hydrocyanic acid	CN^-	Cyanide ion	
	HCO_3^-	Bicarbonate ion	CO_3^{2-}	Carbonate ion	
	H_2O	Water	OH^-	Hydroxide ion	
	NH_3	Ammonia	NH_4^+	Ammonium ion	
Weakest acids	OH^-	Hydroxide ion	H_2O	water	Strongest bases

8.4 Expressing the Strength of Acids and Bases

The strength of an acid or a base is expressed in terms of hydrogen and hydroxide ions concentrations, pH and pOH scales, K_a, K_b, pK_a, and pK_b values.

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8.4.1 Ionic Product of Water (K_w)

Even highly purified water is observed to conduct very small electricity which shows the presence of very small concentration of ions. These ions are produced by the auto-ionization or self-ionization of water molecules.

$$\underset{\text{Acid}}{H_2O_{(l)}} + \underset{\text{Base}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{Acid}}{H_3O^+_{(aq)}} + \underset{\text{Base}}{OH^-_{(aq)}}$$

As water is amphoteric, hence it acts both as a proton donor and proton acceptor. The ionization reaction of water can also be written as:

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

Here pure water ionizes into H^+ and OH^-. According to law of mass action, the equilibrium constant for the reaction is:

$$K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

Since water is in excess, and very few of its molecules undergo ionization, so its concentration remains constant. Therefore:

$$K_c.[H_2O] = [H^+][OH^-] \quad \text{or}$$

$$K_w = [H^+][OH^-]$$

The equilibrium constant K_w is called ionic product of water and its value at 25°C is always $1.0 \times 10^{-14} mol^{-2} dm^{-6}$ obtained by multiplying together the molar concentrations of H^+ ions and OH^- ions present in pure water at room temperature.

$$\text{Ionic product of water } (K_w) = [H^+][OH^-]$$
$$= (10^{-7} mol\, dm^{-3})(10^{-7} mol\, dm^{-3})$$
$$= 1.0 \times 10^{-14} mol^2 dm^{-6}$$

K_w is temperature dependent. Its value increases with increase in temperature and decreases with decrease in temperature and has a constant value at constant temperature.

Table 8.2: Value of K_w at different temperatures

Temperature (°C)	K_w value ($mol^2 dm^{-6}$)
0	1.2×10^{-15}
10	3.0×10^{-15}
25	1.0×10^{-14}
50	5.3×10^{-14}

The relative concentrations of H^+ and OH^- ions indicates the acidic, neutral, or basic character of the aqueous solution. There are three possibilities for all aqueous solutions.

a) An aqueous solution in which the concentration of H^+ ion is equal to OH^- ion is called neutral solution. For neutral solution, the $[H^+]=[OH^-]=10^{-7} mol\, dm^{-3}$.

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b) An aqueous solution in which the concentration of H^+ ion is greater than OH^- ion is called acidic solution. For acidic solution, the $[H^+] > [OH^-]$. In this solution $[H^+] > 10^{-7}$ mol dm^{-3} and $[OH^-] < 10^{-7}$ mol dm^{-3}.

c) An aqueous solution in which the concentration of H^+ ion is less than that of OH^- ion is called basic solution. For basic solution, the $[H^+] < [OH^-]$. In this solution $[H^+] < 10^{-7}$ mol dm^{-3} and $[OH^-] > 10^{-7}$ mol dm^{-3}.

When acid is added to water then $[H^+] > [OH^-]$ and when a base is added to water then $[H^+] < [OH^-]$.

Example 8.1

The concentration of H^+ ions in an orange juice is 5.5×10^{-4} M. Calculate the concentration of OH^- ions; classify the solution as acidic, basic or neutral.

Solution:

$[H^+] = 5.5 \times 10^{-4}$ M

$[OH^-] = ?$

$K_w = [H^+][OH^-]$

or $$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{5.5 \times 10^{-4}} = 1.82 \times 10^{-11} \text{ M}$$

The solution is acidic because the $[OH^-] < 10^{-7}$ M.

Practice Exercise 1:

The concentration of OH^- ions in gastric juice is 1.0×10^{-13} M. Calculate the concentration of H^+ ions; classify the solution as acidic, basic or neutral.

8.4.2 pH, pOH and pK_w

The molar concentrations of hydrogen ions and hydroxide ions are very small in aqueous solutions. Their concentrations generally range from 10 mol dm^{-3} to 10^{-15} mol dm^{-3}. It is, therefore, more convenient to express these concentrations on a logarithm scale, known as the pH scale.

The concept of pH scale was first introduced by the Danish chemist Soren Sorenson (1868 - 1939) in the year 1909 as easy and convenient way for expressing hydrogen ion concentration (acidity and basicity).

The pH of solution is defined as:

The negative logarithm of hydrogen ion concentration in an aqueous solution is called pH.

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

For example, the pH of pure water is 7 and that of apples is 3.1

The pOH of solution may be defined as:

The negative logarithm of hydroxide ion concentration in an aqueous is called pOH.

$pOH = -\log[OH^-]$

For example, the pOH of pure water is 7 and that of apples is 10.9

The pH values range from 0 to 14. However, solutions of negative pH and having pH > 14 are also known.

For Acidic solution the pH value is less than 7(pH < 7).

For Neutral solution the pH value is equal to 7(pH = 7).

For Basic solution the pH value is greater than 7(pH > 7).

Keep in mind

The pH scale is basically the reverse of pOH scale.

The pK_w is the negative logarithm of K_w in the solution.

$pK_w = -\log K_w$

The numerical value of K_w is 1.0×10^{-14} and its pK_w value can be calculated as:

$pK_w = -(\log 1.0 \times 10^{-14})$

$= -(-14)$

$= 14$

The pK_w value can also be calculated as:

$pK_w = pH + pOH = 7 + 7 = 14$

Table 8.3: The pH and pOH Values for a Range of $[H^+]$ and $[OH^-]$ Concentrations

$[H^+]$	pH		$[OH^-]$	pOH	
10^{-14}	14	Decreasing acidity	10^{0}	0	Increasing basicity
10^{-13}	13		10^{-1}	1	
10^{-12}	12		10^{-2}	2	
10^{-11}	11		10^{-3}	3	
10^{-10}	10		10^{-4}	4	
10^{-9}	9		10^{-5}	5	
10^{-8}	8		10^{-6}	6	
10^{-7}	7	Neutral	10^{-7}	7	Neutral
10^{-6}	6		10^{-8}	8	
10^{-5}	5		10^{-9}	9	
10^{-4}	4		10^{-10}	10	
10^{-3}	3		10^{-11}	11	
10^{-2}	2		10^{-12}	12	
10^{-1}	1	Increasing acidity	10^{-13}	13	Decreasing Basicity
10^{0}	0		10^{-14}	14	

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The pH values are the inverse of $[H^+]$. Greater the value of pH, smaller will be the value of $[H^+]$ and weaker will be the acid.

Keep in Mind

- The acids which have pH less than 4 are strong acids (pH < 4).
- The acids which have pH equal to or greater than 4 but less than 6 are weak acids (pH ≥ 4<6).
- The solutions which have pH equal to or greater than 6 but less than 8 are neutral or nearly neutral (pH ≥ 6<8).
- The bases which have pH equal to or greater than 8 but less than 10 are weak bases (pH ≥ 8<10).
- The bases which have pH equal to or greater than 10 are strong bases (pH ≥10).

Table 8.4: The pH of Some Common Substances

Substance	pH	Substance	pH	Substance	pH
Gastric juice (stomach acid)	1.0-3.0	Tomatoes	4.0-4.5	Milk (cows)	6.3-6.6
Lemon juice	1.8-2.4	Bear	4.0-5.0	Pure water	7.0
Soft drinks	2.0-4.0	Banana	4.5-5.7	Blood (human)	7.3-7.5
Vinegar	2.4-3.4	Urine (human)	4.8-8.4	Tears	7.4
Plums	2.8-3.0	Carrots	4.9-5.3	Egg white	7.6-8.0
Apples	2.9-3.3	Peas	5.8-6.4	Sea water	8.0-8.4
Cherries	3.2-4.0	Butter	6.1-6.4	Milk of magnesia	10.6
Peaches	3.4-3.6	Rain water	6.2	Household ammonia	11.5
Pears	3.6-4.0	Potatoes	5.6-6.0	Drain cleaner	13.0
Orange juice	3.5-4.0	Saliva (human)	6.4-6.9	1 M NaOH	14.0

Most of the fruits are acidic in nature. The sour taste is the indication of the acidic character of fruits. When the difference of the pH values of two acids is one then one acid is ten times stronger than other (or it has ten times more hydrogen ion concentration). For example, a lemon with a pH of 2.0 is ten times more acidic than an apple with a pH of 3.0 and is hundred times more acidic than cherry with a pH of 4.0. An increase of one in pH corresponds to a tenfold decrease in $[H^+]$.

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Curdling of Milk with Lemon Juice:

Curdling means to change into curds. Curds are a dairy product obtained by curdling of milk by acid or rennet, used in making cheese or eaten as food.

Milk is actually made up of water, suspended fat, and protein. It contains a specific protein called casein. Casein floats freely in groups (called micelles) throughout the milk and does not usually bond to anything. These grouping (micelles) have negative charge. They repel each other, which stops them from clumping and keeps the casein groupings (micelles) evenly dispersed in the milk. When lemon juice that contains citric acid is added to milk, the pH of milk drops and it becomes more acidic. The positive hydrogen atoms get attracted to the negative micelles, making them neutral. Now instead of pushing one another part, the micelles start to attract one another and stick together. Thus the milk gets curdled. The process of curdling happens much faster when lemon juice is added to hot milk. But it is better to add a lemon juice to milk when both the liquids are cold and lemon juice is added slowly. The more lemon juice you add, the larger your curds will be and the faster they will form.

Example 8.2

Calculate the pH of the carrots juice which has the hydrogen ion concentration 5.5×10^{-6}M.

Solution:

The pH of carrots juice = ?

$[H^+] = 5.5\times10^{-6}$M

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

pH of carrots juice $= -(\log 5.5\times10^{-6})$

$= -[(\log 5.5)+(-6\log 10)]$

$= -[(0.740)+(-6\times1)]$

$= -[0.740-6]$

$= -[-5.26]$

$= 5.26$

Practice Exercise 2:

Calculate the pH and pOH of the egg white having hydrogen ion concentration 2.51×10^{-8}M. Is the solution acidic or basic?

Example 8.3

(a) Calculate the hydrogen ion concentration of banana, which has a pH value of 5.0.

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(b) What are the hydrogen and hydroxide ion concentrations of human blood that has a pH of 7.4?

Solution (a):

If we may be given the pH value of a solution and asked to calculate the hydrogen ion concentration, then we need to take the antilog of the equation.

$[H^+] = 10^{-pH}$

$[H^+] = ?$

pH of banana $= 5.0$

As we know, $[H^+] = 10^{-pH}$

By putting the value of pH we have,

$[H^+] = 10^{-5}$

Solution (b):

$[H^+] = ?$

$[OH^-] = ?$

pH of human blood $= 7.4$

As we know, $[H^+] = 10^{-pH}$

By putting the value of pH in the above equation, we obtain

$[H^+] = 10^{-7.4}$

$[H^+] = 3.98 \times 10^{-8}$

We also know that,

$$[H^+][OH^-] = 1.0 \times 10^{-14} \quad \text{or}$$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{[H^+]}$$

Then, $$[OH^-] = \frac{1.0 \times 10^{-14}}{3.98 \times 10^{-8}}$$

$$[OH^-] = 0.251 \times 10^{-14} \times 10^{8}$$

$$[OH^-] = 0.251 \times 10^{-6}$$

$$[OH^-] = 2.51 \times 10^{-5}$$

Practice Exercise 3:

Calculate the H^+ ions concentrations of the following solutions:

(a) Milk which has pH 6.40.

(b) Sea water which has pH 8.30.

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8.4.3 Acid Ionization Constant, K_a and pK_a

The equilibrium constant which shows the strength of an acid is called ionization constant of an acid (K_a). Let us consider the ionization of an acid, HA in water:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

According to law of mass action, the equilibrium constant for the reaction is given as:

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$ (The bracket shows molar concentration)

In dilute solutions, the concentration of water is almost constant because it is always in excess:

So, $K_c . [H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$

or $K_a = \frac{[H_3O^+][A^-]}{[HA]}$

The K_a is called ionization constant of an acid. Greater the value of K_a, the stronger is the acid and the greater is the concentration of H^+ ions at equilibrium because of its ionization.

Strength of an acid $\propto K_a$

- For weak acids, the K_a value is less than 10^{-3}. ($K_a < 10^{-3}$)
- For moderately weak acids, the K_a values range from 1 to 10^{-3} ($K_a = 1$ to 10^{-3})
- For strong acids, the K_a value is more than 1. ($K_a > 1$)

The negative logarithm of K_a is called pK_a.

$$pK_a = -\log K_a$$

The pK_a is the inverse of K_a.

$$pK_a \propto \frac{1}{K_a}$$

Greater the value of K_a, smaller will be the value of pK_a and stronger will be the acid. When the difference of pK_a values of two acids is equal to one, then one acid is ten times stronger than the other. When difference is two, then one acid is 100 times stronger than the other. When difference is three, then one acid is 1000 times stronger than the other.

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Table 8.5: K_a and pK_a Values for Some Acids at Room Temperature

Acids	Name	K_a	pK_a
HI	Hydroiodic acid	1.0×10^{10}	-10
$HClO_4$	Perchloric acid	1.0×10^{10}	-10
HBr	Hydrobromic acid	1.0×10^{9}	-9
HCl	Hydrochloric acid	1.0×10^{7}	-7
H_2SO_4	Sulphuric acid	1.0×10^{3}	-3
HNO_3	Nitric acid	25	-1.4
H_3O^+	Hydronium ion	1.0	Zero
$(COOH)_2$	Oxalic acid	5.6×10^{-2}	1.25
H_2SO_3	Suphorus acid	1.7×10^{-2}	1.77
$HClO_2$	Chlorus acid	1.2×10^{-2}	1.92
HF	Hydrofluoric acid	6.8×10^{-4}	3.17
HNO_2	Nitrous acid	4.5×10^{-4}	3.35
HCOOH	Formic acid	3.0×10^{-4}	3.52
CH_3COOH	Acetic acid	1.8×10^{-4}	3.74
C_6H_5COOH	Benzoic acid	6.3×10^{-5}	4.20
H_2CO_3	Carbonic acid	4.3×10^{-7}	6.37
H_2S	Hydrogen sulphide	1.0×10^{-7}	7.00
HClO	Hypochlorus acid	6.8×10^{-8}	7.17
H_3BO_3	Boric acid	5.9×10^{-10}	9.23
HCN	Hydrocyanic acid	4.9×10^{-10}	9.31
C_6H_5OH	Phenol	1.3×10^{-10}	9.89
H_2O	Water	1.0×10^{-14}	14

Keep in Mind

You can determine the pH value or H^+ ion concentration of a weak acid solution, if you know the initial concentration of acid and its K_a value. On the other hand, you can determine the K_a value of an acid solution, if you know the pH value and H^+ ion concentration of its solution.

Example 8.4

Calculate the pH of 0.05 M mono-protic acid whose K_a value is 2.5×10^{-5}.

Solution:

Initial concentration of mono-protic acid = 0.05M

The K_a value of mono-protic acid = 2.5×10^{-5}

The pH of mono-protic acid = ?

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The equation for the ionization of an acid is:

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

Initial conc. (M):	0.05	0	0
Equilibrium conc. (M):	$(0.05-x)$	x	x

or

$$K_a = \frac{(x)(x)}{0.05-x} = 2.5\times10^{-5}$$

$$2.5\times10^{-5} = \frac{(x)(x)}{(0.05-x)} = \frac{(x^2)}{(0.05-x)}$$

The value of K_a is small, hence, the ionization of HA is assumed to be very small and the value of x is considered as zero.

$$2.5\times10^{-5} = \frac{x^2}{0.05}$$

$$(2.5\times10^{-5})(0.05) = x^2$$

or

$$x^2 = (2.5\times10^{-5})(0.05)$$

$$x^2 = 0.125\times10^{-5}$$

$$x^2 = 1.25\times10^{-6}$$

by taking under root,

$$x = \sqrt{1.25\times10^{-6}}$$

$$x = 1.12\times10^{-3}\,M$$

$$pH = -\log[H^+] = -\log(1.12\times10^{-3})$$

$$= -(-2.95)$$

$$= 2.95$$

Practice Exercise 4:

Calculate the pH of 0.10 M formic acid whose K_a value is 1.8×10^{-14}.

Example 8.5

Calculate the K_a value of mono-protic acid which has $[HA] = 2.5\times10^{-1}$M, $[H_3O^+]=[A^-]=4.2\times10^{-2}$M at room temperature.

Solution:

$[HA] = 2.5\times10^{-1}$M

$[H_3O^+]=[A^-]=4.2\times10^{-2}$M

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$[A^-] = 4.2 \times 10^{-2} M$

K_a value of mono-protic acid = ?

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_a = \frac{(4.2 \times 10^{-2})(4.2 \times 10^{-2})}{(2.5 \times 10^{-1})}$$

$$K_a = \frac{(0.042)(0.042)}{(0.25)}$$

$$K_a = 7.06 \times 10^{-3}$$

Practice Exercise 5:

A dilute solution of acetic acid has $[H_3O^+] = 4.2 \times 10^{-4} M$ and $[CH_3COO^-] = 4.2 \times 10^{-4} M$. The concentration of unionized acetic acid is $2.1 \times 10^{-2} M$. What is the K_a value for acetic acid at 25°C?

Percentage Ionization of Weak Acids

The strength of an acid can be measured by its %age ionization. We can determine %age ionization of an acid by the formula:

$$\%\text{ age ionization} = \frac{\text{Concentration of ionized acid at equilibrium}}{\text{Initial concentration of acid}} \times 100$$

The greater the %age ionization of an acid, the stronger the acid and vice versa.

The %age ionization of weak acids depends upon the extent of dilution of solution. The extent of dilution increases with decrease in the number of moles of the acid.

$$\text{Extent of dilution} \propto \frac{1}{\text{No. of moles}}$$

When the solution is infinitely diluted, the weak acid gets 100% ionization.

The % ionization of 0.1M acetic acid solution is 1.3% and that of 0.005M acetic acid solution is 5.86%.

8.4.4 Levelling Effect

The strength of acids is not only depending upon the ability of a substance to donate a proton, it also depends upon the ability of solvent to accept protons. The acid strengths are determined by comparing their relative ionizations in water.

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strongest acid that exists in water is the hydronium ion (H_3O^+). Any acid that is stronger than hydronium ion will ionize completely in water and produce H_3O^+ and so appear to be of equal strength and have nearly same pK_a values. Hence, it becomes difficult to tell which acid is stronger, that is, they are levelled out. This phenomenon is called leveling effect. Although strong acids have close pK_a values in water, but they are not equally strong. To compare the strengths of strong acids, a solvent that is weaker proton acceptor than water such as liquid HF or CH_3COOH has to be used. Strong acids show different pK_a values in a solvent that is weaker base than water. For example, the pK_a values of $HClO_4$, H_2SO_4 and HCl in the acetic acid medium are 5.3, 6.8, and 8.8 respectively. The relative strengths of some strong acids in acetic acid (known as glacial acetic acid) medium are:

$$HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$$

Water has no leveling effect on the strength of weak acids such as HCOOH, CH_3COOH, H_2CO_3 and H_3PO_4 etc. because they are not ionized 100% in water and have different pK_a values.

Similarly, the strongest base that is present in water is OH^- ion. Any base that is stronger than OH^- hydrolyzes in water to produce OH^- ions. For example, the amide (NH_2^-) and oxide (O^{2-}) ions are stronger bases than OH^-, and hydrolyze completely in water producing OH^- ions. Water has no leveling effect on the strength of those bases which are weaker than OH^- ions.

Table 8.6: The Strong Bases and Acids that Ionize Completely in the Solution

Strong Bases	Name	Strong Acids	Name
LiOH	Lithium hydroxide	$HClO_4$	Perchloric acid
NaOH	Sodium hydroxide	$HClO_3$	Chloric acid
KOH	Potassium hydroxide	H_2SO_4	Suphuric acid
RbOH	Rubidium hydroxide	HI	Hydroiodic acid
CsOH	Cesium hydroxide	HBr	Hydrobromic acid
$Ca(OH)_2$	Calcium hydroxide	HCl	Hydrochloric acid
$Sr(OH)_2$	Strontium hydroxide	HNO_3	Nitric acid
$Ba(OH)_2$	Barium hydroxide		

Base Ionization Constant, K_b and pK_b

equilibrium constant which shows the strength of a base is called dissociation ant of a base (K_b). Consider the ionization of a base in water:

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

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The equilibrium constant is given as:

$$K_c = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

The water is in excess, so its concentration is constant:

$$K_c \cdot [H_2O] = \frac{[BH^+][OH^-]}{[B]} \quad \text{or}$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

K_b is called ionization or dissociation constant of a base. Greater the value of K_b, stronger is the base and vice versa.

Strength of a base $\propto K_b$

The negative logarithm of K_b is called pK_b.

$$pK_b = -\log K_b$$

The greater the value of K_b, smaller will be the value of pK_b and stronger will be the base.

Table 8.7: K_b and pK_b Values for Some Acids at Room Temperature

Bases	Name	K_b	pK_b
NaOH	Sodium hydroxide	Very large	Very small
KOH	Potassium hydroxide	Very large	Very small
CH_3NH_2	Methyl amine	4.4×10^{-14}	3.36
NH_3	Ammonia	1.8×10^{-5}	4.74
N_2H_4	Hydrazine	1.7×10^{-6}	5.77
NH_2OH	Hydroxylamine	9.1×10^{-9}	8.04
C_5H_5N	Pyridine	1.4×10^{-9}	8.85
C_6H_5NH	Aniline	4.3×10^{-10}	9.37
$CO(NH_2$	Urea	1.3×10^{-14}	13.89

8.4.6 Relation between K_a and K_b

The strength of an acid can be measured by its acid ionization constant (K_a) and the strength of a base can be measured by its base ionization constant (K_b). An important relationship between the acid ionization constant (K_a) and the ionization constant of its conjugate base (K_b) can be derived as follows:

Consider the ionization of a weak acid, HA in water:

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$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

The equilibrium constant for the reaction is given as:

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \quad \text{or} \quad K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \ldots\ldots\ldots\ldots \text{(i)}$$

Consider the ionization of a conjugate base in water:

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

The equilibrium constant is given as:

$$K_c = \frac{[HA][OH^-]}{[A^-][H_2O]} \quad \text{or} \quad K_b = \frac{[HA][OH^-]}{[A^-]} \quad \ldots\ldots\ldots\ldots \text{(ii)}$$

By multiplying equation (i) and (ii), we get

$$K_a . K_b = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]}$$

$$K_a . K_b = [H_3O^+][OH^-]$$

As we know, $K_w = [H^+][OH^-]$, hence,

$$K_a . K_b = K_w \quad \ldots\ldots\ldots\ldots \text{(iii)}$$

The equation (iii) can be expressed as

$$K_a = \frac{K_w}{K_b} \quad \text{or} \quad K_b = \frac{K_w}{K_a}$$

From the above expressions it is clear that the larger the value of K_a, the smaller the value of K_b and vice versa.

If we take negative logarithm of both sides of the equation (iii), then pK values of the conjugate acid and base pairs are related to each other as:

$$pK_a + pK_b = pK_w = 14 \quad \text{(at 25°C)}$$

If we know the pK_a value of an acid we can calculate the pK_b value of its conjugate base as:

$$pK_b = 14 - pK_a$$

If we know the pK_b value of a base we can calculate the pK_a value of its conjugate acid as:

$$pK_a = 14 - pK_b$$

Table 8.8: Relationship of K_a, pK_a, K_b and pK_b Values

Acids	K_a	pK_a	Conjugate bases	K_b	pK_b
H_2SO_3	1.7×10^{-2}	1.7	SO_3^{2-}	5.9×19^{-13}	12.3
HF	6.8×10^{-4}	3.2	F^-	1.5×10^{-11}	10.8
HNO_2	4.5×10^{-4}	3.3	NO_2^-	2.2×10^{-11}	10.7

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Acids	K_a	pK_a	Conjugate bases	K_b	pK_b
CH_3COOH	1.8×10^{-4}	3.7	CH_3COO^-	5.5×10^{-11}	10.3
H_2CO_3	4.3×10^{-7}	6.3	HCO_3^-	2.3×10^{-8}	7.6
HCN	4.9×10^{-10}	9.3	CN^-	2.0×10^{-5}	4.7
C_6H_5OH	1.3×10^{-10}	9.9	$C_6H_5O^-$	7.7×10^{-5}	4.1
H_2O	1.0×10^{-14}	14	OH^-	1.0×10^{0}	0

8.5 Lewis Definitions of Acids and Bases

The Bronsted and Lowry concept failed to explain those acids and bases which do not have hydrogen ions such as $AlCl_3$, and $FeCl_3$. It also failed to explain those acid-base reactions which occur in non-protonic solvents such as liquid SO_2, and liquid BF_3. In 1923, Gilbert N. Lewis, an American chemist focused on the role of electron pair and proposed an even more general concept of acids and bases. This concept is not restricted to any particular element or solvent. According to this concept, an acid is a substance (atom, molecule or ion) that can accept an electron pair to form a coordinate covalent bond and a base is substance that can donate an electron pair and to form a coordinate covalent bond. In short, acids are electron pair acceptors and bases are electron pair donors.

i) All simple cations such as H^+, Li^+, Ni^+, Sn^{2+} and Sn^{4+} act as Lewis acids. Smaller cations such as H^+, Li^+ and Be^{2+} act as stronger Lewis acids because of higher tendency to accept electrons.

ii) The electron deficient molecules which have incomplete octet such as $BeCl_2$, $AlCl_3$, and BF_3 act as Lewis acids.

iii) All anions such as Cl^-, O^{2-}, OH^-, X^- (Halide ion) and NH_2^- (amide ion) act as Lewis bases because they have tendency to donate electron pairs.

iv) The molecules which have lone pair of electrons such as $H_2\ddot{O}$ and $\ddot{N}H_3$ act as Lewis bases.

According to Lewis concept, an acid-base reaction occurs when a base donates an electron pair to an acid with the formation of a coordinate covalent bond between the two substances.

$$\underset{\text{Base}}{Cl^-} + \underset{\text{Acid}}{AlCl_3} \longrightarrow Cl \rightarrow \bar{A}lCl_3 \quad \text{or} \quad AlCl_4^-$$

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Gastric Acidity and use of Anti-acid Drugs

Gastric juice (stomach acid) is essential for the digestion of foods and to kill the bacteria that is ingested. The gastric juice has 0.5% HCl that is secreted by cells in the stomach walls and pH value of the gastric juice is normally 1-3. When too much food is eaten or when the stomach is irritated by very spicy foods, fatty foods, fried foods, acidic foods (tomatoes, oranges), acidic juices (grape fruits, oranges), and alcoholic beverages, or when a person becomes emotional, can cause the stomach to produce too much HCl. Some of acid contents can flow back into the esophagus (the tube that carries food to your stomach) and cause "heart burn". The condition is medically known as "pyrosis" or "acid indigestion".

The symptoms of heart burn include a burning sensation in the chest (just above the stomach) or behind your breast bone (sternum) and some patients experience sour taste in the mouth from gastric juice. Some patients may experience the burning sensation in the throat. Heart burn gets worse when bending over or lying down.

The heart burn is reduced:

- By taking an antacid (anti-acid) to neutralize the stomach acid. The antacid has one or more basic substances which are used to neutralize the excess but not all of the stomach acid.
- By taking acid-inhibitors to reduce the secretion of stomach acid. The acid-inhibitors include famotidine, ranitidine and cimetidine.
- By taking proton pump inhibitors to block the production of acid. The proton pump inhibitors include omeprazole, rabeprazole and esomeprazole.

Bases (neutralizing agents) used as antacids
$NaHCO_3$ (Baking Soda)
$Al(OH)_3$ and $NaHCO_3$
$Mg(OH)_2$ (Milk of Magnesia)
$Al(OH)_3$ and $Mg(OH)_2$

The heart burn can be controlled by some lifestyle change such as:

- To avoid the spicy foods, fatty foods, alcohol, aspirin, ibuprofen, caffeine, beverages, overeating.
- To avoid eating before bedtime, stop smoking, elevate the head of the bed and remain cool in the crisis.

8.6 Buffer Solution

A solution which resists any change in pH when a small amount of an acid or a base is added to it is called buffer solution.

If a solution comes in contact with air, it will absorb CO_2 and become more acidic. If a solution is stored in a glass bottle for long time, the silicates of glass make it more basic. In both cases the pH of solution changes. Buffer solution is used to maintain the pH of solution and prevent these changes.

Composition of Buffer Solution

A buffer solution usually contains:

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i) A weak acid and its salt with strong base.

For example, CH_3COOH and CH_3COONa

ii) A weak base and its salt with strong acid.

For example, NH_4OH and NH_4Cl

Action of Buffer

Consider the buffer solution of acetic acid and sodium acetate:

i) When we add few drops of a strong base (NaOH) to the solution, the OH^- ion of NaOH reacts with acetic acid to give its conjugate base.

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$

ii) When we add few drops of strong acid (HCl) to the solution, the H^+ ion of HCl reacts with acetate ion of acetic acid to give back CH_3COOH.

$$CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$$

Both OH^- and H^+ ions are consumed completely in the above reactions. Hence, pH of the solution remains constant.

Applications of Buffer Solutions

i) They are used on industrial scale in tanning of leather, electroplating and manufacture of sugar where constant pH is essential.

ii) Normal human blood has a pH of about 7.4. It is maintained by use of bicarbonates and phosphates. If it decreases up to 7 or goes up to 8, death may occur.

iii) They are used to study the growth of bacteria at constant pH.

iv) For proper production of crops, the pH control of the soil is essential.

v) They are used in beverage industries.

Buffer Capacity

The number of moles of an acid or a base required by one dm^3 of a buffer solution for changing its pH by one unit is called buffer capacity of a solution. It may also be defined as: the capability of a buffer to resist the change of pH is called buffer capacity. The buffer capacity depends upon the concentration (amount) of acids and salts present in the buffer solution.

Consider a buffer solution having 1.78M CH_3COONa and 1.0M acetic acid. The pH of this solution is 5. A solution having 0.178M CH_3COONa and 0.1M CH_3COOH shall also have pH equal to 5. Since anion/acid ratio is same. But this dilute solution has lower buffer capacity and would more easily be destroyed by

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addition of acid or base. However, the solution with 1M CH_3COOH and 1.78M CH_3COONa has larger buffer capacity and is able to show small pH changes when strong acids or bases are added and is not easily destroyed by such additions.

8.7 Salt Hydrolysis

The neutralization reaction of an acid and a base produces salts and water. The reaction of cations or anions or both cations and anions of salt with water to form acidic or basic or neutral solution is called hydrolysis. Salt hydrolysis usually affects the pH of a solution. For example:

When sodium acetate (CH_3COONa), a salt of weak acid and a strong base, is dissolved in water, its anion (CH_3COO^-) reacts with water as:

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$$

Similarly, NH_4Cl, a salt of weak base and a strong acid when dissolved in water, its cation (NH_4^+) reacts with water as:

$$NH^+_{4(aq)} + H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H^+_{(aq)}$$

There are *four types of salts* on the basis of reactivity with water.

(i) The salts of weak acids and strong bases react with water and give basic solutions. For example, consider the ionization and hydrolysis reactions of CH_3COONa in water.

$$CH_3COONa_{(s)} \xrightleftharpoons{H_2O} CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$$

The sodium acetate solution will be basic due to the formation of OH^- ions. The pH of this solution is more than 7 (pH > 7). The cations of strong bases such as alkali metal and alkaline earth metal ions except Be, have hardly any acidic character; that is to say, these ions do not hydrolyze and has no effect on the pH of the solution.

$$Na^+_{(aq)} + H_2O_{(l)} \rightleftharpoons \text{No reaction}$$

The extent of hydrolysis is determined by the value of K_b for acetate ion. The greater the value of K_b of a base, the more basic the solution it produces.

(ii) The salts of strong acids and weak bases react with water to give acidic solution. For example, consider the ionization of NH_4Cl in water.

$$NH_4Cl_{(s)} \xrightleftharpoons{H_2O} NH^+_{4(aq)} + Cl^-_{(aq)}$$

$$NH^+_{4(aq)} + H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H^+_{(aq)}$$

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The ammonium ion solution is acidic because of the formation of hydrogen ions. The pH of this solution is less than 7 (pH < 7). The anions of strong acids such as Cl^- ions have hardly any basic character; that is to say, these ions do not hydrolyze and has no effect on the pH of the solution.

$$Cl^-_{(aq)} + H_2O_{(l)} \rightleftharpoons \text{No reaction}$$

The extent of hydrolysis is determined by the value of K_a for ammonium ion. The greater the value of K_a of the acid, the more acidic the solution it produces.

(iii) The salts of strong acids and strong bases give neutral solutions. Because these salts are not hydrolyzed in water. For example consider the ionization of NaCl in water.

$$NaCl_{(s)} + H_2O_{(l)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

The sodium ion is a very weak Bronsted base and has no effect on the pH of the solution. On the other hand, the chloride ion is a very weak Bronsted acid and it also has no effect on the pH of the solution. The pH of this solution is equal to 7 (pH=7).

(iv) The salts of weak acids and weak bases may not give neutral solutions, but whether the resulting solution is basic, acidic or neutral depends upon the relative strength of the weak acid and weak base.

To calculate the pH of such solution, you are required to compare the K_a value of the cation with the K_b value of the anion. There are three possibilities:

(a) If the value of K_a of the cation is greater than the value of K_b of the anion ($K_a > K_b$), the solution is acidic. This solution has pH value less than 7 (pH<7).

(b) If the value of K_a of the cation is less than the value of K_b of the anion ($K_a < K_b$) the solution is basic. This solution has pH value greater than 7 (pH> 7).

(c) If the value of K_a of the cation is close to the value of K_b of the anion ($K_a \approx K_b$) the solution is neutral or nearly neutral. This solution has pH value equal to or nearly equal to 7 (pH≈ 7).

To determine whether CH_3COONH_4 solution is acidic, basic, or neutral, you are required to compare the values of K_a of the ammonium ions and K_b of the acetate ions. Consider the ionization and hydrolysis reactions of CH_3COONH_4 in water.

$$CH_3COONH_4 \xrightleftharpoons{H_2O} CH_3COO^-_{(aq)} + NH^+_{4(aq)}$$

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$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)} \qquad K_a = 5.6 \times 10^{-10}$$

$$NH^+_{4(aq)} + H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H^+_{(aq)} \qquad K_b = 5.6 \times 10^{-10}$$

This solution is neutral because the value of K_a is equal to the value of K_b. It means that the number of hydrogen ions produced by ammonium ions is equal to the number of hydroxide ions produced by acetate ions.

Table: 8.9: Types of Salts and the pH of Solutions

Type of Salt	Ions that are Hydrolyzed	pH of the Solution	Examples
Cation from strong base and anion from weak acid	Anion	> 7	CH_3COONa, Na_2CO_3
Cation from weak base and anion from strong acid	Cation	< 7	NH_4Cl, NH_4NO_3
Cation from strong base and anion from strong acid	None	≈ 7	NaCl, KI, KNO_3, Na_2SO_4
Cation from weak base and anion from weak acid	Anion and cation	Depends upon the relative strength of the weak acid and weak base.	NH_4F, CH_3COONH_4, NH_4CN

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Why Essential Elements like Iodine are added to Table Salt?

Iodine is a trace mineral that is naturally present in small amounts in marine organisms, eggs, and dairy products such as yogurt, milk, and cheese. It is essential for the formation of iodine containing hormones (thyroxine and triiodothyronine) secreted by the thyroid gland. Hormones are molecules that are carried in the bloodstream from one part of the body to another part and are responsible for growth, development, and maintenance of all body tissues. Iodine containing hormones regulate the heart rate and blood pressure and can also help the body to burn extra fat deposits. Daily requirement of iodine for adults is placed at 150 micrograms per day or 5 gram (1 teaspoonful) of iodized salt per day. If you do not get enough iodine, your thyroid enlarges and works overtime to produces more hormones, and as a consequence, the person suffers from low energy, low blood pressure, and weight gain. Extreme cases can lead to *goiter*, in which the gland is grossly enlarged. On the other hand, excess iodine in the diet can lead to an overactive metabolism. The addition of small amount of iodine to table salt in the form of NaI or KI at very little cost can prevent the deficiency of iodine. Good quality

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iodized salt provides the right quantity of iodine, therefore regular use of iodized salt cannot lead to excess iodine in the body. Daily consumption of iodized salt can protect entire generations of both humans and animals from mental and physical disabilities caused by Iodine deficiency.

Summary of Facts and Concepts

- Acids have sour taste, turn blue litmus paper red, react with active metals, conduct electricity in aqueous solutions and react with bases to form salts and water.
- Bases have bitter taste, soapy touch, turn red litmus paper blue, conduct electricity in aqueous solutions and react with acids to form salts and water.
- The sour taste of many foods such as vinegar, tomatoes, yogurt, lemons, and oranges is because of the presence of acids in them. The bitter taste of beer and coffee is because of the presence of bases in them. The bases are less common in foods. Both the acids and bases are used on large scale in industries and laboratories.
- According to Arrhenius concept, an acid is a substance that gives H^+ ions in water and a base is substance that gives OH^- ions in water.
- The strength of Arrhenius acid or base depends on the extent of ionization of acid or base in water.
- According to Bronsted-Lowry concept, an acid is a proton donor substance while a base is proton acceptor substance.
- According to Lewis concept, acid is electron pair acceptor substance while a base is electron pair donor substance.
- A strong acid or base is almost completely ionized in the solution while a weak acid or base is ionized to a slight extent in the solution.
- An acid increases the concentration of H^+ ions when dissolved in water while a base increases the concentration of OH^- ions when dissolved in water.
- The pH scale is used to measure acidity and pOH scale is used to measure basicity of solution. One-fold change in pH is equal to ten-fold change in the concentration of hydrogen ion.
- The K_a is the equilibrium constant that describes the ionization of an acid and the K_b is the equilibrium constant that describes the ionization of a base. Acid strength is denoted by the value of K_a and base strength is denoted by the value of K_b. Greater the value of K_a, stronger is the acid and vice versa. Greater

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value of K_a, stronger is the base and vice versa.

- Greater the value of K_a, smaller the value of pK_a, and stronger will be the acid.
- Greater the value of K_b, smaller the value of pK_b, and stronger will be the base.
- A solution that resists pH change when small amounts of acid or base is added to it is called buffer solution. Buffer solutions contain either a mixture of weak acid and a salt of its conjugate base (such as CH_3COOH and CH_3COONa) or a mixture of weak base and a salt of its conjugate acid (such as NH_4OH and NH_4Cl).
- The number of moles of an acid or a base required by one dm^3 of a buffer solution for changing its pH by one unit is called buffer capacity of a solution.
- Salts that have cations of strong bases and anions of strong acids give neutral solutions. Salts that have cations of strong bases and anions of weak acids give basic solutions. Salts that have cations of weak bases and anions of strong acids give acidic solutions.

Questions and Problems

Q.1. Four answers are given for each question. Select the correct one:

i) According to _____ concept, acid is an electron pair acceptor substance.

(a) Arrhenius (b) Bronsted

(c) Lowry (d) Lewis

ii) Ionic product of water is represented by:

(a) K_w (b) K_c

(c) pK_a (d) pK_b

iii) The value of ionic product of water at 25°C is:

(a) $1.0\times10^{-14}mol^2dm^{-6}$ (b) $1.0\times10^{14}mol^2dm^{-6}$

(c) $1.5\times10^{14}mol^2dm^{-6}$ (d) $1.5\times10^{-14}mol^2dm^{-6}$

iv) When an acid is added to water, then

(a) $[H^+]>[OH^-]$ (b) $[H^+]<[OH^-]$

(c) $[H^+]=[OH^-]$ (d) $[H^+]\approx[OH^-]$

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v) The pH of the aqueous solution of 10^{-2} M HCl is:

(a) 1.0 (b) 1.5

(c) 2.0 (d) 2.5

vi) The pH value of tears is 7.4, and pOH value is

(a) 4.6 (b) 6.6

(c) 7.0 (d) 7.6

vii) Which one of the following is **NOT** the Arrhenius acid:

(a) HCl (b) HNO_3

(c) $AlCl_3$ (d) H_2SO_4

viii) When the difference of pK_a values of two acids is equal to 2 then one acid is stronger than the other.

(a) 10 times (b) 100 times

(c) 1000 times (d) 10000 times

ix) Which one of the following statements is **NOT** correct for bases:

(a) Have bitter taste (b) turn blue litmus red

(c) have high pH values (d) reacts with acids to form salts

x) Which salt in water has pH value less than 7:

(a) NaCl (b) NH_4Cl

(c) CH_3COONa (d) CH_3COONH_4

Q.2. Fill in the blanks with suitable words given in the brackets:

i) A substance is termed as amphoteric when it acts _____. (as proton acceptor/as proton donor/both as proton acceptor and proton donor)

ii) Pure water is _____ conductor of electricity. (poor/good)

iii) The basic solution has pH _____ than seven. (less/greater)

iv) The sum of pH and pOH is _____ 14. (equal to/less than)

v) The ionic product of water increases by _____ temperature. (decrease/increase)

vi) The stronger acids have _____ value of pK_a. (smaller/greater).

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vii) The value of pH is _____ proportional to $[H^+]$. (directly/inversely)

viii) Weak acids are _____ electrolytes. (weak/strong)

ix) The electron deficient molecules act as Lewis _____. (acids/bases)

x) Aqueous solution of Na_2CO_3 is _____ while that of NH_4NO_3 is _____. (acidic/basic)

Q.3. Label the following statements as True or False:

i) The pH of the normal human blood is 7.4.

ii) The conjugate base of HCl is Cl^- *ion*.

iii) A strong base has a pH value of 14.

iv) The strength of an acid depends on the conjugate base: the stronger the conjugate base, the weaker the acid.

v) Orange is more acidic than apple.

vi) The antacids are used to reduce the secretion of stomach acid.

vii) Milk of magnesia has sour taste.

viii) For the neutralization of the stomach acid most of the people take NaOH.

ix) The larger the value of K_a, the smaller the value of K_b and vice versa.

x) The acids which have pH less than 4 are strong acids.

Q.4: What are the properties of acids and bases? Give some examples of acid containing foods and base containing substances.

Q.5: Define Arrhenius acids and bases and make it clear with examples.

Q.6: What is amphoteric substance? Give examples of substances that have amphoteric characteristics.

Q.7: Define Bronsted-Lowry acids and bases. Give a demonstration of each by chemical equations.

Q.8: What is a conjugate acid-base pair? Give relationship between the strength of an acid and its conjugate base.

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Q.9: Write the conjugate base for each of the following acids:

(a) HNO_2 (b) H_2SO_3 (c) HSO_4^-

(d) H_2CO_3 (e) HF (f) HCO_3^-

Q.10: Write the conjugate acids for each of the following bases:

(a) NH_3 (b) Br^- (c) $CH_3CH_2NH_2$

(d) NO_3^- (e) NH_2^- (f) H_2O

Q.11: What is the difference between Arrhenius and Bronsted-Lowry definition of acids and bases?

Q.12: What do you know about Lewis acid-base concept? Explain it.

Q.13: What is the difference between strong and weak acids?

Q.14: What do you know about the strongest acid and strongest base which can exist in water?

Q.15: How do you measure the strength of an acid or base?

Q.16: What is the ionic product constant of water? Why the ionic product of water increases by increasing temperature? Write an expression for K_w what is its value at room temperature?

Q.17: Calculate the H^+ ions and OH^- ions concentrations of each of the following solutions:

(a) 0.1M HNO_3 solution ($K_a = 25$)

(b) 0.05 M NaOH solution. ($K_b = 10^{20}$)

Q.18: Calculate the concentration of H^+ ions in ammonia solution used for floor and glass cleaning whose hydroxide ion concentration is 0.025M.

Q.19: What do you mean by the pH and pOH? How are they related? Write an equation relating pH and pOH with pK_w.

Q.20: What is pOH of the plum having hydrogen ion concentration 1.58×10^{-3}M? Is the solution acidic or basic?

Q.21: What is the pH of 2.0×10^{-4}M NaOH solution?

Q.22: What is H^+ and OH^- concentrations of a sample of tomatoes that has a pH value of 4.50?

Q.23: Calculate the pH of each of the following solution and classify each solution as acidic or basic:

(a) $[H^+] = 1.0\times10^{-10}$M (b) $[H^+] = 3.2\times10^{-8}$M

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(c) $[H^+] = 4.3\times10^{-5}M$ (d) $[H^+] = 6.7\times10^{-3}M$

(e) $[H^+] = 9.5\times10^{-1}M$

Q.24: Calculate the pOH of each of the following solution and classify each solution as acidic, basic or neutral:

(a) $[OH^-] = 1.0\times10^{0}M$ (b) $[OH^-] = 2.4\times10^{-3}M$

(c) $[OH^-] = 1.0\times10^{-7}M$ (d) $[OH^-] = 7.8\times10^{-11}M$

(e) $[OH^-] = 1.0\times10^{-14}M$

Q.25: Calculate the pH of each of the following solution and classify each solution as acidic, basic or neutral:

(a) pOH = 0.00 (b) pOH = 1.62

(c) pOH = 3.33 (d) pOH = 7.00

(e) pOH = 13.92

Q.26: Calculate the pOH of each of the following solution and classify each solution as acidic, basic or neutral:

(a) pH = 14.02 (b) pH = 12.14

(c) pH = 7.61 (d) pH = 7.00

(e) pH = 11.44

Q.27: What is meant by K_a and K_b? What is their relation to the strength of acids and bases?

Q.28: Calculate the pH of 0.01M acetic acid whose K_a value is 1.7×10^{-5}.

Q.29: Formic acid has 2.45×10^{-6}M hydrogen ion concentration and 2.45×10^{-6}M formate ion concentration. The concentration of unionized formic acid is 0.025M at equilibrium. Find out the value of K_a for acid at room temperature.

Q.30: What are buffer solutions? Why buffers resist changes in pH? What are the applications of buffer solution?

Q.31: What is salt hydrolysis? Classify the salts on the basis of reactivity with water.

Q.32: Define and explain leveling effect.

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Q.33: Answer the following questions:

(a) Why water is considered as a base in the Bronsted-Lowry concept?

(b) Why the value of K_b of a conjugate base decreases by increasing the value of K_a of a substance?

(c) Why a strong acid has a weak conjugate base and a weak acid has relatively a strong conjugate base?

(d) The aqueous solution of NH_4Cl is acidic and that of Na_2CO_3 is basic, why?

(e) $AlCl_3$ is said to be Lewis acid but not Bronsted-Lowry acid, why?

(f) Why the sum of pH and pOH of the aqueous solution at 25°C equal to 14?

(g) Why the HCl has different pH values in water and acetic acid?

(h) Which has the larger value of the pK_a, a strong acid or the weak acid?

(i) Why chemists prefer to show the acid strength in terms of pH rather than $[H^+]$?

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Chapter # 09

Chemical Kinetics

Major Concepts

9.1 Chemical Kinetics
9.2 Rates of Reactions
9.3 Collision Theory, Transition State and Activation Energy
9.4 Catalysis

Learning Outcomes

The students will be able to:

- Define chemical kinetics. (Remembering)
- Explain and use the terms rate of reaction, rate equation, order of reaction, rate constant and rate determining step. (Understanding)
- Explain qualitatively factors affecting rate of reaction. (Applying)
- Given the order with respect to each reactant, write the rate law for the reaction. (Applying)
- Explain what is meant by the terms activation energy and activated complex. (Understanding)
- Relate the ideas of activation energy and the activated complex to the rate of a reaction. (Applying)
- Use the collision theory to explain how the rate of a chemical reaction is influenced by the temperature, concentration, size of molecules and. (Applying)
- Given a potential energy diagram for a reaction, discuss the reaction mechanism for the reaction. (Applying)
- Explain effects of concentration, temperature and surface area on reaction rates. (Applying)
- Explain the significance of the rate-determining step on the overall rate of a multi-step reaction. (Analyzing)
- Describe the role of the rate constant in the theoretical determination of reaction rate. (Applying)

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- Describe that increase in collision energy by increasing the temperature can improve the collision frequency. (Applying)
- Define terms catalyst, catalysis, homogeneous catalysis and heterogeneous catalysis. (Understanding)
- Explain that a catalyst provides a reaction pathway that has low activation energy. (Applying)
- Describe enzymes as biological catalysts. (Understanding)
- Explain why powdered zinc reacts faster. (Analyzing)

9.1 Introduction to Chemical Kinetics

The different chemical reactions occur at very different rates. Some reactions occur very slowly and some occur very quickly. The reactions may take seconds, weeks or months to occur. The rusting of iron, the conversion of graphite into diamond, the setting of cement and the decay of plants into coal occur very slowly. Similarly the cooking of food, formation of yogurt, the fermentation of glucose to give ethanol and carbon dioxide; and the hydrolysis of an ester to give acid and ethanol are also the examples of slow reactions. On the other hand, the combustion of petrol, the explosion of gun powder, the neutralization of an acid (HCl) by a base (NaOH), and the reaction of hemoglobin with oxygen and CO occur very quickly and are called fast reactions. Chemical kinetics is the branch of chemistry which deals with the study of reaction rate (speed), reaction mechanism and factors that affect the reaction rate. The laws of thermodynamics support us to decide whether the reaction is feasible or not but chemical kinetics helps us to know:

i) How fast chemical reactions occur?
ii) How reactions speed can be controlled?
iii) What are the factors (variables) that affect reactions rate?

For example, when the food is stored in the refrigerator, the temperature of food is slowed down and the food is preserved. Here the reaction speed (decomposition of food) is controlled by decreasing the temperature. Chemical kinetics not only plays an important role in our daily life but it also plays a vital role in industries. For example, it helps to predict the expiry date of medicines. The medicines lose their effectiveness with the passage of time due to the decomposition of active ingredients. It also helps us to get the maximum yield during industrial process. It is the chemical kinetics that decides whether a certain chemical reaction is economical or not. For example, the economical synthesis of ammonia in the industry mainly depends on the speed of reaction at which reactants (N_2 and H_2) are converted into product (NH_3). In this chapter we mainly focus on the reaction rate, the mechanism and the variables that influence the reaction rate.

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9.2 Rates of Reactions

The change in the concentration of reactants or products per unit time is called rate or speed of reaction.

$$\text{Rate of reaction} = \frac{\text{Change in concentration of reactants (or products)}}{\text{Change in time}} = \frac{\Delta C}{\Delta t}$$

The unit of rate of reaction depends on the concentration unit of reactants or products and the unit of time. The usual unit of rate of reaction is moles per decimeter cube per second (mol $dm^{-3} s^{-1}$). The usual unit for gaseous reaction is atm sec^{-1}.

Consider a general chemical reaction in which the reactant A is converted into product B.

$$A \longrightarrow B$$

When the reaction proceeds, then the concentration of reactant *A* decreases and that of product *B* increases with the passage of time. It can be best understand by the graph. When we plot a graph between concentration (of reactants and products) on y-axis and time on x-axis, then we will able to show the change in the concentration of reactants or products of a reaction with the passage of time. At the beginning, the slope of the graph for the molar concentration of reactants or products is the steepest which indicates that the reactants are converted into products at greater speed. After some times, the slope becomes less steep which shows that the change in concentration of reactants or products is slowing down. At the end of a reaction, the concentration of the reactant becomes zero and that of product becomes the maximum and the reaction stops. The change in the concentration of reactants or products with time gives us an idea about the rate of chemical reaction.

There are two types of rates of reactions:

1. Instantaneous rate of reaction
2. Average rate of reaction.

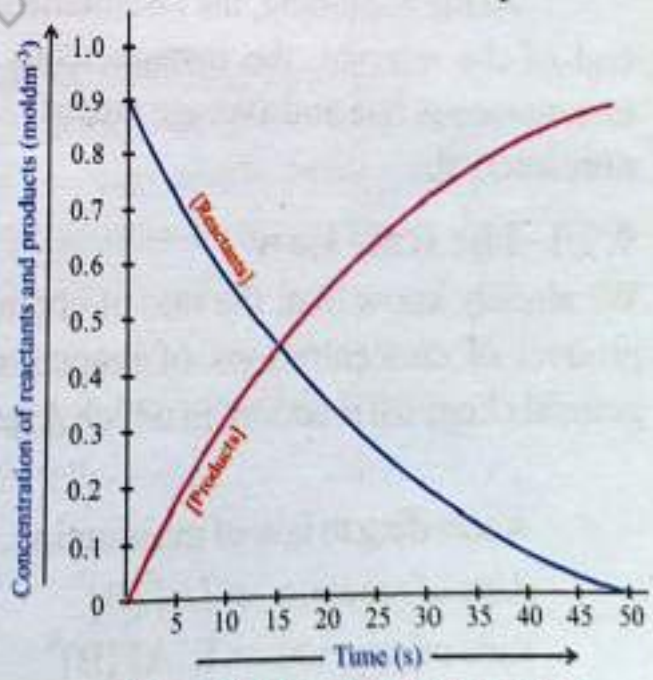

Figure 9.1: Change in the molar concentration of reactants and products with time for the reaction

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i) Instantaneous Rate of Reaction

The rate of reaction at a particular instant during the time interval is called instantaneous rate of reaction. The instantaneous rate of reaction goes on changing every moment. It is very fast at the beginning and very slow at the end of reaction.

The instantaneous rate of reaction can be calculated from the following expressions:

$$\text{Instantaneous rate of reaction} = \frac{-d[A]}{dt} \quad \text{or}$$

$$\text{Instantaneous rate of reaction} = \frac{d[B]}{dt}$$

Where d[A] and d[B] show a very small change in the concentration (of reactant A and product B) and dt shows a very small change in time. The d[A] has minus sign in the rate expression which shows the decrease in the concentration of reactant during the passage of time. The d[B] has no minus sign in the rate expression which shows that the concentration of product *B* increases during the passage of time.

ii) Average Rate of Reaction

The total change in concentration divided by total time is called average rate of reaction.

$$\text{Average rate of reaction} = \frac{\text{Total change in concentration}}{\text{Total change in time}}$$

At the beginning, the instantaneous rate is higher than the average rate. At the end of the interval, the instantaneous rate is lower than the average rate. The instantaneous rate and average rate of reactions are equal for only one instant in any time interval.

9.2.1 The Rate Law

We already know that, the rate of chemical reaction is directly proportional to the product of concentrations of reactants each raised to some power. Consider a general chemical reaction, in which A reacts with B to produce C and D.

$$aA + bB \longrightarrow cC + dD$$

According to law of mass action,

$$\text{Rate of reaction} \propto [A]^a[B]^b \quad \text{or}$$

$$\text{Rate of reaction} = K[A]^a[B]^b$$

This equation is called rate equation or rate law. Here K is called rate constant.

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The rate equation is generally written in the form:

$$\text{Rate of reaction} = K[A]^m[B]^n$$

Keep in Mind

The K is the proportionality constant of rate equation and is known as the rate constant or specific rate constant. We can determine its value, if we know the concentration of reactants and order of reaction. Its value is directly proportional to the rate of reaction, that is, the reactions with higher rate has higher value of K and the reactions which proceeds slowly have lower value of K. The value of K remains same for a specific reaction and is independent of reactants or products concentrations and does not change with time at constant temperature. The value of K increases by increase in temperature and decreases by decrease in temperature. The magnitude of K alters when a catalyst is added to the reaction mixture.

In the rate equation, it is not necessary that the powers (exponents m and n) are always equal to the co-efficient (a and b) of balanced chemical equations. Rate law can be defined as: An expression which shows how the reaction rate is related to concentration of reactants is called rate law or rate expression. It is determined experimentally. It is not predicted from a balanced chemical equation, because as we know that the sum of exponents in the rate equation may or may not be equal to the co-efficient of balanced chemical equation. The value of the exponents in the rate law shows the order of reaction with respect to each other. For example, consider the reaction of nitric oxide with hydrogen:

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O \qquad \text{Rate} = K[H_2][NO]^2$$

The exponent of 1 for hydrogen concentration shows that the reaction is first order with respect to hydrogen. The exponent of 2 for the nitric oxide (NO) concentration shows that the reaction is second order with respect to nitric oxide. The sum of the exponents of both the reactants shows the overall order of reaction, hence, this reaction is of third order (1 + 2 = 3) overall.

Some examples of rate law are:

	Reactions	Rate Law
i)	$2NO_2 \longrightarrow 2NO + O_2$	$\text{Rate} = K[NO_2]^2$
ii)	$2N_2O_5 \longrightarrow 4NO_2 + O_2$	$\text{Rate} = K[N_2O_5]$
iii)	$H_2 + I_2 \longrightarrow 2HI$	$\text{Rate} = K[H_2][I_2]$

9.2.2 Elementary and Overall Reactions

Some reactions occur in single step but most of the reactions occur by a series of steps. The steps involved in a several step reaction are called mechanism of reaction

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or reaction pathway. A single step in a mechanism of reaction is called an elementary reaction or elementary step.

Keep in Mind

How do Chemists Determine the Mechanism of Chemical Reactions? It is not an easy work to determine the mechanism of chemical reaction, that is, it needs expertness. The chemists determine the rate law by experiments at first, and then they propose mechanism for chemical reactions. The elementary steps of the reaction are added up, if it gives the overall balanced chemical equation, then this mechanism is accepted, if not, then rejected. They also compare the proposed mechanism with experimentally determined rate law, if they do agree, then this mechanism is accepted, if do not agree, then this mechanism is rejected and work out for another mechanism.

To understand the chemical reaction, the chemists must know the step by step sequence of reactions by which the overall chemical change occurs. Consider the following reaction

$$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$$ Overall reaction

According to law of mass action,

Rate of reaction $= K[NO_2][CO]$

But experimentally determined rate equation of the reaction is:

Rate of reaction $= K[NO_2]^2$

This equation shows that the rate of reaction depends upon the concentration of NO_2 and it does not depend upon the concentration of CO. The reaction is of second order. The proposed mechanism for this reaction is:

$$NO_{2(g)} + NO_{2(g)} \xrightarrow{Slow} NO_{3(g)} + NO_{(g)}$$ Elementary reaction

$$NO_{3(g)} + CO_{(g)} \xrightarrow{Fast} NO_{2(g)} + CO_{2(g)}$$ Elementary reaction

We get the overall reaction by taking the sum of the elementary reactions:

$$\cancel{NO_{2(g)}} + NO_{2(g)} \xrightarrow{Slow} \cancel{NO_{3(g)}} + NO_{(g)}$$ Elementary reaction

$$\cancel{NO_{3(g)}} + CO_{(g)} \xrightarrow{Fast} \cancel{NO_{2(g)}} + CO_{2(g)}$$ Elementary reaction

$$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$$ Overall reaction

In the several steps reaction, all the elementary steps do not have the same rate, that is, one step is much slower than the others. The slowest step which determines the rate of chemical reaction in a several step reaction is called rate determining step or rate limiting step. Note that, the overall reaction cannot be faster than the rate of determining step (the slowest elementary reactions step). In the above reaction, the slowest step (first step) is the rate determining step and NO_3 which does not appear in the balanced equation is called reaction intermediate. The

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reaction intermediate has temporary existence and is unstable. It is neither a reactant nor a product but it is produced during the path of reaction, that is, it is formed in one step and completely consumed in the later step. NO_3 has normal bonds and it can be isolated (separated) under special conditions.

9.2.3 Order of Reaction and its Determination

The number of atoms or molecules whose concentrations determines the rate of reaction is called order of reaction. It may also be defined as:

The sum of all the exponents of the concentration terms in a rate equation is called order of reaction. For example:

Rate of reaction $= K[A]^m[B]^n$

Order of reaction $= m + n$

Order of reaction is determined experimentally. Order of reaction is not predicted from a balanced chemical equation because the sum of exponents in the rate equation may or may not be the same as in a balanced chemical equation.

Important types of order of reaction are discussed below:

First Order Reaction

The reaction in which the rate of chemical reaction is directly proportional to the first power of the concentration of one reacting substance is called first order reaction.

Rate of reaction $= K[A]^1$

The rate of first order reaction doubles by doubling the concentration of reactant.

For example:

i) $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$ Rate of reaction $= K[N_2O_5]$

ii) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$ Rate of reaction $= K[NH_4NO_2]$

Second Order Reaction

The reaction in which rate of a chemical reaction is directly proportional to the square of the molar concentration of one reacting substance (or to the product of molar concentrations of two reacting substances) is called second order reaction.

Rate of reaction $= K[A]^2$ or Rate of reaction $= K[A][B]$

The rate of second order reaction quadruples by doubling the concentrations of reactants.

For example:

i) $H_2 + I_2 \longrightarrow 2HI$ Rate of reaction $= K[H_2][I_2]$

$2O_3 \longrightarrow 3O_2$ Rate of reaction $= K[O_3]^2$

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Third Order Reaction

The reaction in which rate of a chemical reaction is directly proportional to the product of molar concentration of three reacting substances (or to the first power of molar concentration of one reacting substance and square of the other reacting substance) is called third order reaction.

$$\text{Rate of reaction} = K[A][B][C] \quad \text{or} \quad \text{Rate of reaction} = K[A]^2[B]$$

The rate of third order reaction octuples by doubling the concentrations of reactants.

For example:

i) $2NO + O_2 \longrightarrow 2NO_2$ Rate of reaction $= K[NO]^2[O_2]$

ii) $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$ Rate of reaction $= K[NO]^2[H_2]$

Zeroth Order Reaction

The reaction whose rate does not depend upon the concentration of any reactant is called zeroth order reaction.

$$\text{Rate of reaction} = K[A]^0$$

The reactions catalyzed by enzymes and thermal decomposition reactions may be zero order.

For example:

i) Photosynthesis (Photochemical reactions).

ii) $2NH_3 \xrightarrow{\text{Tungsten}} N_2 + 3H_2$ Rate of reaction $= K[NH_3]^0$

Experimental Determination of Order of Reaction

We can calculate order of reaction, if we know the rate of reaction. The rate of reaction is the change in concentrations of the reactants or products. The rate of reaction is generally determined by physical and chemical methods. The physical methods include spectrometry, electrical conductivity, dilatometry, refractometry, optical rotation method, pH metric method, and gas chromatography method etc. The method used to monitor changes in the concentration of reactant or product depends on the specific reaction. Suppose a series of experiments is conducted and observed the effect of concentration on the rate of reaction to predict the order of reaction.

i) Suppose a reaction has only one reactant and its rate constant K value is 0.2...

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Table 9.1: Initial rate and concentration of reactants A and B

Experiments	Initial Concentration (mol dm^{-3})	Initial Rate (mol $dm^{-3}s^{-1}$)
	[A]	
1	0.01	0.0025
2	0.02	0.005
3	0.04	0.01

Experiments 1 and 2 show that when we double the initial concentration of A from 0.01 to 0.02, doubles the rate of reaction from 0.0025 to 0.005.

Experiments 1 and 3 shows that when we quadruples the initial concentration of A from 0.01 to 0.04, quadruples the rate of reaction from 0.0025 to 0.01. It means that the rate of reaction is directly proportional to the first power of concentration of reactant A.

$$\text{Rate} \propto [A]^1$$

A reaction whose rate of reaction depends on the concentration of a single reactant raised to the first power is known as first order reaction.

ii) Consider the reaction between reactants A and B. the value of the rate constant K is 1.20$mol^{-1}dm^3s^{-1}$.

Table 9.2: Initial rate and concentration of reactants A and B

Experiments	Initial Concentration (mol dm^{-3})		Initial Rate (mol $dm^{-3}s^{-1}$)
	[A]	[B]	
1	0.20	0.02	0.0048
2	0.20	0.08	0.0192
3	0.40	0.02	0.0096

Experiment 1 and 2 show that when we keep the concentration of reactant A constant and quadruples the initial concentration of B from 0.02 to 0.08, quadruples the rate of reaction from 0.0048 to 0.0192. It means that the rate of reaction is directly proportional to the first power of the molar concentration of reactant B.

$$\text{Rate} \propto [B]^1 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (i)$$

Experiments 1 and 3 show that when we keep the concentration of reactant B constant and double the initial concentration of A from 0.20 to 0.40, doubles the rate of reaction from 0.0048 to 0.0096. It means that the rate of reaction is directly

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proportional to the first power of concentration of reactant A.

$$\text{Rate} \propto [A]^1 \quad \ldots\ldots\ldots\ldots \quad \text{(ii)}$$

By comparing equation (i) and (ii), we have

$$\text{Rate} \propto [A]^1[B]^1 \quad \text{or}$$

$$\text{Rate} = K[A]^1[B]^1$$

The sum of the exponents of both the reactants shows the overall order of reaction, hence this reaction is of second order $(1+1=2)$ overall.

iii) Consider the reaction between reactants *A* and *B*. the value of the rate constant *K* is $1.20 mol^{-2} dm^6 s^{-1}$.

Table 9.3: Initial rate and concentration of reactants A and B

Experiments	Initial Concentration (mol dm^{-3})		Initial Rate (mol $dm^{-3} s^{-1}$)
	[A]	[B]	
1	0.20	0.02	0.0048
2	0.20	0.04	0.0192
3	0.40	0.02	0.0096

Experiments 1 and 2 show that when we keep the concentration of reactant *A* constant and double the initial concentration of *B* from 0.02 to 0.04, quadruples the rate of reaction from 0.0048 to 0.0192. It means that the rate of reaction is directly proportional to the square of the molar concentration of reactant *B*.

$$\text{Rate} \propto [B]^2 \quad \ldots\ldots\ldots\ldots \quad \text{(i)}$$

Experiments 1 and 3 show that when we keep the concentration of reactant *B* constant and double the initial concentration of *A* from 0.20 to 0.40, doubles the rate of reaction from 0.0048 to 0.0096. It means that the rate of reaction is directly proportional to the first power of concentration of reactant *A*.

$$\text{Rate} \propto [A]^1 \quad \ldots\ldots\ldots\ldots \quad \text{(ii)}$$

By comparing equation (i) and (ii), we have

$$\text{Rate} \propto [A]^1[B]^2 \quad \text{or}$$

$$\text{Rate} = K[A]^1[B]^2$$

The sum of the exponents of both the reactants shows the overall order of reaction, hence this reaction is of third order $(1+2=3)$ overall.

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Example 9.1

Consider the reaction between hydrogen and nitric oxide:

$$2NO + H_2 \longrightarrow 2H_2O + N_2$$

Initial rate data for the reaction between NO and H_2 is given below in the table:

Experiments	Initial Concentration (mol dm^{-3})		Initial Rate (mol dm^{-3}s^{-1})
	$[H_2]$	[NO]	
1	0.025	0.050	2.5×10^{-3}
2	0.050	0.050	5.0×10^{-3}
3	0.025	0.100	1.0×10^{-2}

From the above data, determine (a) the rate equation for reaction, and the overall order of reaction and (b) the rate constant value at room temperature.

(a) Experiments 1 and 2 show that by doubling the concentration of H_2 from 0.025 to 0.050, doubles the rate from 2.5×10^{-3} to 5.0×10^{-3}, hence the rate of reaction is directly proportional to the first power of concentration of reactant H_2.

$$\text{Rate} \propto [H_2]^1 \quad \ldots\ldots\ldots\ldots\ldots \text{(i)}$$

Experiments 1 and 3 show that by doubling the concentration of NO from 0.050 to 0.100, quadruples the rate from 2.5×10^{-3} to 1.0×10^{-2}, hence the rate of reaction is directly proportional to the square of concentration of NO.

$$\text{Rate} \propto [NO]^2 \quad \ldots\ldots\ldots\ldots\ldots \text{(ii)}$$

By comparing equation (i) and (ii), we obtain the overall rate equation.

$$\text{Rate} \propto [H_2]^1[NO]^2 \quad \text{or}$$

$$\text{Rate} = K[H_2]^1[NO]^2$$

The sum of the exponents of both the reactants shows the overall order of reaction, hence this reaction is of third order $(1 + 2 = 3)$ overall.

(b) We know that the rate equation for the reaction is:

$$\text{Rate} = K[H_2]^1[NO]^2 \quad \text{or} \quad K = \frac{\text{Rate}}{[H_2]^1[NO]^2}$$

By putting the values in the above equation, we get:

$$K_1 = \frac{2.5 \times 10^{-3} \text{ mol dm}^{-3}\text{s}^{-1}}{(0.025 \text{ mol dm}^{-3})(0.050 \text{ mol dm}^{-3})^2} = 40 \text{ mol}^{-2}\text{dm}^6\text{s}^{-1}$$

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$$K_2 = \frac{5.0 \times 10^{-3} \text{ mol dm}^{-3}\text{s}^{-1}}{(0.050 \text{ mol dm}^{-3})(0.050 \text{ mol dm}^{-3})^2} = 40 \text{ mol}^{-2}\text{dm}^6\text{s}^{-1}$$

$$K_3 = \frac{1.0 \times 10^{-2} \text{ mol dm}^{-3}\text{s}^{-1}}{(0.025 \text{ mol dm}^{-3})(0.100 \text{ mol dm}^{-3})^2} = 40 \text{ mol}^{-2}\text{dm}^6\text{s}^{-1}$$

As discussed earlier, the rate constant is independent of concentration at constant temperature. Note that the units of rate constant (K) depend on the number of concentration terms in the rate equation and on the values of exponents. Some of the common units of rate constant are given in the table:

Overall Order of Reaction	Rate Equation	Units of *K*
First order	Rate = K[A]	s^{-1}
Second order	Rate = K[A][B]	$mol^{-1}dm^3s^{-1}$
Third order	Rate = $K[A]^2[B]$	$mol^{-2}dm^6s^{-1}$
Zeroth order	Rate = K	$mol\ dm^{-3}s^{-1}$

Practice Exercise 1:

Consider the reaction between oxygen and nitric oxide:

$$2NO + O_2 \longrightarrow 2NO_2$$

Initial rates data for the reaction between NO and O_2 is given below in the table:

Experiments	Initial Concentration (mol dm^{-3})		Initial Rate (mol $dm^{-3}s^{-1}$)
	[NO]	$[O_2]$	
1	0.022	0.012	1.25×10^{-3}
2	0.022	0.024	2.50×10^{-3}
3	0.044	0.012	5.00×10^{-3}

(a) What is the rate law and overall order of reaction?

(b) What is the value of the rate constant at 25°C?

9.2.4 Factors Affecting Rate of Reaction

The rates of chemical reactions are influenced by five major factors:

i) The nature of the reactants.
ii) The concentration of the reactants.
iii) The surface area of the reactants.
iv) The temperature of the reactants.
v) The action of the catalysts.

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In this topic we are going to discuss the first four and the action of the catalysts will be discussed in the forthcoming topic (9.4).

i) The Nature of the Reactants

The rate of chemical reactions depends upon the nature of the reactants. Some substances react swiftly while others react slowly. For example, the reaction of potassium with water is very fast than that of calcium.

$$2K + 2H_2O \xrightarrow{\text{Fast}} 2KOH + H_2$$

$$Ca + 2H_2O \xrightarrow{\text{Slow}} Ca(OH)_2 + H_2$$

The reactions between ionic compounds are fast. For example, the reaction between NaCl and $AgNO_3$ in the solution is very fast. In the solution, the silver ions and chloride ions have no bonds to break. In this case only new bonds are formed between silver ions and chloride ions to produce silver chloride.

$$NaCl_{(aq)} + AgNO_{3(aq)} \xrightarrow{\text{Fast}} AgCl_{(s)} + NaNO_{3(aq)}$$

On the other hand, the reactions between covalent compounds are usually slow. For example, the reaction between secondary propyl alcohol and HCl in the presence of $ZnCl_2$ is slow and takes five to ten minutes for completion because they have a lot bonds that have to be broken.

$$(CH_3)_2CH-OH + HCl \xrightarrow[5-10 \text{ minutes}]{ZnCl_2} (CH_3)_2CH-Cl + H_2O$$

ii) The Concentration of the Reactants

The rate of chemical reactions increases by increasing the concentration of all or any one of the reactants. For example, wood burn much more rapidly in pure O_2 (100%) than in the air in which only 21% oxygen is present. Because the concentration of oxygen in pure oxygen is five times greater than air.

By increasing the concentration of reacting substances, the chances of collision between the molecules increases and the rate of reaction increases. This is because of the greater number of molecules per unit volume.

Rate of reaction $\propto$ [A][B]

Quantitative effect of concentration on the rate of chemical reaction is given by order of reaction.

iii) The Surface Area of the Reactants

The actual reactions occur at the surface area between the reactants. The rate of reaction is directly proportional to the surface area of the reactants. The larger the surface area the higher is the reaction rate and the smaller the surface area the lower is the reaction rate. This is because, by increasing the surface area, more atoms or

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molecules come in contact with each other. The surface area can be increased by grinding the big crystals into smaller ones. For example, the reaction of zinc granules with hydrochloric acid is very slow and that of zinc dust (powder) is very fast.

$$Zn_{(s)}(\text{Granules}) + 2HCl_{(aq)} \xrightarrow{\text{Slow}} ZnCl_{2(aq)} + H_{2(g)}$$

$$Zn_{(s)}(\text{Dust}) + 2HCl_{(aq)} \xrightarrow{\text{Fast}} ZnCl_{2(aq)} + H_{2(g)}$$

Likewise, the reaction of marble chips (big pieces of $CaCO_3$) with sulphuric acid is slow and that of marble powder is fast. You know that it is difficult to ignite the big log. This is due to small surface area. If we break the log into smaller thin sticks (kindling), then the surface area increases and it will become easy to ignite the kindling.

iv) The Temperature of the Reactants

The kinetic energy of the particles of the substance is directly proportional to the temperature of the substance. By increasing temperature, the kinetic energy of a substance increases which in turn increase the rate of reaction of both the endothermic and exothermic reactions. Why we keep milk inside the refrigerator? We know that the rate of reaction decreases with decrease in temperature. When we keep milk at lower temperature inside the refrigerator, the chemical reactions that cause the milk to spoil are slow down and hence the milk remains fresh for a longer time. If we keep it in the kitchen at room temperature, the milk will spoil much more readily and becomes sour. On the other hand, food cooks more quickly in pressure cooker (airtight pot) than an open pot. The boiling point of water in pressure cooker is higher than its normal boiling point of 100°C. At higher temperature, the heat of decomposition of food (rate of reaction) is high and hence, the food cooks in short period of time.

At room temperature, the rates of many reactions roughly double with every 10°C rise in temperature. If the temperature is increased by 20°C, the rate of reaction will be increased four times. However, the actual rise in the rate of chemical reaction can be determined by experiments.

9.3 Collision Theory, Transition State and Activation Energy

9.3.1 Collision Theory

According to the collision theory of chemical kinetics, chemical reactions generally take place by collisions between the reacting substances (atoms, molecules or ions). By increasing the concentration of reacting substances, the chances of collision between particles increase due to greater number of particles per unit volume, and

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hence the rate of reaction increases. The rate of collision is directly proportional to the concentration of reactants A and B.

$$\text{Rate of collision} \propto [A][B]$$

The rate of reaction is directly proportional to the number of collision between the reactant molecules per second.

$$\text{Rate of reaction} \propto \text{Number of collisions per second}$$

We may say that by increasing the concentration of reacting substances, the rate of collision increases which in turn increase the rate of reaction and vice versa. Consider the formation of a product by the reaction of reactants A and B. If the concentration of reactant A is doubled, the rate at which B molecules collide with A molecules is also doubled. Likewise, if the concentration of reactant B is doubled, the rate at which A molecules collide with B molecules is also doubled. The reaction is second order overall. The rate of some reactions is directly proportional to the square of molar concentration of reactants.

By collision old bonds can be broken and new bonds can be formed. All the collisions of molecules do not give products. There are two types of collisions:

(a) Effective Collisions (b) Ineffective Collisions

The collisions which give products are called effective or fruitful collisions.

The collisions which do not give products are called ineffective collisions.

Three main conditions of this theory are:

i) The reacting substances must collide with one another to react.

ii) For effective collisions, the molecules must have sufficient amount of energy to start the reaction by breaking old bonds and forming new bonds during the process.

iii) The reactant molecules must collide with proper orientation that could enable them to react with one another.

If all the collisions among the reactant molecules are effective, the reaction will be completed in a short time.

9.3.2 Transition State

The unstable high energy specie which is formed by collision of reactant molecules is called an activated complex. It is short-lived specie and decomposes into products immediately. It has a transient existence that is why; it is also called a transition state. The amount of energy needed to convert the reactants into the activated complex (Transition State) is called activation energy (E_a). When molecules collide, some of kinetic energy of colliding molecules is converted into potential energy and the molecules slow down. If this potential energy is equal to or

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more than activation energy, then the molecules may be activated and the activated complex is formed. If this potential energy is less than activation energy, then the molecules upon collision bounce back and do not form the activated complex and the reaction does not occur. The activated complex has partial bonding of both the reactants and products. When activated complex is formed, then there are two possibilities:

(a) It may reconstruct the original bonds and change back into the reactants;

(b) It may construct new bonds and change in to products.

Both forward and reverse reactions produce the same activated complex. For example, molecules A_2 react with B_2 to give product, AB. The activated complex is formed when molecules of A_2 collide with molecules of B_2. The activated complex has partially broken and partially formed bonds. In this process, old bonds are broken between the reactants atoms (A-A and B-B) and new bonds are formed between the atoms A and B to produce the product (AB).

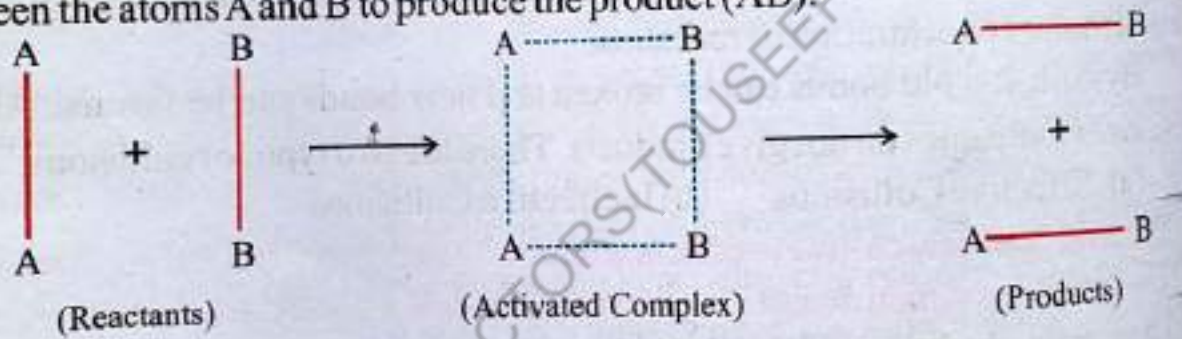

Figure 9.2: Activated Complex of Reactants A_2 and B_2

The transition state (activated complex) is always at higher energy state than the reactants and products.

9.3.3 Activation Energy

The minimum amount of energy required which the molecules must have to form an activated complex is called activation energy. It is represented by E_a. Its units are joules or kilojoules per mole ($kJ\ mol^{-1}$).

The reactants are not directly converted into products. They first gain energy to form an activated complex and then this activated complex decomposes into products. We can say that activation energy is an energy barrier (or energy hill) between the reactants and products. The reactant molecules must cross this energy barrier before they can form the products.

Crossing this barrier is similar to carrying a ball to the top of the hill and then rolling down the other side. But if the ball will not reach at the top of hill, it will roll back. Similarly, if activation energy is not provided, the reaction will not start and the reactants will not converted into products. It can be best understood by the

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energy diagram.

In case of exothermic reactions, the potential energy of reactants is higher than products. This difference is shown by ΔH. To start the reaction, we have to provide the energy E_a to reach at the top of the barrier.

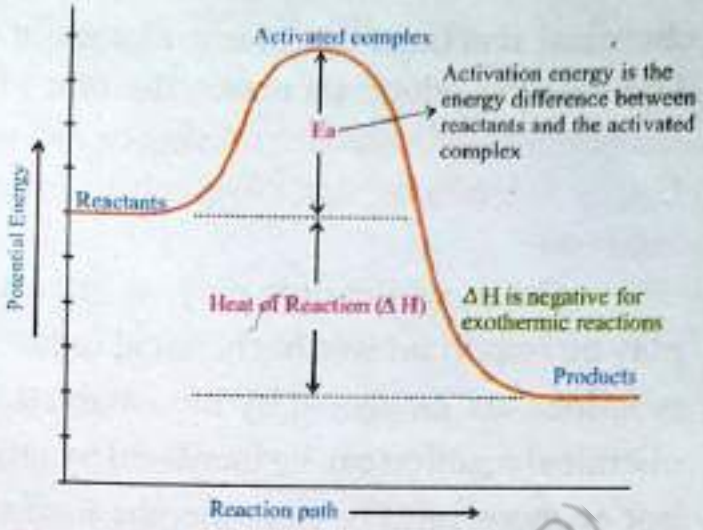

Figure 9.3: A graph between reaction path and potential energy for exothermic reaction

In case of endothermic reactions, the potential energy of reactants is lower than products. This difference is shown by ΔH. To start the reaction, we have to provide the energy E_a to form an activated complex.

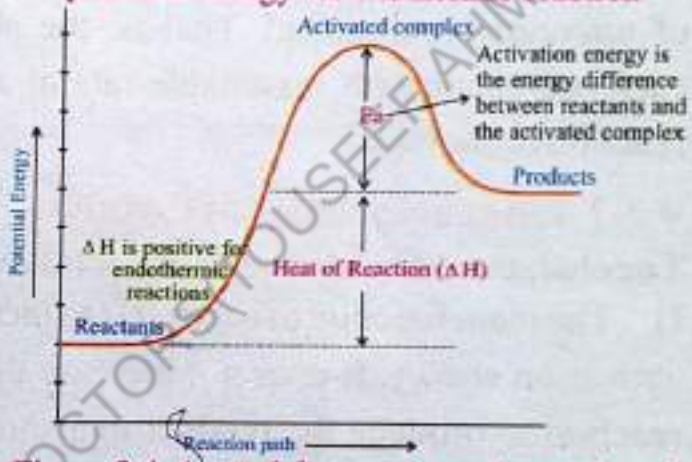

Figure 9.4: A graph between reaction path and potential energy for endothermic reaction

The activation energy for the forward and reverse reactions is not same for all of the reactions. For exothermic reactions, the activation energy for the forward reaction is less than that of reverse reaction because the reactants are at higher energy level than the products. On the other hand, the activation energy for the reverse reaction is higher than that of forward reaction because the products are at higher energy level than that of reactants. For endothermic reactions, the activation energy for the forward reaction is higher than that of reverse reaction because the reactants are at lower energy level than that of products. On the other hand, the activation energy for the reverse reaction is lower than that of forward reaction because the products are at lower energy level than reactants. Note that:

(a) The reactions which are exothermic in forward direction will be endothermic in the reverse direction,

(b) Fast reactions usually have low activation energies, and slow reactions have high activation energies.

9.4 Catalysis (Effect of Catalysts)

A substance which is not consumed in a reaction but alters the rate of chemical reaction is called Catalyst. In most of the cases, the catalyst increases the rate of

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chemical reactions but in some cases, it decreases the rate of chemical reactions. The catalyst which increases the rate of reaction is called positive catalyst. The catalyst which decreases the rate of reaction is called negative catalyst or inhibitor. The increase in the rate of chemical reaction by the addition of a catalyst is called catalysis.

Catalysts not only play an important role in living organisms but they also play an important role in chemical industries too. In living organisms, the chemical reactions are catalyzed by bio-catalysts called enzymes. In industries, the rate of chemical reaction can be increased by raising the temperature of the reaction but it is not economical. For example, the formation of ammonia by Haber process in the absence of catalyst is very expensive. The addition of catalyst makes the formation of ammonia economical. That is, the chemical reactions that are catalyzed by catalysts occur with reasonable rate at a much lower temperature and make the reaction economical.

9.4.1 Characteristics of Catalyst

The characteristics of catalyst are as follows:

I) The main function of catalyst is to increase the rate of reaction by decreasing the activation energy. It does not increase the amount of product but it speeds up the reaction to produce the product in a short time. In the presence of a catalyst, the reaction occurs at higher rate and at lower temperature. It changes path or mechanism of chemical reaction and a new reaction path is provided to the reaction. In this way, greater number of reactant molecules can cross the lower energy barrier. As a result of this, rate of reaction increases. For example, oxygen gas can be obtained by the thermal decomposition of potassium chlorate ($KClO_3$) in the laboratory:

$$2KClO_{3(s)} \longrightarrow 2KCl_{(s)} + 3O_{2(g)}$$

The decomposition of $KClO_3$ at room temperature is very slow when heated in the absence of a catalyst.

$$2KClO_{3(s)} \xrightarrow[\text{Slow}]{\text{Heat}} 2KCl_{(s)} + 3O_{2(g)}$$

On industrial scale, the reaction must occur at an appreciable rate and it must have a high yield of the product. Hence, the rate of decomposition can be increased when a small amount of manganese dioxide (MnO_2), a black powder, is added to it.

$$2KClO_{3(s)} \xrightarrow[\text{Fast}]{\text{Heat} + MnO_2} 2KCl_{(s)} + 3O_{2(g)}$$

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It is clear from the figure 9.5 that the catalyst lowers the activation energy and provides a new path to the reaction but ΔH remains same.

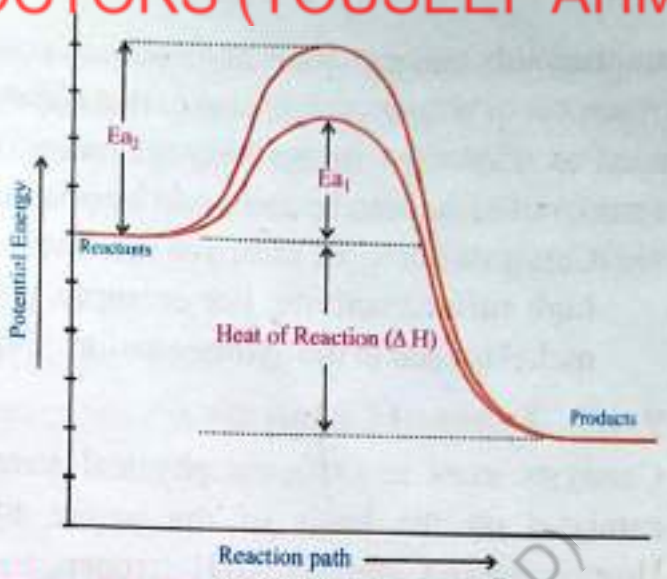

Figure 9.5: Effect of catalyst on activation energy of reaction

ii) The catalyst (MnO_2) is not consumed in the reaction as discussed earlier and can be recovered at the end of reaction. The catalysts recovered can be used again. Hence, catalyst is not written into the equation because it neither acts as a reactant nor as a product. It is usually written above the arrow.

iii) A catalyst only reduce the time of equilibrium, it does not change the equilibrium position of reversible reactions.

iv) A catalyst has no effect on the total enthalpy (ΔH) of reaction. Hence, it can not start those reactions which are not thermodynamically feasible.

v) A particular catalyst works for a particular reaction. A catalyst can catalyzes only specific reaction and cannot be used for every reaction. Change of catalyst also changes the nature of the reaction. For example, in the presence of nickel (Ni), the carbon monoxide and oxygen gases of water gas ($CO+H_2$) react to produce CH_4 and H_2O while in the presence of ZnO catalyst, they react to produce CH_3OH.

$$CO_{(g)} + 3H_{2(g)} \xrightarrow{Ni} H_2O_{(l)} + CH_{4(g)}$$

$$CO_{(g)} + 2H_{2(g)} \xrightarrow{ZnO} CH_3OH_{(l)}$$

If iron coated alumina is used as a catalyst, then the mixture of carbon monoxide and hydrogen gases produce octane (gasoline).

$$8CO_{(g)} + 17H_{2(g)} \xrightarrow{Fe/Al_2O_3} C_8H_{18(l)} + 8H_2O_{(l)}$$

vi) Catalyst can be deactivated by small amount of impurity. Deactivation of a catalyst by small amount of impurity is called poisoning of a catalyst. A substance which deactivates the catalyst is called poison. For example, in contact process of H_2SO_4, the presence of small amount of As_2O_3 (impurity) in sulphur dioxide gas decreases the catalytic behaviour of V_2O_5 (vanadium pentaoxide). Here Arsenic oxide (As_2O_3) acts as a poison.

vii) The catalytic behavior of catalyst can be increased by the introduction of

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another substance. A substance which increases the activity of a catalyst is called promoter or activator. It is also called Catalyst for a catalyst. For example, nickel is used as a catalyst in the hydrogenation of vegetable oil to ghee. The catalytic activity of nickel can be increased by using copper and tellurium.

viii) Catalysts are more effective in a finely divided form (powder form) because of high surface activity. For example, a finely divided nickel also called Raney nickel is used in the hydrogenation of vegetable oil to form ghee.

9.4.2 Types of Catalysis

Catalysts exist in different physical states; therefore, there are three types of catalysis on the basis of the nature of the rate increasing substances: (a) Homogeneous Catalysis, (b) Heterogeneous Catalysis, and (c) Enzyme Catalysis.

a) Homogeneous Catalysis

In homogeneous catalysis, the reactants and catalysts are in same phase. Homogeneous catalysis occurs either in gaseous phase or in the liquid (solution) phase. Consider the example of the formation of sulphuric acid by lead chamber process. In lead chamber process, sulphuric acid is produced by dissolving SO_3 gas in water. The SO_3 gas is obtained by the oxidation of SO_2 gas. Such reaction is catalyzed by nitric oxide (NO).

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{NO_{(g)}} 2SO_{3(g)}$$

In this reaction both the reactants and catalyst are gases.

Consider another example of the hydrolysis of an ester (ethyl acetate) in the presence of an acid (sulphuric acid) or a base (KOH).

$$CH_3COOC_2H_{5(aq)} + H_2O_{(l)} \xrightleftharpoons{H_3O^+ \text{ or } OH^-} CH_3COOH_{(aq)} + C_2H_5OH_{(aq)}$$

Here both the reactants and catalyst are in solution.

b) Heterogeneous Catalysis

In heterogeneous catalysis, the reactants and catalysts are in different phases. In heterogeneous catalysis, the reactants are mostly in gaseous or in liquid states while catalysts are in solid states. Heterogeneous catalysis most often involves gaseous reactants which are being on the surface of the solid catalyst. The atoms and ions of the surface of catalyst are very reactive and provide a site for the reaction. The adsorption may either be physical or chemical. In physical adsorption, the reactants are attached to catalysts surface by weak intermolecular forces while in chemical adsorption, the reactants are attached to the surface of the reactants by chemical bonding. The bonds in the reactant species during chemical adsorption may either be broken or weakened. The adsorption of reactants on the surfaces of

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solid catalyst increases the concentration of reactants which in turn increases the rate of reaction. Consider the manufacture of sulphuric acid by contact process. In contact process, sulphuric acid is produced by dissolving SO_3 gas in water. The SO_3 gas is obtained by the oxidation of SO_2 gas in the presence of vanadium pentaoxide (V_2O_5) catalyst.

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{V_2O_{5(s)}} 2SO_{3(g)}$$

Here reactants are gases and catalyst is solid.

Consider another example of the hydrogenation of ethene to ethane in the presence of nickel catalyst.

$$CH_2=CH_{2(g)} + H_{2(g)} \xrightarrow{Ni_{(s)}} CH_3-CH_{3(g)}$$

Here reactants are gases and catalyst is solid. Most of the catalysts used in industrial chemical processes are heterogeneous, because such catalysts can be easily separated from the reaction products to some extent.

Table 9.4: The Uses of Some Heterogeneous Catalysts

Catalysts	Uses	Reactions
V_2O_5 or Pt	Contact process (in the manufacture of sulphuric acid)	$2SO_2 + O_2 \rightleftharpoons 2SO_3$
Ni, Pd, or Pt	Hydrogenation of alkenes	$CH_2=CH_2 + H_2 \longrightarrow CH_3-CH_3$
Fe, Al_2O_3, and K_2O	Haber process (in the manufacture of NH_3)	$N_2 + 3H_2 \rightleftharpoons 2NH_3$
Cr_2O_3 and ZnO	Formation of methanol from water gas ($CO + H_2$)	$CO + 2H_2 \longrightarrow CH_3OH$
Pt and Rh	In the formation of NO gas which is further used in the manufacture of nitric acid by Ostwald process	$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$
Cu	Oxidation of alcohols to aldehydes.	$CH_3CH_2OH + [O] \longrightarrow CH_3\text{-}CHO + H_2O$

e) Enzyme Catalysis

The complex protein molecules which catalyze the chemical reactions in the living cells are called enzymes. The chemical reaction which is catalyzed by enzymes is called enzyme catalysis. Each enzyme is produced in a particular living cell to catalyze a reaction taking place in that cell. Many enzymes have been

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identified and obtained in pure crystalline state from the cells to which they belong. However, the first enzyme was prepared in the laboratory in 1960. Some common examples of enzyme catalysis are:

i) The starch is hydrolyzed into maltose by diastase enzyme present in the yeast.

$$\underset{\text{(Starch)}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[\text{Yeast}]{\text{Diastase}} \underset{\text{(Maltose)}}{nC_{12}H_{22}O_{11}}$$

ii) The maltose can be converted into glucose and fructose by maltase enzyme present in the yeast.

$$\underset{\text{(Maltose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Yeast}]{\text{Maltase}} \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$$

iii) The cane sugar juice can also be converted into glucose and fructose by invertase enzyme present in the yeast.

$$\underset{\text{(Sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Yeast}]{\text{Invertase}} \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$$

iv) Glucose can be converted into ethyl alcohol by the zymase enzyme present in the yeast.

$$C_6H_{12}O_6 \xrightarrow[\text{Yeast}]{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

v) The urea is hydrolyzed into ammonia and carbon dioxide by urease enzyme present in the soya bean.

$$\underset{\text{Urea}}{(NH_2)_2CO} + H_2O \xrightarrow[\text{Soya bean}]{\text{Urease}} \underset{\text{Ammonia}}{2NH_3} + CO_2$$

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Enzymes can be Effective in Removing Stains From Fabrics:

Some laundry detergents have added enzymes that break down proteins, helping to remove them from the cloth fibers, and thus remove stains. The enzymes such as proteases, amylases, lipases and cellulases are some of the active ingredients in the laundry detergents. The enzyme amylase catalyzes the breakdown of starch based stains to smaller segments. Amylases remove starch-based soils that contain eggs, sugars, sauces, ice cream and gravy. The action of proteases is similar to that of amylase, except that a large protein molecule is hydrolyzed. Proteases remove soils and protein-based stains that contain blood, foods, urine, feces, wines, and other beverages. Lipases are effective in removing oily body and food stains. Cellulases remove dust and mud and are used to soften fabric and restore colour of fibers.

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Summary of Facts and Concepts

- Chemical kinetics concern with the study of reaction rate, reaction mechanism, and factors that affect the reaction rate.
- Reaction rate is the change in the concentration of reactants or products per unit time. The rate of reaction is not constant. The rate of reaction is influenced by concentration of reactants, surface area, temperature, nature of reactants, and the action of catalysts.
- The rate of reaction between two specific time intervals is called average rate of reaction while the rate of reaction at any one instant during the interval is called instantaneous rate of reaction.
- Rate law or rate equation is an equation that shows the relationship between the rate of a chemical reaction and the molar concentrations of the reactants each raised to some power.

  Rate of reaction $\propto [A]^m[B]^n$ or

  Rate of reaction $= K[A]^m[B]^n$
- The rate constant (K) is a proportionality constant that relates the rate of chemical reaction to the molar concentrations of reactants. The exponents *m* and *n* are called reaction orders for the reactants.
- The overall order of reaction is the sum of all the exponents of the concentration terms in the rate equation. It is determined experimentally. The sum of the exponents in the rate equation may or may not be equal to the coefficients of balance chemical equation. Order of reaction may be whole number, zero, or fractional.
- Reaction mechanismis the step-by-step process by which reactants are converted into products. A single step in a reaction mechanism is called an elementary reaction or elementary step.
- The slowest step which controls the rate of reaction in a multistep reaction is called rate determining step.
- Activation energy is the amount of energy required for molecules to form an activated complex so that a reaction can occur.
- Activated complex (or transition state) is unstable intermediate complex with very high energy and is formed by the collision of reactant molecules.
- According to collision theory, the reactant molecules must collide effectively for reaction to occur.
- The collision that results in the formation of an activated complex and produce

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product is called effective collision.

- Catalyst is a substance that usually speeds up a chemical reaction by lowering activation energy. The catalyst is not used up by the reaction and can be recovered at the end of reaction.
- The process by which a catalyst increases the rate of chemical reaction is called catalysis. Catalysis may either be homogeneous or heterogeneous. In homogeneous catalysis, the catalyst and reacting substances exist in the same phase while in heterogeneous catalysis, the catalyst and reacting substances exist in different substances.
- Enzymes are usually the complex protein molecules and are present in all living cells. They are also known as biological catalysts because they catalyze the reactions in the living cells.

Questions and Problems

Q.1. Four answers are given for each question. Select the correct one:

i) Chemical kinetics deals with the study of:

(a) Reaction rate (b) reaction mechanism

(c) factors that affect the reaction rate (d) all of them

ii) The energy of activated complex is:

(a) Lower than the energy of reactants and higher than the energy of products

(b) lower than the energy of products and higher than the energy of reactants

(c) lower than the energy of both the reactants and products

(d) higher than the energy of both the reactants and products

iii) A substance that alters the rate of chemical reaction without being consumed in the reaction is called:

(a) Catalyst (b) reactant

(c) product (d) activated complex

iv) The slowest step in a step-by-step reaction is called

(a) Rate determining step (b) rate limiting step

(c) rate controlling step (d) all of them

v) The rate of which reaction increases four times by doubling the concentration(s) of reactant(s)?

(a) First order (b) second order

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(c) third order (d) zero order

vi) Decomposition of N_2O_5 is an example of:

(a) First order (b) second order

(c) third order (d) zero order

vii) The collision that results in the formation of product is called:

(a) Fruit full collision (b) effective collision

(c) both a and b (d) ineffective collision

viii) Which one of the following does **NOT** influence rate of reaction?

(a) Concentration (b) temperature

(c) catalyst (d) activation energy

ix) The unit of rate constant for third order reaction is:

(a) s^{-1} (b) $mol^{-1}dm^3s^{-1}$

(c) $mol^{-2}dm^6s^{-1}$ (d) $mol\,dm^{-3}s^{-1}$

x) Which one of the following reactions is **NOT** the example of heterogeneous catalysis?

a) $2SO_2 + O_2 \overset{Pt}{\rightleftharpoons} 2SO_3$

b) $CH_2 = CH_2 + H_2 \xrightarrow{Ni} CH_3 - CH_3$

c) $CO + 2H_2 \xrightarrow{Cr_2O_3 + ZnO} CH_3OH$

d) $2SO_2 + O_2 \overset{NO}{\rightleftharpoons} 2SO_3$

Q.2. Fill in the blanks with suitable words given in the brackets:

i) The change in the concentration of reactants or products over time is called _____. (reaction rate/reaction mechanism)

ii) At the beginning the instantaneous rate is _____ than the average rate. (lower/higher)

iii) A catalyst that increases the rate of chemical reaction is called _____ catalyst. (positive/negative)

iv) The rate of reaction _____ by increasing temperature. decreases/increases)

v) A catalyst _____ the activation energy of the chemical reaction. (decreases/increases)

vi) he amount of energy needed for molecules to undergo reaction is _____. (internal energy/activation energy)

vii) The smaller the surface area of the reacting substances, the _____ is the reaction rate. (higher/lower)

viii) Alkali metals (group IA elements) react with water swiftly than alkaline earth metals (group IIA elements) due to _____

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atomic sizes. (smaller/larger)

ix) At room temperature, the rates of many reactions roughly double with every 10°C rise in temperature due to _____ in the number of effective collisions. (decrease/increase)

x) A substance which increases the activity of a catalyst is called _____. (activator/inhibitor)

Q.3. Label the following statements as True or False:

i) The neutralization of acids by bases is the example of slow reactions.

ii) Order of reaction is predicted from a balanced chemical equation because the sum of exponents in the rate equation is equal to the coefficient of balanced chemical equation.

iii) For exothermic reactions, the potential energy of reactants is higher than the potential energy of products.

iv) The activation energy is the minimum when all the collisions among the molecules of reactants are effective.

v) The rate of both forward and reverse reaction increases by increasing temperature.

vi) It is easy to ignite the match stich than a big log.

vii) The reaction intermediate has temporary existence and is unstable.

viii) The activation energy for the forward and reverse reactions is same for all of the reactions.

ix) A substance which slows down a reaction is called inhibitor.

x) A particular catalyst works for a particular reaction.

Q.4: What is chemical kinetics? What information it gives for the chemical reactions?

Q.5: What is meant by the reaction rate? What are the usual units of reaction rate?

Q.6: How can you differentiate between average rate and instantaneous rate of chemical reaction?

Q.7: Name the factors that affect the reaction rate. Discuss the effects of the concentration, temperature, and surface area on reaction rates.

Q.8: What is reaction mechanism? Discuss the reaction mechanism for the reaction.

Q.9: What is order of reaction? What do you know about first order, second order, third order and zero order chemical reactions? Give an example for each.

Q.10: Consider the formation of phosgene gas from CO and Cl_2:

$$CO_{(g)} + Cl_{2(g)} \longrightarrow COCl_{2(g)}$$

The initial rates obtained from three experiments at a given temperature are given in the table.

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Experiments	Initial Concentration (mol dm^{-3})		Initial Rate (mol $dm^{-3}s^{-1}$)
	[CO]	[Cl_2]	
1	0.015	0.0068	1.7×10^{-10}
2	0.030	0.0068	3.40×10^{-10}
3	0.015	0.0204	5.10×10^{-10}

By using the data, determine (a) the reaction orders for both the reactants, the overall order of reaction and the rate law, and (b) the value of the rate constant at a given temperature.

Q.11: Define rate determining step, elementary step, and reaction intermediate.

Q.12: Explain the significance of the rate determining step on the overall rate of a multistep reaction.

Q.13: Explain collision theory and give main conditions of this theory.

Q.14: Explain the following:

(a) Rate law (b) Transition state (c) Activation energy

Q.15: Explain how activation energy influences the rate of chemical reaction?

Q.16: What is catalysis? Explain the difference between homogeneous and heterogeneous catalysis. Give an example of each.

Q.17: What is catalyst? What are the characteristics of catalyst? What is the effect of a catalyst on the activation energy?

Q.18: Describe some of the important industrial processes that are dependent on catalysts.

Q.19: Explain the following statements:

a) The reaction of thick copper wire with hot concentrated sulphuric acid is slow and that of thin copper wire is fast.

b) All collisions of reactant molecules do not result in the formation of product. Give reasons.

c) The rate expression for a reaction is determined from experiment and not from the balanced chemical equation.

d) The rate of reaction can be increased without changing the temperature.

e) The order of reaction is not necessarily equal to the sum of the coefficients in the balanced chemical equation.

f) Catalyst is neither a reactant nor a product.

g) The radioactive decay is the example of first order reaction.

h) The second order and third order reactions have different units.

i) Which sugar dissolves the fastest, the granular sugar or the powder sugar? Give reason.

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Chapter # 10

Solutions and Colloids

Major Concepts

10.1 General Properties of Solutions
10.2 Concentration Units
10.3 Raoult's Law
10.4 Colligative Properties of Non-Electrolyte in Solutions
10.5 Colloids

Learning Outcomes

The students will be able to:

- List the characteristics of colloids and suspensions that distinguish them from solutions. (Applying)
- Define hydrophilic and hydrophobic molecules. (Remembering)
- Explain the nature of solutions in liquid phase giving examples of completely miscible, partially miscible and immiscible liquid-liquid solutions. (Applying)
- Explain the effect of temperature on solubility and interpret the solubility graph. (Analyzing)
- Express solution concentration in terms of mass percent, molality, molarity, parts per million, billion and trillion and mole fraction. (Remembering)
- Define the terms colligative. (Remembering)
- Describe on a particle basis why a solution has a lower vapor pressure than the pure solvent. (Applying)
- Explain on a particle basis how the addition of a solute to a pure solvent causes an elevation of the boiling point and depression of the freezing point of the resultant solution. (Applying)
- Describe the role of solvation in the dissolving process. (Understanding)
- Define the term water of hydration. (Remembering)
- Explain concept of solubility and how it applies to solution saturation. (Applying)
- Distinguish between the solvation of ionic species and molecular substances. (Understanding)

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Introduction

Anything that has mass and occupies space is called matter. Matter is of two types: (I) substance (pure substance), and (ii) mixture (impure substance). Mixtures are classified as either homogeneous (uniform composition throughout) or heterogeneous (different composition in different regions). Solution is a homogeneous mixture of two or more than two different substances consisting of ions or molecules. A solution has at least two components. The component of solution which is in lesser amount is called solute and the component which is in larger amount is called solvent. For example, NaCl is solute and water is solvent in salt-water solution. In the everyday routine, we make or use solutions very often. In the start of the day, we drink a cup of tea which is the solution of water (solvent), sugar (solute) and soluble extracts of tea (solute). Other common examples of solutions are natural gas (homogeneous mixture of gaseous lower hydrocarbons), gasoline (homogeneous mixture of liquid hydrocarbons), soda water (solution of CO_2 in water), milk, sea water, steel, shampoo, and the air we breathe. The amount of solute in the given amount of solvent or solution is called concentration of solution. The solution which has relatively lesser amount of solute is called dilute solution and the solution which has relatively a larger amount of solute is called concentrated solution. For example, 5% aqueous solution of sugar is dilute than 10% aqueous solution of sugar. Likewise, the 10% aqueous solution of sugar is concentrated than 5% aqueous solution of sugar.

The solution of a substance in water is called aqueous solution. Aqueous solutions are the most common solutions and play an important role in chemistry. Common examples of aqueous solutions are sugar-water and salt-water solutions. Solutions may be gases, liquids or solids. There are nine types of solutions on the bases of physical states (i.e. solid, liquid and gaseous nature) of solute and solvent.

Table 10.1: Types of Solutions on the basis of physical states

State of Solute	State of Solvent	State of Resulting Solution	Examples
Gas	Gas	Gas	Air, natural gas
Gas	Liquid	Liquid	CO_2 in water (Soda water)
Gas	Solid	Solid	Hydrogen in palladium, hydrogen in platinum
Liquid	Gas	Gas	Mist, fog, clouds, sprays
Liquid	Liquid	Liquid	Alcohol in water, milk, gasoline, gas oil, antifreeze

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State of Solute	State of Solvent	State of Resulting Solution	Examples
Liquid	Solid	Solid	Mercury in Silver (dental amalgam), Cheese, Butter
Gas	Gas	Gas	Dust in smoke
Solid	Liquid	Liquid	Sugar in H_2O, Jellies, Paints, vinegar, sea water
Solid	Solid	Solid	Metal alloys, steel, pearls, opals, ruby, garnet, Brass (Cu/Zn), Solder (Sn/Pb)

Keep in Mind

In the atmosphere there are at least three kinds of solutions. These are (i) gas in gas-oxygen dissolved in nitrogen, (ii) liquid in gas-water vapour dissolved in air, and (iii) solid in gas-tiny particles of smoke dissolved in the air.

In general, polar solutes are dissolved in polar solvents and non-polar solutes are dissolved in non-polar solvents. The common polar solvents that are used in the laboratory are water, acetone, methyl alcohol, and ethyl alcohol. The common non-polar solvents are ether, chloroform, carbon tetrachloride, hexane, toluene, benzene.

10.1 General Properties of Solutions

Some of the general properties of solutions are:

i) A solution has at least two components: a solvent and a solute. It may have more than two components: a solvent and two or more solutes.

ii) A solution does not have fixed composition; that is, the ratio of solute can be different from solvent.

iii) The solutes particles consist of ions or molecules.

iv) Solutions may either be colourless or coloured and are usually transparent.

v) The properties of a solution do not remain same when the ratio of solute to solvent is changed.

vi) The solute particles are uniformly distributed in the whole solution and the solution is homogeneous throughout. The solute particles will not "settle out" after a time. The composition and properties of the every part of the solution is exactly the same as every other part.

vii) The solute can generally be separated from the solvent by physical techniques such as evaporation and distillation.

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10.1.1 Solution, Suspension and Colloids

Mixtures are classified into homogeneous mixtures and heterogeneous mixtures. Homogeneous mixtures are further classified into solutions and colloids.

A solution is a homogenous mixture of two or more components. The solute particles of solutions are so small that they cannot be seen by the naked eye and microscope. Due to small size, the solute particles pass through filter paper and are not separated from the solution by filtration. The size of solute particles ranges from about 0.01nm to 1nm. Examples of some common solutions are sugar in water, soft drinks, gasoline, and air.

A suspension, on the other hand, is a heterogeneous mixture and the particles are so large that can be seen with microscope and can often be seen with the naked eye. Due to bigger size, the particles cannot pass through filter paper and can be separated from heterogeneous mixtures. The particles of suspension are heavy enough and will settle out under the influence of gravity after a time. The size of particles is more than 1000nm. A common example of suspension is muddy water. Other examples of suspensions are soot, chalk powder in water, sand in water, flour in water and milk of magnesia. Many of the medicinal solutions are marketed as a suspension that are labeled as "suspension" and instructed "shake well before using". You may be familiar with antibiotics that are aqueous suspensions and are well shaken before using. The main purpose of shaking the antibiotics is to mix the substance uniformly in a solvent.

A colloid (or colloidal dispersion) is also a homogeneous mixture of two or more components like solution. The word colloidal means "glue-like" and was originally applied to sticky substances such as starch, gelatin and glue. We cannot use the terms solute and solvent for the components of colloids because the solute particles are not dissolved in the solvent and is present in the form of tiny particles that are suspended in the medium. We, therefore, use the terms dispersed phase for solute and dispersing medium (or continuous phase) for solvent. The dispersed particles are present in lesser amounts than dispersing medium in colloids. Examples of colloids are milk, hair sprays, fog, smoke, clouds, butter, face cream, toothpaste, starch and blood serum. The dispersed particles are intermediate in size between those of a true solution and those of suspension. The dispersed particles of colloids are so small that are not usually seen by the naked eye and ordinary microscope. However, they can be detected by electron microscope. Due to relatively small size, the dispersed particles pass through filter paper of large pores and will not settle out under the influence of gravity over time. The size of dispersed particles is about 2 nm to 1000 nm.

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10.1.2 Hydrophilic and Hydrophobic Molecules

Hydrophilic (adj.) (Greek = 'water loving') molecules are polar and having affinity for water. They have ability to form hydrogen bonds or ion dipole forces with water and are readily soluble in water. Hydrophilic substances are also known as polar substances. Examples of hydrophilic molecules are sugars, salts (NaCl), alcohols (ethanol).

Hydrophobic (adj.) (Greek = 'water hating') molecules are non-polar and are repelled by water. The word hydrophobic does not actually mean that they hate water but it means that they are unable to form hydrogen bonds with water and are not dissolved in water. They are dissolved in non-polar solvents such as ether, carbon tetrachloride, benzene. Hydrophobic substances are also known as non-polar substances. Examples of hydrophobic molecules are oils, fats, alkanes (hexane), and greasy substances.

What happens when we add a lump of sugar in water and stir it? The sugar forms hydrogen bonds with water and is dissolved. What happens when we add half test tube of oil in another test tube containing water? The oil does not mix with water. Sugar is hydrophilic and oil is hydrophobic.

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The use of Soap and Detergents

The soap is generally used for bathing and detergents are used for washing. Soaps are mixtures of sodium or potassium salts of fatty acids. A soap molecule is amphipathic and has two ends, the head and the tail. The head of the soap is hydrophilic and the tail of the soap is hydrophobic. When we put soap in water. The hydrophilic end is attracted to water and the hydrophobic end is repelled by water. Hydrophobic end that consists of long chains hydrocarbon and structurally similar to oil is out of water and is attracted by other hydrophobic substances such as oil droplets and grease that are present at the surface of skin or cloth. The soap in this way forms an emulsion (colloid) with water which is used to wash skin, clothes or greasy dishes to remove stain or dirt from their surfaces. Like soaps, detergents also have molecules with a polar end and a non-polar end.

10.1.3 The Nature of Solutions in Liquid Phase

Solutions may be gaseous, liquid, or solid as we know. But here we will focus on liquid solutions because they are in the interests of chemists as lots of reactions of great significance occur in liquid solutions and are undoubtedly the most common and important. Liquid solutions are formed by dissolving a gas

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liquid, or solid in a liquid solvent. The process of dissolving of solute in a solvent is called dissolution. Examples of liquid solutions are soda water, iodine tincture, tap water, sea water, house hold ammonia, brine, sodium-potassium alloy. Liquid solutions are the most common types that you found in laboratory of chemistry, super market and at your home. In our daily life we dissolve sugar in water to make tea, salt in water to cook food, CO_2 in water to make soda water. Soda water is an example of gas-liquid solution where carbon dioxide gas is dissolved in water. Antifreeze is an example of liquid-liquid solution where ethylene glycol (a viscous hygroscopic liquid) is dissolved in water. Brine is an example of solid-liquid solution where NaCl (a solid salt) is dissolved in water.

The solutions of liquids in liquids are divided into three classes as follows:

(a) Completely Miscible liquids
(b) Partially Miscible liquids
(c) Practically Immiscible liquids

(a) Completely Miscible Liquids

Liquids which dissolve in each other in all proportions are called completely miscible liquids. For example:

i) Alcohol and water
ii) Alcohol and ether
iii) Benzene and toluene
iv) Phenol and H_2O above 67°C.

The properties of such solutions are not additive. Generally, the volume decreases on mixing but sometimes it increases. During the formation of solution, heat may either be evolved or absorbed. Such solutions can usually be separated by fractional distillation.

(b) Partially Miscible Liquids

Liquids which are slightly soluble in each other are called partially miscible liquids.

For example:

i) Ether and water
ii) Bromine and water
ii) Phenol and water below 67°C
iv) Aniline and water

When equal volumes of ether and water are shaken in separating funnel, then two layers are formed. Each liquid layer is a saturated solution of the other liquid. Such solutions are called conjugate solutions. Solubility of these conjugate solutions is affected by temperature changes.

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(c) Practically Immiscible Liquids

Liquids which are completely insoluble in one another are called immiscible liquids. For example:

i) Benzene and water
ii) Carbon tetrachloride and water
iii) Chloroform ($CHCl_3$) and water
iv) Carbon disulphide (CS_2) and water

10.1.4 Solubility

The concentration of the solute in the solution when it is in equilibrium with the solid substance at a definite temperature is called solubility. For example, the solubility of NaCl in 100g of water at 0°C is 35.7g.

It can also be defined as:

The amount of solute dissolved in 100g of solvent to make a saturated solution at a definite temperature is called solubility.

Units of solubility are:

i) No. of grams of solute in 100g of solvent
ii) Mole dm^{-3}

Various methods are used for the determination of solubility. One of them is given here:

The saturated solution of a solid mass is prepared at a constant temperature. Then this solution is filtered. A known volume of this solution is evaporated in a china dish and from the mass of residue, the solubility is determined.

The extent of solubility of solute in a particular solvent depends on the nature of solute and solvent particles whether they are polar or non-polar, the temperature at which the solution is formed, and the pressure of the gaseous solute.

The Nature of Solute and Solvent

The intermolecular attractive forces that are present among liquids and solids play a key role in the formation of solutions. The intermolecular forces will enable us to understand, why water dissolves table salt (or sugar) but not dissolve cooking oil (or motor oil). A general rule of thumb that, "like dissolves like" is applied here. This means that polar solvents dissolve polar solutes and non-polar solvents dissolve non-polar solutes. For example, polar solutes such as NaCl and sugar are dissolved in water (polar solvent) and non-polar solutes such as cooking oil and motor oil are not dissolved in water (polar solvent).

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When NaCl an ionic compound is dissolved in water, the inter-ionic attractive forces among NaCl particles are overcome and they are split up into positive and negative ions. Positive ions are attracted by negative pole of water molecules and negative ions are attracted by positive pole of water molecules. In this way all negative and positive ions are surrounded by water molecules. The process in which an ion or molecule is surrounded by water molecules is called hydration. In a broader way, the process in which an ion or molecule is surrounded by solvent molecules is called solvation.

Sugar (sucrose) and water are soluble in each other because the major force between molecules is hydrogen bonding involving –OH groups. When they both are mixed, the sugar molecules that have –OH groups form hydrogen bonds with water molecules and are dissolved. In this case each molecule of sugar (sucrose) stays together as a single unit and the ions in the solution do not form. The non-polar solutes have London dispersion forces while water has hydrogen bonding that is why neither cooking oil nor motor oil is dissolved in water and float on the surface of water because they do not attract each other significantly.

The non-polar solutes such as cooking oil and motor oil are dissolved in non-polar solvents such as gasoline and benzene. The solutes and solvents both, in this case, has the same attractive forces (London dispersion forces), that is why; they are soluble in one another.

Keep in Mind

The solution is formed when solute-solvent attractions are either comparable to or stronger than solute-solute and solvent-solvent attractions.

We have main focus on solid-liquid solutions and liquid-liquid solutions because the solutions of gases in water are unusual.

10.1.4.1 The Effect of Temperature on Solubility

We have observed that the solubility of tea leaves, coffee beans or sugar increases with rise in temperature and decreases with fall in temperature; that is, they are more soluble in hot water and less soluble in cold water. But the solubilities of some substances such as cerium sulphate and cesium sulphate decrease with rise in temperature.

Keep in Mind

The temperature is not only affecting the rate of dissolving, it also affects the solubility. The rate of dissolving of solute is directly proportional to temperature; that is, the rate of dissolving of solute increases by increase in temperature and decreases by decrease in temperature. But the amount of dissolved solute in the solution may decrease or increase by raising temperature of the solution.

Solubility of Solids in Liquids

The solids have strong attractive forces among their particles. The energy is required to overcome these attractive forces among particles of solids when a solid

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is dissolved in liquid. The rise in temperature usually increases the solubility of solids in liquids. For example, the solubility of sugar (sucrose) in 100g of water at 0°C is 179g, at 40°C is 238g and at 100°C is 487g. The solubility of some solids like NaCl is little affected by rise in temperature. The solubility of NaCl in 100g of water at 0°C is 35.7g, at 40°C is 36.4g and at 100°C is 39.2g. The solubility of sodium chloride increases only about 3.5g. On the other hand, the solubility of some solids decreases by rise in temperature. For instance, the solubility of cerium sulphate at 0°C is 20.8g, at 40°C is about 6.7g and at 100°C is about 3.87g. The solubility of cerium sulphate decreases about 17g. The solubility curves are shown in the figure. The solubility curve is a graphical representation between temperature and solubility of solute in a particular solvent.

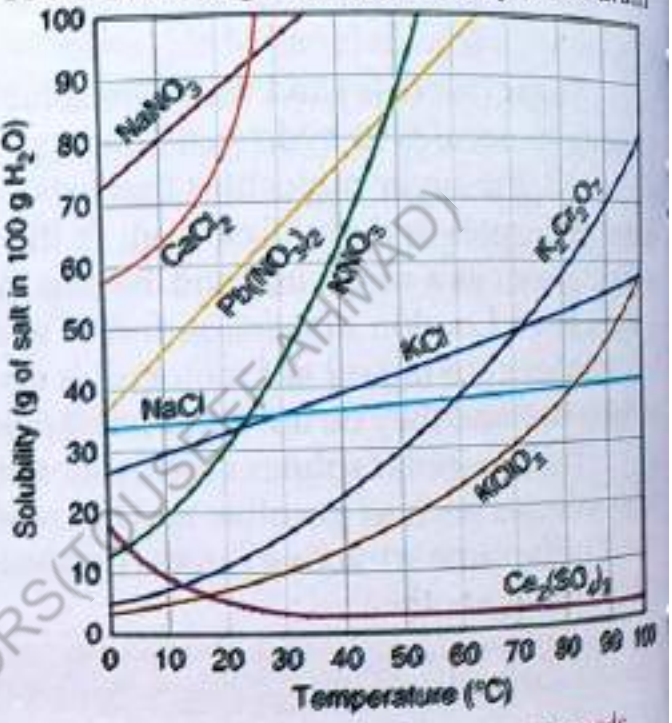

Fig. 10.1: Solublity of most compounds increase by increasing temperature

Table 10.2: Solubility in Gram of Solutes in 100g of Water

Substance	Temperature					
	0°C	20°C	40°C	60°C	80°C	100°C
NaCl	35.7	35.9	36.4	37.1	38.0	39.2
$C_{12}H_{22}O_{11}$	179	204	238	287	362	487
KNO_3	13.9	31.6	61.3	106	167	245
$AgNO_3$	122	216	311	440	585	733
$LiCO_3$	1.54	1.33	1.17	1.01	0.85	0.72
$Ce_2(SO_4)_3$	20.8	10.1	–	3.87	–	–
CO_2 at SP	0.335	0.169	0.0973	0.058	–	–
O_2 at SP	0.00694	0.00537	0.00308	0.00227	0.00138	0.00

Solubility of Liquids in Liquids

The attractive forces among the particles of liquids are weaker than solids. The additional energy is not required to overcome these attractive forces among

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particles of liquids when it is dissolved in another liquid. We can say that the rise in temperature usually does not affect the solubility of most of the liquids in liquids.

Solubility of Gases in Liquids

There are weak attractive forces between gas molecules, so the additional energy is not required to overcome these forces among the molecules of gases when they are dissolved in liquid such as water. The energy as heat is released when a gas is dissolved in water due to forces of attractions between gases molecules and solvent molecules. It means that this is an exothermic process and is favoured by fall in temperature. We may say that the solubilities of gases in water are decreased by rise in temperature (except helium). This is because as the temperature increases the kinetic energy of the gas molecules increase and as a result of this the forces of attractions between gases and water molecules decrease.

Heat of Solution

The energy changes during the formation of a solution are called energetics of solutions or heat of solution or enthalpy of solution.

The solution formation may either be endothermic or exothermic.

The heat of solution is negative for an exothermic process and is positive for an endothermic process. Heat of solution measure the intermolecular attraction between solute and solvent molecules. When KNO_3 is added to water, the temperature of the solution decreases which shows that it is an endothermic process.

$$KNO_{3(s)} + H_2O_{(l)} \rightleftharpoons K^+_{(aq)} + NO^-_{3(aq)} \qquad \Delta H = +35.7 \text{ kJ mol}^{-1}$$

The solubility of potassium nitrate in water is increased by rise in temperature. The solubility of solutes that has positive heats of solution is usually raised by rise in temperature.

When LiCl is added to water, the temperature of the solution increases which shows that it is an exothermic process.

$$LiCl_{(s)} + H_2O_{(l)} \rightleftharpoons Li^+_{(aq)} + Cl^-_{(aq)} \qquad \Delta H = -37 \text{ kJ mol}^{-1}$$

The solubility of lithium chloride in water is increased by fall in temperature. The solubility of solutes that has negative heats of solution is usually raised by fall in temperature. By increasing temperature, the solubility of solutes usually falls in this case.

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Table 10.3: Heat of Solution of Some Substances at Room Temperature

Substance	Heat of Solution (kcal/mol)	Substance	Heat of Solution (kcal/mol)
$NaCl_{(s)}$	+3.88	$CH_3COOH_{(l)}$	−1.51
$NaOH_{(s)}$	−44.51	$H_2SO_{4(l)}$	−74.32
$KNO_{3(s)}$	+34.89	$HCl_{(g)}$	−74.84
$NH_4NO_{3(s)}$	+25.69	$NH_{3(g)}$	−30.50
$KOH_{(s)}$	−57.61	$NH_4Cl_{(s)}$	+14.78
$KClO_{3(s)}$	+41.38	$AgNO_{3(s)}$	+22.59
$CuSO_4.5H_2O_{(s)}$	+11.51	$NaNO_{3(s)}$	+20.50
$MgSO_4.7H_2O_{(s)}$	+15.90	$Na_2SO_4.10H_2O_{(s)}$	+78.54

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Use of Cold and Hot Pouches

Heat is either given off or absorbed when ionic substances are dissolved in water. The endothermic solution process is used in the "instant cold pouches" and the exothermic solution process is used in the "instant hot pouches". These instant cold and hot pouches are used in hospitals and at other places for the treatment of minor injuries, sprains, and bruises to reduce swelling. In instant cold pouches, the NH_4NO_3 (or NH_4Cl) is packed in a stronger bag that is placed inside a plastic bag of water. When the inner bag that contains ammonium nitrate is broken by squeezing, the ammonium nitrate dissolves in the water in the outer bag. In this case, the heat is absorbed and the pouch becomes cold. On the other hand, the hot pouches generally contains $CaCl_2$ (or $MgSO_4$), which on dissolving in water, release heat and the pouch becomes hot.

10.1.4.2 The Effect of Pressure on Solubility

The solubilities of solids or liquids are affected very little or not affected by changing pressure that is why the effect of pressure on the solubility of solids or liquids in liquid solvent is neglected. However, pressure has a great effect on the solubility of gases. The English chemist William Henry studied the effect of gases on the solubility of gases. According to Henry's law, the solubility of a gas in a liquid is directly proportional to the pressure of the gas above the liquid at a given temperature.

William Henry (1774-1836)

$$S \propto P \quad \text{or} \quad S = K.P$$

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Where, K is proportionality constant, S is the solubility of the gas in the solvent, and P is the partial pressure of the gas.

The solubility of the gas is doubled by doubling the partial pressure of the gas above the solution and is tripled by tripling the partial pressure of the gas above the solution, and so on. The solubility of CO_2 gas at one atmosphere in 100g of water is 0.169g at 20°C. The solubility of CO_2 gas will be doubled (0.338g) by doubling the pressure of the gas to two atmospheres at same temperature.

Suppose we have a gas in equilibrium with a solution at which the number of molecules entering the solution is equal to the number of molecules leaving the solution. When the pressure of the gas above the solution is increased, the more molecules are forced into the solution. Thus, the concentration of the gas in the solution increases until the equilibrium is restored again; that is, the solubility increases until the rate at which the number of gas molecules enteri..g the solution is equal to the number of gas molecules leaving from the solution. Thus, we can say that the solubility of gas in a liquid increases by increasing pressure above the solution.

Figure: 10.2: This diagram shows the concentration of dissolved gas is proportional to the pressure of the gas above the solution

Interesting Information

Carbonated beverages are the saturated solutions of carbon dioxide in water under pressure. Carbonated beverages are bottled at a pressure of 5-10 atmospheres. When a bottle of carbonated beverage is uncapped, the pressure on the surface of the beverage is reduced to one atmosphere, and the bubbles of carbon dioxide come out suddenly of the solution. This rapid escape of dissolved gas from a liquid is known as effervescence.

10.2 Concentration Units of Solutions

Concentration of solution means the amount of solute present in a given amount of solution. We commonly deal with dilute (a solution which has relatively

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small amount of solute) and concentrated solution (a solution which has relatively large amount of solute) in our daily life. Sometimes we use unsaturated (a solution which can dissolve further solute on addition), saturated (a solution which is fully loaded up with solute and cannot dissolve more solute at a given temperature) and supersaturated (a solution which has more of the solute than the usual maximum amount and are unstable). They are prepared at an elevated temperature or pressure to describe the concentration of solution. But in chemistry lab we have to know the exact concentration of a solution; that is, the exact amount of solute in the given amount of solution. Chemists use several different concentration units, each of which has its own benefits and drawbacks. The amount of solutes or solvents in a solution is generally measured in terms of volume, mass or moles and these units are usually called concentration units. The concentration of solution can be expressed by percentage composition, molarity, molality, mole fraction, and parts per million, billion and trillion.

10.2.1 Percentage Composition

The term percent means "parts per hundred". The number of parts of solute present in 100 parts of solvent or solution is called %age composition.

It can be expressed by four different ways:

i) Weight by Weight Percent (W/W %)

The weight by weight percent also called weight percent or percent by weight or percent by mass is defined as the number of grams of solute present in 100 grams of solution. For example, a 10% W/W sugar solution means contains 10 g of sugar in 100g of solution. The solution has 10 g of sugar (solute) and 90 g of water (solvent).

$$\text{\% age by weight} = \frac{\text{Mass of solute}}{\text{Mass of solution (mass of solute + mass of solvent)}} \times 100$$

The solute and solution masses must be measured in the same unit; that is, in grams.

Example 10.1

What is weight percent of solution containing 100g of water and 2.5g of glucose?

Solution:

Mass of glucose = 2.5g
Mass of water = 100g
Mass of solution = 100 + 2.5 = 102.5g

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Weight percent of glucose solution = ?

$$\text{Weight percent of glucose solution} = \frac{\text{Mass of glucose}}{\text{Mass of solution}} \times 100$$

$$= \frac{2.5\text{g}}{102.5\text{g}} \times 100$$

$$= 2.45\%$$

Practice Exercise 1:

Calculate the weight percent of sugar (sucrose) when 15g of sugar is added to 85g of water?

ii) Weight by Volume Percent (W/V %)

The weight by volume percent is defined as the number of grams of solute present in 100mL of solution. For example, a 10% W/V sugar solution means that 10g of sugar in each 100mL of solution.

$$\text{\% age by weight – volume} = \frac{\text{Mass of solute (g)}}{\text{Volume of solution (mL)}} \times 100$$

The units do not cancel because the concentration unit of solute is always given in grams and that of solution is milliliters. This concentration unit is normally used when the solute is a solid and the solvent or resulting solutions are liquids.

Example 10.2

Calculate the mass by volume percent of 70mL of solution that has 20g of NaOH.

Solution:

Mass of NaOH = 20g

Volume of solution = 70mL

Mass by volume percent of solution = ?

$$\text{Mass by volume percent of solution} = \frac{\text{Mass of NaOH in g}}{\text{Volume of solution in mL}} \times 100$$

$$= \frac{20\text{g}}{70\text{mL}} \times 100$$

$$= 28.57\%$$

Practice Exercise 2:

A 50mL solution is prepared by dissolving 0.75g of NaCl in enough water. What is the W/V% of the solution?

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iii) Volume by Weight Percent V/W %

The Volume by Weight Percent is defined as the number of milliliters of solute in 100 g of solution. For example, a 10% V/W solution means that 10mL of alcohol in water to make the total mass of the solution 100g.

$$\%\text{ age by volume – weight} = \frac{\text{Volume of solute}}{\text{Mass of solution}} \times 100$$

In this type of solution, we know the total mass of solution but we do not know the total volume of solution.

iv) Volume by Volume Percent (V/V %)

The volume by volume percent (also called volume percent or percent by volume) is defined as the volume in milliliter of solute in 100 milliliter of solution. For example, 10% V/V alcohol-water solution means that 10mL of alcohol dissolved in enough water to make the total volume of solution 100mL. Keep in mind that 10% V/V alcohol-water solution cannot be prepared by dissolving 10mL of alcohol in 90mL of water because the total volume of the solution may not be necessarily equal to the sum of volumes of solute and solvent.

$$\%\text{age by volume} = \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100$$

The solute and solution masses must be measured in the same unit; that is, in milliliters.

Example 10.3

An alcoholic beverage has 25mL of ethyl alcohol. What is V/V % of 75mL of the beverage?

Solution:

Volume of ethyl alcohol = 25mL

Volume of beverage = 75mL

Volume percent = ?

$$\text{Volume percent} = \frac{\text{Volume of ethyl alcohol}}{\text{Volume of beverage}} \times 100$$

$$= \frac{25\text{mL}}{75\text{mL}} \times 100$$

$$= 33.33\%$$

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Practice Exercise 3:

Calculate the V/V % of 0.250L of vinegar solution containing 12.5mL of acetic acid.

10.2.2 Molarity

Molarity is the most useful unit of concentration in chemistry. The number of moles of solute dissolved in one liter of solution is called molarity. It is denoted by 'M'. The molarity has the units of mole per liter (mol/L). The mathematical equation for the calculation of molarity is as follows:

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute (n)}}{\text{Volume of solution in liter (V)}} \quad \text{or}$$

$$\text{Molarity (M)} = \frac{\text{Mass of solute in gram}}{\text{Molar mass of solute}} \times \frac{1}{\text{Volume of solution in liter}}$$

In order to calculate the molarity of solution, the number of moles of solute and the volume of the solution in liters are required. Keep in mind that a solution of a given molarity is prepared by dissolving the solute in enough solvent to make the total volume of the solution one liter. We are not allowed to dissolve the solute in one liter of solvent, because the total volume of solution in this case might be a bit larger than one liter due to additional volume of solute. If the volume of the solution is larger than one liter, then the molarity will be less than 1M for the solution.

Keep In mind

To prepare one molar (1M) aqueous solution of NaOH, we are required to dissolve 1 mol (40g) of NaOH in enough water to make the total volume of the solution one liter. If we want to prepare 2M NaOH solution, then we are required to dissolve 2 moles (80g) of NaOH in enough water to make the total volume of the solution one liter. The solution whose molarity is one is called one molar solution.

Molarity is very useful to us because the number of moles of solute dissolved can be calculated by multiplying the molarity of solution with the volume of solution.

$$\text{No. of moles of solute (n)} = \text{Molarity (M)} \times \text{Volume of solution in liter (V)}$$

The number of moles of solutes enables us to calculate the number of particles and to solve those problems that involve quantities in chemical reactions.

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Table 10.4: Concentration of Solution in Molarity

Solute	of Solute	Moles of Solute	Solvent	Volume of Solution (mL)	Volume of Solution (L)	Molarity (M)
Iodine	2.54	0.01	CCl_4	500	0.50	0.02
KNO_3	750	7.42	H_2O	15×10^2	1.50	4.95
Sucrose	250	0.73	H_2O	750	0.75	0.97
NH_3	8.5	0.50	H_2O	180	0.18	2.78

Example 10.4

What is the molarity of 2.5L of solution containing 2.0mol of ethyl alcohol?

Solution:

Molarity of solution = ?

Volume of solution = 2.5L

Moles of ethylalcohol = 2.0mol

$$\text{Molarity (M) of solution} = \frac{\text{Moles of ethyl alcohol}}{\text{Volume of solution in dm}^3}$$

$$= \frac{2.0\text{mol}}{2.5\text{ L}}$$

$$= 0.8\text{M}$$

Practice Exercise 4:

Calculate the molarity of the sulphuric acid solution when 49g of sulphuric acid is dissolved in 2.5×10^2mL of solution.

Example 10.5

Prepare 1 M and 0.50M solutions of glucose.

Solution:

Molar mass of glucose $(C_6H_{12}O_6) = 72 + 12 + 96 = 180\text{g mol}^{-1}$

- **1 M glucose solution** is prepared by dissolving 180g (1 mol) of glucose in one liter of solution.
- **0.50M glucose solution** is prepared by dissolving 0.50mol ($0.50 \times 180 = 90$g) of glucose in one liter of solution.

Practice Exercise 5:

How can you prepare 0.25M and 2.50M NaOH solution?

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10.2.3 Molality

The number of moles of solute dissolved in one kilogram of solvent is called molality. It is denoted by lower case 'm'. The molality has the units of moles per kilogram (mol/kg). The mathematical equation for the calculation of molality is as follows:

$$\text{Molality (m)} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kilogram}} \quad \text{or}$$

$$\text{Molality (m)} = \frac{\text{Mass of solute in gram}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent in kilogram}}$$

The one molal solution of a solute is prepared by dissolving one mole of solute in one kilogram of solvent.

For example, 1 molal HCl solution is prepared when one mole of HCl (36.5g) is dissolved in 1kg of solvent. If we dissolve one mole (60g) of urea, $(NH_2)_2CO$ in 500 g (0.50kg) of water, the solution in hand will be 2 molal.

Note that the molarity of solution is temperature dependent but molality is temperature independent. It means that molarity of a solution changes slightly when temperature of the solution changes, but molality does not. Hence, molality is more convenient in those experiments that involve temperature changes.

The mass of one liter of water at room temperature is nearly equal to one kilogram that is why, in dilute solutions the number of moles of solute in one liter is about equal to the number of moles of solute in one kilogram of water. Hence, molarity is about equal to molality in dilute aqueous solutions.

Table 10.5: Concentration of Solution in Molality

Solute	Amount of Solute (g)	Moles of Solute	Solvent	Amount of Solvent (g)	Amount of Solvent (kg)	Molality (m)
CH_3OH	16.0	0.50	C_2H_5OH	1000	1.00	0.50
$CuSO_4$	159.6	1.00	H_2O	10^4	10.00	0.10
H_2O_2	68	2.00	H_2O	2×10^3	2.00	1.00
HCl	3.65	0.10	H_2O	1×10^2	0.10	1.00

Example 10.6

What is the molality of solution made by dissolving 290g of acetone (CH_3COCH_3) in 500 g of water?

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Solution:

Molality of acetone solution = ?

Mass of acetone = 290g

Mass of water = 500g = 0.50kg

$$\text{Molality of acetone solution} = \frac{\text{Given mass of acetone}}{\text{Molar mass of acetone}} \times \frac{1}{\text{Mass of solvent in kg}}$$

$$\text{Molality of acetone solution} = \frac{290\ \text{g}}{58\ \text{g}} \times \frac{1}{0.50\text{kg}} = 10\text{m}$$

Practice Exercise 6:

What is the molality of solution that is made by dissolving 96g of SO_2 gas in 750g of water?

10.2.4 Mole Fraction

It can be defined as:

The number of moles of a particular component divided by total number of moles of all the components present in the solution is called mole fraction. It is denoted by 'X'. Mole fraction has no unit.

$$\text{Mole fraction (X)} = \frac{\text{Number of moles of one component}}{\text{Total number of moles of all the component}}$$

The mole fraction of a particular component can be calculated as:

$$X_A = \frac{n_A}{n_A + n_B + n_C} = \frac{n_A}{n_t}$$

i) The mole fraction of a particular component is always less than 1.

ii) The sum of mole fraction of the entire components is always unity.

$$X_A + X_B + X_C = 1$$

If a solution has 2 moles of NH_3 in 7 moles of water, the mole fraction of NH_3 is shown as X_{NH_3} and the mole fraction of water is shown as X_{H_2O}. The total number of moles of ammonia and water in the solution are (2 mol + 7 mol) = 9.00 moles. The mole fractions of ammonia and water in the solution are calculated as:

$$\text{The mole fraction of ammonia} = X_{NH_3} = \frac{\text{No. of moles of ammonia}}{\text{Total number of moles}} = \frac{2\text{mol}}{9\text{mol}} = 0.2$$

$$\text{The mole fraction of water} = X_{H_2O} = \frac{\text{No. of moles of water}}{\text{Total number of moles}} = \frac{7\text{mol}}{9\text{mol}} = 0.7$$

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The sum of the mole fractions of both the components of solution is equal to one.

Mole fractions are specially used for the calculations of concentrations of gas mixtures but not for liquid solutions because other units of liquid solutions are generally more appropriate. Mole fractions do not depend on temperature.

Example 10.7

Calculate the mole fraction of each component of solution prepared by dissolving 1.22g of benzoic acid (C_6H_5COOH), in 11.95g of chloroform ($CHCl_3$).

Solution:

Mole fraction of benzoic acid $= X_{C_6H_5COOH} = ?$

Mole fraction of chloroform $= X_{CHCl_3} = ?$

Mass of benzoic acid $= 1.22g$

Mass of chloroform $= 11.95g$

$$\text{Moles of benzoic acid} = \frac{\text{Mass of benzoic acid}}{\text{Molar mass of benzoic acid}} = \frac{1.22\ g}{122 g.mol^{-1}} = 0.01\ mol$$

$$\text{Moles of chloroform} = \frac{\text{Mass of chloroform}}{\text{Molar mass of chloroform}} = \frac{11.95\ g}{119.5 gmol^{-1}} = 0.1\ mol$$

Total number of moles $= 0.01mol + 0.1mol = 0.11moles$

$$\text{Mole fraction of benzoic acid} = \frac{\text{Moles of benzoic acid}}{\text{Total number of moles}} = \frac{0.01mol}{0.11mol} = 0.09$$

$$\text{Mole fraction of chloroform} = \frac{\text{Moles of chloroform}}{\text{Total number of moles}} = \frac{0.1\ mol}{0.11mol} = 0.91$$

Practice Exercise 7:

A can of 2kg antifreeze contains 0.8 kg of ethylene glycol ($C_2H_6O_2$), and 1.2kg of water. What are the mole fractions of both the components of antifreeze?

10.2.5 Parts Per Million, Billion and Trillion

These units are used for very dilute solutions in which solutes have very low mass concentrations. These units can be used to express the amounts of pollutant gases in the air, the impurities present in the water, and the drugs in the human body.

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Parts per million

The number of parts by mass (or volume) of solute present in one million (10 lac) parts by mass (or volume) of the solution is called parts per million. It is abbreviated as ppm. One ppm is equal to one milligram of solute in one kilogram of solution (1 ppm = 1 mg/kg).

$$\text{Parts per million (ppm)} = \frac{\text{Mass of solute in grams}}{\text{Mass of solution in grams}} \times 10^6 \quad \text{or}$$

$$\text{Parts per million (ppm)} = \frac{\text{Volume of solute in mL}}{\text{Volume of solution in mL}} \times 10^6 \quad \text{or}$$

$$\text{Parts per million (ppm)} = \frac{\text{Mass of solute in grams}}{\text{Volume of solution in mL}} \times 10^6$$

It is used for very low concentrations of the solution. The impurities of the substances are usually expressed in ppm. For example, the maximum allowable amount of arsenic in water is 0.05ppm. A concentration of 0.05ppm means that if you drink 10 lac grams of water, then 0.05g of those is arsenic and other 999999.95g are consist of water and other minerals and contaminants.

Table 10.6: The Maximum Allowable Amounts of Minerals in Drinking Water

Mineral	Amount in ppm	Mineral	Amount in ppm
Sodium	160.00	Lead	0.05
Barium	1.00	Cadmium	0.01
Arsenic	0.05	Selenium	0.01
Chromium	0.05	Mercury	0.002
Silver	0.05		

Parts per Billion

The number of parts by mass (or volume) of solute present in one billion (1000million) parts by mass (or volume) of the solution is called parts per billion. It is abbreviated as ppb. One ppb is equal to one microgram of solute in one kilogram of solution (1 ppb = 1μg/kg).

$$\text{Parts per billion (ppb)} = \frac{\text{Mass of solute in grams}}{\text{Mass of solution in grams}} \times 10^9 \quad \text{or}$$

$$\text{Parts per million (ppb)} = \frac{\text{Volume of solute in mL}}{\text{Volume of solution in mL}} \times 10^9 \quad \text{or}$$

$$\text{Parts per million (ppb)} = \frac{\text{Mass of solute in grams}}{\text{Volume of solution in mL}} \times 10^9$$

It is used for very low concentrations of the solution.

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Parts per Trillion

The number of parts by mass (or volume) of solute present in one trillion (1000 billion) parts by mass (or volume) of the solution is called parts per billion. It is abbreviated as ppt. One ppt is equal to one nanogram of solute in one kilogram of solution (1 ppt = 1ng/kg).

$$\text{Parts per trillion (ppt)} = \frac{\text{Mass of solute in grams}}{\text{Mass of solution in grams}} \times 10^{12} \quad \text{or}$$

$$\text{Parts per million (ppt)} = \frac{\text{Volume of solute in mL}}{\text{Volume of solution in mL}} \times 10^{12} \quad \text{or}$$

$$\text{Parts per million (ppt)} = \frac{\text{Mass of solute in grams}}{\text{Volume of solution in mL}} \times 10^{12}$$

It is also used for very low concentrations of the solution.

Example 10.8

The concentration of gold in one liter of sea water is 0.001mg. What is the concentration of this solution is ppm, ppb, and ppt?

Solution

Mass of gold = 0.001mg = 0.000001g
Volume of sea water = 1L = 1000mL

Concentration of gold in sea water in ppm $= \frac{0.000001\ g}{1000\ mL} \times 10^{6} = 0.001$ ppm

Concentration of gold in sea water in ppb $= \frac{0.000001\ g}{1000\ mL} \times 10^{9} = 1$ ppb

Concentration of gold in sea water in ppt $= \frac{0.000001\ g}{1000\ mL} \times 10^{12} = 1000$ ppt

Practice Exercise 8:

A college student added one tea spoon of table sugar in the swimming pool. The concentration of table sugar is about 4×10^{-6}g per liter of water. Determine concentration of table sugar in water of swimming pool in ppm, ppb, and ppt.

10.3 Raoult's Law

In 1886, the French chemist François Marie Raoult (1830-1901) discovered a relation between the vapour pressure of pure solvent and that of a solution. He observed that the vapour pressure of solvent above a solution of a non-volatile, non-electrolyte solute depends on the mole fraction of solvent in the solution.

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10.3.1 Non-volatile, Non-electrolyte Solute in Volatile Solvents

Raoult's law can be defined in three ways:

i) The vapour pressure of solvent above a solution is equal to the product of the vapour pressure of pure solvent and its mole fraction in the solution.

$$P = P^\circ X_1$$

Where,

P is vapour pressure of solvent above solution, P° is vapour pressure of pure solvent, and X_1 is mole fraction of the solvent in the solution.

ii) The lowering of vapour pressure of a solvent is directly proportional to the mole fraction of solute.

$$\Delta P = P^\circ X_2$$

Where, Lowering of vapour pressure $(\Delta P) = P^\circ - P$

The lowering of vapour pressure depends on the number of non-volatile, non-electrolyte solute particles (atoms, molecules, or ions) in the solution but does not depend on the nature of the solute particles; that is, no matter what types of particles (atoms, molecules, or ions) are present in the solution.

iii) The relative lowering of vapour pressure $(\Delta P / P^\circ)$ is equal to the mole fraction of solute. By increasing mole fraction of solute, vapour pressure of solvent or solution decreases.

$$\Delta P / P^\circ = X_2$$

The solutions that obey Raoult's law are said to be ideal solutions.

The relative lowering of vapour pressure $(\Delta P / P^\circ)$ has three properties.

i) It is independent of temperature.
ii) It is proportional to the concentration of solute.
iii) It is constant when equimolar proportions of different solutes are dissolved in the same solvent.

The composition of vapours formed above a solution is different from the composition of liquid mixture at a given temperature. In order to obey the Raoult's law for the ideal solutions, the solute should be non-electrolyte and solution should be dilute.

10.3.2 When Both of the Components are Volatile

According to Dalton's law of partial pressure, the total pressure of a mixture of two or more volatile liquids such as petrol is equal to the sum of the individual vapour pressures of all the components (liquids) present in the mixture

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(liquid solutions).

$$P_{total} = P_A + P_B \quad \text{.....(i)}$$

The individual vapour pressures P_A and P_B are determined by Raoult's law. In case of components A and B, it makes no difference which we call the solute and which the solvent. According to Raoult's law, the individual vapour pressure of a particular component above a solution is equal to the product of the vapour pressure and its mole fraction in the solution.

$$P_A = P_A^\circ . X_A$$

$$P_B = P_B^\circ . X_B$$

By putting the values of P_A and P_B in equation (i) we get

$$P_t = P_A^\circ X_A + P_B^\circ X_B$$

Since,

$$X_A + X_B = 1$$

or $$X_A = 1 - X_B$$

Therefore,

$$P_t = P_A^\circ (1 - X_B) + P_B^\circ X_B$$

or $$P_t = P_A^\circ - P_A^\circ X_B + P_B^\circ X_B$$

or $$P_t = P_B^\circ X_B - P_A^\circ X_B + P_A^\circ$$

or $$P_t = X_B(P_B^\circ - P_A^\circ) + P_A^\circ$$

Graphical Representation of Raoult's Law

Consider the following six solutions with their mole fraction and vapour pressure values in the table.

Table 10.7: Six solutions with their Mole Fraction and Vapour Pressure Values

Mole Fraction of Component (X_A)	Vapour Pressure of Component A (P_A°)	Mole Fraction of Component B (X_B)	Vapour Pressure of Component B (P_B°)	Vapour Pressure of Solution ($P_t = P_A^\circ + P_B^\circ$)
0.0	0	1.0	50	50
0.2	5	0.8	40	45
0.4	10	0.6	30	40
0.6	15	0.4	20	35
0.8	20	0.2	10	30
1.0	25	0.0	0	25

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All of the above solutions have their own vapour pressures. We know that the total vapour pressure is equal to the sum of the vapour pressures of all the components present in the solution.

When a graph is plotted between mole fractions of A and B; that is, X_A and X_B on x-axis and vapour pressures of solutions; that is, P_A° and P_B° on y-axis, then a straight line is obtained.

The graph shows that component B is more volatile than component A. Hence, it has high vapour pressure and low boiling point as compared to component A. The two dotted lines show the partial pressures of the individual components of the solution. The vapour pressure of the components increases with increase in its mole fraction in the solution.

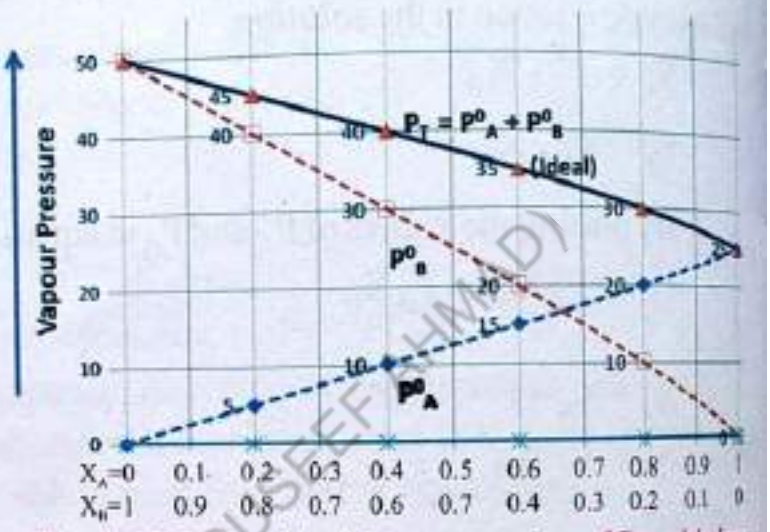

Figure 10.3: Graphical Representation of Raoult's Law

The total pressure is equal to the sum of the vapour pressures of the individual components ($P_t = P_A^\circ + P_B^\circ$) as shown in the graph.

Deviations of Solutions

Only the ideal solutions obey Raoult's law. The ideal behaviour is shown by those solutions which have nearly the same forces of attractions between the particles of solute-solute, solute-solvent, solvent-solvent. Hence, the enthalpy change during the formation of solution is zero. For real solutions, the forces of attractions between the particles of solute-solvent are much stronger or weaker than solute-solute and solvent-solvent. Consequently, the enthalpy change may either be negative or positive. Therefore, a non-ideal solution shows two types of deviations from Raoult's law.

Positive Deviation

A non-ideal solution in which solute-solvent attraction is weaker than solute-solute and solvent-solvent attraction shows positive deviation from Raoult's law.

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In this type of deviation,

i) Vapour pressure of solution is higher than its individual components.

ii) Boiling point of solution is lower than its individual components. For example, the boiling point of the solution of ethanol + water is 78.1°C which is lower than the boiling point of both ethanol (78.5°C) and water (100°C).

Figure 10.4: Positive Deviation from Raoult's Law

Negative Deviation

A solution in which solute-solvent attraction is stronger than solute-solute and solvent-solvent attraction shows negative deviation from Raoult's law.

In this type of deviation:

i) The vapour pressure of solution is lower than that of its individual components.

ii) The boiling point of solution is higher than that of its individual components. For example, the boiling point of the solution of Water + HCl is 108.5°C which are higher than the boiling point of both water and HCl.

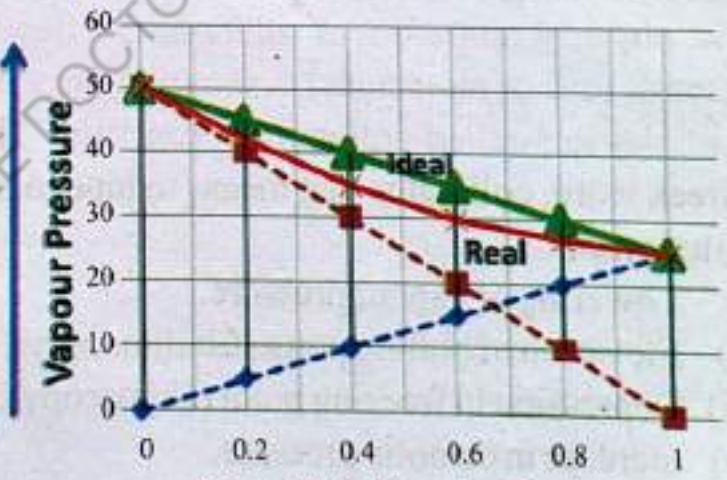

Figure 10.5: Negative Deviation from Raoult's Law

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Table 10.8: Difference Between Ideal and Non-ideal Solutions

Ideal Solution	Non-ideal Solution
A solution which obeys Raoult's law is called ideal solution.	A solution which does not obey Raoult's law is called non-ideal solution.
The forces of attractions between the molecules of different components (i.e. solute-solute, solute-solvent, solvent-solvent) are same.	The forces of attractions between the molecules of different components are not same.
The sum of volumes of individual components is equal to the volume of solution. $V_1 + V_2 = V_{solution}$	The sum of volumes of individual components is not equal to the volume of solution. $V_1 + V_2 \neq V_{solution}$
There is no enthalpy change during the formation of solution. $\Delta H = 0$	There is an enthalpy change during the formation of solution. $\Delta H \neq 0$
Examples are: Benzene-Toluene, Benzene-ether.	Examples are: Acetone-water, ethanol-Hexane.

10.4 Colligative Properties of Dilute Solutions

The physical properties of solutions that depend on the number of solute particles (atoms, ions or molecules) in the solution and do not depend on the kind of solute particles are called colligative properties. The word colligative is derived from Greek word, colligatus that means to bind together. Colligative properties of dilute solution are:

i) Lowering of vapour pressure.
ii) Elevation of boiling point (Ebullioscopy).
iii) Depression in freezing point (Cryoscopy).
iv) Increase in osmotic pressure.

It is important to keep in mind the conditions for colligative properties given below:

i) Solution should be dilute; that is, the concentration of the solution should be less than or equal to 0.2 M.
ii) Solute should be non-volatile.
iii) Solute should be non-electrolyte.

10.4.1 Lowering of Vapour Pressure

Vapour pressure is the pressure exerted by the vapour in equilibrium on

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liquid in a closed container. A substance which has a measureable vapour pressure is volatile and a substance which does not have a measureable vapour pressure is non-volatile. If a non-volatile and non-electrolyte solute is added to a solvent, then evaporating tendency of solvent molecules from the surface of solution decreases. Thus vapour pressure of solution decreases. This is known as lowering of vapour pressure. The vapour pressure of a volatile solvent that has a non-volatile solute is inversely proportional to number of solute particles in the solution.

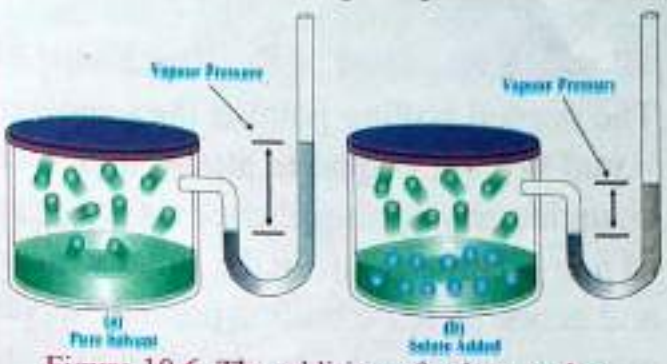

Figure 10.6: The addition of solute to the liquid solvent decreases the evaporating tendency of solvent

$$\text{Vapour pressure} \propto \frac{1}{\text{No. of non-volatile solute particles}}$$

It means the vapour pressure of solvent decrease by increase in the number of solute particles and vice versa.

According to Raoult's law,

The relative lowering of vapour pressure is equal to the mole fraction of solute.

$$\Delta P / P^\circ = X_2$$

We know that, $X_2 = \frac{n_2}{n_1 + n_2}$

Therefore,

$$\frac{\Delta P}{P^\circ} = \frac{n_2}{n_1 + n_2}$$

So, for a dilute solution, n_2 can be ignored in denominator, hence

$$\frac{\Delta P}{P^\circ} = \frac{n_2}{n_1}$$

As we know, $n_1 = W_1 / M_1$ and $n_2 = W_2 / M_2$

Hence, $$\frac{\Delta P}{P^\circ} = \frac{W_2 / M_2}{W_1 / M_1}$$

or $$\frac{\Delta P}{P^\circ} = \frac{W_2}{M_2} \times \frac{M_1}{W_1}$$

or $$\mathbf{M_2 = \frac{P^\circ}{\Delta P} \times \frac{W_2 M_1}{W_1}}$$

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The molecular mass of a non-volatile solute (M_2) can be calculated by the above equation.

10.4.2 Elevation of Boiling Point of the Solvent

The normal boiling point is the temperature at which the vapour pressure of the liquid becomes equal to atmospheric pressure. Boiling point can be changed by changing either atmospheric pressure or vapour pressure of the liquid. The presence of non-volatile solute in the solution decreases the vapour pressure of the solvent and hence increase boiling point of solvent. This is known as elevation of boiling point of the solvent. The elevation of boiling point (ΔT_b) is the difference between the normal boiling point of pure solvent and elevated boiling point of a solution.

$$\Delta T_b = T_{b(solution)} - T_{b(solvent)}$$

Where, ΔT_b is the elevation in the boiling point of solution, $T_{b(solution)}$ is the boiling point of solution, and $T_{b(solvent)}$ is the boiling point of the pure solvent.

The elevation of boiling point (ΔT_b) is directly proportional to the concentration of the solute in the solution (molality).

$$\Delta T_b \propto m \quad \text{or}$$

$$\Delta T_b = K_b m \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (i)$$

Where,

K_b is called molal boiling point constant or ebullioscopic constant.

We know,

$$\text{Molality (m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent in Kg}}$$

or $$m = \frac{W_2}{M_2} \times \frac{1}{W_1}$$

or $$m = \frac{W_2}{M_2 W_1}$$

By putting the value of 'm' in equation (i), we get

$$\Delta T_b = K_b \times \frac{W_2}{M_2 W_1}$$

or $$M_2 = \frac{K_b}{\Delta T_b} \times \frac{W_2}{W_1}$$

This equation can be used to determine the molar mass of a non-volatile non-electrolyte solute in a volatile solvent.

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Example 10.9

Calculate the boiling point of the solution when 18.5g of phenol (C_6H_5OH) is dissolved in 500g of water. The boiling point of pure water is 100°C and the boiling point elevation constant for water is 0.51°C kg/mol.

Solution:

Elevation in the boiling point of the water $= \Delta T_b = ?$

Mass of phenol $= W_2 = 18.5g$

Molar mass of phenol (C_6H_5OH) $= M_2 = 72 + 5 + 16 + 1 = 94 g mol^{-1}$

Boiling point elevation constant for water $= K_b = 0.51°C\ kg\ mol^{-1}$

Mass of water $= W_1 = 500g = 0.5kg$

The equation for the calculation of ΔT_b is:

$$\Delta T_b = K_b \times \frac{W_2}{M_2 W_1}$$

By putting the values, we obtain

$$\Delta T_b = 0.51°C\ kg\ mol^{-1} \times \frac{18.5g}{(94g\ mol^{-1})(0.5kg)}$$

$$\Delta T_b = \frac{9.435°C}{47}$$

$$\Delta T_b = 0.20°C$$

The boiling point of the solution is equal to the sum of the original boiling point and elevation in the boiling point of the solvent.

The boiling point of the solution $= 100.00°C + 0.20°C = 100.20°C$

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Practice Exercise 9:

A solution is made in which 100g of ethylene glycol ($C_2H_6O_2$) is dissolved in 500g of water. The boiling point elevation constant for water is 0.51°C kg/mol. What is the boiling point elevation of the water? What is the boiling point of aqueous solution?

Keep in Mind

We use molality instead of molarity in boiling point elevation calculations because the molality of a solution does not change by changing temperature, but the molarity of solution changes.

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Table 10.9: Molal Boiling Point Elevation Constants (K_b) for Some Common Substances

Substance	Formula	Normal Boiling Point (°C)	Molal Boiling Point Constant, K_b (°C Kg/mol)
Acetic acid	CH_3COOH	118.5	3.07
Acetone	CH_3COCH_3	56.0	1.71
Aniline	$C_6H_5NH_2$	184.4	3.22
Benzene	C_6H_6	80.15	2.53
Camphor	$C_{10}H_{16}O$	207.4	5.61
Carbon disulphide	CS_2	46.3	2.34
Carbon tetrachloride	CCl_4	76.5	5.02
Chloroform	$CHCl_3$	61.2	3.63
Diethyl ether	$CH_3CH_2OCH_2CH_3$	34.42	2.02
Ethyl alcohol	CH_3CH_2OH	78.26	1.22
Naphthalene	$C_{10}H_8$	218.0	5.65
Nitrobenzene	$C_6H_5NO_2$	210.9	5.24
Phenol	C_6H_5OH	181.8	3.56
Water	H_2O	100.0	0.51

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Example 10.10

A solution consists of 270g of solute dissolved in 250g of water. The boiling point elevation and the boiling point elevation constant values for water are 3.06°C and 0.51°C kg/mol respectively.

Solution

Elevation in the boiling point of the water $= \Delta T_b = 3.06°C$

Mass of glucose $= W_2 = 270g$

Molar mass of solute $= M_2 = ?$

Boiling point elevation constant for water $= K_b = 0.51°C\,kg\,mol^{-1}$

Mass of water $= W_1 = 250g = 0.25kg$

The equation for the calculation of molar mass of solute is:

$$M_2 = \frac{K_b}{\Delta T_b} \times \frac{W_2}{W_1}$$

By putting the value, we have

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$$M_2 = \frac{0.51^\circ C\ kg\ mol^{-1}}{3.06^\circ C} \times \frac{270g}{0.25kg}$$

$$M_2 = 180g\ mol^{-1}$$

Practice Exercise 10:

The boiling point of chloroform is increased by 2.42°C when 15.2g of camphor is dissolved in 150g chloroform. What is the molar mass of camphor? The value of K_b for chloroform is 3.63 °C kg/mol.

10.4.3 Depression in Freezing Point

The temperature at which the solid and liquid states of a substance exist in equilibrium with each other is called freezing point. It may also be defined as: the temperature at which its solid and liquid phases have the same vapour pressure is called freezing point.

When a non-volatile solute is added to a solvent, its vapour pressure is decreased. As a result of this freezing point of solvent decreases, this is known as depression of freezing point. At the freezing point, there are two things in the vessel; that is, liquid solution and the solid solvent. The solution will freeze at that temperature at which the vapour pressures of both liquid solution and solid solvent are same. It means that a solution should freeze at lower temperature than pure solvent.

The depression of a freezing point is directly proportional to the concentration (molality) of the solution.

$$\Delta T_f \propto m$$

or $$\Delta T_f = K_f m \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (i)$$

Where,

K_f is called molal freezing point constant or cryoscopic constant.

We know,

$$\text{Molality (m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent in kilogram}}$$

or $$m = \frac{W_2}{M_2} \times \frac{1}{W_1}$$

or $$m = \frac{W_2}{M_2 W_1}$$

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By putting the value of 'm' in eq. (i), we have

$$\Delta T_f = K_f \times \frac{W_2}{M_2 W_1}$$

or $$M_2 = \frac{K_f}{\Delta T_f} \times \frac{W_2}{W_1}$$

The molar mass of solute can be calculated by this equation.

Table 10.10: Molal Freezing Point Depression Constants (K_f) for Some Common Substances

Substance	Formula	Normal Freezing Point (°C)	Molal Freezing Point Constant, K_f (°C Kg/mol)
Acetic acid	CH_3COOH	16.6	3.90
Acetone	CH_3COCH_3	–94.8	-
Aniline	$C_6H_5NH_2$	–6.1	5.87
Benzene	C_6H_6	5.5	5.12
Camphor	$C_{10}H_{16}O$	178.8	–39.70
Carbon disulphide	CS_2	–111.5	3.80
Carbon tetrachloride	CCl_4	–2.96	-
Chloroform	$CHCl_3$	–63.5	4.70
Diethyl ether	$CH_3CH_2OCH_2CH_3$	–116.3	1.79
Ethyl alcohol	CH_3CH_2OH	–114.6	1.99
Naphthalene	$C_{10}H_8$	80.2	6.90
Nitrobenzene	$C_6H_5NO_2$	5.7	5.12
Phenol	C_6H_5OH	40.9	7.27
Water	H_2O	0.0	1.86

Applications of Freezing Point Depression and Boiling Point Elevation

i) Ethylene glycol is used as antifreeze in automobile radiators because it lowers the freezing point of the coolant. In cold climates, it prevents the solution in the radiators, coolant lines and engine blocks from freezing. Besides lowering the freezing point, it elevates the boiling point of the solution when added to water and prevents the water in the radiator from boiling off in hot summer days and

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the engine is not overheated.

ii) A salt such as NaCl or $CaCl_2$ is sprinkled on icy roadways and walkways in the winter to lower the melting point of ice and snow so that the water on the roads will not freeze at normal freezing point of water (0°C).

iii) A freezing mixture (Ice + NaCl or KNO_3) is used in making ice cream and kulfa. A freezing mixture lowers the freezing point of the solution well below the freezing point of pure water and freezes the ice cream rapidly.

iv) Sea water has freezing point below 0°C because it is the solution and contains higher concentration of various salts.

Example 10.11

A salt solution is prepared by adding 58.5g of NaCl in 0.75kg of water. Determine the freezing point of the solution. The freezing point constant of water is 1.86°C kg/mol and the normal freezing point of water is 0.00°C.

Solution:

Depression in the freezing point of the water $= \Delta T_f = ?$

Freezing point of solution $= ?$

Mass of sodium chloride $= W_2 = 117g$

Molar mass of sodium chloride (NaCl) $= M_2 = 23 + 35.5 = 58.5 g\,mol^{-1}$

Freezing point depression constant for water $= K_f = 1.86°C\,kg\,mol^{-1}$

Mass of water $= W_1 = 0.75kg$

The equation for the calculation of ΔT_f is:

$$\Delta T_f = K_f \times \frac{W_2}{M_2 W_1}$$

By putting the values, we get

$$\Delta T_f = 1.86°C\ Kg\ mol^{-1} \times \frac{117g}{(58.5 g mol^{-1})(0.75kg)}$$

$$\Delta T_b = \frac{217.62°C}{43.87}$$

$$\Delta T_b = 4.96°C$$

The freezing point of the solution is equal to the difference of the original freezing point and depression in the freezing point of the solvent.

The freezing point of the solution $= 0.00°C - 4.96°C = -4.96°C$

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Example 10.12

A solution is prepared in which 51.2g of sulphur is placed in 0.22kg of carbon disulphide. i.e. ΔT_f value for carbon disulphide is 3.45°C and K_f value for carbon disulphide is 3.80°C kg/mol. What is the molar mass of sulphur?

Solution:

Depression in the freezing point of the carbon disulphide $= \Delta T_f = 3.45°C$

Mass of sulphur $= W_2 = 51.2g$

Molar mass of sulphur $= M_2 = ?$

Freezing point depression constant for carbon disulphide $= K_f = 3.80°C\,kgmol^{-1}$

Mass of carbon disulphide $= W_1 = 0.22kg$

The equation for the calculation of molar mass of sulphur is:

$$M_2 = \frac{K_f}{\Delta T_f} \times \frac{W_2}{W_1}$$

By putting the value, we have

$$M_2 = \frac{3.80°C\,kg\,mol^{-1}}{3.45°C} \times \frac{51.2g}{0.22kg}$$

$$M_2 = 256g\,mol^{-1}$$

Practice Exercise 11:

An aqueous solution of glycerin contains 64.4g of glycerin in 0.644kg of water. What is the molar mass of the glycerin? The ΔT_f value for water is 2.02°C and K_f value for water is 1.86 °C kg/mol.

Practice Exercise 12:

Antifreeze contains 300g of ethylene glycol in 700g of water. What is the freezing point of antifreeze? The molar mass of ethylene glycol is 250g. The freezing point constant of water is 1.86°C kg/mol and the normal freezing point of water is 0.00°C.

10.4.4 Osmotic Pressure and Reverse Osmosis

Osmosis is the spontaneous process whereby the solvent molecules pass through a semipermeable membrane from a solution of lower concentration of solute (higher concentration solvent) into a solution of higher concentration of solute (lower concentration of solvent). Osmosis takes place, when two solutions of different concentrations (a pure solvent and a solution) are separated by semipermeable membrane. A semipermeable membrane is a thin layer of material that allows

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solvent particles to pass through it in the both directions and prevent solute particles to pass through. The rate of passage of solvent particles from the pure solvent side toward the solution side is high enough, because of this, the quantity of liquid on the pure solvent side decreases and the quantity of liquid on the solution side increases; hence the concentration of solution decreases. Animal bladder, cell membranes in the cells of living things (plants and animals) and cellophane (a polymer derived from cellulose) are the examples of semipermeable membranes. Consider an experiment in which a 10% concentrated sugar (glucose) solution is taken in a thistle funnel whose mouth is sealed with a semipermeable membrane. The funnel containing sugar solution is then place in a beaker of pure water. In the start the rate of flow of solvent (water) from beaker into the funnel (sugar solution) is greater than the rate of flow of solvent from funnel to beaker. The solvent starts flowing from the beaker through the semipermeable membrane into the sugar solution side (funnel).

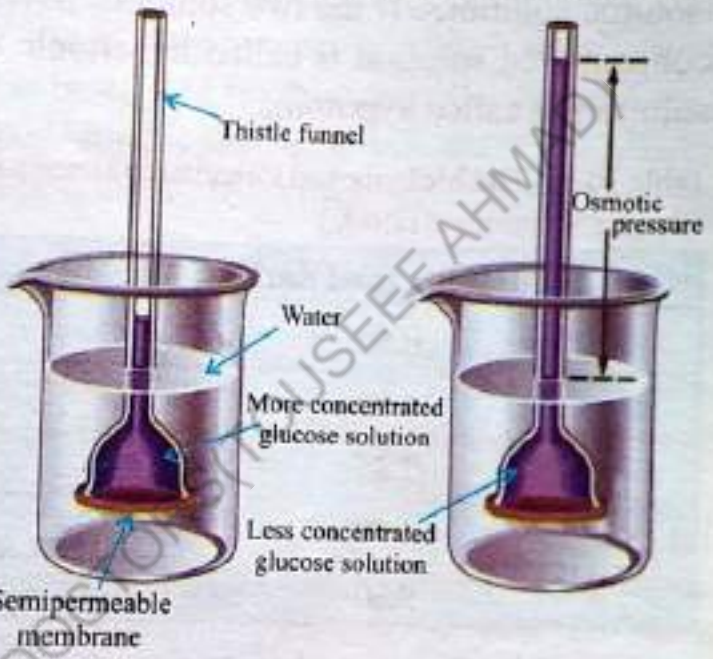

Figure: 10.7: Demonstration of Osmotic Pressure

Overtime, the volume of the sugar solution increases in the stem of the funnel while the water level in the beaker decreases. The process remains in operation until the pressure created by the weight of the water on the semipermeable membrane is enough to stop the upward flow of water. At this stage the rate of flow of water from beaker to funnel becomes equal to the rate of flow of water from funnel to beaker and the solution level stops rising and the equilibrium is established. Now the solvent flows at an equal rate in both directions across the semipermeable membrane and the volume of the liquid on each side of the membrane does not change. The amount of pressure required to attain equilibrium is called osmatic pressure. Osmotic pressure is defined as the pressure that must be applied on the high solute concentration side to stop the flow of solvent through a semipermeable membrane. It is denoted by capital pi (π). The osmotic pressure of the solution is given by:

$$\pi = (n/V)RT \quad \text{or}$$

$$\pi = MRT$$

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Where, M is the molarity of solution, R is the general gas constant (0.08206atm dm^3/mol K) and T is the absolute temperature. The osmotic pressure is expressed in atmospheres. The osmotic pressure increases by rise in the concentration of solute particles in the solution at a specific temperature. It also increases by rise in temperature and decrease by fall in temperature. Osmotic pressure depends on the number of solute particles in the solution but not on the type of solute particles. The two different solutions of equal concentration have the same osmotic pressure. The solutions that have the same osmotic pressures are called isotonic solutions. If the two solutions have different osmotic pressures, the more concentrated solution is called hypertonic and less concentrated solution (dilute solution) is called hypotonic.

Table 10.11: The Molarity and Calculated Osmotic Pressure Values of Variable Concentrations of Glucose Solutions at (298K)

Molarity (mol/dm^3)	Osmotic Pressure (atm)
0.50	12.23
1.00	24.45
2.25	55.02
4.50	110.04
9.00	220.08

Some of the Interesting Examples of Osmosis

i) The leaves of plants give off water vapours that lead to the rise in solute concentration in the leaf fluids. Water rises up from soil into plant leaves through roots, trunk, branches and stem creating an osmotic pressure.

ii) If plants are watered with salt water whose concentration is greater than the solution in the root, the roots will lose water rather than absorb it. Hence, the plants become dehydrated and sooner or later the plants die.

iii) The meat can be preserved by treating its surface with salt. The meat becomes dehydrated and does not go bad and remain in a good condition for a long time and there is no need of refrigeration for meat. The salt present on the surface of meat produces a concentrated solution which is hypertonic to bacteria cells. The bacteria on the surface of salted meat then tend to shrivel up and die.

iv) You are advised never drink excessive amount of sea water, even if your body is badly damaged and you are in the middle of the sea. When sea water (concentrated salt solution) is taken into stomach and intestine, the sea water extracts the water

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out of the stomach and intestine and the tissues become dehydrated. As a consequence of dehydration thirst increases but not decreases because the body will lose water instead absorb it.

Reverse Osmosis

The reverse of osmosis is said to be reverse osmosis. In normal osmosis, the solvent flows through a semipermeable membrane from a lower solute concentration to one of higher solute concentration but in reverse osmosis, the pressure greater than osmotic pressure is applied to flow the solvent through a semipermeable membrane from a higher solute concentration to one of lower solute concentration. The process of reverse osmosis is used to purify water. This process is particularly used to remove contaminates from sea water to make it fit for drinking. The world largest desalination plants are present in Saudi Arabia that treat salt water by reverse osmosis to produce fresh water and fulfill at about 50% requirements of the country.

10.5 Colloids

10.5.1 Types of Colloids

There are eight types of colloids on the basis of phase (solid, liquid, or gas) of the dispersed substance and of the dispersing medium.

Keep in mind

A colloid (or colloidal dispersion) is a homogeneous mixture of two or more components like solution.

i) Liquid aerosols may be formed when liquid droplets are dispersed in a gas. Examples of liquid aerosols are fog, mist, and aerosol sprays.

ii) Solid aerosols may be formed when solid particles are dispersed in a gas. Examples of solid aerosols are dust, and smoke in air.

iii) Liquid foams may be formed when a gas is dispersed in a liquid. Examples of liquid foams are beaten egg white, and shaving lather.

iv) Solid foams may be formed when solid particles are dispersed in a liquid. Examples of solid foams are Styrofoam, and marshmallow.

v) Emulsions may be formed when liquid particles are dispersed in another liquid. Examples of emulsions are mayonnaise, and face cream.

vi) Gels may be formed when liquid particles are dispersed in a solid. Examples of gels are butter, and jellies.

vi) Liquid sols may be formed when solid particles are dispersed in a liquid. Examples of liquid sols are pudding, and ink.

vii) Solid sols may be formed when solid particles are dispersed in a solid. Examples of solid sols are steel, and pearls.

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Table 10.12: Types of Colloids and their examples

State of Dispersed Phase	State of Dispersing Medium	State of Resulting Colloid	Name	Example
Gas	Liquid	Liquid	Foam	Whipped cream, shaving lather, soap lather, beaten egg white
Gas	Solid	Solid	Solid foam	Styrofoam, marshmallow, sponge, rubber
Liquid	Gas	Gas	Aerosol	Mist, fog, clouds, sprays
Liquid	Liquid	Liquid	Emulsion	Mayonnaise, milk, face cream
Liquid	Solid	Solid	Gel	Jelly, Cheese, Butter, gelatin
Solid	Gas	Gas	Aerosol	Smoke, airborne viruses
Solid	Liquid	Liquid	Sol	Paint, ink, puddings
Solid	Solid	Solid	Solid sol	Pearls, opals, ruby, porcelain, coloured glass, some metal alloys such as steel

Colloids in which the dispersing phase is water may be classified as hydrophilic or hydrophobic. A colloid in which there is strong attractive force between dispersed phase and the dispersing medium (water) is known as hydrophilic colloid. The examples of hydrophilic colloids are gelatin in water, and jellies. A colloid in which there is a very weak attractive force between dispersed phase and the dispersing medium (water) is known as hydrophobic colloid. The examples of hydrophobic colloids are milk and mayonnaise.

10.5.2 Properties of Colloids

Some of the important properties of colloids are as follows:

I) Colloids are also homogeneous like that of solutions but borderline; that is, the particles of dispersed phase may be uniformly distributed among the particles of dispersing medium. A colloid is also known as colloidal dispersion because the particles of dispersed phase remain dispersed in the dispersing medium but not dissolved.

ii) The colloidal suspensions are often translucent or opaque but may be transparent.

iii) Colloidal particles are intermediate in size; that is, the size of colloidal particles is greater than the size of the particles of the true solutions and

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smaller than particles of suspensions that can be seen by naked eye. Colloidal particles have dimensions ranging from approximately 2nm to 1000nm. Particles with diameters 0.01nm to 1nm are true solution particles and those larger than 1000nm are suspension particles.

iv) The colloidal suspensions and true solutions look similar to the naked eye. But the colloidal particles are too small that are not usually seen by the naked eye and even with an ordinary microscope. However, they can be detected by electron microscope. On the other hand, the particles of true solutions are so small that they cannot be seen by the naked eye and microscope but the particles of suspensions are so large that can be seen with microscope and can often be seen with the naked eye.

v) The particles of colloidal suspensions are not settling out under the influence of gravity because their particles are in constant random motion, called Brownian motion, which keeps them from settling. This is due to small sized-suspended particles of colloids. The motion of colloidal particles increases by rise in temperature and decreases by increase the viscosity of the colloidal suspension. The motion of colloidal particles can be detected by ultra-microscope.

vi) The diffusion of colloidal suspensions is very slow due to large sized-suspended particles of dispersed phase than that of solution which is fast due to small size of solute particles. The suspensions do not diffuse. Diffusion is due to Brownian motion of particles which is more rapid for small sized-particles.

vii) Colloidal suspensions pass through filter paper but do not pass through semipermeable membrane.

viii) One of the most important properties that distinguish colloids from solutions is its ability to scatter light. When a beam of light is passed through a true solution, we cannot see the path of the beam of visible light because the light is not scattered due to small size of solute molecules. However, when a beam of light is passed through a colloidal suspension, we can see the path of the beam of visible light because the light is scattered by the dispersed phase. This phenomenon was first observed by the Irish physicist John Tyndall (1820-1893), and is termed as the Tyndall effect. Consider the examples of Tyndall effects. The visibility of headlights of cars is not better in the fogging weathers because the colloidal-sized particles in the fog scatter the light. The particles of dust can easily be seen in a beam of sunlight in the air of a room because the colloidal-sized dust particles

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(a) (b) (c)

Figure 10.8: (a) Light passing through solution, (b) Light Scattering by Colloidal Suspensions, (c) Light Scattering by Colloidal Suspensions

scatter the light. The sky looks blue because the colloidal-sized particles in the air scatter the light.

Some of the properties of solutions, colloids and suspensions are compared in the table 10.13.

Table 10.13: properties of solutions, colloids and suspensions

Property	Solution	Colloid	Suspension
Type of mixture	Homogeneous	Homogeneous	Heterogeneous
Size of particles	0.01 nm to 1 nm	2 nm to 1000 nm	Greater than 1000 nm
Effect of light	Cannot scatter light	Scatter light	Scatter light
Transparency	Transparent	Cloudy (translucent)	Opaque
Settling properties of particles	Do not settle down on standing	Do not settle down on standing	Settle down on standing
Filterability	Non-filterable	Non-filterable	Filterable
Separation	The solute can be separated from the solvent by evaporation and distillation.	The dispersed phase can be separated from dispersing medium by semipermeable membrane; that is, cellophane and cell walls	Can easily be separated by filtration
Visibility of particles	Invisible by naked eye and microscope	Invisible by naked eye and with an ordinary microscope	Visible by naked eye

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Summary of Facts and Concepts

- Solution is a homogeneous mixture of two or more substances that may be gases, liquids or solids. The component of solution that is in larger amount is the solvent. The component of solution that is in smaller amount as compared to solvent is called solute. The solution of substances in water is called aqueous solution (aqua means water). Liquids solutions may be coloured or colourless but clear and transparent. The solute particles of solutions are very small and cannot be seen by the naked eye and microscope.
- A suspension is a heterogeneous mixture and the particles are so large that can be seen with microscope and can often be seen with the naked eye. The particles of suspensions are large enough that they settle out under the influence of gravity.
- A colloid is a homogeneous mixture of two or more components like solution. The dispersed particles are intermediate in size between those of a true solution and suspension and do not settle out under the influence of gravity. The dispersed particles of colloids are so small that are not usually seen by the naked eye and ordinary microscope. But can be detected by electron microscope.
- The solubility of solute is the maximum amount of solute dissolved in given amount of solvent to make a saturated solution at a given temperature. The solubility of solids and liquids in a solvent is usually increases by increase in temperature. In contrast, the solubility of gases decreases by increasing temperature. The solubility of gases increases by increasing the pressure over the solution of the gas.
- Concentration is the amount of solute dissolved in the given amount of solvent or solution at a given temperature. The concentration of the solution can be expressed by percentage composition, molarity, molality, mole fraction, parts per million, parts per billion, and parts per trillion.
- A substance which has measureable vapour pressure is said to be volatile while a substance which has no measureable vapour pressure is said to be non-volatile.
- Osmosis is the flow of solvent molecules through a semipermeable membrane from a low concentrated solution to a high concentrated solution.
- Osmotic pressure is the pressure that is applied on the high solute concentration side to prevent osmosis from happening.
- In *reverse osmosis*, the pressure on the more concentrated side is applied to pass the solvent molecules but not the solute particles through a semipermeable membrane. This process is used for desalination of sea water.

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Questions and Problems

Q.1. Four answers are given for each question. Select the correct one:

i) One molar solution has one mole of solute in the solution of:

(a) 1000 ml (b) 1L

(c) both a and b (d) 1000g

ii) Which one of the following is more concentrated:

(a) 0.1M (b) 0.25M (c) 0.5M (d) 0.75M

iii) Which one of the following is the example of colloid:

(a) Ink (b) milk of magnesia

(c) glucose solution (d) soda water

iv) The mole fraction of ethyl alcohol in the solution consisting 23g ethyl alcohol and 3.2g methyl alcohol is:

(a) 0.17 (b) 0.37 (c) 0.63 (d) 0.83

v) Which one of the following is **NOT** soluble in water:

(a) Benzene (b) phenol

(c) ethyl alcohol (d) table salt

vi) Which one of the following is a colligative property:

(a) Melting point (b) density

(c) boiling point (d) elevation in boiling point

vii) Elevation of boiling point is directly proportional to:

(a) molal concentration of solution

(b) molal concentration of solvent

(c) molar concentration of solvent

(d) molar concentration of solution

viii) The solubility of which one of the following substances increases by rise in temperature:

(a) CO_2 (b) $Ce_2(SO_4)_3$ (c) KNO_3 (d) O_2

ix) The solution cools when water is added:

(a) KNO_3 (b) $CuSO_4$ (c) H_2SO_4 (d) LiCl

x) Which of the following can **NOT** scatter light:

(a) sugar in water (b) milk of magnesia

(c) starch solution (d) fog

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Q.2. Fill in the blanks with suitable words given in the brackets:

i) The oxygen gas is _____ soluble in water. (completely / slightly)

ii) The solubility of the gas is _____ by doubling the partial pressure of the gas above the solution. (doubled/quadrupled)

iii) Sponge is an example of _____. (suspension/colloid)

iv) The component of solution which is in _____ amount is called solute. (larger/smaller)

v) The concentration of solution of 6g of urea per liter is _____. (0.1 M/1 M)

vi) The relative lowering of vapour pressure is _____ proportional to the mole fraction of solute. (directly/inversely)

vii) 15% W/W sugar solution contains 15g of sugar in 100g of _____. (solvent/solution)

viii) _____ is a process in which an ion or molecule is surrounded by solvent molecules. (hydration/solvation)

ix) The freezing mixture, which is used to freeze the ice cream, is prepared when _____ is mixed with ice. (KNO_3/$AgNO_3$)

x) A semipermeable membrane is a thin layer of material that allows _____ particles to pass through it. (solute/solvent)

Q.3. Label the following sentences as True or False:

i) AgCl is completely soluble in water.

ii) Glycerin is used as antifreeze in the radiators of automobiles.

iii) The amount of NH_4Cl needed to make 500mL of 0.25M solution is 6.69g.

iv) We can see the path of visible light when a beam of light is passed through a colloidal suspension.

v) Beaten egg white is the example of liquid foam.

vi) The impurities of the substances are usually expressed in parts per hundred.

vii) 20% V/V alcohol-water solution means that 20mL of alcohol dissolved in enough water to make the total volume of solution 100mL.

viii) The heat is absorbed when sulphuric acid is dissolved in water.

ix) A solution which can dissolve further solute on addition is known as saturated solution.

x) The completely miscible solutions can usually be separated by fractional distillation.

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Q.4: Define solution. What are the general properties of solutions?

Q.5: Distinguish between hydrophilic and hydrophobic molecules. What is the function of soaps and detergents?

Q.6: What are liquid solutions? Explain in your own words with examples.

Q.7: What are the different types of liquid solutions? Explain in detail.

Q.8: What is the meaning of "like dissolves like"? Explain with examples.

Q.9: Explain why table sugar is dissolved in water but not in benzene?

Q.10: What is the effect of temperature on the solubility of liquids in liquids and solids in liquids?

Q.11: What is the effect of the pressure on the solubility of gases in liquids?

Q.12: What is the effect of the temperature on the solubility of gases in liquids?

Q.13: What happens:

(a) When the pressure of CO_2 gas above the solution of carbonated beverage is increased and

(b) When the temperature of the carbonated beverage is increased?

Q.14: Why we drunk carbonated beverages only cold but not hot?

Q.15: Why does a bottle of carbonated beverage effervescence when you uncapped the bottle?

Q.16: The carbonated beverage is kept in closed vessel, why?

Q.17: Discuss and explain the heat of solution. The heat of solution is either negative or positive for solution, explain.

Q.18: What do you think, the rise in temperature will increase or decrease the solubility of NH_4Cl and NaOH in water?

Q.19: What do you know about concentration units of solution? Describe the compositions of solutions in terms of weight by weight, weight by volume, volume by weight, and volume by volume percent.

Q.20: What do you mean by molarity and molality of solution? Give their mathematical equations to calculate molarity and molality of solutions.

Q.21: The molarity of solution is affected by temperature change and molality of solution is not affected by temperature change. Explain.

Q.22: Why the sum of the volumes of individual components is not necessarily equal to the total volume of solution?

Q.23: What is mole fraction? Why the sum of all the components present in the solution is equal to one?

Q.24: Describe and explain the concentration units, parts per million, billion, and trillion.

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Q.25: Explain Raoult's law with the help of three statements when solute is non-volatile and solvent is volatile.

Q.26: Explain Raoult's law when both of the components of solution; that is, solute and solvent are volatile.

Q.27: A non-ideal solution shows two types of deviations from Raoult's law; that is positive and negative. Explain with the help of graphs.

Q.28: What is the difference between ideal and non-ideal solutions?

Q.29: What is the meaning of the term colligative? Define the term colligative property and name the four colligative properties of solution. What are the conditions for colligative properties?

Q.30: The vapour pressure of a solution containing a non-volatile solute is always less than that of pure solvent, justify.

Q.31: Why is the vapour pressure of sea water less than that of pure water?

Q.32: How can you calculate the molar mass of non-volatile and non-electrolyte solute in a volatile solvent?

Q.33: Explain freezing point depression and boiling point elevation in your own words. Give applications of freezing point depression and boiling point elevation.

Q.34: Explain osmosis, osmotic pressure, and reverse osmosis. Give their daily life applications.

Q.35: What is colloid? Describe the types and properties of colloids.

Q.36: What is the difference between solution, colloid and suspension?

Q.37: Explain why a solution and a colloid are considered as homogeneous mixtures while suspension is considered as heterogeneous mixture?

Q.38: What is the Tyndall effect? Give two examples of this effect.

Q.39: Define the terms solute and solvent. Identify the solute and solvent in the solutions given below:

(a) 10g of sugar and 100g of water
(b) 5g of oxygen and 20g of nitrogen
(c) 5mL of water and 30mL of ethanol
(d) Air
(e) Soda water

Q.40: Calculate the weight percent of gold ring containing 2g of platinum and 7g of gold.

Q.41: Calculate the W/V % of 0.5 liter of soft drink that has 55g of dissolved carbon dioxide gas.

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Q.42: A cup of 200mL of hot milk tea contains 50mL of milk. What is the V/V% of the tea?

Q.43: A solution contains 12.25g of $KClO_3$, dissolved in 5×10^3 g of water. What is the molality of the solution?

Q.44: How many grams of calcium chloride are required to prepare 0.01M and 0.025M solutions?

Q.45: If 15g of urea (N_2H_4CO)is dissolved in 5×10^2mL of solution, calculate the molarity of the urea solution.

Q.46: Calculate the molality of each of the following solutions containing:

(a) 0.1 mol of solute in 0.25kg of solvent

(b) 0.25 mol of solute in 0.1kg of solvent

Q.47: Calculate the molarity of each of the following solutions containing:

(a) 1.50 mol of NaCl in 0.50L of water

(b) 2.25 mol of rock candy in 4.50L of water.

Q.48: A solution is prepared by dissolving 9.2g of toluene (C_7H_8) in 39g of benzene (C_6H_6). What is the mole fraction of toluene in this solution?

Q.49: The bottle of one liter mineral water contains 78mg calcium, 24mg magnesium, 5mg sodium, and 1mg potassium. Calculate the concentration of each mineral in the mineral water in ppm, ppb, and ppt.

Q.50: What is the boiling point of the solution that contains 23.25g of aniline ($C_6H_5NH_2$) in 0.75kg of ethyl alcohol? The boiling point of pure ethyl alcohol is 78.26°C. The boiling point elevation constant for ethyl alcohol is 1.22°C kg/mol.

Q.51: A solution prepared by adding 11.30g of an organic compound in 0.1kg of ether has ΔT_b and K_b values for ether 3.06°C and 2.02°C kg/mol respectively. Find out the molar mass of the organic compound.

Q.52: Calculate the freezing point of sugar solution containing 855g of sucrose ($C_{12}H_{22}O_{11}$) and 2.50kg of water. The K_f value for water is 1.86°C kg/mol.

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Chapter # 11

Thermochemistry

Major Concepts

11.1 Energy in Chemical Reactions
11.2 Thermodynamics
11.3 Internal Energy
11.4 First Law of Thermodynamics
11.5 Standard State and Standard Enthalpy Changes
11.6 Heat Capacity
11.7 Calorimetry
11.8 Hess's Law
11.9 Born-Haber Cycle

Learning Outcomes

The students will be able to:

- Define thermodynamics. (Remembering)
- Classify reactions as exothermic or endothermic. (Understanding)
- Define the terms system, surrounding, boundary, state function, heat, heat capacity, internal energy, work done and enthalpy of a substance. (Remembering)
- Name and define the units of thermal energy. (Remembering)
- Relate a change in enthalpy to the heat of reaction or heat of combustion of a reaction. (Applying)
- Relate change in internal energy of a system with thermal energy at constant temperature and constant pressure. (Applying)
- Define bond dissociation energy. (Remembering)
- Use the experimental data to calculate the heat of reaction using a calorimeter. (Applying)
- Specify conditions for the standard heat of reaction. (Applying)
- Apply Hess's Law to construct simple energy cycles. (Understanding)
- Describe how heat of combustion can be used to estimate the energy available from foods. (Analyzing)
- Explain reaction pathway diagram in terms of enthalpy changes of the reaction. (Born Haber's Cycle) (Applying)

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Introduction

The branch of chemistry which deals with heat changes during a chemical reaction is called thermochemistry.

The ability or capacity of a body to do work is called energy. There are two main types of energy; that is potential energy, and the kinetic energy.

The energy of an object due to its position relative to other objects or stored in a molecule due to its chemical bonds is called potential energy. The water held behind a dam has potential energy because of its height. The potential energy of water increases when the level (position) of water in the dam increases and the potential energy of water decreases when the level (position) of water decreases. This water has no kinetic energy because it is not moving.

The energy of a system due to its motion is called kinetic energy. All the moving objects have kinetic energy. The magnitude of the kinetic energy of a body depends on its mass and velocity. The greater the velocity of objects, the higher the kinetic energy or/and the heavier the objects, the higher the kinetic energy. When water is allowed to fall over the dam, its potential energy is converted into kinetic energy. The kinetic energy of falling water increases when the speed of flow of water increases. Kinetic energy of the given mass of water is directly proportional to the square of its speed.

The SI unit of energy and heat is joule which is defined as: the amount of energy expended when a force of one Newton moves an object (body) of 1kg through one meter in the direction of force. Joule (1818-1889) was a British scientist who probed work and heat. Joule is a small unit of energy; we therefore, use the unit kilojoule for energy (1kJ = 1000J). The non-SI unit of energy and heat which is used in large scale is calorie. It is denoted by cal and is defined as the amount of energy required to raise the temperature of one gram of water from 14.5°C to 15.5°C (1kcal = 1000cal).

Energy is very important for us on the earth. For example, the food we eat provides the energy in the form of heat to regulate our body temperature and carry out all other bodily functions. The burning of logs, coal and natural gas provides energy in the form of heat to warm our homes. The burning of gasoline and diesel in the engine of automobiles provide energy to run engines. The energy released by the burning of fuel is used to generate electricity which in turn is used to light bulbs, run computers, refrigerators and other appliances. The main source of energy is sun and after that a large amount of energy comes from chemical reactions.

The transfer of energy between two objects due to difference in temperature is called heat. Heat flows from a hot body to cold body until both are at the same

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temperature. Let us understand how energy is transferred from one piece of matter to another. When a red hot iron bar is placed in cold water, the temperature of the water increases, because the energy in the form of heat flows from iron bar (hot body) to water. On the other hand, the temperature of hot iron bar decreases, because the energy in the form of heat flows away from it to surrounding (water). This process of transferring of heat is continued till the temperature of the iron bar becomes equal to water.

11.1 Energy in Chemical Reaction

Chemical reactions may either be exothermic or endothermic. Those reactions or processes in which heat is evolved (from system to surrounding) are called exothermic reactions or processes (Greek: **exō** = outside; hence heat flows out). The burning of gasoline, coal, and wood are the examples of exothermic reactions. The other examples of exothermic processes are freezing, condensation, and deposition. Some of the exothermic reactions are:

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow 2H_2O_{(g)} + CO_{2(g)} \qquad \Delta H = -890.4kJ$$

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -393.51kJ$$

Amount of heat released is indicated by ΔH with negative sign because heat flows from system to surroundings. Majority of reactions which take place at ordinary temperature are exothermic.

During chemical reactions old bonds are broken and new bonds are formed. Bond breakage is an endothermic process while bond formation is an exothermic process. If the energy needed to break old bonds in the reactants is less than the energy evolved by new bond formation in the products, then the reaction is exothermic. In this case some of the potential energy is converted into thermal energy. The potential energy of the products is less than reactants, that is why, the products are more stable than reactants; that is, the bond in the products are more stronger than those of the reactants.

Keep in mind

A process that is endothermic in forward direction is exothermic in reverse direction, that is, evaporation is an endothermic process while condensation, the reverse of evaporation, is an exothermic process.

Those reactions or processes in which heat is absorbed (from surrounding to system) are called endothermic reactions or processes (Greek: **endon** = within; hence, heat flows in). The process of photosynthesis in plants is the example of endothermic reaction. The other examples of endothermic processes are melting, evaporation, and sublimation. Some of the endothermic reactions are:

E ↓ ← exo — solid-liquid-gas — endo → ↑ E

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$C_{(s)} + H_2O_{(g)} \longrightarrow CO_{(g)} + H_{2(g)}$ $\Delta H = +131.4kJ$

$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$ $\Delta H = +180.51kJ$

Amount of heat absorbed is indicated by ΔH with positive sign, because heat flows from surrounding to system.

If the energy needed to break old bonds in the reactants is greater than the energy evolved by new bond formation in the products, then the reaction is endothermic. In this case some of the thermal energy is converted into potential energy. The potential energy of the products is greater than reactants, that are why, the products are less stable than reactants; that is, the bond in the products are weaker than those of the reactants.

The amount of heat evolved or absorbed when reactants are converted into products during a chemical reaction is called heat of reaction. It may also called chemical energetic. The equation which shows the amount of heat evolved or absorbed during a chemical reaction is called thermochemical equation or reaction.

11.2 Thermodynamics

The study of energy, work, heat, temperature and their relationship is known as thermodynamics (Greek: thermē = heat; dunamis = power). It may also concerned with energy transformation; that is, the transfer of energy from one object (or substance) to another. Chemists give preference to the branch of thermodynamics that is, thermochemistry.

There are four laws of thermodynamics, but only the first law of thermodynamics will be discussed in this chapter.

Some Thermodynamic Terms

System

Anything (substance or mixture) which is under observation or experiment (in the laboratory) is called system.

Types of System

i) Open system: It can exchange both energy and matter (mass) with its surroundings. Examples are open reaction flask, rocket, and an uncovered cup of tea. The energy and matter do not remain same in an open system.

ii) Closed system: It can exchange only energy but not the matter (mass) with its surroundings. For example, a sealed reaction flask, a gas in a closed container. This system is most readily study in thermochemistry.

iii) Isolated system: It can exchange neither energy nor matter with its surroundings. A thermos flask containing hot green tea approximates an isolated system.

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Surrounding

Everything in the universe which is not part of the system is called surrounding.

Universe

The system plus its surrounding is called universe. It is different from the astronomical universe.

Universe = System + Surrounding

Boundary

The real or imaginary surface which separates the system from surroundings is called boundary.

i) Suppose we have a cup full of tea, the tea is system, the cup and other things are surroundings. The tea plus cup and all other things is universe.

ii) Suppose we are studying the thermal decomposition of $Pb(NO_3)_2$ in a beaker.

System : $Pb(NO_3)_2$

Surrounding : Beaker + Source of heat + every thing else.

Universe : $Pb(NO_3)_2$ + Beaker + Source of heat + Everything else.

States of System

The condition of the system is called state of system. The variables such as temperature, pressure, volume, enthalpy etc. describe the state of system. State is of two types:

i) **Initial State of System:** The state of system before it undergoes a change is called initial state of system. Suppose we have a beaker of water. It has some temperature and volume, which is its initial state.

ii) **Final State of System:** The state of system after it undergoes a change is called final state of system. Suppose we heat the water, as a result of this temperature changes. It is its final state.

Change in State

The difference between two states (initial and final states) is called change in state. For example:

Change in temperature $(\Delta T) = T_2 - T_2$

Change in pressure $(\Delta P) = P_2 - P_1$

Change in volume $(\Delta V) = V_2 - V_1$

Change in enthalpy $(\Delta H) = H_2 - H_1$

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PTVEHS

State Functions (State Variables)

A property which depends upon initial and final states of system and is independent of the path followed by the system is called state function.

For example, temperature, pressure, volume, enthalpy, internal energy are all state functions. The properties such as heat and work are path dependent and are not state functions.

q W

11.3 Internal Energy

The sum of all kinds of energies (kinetic and potential energies) of the components of the system (particles) is called internal energy (E = P.E + K.E). It is represented by symbol E. The SI unit of internal energy is joule and non-SI unit is calorie. The internal energy depends upon motion of particles, their arrangement, intermolecular and intra molecular forces. Internal energy is the sum of kinetic and potential energies as we know. Now we should know that, potential energy is due to intermolecular and intra molecular forces whereas the kinetic energy is due to translational, vibrational and rotational motions.

$$K.E = E_{Vibrational} + E_{Translational} + E_{Rotational}$$

Vibrational energy is due to vibrational motion, translational energy is due to translational motion and rotational energy is due to rotational motion.

The internal energy of a system cannot be measured. However change in internal energy (ΔE) can be calculated.

$$\Delta E = E_2 - E_1$$

Internal energy change (ΔE) of a system is the amount of energy evolved or absorbed by the system at constant volume. The change in internal energy has three portions:

i) A number which shows the magnitude of the change.
ii) A unit which also shows the magnitude of the change.
iii) A sign that is used to give the direction.

If E is positive, then E_2 is greater than E_1 ($E_2 > E_1$) and if E is negative, then E_2 is less than E_1 ($E_2 < E_1$).

Keep in mind that the increase in the energy of the system occurs with the decrease in the energy of the surrounding and vice versa.

An increase in internal energy:

i) Can cause a chemical reaction when it is enough to break the bonds.
ii) Can change the phase of the system; that is, fusion or evaporation may occur.
iii) Can increase the temperature of the system which in turn increases the kinetic energy of the system.

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11.4 First Law of Thermodynamics

First law of thermodynamics is the law of conservation of energy and is stated as: energy can neither be created nor destroyed but can be changed from one form to another form. It may also be defined as: the energy lost by the system is equal to the energy gained by the surrounding but the total energy of the universe is always constant.

$$\Delta E_{Universe} = \Delta E_{System} + \Delta E_{Surrounding} = Zero$$

The internal energy changes when a system either gives off or gains energy (heat). Similarly, the internal energy changes when a work is either done by the system on the surrounding or done by the surrounding on the system. The total change in the internal energy is the sum of work (w) and energy (q).

$$\Delta E = q + w$$

This is the mathematical form of first law of thermodynamics. The internal energy of the system increases when work is done by the system on its surrounding and vice versa.

Work has to be done when:

i) We increase the speed of car from 0 to 80 km/hour.
ii) We walk upstairs.
iii) We lift a hammer.
iv) An electron in an atom is forced to go away from the nucleus.
v) A cation is isolated from anion in an ionic compound.
vi) A fixed amount of gas is compressed in to a smaller volume under the influence of an external pressure; that is, the pumping of air in the tyre.

In all of the above cases, the work has been done on the objects (system), hence the energy (P.E.) of the objects increase.

The work has to be done when:

i) The stone throws down the mountain.
ii) Tears stream down the face.
iii) Water flows down the hill.
iv) Petrol burns inside the engine.
v) The wood and coal burns inside the stove.
vi) The tyre of the car bursts.

In these cases, the work has been done by the system on the surrounding, hence, the energy of the system decreases.

The sign conventions for heat (q) and work (w) are as under:

The q is positive when system absorbs energy; that is, for an endothermic

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process and q is negative when system releases energy, that is, for an exothermic process.

The w is positive when the work is done on the system by the surroundings and w is negative when the work is done by the system on the surroundings.

The ΔE is positive when the system absorbs energy (heat) and ΔE is negative when the system loses energy.

Pressure-Volume Work

The product of force and distance is called work.

$$\text{Work (w)} = \text{Force (F)} \times \text{distance (S)} \quad \ldots\ldots\ldots\ldots \text{(i)}$$

SI unit of work is joule.

There are various kinds of work but in chemistry we most commonly deal with Pressure-Volume Work. Let us consider a gas confined in a cylinder with movable piston as shown in the figure. The internal energy of the system is E_1 at initial state. A quantity of heat (q) is given to the system. The internal energy of the system changes from E_1 to E_2 and the piston moves upward.

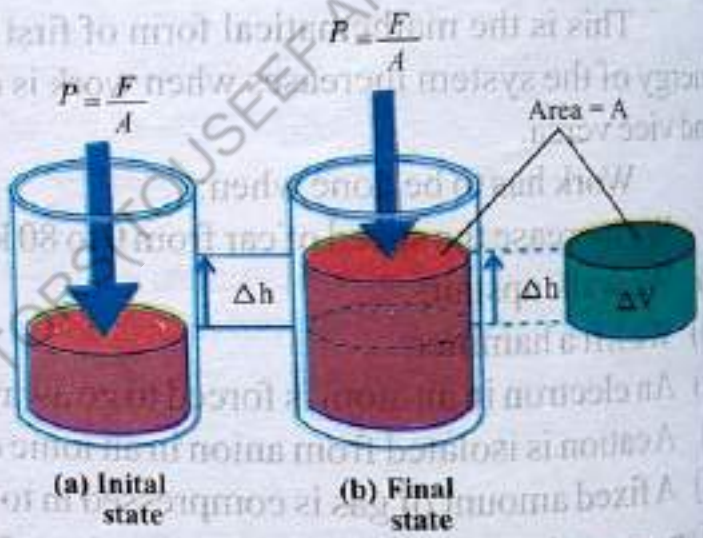

Figure 11.1: Pressure-volume Work

In the figure, A is the area of the piston, P is the external pressure on the piston, F is force exerted by the gas on piston and q is the heat absorbed by the gas.

As pressure is force per unit area, hence:

$$P = \frac{F}{A}$$

Therefore,

$$F = P \times A \quad \ldots\ldots\ldots\ldots\ldots \text{(ii)}$$

Let us assume that, the gas expands. As a result of this, the piston moves from h_i (initial height) to h_f (final height). The difference of these heights is equal to Δh.

$$\Delta h = h_f - h_i \quad \ldots\ldots\ldots\ldots\ldots \text{(iii)}$$

We know that, the volume of the gas in the cylinder is equal to cross section area (A) multiplied by the height of the column of the gas(h).

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Hence,

$\Delta V = A \times h$ (Area = length × width)

By applying the initial and final states of system, we get

$V_i = A \times h_i$ ..... (iv)

$V_f = A \times h_f$ ..... (v)

Change in volume (V) is

$\Delta V = V_f - V_i$ ..... (vi)

By putting the values of equation (iv) and (v) in equation (vi), we get

$\Delta V = Ah_f - Ah_i$

$\Delta V = A(h_f - h_i)$

$\Delta V = A\Delta h$ ..... (vii)

By rearranging the equation (vii), we get

$\Delta h = \Delta V / A$ ..... (viii)

Where, h is change in height or the distance traveled by gas due to force.

By putting the values of equation (ii) and (viii) in equation (i), we get:

$w = PA \times \Delta V/A$

$w = +P\Delta V$

(Positive sign shows that work has been done on the system (gas) by the surrounding).

As, $w = P\Delta V$

Therefore,

$\Delta E = q + P\Delta V$

If the work is done by the system, then

$\Delta E = q - P\Delta V$ (OR) $\Delta E = q - w$

1.4.1 Heat Changes at Constant Pressure

The heat content of a system is called enthalpy. It may also be defined as: the internal energy E plus product of pressure (P) and volume (V) is called enthalpy. It is represented by H. Mathematically,

$H = E + PV$

It is impossible to measure enthalpy of a system. However change in enthalpy (ΔH) can easily be measured.

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$\Delta H = H_2 - H_1$ ..... (vi)

$H_2 = E_2 + P_2V_2$

$H_1 = E_1 + P_1V_1$

By putting the values of H_2 and H_1 in eq. (i)

$\Delta H = (E_2 + P_2V_2) - (E_1 + P_1V_1)$ ..... (ii)

or $\Delta H = (E_2 - E_1) + (P_2V_2 - P_1V_1)$

or $\Delta H = \Delta E + \Delta PV$

When P is constant whereas the gas is expanding, then we can write,

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

or $\Delta H = \Delta E + w$ ..... (iii) (Where $P\Delta V = w$)

According to the first law of thermodynamics,

$\Delta E = q - w$

By putting the value of ΔE in equation (iii), we get

$\Delta H = q - w + w$

or $\Delta H = q$ (q = Amount of heat supplied)

This relationship is usually written as,

$\Delta H = q_P$

Where, subscript p means constant pressure.

11.4.2 Heat Changes at Constant Volume

Consider a gas in a closed container, the volume of the gas is not changed. Therefore $\Delta V = O$

According to first law of thermodynamics:

$\Delta E = q - w$

or $\Delta E = q - P\Delta V$

As volume is constant i.e. $\Delta V = O$, therefore,

$\Delta E = q - P \times O$

or $\Delta E = q - O$ or $\Delta E = q$

This relationship is usually written as:

$\Delta E = q_v$

Where, subscript v means constant volume. All the heat given to the system (gas) is used to increase internal energy of the system.

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11.5 Standard State and Standard Enthalpy Changes

The physical state of substance at 25°C and at one atmosphere which is the most stable state is called standard state. It is denoted by $\Delta H°$. Where, Δ (delta) stands for change, the symbol H for enthalpy, and the superscript degree sign (°) for standard states. Hence, the $\Delta H°$ means standard enthalpy change.

The amount of heat released or absorbed (enthalpy change) during a chemical reaction when all the reactants and products are in their standard states is called standard enthalpy of reaction. It may also called heat of reaction. It is denoted by $\Delta H°_{rxn}$. Substances are said to be in the standard state at 1 atm; hence we use the term "standard enthalpy." Here the subscript "rxn" stands for reaction. Hence, is read as the standard enthalpy change of reaction. Its unit is $kJmol^{-1}$.

For exothermic reactions $\Delta H°_{rxn}$ values are shown by negative signs and for endothermic reactions the $\Delta H°_{rxn}$ values are shown with positive signs.

For example:

$$2H_2 + O_2 \longrightarrow 2H_2O \qquad \Delta H°_{rxn} = -285.8\ kJmol^{-1}$$

$$C + O_2 \longrightarrow CO_2 \qquad \Delta H°_{rxn} = -393.51\ kJmol^{-1}$$

The magnitude of ΔH is directly proportional to the quantity of reactant consumed in the process (or to the quantity of product formed in the process). For example, 393.51kJ of heat is produced when 1 mol of carbon is burnt at standard states. Because the combustion of 1 mol of carbon with 1 mol of O_2 releases 393.51kJ of heat, the combustion of 2 mol of carbon with 2 mol of O_2 releases twice as much heat, 787.02kJ.

$$2C + 2O_2 \longrightarrow 2CO_2 \qquad \Delta H°_{rxn} = -787.02\ kJ$$

11.5.1 Standard Enthalpy of Atomization ($\Delta H°_{at}$)

The enthalpy change when one mole of gaseous atoms is formed from the element at standard states is called standard Enthalpy of atomization. It is denoted by $\Delta H°_{at}$. Its unit is kJ mol^{-1}. For example, the standard enthalpy of atomization of hydrogen is:

$$1/2\ H_{2(g)} \longrightarrow H_{(g)} \qquad \Delta H°_{at} = 218kJmol^{-1}$$

The standard enthalpy of atomization of sodium is:

$$Na_{(s)} \longrightarrow Na_{(g)} \qquad \Delta H°_{at} = 107kJmol^{-1}$$

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11.5.2 Standard Enthalpy of Formation (ΔH_f°)

The enthalpy change when one mole of a compound is formed from its elements in their standard states is called standard enthalpy of formation. It is denoted by ΔH_f° and its unit is $kJmol^{-1}$.

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_f^\circ = -393.51\ kJmol^{-1}$$

$$Mg_{(s)} + 1/2O_{2(g)} \longrightarrow MgO_{(s)} \qquad \Delta H_f^\circ = -692\ kJmol^{-1}$$

A negative ΔH_f° means that the compound is more stable than reactants. For example, CO_2 and MgO are more stable than their reactants. On the other hand, the positive ΔH_f° means that the compound is less stable than their reactants. For example, NO is less stable than their reactants. Consider the reaction.

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)} \qquad \Delta H_f^\circ = +90.37\ kJmol^{-1}$$

The reactions which are exothermic in forward direction will be endothermic in reverse direction. The enthalpy change for a reverse reaction is equal in magnitude to that for the corresponding forward reaction but opposite in sign; that is, heat of decomposition of a compound is equal and opposite to heat of formation of that compound. For example, the amount of heat released is 46.11kJ for the formation of one mole of ammonia. The amount of heat required to decompose one mole of ammonia is 46.11kJ which is equal to heat of formation of ammonia but apposite in sign because the reaction in reverse direction is endothermic.

$$N_2 + 3H_2 \longrightarrow 2NH_3 \qquad \Delta H^\circ = -46.11\ kJmol^{-1}$$

$$2NH_3 \longrightarrow N_2 + 3H_2 \qquad \Delta H^\circ = +46.11\ kJmol^{-1}$$

Table 11.1: Standard Enthalpies of Formation of Some Common Substance at 25°C

Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$C_2H_{2(g)}$	226.7	Glucose	$C_6H_{12}O_{6(s)}$	-1273
Ammonia	$NH_{3(g)}$	-46.19	Hydrogen chloride	$HCl_{(g)}$	-92.30
Benzene	$C_6H_{6(l)}$	49.00	Methane	$CH_{4(g)}$	-74.80
Carbon dioxide	$CO_{2(g)}$	-393.51	Sodium chloride	$NaCl_{(s)}$	-410.9
Ethyl alcohol	$C_2H_5OH_{(l)}$	-277.7	Sucrose	$C_{12}H_{22}O_{11(s)}$	-2221
Ethylene	$C_2H_{4(g)}$	52.26	Water	$H_2O_{(l)}$	-285.8

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The stability of a compound has close relation with enthalpy of formation. The enthalpy of formation of a compound will enable you to identify a stable compound. A compound is said to be unstable which has positive or low negative values of enthalpy of formation and a compound is said to be very unstable which has high positive values of enthalpy of formation. On the other hand, the compound with high negative values of enthalpy of formation is said to be very stable.

11.5.3 Standard Enthalpy of Combustion (ΔH_c°)

The enthalpy change when one mole of a substance is completely burnt in excess of oxygen at standard states is called standard enthalpy of combustion. It is denoted by ΔH_c°. Its unit is $kJmol^{-1}$. For example, heat of combustion of CH_4, CO_2 and CO is shown by the reactions:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2HO_2 \qquad \Delta H_c^\circ = -890\ kJmol^{-1}$$

$$C + O_2 \longrightarrow CO_2 \qquad \Delta H_c^\circ = -393.51\ kJmol^{-1}$$

$$C + 1/2O_2 \longrightarrow CO \qquad \Delta H_c^\circ = -110.5kJ\ mol^{-1}$$

Table 11.2: Standard Enthalpies of Combustion of Some Common Substance at 25°C

Substance	Formula	ΔH_c° (kJ/mol)	Substance	Formula	ΔH_c° (kJ/mol)
Hydrogen	$H_{2(g)}$	–286	Ethylene	$C_2H_{4(g)}$	–1412
Methane	$CH_{4(g)}$	–891	Acetylene	$C_2H_{2(g)}$	–1300
Butane	$C_6H_{6(l)}$	–2880	Benzene	$C_6H_{6(l)}$	–3270
Octane	$C_8H_{18(l)}$	–5474	Carbon monoxide	$CO_{(g)}$	–283

11.5.4 Standard Enthalpy of Neutralization (ΔH_n°)

The enthalpy change when one mole of hydrogen ions (H^+) from an acid react with one mole of hydroxide ions (OH^-) from a base to form one mole of water at standard states is called standard enthalpy of neutralization. It is denoted by ΔH_n°. Its unit is $kJmol^{-1}$. The strong acids and bases are ionized completely when dissolved in water as:

$$HCl_{(g)} \xrightleftharpoons{H_2O} H^+_{(aq)} + Cl^-_{(aq)}$$

$$NaOH_{(s)} \xrightleftharpoons{H_2O} Na^+_{(aq)} + OH^-_{(aq)}$$

By mixing the hydrochloric acid and sodium hydroxide solutions, the following situation occurs:

$$\left(H^+_{(aq)} + Cl^-_{(aq)}\right) + \left(Na^+_{(aq)} + OH^-_{(aq)}\right) \rightleftharpoons H_2O_{(l)} + Na^+_{(aq)} + Cl^-_{(aq)}$$

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In the above reaction, the H^+ ions react with OH^- ions to form water. The sodium ions and chloride ions remain as such. Hence, the actual reaction is:

$$H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)} \qquad \Delta H^\circ_n = -57.4 kJmol^{-1}$$

The heat of neutralization of any strong acid with any strong base is approximately equal to –57.4kJ/mol, because the reaction involves only the combination of hydrogen and hydroxide ions.

11.6 Heat Capacity

The amount of energy required to raise the temperature of an object or a substance by one degree Celsius (or one Kelvin) is called heat capacity. It is denoted by C. Its unit is joules per gram per degree Celsius (J/g °C) or joules per mole per degree Celsius (J/mol °C). It is measured at constant pressure or constant volume.

Heat capacity may further be classified into specific heat capacity and molar heat capacity.

The amount of energy required to raise the temperature of one gram of a substance (element or compound) by one degree Celsius (1°C) or one Kelvin (1K) at constant pressure is called specific heat capacity or just specific heat. It is denoted by C_s. Its unit is J/g °C. The specific heat for water at 15°C is 4.184J/g°C and that of iron is 0.45J/g °C. It means 4.184 Joules energy is required to raise the temperature of one gram of water by one degree Celsius and 0.45 Joules energy is required to raise the temperature of one gram of iron by one degree Celsius; that is, water needs about nine times more heat to raise the temperature of one gram of water by one degree Celsius as compared to iron metal. It can be determined experimentally by measuring the temperature change (ΔT), the mass of substance and quantity of heat released or absorbed. The following equation is used to calculate the specific heat:

$$C_s = \frac{q}{m \times \Delta T}$$

Where, C_s is the specific heat capacity, m is the mass of a substance, ΔT is the change in temperature, and q is the amount of heat released or absorbed. The q is positive for an endothermic process and negative for an exothermic process.

The amount of energy required to raise the temperature of a substance is equal to the product of specific heat, mass of a substance and rise in temperature:

$$q = C_s \times m \times \Delta T$$

As C_s is the specific heat capacity, by taking mass constant, the amount of heat (q) released (or absorbed) by an object (or a substance) is directly proportional

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to its temperature change. The increase in temperature increases the quantity of heat of an object.

The amount of energy required to raise the temperature of one mole of a substance by one degree Celsius (1°C) or one Kelvin (1K) is called molar heat capacity. It is denoted by C_m. its unit is J/mol °C.

The specific heat capacity of a substance can easily be converted into molar heat capacity by multiplying specific heat capacity of a substance with its molar mass.

Molar heat capacity = Specific heat capacity × molar mass of a substance

Every object or substance has its own heat capacity.

Table 11.3: The heat capacities of some common substances and objects at room temperature (25°C)

Element	Heat Capacity (J/g °C)	Compound	Heat Capacity (J/g °C)	Object	Heat Capacity (J/g °C)
Aluminum (s)	0.900	Ammonia (g)	2.09	Cement	0.88
Copper (s)	0.385	Benzene (*l*)	1.74	Glass	0.84
Gold (s)	0.129	Carbon tetrachloride(*l*)	0.862	Granite	0.79
Graphite (s)	0.711	Ethanol (*l*)	2.44	Steel	0.45
Iron (s)	0.450	Ethylene glycol (*l*)	2.42	Wood	1.76
Mercury (l)	0.140	Water (*l*)	4.184		

The water has high value of specific heat capacity, hence

i) It plays an important role in regulating the temperature of the earth.

ii) It is also used in the radiators of automobiles as a coolant.

iii) It keeps our body temperature constant to a certain degree. Hence, our body needs much energy transfer to increase or decrease the temperature of our body.

11.7 Calorimetry

The measurement of heat of reaction is called calorimetry. The amount of heat released or absorbed (ΔH) during a physical and chemical process can be measured with a device, known as calorimeter. For example, a calorimeter is used to measure the heat of neutralization of a strong acid with a strong base and heat of combustion of an organic compound burnt in oxygen. There are two types of calorimeters.

i) Simple calorimeter

ii) Bomb calorimeter

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i) Simple Calorimeter

It consists of an insulated container with a thermometer and stirrer. It can be used to measure heat of neutralization of a strong acid with a strong base and heat of solution. The known quantities of reactants are placed in the calorimeter. The amount of heat released or absorbed during a chemical reaction is calculated from the temperature change. Knowing the mass of reactants in the calorimeter, the specific heat of the reaction mixture and the temperature change, we can calculate the heat of reaction using the equation:

$$q = C_s \times m \times \Delta T$$

Because the pressure inside the calorimeter is constant (1atm), hence, heat change (q) for the process is equal to enthalpy change.

$$q = \Delta H_p = C_s \times m \times \Delta T$$

The heat of neutralization of a strong acid with a strong base is calculated by simple calorimeter.

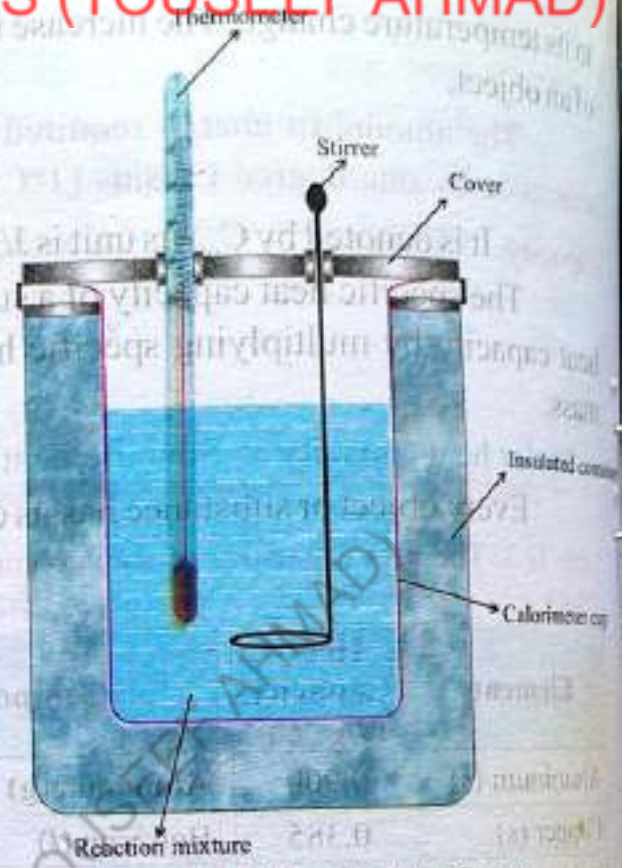

Figure 11.2: Simple Calorimeter

ii) Bomb Calorimeter

It consists of an insulated steel vessel called a bomb. It has an ignition coil and a platinum cup inside the bomb. The bomb has an inlet valve for adding oxygen and electrical leads for the ignition of mixture. It is generally used to measure the enthalpy of combustion of food, fuel and other compounds.

The known quantity of a sample is placed in a small platinum

Figure 11.3: Bomb Calorimeter

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cup inside the bomb. The bomb is sealed and oxygen is added in through an inlet valve until the pressure inside the bomb is about 20atm. The bomb is then placed in an insulated steel vessel containing known mass of water. The initial temperature of water is noted by thermometer. The sample is ignited by passing an electric current through the ignition coil. The heat evolved during the combustion of sample raises the temperature of bomb, water and other parts of the calorimeter. The rise in temperature of water is noted after every 30 seconds. Knowing the mass of sample in the calorimeter, the heat capacity of the calorimeter and the temperature change, we can calculate the heat of combustion by the following equation:

$$q = C_s \times m \times \Delta T$$

Example 11.1

Calculate the heat of neutralization when 50mL of 0.5M HCl is mixed with 50mL of 0.5M NaOH in a calorimeter at 25°C. The final temperature after stirring the reaction mixture is 27.25°C. The specific heat of water is 4.184 J/g°C and the density of solution is 1g/mL.

Solution:

Change in temperature (ΔT) $= T_2 - T_1 = 27.25°C - 25.00°C = 2.25°C$

Total volume of solution $= 50mL + 50mL = 100mL$

Total mass of solution $=$ Density $\times$ Total volume $= 1g/mL^{-1} \times 100mL = 100g$

Number of moles of HCl or NaOH $= \frac{50mL}{1000mL\ L^{-1}} \times 0.5mol\ L^{-1} = 0.025mol$

Heat of a neutralization of solution $= \Delta H_n = ?$

The equation used to calculate heat of neutralization is:

$$\Delta H_n = q_p = C_s \times m \times \Delta T$$

By putting the values we get,

$$\Delta H_n = -(4.184 Jg^{-1}°C^{-1} \times 100g \times 2.25°C)$$
$$= -941.4J$$

The value of ΔH_n in kilo joule $= \frac{-941.45J}{1000J/kJ} = -0.9414kJ$

ΔH_n for one mole of HCl and NaOH $= \frac{-0.9414kJ}{0.025mol} = -37.656kJ/mol$

The value of ΔH_n is negative because the heat is released.

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Practice Exercise 1:
When 50mL of 1.00M HNO_3 is added to 50mL of 1.00 M KOH solution at 25°C in a calorimeter; the temperature of the aqueous increases to 38°C. Find out the heat of neutralization in kilojoules per mole for the reaction. The specific heat of the solution is 4.184 J/g.°C and density is 1.00g/mL.

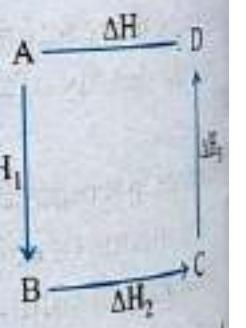
11.8 Hess's Law of Constant Heat Summation

Consider the formation of two moles of carbon monoxide from two moles of carbon and one mole of oxygen.

$$2C_{(Graphite)} + O_{2(g)} \longrightarrow 2CO_{(g)}$$

The enthalpy change for this reaction cannot be measured directly although the CO gas is the major product, because the CO gas formed during the reaction further reacts with oxygen and forms some CO_2 gas. The enthalpy change for the above reaction can be measured indirectly using Hess's law.

In 1840, the Swiss chemist German Henri Hess (1802-1850), a professor of St. Petersburg university, Russia formulated this law. He is known as the father of thermochemistry. **Hess's law states that the enthalpy change during chemical reaction is same whether reaction takes place in one step or in a series of steps.** Enthalpy is a state function; hence, its change is independent of the path between initial and final states.



Consider a general reaction in which *A* is reactant and *D* is product. In this reaction *A* is converted into *D* by direct and indirect methods. In a multi-step reaction *B* and *C* are intermediate states.

According to Hess's Law, the enthalpy change for the overall reaction is equal to the sum of the enthalpy changes of the individual steps in a multistep reaction.

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Applications of Hess's Law

The enthalpy change (heat of formation) of methane, ethyne, CO, benzene, ethyl alcohol etc. cannot be calculated directly. They can be determined indirectly by using Hess's law. Some examples of Hess's law are:

Formation of CO_2

The formation of CO_2 takes place by two methods:

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Direct method:

$$C + O_2 \longrightarrow CO_2 \qquad \Delta H = -393.51 kJmol^{-1}$$

Indirect method:

$$C + 1/2O_2 \longrightarrow CO \qquad \Delta H_1 = -110.5 kJmol^{-1}$$

$$CO + 1/2O_2 \longrightarrow CO_2 \qquad \Delta H_2 = -283.0 kJmol^{-1}$$

$$C + O_2 \longrightarrow CO_2 \qquad \Delta H = -393.5 kJmol^{-1}$$

The enthalpy change remains same whether reaction takes place in one step or in several (many) steps.

Formation of Sodium Carbonate

It takes place by two methods:

Direct Method:

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O \qquad \Delta H = -89.08 kJmol^{-1}$$

Indirect Method:

$$NaOH + CO_2 \longrightarrow NaHCO_3 \qquad \Delta H_1 = -48.06 kJmol^{-1}$$

$$NaOH + NaHCO_3 \longrightarrow Na_2CO_3 + H_2O \qquad \Delta H_2 = -41.02 kJmol^{-1}$$

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O \qquad \Delta H = -89.08 kJmol^{-1}$$

The enthalpy change remains same whether reaction takes place in one step or in several steps.

11.9 Born-Haber Cycle

The Born-Haber cycle was developed by the German physicist Max Born and the German chemist Fritz Haber to calculate the lattice energies of binary ionic compounds such as M^+X^-. The Born-Haber cycle states that the sum of all the enthalpy changes is always equal to zero. It is a special application of Hess's law.

Calculation of Lattice Energy of NaCl

The formation of NaCl occurs by two methods:

Direct method:

One mole of sodium combines with half mole of chorine to produce one mole of NaCl. The amount of energy released when one mole of NaCl is produced from its elements is called heat of formation of NaCl. The heat of formation of sodium chloride is -411kJ/mol.

$$Na_{(S)} + \tfrac{1}{2} Cl_{2(g)} \longrightarrow NaCl_{(s)} \qquad \Delta H_f = -411 kJmol^{-1}$$

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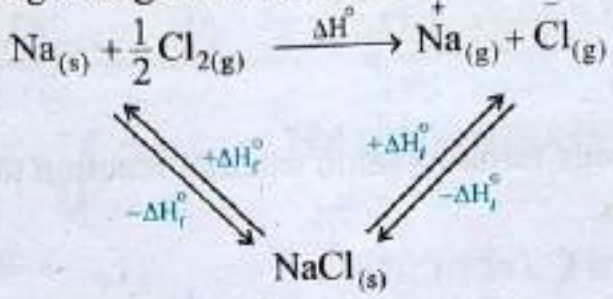
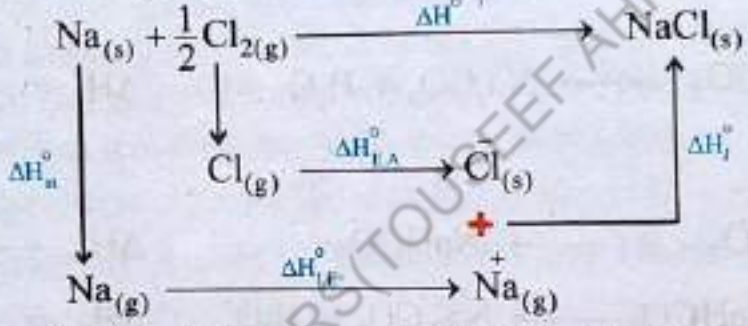
Indirect method:

Lattice energy of compounds cannot be determined directly by experiments. It can be determined indirectly by means of an energy cycle because an ionic compound is thought to be formed in a series of steps.

The energy triangle diagram for NaCl is:



The complete energy cycle called Born-Haber cycle for the formation of NaCl is:



We can calculate the lattice energy of NaCl with help of five steps that are given below:

i) One mole of solid sodium is directly converted into sodium vapours. This process is called sublimation. It is an endothermic process. The enthalpy of sublimation for sodium is 107.7kJ/mol.

$Na_{(s)} \longrightarrow Na_{(g)}$ $\qquad \Delta H_1^\circ = +107.7 kJ/mol$

ii) One mole of sodium ions are obtained by the ionization of one mole of gaseous sodium atoms. It is an endothermic process. The enthalpy of ionization for sodium is 496kJ/mol. This is the first ionization energy of sodium.

$Na_{(g)} \longrightarrow Na^+_{(g)} + 1\bar{e}$ $\qquad \Delta H_2^\circ = +496.0 kJ/mol$

iii) One mole of chlorine atoms are obtained by the dissociation of half mole of Cl_2 gas. It is also an endothermic process. The enthalpy of atomization for Cl_2 gas is 121.7 kJ/mol.

$\frac{1}{2} Cl_2 \longrightarrow Cl_{(g)}$ $\qquad \Delta H_3^\circ = +121.7 kJ/mol$

iv) One mole of chloride ions are formed from chlorine atoms by the addition of electrons. It is an exothermic process. The enthalpy of ionization for chlorine is –349 kJ/mol. This is the electron affinity of chlorine.

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$Cl_{(g)} + 1\bar{e} \longrightarrow Cl^-_{(g)}$ $\quad \Delta H_4^\circ = -349.0 kJ/mol$

v) One mole of solid sodium chloride is formed by the combination of one mole of sodium ions and one mole of chloride ions. This is the process of lattice formation. It is an exothermic process. The amount of energy released during the formation of NaCl is called lattice energy.

$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)}$ $\quad \Delta H_5^\circ = ?$

We cannot determine lattice energy directly. It can be determined by using Hess's law as:

$$\Delta H_f = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ + \Delta H_4^\circ + \Delta H_5^\circ$$
$$-411 = 107.7 + 496.0 + 121.7 + (-349.0) + \Delta H_5^\circ$$
$$-411 = 725.4 - 349.0 + \Delta H_5^\circ$$
$$-411 = 376.4 + \Delta H_5^\circ$$
$$\Delta H_5^\circ = -411 - 376.4 = -787.4 kJ/mol$$

The lattice energies of other compounds can be calculated in the same way.

Practice Exercise 2:

Calculate the lattice energy of KBr with the help of the following information:

i) The enthalpy of formation for KBr is –392.2kJ/mol
ii) Heat of sublimation for potassium is 89kJ/mol
iii) The ionization energy for potassium is 419kJ/mol
iv) The enthalpy of atomization for bromine is 112kJ/mol
v) The electron affinity of bromine is –324kJ/mol

Summary of Facts and Concepts

- Thermochemistry is the study of heat changes associate with chemical reactions and physical changes.
- Energy is the capacity of a body to do work or heat transfer. It includes kinetic energy and potential energy. The SI unit of energy is joule.
- Kinetic energy is due to motion of the object or particles of substance. It depends on mass and velocity of an object or particle of substance. ($K.E = 1/2mv^2$). Potential energy is due to the position of an object or stored in a molecule because of its composition.
- Internal energy is the sum of the kinetic energies and potential energies of the particles of the substance.

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- According to first law of thermodynamics, the energy of the universe is constant and the internal energy change (ΔE) is the sum of heat (q) and work (w): $\Delta E = q + w$
- The change in internal energy (ΔE) is the amount of energy (heat) evolved or absorbed by the system at constant volume: $\Delta E = q_v$
- In an exothermic process, the heat flows out of the system while in an endothermic process, the heat flows into a system.
- Enthalpy is a state function. It is the heat content of a system. It is equal to the sum of internal energy (E) and product of pressure (P) and volume (V).
- Enthalpy change (ΔH) is the amount of heat evolved or absorbed by the system at constant pressure: $\Delta H = q_p$
- Thermochemical equation is the equation that shows the amount of heat change during a chemical reaction.
- The enthalpy change for exothermic reaction is negative and for endothermic reaction it is positive.
- The amount of heat evolved or absorbed during a chemical reaction or physical process is measured experimentally by using calorimeter.
- According to Hess's law of constant heat summation, the enthalpy change during chemical reaction is same whether reaction occurs in a single step or in a series of steps.
- The standard enthalpy of formation is the enthalpy change when one mole of a compound is formed from its elements in their standard states; that is, at 25 °C and 1 atm.
- The amount of energy required to break all bonds in mole of substance is called bond dissociation energy.

Questions and Problems

Q.1. Four answers are given for each question. Select the correct one:

(i) The study of heat changes that accompany a chemical reaction is called:

(a) Thermochemistry (b) electrochemistry
(c) nuclear chemistry (d) chemical kinetics

(ii) Which one of the following is **NOT** the unit of heat:

(a) Joule (b) Kelvin (c) calorie (c) kilojoule

(iii) Anything which is under observation or experiment is called:

(a) Universe (b) boundary (c) system (d) surrounding

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(iv) The energy of the system during endothermic reactions is:

(a) Increased (b) decreased

(c) neither increased nor decreased

(d) first increased and then decreased

(v) The sum of kinetic energy and potential energy of the particles of substance is called:

(a) Heat capacity (b) specific heat

(d) enthalpy of the system (d) internal energy

(vi) Internal energy depends upon:

(a) Intermolecular forces (b) intramolecular forces

(c) motion of particles (d) all of them

(vii) The enthalpy change is positive for:

(a) Combustion (b) exothermic process

(c) ionization energy (d) electron affinity

(viii) One calorie is equal to:

(a) 4.184 J (b) 41.84 J (c) 418.4 J (d) 4184.0 J

(ix) The heat of formation of carbon dioxide is:

(a) 3.9351kJ/mol (b) 39.351kJ/mol

(c) 393.51kJ/mol (d) 3935.1kJ/mol

(x) Which one of the following is **NOT** a state function:

(a) Temperature (b) work

(c) pressure (d) internal energy

Q.2. **Fill in the blanks with suitable words given in the brackets:**

(i) The majority of reactions which give stable products are _____. (Endothermic/exothermic)

(ii) The *w* is _____ when the work is done on the system by the surroundings. (positive/negative)

(iii) The energy of the system is _____ during an endothermic process. (decreased/increased)

(iv) Melting of ice is an _____ process. (exothermic / endothermic)

(v) The amount of energy required to raise the temperature of one gram of a substance one Kelvin at constant pressure is called _____. (specific heat capacity/molar heat capacity)

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(vi) The energy is provided to the system at constant _____ to change the enthalpy of the system. (pressure/volume)

(vii) The energy is provided to the system at constant _____ to change the internal energy of the system. (pressure/volume)

(viii) The heat of formation of a compound is _____ . to heat of decomposition of a compound. (equal/not equal)

(ix) The equation for first law of thermodynamics is _____. ($E = q + w / \Delta E = q + w$)

(x) The enthalpy change when one mole of a _____ is formed from its elements is called standard enthalpy of formation. (Substance / compound)

Q.3. Label the following statements as True or False:

(i) Thermochemistry is the study of heat, energy and work.

(ii) Enthalpy is not a state function.

(iii) A balanced chemical equation which shows the enthalpy change of a reaction is called thermochemical equation.

(iv) According to Hess's law, the enthalpy change is equal to the sum of the enthalpy changes of the individual steps in a multi-step reaction.

(v) The energy can be created or destroyed during a physical change or chemical change.

(vi) In chemistry, we most commonly deal with pressure-volume work.

(vii) The Born-Haber cycle is different from Hess's law.

(viii) The heat of neutralization for a strong acid and a strong base is equal to –57.4kJ/mol.

(ix) The unit of specific heat capacity is *J/mol°C*.

(x) Bomb calorimeter is used to determine the heat transfer at constant volume.

Q.4: Define the following terms: thermochemistry, joule, and calorie.

Q.5: Define heat. Explain with example, how energy is transferred from one piece of matter to another?

Q.6: Define energy. What is the difference between kinetic energy and potential energy? Give the importance of energy.

Q.5: What is the difference between temperature and heat?

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Q.6: What is thermochemical equation? What are exothermic and endothermic reactions? Give an example of each.

Q.7: What is system? What do you know about types of system?

Q.8: Give definitions for the following terms:

(a) Thermodynamics (b) Surrounding

(c) Boundary (d) Universe

(e) State of system

Q.9: What is meant by state function? Explain enthalpy is a state function but heat is not a state function.

Q.10: Define and explain internal energy of the system.

Q.11: What is first law of thermodynamics? Prove that:

(a) $\Delta H = q_p$ (b) $\Delta E = q_v$

Q.12: What is meant by enthalpy? What is the difference between ΔH and ΔE? The value of $\Delta H \approx \Delta E$ in case of solids and liquids, why?

Q.13: Give the sign of ΔH for exothermic and endothermic reactions.

Q.14: Give precise definitions for the terms given below:

(a) Standard enthalpy change

(b) Standard enthalpy of atomization

(c) Standard enthalpy of combustion

(d) Standard enthalpy of formation

(e) Standard enthalpy of neutralization

Q.15: What is meant by the term heat capacity of a substance? Define and explain specific heat capacity and molar heat capacity. Give units of each.

Q.16: Why we prefer to sit on a bench made of wood rather than a bench made of iron in a hot summer day?

Q.17: Define calorimetry.

(a) How do you measure the enthalpy of neutralization by simple calorimeter?

(b) How do you measure the enthalpy of combustion by bomb calorimeter?

Q.18: What is Hess's law of constant heat summation? Give its applications.

Q.19: What is lattice energy? How does the Born-Haber cycle helps to calculate the lattice energy of NaCl?

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Q.20: Why it is essential to mention the physical states of reactants and products in a thermochemical equation?

Q.21: Why the heat of neutralization of any strong acid with any strong base is approximately equal to $-57.4 kJ\ mol^{-1}$?

Q.22: The white precipitate of AgCl is formed when 20mL of $0.50 mol/dm^3$ solution of $AgNO_3$ is added to 20mL of $0.50\ mol/dm^3$ solution of NaCl. The rise in temperature is 8.0 °C. Calculate the heat of solution in kilojoules per mole. The specific heat of the solution is assumed to be 4.184 J/g. °C and density is 1.00g/mL.

Q.23: Calculate the lattice energy of lithium fluoride (LiF) with the help of the following information:

a) The enthalpy of formation for LiF is $-594 kJ\ mol^{-1}$.
b) Heat of sublimation for lithium is $155 kJ\ mol^{-1}$.
c) The ionization energy for lithium is $520\ kJ\ mol^{-1}$.
d) The enthalpy of atomization for F_2 is $75 kJ\ mol^{-1}$.
e) The electron affinity of fluorine is $-328 kJ\ mol^{-1}$.

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Chapter # 12

Electrochemistry

Major Concepts

12.1 Oxidation-Reduction Concepts
12.2 Electrode
12.3 Electrochemical Cells
12.4 Standard Cell Potential and Standard Electrode Potential
12.5 Modern Batteries
12.6 Corrosion

Learning Outcomes

The students will be able to:

- Give the characteristics of a Redox reaction. (Understanding)
- Determine the oxidation number of an atom of any element in a pure substance. (Applying)
- Define oxidation and reduction in terms of a change in oxidation number. (Applying)
- Use the oxidation-number change method to identify atoms being oxidized or reduced in redox reactions. (Applying)
- Use the oxidation-number change method to balance redox equations. Applying)
- Balance redox reactions that take place in acid solutions. (Applying)
- Break a redox reaction into oxidation and reduction half reactions. (Applying)
- When given an unbalanced redox equation, use the half reaction method to balance the equation. (Applying)
- Define cathode, anode, electrode potential and S.H.E. (Standard Hydrogen Electrode). (Remembering)
- Identify the substance oxidized and the substance reduced in a dry cell. (Applying)
- Use the activity series of metals to predict the products of single replacement reactions. (Analysis)
- Define cell potential, and describe how it is determined. (Understanding)
- Describe the reaction that occurs when a lead storage battery is recharged. (Applying)
- Explain how a fuel cell produces electrical energy. (Applying)
- Define the standard electrode potential of an electrode. (Remembering)

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Introduction

Electrochemistry is the branch of chemistry which deals with the conversion of electrical energy into chemical energy in electrolytic cells and chemical energy into electrical energy in galvanic or voltaic cells. Electrochemistry has lots of important applications but we are going to discuss few of them.

A cell consists of two electrodes that are dipped into an electrolyte used for interconversion of chemical and electrical energy. Battery is a device that consists of one or more cells and is used to produce electric current by converting chemical energy to electrical energy. Some examples of batteries are dry cell, silver batteries, NiCad battery, lead storage battery, and fuel cells. These batteries are used to power radios, digital watches, calculators, cell phones, laptops, CD players, flashlights, toys and hybrid cars.

Furthermore many essential industrial chemicals and materials such as caustic soda (NaOH), chlorine, aluminum, hydrogen, oxygen, and hydrogen peroxide are manufactured by electrolytic processes.

Electrochemical processes are not always advantageous; that is, there are some electrochemical processes that damage the materials such as corrosion of iron. The main target of electrochemistry is to prevent the corrosion to reduce the loss of materials.

12.1 Oxidation-reduction Concepts

12.1.1 Oxidation and Reduction

Oxidation and reduction can be defined in three different ways:

i) The addition of oxygen to a substance during a chemical reaction is called oxidation while the removal of oxygen from a substance during a chemical reaction is called reduction. Reduction is the reverse of oxidation.

$$PbO + C \longrightarrow Pb + CO$$

In this reaction, lead oxide is reduced to lead by losing oxygen while carbon is oxidized to carbon monoxide by gaining oxygen.

ii) The addition of hydrogen to a substance during a chemical reaction is called reduction while the removal of hydrogen from a substance during a chemical reaction is called oxidation.

$$H_2S + Cl_2 \longrightarrow S + 2\,HCl$$

In this example, hydrogen sulphide gas is oxidized to sulphur by losing hydrogen while chlorine is reduced to HCl by gaining hydrogen.

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iii) Loss of one or more electrons by a substance is called oxidation while the gain of one or more electrons from a substance is called reduction.

$$2Na + Cl_2 \longrightarrow 2NaCl$$

In this reaction, sodium is oxidized to sodium ion by losing electrons and chlorine is reduced to chloride ion by gaining electrons. The element that loses the electrons during the reaction is said to be oxidized. Its oxidation number increases. The element that gains electrons during the reaction is said to be reduced. Its oxidation number decreases.

12.1.2 Oxidation Numbers

The apparent charge, positive or negative, which an atom would have in a compound, is called oxidation number. It is also known as the oxidation state. It enables us to identify the elements that are oxidized or reduced. The elements that show an increase in the oxidation state are oxidized while the elements that show decrease in the oxidation state are reduced.

Rules for Assigning Oxidation Numbers

i) The oxidation number of an atom of a free element is zero. Hence, each atom in H_2^0, N_2^0, O_2^0, Br_2^0, Na^0, Mg^0, Fe^0 and Zn^0 has zero oxidation numbers.

ii) In compounds, the oxidation number of hydrogen is +1 except in metal hydrides where it is –1. Hence, the oxidation number of hydrogen is –1 in LiH, NaH, and CaH_2.

iii) The oxidation number of oxygen is –2 in all its compounds (e.g. CO_2 and CaO) except in peroxides and superoxides. In peroxides, it is –1 (e.g. H_2O_2 and Na_2O_2) and in superoxides, it is –1/2 (e.g. KO_2). The oxidation number of oxygen in oxygen difluoride, OF_2 is +2.

iv) The oxidation numbers of alkali metals, alkaline earth metals (Group IIA) and group IIIA elements are +1, +2 and +3 respectively.

v) The oxidation number of halogens (Group VIIA elements) is –1 in their binary compounds (NaCl, KBr, and $AlCl_3$). The halogens except fluorine show positive oxidation numbers when they are bonded with oxygen.

vi) The oxidation number of a monoatomic ion is equal to the charge on it. Hence, Na^+, Mg^{2+}, Al^{3+} and O^{2-} have +1, +2, +3 and –2 oxidation states respectively.

vii) In polyatomic ions such as CO_3^{-2}, SO_4^{-2} and PO_4^{-3} the sum of oxidation

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number of atoms of different elements is equal to the net charge on the ion. For example, in the carbonate ion (CO_3^{-2}), the oxidation number of carbon is +4 and that of oxygen is –2. Hence, the sum of oxidation numbers is $1(+4)+3(-2)=-2$.

viii) The sum of oxidation numbers of all the elements in a neutral compound is equal to zero. For example, in potassium permanganate ($KMnO_4$), the oxidation number of potassium is +1, manganese is +7 and that of oxygen is –2. Hence, the sum of the oxidation numbers is $1(+1)+1(+7)+4(-2)=0$.

ix) In any substance, the more electronegative atom has the negative oxidation number while the less electronegative atom has the positive oxidation number.

x) The same element may show different oxidation numbers in different compounds. For example, the oxidation numbers of *sulphur* in disulphur dichloride (S_2Cl_2), sulphur dioxide (SO_2), sulphuric acid (H_2SO_4), and hydrogen sulphide (H_2S) are +1, +4, +6, and –2 respectively.

Example 12.1

Calculate the oxidation number of nitrogen in HNO_3.

Solution

The oxidation number of hydrogen is +1 and that of oxygen is –2. The oxidation number of nitrogen in HNO_3 is calculated as:

$$1(+1)+1(N)+3(-2) = 0$$
$$+1 + N - 6 = 0$$
$$N - 5 = 0$$

Example 12.2

Find out the oxidation number of chromium in $K_2Cr_2O_7$.

Solution:

The oxidation number of potassium is +1 and that of oxygen is –2. The oxidation number of chromium in $K_2Cr_2O_7$ is calculated as:

$$2(+1) + 2(Cr) + 7(-2) = 0$$
$$+2 + 2Cr - 14 = 0$$
$$2Cr - 12 = 0$$
$$2Cr = +12$$
$$Cr = +12/2$$
$$Cr = +6$$

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Example 12.3

Find out the oxidation number of nitrogen in NH_4^{+1}.

Solution:

The oxidation number of hydrogen is +1 and that of nitrogen in NH_4^{+1} is calculated as:

$$1(N) + 4(+1) = +1$$
$$N + 4 = +1$$
$$N = +1 - 4$$
$$N = -3$$

Example 12.4

What is the oxidation number of carbon in HCO_3^{-1}?

Solution:

The oxidation number of hydrogen is +1 and that of oxygen is –2. The oxidation number of carbon in HCO_3^{-1} is calculated as:

$$1(+1) + 1(C) + 3(-2) = -1$$
$$+1 + C - 6 = -1$$
$$C - 5 = -1$$
$$C = -1 + 5$$
$$C = +4$$

Practice Exercise 1:

Calculate the oxidation number of Chromium in the following species:

(i) $CrCl_3$ (ii) Cr_2O_3 (iii) $Cr_2(SO_4)_3$ (iv) CrO_4^{-2}

12.1.3 Recognizing Oxidation-Reduction Reactions

The reactions that involve oxidation and reduction are called oxidation-reduction reactions. They are also known as redox reactions. Oxidation-reduction reactions can be considered as electron transfer reactions. In the process, the electrons may either be transferred from one substance to another to form ionic bonds or shared to form covalent bonds. The process of oxidation and reduction occur simultaneously during a chemical reaction. Both of these processes occur in equivalent amounts.

Keep in mind

The number of electrons shared, gained or lost by an atom of an element is called valency whereas the apparent charge, positive or negative which an atom would have in a compound is called oxidation state.

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To identify the oxidation-reduction reactions, one should know that the change in oxidation number occurs during the oxidation-reduction reaction.

Consider the reaction in which zinc metal reacts with a solution of aqueous copper sulphate containing copper ions:

$$Zn_{(s)} + CuSO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + Cu_{(s)}$$

This reaction can also be shown as:

$$Zn^{0}_{(s)} + Cu^{+2}_{(aq)} + SO^{-2}_{4(aq)} \longrightarrow Zn^{+2}_{(aq)} + SO^{-2}_{4(aq)} + Cu^{0}_{(s)}$$

This is a redox reaction in which zinc metal is oxidized; that is, the zero oxidation number of zinc is converted to +2. The copper ion is reduced; that is, the +2 oxidation number of copper ion is converted to zero.

A redox reaction is the sum of two half- reactions; that is, an oxidation half-reaction and a reduction half-reaction.

Redox reaction = Oxidation half reaction + Reduction half reaction

An equation which shows either loss or gain of electrons is called half-reaction. A half-reaction which shows the reactant that loses electrons is called oxidation half-reaction whereas a half-reaction which shows the reactant that gains electrons is called reduction half-reaction. In oxidation half-reaction, the electrons appear on the product side of the equation whereas in reduction half-reaction, the electrons appear on the reactant side of the equation. The above reaction can be separated into two half reactions as:

Oxidation half-reaction: $Zn^{0}_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^{-}$

Reduction half-reaction: $Cu^{+2}_{(aq)} + 2\,e^{-} \longrightarrow Cu^{0}_{(s)}$

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Applications of Redox Reactions in Daily Life

Applications of redox reactions are numerous but we are going to discuss few of them.

- The burning of wood, paper, coal, and gasoline in the presence of air is called combustion, which is rapid redox reaction.
- Many biological redox reactions provide energy that is required by living organisms to sustain life. The most familiar is the process of metabolism, which is a complex process. The oxidation of carbohydrate is an example of metabolic redox process. In this process, a carbohydrate such as glucose reacts with oxygen to produce CO_2 and water with the evolution of energy.

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{energy}$$

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- Redox process is also responsible for the operation of batteries. There is a lot of variety of batteries that are used to power many useful devices such as flashlights, radios, laptop computers, watches, and portable music players.
- Bleaching agents are oxidizing agents that are used to decolourize or lighten the colour of materials such as paper, fabrics and human hair. By redox reactions, elemental chlorine is used to bleach wood pulp to make white paper, sodium hypochlorite (NaOCl) is used to remove stains from clothes, and hydrogen peroxide is used to convert redheads into blondes of sort.
- Redox reactions are not always beneficial. The decay of metals by oxidation such as rusting of iron in the moist air is called corrosion. Corrosion is a spontaneous redox reaction and damages especially those materials which are made of iron.
- Electroplating is redox process that is used to improve the hardness, stability and appearance of metals (objects) and to protect them from corrosion.

12.1.4 Balancing Oxidation-Reduction Equations by Oxidation Number Method:

The following rules are used for balancing of redox equations by oxidation number method.

i) Write down the skeleton equation for the reaction under consideration.

ii) Write down the oxidation number of each atom above it.

iii) Identify those atoms whose oxidation numbers are changed during redox reaction.

iv) Record the oxidation numbers above the atoms whose oxidation numbers have changed.

v) Indicate the change in oxidation number by arrows joining the atoms on both sides of the equation. Arrows show the number of electrons gained or lost by single atom only.

vi) Equate (to make balance) the number of electrons gained or lost by multiplying with a suitable number.

vii) Balance rest of the equation by inspection method.

Example 12.5

Balance the following equations by oxidation number method:

(a) $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$

(b) $K_2Cr_2O_7 + HCl \longrightarrow KCl + CrCl_3 + Cl_2 + H_2O$

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Solution: (a)

i) Write down the skeleton equation for the reaction.

$$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$$

ii) Write down the oxidation number of each atom above it.

$$\overset{0}{Cu} + \overset{1(+1)\ 1(+5)\ 3(-2)}{\overset{+1}{H}\ \overset{+5}{N}\ \overset{-6}{O_3}} \longrightarrow \overset{1(+2)\ 2(-5)\ 6(-2)}{\overset{+2}{Cu}\ (\overset{+10}{N}\ \overset{-12}{O_3})_2} + \overset{1(+4)\ 2(-2)}{\overset{+4}{N}\ \overset{-4}{O_2}} + \overset{2(+1)\ 1(-2)}{\overset{+2}{H_2}\ \overset{-2}{O}}$$

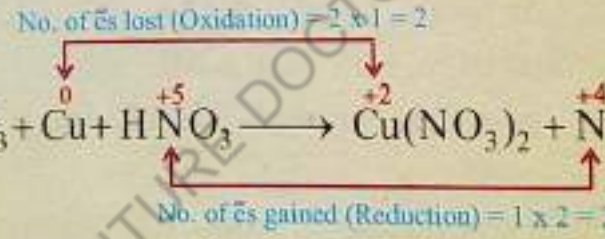
iii) Identify those atoms whose oxidation numbers have changed during the reaction.

$$\overset{0}{Cu} + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+4}{N}O_2 + H_2O$$

In this equation, the oxidation number of copper has changed from zero to +2 and that of nitrogen has changed from +5 to +4. We should write HNO_3 twice on the left hand side because the oxidation number of nitrogen remains same (+5) in $Cu(NO_3)_2$ and changes (+4) in NO_2.

$$HNO_3 + \overset{0}{Cu} + \overset{+5}{HNO_3} \longrightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+4}{NO_2} + H_2O$$

iv) Draw arrows between the same atoms whose oxidation numbers have changed, and show the number of electrons lost, or gained by an atom.



One copper atom lost 2 electrons and two nitrogen atoms gained 2 electrons.

v) Multiply HNO_3 and NO_2 by 2 to balance the number of electrons lost or gained during the reaction.

$$HNO_3 + Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$

This equation can also be written as:

$$Cu + 3HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$

vi) Now balance rest of the equation by inspection method.

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

Solution: (b)

i) Write down the skeleton equation for the reaction.

$$K_2Cr_2O_7 + HCl \longrightarrow KCl + CrCl_3 + Cl_2 + H_2O$$

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ii) Write down oxidation numbers of each atom above it.

$$\overset{2(+1)}{\overset{+2}{K_2}}\ \overset{2(+6)}{\overset{+12}{Cr_2}}\ \overset{7(-2)}{\overset{-14}{O_7}} + \overset{+1\ -2}{HCl} \longrightarrow \overset{+1\ -1}{KCl} + \overset{3(-1)}{\overset{+3\ -3}{CrCl_3}} + \overset{0}{K_2} + \overset{2(+1)}{\overset{+2\ -2}{K_2O}}$$

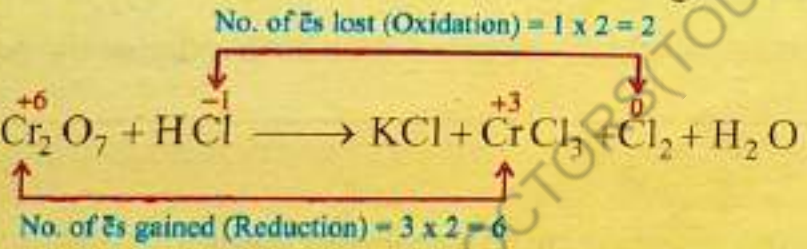
iii) Identify those atoms whose oxidation numbers have changed during the reaction.

$$\overset{+6}{K_2Cr_2O_7} + \overset{-1}{HCl} \longrightarrow KCl + \overset{+3}{CrCl_3} + \overset{0}{Cl_2} + H_2O$$

In this equation, oxidation number of chromium has changed from +6 to +3 and that of chlorine has changed from –1 to zero. The oxidation numbers of chlorine in KCl and $CrCl_3$ remain same (–1). We should, therefore, write HCl twice on the left hand side. One HCl for those chlorine atoms whose oxidation numbers have changed and one HCl for those chlorine atoms whose oxidation numbers have not changed.

$$HCl + \overset{+6}{K_2Cr_2O_7} + \overset{-1}{HCl} \longrightarrow KCl + \overset{+3}{CrCl_3} + \overset{0}{Cl_2} + H_2O$$

iv) Draw arrows between the same atoms whose oxidation numbers have changed and show the number of electrons lost or gained by an atom.



Here, two chlorine atoms have lost 2 electrons while two chromium atoms have gained 6 electrons.

v) Multiply HCl by 6, Cl_2 by 3 and $CrCl_3$ by 2 to balance the number of electrons lost or gained.

$$HCl + K_2Cr_2O_7 + 6\,HCl \longrightarrow KCl + 2CrCl_3 + 3Cl_2 + H_2O$$

vi) Now balance rest of the equation by inspection method.

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

Practice Exercise 2:

Balance the following equation by oxidation number method:

$$Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO + H_2O$$

12.1.5 Balancing of Oxidation Reduction Equations by the Half Reaction Method:

This method of balancing the oxidation-reduction equations is also known as the ion-electron method. The following rules are used for balancing of redox

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equations by the half reaction method:

i) Write down the skeleton equation which shows only those species that are actually involved in the reaction.

ii) Split up the equation into two half reactions i.e. oxidation and reduction half reactions.

iii) Those atoms, molecules or ions should be written which really exist. Remove all unnecessary species.

iv) Balance all atoms on either side of the equation other than hydrogen and oxygen.

v) Balance oxygen atoms by adding H_2O molecules.

vi) Balance hydrogen atoms by adding H^+ ions in acidic solution or OH^- ions in basic solution.

vii) Balance the charges by adding electrons.

viii) Balance the number of electrons lost or gained during reaction by multiplying each half reaction with a suitable number.

ix) Add both half reactions in such a way that the electrons must not appear in the final equation.

x) Cancel out substances which are present on both sides of the equation.

Example 12.6

Balance the following equation by half reaction method:

$$KMnO_4 + HCl \longrightarrow H_2O + MnCl_2 + Cl_2$$

Solution:

(i) Write down the skeleton equation.

$$KMnO_4 + HCl \longrightarrow H_2O + MnCl_2 + Cl_2$$

(ii) Now write the species which are actually involved in the reaction and remove all un-necessary species.

$$MnO_4^- + Cl^- \longrightarrow Mn^{+2} + Cl_2$$

(iii) Split up the equation into two half reactions

$MnO_4^- \longrightarrow Mn^{+2}$ (Reduction half reaction)

$Cl^- \longrightarrow Cl_2$ (Oxidation half reaction)

(iv) Balance chlorine atoms by multiplying 2 on left hand side.

$$2Cl^- \longrightarrow Cl_2$$

(v) Balance the charge by adding 2 electrons on right hand side.

$$2Cl^- \longrightarrow Cl_2 + 2e^- \quad \ldots\ldots\ldots\ldots\ldots \quad (A)$$

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(vi) Balance oxygen atoms by adding $4H_2O$ molecules on R.H.S.

$$MnO_4^- \longrightarrow Mn^{+2} + 4\,H_2O$$

(vii) Balance hydrogen atoms by adding eight H^+ ions on L.H.S.

$$MnO_4^- + 8\,H^+ \longrightarrow Mn^{+2} + 4\,H_2O$$

(viii) Balance the charge by adding 5 electrons on L.H.S.

$$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{+2} + 4\,H_2O \quad \ldots\ldots\ldots\ldots \text{(B)}$$

(ix) Multiply equation (A) by 5 and equation (B) by 2 to balance the number of electrons lost or gained.

$$\left[2\,Cl^- \longrightarrow Cl_2 + 2\,e^-\right] \times 5$$

$$\left[MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{+2} + 4\,H_2O\right] \times 2$$

(x) Add both equations and cancel out the common species on both sides.

$$10\,Cl^- \longrightarrow 5\,Cl_2 + 10\,e^-$$

$$2MnO_4^- + 16\,H^+ + 10\,e^- \longrightarrow 2Mn^{+2} + 8H_2O$$

$$10Cl^- + 2MnO_4^- + 16H^+ \longrightarrow 5Cl_2 + 2Mn^{+2} + 8H_2O$$

Practice Exercise 3:

Balance the following equation by half reaction (ion-electron) method:

$$Cu + Ag^+ \longrightarrow Ag + Cu^{+2}$$

12.1.6 Chemistry of Some Important Reducing and Oxidizing Agents

A substance that loses electrons during a chemical reaction is called reducing agent or reductant where as a substance that gains electrons during a chemical reaction is called oxidizing agent or oxidant. The oxidizing agent oxidizes other substances (increases the oxidation state of other substances) and is reduced itself. The reducing agent reduces other substances (decreases the oxidation state of other substances) and is oxidized itself. The total number of electrons gained by oxidizing agent is always equal to the total number of electrons lost by the reducing agent.

Consider the following reaction in which sulphurous acid (H_2SO_3) reacts with nitric oxide (NO) to produce sulphuric acid and nitrous oxide (N_2O).

$$H_2SO_3 + 2NO \longrightarrow H_2SO_4 + N_2O$$

In this reaction, sulphurous acid is oxidizing agent because it (sulphur) loses electrons while nitric oxide is reducing agent because it gains (nitrogen) electrons. The electrons are transferred from sulphur to nitrogen.

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Among elements, the metals are good reducing agents while non-metals are good oxidizing agents. In the periodic table, the alkali metals are strong reducing agents because they form positive ions readily and halogens are strong oxidizing agents because they have strong attractions for electrons and form negative ions readily.

Among compounds, the potassium dichromate ($K_2Cr_2O_7$) and potassium permanganate ($KMnO_4$) are the most important strong oxidizing agents whereas hydrogen sulphide (H_2S), sulphur dioxide (SO_2) and ferrous sulphate ($FeSO_4$) are some important reducing agents. Some of the reactions of oxidizing and reducing agents are:

i) Magnesium reacts with cold dilute nitric acid to form hydrogen gas.

$$2HNO_3 + Mg \longrightarrow Mg(NO_3)_2 + H_2$$

In this reaction, nitric acid acts as oxidizing agent and magnesium atom acts as reducing agent.

ii) Hydrogen sulphide reacts with chlorine to form hydrogen chloride and sulphur.

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$

In this reaction, hydrogen sulphide acts as reducing agent and chlorine as oxidizing agent.

iii) Potassium dichromate reacts with sulphur dioxide in acidic medium to produce chromic sulphate, $Cr_2(SO_4)_3$.

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

In this reaction potassium dichromate acts as an oxidizing agent while sulphur dioxide acts as a reducing agent.

iv) $KMnO_4$ reacts with concentrated HCl to produce chlorine gas.

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

In this reaction, potassium permanganate acts as an oxidizing agent.

12.2 Electrode

The surfaces, in a cell, at which reactions (oxidation or reduction half-reactions) take place, are called electrodes. An electrode, in a cell, is a metal plate, wire, rod, or a piece of graphite through which the electric current enters into or leave out the electrolyte. The electrodes may or may not involve in the reactions. The electrodes that do not involve in the reactions are called inert electrodes. Electrodes are of two types; anode and cathode. The positive electrode is called anode because anions are attracted to it while negative electrode is called cathode because cations are

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attracted to it. Oxidation takes place at anode and reduction takes place at cathode. Electrons move from anode to cathode through an external circuit.

12.3 Electrochemical Cells

A cell consisting of two electrodes dipped into an electrolyte in which a chemical reaction either produces or utilizes an electric current is called electrochemical cell.

Electrochemical cells are of two types:

i) Electrolytic cell
ii) Galvanic or Voltaic cell

12.3.1 Electrolytic Cells

The electrochemical cell which utilizes an electric current to produce chemical reaction is called electrolytic cell. It may also be defined as: the cell in which non-spontaneous redox reaction takes place by the passage of electricity is called electrolytic cell. Examples are Down's cell, Nelson's cell.

Working of Electrolytic Cell

Consider an electrolytic cell which is used to determine the conductivity of solution.

An electrolytic cell consists of a beaker with two electrodes which are dipped in electrolyte and connected to a direct current (DC) source. When an electric current is passed through an electrolyte, the positively charged ions (cations) move towards cathode and negative charged ions (anions) move towards anode. The solution of the ions results in the passage of a current and the bulb glows. (The bulb will glow brightly in strong electrolyte and glow dimly in weak electrolytes.)

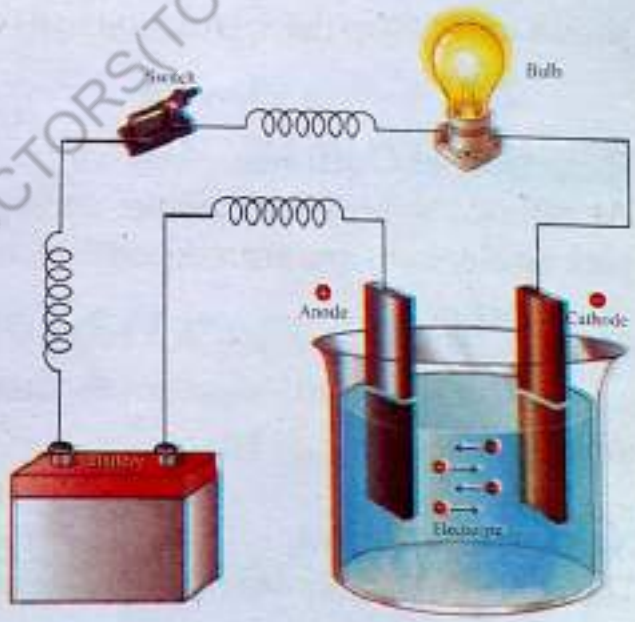

Figure 12.1: Electrolytic Cell

This movement of ionic charges through the solution due to the passage of electric current is called Electrolytic Conduction (Conduction of electricity).

12.3.2 Electrolysis of Aqueous Solution of NaCl

The electrolysis of aqueous NaCl is carried out in an electrolytic cell. This cell consists of a beaker with two electrodes which are connected to a direct current

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(DC) source. When solution of concentrated NaCl is placed in the cell and the electrodes are connected to DC. As a result of this H_2 gas is produced at cathode and Cl_2 gas at anode.

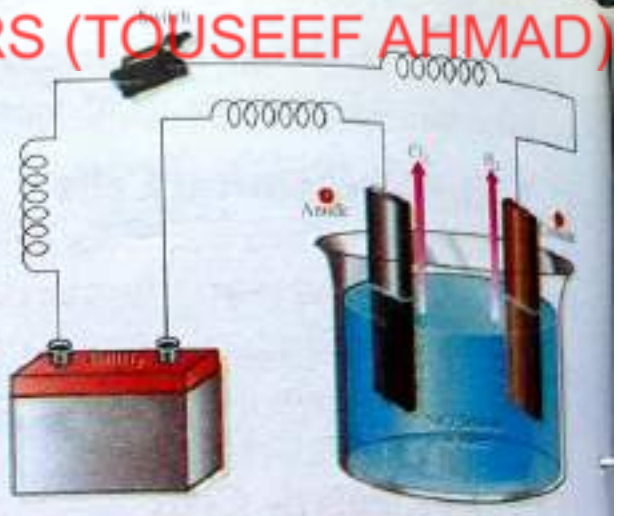

Figure 12.2:
Electrolysis of sodium chloride in water

Explanation

When NaCl is dissolved in water, it dissociates into ions as:

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

When electric current is passed through the solution, the following reactions take place at electrodes.

Reaction at Anode

At anode chloride ions (negative ions) lose electrons and are oxidized. As it shows only half of the net reaction so it is called oxidation half reaction.

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

Reaction at Cathode

At cathode sodium ions are not undergoing reduction. Actually water molecules pick up electrons and are reduced to H_2 and OH^- ions. It is reduction half reaction.

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

The H^+ ions of water act as stronger oxidizing agents as coimpared to Na^+ ions.

Net Cell Reaction

The net cell reaction which involves the oxidation and reduction half reactions are called redox reactions.

$$2NaCl + H_2O \longrightarrow H_2 + Cl_2 + NaOH$$

The net cell reaction produces hydrogen gas, chlorine gas and aqueous solution of NaOH. Pure NaOH is then obtained by evaporation of the solution.

In the above reactions, it is clear that H_2O is more easily reduced than Na^+. The reduction potential of water is –0.828 V while that of Na^+ is –2.714 V.

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12.3.3 Difference Between Coulomb, Ampere, and Volt

The flow of electrons through an external circuit is called the electrical current. The SI unit of electric current is ampere (A) that is defined as a charge of one coulomb flowing through a conductor in one second.

1 Ampere = 1 coulomb / second or 1A = 1C / sec

The quantity of electric current is known as electric charge. The SI unit of electric charge is coulomb (C) that is defined as the product of the current in amperes (A) and time in seconds (t).

1 coulomb = 1 ampere × 1 second or 1C = 1A × sec

For example, 75 coulomb current is passed in the wire when 5A current flows through a wire for 15 seconds.

Charge in coulomb = current in amperes × time in seconds

= 5A × 15sec

= 75C

An electrical potential difference is called voltage. The SI unit of potential difference (voltage) is the volt (V) that is equal to one joule (J) of energy per coulomb of charge (C).

$$1\text{ volt} = \frac{1\text{ joule}}{1\text{ coulomb}} \quad \text{or} \quad 1V = \frac{1J}{C}$$

Thus, a 1.5V cell produces 1.5 Joule of energy to every 1 coulomb of charge flowing through the cell.

12.3.4 Voltaic (or Galvanic) Cells

The electrochemical cell in which electric current is produced by spontaneous redox reaction is called galvanic cell or voltaic cells. They are commonly known as batteries. The names "galvanic" and "voltaic" honor the Italian scientists Luigi Galvani (1737-1798) and Alessandro Volta (1745-1827), who assembled the first version of the cells. Examples of galvanic cells are Daniel cell, Dry cell, Ni-Cd cell, Fuel cell.

Construction of Galvanic Cell

This cell consists of two half cells (half reactions) and placed in two beakers A and B containing solution of $ZnSO_4$ and $CuSO_4$ respectively. Zn electrode is dipped in solution of beaker A and Cu electrode in solution of beaker B. Each beaker makes a half cell and two beakers together make a complete cell. These two half cells are separate from each other and connected electrically by a salt bridge.

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Working of Galvanic Cell

When these two electrodes are connected externally by a wire, electrons flow from Zn-electrode to Cu-electrode. Hence Zn acts as an anode. The Cu^{2+} ions, from the solution, pick up the electrons at Cu-electrode and get reduced to copper atoms, Hence Cu acts as a cathode.

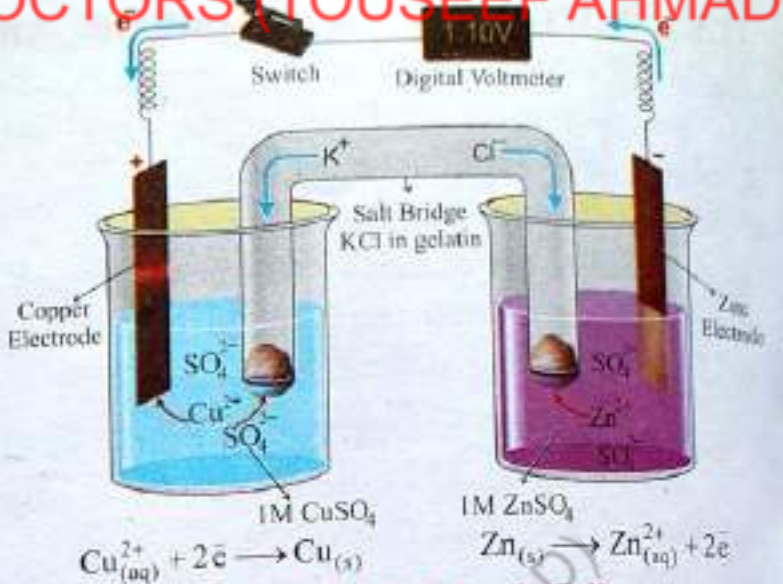

Figure 12.3: Galvanic Cell

Due to flow of electrons from Zn to Cu, the cell produce an electric current and it serves as a source of electricity. Following reactions take place in the cell:

Reaction at anode: $Zn^{0}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2e^{-}$ (Oxidation)

Reaction at cathode: $Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu^{0}_{(s)}$ (Reduction)

Net cell reaction: $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu^{0}_{(s)}$

The net cell reaction involves oxidation and reduction, hence called redox reaction. Conventionally the cell is represented as:

$$Zn^{0}_{(s)} / Zn^{2+}_{(aq)}\,1M \;\;\|\;\; Cu^{2+}_{(aq)}\,1M / Cu^{2+}_{(aq)}$$

anode — salt bridge — cathode

'||' lines indicate salt bridge.

KNO_3, Na_2SO_4

Salt Bridge

A U-shaped tube filled with electrolyte like KCl or $NaNO_3$ in gelatin and sealed at both ends by porous glass wool is called salt bridge.

i) It connects two half cells electrically and it prevents mixing of two electrode solutions.

ii) It maintains the electrical neutrality in each half cell.

iii) It prevents charge accumulation in either solution. In the salt bridge, the ions migrate and carry the charge.

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12.4 Standard Cell Potential and Standard Electrode Potential

12.4.1 Standard Cell Potential

The ability of cell to push electrons through the external circuit is expressed as potential. Electrons moves through the external circuit from anode (high pressure region) to cathode (low pressure region). The pressure of electrons at cathode is kept low by the process of reduction and the pressure of electrons at anode is kept high by the process of oxidation. The driving force that pushes the electrons from the anode and pulls them toward the cathode through the external circuit is an electrical potential, called electromotive force (emf). It is also known as cell voltage or cell potential (E).The cell potential may also be defined as the potential difference between the two electrodes in a voltaic cell. If there is no potential difference between the electrodes of the cell, then the current will not flow. The SI unit of potential difference (voltage) is the volt (V). The cell potential (or voltage) depends upon the nature of electrodes and the ions. It also depends on the concentrations of the ions and the temperature at which the cell is operated. The standard cell potential is the cell potential when both reactants and products are in their standard states. Standard cell potential is symbolized by E°. The superscript degree sign (°) indicates standard state conditions. Standard conditions include 1 M concentrations for solutions, 1atm pressure for gases and usually 25°C temperature for the system. The liquids and solids must be present in their pure forms. The cell potential is measured by voltmeter.

12.4.2 Standard Electrode Potential

Keep in mind

The standard oxidation potential and standard reduction potential values are always equal but opposite in signs.

The difference of potential between an electrode and its salt solution in which the electrode is placed is called electrode potential or single electrode potential or half-cell potential. It may also be defined as:

The tendency of an electrode (substance) to lose or gain electrons when it is in contact with its own ions is called electrode potential. The magnitude of standard electrode potential values depends upon:

i) Nature of electrode and the ions and
ii) Concentration of the solution in which the electrode is placed.
iii) The temperature of the cell.

The potential difference between an electrode and 1M solution of its ions at 25°C (298 K) is called Standard electrode potential.

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12.4.3 Standard Reduction Potential

The standard cell potential is the sum of standard oxidation potential and standard reduction potential.

$$E^{\circ}_{cell} = E^{\circ}_{ox} + E^{\circ}_{red}$$

The potential of an electrode at which reduction occurs is called reduction potential. It is symbolized by E°_{red}. When electrode of copper is placed in a solution of copper ions, then reduction occurs.

$$Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)}$$

Reduction potential of copper is 0.34 V and that of zinc is –0.76 V.

The potential of an electrode at which oxidation occurs is called oxidation potential. It is symbolized by E°_{ox}. When electrode of zinc is placed in a solution of zinc ion, then oxidation occurs.

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^{-}$$

Oxidation potential of zinc is 0.76 V and that of copper is –0.34 V.

Keep In mind

Note that the standard oxidation potential and standard reduction potential values are always equal but opposite in signs.

The reduction potential at their standard states is called standard reduction potential and the oxidation potential at their standard states is called standard oxidation potential.

12.4.4 Measurement of Electrode Potential

There is no method to measure the potential for a single electrode; only the cell potentials can be measured. However it can be measured with reference to some standard electrode such as Standard Hydrogen Electrode (SHE). Standard electrode potential of hydrogen is taken as zero at all temperatures.

Standard Hydrogen Electrode (SHE)

It consists of platinum foil which is coated with finely divided black platinum and encased with a glass sleeve. It is dipped in 1M HCl solution. Pure hydrogen gas at 1atm pressure is bubbled into 1M HCl solution. The hydrogen gas is absorbed on the platinum foil. The platinum acts as a conductor and facilitates the establishment of equilibrium between hydrogen gas and its ions in solution.

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$H_2 \rightleftharpoons 2H^+ + 2e^-$ [Oxidation (SHE acts as anode)]

$2H^+ + 2e^- \rightleftharpoons H_2$ [Reduction (SHE acts as cathode)]

The double arrows show only that the reaction is reversible, but not that there is true equilibrium.

The potential of this electrode is arbitrarily taken as zero at all temperatures. By convention this half-cell is written as oxidation and all other half cell reactions as reductions.

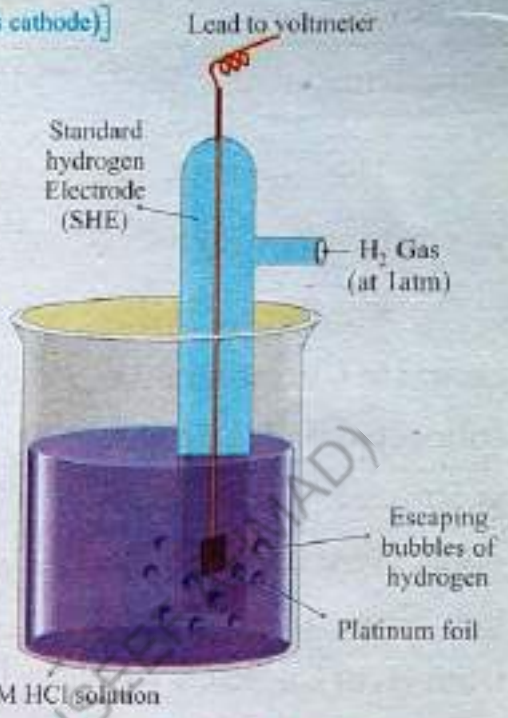

Figure 12.4: Standard Hydrogen Electrode (SHE)

Working with SHE

The electrode whose electrode potential is to be determined is connected with SHE and a galvanic cell is established. The two solutions are separated by a salt bridge. As the potential of SHE is zero, therefore, the voltmeter reading gives electrode potential of the electrode under test. The SHE may act as the anode or cathode depending upon the nature of electrode coupled with it.

To measure the electrode potential of zinc, a galvanic cell is established between zinc electrode dipped in 1M solution of its ions and SHE at 25°C. Zn acts as anode and hydrogen cathode act as inert electrode on which hydrogen gas is bubbled at 1 atmosphere. The electrode potential (E°) value of Zn is −0.76 volts as shown by voltmeter. The cell reactions are:

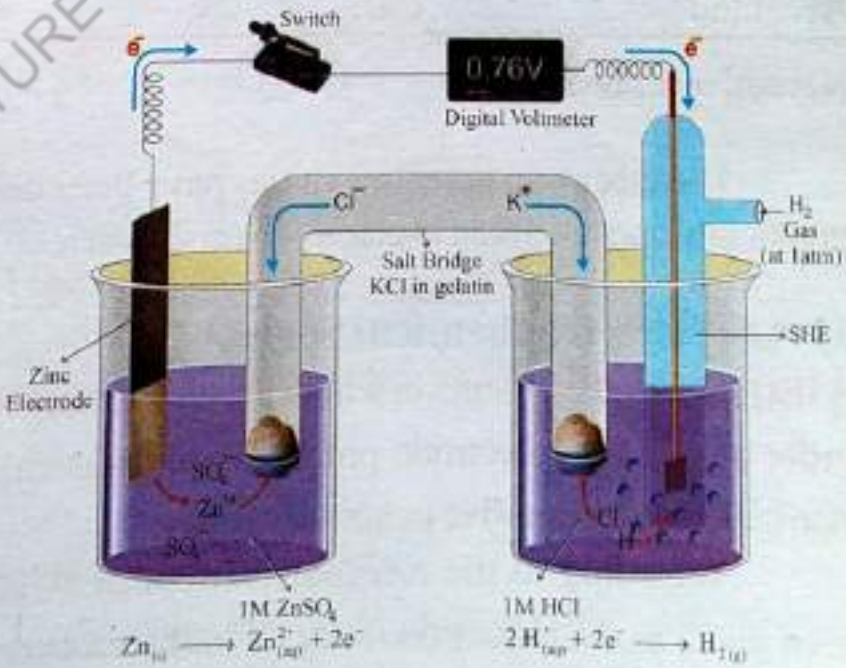

Figure 12.5: Galvanic Cell for measuring the electrode potential of zinc.

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At anode: $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$ (Oxidation)

At cathode: $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$ (Reduction)

Net cell reaction: $Zn^0_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + H_{2(g)}$ (Redox Reaction)

The elements which have negative value of E° have tendency to lose electrons (not to gain electrons).

Similarly when Cu in 1M Cu^{2+} solution is connected with *SHE*, the voltmeter reads 0.34 volts. Here meter shows the flow of electrons from H_2 to Cu, so Cu acts as a cathode. The cell reactions are:

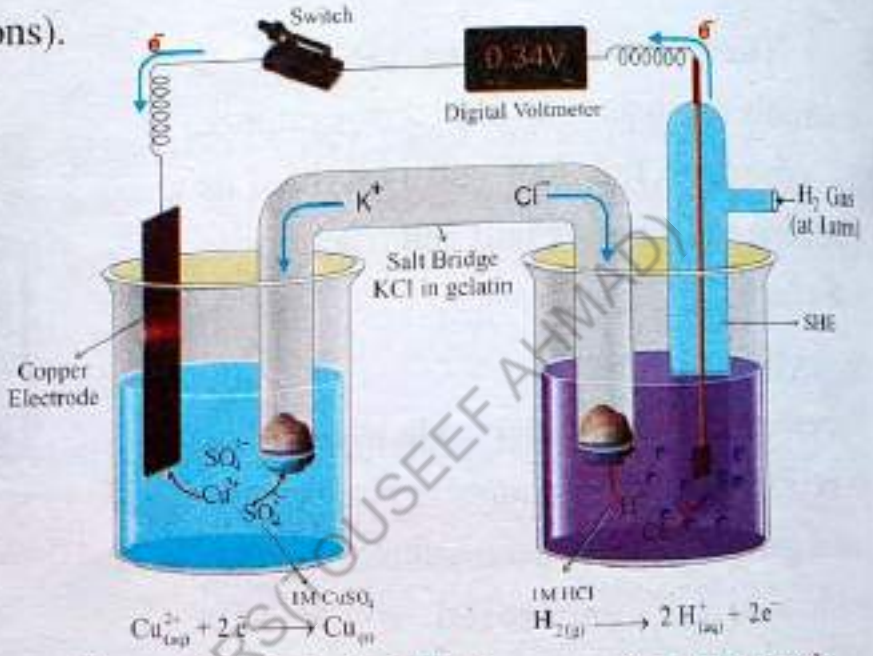

Figure 12.6: Galvanic Cell for measuring the electrode potential of copper.

At anode: $H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^-$ (Oxidation)

At cathode: $Cu^{2+}_{(aq)} + 2\bar{e} \longrightarrow Cu_{(s)}$ (Reduction)

Net cell reaction: $H_{2(g)} + Cu^{2+}_{(aq)} \longrightarrow 2H^+_{(aq)} + Cu^0_{(s)}$ (Redox reaction)

The electrode potential values have been determined for all of the elements practically and are given in electrochemical series.

12.4.5 Electrochemical Series

A list (series) of elements in which they are arranged in the increasing or decreasing order of standard electrode potential values is called electrochemical series. It is also called electromotive or activity series.

According to the recommendation of IUPAC, the electrode potential has been given in the reduction mode. If half -reactions are written in oxidation mode, their potentials are oxidation potentials. By changing mode, magnitude of the potential does not change, only signs are reversed.

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Table 12.1: Standard Reduction Potentials in Water at 25°C

Reduction Half Reaction	E° (V)
$F_{2(g)} + 2e^- \rightleftharpoons 2F^-_{(aq)}$	+2.87
$O_{3(g)} + 2H^+_{(aq)} + 2e^- \rightleftharpoons O_{2(g)} + H_2O$	+2.07
$Co^{3+}_{(aq)} + e^- \rightleftharpoons Co^{2+}_{(aq)}$	+1.82
$Ce^{4+}_{(aq)} + e^- \rightleftharpoons Ce^{3+}_{(aq)}$	+1.61
$Au^{3+}_{(aq)} + 3e^- \rightleftharpoons Au_{(s)}$	+1.50
$Cl_{2(g)} + 2e^- \rightleftharpoons 2Cl^-_{(aq)}$	+1.36
$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightleftharpoons 2H_2O$	+1.23
$Br_{2(l)} + 2e^- \rightleftharpoons 2Br^-_{(aq)}$	+1.07
$2Hg^{2+}_{(aq)} + 2e^- \rightleftharpoons Hg^{2+}_{2(aq)}$	+0.92
$Hg^{2+}_{2(aq)} + 2e^- \rightleftharpoons 2Hg_{(l)}$	+0.85
$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)}$	+0.80
$Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)}$	+0.77
$O_{2(g)} + 2H^+_{(aq)} + 2e^- \rightleftharpoons H_2O_{2(aq)}$	+0.68
$I_{2(s)} + 2e^- \rightleftharpoons 2I^-_{(aq)}$	+0.53
$O_{2(g)} + 2H_2O_{2(aq)} + 4e^- \rightleftharpoons 4OH^-$	+0.40
$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$	+0.34
$Cu^{2+}_{(aq)} + e^- \rightleftharpoons Cu^+_{(aq)}$	+0.15
$Sn^{4+}_{(aq)} + 2e^- \rightleftharpoons Sn^{2+}_{(aq)}$	+1.03
$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}$	0.00
$Pb^{2+} + 2e^- \rightleftharpoons Pb_{(s)}$	−0.13
$Sn^{2+}_{(aq)} + 2e^- \rightleftharpoons Sn_{(s)}$	−0.14
$Ni^{2+}_{(aq)} + 2e^- \rightleftharpoons Ni_{(s)}$	−0.25
$Co^{2+}_{(aq)} + 2e^- \rightleftharpoons Co_{(s)}$	−0.28
$Cd^{2+}_{(aq)} + 2e^- \rightleftharpoons Cd_{(s)}$	−0.40
$Fe^{2+}_{(aq)} + 2e^- \rightleftharpoons Fe_{(s)}$	−0.44
$Cr^{3+}_{(aq)} + 3e^- \rightleftharpoons Cr_{(s)}$	0.74
$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$	−0.76
$2H_2O + 2e^- \rightleftharpoons H_{2(g)} + 2OH^-_{(aq)}$	−0.83
$Mn^{2+}_{(aq)} + 2e^- \rightleftharpoons Mn_{(s)}$	−1.18
$Al^{3+}_{(aq)} + 3e^- \rightleftharpoons Al_{(s)}$	−1.66
$Be^{2+}_{(aq)} + 2e^- \rightleftharpoons Be_{(s)}$	−1.85
$Mg^{2+}_{(aq)} + 2e^- \rightleftharpoons Mg_{(s)}$	−2.37
$Na^+_{(aq)} + e^- \rightleftharpoons Na_{(s)}$	−2.71
$Ca^{2+}_{(aq)} + 2e^- \rightleftharpoons Ca_{(s)}$	−2.87
$Sr^{2+}_{(aq)} + 2e^- \rightleftharpoons Sr_{(s)}$	−2.89
$Ba^{2+}_{(aq)} + 2e^- \rightleftharpoons Ba_{(s)}$	−2.90
$K^+_{(aq)} + e^- \rightleftharpoons K_{(s)}$	−2.93
$Li^+_{(aq)} + e^- \rightleftharpoons Li_{(s)}$	−3.05

Increasing strength as reducing agent / Increasing ease of oxidation

Increasing strength as oxidizing agent / Increasing ease of reduction

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Applications of Electrochemical Series

i) Calculation of the Voltage of Cells

From the series we can calculate the cell voltage (cell potential). The sum of the oxidation potential and reduction potential is called cell voltage.

Mathematically,

$$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$$

Let us find out cell voltage of Cu - Zn (Daniel) cell.

At anode (Oxidation): $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$ $\quad E^\circ_{ox} = +0.76V$

At cathode (Reduction): $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ $\quad E^\circ_{red} = +0.34V$

The voltage of the cell (E°_{cell}) is calculated as:

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$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$

$E^\circ_{cell} = 0.76 + 0.34$

$= 1.10V$

ii) Prediction of the Feasibility of a Chemical Reaction:

From the electrochemical series, we can determine whether the reaction is possible or not. We sum up the voltages of two half reactions, if voltage of the cell is positive, the reaction is possible and if negative, the reaction is not possible. Let us see the reactions:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

From the electrochemical series, we have

$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$	$E^\circ_{ox} = +0.76V$
$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$	$E^\circ_{red} = +0.34V$
$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$	$E^\circ_{cell} = +1.10V$

The voltage is positive, hence the reaction is feasible (possible).

Consider another example:

$$Zn^{2+}_{(aq)} + Cu_{(s)} \longrightarrow Zn_{(s)} + Cu^{2+}_{(aq)}$$

From the electrochemical series, we have:

$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$	$E^\circ_{red} = -0.76V$
$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$	$E^\circ_{ox} = -0.34V$
$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$	$E^\circ_{cell} = -1.10V$

The sum of E° values of the two half-cell reactions is negative, hence the reaction is not feasible (possible).

iii) Comparison of Relative Tendency of Metals and Non-Metals to get Oxidized or Reduced:

Greater the value of standard reduction potential (E°_{red}) of a given specie, greater is its tendency to accept electrons to undergo reduction and hence to act as an oxidizing agent. For example, the ions such as Cu^{2+}, Ag^+, Hg^{++} and non-metals like F_2, Cl_2, and Br_2 act as oxidizing agents. On the other hand, the species having lower value of standard reduction potential (E°_{red}) show greater tendency to lose electrons. They undergo oxidation and hence act as reducing agents. For example, metals lying below SHE such as Zn, Mg, and Li readily lose electrons and act as reducing agents.

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iv) Reaction of Metals with Dilute Acids

Greater the value of E°_{red} of metal, lesser is its tendency to lose electrons to form metal cations and so weaker is its tendency to displace H_2. For example, metals like Cu, Ag and Au which have sufficiently high positive values of E°_{red} do not liberate hydrogen from acids. While metals like Zn, Mg and Ca having low E°_{red}, liberate hydrogen gas when they react with acids.

$$Au + HCl \longrightarrow \text{No Reaction}$$

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$

v) Displacement of One Metal by another from its Solution

From electrochemical series, we can determine whether a given metal will be displaced by another metal or not. A metal will displace another metal from the aqueous solution of its salt that lies below it in the series. For example, Zn will displace Cu.

$$Zn^0_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu^0_{(s)}$$

12.5 Modern Batteries

The cells which are used to produce electric current by chemical change are called batteries.

Batteries are of two types:

Primary and secondary batteries

12.5.1 Primary Batteries

The galvanic cells which cannot be recharged are called *primary cells*. For example, dry cell batteries.

Dry Cell Batteries

Dry cell batteries are used in torch lights, portable radios, toys, calculators, electronic watches etc. They are called dry cells because they do not have a liquid electrolyte. Some important types of dry cells are:

i) Leclanche dry cell
ii) Alkaline battery
iii) Nickel - Cadmium (NiCd) cell

i) Leclanché Dry Cell

The first dry cell was invented by Georges Leclanché (1839 - 1882) in

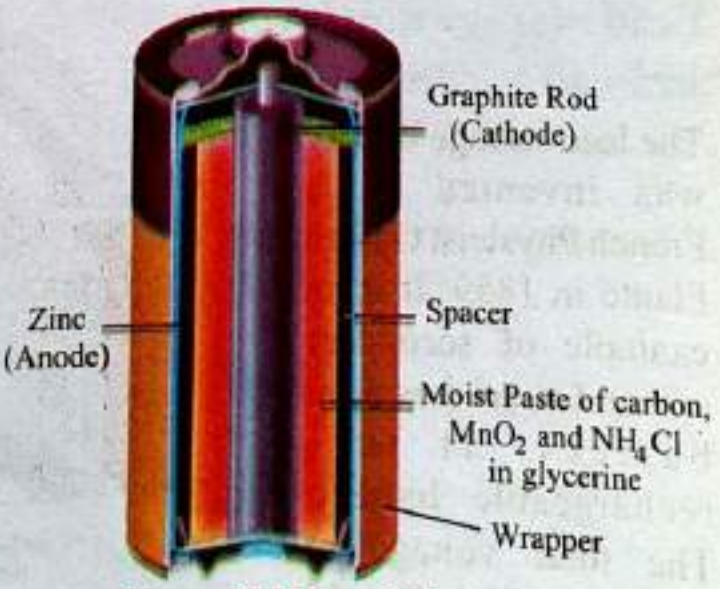

Figure 12.7: Dry Cell

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1866. This dry cell battery has a zinc container which acts as anode and a moist paste of carbon powder, solid MnO_2 and solid NH_4Cl in glycerin around a carbon (graphite) rod which acts as cathode. When both electrodes (zinc container and carbon rod) are connected, electrons are released from zinc and current is produced. The reactions are:

At anode: $Zn \longrightarrow Zn^{2+} + 2e^-$ (Oxidation)

At cathode: $2NH_4^+ + 2MnO_2 + 2e^- \longrightarrow Mn_2O_3 + 2NH_3 + H_2O$ (Reduction)

This cell produces a potential of about 1.5 volts.

ii) Alkaline Battery

Batteries with alkaline electrolyte were first invented by Waldemar Jungner in 1899. This is a type of dry cell. In this cell, zinc acts as anode and MnO_2 acts as cathode. KOH (or NaOH) is used as an electrolyte because of which it is known as alkaline battery. The battery is enclosed in a steel container. The zinc anode is slightly porous giving it a larger effective area. This cell delivers more current and has longer life than a common zinc cell.

The following reactions take place in this cell:

At Anode: $Zn_{(S)} + 2OH^-_{(aq)} \longrightarrow Zn(OH)_{2(S)} + 2e^-$ (Oxidation)

At Cathode: $2MnO_{2(s)} + H_2O_{(l)} + 2e^- \longrightarrow Mn_2O_{3(s)} + 2OH^-_{(aq)}$ (Reduction)

Net Reaction: $Zn_{(s)} + 2MnO_{2(s)} + H_2O_{(l)} \longrightarrow Zn(OH)_{2(s)} + Mn_2O_{3(s)}$

The voltage of this cell is 1.5 volt.

12.5.2 Secondary Batteries

The galvanic cells which can be recharged are called *secondary cells*. Examples are lead storage battery and NiCad battery.

Lead Storage Battery or Lead Accumulator

The lead storage battery was invented by a French Physicist Gaston Planté in 1859. It is an example of secondary cell and is used as a car battery. It is a rechargeable battery. The total voltage of battery is either 6 or 12

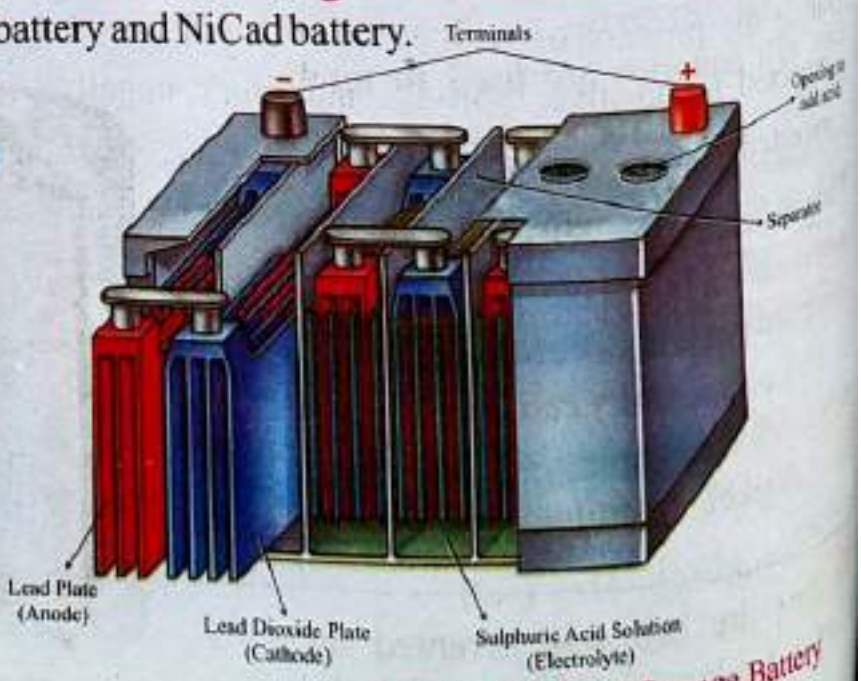

Figure 12.8: Lead Storage Battery

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volts depending upon the number of cells used in its construction. The voltage of each cell is 2 volt. In the lead storage battery, the anodes are made up of lead metal (Pb) and cathodes are made up of lead dioxide (PbO_2). These electrodes are dipped in 30% H_2SO_4 solution (density = $1.25 gcm^{-3}$).

Discharging

At anode, lead atoms lose two electrons each to form Pb^{2+} ions which combine with SO_4^{2-} ions present in the solution to give solid $PbSO_4$. $PbSO_4$ deposits on anode.

At anode: $Pb_{(s)} \longrightarrow Pb^{2+}_{(aq)} + 2e^-$

(Oxidation) $Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)}$

$$Pb_{(s)} + SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)} + 2\bar{e}$$

The electrons released in the reaction pass round an external circuit as an electric current. This electric current is used for starting the engine of vehicle and for lighting up of car lights and so on.

At cathode, the electrons from the anode are accepted by PbO_2 and H^+ ions to produce lead ions and water as:

At cathode: $PbO_{2(s)} + 4H^+_{(aq)} + 2e^- \longrightarrow Pb^{2+}_{(aq)} + 2H_2O_{(l)}$

Reduction: $Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)}$

$$PbO_{2(s)} + 4H^+_{(aq)} + SO^{2-}_{4(aq)} + 2\bar{e} \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)}$$

When both the electrodes are covered with $PbSO_4$ deposits, then the cell is unable to produce any more current until it is recharged.

Recharging

During the process of recharging, the red positive (+) lead of the charger is connected to positive terminal and black negative (–) lead of the charger is connected to negative terminal of the battery. So, the reverse reaction takes place and cell starts recharging. The reactions which occur at electrodes are:

At anode: $PbSO_{4(s)} \longrightarrow Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)}$

$Pb^{2+}_{(aq)} + 2H_2O_{(l)} \longrightarrow PbO_{2(s)} + 4H^+_{(aq)} + 2\bar{e}$

At cathode: $PbSO_{4(s)} \longrightarrow Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)}$

$Pb^{2+}_{(aq)} + 2e^- \longrightarrow Pb_{(s)}$

Net reaction: $PbSO_{4(s)} + 2H_2O_{(l)} \longrightarrow Pb_{(s)} + PbO_{2(s)} + 4H^+_{(aq)} + 2SO^{2-}_{4(aq)}$

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During discharging the density of acid (30% H_2SO_4) falls to 1.15g cm^{-3}. After recharging, the H^+ and SO_4^{2-} ions go back in solution and increase the density of acid again up to 1.25gcm^{-3}. The voltage of each cell returns to around 2 volts. Now this battery is used again.

Nickel Cadmium Cell (Rechargeable)

Nickel cadmium battery was invented by Waldemar Jungner in 1899 of Sweden. Nickel cadmium (or NiCd) cell is an important type of dry cell. It has acquired wide spread use in recent years. In this cell cadmium acts as anode. It undergoes oxidation in an alkaline (basic) electrolyte. The NiO_2 acts as cathode which undergoes reduction.

The reactions are:

At anode: $Cd_{(s)} + 2OH^-_{(aq)} \longrightarrow Cd(OH)_{2(s)} + 2\bar{e}$ (Oxidation)

At cathode: $2NiO_{2(s)} + 2H_2O_{(l)} + 2\bar{e} \longrightarrow Ni(OH)_{2(s)} + 2OH^-_{(aq)}$ (Reduction)

Net reaction: $Cd_{(s)} + NiO_{2(s)} + 2H_2O_{(l)} \longrightarrow Cd(OH)_{2(s)} + Ni(OH)_{2(l)}$

It is a rechargeable battery and is used in mobile phones, electronic calculators, electrical shutters, portable computers etc. It is more expensive than lead storage battery.

12.5.3 Fuel Cells

It is voltaic cell in which gaseous fuel (chemical energy) is converted into electrical energy (electricity).

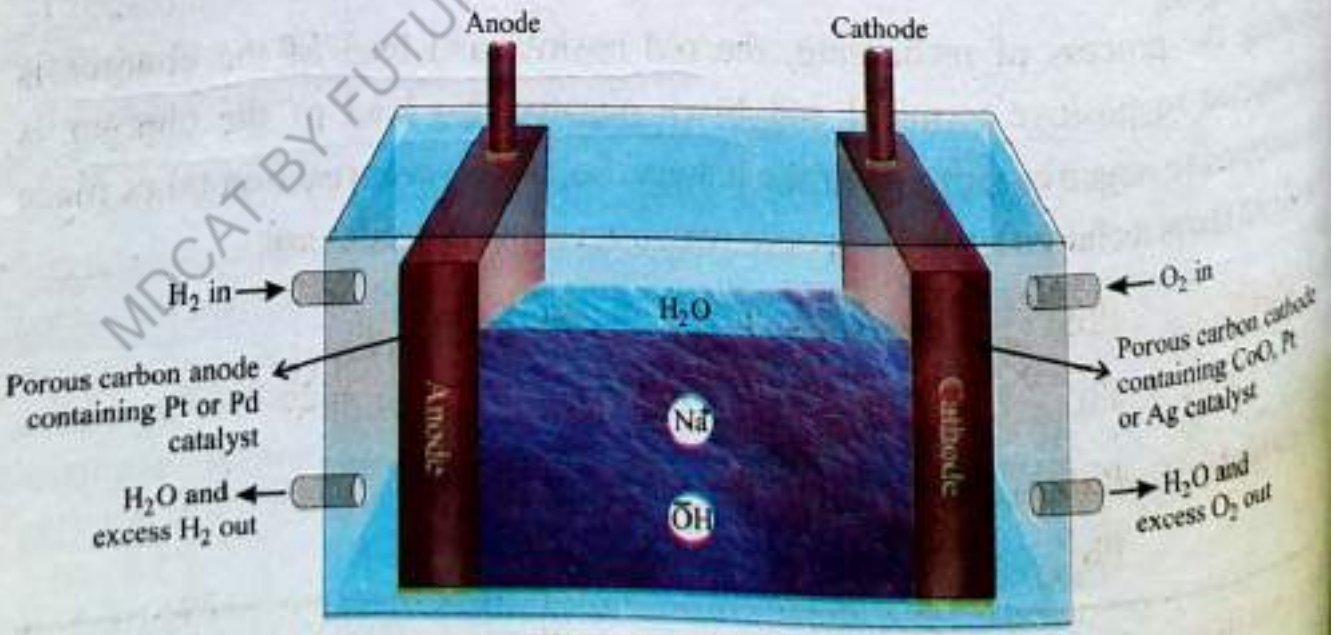

Figure 12.9: Fuel Cell

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In this cell, gaseous fuels such as hydrogen and oxygen are allowed to undergo redox reactions. As a result of this electrical energy is produced.

This cell consists of three compartments separated from each other by porous electrodes. The electrodes are hollow tubes made of porous compressed carbon filled by platinum or palladium catalysts at the anode and cobalt oxide, platinum, or silver catalyst at the cathode.

An electrolyte such as KOH or NaOH is placed in the central compartment. Hydrogen is passed through anode and oxygen through the cathode. These gases diffuse slowly through the electrodes and react with electrolyte at 150°C and at high pressure. Hydrogen is oxidized to water at anode and oxygen is reduced to hydroxide ions at cathode.

The reactions are:

At anode: $2H_{2(g)} + 4OH^-_{(aq)} \longrightarrow 4H_2O_{(l)} + 4\bar{e}$ (Oxidation)

At cathode: $O_{2(g)} + 2H_2O_{(l)} + 4\bar{e} \longrightarrow 4OH^-_{(aq)}$ (Reduction)

Net reaction: $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$ (Redox reaction)

Such cells run continuously as long as reactants are supplied.

A number of cells are connected together to obtain several kilowatts of power.

Advantages of Fuel Cells

i) The fuel cells are very efficient. They convert 75% fuel (i.e. chemical energy) into electricity. The ordinary electricity generator using oil or natural gas has an efficiency of 35-40%, whereas a diesel engine has an efficiency of 25-30%. Rest of the energy is lost as heat.

ii) The fuel cells are free from (noise and thermal) pollution.

iii) The water formed as an end product can be used for drinking purpose for an astronaut in space vehicles.

iv) Oxygen and hydrogen can be continuously supplied to the cell and there is no need for replacement of any electrical energy.

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Solar Cells as the Source of Energy in Future:

Solar cells (also called photovoltaic cells) are electronic devices that convert the solar energy into electricity. Solar energy is the energy obtained from the sun's radiation (sunlight) that is used to generate electricity, to heat or cool homes, or cause chemical reactions. The solar cells are connected together to form a panel. Solar panels

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can be linked to a rechargeable battery that collects energy in the day to be used at any time, even at night when there is no sun. Solar energy is a type of renewable energy; it will never run out. Solar energy is clean and pollution free. Solar panels are extremely reliable, need little maintenance and have a long life. Solar energy can be used in remote areas to generate electricity where it is too difficult to provide much needed electricity by using traditional methods.

If we compare these characteristics to those of fossil fuels such as coal, oil, gas and nuclear power, then we will able to decide which source is better for us. Solar energy is a rapidly growing way to generate electricity.

12.6 Corrosion

The process of chemical decay of metals by an electrochemical process is usually known as corrosion. Corrosion is a spontaneous redox reaction that occurs when metal comes in contact with oxygen in the presence of moisture. The metal is oxidized and converted to an unwanted compound; that is, to an oxide. This is the most common form of corrosion. The corrosion is generally a surface phenomenon.

Corrosion of Iron (Rusting)

The most familiar example of corrosion is the rusting of iron. Rusting of iron needs both oxygen gas and moisture. It does not occur in moisture free air (dry air) and air free water (oxygen-free water). Iron which is a silver white metal is converted to red-brown mass (rust) when comes in contact with moist air. The rust is hydrated iron (III) oxide ($Fe_2O_3.x\ H_2O$ where x varies from 2 to 4, it is not fixed). The iron corrodes (rusts) rapidly when comes in contact with less active metal such as copper and corrodes slowly when comes in contact with a more active metal such as zinc.

When iron comes in contact with moist air, a galvanic cell is produced where one part of iron acts as cathode and other part of iron acts as anode.

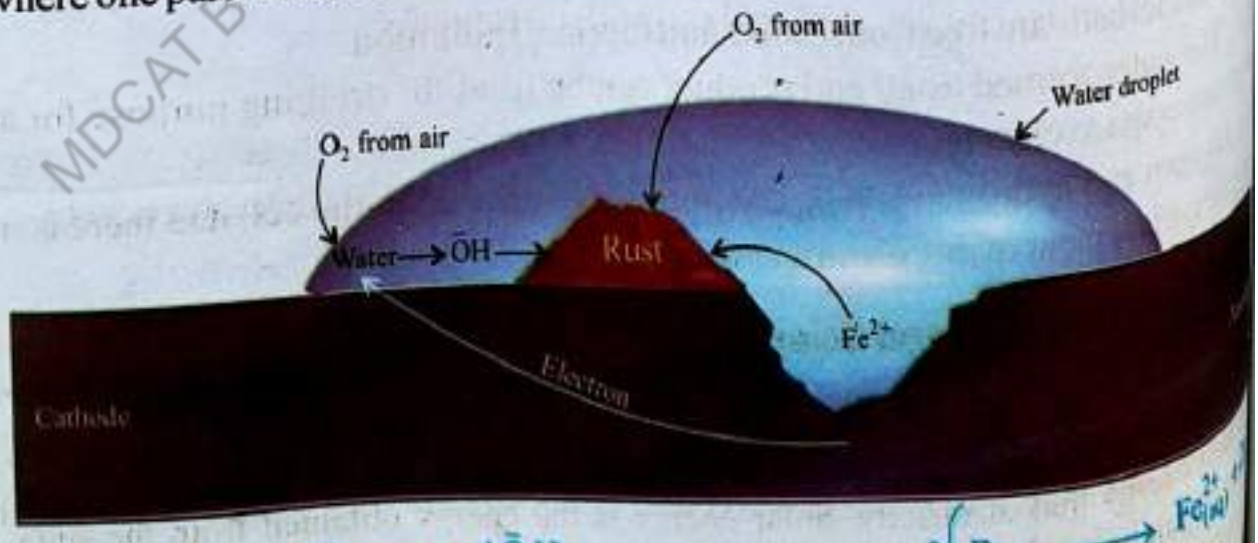

Figure 12.10: Rusting of Iron

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The electrons flow from anode to cathode. The following reactions occur:

At anode: $2Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^-$

At cathode: $2H_2O_{(l)} + O_{2(g)} + 4e^- \longrightarrow 4OH^-_{(aq)}$

Net cell reaction: $2Fe_{(s)} + O_{2(g)} + 2H_2O_{(l)} \longrightarrow 2Fe^{2+}_{(aq)} + 4OH^-_{(aq)}$

The iron (II) ions are further oxidized by oxygen and forms iron (III) ions that react with hydroxide ions to form rust.

$$2Fe^{2+}_{(aq)} + 4OH^-_{(aq)} + \tfrac{1}{2}O_{2(g)} \longrightarrow \underset{\text{(Rust)}}{Fe_2O_3.2H_2O_{(s)}}$$

The overall reaction can also be written as:

$$2Fe_{(s)} + \tfrac{3}{2}O_{2(g)} + x\,H_2O_{(l)} \longrightarrow Fe_2O_3.x\,H_2O_{(s)}$$

Interesting information:

Corrosion of iron forms oxide layer on the surface which protects the iron from further corrosion. The oxide layer on the surface of aluminum also protects it from corrosion. The aluminum has low reduction potential value and is therefore, more reactive than iron and we expect to be corrode readily. But in actual practice, it corrodes slowly. The exceptional stability of aluminum is due to the formation of compact layer of oxide (Al_2O_3), which protects the metal from further corrosion. On the other hand, the oxide layer of iron is permeable and allows oxygen and moisture to penetrate further into the metal and promotes corrosion.

Prevention of Corrosion

The methods that are used to prevent the metal from corrosion are listed below:

Alloying

The corrosion of metal can be prevented or minimized by lowering its reactivity through alloying. For example, stainless steel which is an alloy of iron, chromium, silicon, and nickel is resistant to corrosion. Stainless steel is used for making knives, spoons, forks, utensils, scissors, and surgical instruments.

Oil or Grease Coating

The corrosion of metal can be prevented or minimized by covering the surface of metal with grease or oil. For example, the nuts, bolts, tools, parts of machinery, and parts of engines are coated with grease or oil to protect them from rusting.

Paint Coating

The corrosion of metal can be prevented or minimized by covering the surface of metal with paint. For example, the iron bridges, windows, doors, gates, and the bodies of rickshaws, cars, buses, and trucks are coated with paints to protect them from corrosion (rusting).

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Galvanizing

The process in which sheets of metals (iron) are coated with thin layer of zinc to prevent corrosion is called galvanizing. It is also known as zinc coating or anode coating. This process can be done by dipping a clean sheet of iron into a bath of molten zinc. If zinc coating is damaged by a scratch or a dent, corrosion starts. The standard reduction potential value of zinc is less than iron, so zinc is more easily oxidized and the iron is therefore protected. This method is used to protect underground storage tanks, pipes, oil rigs and ships from rusting. This method is also used to protect dust-bins, drums, and buckets from corrosion (rusting). The metals most frequently used for this purpose are aluminum and magnesium, because these metals are much more reactive than iron and form a compact layer which minimizes their own corrosion.

Electroplating

The process in which a thin layer of one metal is deposited on another metal (object) by means of electrolysis to prevent corrosion is called electroplating.

Electroplating is carried out by using the metal (object) to be plated as a cathode and the metal to be deposited as an anode. The electrolyte is an aqueous solution of salt of the metal being deposited. The electrodes are connected with a battery. When electric current is passed through the solution, the metal to be deposited (anode) is oxidized to its cations and enters into the solution. These cations are reduced and deposited onto the object to be plated (cathode). In this process, a thin layer of metal is deposited onto the object which is then pulled out from the solution. The process of electroplating is used to improve the hardness, stability and appearance of objects and to protect them from corrosion. Some examples of electroplating are tin-plating, chromium-plating, silver-plating, and gold-plating.

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Tin is non-poisonous and is used for plating tiffin-boxes. Chromium is often plated onto a bicycle handle, bars and car bumpers made of iron and steel to protect them from corrosion and give them a shiny appearance. The jewelries, trophies, and medals are commonly silver-plated. Some other common examples of silver-plating are cups, dishes, spoons, and objects made of steel. Silver is a stable metal and does not react with oxygen and vapours of water present in the atmosphere. The silver-plated objects lose luster (chamak) and turn black when kept for a long time in the air due to formation of a thin layer of silver sulphide (Ag_2S) by the action of hydrogen sulphide (H_2S) gas present in the air. Gold is a very stable metal and do not react with water vapours, and gases that are present in the atmosphere. Gold is used for decorative plating. The gold-plated objects do not lose luster and look new for several years.

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Summary of Facts and Concepts

- Electrochemistry is the branch of chemistry in which we study about the interconversion of chemical and electrical energy.
- The reactions in which electrons are transferred from one reactant to another are called oxidation-reduction (or redox) reactions.
- Oxidation is the loss of electrons and reduction is the gain of electrons. Oxidation occurs at anode and reduction occurs at cathode. The electrons flow from anode to cathode.
- Oxidation state (or oxidation number) is defined as the apparent charge, positive or negative, which an atom would have in a compound. An atom may have different oxidation states in different compounds.
- Oxidizing agent is a substance that oxidizes other substances and gets reduced itself in a chemical reaction. Examples of oxidizing agents are non-metals.
- Reducing agent is a substance that reduces other substances and gets oxidized itself in a chemical reaction. Examples of reducing agents are metals.
- The flow of electrons is called electric current or electricity.
- A substance through which electric current can pass is called conductor while a substance through which an electric current cannot pass is called non-conductor or insulator. Metals are conductors while non-metals are insulators.
- Redox reaction is the sum of oxidation-half reaction and reduction-half reaction. Oxidation-half reaction is a half reaction in which a substance loses electrons whereas the reduction-half reaction is a half reaction in which a substance gains electrons.
- Redox potential is a combined term involving oxidation potential and reduction potential. Oxidation potential is the potential of an electrode at which oxidation occurs while reduction potential is the potential of an electrode at which reduction occurs.
- Electrode potential is the difference of potential between an electrode and its salt solution in which the electrode is placed. The potential difference between an electrode and 1M solution of its ions at 25°C is called standard electrode potential.
- Electromotive force is a force that moves the electrons from the anode to the cathode through the external circuit (wire). It is abbreviated by emf.
- The emf of a galvanic cell is called cell potential or cell voltage and is measured in volts. The cell potential under standard conditions is called standard cell potential.
- Electrochemical cells are of two types: galvanic and electrolytic. Chemical energy is converted to electrical energy in galvanic cell while electrical energy

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is converted to chemical energy in electrolytic cell.

- Galvanic (or voltaic) cell is a cell in which electric current is produced by spontaneous redox reaction. Electrolytic cell is a cell in which non-spontaneous redox reaction occurs by the passage of electricity.
- A battery is a galvanic cell or a group of cells connected in a series.
- Corrosion is the process of chemical decay of metals due to action of surrounding medium. The most common example of corrosion is the rusting of iron.
- The corrosions of metals can be reduced or prevented by number of methods but the most important is electroplating.
- Electroplating is an electrolytic process in which a thin layer of one metal is deposited on another metal.

Questions and Problems

Q.1. Four answers are given for each question. Select the correct one:

i) The cell in which electrical energy is converted into chemical energy is:

(a) Electrolytic cell (b) galvanic cell
(c) NiCd cell (d) fuel cell

ii) Which one of the following reactions is **NOT** a redox reaction:

(a) $C + O_2 \longrightarrow CO_2$

(b) $NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$

(c) $ZnSO_4 + Cu \longrightarrow CuSO_4 + Zn$

(d) $2Na + Cl_2 \longrightarrow 2NaCl$

iii) The oxidation state of manganese is +3 in:

(a) MnO (b) MnO_2 (c) Mn_2O_3 (d) Mn_2O_7

iv) In the following reaction, the substance that undergoes reduction is:

$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

(a) H_2O (b) CO_2 (c) $C_6H_{12}O_6$ (d) O_2

v) Which one of the following is the strongest oxidizing agent?

(a) Oxygen (b) chlorine (c) fluorine (d) nitrogen

vi) Which one of the following substances is oxidized in the reaction given below:

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$Mg + 2HCl \longrightarrow MgCl_2 + H_2$

(a) Mg (b) HCl (c) $MgCl_2$ (d) H_2

vii) Which statement is *correct* about the Daniel cell (Zn-Cu cell)?

(a) The Daniel cell is an example of an electrolytic cell.

(b) The spontaneous cell reaction involves the oxidation of Cu by Zn^{2+}

(c) The spontaneous cell reaction involves the reduction of Zn^{2+} to Zn

(d) The spontaneous cell reaction involves the reduction of Cu^{2+} to Cu

viii) The reaction that occurs at cathode is known as:

(a) Redox (b) oxidation

(c) reduction (d) decomposition

ix) Which of the following statement is **NOT** correct for a galvanic cell:

a) Oxidation occurs at anode

b) reduction occurs at cathode

c) both '*a*' and '*b*'

d) electrons flow from cathode to anode

x) Galvanizing is a process in which sheets of metals are coated with thin layer of ..... to prevent corrosion:

(a) Tin (b) zinc (c) copper (d) silver

Q.2. Fill in the blanks with suitable words given in the brackets:

i) A substance through which electric current _____ pass is called conductor. (can/cannot)

ii) The _____ electrode is called anode. (positive/negative)

iii) Spontaneous chemical reactions take place in _____ cell. (electrolytic/galvanic)

iv) Ionic compounds conduct electricity in _____ state. (solid/molten)

v) Oxidation occurs during chemical reaction by _____ of electrons. (gain/loss)

vi) The tendency of an electrode to gain electrons is called reduction potential. (gain/lose)

vii) The cells that can be recharged are called _____ cells. (primary/secondary)

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viii) The oxidation number of chlorine in $KClO_4$ is _____. (-1/+7)

ix) The method of electroplating is used to protect _____ from corrosion. (metal/non-metal)

x) Aluminum is _____ reactive than iron. (less/more)

Q.3. Label the following statments as True or False:

i) Oxidation takes place at anode.

ii) The reduction potential of zinc is 0.34 V.

iii) Oxidizing agent oxidizes other substances.

iv) Fluorine is the strongest oxidizing agent.

v) Half-cell of an active metal acts as cathode.

vi) The element is reduced when its oxidation number is increased.

vii) Fuel cell is the example of voltaic cell.

viii) The moist air is necessary for rusting of iron.

ix) The SI unit of voltage is coulomb.

x) Corrosion is a spontaneous redox reaction.

Q.4: What is electrochemistry? Give its important applications.

Q.5: Is electrochemical process always advantageous?

Q.6: What are redox reactions? Give applications of redox reactions in daily life.

Q.7: Define oxidation number and describe the rules for assigning the oxidation numbers.

Q.8: Calculate the oxidation number of 'S' in the following species:

(i) H_2S (ii) SO_2 (iii) SO_3 (iv) $Na_2S_2O_3$

Q.9: How can you recognize oxidation reduction reactions? Explain briefly.

Q.10: Write down the rules, which are used for balancing of redox equations by oxidation number method and by the half reaction method.

Q.11: Balance the following equations by oxidation number method:

a) $Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$

b) $HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O$

c) $MnO_2 + HCl \longrightarrow MnCl_2 + Cl_2 + H_2O$

d) $NaCl + H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + Cl_2 + H_2O$

Q.12: Balance the following equations by half reaction (ion-electron) method:

a) $Br_2 + NaOH \longrightarrow NaBr + NaBrO_3 + H_2O$

b) $HNO_3 + HI \longrightarrow NO + H_2O + I_2$

c) $Cu + NO_3^{-1} \longrightarrow Cu^{+2} + 2NO_2$

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Q.13: What is meant by the terms oxidizing and reducing agents? Give some important reactions of oxidizing and reducing agents.

Q.14: Define the terms anode and cathode with reference to a specific voltaic cell.

Q.15: What are electrochemical cells? What is the difference between galvanic cell and electrolytic cell?

Q.16: Describe the construction and working of galvanic cell.

Q.17: Describe the electrolysis of aqueous solution of NaCl.

Q.18: Distinguish between electrical terms coulomb, ampere, and volt.

Q.19: Define salt bridge. What is the function of salt bridge?

Q.20: Explain briefly:

a) Standard cell potential.

b) Standard electrode potential.

c) Standard reduction potential.

Q.21: Describe the construction and working of standard hydrogen electrode.

Q.22: What is electrochemical series? Give its important applications.

Q.23: What are dry cells? What are the important types of dry cells? Explain.

Q.24: Write a short note on lead storage battery.

Q.25: What are fuel cells? What are the advantages of fuel cells?

Q.26: Define and explain corrosion. What do you know about the corrosion (rusting) of iron? What are the methods to prevent the metal from corrosion?

Q.27: Answer the following questions briefly:

a) Why is it necessary to use a salt bridge in a galvanic cell?

b) Why is the cathode of a galvanic cell considered to be the positive electrode?

c) Why sodium ion (Na^+) acts as an oxidizing agent whereas sodium atom (Na) acts as a reducing agent?

d) SHE acts as cathode when connected with zinc electrode but acts as anode when connected with copper electrode, why?

e) Zinc displaces hydrogen from acids but copper cannot, why?

f) Why iron doors and bodies of cars are painted routinely?

g) Why damp air is necessary for rusting of iron?

h) Why the bracelets and rings made of gold look new even after several years of use?

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Answers to the Selected Practice Exercises

Chapter No.1

(1) 157.9g (2) 0.1mol
(3) 111g (4) 91mol
(5) 1.505×10^{24} molecules
(6) 6.69×10^{24} molecules
(7) $50.43dm^3$ (8) $25.47dm^3$
(9) 182.5g (10) 7.5mol
(11) 130.37g (12) $700.44dm^3$
(13) % of N in NH_3 = 82.35%, % of N in HNO_3 = 22.22%
(14) e (15) 90.79%

Chapter No.4

(1) (a) 0.355atm (b) 360mbar
(c) 5.22psi
(2) $17.5dm^3$ (3) $26.77cm^3$
(4) 56000mL (5) 44.89atm
(6) 3.99kg (7) $1.89gdm^{-3}$
(8) 101.59atm (9) 1.46

Chapter No.7

(2) 24.24 (3) 0.0024M
(4) 9.33×10^{-10}M (5) 4.56×10^{-8}

Chapter No.8

(1) Acidic, $[H^+] > 10^{-7}$M
(2) Basic, pH > 7
(3) (a) 2.5×10^6 (b) 1.99×10^8
(4) 7.37 (5) 8.4×10^{-6}

Chapter No.9

(1)(a) Rate = $K[NO]^2[O_2]^1$ Third Order
(b) $K = 215mol^{-2}dm^6S^{-1}$

Chapter No.10

(1) 15% (2) 1.5%
(3) 5% (4) 2M
(6) 2m
(7) $X_{C_2H_6O_2} = 0.162$, $X_{H_2O} = 0.838$
(8) 0.004ppm = 4ppb = 4000ppt
(9) $\Delta T_b = 1.65°C$
b.p of aq. Solution = 101.65°C
(10) $152gmol^{-1}$ (11) $92gmol^{-1}$
(12) $\Delta T_f = 3.19°C$
freezing point depression of antifreeze = −3.19°C

Chapter No.11

(1) $\Delta H_n = 1087.8kJmol^{-1}$
(2) $-688.2kJmol^{-1}$

Chapter No.12

(1) (i) +3 (ii) +3

Answers to the Selected Problems

Chapter No.1

(14) 55.8g
(15) (b) 14g of O_2 is required
(c) 49g of CaO is produced
(16) (a) 1.375mol (b) 1.375mol
(17) 240g (18) 56L
(19) 31.25mol (20) 3.97mol
(25) $CO_3^{-2} = 1.505\times10^{24}$ particles
$C_9H_8O_4 = 1.204\times10^{27}$ particles
(26) $V_{SO_2} = 28.02dm^3$
$V_{Ar} = 11.207dm^3$
(28) (i) 50% (ii) 53.33%
(iii) 26.67% (iv) 66.67%
(v) 53.33%
(29) Br_2 is limiting reactant and Mass of HBr 16.02g
(30) 56.16g
(31) Carbon is limiting reactant and mass of SiC is 13.2g
(32) Mass of N_2O = 124.85g
Mass of H_2O = 102.15g
(33) (a) Theoretical yield of Cu = 5.28g
(b) Percentage yield of Cu = 94.7%
(34) 83.34%

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Chapter No.2

(41) $E = 4.05\times10^{-19}$ J

(42) $\nu = 5.26\times10^{14}$ Hz

$E = 3.49\times10^{-19}$ J

$= 1.75\times10^{6}$ m^{-1}

(44) $\Delta E = 1.635\times10^{-18}$ J

(45) $\nu = 4.57\times10^{14}$ Hz,

λ = 656nm

Chapter No.3

(50) Percent ionic character of HF = 41.36%

HF is more ionic than HCl

(51) 6.08D (52) 1.80×10^{-20} C

Chapter No.4

(28) 1.47 psi and 101.325mbar

(29) 110.92 atm (30) 15.2mmHg

(31) 8.15dm^3 (32) 2.83mL

(33) 579.16K (35) 682.56dm^3

(36) 28dm^3 (37) 61.64dm^3

(38) 56.73m^3 (39) 221.47K

(40) 1.81mol (41) 17gmol^{-1}

(42) 128.81gmol^{-1} (44) 760mmHg

(45) 4 psi

(46) $P_{}$ = 0.744atm

$P_{Ne}^{H_2}$ = 0.149atm

P_{Kr} = 0.107 atm

(47) 2.65

(48) $M_x = 44$gmol^{-1}

The unknown gas is CO_2

(49) 15.9gmol^{-1}

Chapter No.7

(5) 2.118×10^{20}

(25) 4.99

(26) 2.08×10^{-3} M (27) 6.87×10^{-3} M

(28) 1.304×10^{-5} M (29) 6.91×10^{-9}

(30) 3.73

Chapter No.8

(17) (a) $[H^+] = 1.58$M

$[OH^-] = 6.33\times10^{-15}$ M

(b) $[OH] = 2.236\times10^{9}$ M

$[H^+] = 4.47\times10^{-24}$ M

(18) $[H^+] = 4.0\times10^{-15}$ M

(20) pOH = 12.2, the solution is acidic

(21) pH = 10.3

(22) $[H^+] = 3.16\times10^{-5}$

$[OH^-] = 3.16\times10^{-10}$

(28) pH = 3.385 (29) $K_a = 2.401\times10^{-10}$

Chapter No.9

(10) (a) Reaction order for CO = First Order

Reaction order for Cl_2 = First Order

Over all order for reaction = Second Order

Rate = $K[CO]^1[Cl_2]^1$

(b) $K = 1.6710^{-6}$ mol^{-1}dm^{3}S^{-1}

Chapter No.10

(40) 22.22% (41) 11%

(42) 5% (43) 0.02m

(45) 0.5M

(46) (a) 0.4m (b) 2.5m

(47) (a) 3M (b) 0.5M

(48) $X_{C_7H_8} = 0.17$ (50) 78.667°C

(51) 74.56gmol^{-1} (52) −1.86°C

Chapter No.11

(22) $\Delta H_n = 133.9$KJmol^{-1}

(23) −1016KJmol^{-1}

Chapter No.12

(8) (i) S = −2 (ii) S = +4

(iii) S = +6 (iv) S = +2

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Index

A

Absolute temperature: 143, 144, 145
Absolute zero: 143, 144, 145
Acid: 279 - 305
Action of the catalyst: 322
Activation energy: 326-327
Activated complex: 325-326
Activator: 330
Active mass: 248
Actual yield: 25
Alkaline earth metals: 231
Allotropy: 222-223
Alloying: 439
Amorphous solids: 218-219
Ampere: 425
Amphoteric substance: 280-281
Amplitude: 48
Anisotropy: 221
Anode: 422
Antifreeze: 343
Aqueous solution: 339
Atomic number: 48-49
Aufbau (or building up) principle: 72
Average rate of reaction: 314
Avogadro's law: 146-148
Avogadro's number: 9
Azimuthal quantum number: 66

B

Balmer series: 59
Barometer: 138
Base: 279-305
Battery: 433-438
Bohr's atomic model: 49
Boiling point: 196
Boiling point elevation: 366
Bomb calorimeter: 400
Bond length (or bond distance): 116
Bond energy (or bond enthalpy): 113
Bond order: 109
Bond pair of electrons: 86
Born-Haber cycle: 403
Boyle's law: 141
Bracket series: 59
Brine: 343
Bronsted-Lowry acid-base concept: 281-282
Buffer capacity: 300-301
Buffer solution: 299-300

C

Calorimetry: 399
Catalysis: 327-332
Catalyst: 327-332
Catalyst for a catalyst: 330
Cathode: 422
Cathode rays: 35-38
Cell: 412
Characteristic of catalyst: 328
Charles law: 143
Chemical adsorption: 330
Chemical energetics: 388
Chemical equilibrium: 245-247
Cleavage plane: 221
Colligative properties: 364
Collision theory: 324-325
Colloids: 341, 375-378
Common ion effect: 270
Completely miscible liquids: 343
Concentrated solution: 339
Concentration of reactant: 323
Concentration of solution: 339
Conjugate acid: 282-284
Conjugate base: 282-284
Continuous phase: 341
Coordinate covalent bond: 298
Corrosion: 438-440
Covalent bond: 85
Covalent solids: 232
Coulomb: 425
Crystal lattice (or space lattice): 224
Crystalline solid: 218
Critical pressure: 168
Critical temperature: 168
Critical volume: 168
Crystal: 224
Cubic system: 225

D

Dalton's law of partial pressure: 159

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Degenerate orbitals: 69
Deviation from ideal gas behaviour: 155-157
Diamagnetic substances: 108
Diffusion of gases: 164-166
Dilute solution: 339
Dipole-dipole forces: 183-184
Dipole moment: 120-125
Discharge tube: 36
Discovery of electron: 36-41
Discovery of neutron: 43-44
Discovery of nucleus: 45-46
Discovery of proton: 41-42
Dissolution: 343
Ductility: 233

E

Effusion of gases: 164-166
Electrochemical cell: 423
Electrochemical series: 430-433
Electrochemistry: 411-440
Electrodes: 422-423
Electrode potential: 427
Electrolysis of aqueous NaCl solution: 423-424
Electrolytic cell: 423
Electrolytic conduction: 423
Electronegativity: 118
Electroplating: 440
Elementary reaction: 315-316
Endothermic reactions: 387-388
Energetic of phase changes: 204-205
Enthalpy: 393
Enzyme: 328, 331, 334
Enzyme catalysis: 331-332
Equilibrium constant, K_c: 249-250
Equilibrium position: 259
Evaporation: 191-193
Exothermic reactions: 387

F

First law of thermodynamics: 391
First order reaction: 317
Freezing point: 369
Freezing point depression: 369
Fuel cells: 436-437

G

Galvanic (or voltaic) cell: 425-426
Galvanizing: 440
Graham's law of diffusion and effusion: 164-166
Ground state and excited state: 58

H

Haber's process: 264-265
Heat: 386-387
Heat capacity: 398-399
Heat of solution (or enthalpy of solution): 347-348
Hess's law of constant heat summation: 402-403
Heterogeneous equilibrium: 247-248
Heterogeneous catalysis: 330-331
Hexagonal system: 226
Homogeneous equilibrium: 247
Homogeneous catalysis: 330
Hund's rule: 73-74
Hybridization: 98-104
Hydration: 126
Hydrogen bonding: 184-188
Hydrophilic molecules: 342
Hydrophobic molecules: 342
Hypertonic solution: 374
Hypotonic solution: 374

I

Ideal gas equation (or general gas equation): 149-151
Ideal solutions: 364
Inert electrodes: 422
Inhibitor: 328
Instantaneous rate of reaction: 314
Inter and intramolecular forces: 182
Internal energy, (E): 390
Ionic bond: 85
Ionic character (or polarity of molecule): 118
Ionic product of water: 285
Irreversible reactions: 244
Isomorphism: 222
Isotonic solution: 374
Isotopes: 44

J

Joule-Thomson effect: 169

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K

K_a and pK_a: 291

K_b and pK_b: 295-296

Kinetic energy: 386

Kinetic molecular theory of gases: 136-137

L

Lattice energy: 229-230

Law of conservation of energy: 391

Law of conservation of mass: 15

Law of definite proportions: 15

Law of mass action: 248-249

Le Chatelier's Principle: 259-265

Levelling effect: 294-295

Lewis acid-base concept: 298

Limiting reagent: 21-22

Lind's method: 169-170

Liquefaction of gases: 167-169

Liquid crystal: 207-209

London dispersion forces: 188-191

Lone pair of electrons: 86

Lyman series: 59

M

Magnetic quantum number: 66-67

Mass number: 44

Mechanism of reaction: 315-316

Metallic bond: 232-233

Metallic solids: 232-233

Molality: 355

Molar heat of fusion: 205

Molar heat of sublimation: 206

Molar heat of vaporization: 205-206

Molarity: 353

Molar mass: 10

Molar volume: 10

Mole: 8-9

Molecular orbital theory (MOT): 104-113

Molecular solids: 236-337

Mole fraction: 356-357

Monoclinic system: 226

N

Nature of the reactant: 323

Non-ideal solution: 364

O

Orbital: 64, 69

Order of reaction: 317

Orthorhombic system: 225

Osmotic pressure: 372-374

Overall reaction: 315-316

Overlapping: 94-96

Oxidation: 412-413

Oxidation number: 413-414

Oxidizing agent: 421-422

P

Paschen series: 59

Paramagnetic substances: 108

Partial pressure: 160

Partially miscible liquids: 343

Parts per billion (ppb): 358

Parts per million (ppm): 358

Parts per trillion (ppt): 359

Pauli Exclusion Principle: 73

Percentage composition: 20-21

Pfund series: 59-60

pH scale: 286-288

Physical adsorption: 330

Pi-bond: 96

Planck's quantum theory: 47

Plasma: 170-172

pOH scale: 286-288

Poison: 329-330

Poisoning of catalyst: 329

Polymorphism: 222

Positive rays: 42

Potential energy: 386

Practically miscible liquids: 344

Pressure: 137-139

Primary batteries: 433-434

Principal quantum number: 65

Promoter: 330

Q

Quantum: 47

Quantum numbers: 64-67

R

Raoult's law: 359-363

Rate determining step or rate limiting step: 316

Rate law or rate expression: 314-315

Reaction intermediate: 316-317

Relative strength of acids and bases: 283-284

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Rate of reaction: 313-314
Reaction quotient: 257-258
Redox reaction: 415-416
Reducing agent: 421-422
Reduction: 412-413
Resonance: 92-93
Reverse osmosis: 375
Reversible reactions: 344
Rutherford's atomic model: 46

S

Salt bridge: 426
Salt hydrolysis: 301-303
Saturated solution: 350
Secondary batteries: 434-436
Second order reaction: 317
Shell (or orbit): 49, 68
Sigma bond: 94-95
Soda water: 339
Solubility: 344-349
Solubility product, K_{sp}: 266-268
Solute: 339
Solvation: 345
Solvent: 339
Spectrum: 77
Spin quantum number: 67
Standard cell potential: 427
Standard electrode potential: 427
Standard enthalphy change: 395
Standard Hydrogen Eletrode (SHE): 428-430
Standard enthalpy (or heat) of atomization: 395
Standard enthalpy (or heat) of combustion: 397
Standard enthalpy (or heat) of formation: 396
Standard enthalpy (or heat) of neutralization: 397-398
Standard enthalpy (or heat) of reaction: 395
Standard reduction potential: 428
Standard temperature and pressure (STP): 173
Stark effect: 61
State function: 390
Strong electrolyte: 270
Subshell: 66, 68
Super saturated solution: 350
Surface area of the reactant: 323-324
Surface tension: 202-204
Surrounding: 389
Suspension: 341, 378
Symmetry: 220
System: 388

T

Temperature of the reactant: 324
Tetragonal system: 225
Theoretical yield: 25
Thermochemical equation: 388
Thermochemistry: 386
Thermodynamics: 388
Third order reaction: 318
Transition state: 325-326
Transition temperature: 223
Triclinic system: 226
Trigonal system: 225

U

Unit cell: 224-225
Universe: 389
Unsaturated solution: 350

V

Valence bond theory (VBT): 94
Van der Waal's equation: 157-159
Vapour pressure: 193-196
Viscosity: 199-202
Volt: 425
Voltaic cell: 425-426
VSEPR theory: 86-92

W

Wavelength: 48
Wave number: 48
Weak electrolytes: 270

X

X-rays: 61-64

Y

yield: 25

Z

Zeeman Effect: 60
Zeroth order reaction: 318

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Table of Metric Units

Quantity	Unit	Symbol
Energy	Calorie	cal
Pressure	Millimeter of mercury	mm Hg
Specific heat	Joule per kilogram degree Celsius	J/kg.°C
Temperature	Degree Celsius	°C
Volume	Litre	L

Table of SI Base Units

Quantity	Unit	Symbol
Length	Metre or Meter	m
Mass	Kilogram	Kg
Time	Second	s
Electric current	Ampere	A
Temperature	Kelvin	K
Amount of substance	Mole	mol
Luminous intensity	Candela	cd

Table of some Important Derived Units

Quantity	Unit	Symbol
Area	Square metre	m^2
Force	Newton	N
Volume	Cubic metre	m^3
Density	Kilogram per cubic metre	kg/m^3
Energy or heat	Joule	J
Pressure	Pascal	Pa
Electric potential	Volt	V
Electric charge	Coulomb	C
Specific heat	Joule per kilogram-kelvin	J/kg.K
Frequency	Hertz	Hz

Table of SI Prefixes

Prefix	Symbol	Meaning	Multiplier	Prefix	Symbol	Meaning	Multiplier
exa	E	Quintillion	10^{18}	deci	d	Tenth	10^{-1}
peta	P	Quadrillion	10^{15}	centi	c	Hundredth	10^{-2}
tera	T	Trillion	10^{12}	milli	m	Thousandth	10^{-3}
giga	G	Billion	10^{9}	micro	μ	Millionth	10^{-6}
mega	M	Million	10^{6}	nano	n	Billionth	10^{-9}
kilo	k	Thousand	10^{3}	pico	p	Trillionth	10^{-12}
hecto	h	Hundred	10^{2}	femto	f	Quadrillionth	10^{-15}
deca	da	Ten	10^{1}	atto	a	Quintillionth	10^{-18}

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Table of Physical Constants

Quantity	Symbol	Value
Acceleration due to gravity	g	$9.80665\ m/s^2$
Atomic mass unit	amu	$1.660539 \times 10^{-24} g$ $1.660539 \times 10^{-27} kg$
Avogadro's number	N_A	6.0221367×10^{23} particles/mol
Bohr radius	a_o	$5.291772949 \times 10^{-11} m$
Charge-to-mass ratio of electron	e/m	$1.75881962 \times 10^{11} C/kg$
Electron or proton charge	e	$1.602176 \times 10^{-19} C$
Faraday's constant	F	$9.6485309 \times 10^{4} C/mol$
General gas constant	R	8.3145 J/(mol.K) 0.082058 dm^3. atm/(mol.K)
Mass of electron	m_e	5.485799×10^{-4} amu $9.109382 \times 10^{-31} kg$
Mass of neutron	m_n	1.008665 amu $1.674927 \times 10^{-27} kg$
Mass of proton	m_p	1.007276 amu $1.672622 \times 10^{-27} kg$
Molar volume	V_m	$22.414 \times 10^{-3} m^3/mol$ 22.414 dm^3/mol
Pi	π	3.1415926536
Planck's constant	h	$6.626069 \times 10^{-34} J.s$
Rydberg constant	R_∞	$3.28984 \times 10^{15} Hz$ $1.09737315685 \times 10^{-7} m^{-1}$ $1.09737315685 \times 10^{-2} nm^{-1}$
Speed of light (m vacuum)	c	$2.99792 \times 10^{8} ms^{-1}$
Vacuum permittivity	ε	$8.85419 \times 10^{-12} J^{-1} C^2 m^{-1}$

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Table of important Conversion Factors

Length (SI unit = meter)

1 kilometer (km)	= 1000 m
	= 0.62137 mile (mi)
1 meter (m)	= 1.0936 yards
	= 39.37 inch (in.)
	= 100 centimeters (cm)
	= 1000 millimeters (mm)
1 inch	= 2.54 centimeters (cm)
1 mile	= 1.609 km = 5280 feet (ft)
1 foot	= 12 in.
	= 30.48 cm
1 yard (yd)	= 36 in.
	= 0.9144 m

Mass (SI unit = kilogram)

1 kilogram (kg)	= 1000 grams (g)
	= 2.2046 pounds (lb)
1 pound	= 0.45359 kg
	= 453.59 g
	= 16 ounces
1 gram	= 1000 milligrams (mg)
	= 6.02×10^{23} amu
1 ton	= 2000 lb
	= 907.185 kg
1 metric ton	= 1000 kg
	= 1.103 tons
	= 2204.62 lb
1 ounce (oz)	= 28.3 g

Volume (SI unit = cubic meter)

1 liter (L)	= 1 decimeter cube (dm^3)
	= 1000 milliliters (mL)
	= 10^{-3} cubic meter (m^3)
	= 1.0567 quarts (qt)
1 gallon (gal)	= 4 qt
	= 8 pints (pt)
	= 3.785 L
	= 128 fluid ounces (liq. oz)
1 quart (qt)	= 2 pt
	= 0.946 L
	= 32 liq. oz
1 fluid ounce	= 29.6 mL
1 milliliter	= 1 centimeter cube (cm^3)
	= 10^{-3} L

Pressure (SI unit = pascal)

1 pascal (Pa)	= N/m^2
	= 1 kg/ms^2
1 atmosphere	= 760 millimeter of mercury (mmHg)
	= 760 torr
	= 76 centimeter of mercury (cmHg)
	= 101325 Pa
	= 101.325 kilopascals (kPa)
	= 14.7 pound per square inch (lb/in^2)
1 bar	= 100000 Pa
	= 0.98692 atmospheres (atm)
1 torr	= 1 mm Hg

Energy (SI unit = joule)

1 joule (J) (Nm)	= 1 Newton meter
	= 1 kg m^2/s^2
	= 0.23901 calorie
	= coulomb volt (CV)
	= 10^7 erg
1 calorie (cal)	= 4.184 J
1 electron volt (eV)	= 96.485 kJ/mol
	= 1.60218×10^{-19} J
1 kilowatt hour (kWh)	= 3600 kJ

Temperature (SI unit : Kevin)

0 kelvin (K) = -273.15°C = -459.67°F

$K = {}^\circ C + 273.15$

${}^\circ C = K - 273.15$

$${}^\circ C = \frac{({}^\circ F - 32)}{1.8}$$

$${}^\circ F = 1.8 \times {}^\circ C + 32$$

Time (SI unit = second)

1 minute (min)	= 60 seconds (s)
1 hour (hr)	= 60 minutes
	= 3600 seconds
1 day (d)	= 24 h
	= 1440 min
	= 86400 s
1 year (yr)	= 365.25 d
	= 8766 hr

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Names, Formulas and Valencies of Some Common Ions

Monovalent positive ions (cations)		Monovalent negative ions (anions)	
Ammonium	NH_4^+	Acetate	$C_2H_3O_2^-$ or CH_3COO^-
Cesium	Cs^+	Bisulphate or Hydrogen sulphate	HSO_4^-
Cuprous or Copper (I)	Cu^+	Bisulphite or Hydrogen sulphite	HSO_3^-
Hydrogen	H^+	Bicarbonate or Hydrogen carbonate	HCO_3^-
Lithium	Li^+	Bromate	BrO_3^-
Silver	Ag^+	Bromide	Br^-
Sodium	Na^+	Chlorate	ClO_3^-
Divalent positive ions		Chloride	Cl^-
Barium	Ba^{2+}	Chlorite	ClO_2^-
Cadmium	Cd^{2+}	Cyanide	CN^-
Calcium	Ca^{2+}	Fluoride	F^-
Chromous or Chromium (II)	Cr^{2+}	Hydride	H^-
Cobaltous or Cobalt (II)	Co^{2+}	Hydroxide	OH^-
Cupric or Copper (II)	Cu^{2+}	Hypochlorite	ClO^-
Cuprous or Copper (I)	Cu_2^{2+}	Iodate	IO_3^-
Ferrous or Iron (II)	Fe^{2+}	Iodide	I^-
Magnesium	Mg^{2+}	Nitrate	NO_3^-
Manganous or Manganese (II)	Mn^{2+}	Nitrite	NO_2^-
Mercuric or Mercury (II)	Hg^{2+}	Perchlorate	ClO_4^-
Mercurous or Mercury (I)	Hg_2^{2+}	Permanganate	MnO_4^-
Plumbous or Lead (II)	Pb^{2+}	Thiocyanate	SCN^-
Strontium	Sr^{2+}	**Divalent negative ions**	
Nickel (II)	Ni^{2+}	Carbonate	CO_3^{2-}
Stannous or Tin (II)	Sn^{2+}	Chromate	CrO_4^{2-}
Zinc	Zn^{2+}	Dichromate	$Cr_2O_7^{2-}$
Trivalent positive ions		Oxalate	$C_2O_4^{2-}$
Aluminum	Al^{3+}	Oxide	O^{2-}
Antimony (III)	Sb^{3+}	Peroxide	O_2^{2-}

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Arsenic (III)	As^{3+}	Silicate	SiO_3^{2-}
Bismuth (III)	Bi^{3+}	Sulphide	S^{2-}
Chromic or Chromium (III)	Cr^{3+}	Sulphate	SO_4^{2-}
Ferric or Iron (III)	Fe^{3+}	Sulphite	SO_3^{2-}
Titanous or Titanium	Ti^{3+}	Thiosulphate	$S_2O_3^{2-}$
Tetravalent positive ions		**Trivalent negative ions**	
Manganic or Manganese (IV)	Mn^{4+}	Arsenate	AsO_4^{3-}
Plumbic or Lead (IV)	Pb^{4+}	Borate	BO_3^{3-}
Stannic or Tin (IV)	Sn^{4+}	Phosphate	PO_4^{3-}
Titanic or Titanium (IV)	Ti^{4+}	Phosphide	P^{3-}
Pentavalent positive ions		Phosphite	PO_3^{3-}
Antimony (V)	Sb^{5+}	**Tetravalent negative ions**	
Arsenic (V)	As^{5+}	Carbide	C^{4-}

Formulas and Molecular Masses of some Common Substances

Substances	Formulas	Molecular Masses (amu)	Substances	Formulas	Molecular Masses (amu)
Chlorine	Cl_2	71	Hydrogen	H_2	2
Bromine	Br_2	160	Oxygen	O_2	32
Iodine	I_2	254	Nitrogen	N_2	28
Hydrogen monoxide	H_2O	18	Sodium chloride	NaCl	58.5
Ammonia	NH_3	17	Sulphuric acid	H_2SO_4	98
Methane	CH_4	16	Sodium hydroxide	NaOH	40
Carbon dioxide	CO_2	44	Magnesium sulphate	$MgSO_4$	120
Carbon monoxide	CO	28	Magnesium carbonate	$MgCO_3$	84
Glucose	$C_6H_{12}O_6$	180	Hydrogen peroxide	H_2O_2	34
Benzene	C_6H_6	78	Potassium iodate	KIO_3	214
Acetylene	C_2H_2	26	Potassium permanganate	$KMnO_4$	158
Potassium iodide	KI	166	Manganese dioxide	MnO_2	87
Cholestrol	$C_{27}H_{46}O$	386	Magnesium sulphide	MgS	56.4
Caffeine	$C_8H_{10}O_2N_4$	194	Copper sulphate	$CuSO_4$	159.6

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Glossary

A

Absolute temperature: A temperature scale on which zero kelvins is the lowest possible temperature.

Absolute zero: The lowest possible temperature, 0K. The temperature at which all molecular motion stops.

Acid: (i) Arrhenius concept: a substance that produces hydrogen ions when dissolved in water (ii) Bronsted-Lowry concept: a proton donor (iii) Lewis concept: an electron pair acceptor.

Acidic solution: A solution which has pH value less than 7 (pH < 7) at 25°C; an aqueous solution in which the concentration of hydrogen ions (H^+) is greater than the concentration of hydroxide ions (OH^-).

Activation energy: The minimum amount of energy to start the chemical reaction.

Active mass: In the early days of chemistry concentration was called active mass.

Actual yield: The amount of product actually obtained from a chemical reaction.

Adhesive force (or adhesion): The forces of attractions between unlike particles; the forces that bind a substance to the surface.

Alkali: A water soluble base such as NaOH.

Alkali metals: The elements in group 1(IA) of the periodic table except hydrogen (lithium, sodium, potassium, rubidium, cesium and francium).

Alkaline earth metals: The elements in group 2(IIA) of the periodic table (beryllium, magnesium, calcium, strontium, barium and radium).

Alkaline solution (also basic solution): A solution which has pH value greater than 7 (pH > 7) at 25°C; an aqueous solution in which the concentration of hydroxide ions (OH^-) is greater than the concentration of hydrogen ions (H^+).

Allotropes: The different crystalline forms of the same element, such as diamond and graphite (allotropes of carbon).

Alloy: A solid solution of two or more different metals, or of metals with one or more non-metals. It has the properties of metals.

Amorphous solids: A solid which has non-repetitive three dimensional arrangements of particles.

Amphoteric: A substance that shows both acidic and basic properties such as water.

Anion: A negatively charged ion.

Anode: The electrode at which oxidation (loss of electrons) occurs.

Antibonding molecular orbital: A molecular orbital, which is of higher energy and lower stability than parent atomic orbitals.

Atom: The smallest particle of an element that can enter into a chemical reaction.

Atomic mass: The average mass of the atoms of an element.

Atomic mass unit (amu): One-twelfth of the mass of carbon-12 atom. ($1\ amu = 1.66 \times 10^{-24}\ g$)

Atomic number (Z): The number of protons in the nucleus of an atom.

Atomic radius: The average distance between centre of nucleus and the outermost electronic shell of an atom.

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Avogadro's law: Equal volumes of all gases contain equal numbers of molecules at the same temperature and pressure.

Avogadro's number (N_A): The number of particles in one of a substance. Its value is equal to 6.02×10^{23}.

B

Balanced equation: A chemical equation in which the numbers of atoms of each element on both sides of the equation are equal.

Barometer: An instrument that is used to measure atmospheric pressure.

Base: (i) Arrhenius concept: a substance that produces hydroxide ions when dissolved in water (ii)Bronsted-Lowry concept: a proton acceptor (iii) Lewis concept: an electron pair donor.

Basic solution: See alkaline solution.

Battery: A galvanic cell or group of galvanic cells that can be used to produce an electric current.

Beta particle ($^{0}_{1}e$): A particle identical in charge and mass to an electron and emitted by radioactive decay.

Binary compounds: Compounds having atoms of two different elements such as HCl and Nh_3.

Boiling point: The temperature at which the vapour pressure of liquid becomes equal to the pressure above the liquid.

Bond energy: The amount of energy required to break the bonds in one mole when the substance is in the gas phase.

Bonding molecular orbital: A molecular orbital, which is of lower energy and greater stability than parent atomic orbitals.

Bond length (or bond distance): The distance between the nuclei of two bonded atoms.

Bond order: Half of the difference between the numbers of electrons in bonding molecular orbitals and antibonding molecular orbitals.

Bond pair of electrons: Shared pair of electrons.

Boyle's law: The volume of a fixed amount of gas is inversely proportional to gas pressure at constant temperature.

Buffer solution: A solution that resists changes in pH when small amounts of a strong acid or strong base are added to it.

C

Calorie (cal): The amount of heat required to raise the temperature of 1 gram of water by 1°C from 14.5°C to 15.5°C; 1 cal = 4.184 J.

Capillary action: The rise of a liquid in a narrow tube as a result of adhesive forces between the liquid and the tube and cohesive forces within the liquid.

Catalysis: The acceleration of a chemical reaction by a catalyst.

Catalyst: A substance that usually increases the rate of a chemical reaction but is not consumed by the reaction.

Cathode: The electrode at which reduction (gain of electrons) occurs.

Cation: A positively charged ion.

Cell potential: The potential (voltage) difference between the anode and the cathode of a galvanic

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cell.

Charles's law: The volume of a fixed amount of gas is directly proportional to absolute temperature at constant pressure.

Chemical equation: The symbolic representation of a chemical reaction.

Chemical equilibrium: The state in which the rate of the forward reaction is exactly equal to the rate of the reverse reaction.

Chemical kinetics: The study of reaction rates and reaction mechanisms.

Chemical reaction: The process in which one or more substances are converted into other substances.

Chemistry: The science of the composition, structure, properties and reactions of matter.

Cohesive force (or cohesion): The forces of attractions between like particles; the forces that bind the molecules of a substance together.

Colligative properties: Physical properties of solutions that depend on the number of solute particles in solution but not on the type of solute particles.

Colloids: A mixture that contains particles that are intermediate in size between those in true solutions and those in suspensions and that are suspended in a solid, liquid, or gas.

Combustion: A chemical reaction in which heat (usually a flame) and light are produced by the burning of a substance in air (or oxygen) such as the burning of match stick.

Common ion effect: The shift in equilibrium position that results by the addition of an ion common to the ions in the equilibrium.

Conjugate acid: An acid formed by the addition of a proton to a base.

Conjugate acid-base pair: An acid and a base that differ only in the presence or absence of a proton.

Conjugate base: A base formed by the loss of a proton from an acid.

Corrosion: The chemical decay of metals when exposed to air or water.

Covalent bond: A bond formed by sharing of electrons between two or more atoms.

Covalent solids: The solids in which atoms are held together by covalent bonds.

Critical pressure: The pressure at which a gas is conyerted to a liquid state at its critical temperature.

Critical temperature: The temperature above which a gas cannot be liquefied no matter how much pressure is applied. The critical temperature increases with an increase in the magnitude of intermolecular forces.

Critical volume: The volume of one mole of a gas at its critical temperature and pressure.

Crystal: A solid that has regular, repetitive three dimensional arrangements of particles; that is, atoms, molecules or ions.

Crystal lattice (or space lattice): A three dimensional array of points representing particles (atoms, ions, or molecules) of a crystalline solid.

Crystalline solid: A solid that consists of crystals.

D

Dalton's law of partial pressure: The total pressure of a mixture of gases is equal to the sum of partial pressures of the gases present in the mixture.

Dehydration: Removal of water from a substance.

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Density: The mass of substance divided by its volume.

Diamagnetic: A substance repelled by a magnet.

Diffusion: The spontaneous mixing of gases and liquids due to random motion of their particles.

Diffusion of gases: The spontaneous mixing of gases due to random motion of their particles.

Dilution: The process by which a more concentrated solution is made less concentrated by adding solvent.

Dipole: A molecule or a part of molecule that has both positively and negatively charged regions; a polar molecule

Dipole-dipole forces: The attractive forces between polar molecules.

Dipole moment: The product of charge and the distance between the charges in a molecule.

Double bond: A covalent bond formed by the sharing of two electrons pairs. It has one sigma and one pi bond.

Ductile: Can be drawn into thin wires.

Ductility: The ability of metals to be drawn into thin wires.

Dynamic equilibrium: The process in which two opposing forces are taking place at the same rate.

E

Effusion of gases: The escape of gas molecules through a tiny hole into a region of lower pressure.

Electric current: The flow of electric charge – for example, the flow of electrons through a wire or ions through a solution.

Electrochemical cell: A cell consisting of two electrodes dipped into an electrolyte in which a chemical reaction either produces or utilizes an electric current.

Electrochemical series: A list in which they are arranged in the increasing or decreasing order of standard electrode potential values.

Electrochemistry: The branch of chemistry which deals with the conversion of electrical energy into chemical energy in electrolytic cells and chemical energy into electrical energy in galvanic or voltaic cells.

Electrode: The anode or cathode in an electrochemical cell.

Electrode potential: The potential difference between an electrode and its salt solution.

Electrolysis: A process in which electrical current is used to produce a non-spontaneous redox reaction, such as the decomposition of water.

Electrolytic cell: A cell in which non-spontaneous redox reaction occurs by the passage of electricity.

Electrolyte: A substance that conducts electric current either in solution or in the molten state.

Electrolytic conduction: The passage of electrical charge by ions.

Electron affinity: The energy change when one mole of electrons is added to one mole of isolated gaseous atoms or ions.

Electronegativity: The measure of the ability of an atom to attract a bond pair of electrons towards itself in a molecule.

Electronic configuration: The arrangement of electrons in the subshells or orbitals of an atom or ion.

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Electroplating: The deposition of a thin layer of one metal on another metal (object) by electrolysis.

Elementary step: One of the individual steps in the mechanism of a reaction.

Empirical formula: The formula that shows the smallest whole number ratio of different atoms in the compound.

Endothermic reactions: A reaction that absorbs heat from surroundings.

Energy: The capacity to do work or transfer heat.

Energy level: The space around nucleus where electrons can move.

Enthalpy (H): The heat content of a system.

Enthalpy change: The energy difference between the initial and final states of system.

Enzyme: A substance consists of proteins and acts as a catalyst to speed up the reactions in plants and animals.

Equilibrium: A state in which two opposing process are occurring at the same time and at the same rate such that the concentrations of reactants and products do not change.

Equilibrium constant, K_c: The ratio, at equilibrium, of the concentrations of products raised to the powers of their coefficients divided by the concentrations of reactants raised to the powers of their coefficients.

Evaporation: The spontaneous conversion of liquid molecules into vapours.

Excited state: The unstable state of an atom or molecule in which at least one of the electrons is in their highest possible energy level.

Exothermic reactions: A reaction that releases heat to surroundings.

F

First law of thermodynamics: Energy can neither be created nor destroyed but can be converted from one form to another.

First order reaction: A reaction whose rate depends on reactant concentration raised to the first power.

Formula mass: The sum of atomic masses of all atoms present in the chemical formula of molecule or formula unit or ion.

Formula unit: The basic unit of ionic compounds.

Freezing point: The temperature at which the solid and liquid phases of a substance coexist in equilibrium.

Frequency: The number of waves passing through a point in one second.

G

Gamma rays: The high energy photon emitted by a nucleus.

Galvanic cell: (also called voltaic cell) a cell in which a spontaneous redox reaction occurs to produce electric current.

Graham's law of diffusion and effusion: The rate of diffusion or effusion of a gas is inversely proportional to the square root of its molecular mass or density at constant temperature and pressure.

Ground state: The stable state of an atom or molecule in which all of the electrons are in their lowest possible energy levels.

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Groups: The vertical columns of elements in the periodic table.

H

Half-reaction: A reaction that represents either an oxidation or reduction process.

Heat: The transfer of energy from a hot object to a cold object because of a difference in their temperatures.

Heat of fusion: The amount of heat required to melt one mole of solid at its melting point.

Heat of sublimation: The amount of heat required to vaporize one mole of solid at a given temperature.

Heat of vaporization: The amount of heat required to vaporize one mole of liquid at its boiling point.

Hess's law: In a multistep reaction, the enthalpy change is the same, whether the reaction occurs in one step or in several steps.

Heterogeneous equilibrium: An equilibrium state in which all the reactants and products are in the same phase.

Homogeneous equilibrium: An equilibrium state in which all the components are in two or more different phases.

Hybrid orbitals: A set of equivalent orbitals that is produced from the combination of two or more non-equivalent orbitals of an atom.

Hybridization: The process of mixing of different types of atomic orbitals to produce a new set of equivalent hybrid orbitals.

Hydration: The process in which water molecules surround and interact with solute molecules or ions.

Hydrogen bonding: The attractive force between hydrogen atom of one molecule and the highly electronegative atom of another molecule.

Hydrophilic: Water-loving. A polar molecule or part of molecule, which is attracted to water molecules. These molecules are soluble in water.

Hydrophobic: Water fearing. A non-polar molecule or part of molecule, which is not attracted to water molecules. These molecules are insoluble in water.

I

Ideal gas: A gas that obeys gas laws completely at all temperatures and pressures.

Ideal solutions: The solutions that obey Raoult's law.

Intermolecular forces: The attractive forces between neighbouring molecules.

Intramolecular forces: The attractive forces between atoms within a molecule.

Internal energy (E): The sum of all kinds of possible energies (kinetic and potential) of all of the particles present in the substance.

Ion: A particle which has either positive or negative charge.

Ionic bond: The force of attraction between oppositely charged ions.

Ionic solids: Solids that are composed of cations and anions joined by ionic bonds.

Ionic compound: A compound that consists of cations and anions such as NaCl.

Ionization: The process of formation of ions.

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Ionization energy: The amount of energy required to remove one mole of electrons from one mole isolated gaseous atoms.

Isotopes: Atoms that have same atomic number but different mass numbers. Isotopes have same number of protons and electrons but different number of neutrons.

J

Joule (J): The SI unit of energy; 4.184 J = 1 cal.

K

Kilocalories: 1000 calories.

Kilojoule: 1000 joules.

Kilopascal (kP_a): 1000 Pascals.

Kinetic energy: The energy of an object (or particle) in motion because of its mass (m) and its velocity (v): $K.E = 1/2mv^2$.

Kinetic molecular theory of gases: A set of postulates used to explain the behaviour of gases.

L

Lattice energy: The amount of energy required to convert one mole of ionic solid into gaseous ions or the amount of energy released when one mole of ionic solid is formed from its isolated oppositely charged gaseous ions.

Levelling effect: Strong acids have the same strength (very close pK_a values) in water and are completely converted into solutions of H_3O^+ ions. This phenomenon is known as levelling effect. Strong bases are likewise leveled in water and are completely converted into solutions of OH^- ions.

Limiting reagent: The reactant that is present in insufficient amount when it is consumed, the reaction stops and no further product is formed.

Liquid crystal: An intermediate state that has both the properties of solids and liquids.

London dispersion forces: The attractive forces between non-polar molecules produced due to temporary dipoles.

Lone pair of electrons: Unshared pair of electrons.

M

Malleable: Can be hammered or rolled into thin sheets.

Malleability: The ability of metals to be hammered or rolled into thin sheets.

Mass: Quantity of matter in a body.

Mass number (A): The total number of protons and neutrons present in the nucleus of an atom.

Matter: Anything that has mass and occupies space.

Metallic bond: The attraction between negatively charged electronic cloud and metal cations.

Metallic solids: The solids in which atoms are held together by metallic bonds.

Metalloids: The elements that have both the properties of metals and non-metals.

Metals: The elements that have luster, conduct heat and electricity, and are malleable and ductile.

Millimeters of mercury (mmHg): Also called torr. A unit of pressure where,
1 atm = 760 mmHg = 760 torr.

Miscible: Two or more liquids that can dissolve into each other in all proportions.

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Molality (m): The number of moles of solute per kilogram of solution.

Molarity (M): The number of moles of solute per liter of solution.

Molar mass: The mass of one mole of a substance.

Molar volume (of a gas): The volume of one mole of a gas at STP.

Mole: The amount of substance that contains same number of particles as there are exactly 12 g of carbon-12. One mole is equal to molar mass in grams of a substance.

Molecular formula: The formula that shows actual number of atoms in one molecule of a substance.

Molecular solids: The solids in which molecules are held together by intermolecular forces.

Molecular mass: The sum of atomic masses of all the atoms present in the molecule.

Mole fraction: The ratio of number of moles of one component of a mixture to the total number of moles of all the components in the mixture. It is denoted by X.

Momentum: The product of mass (m) and velocity (v) of an object.

N

Neutral solution: A solution which has pH value equal to 7(pH=7) at 25°C; an aqueous solution in which the concentration of hydrogen ions (H^+) is equal to the concentration of hydroxide ions (OH^-).

Neutralization reaction: The reaction of an acid with a base to form salt plus water. For example;

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

Non-electrolyte: A substance that does not conduct electric current either in solution or in the molten state.

Non-ideal solution: A solution that does not obey Raoult's law.

Non-metals: The elements that do not have luster, are poor conductors of heat and electricity and are neither malleable nor ductile.

Non-polar bond: A covalent bond between the two atoms in which the electrons are shared equally.

Non-polar molecule: A molecule that does not have a net dipole moment.

Non-volatile: A substance that does not vaporize easily; does not have a measureable vapour pressure.

O

Osmosis: The passage of solvent but not those of solutes, through semipermeable membrane, from a region of lower solute concentration to a region of higher solute concentration.

Osmotic pressure (Π): The pressure that is applied to stop osmosis.

Oxidation: The loss of electrons; the increase in the oxidation state of specie.

Oxidation number: (Also called oxidation state) the apparent charge, positive or negative, which an atom would have in a compound.

Oxidation state: See oxidation number.

Oxidizing agent (oxidant): A substance that accepts electrons from another substance in a redox reaction. It is reduced in the reaction.

P

Paramagnetic substance: A substance that is attracted to a magnetic field; a substance with unpaired electrons.

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Partial pressure: The pressure of each gas in the mixture of gases.

Pascal (P_a): The SI unit of pressure: $1\ P_a = 1\ N/m^2$.

Periods: The horizontal rows of elements in the periodic table.

pH: The negative log of hydrogen ion concentration in base 10. $pH = -\log[H^+]$

Plasma state: The fourth state of matter which has an ionized gas mixture.

Pi (π) bond: A bond formed by side-to-side overlap of two p-orbitals.

pOH: The negative log of hydroxide ion concentration in base 10. $pOH = -\log[OH^-]$

Polar molecule: A molecule that has a net dipole moment.

Positive ion: A cation; an ion that is formed by loss of one or more electrons from an atom or molecule.

Potential energy: The energy of an object due to its relative position.

Pressure: The force per unit area. $P = F/A$

Product: A substance that is formed in a chemical reaction.

Q

Quantum: A packet of energy.

Quantum number: One of four related numbers that specify the shape, energy and orientation of an orbital, or that is related to the spin of an electron.

R

Radioactivity: The process spontaneous emission of radiations from the unstable nuclei of atoms.

Radioactive substance: A substance that emits radiations from the nuclei of its component atoms.

Rate of reaction: The change in the concentration of reactant or product per unit time.

Reactant: A substance that undergoes a reaction.

Real gas: (Also called non-ideal or actual gas) a gas that does not obey gas laws completely at all temperatures and pressures.

Redox reaction: A reaction in which oxidation and reduction occur.

Reducing agent (or reductant): A substance that loses electrons to another substance in a redox reaction. It is oxidized in the reaction.

Reduction: The gain of electrons; the decrease in the oxidation state of specie.

Resonance: The process in which two or more Lewis structures are drawn for a compound or polyatomic ion, which differ only in the arrangement of electrons.

Resonance hybrid: The actual structure of a molecule or a polyatomic ion that can be represented by two or more Lewis structures.

Resonance structures: Two or more Lewis structures, which have same arrangement of atoms but different arrangement of bonding electrons.

Reverse osmosis: The process by which water molecules move under high pressure, greater than osmotic pressure, through a semipermeable membrane from the more concentrated to the less concentrated solution.

Reversible reactions: A reaction that can occur in both forward and reverse directions.

S

Saturated solution: The solution that contains maximum amount of solute at a given temperature. If more solute is added to a saturated solution, it will settle down and will not dissolve.

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Second order reaction: A reaction whose rate depends on reactant concentration raised to the second power or on the concentrations of two different reactants, each raised to the first power.

Shielding effect: (Also called screening effect): The effect when inner shell electrons prevent the attraction of nucleus for the outer most shell electrons.

Sigma (σ) bond: A bond formed by head-to-head overlap of two orbitals.

Single covalent bond: A covalent bond formed by sharing of one electron pair. It has one sigma bond only.

Solubility: The amount of solute dissolved in 100g of solvent to make a saturated solution at a particular temperature.

Solubility product (K_{sp}): The product of the molar concentrations of the ions, each raised to a power equal to the coefficient in the equilibrium equation.

Solute: The component of solution which is in lesser amount; a substance dissolved in a solvent to make a solution. A solution may contain one or more solutes.

Solution: Homogeneous mixture of two or more substances. Solutions are often liquids, but they may also be found in solid or gaseous states.

Solvent: The component of solution which is in larger amount; the component of solution in which the other components (solutes) are dissolved to make a solution.

Specific heat: The amount of heat required to raise the temperature of one gram of any substance by 1°C.

Spontaneous process: The process that occurs by itself without outside assistance.

Standard enthalpy (or heat) of combustion: The enthalpy change when one mole of a substance is completely burnt in excess of oxygen below under standard conditions.

Standard enthalpy (or heat) of formation: The enthalpy change when one mole of a compound is formed from its elements under standard conditions.

Standard enthalpy (or heat) of neutralization: The enthalpy change when one mole of hydrogen ions from an acid react with one mole of hydroxide ions from a base to form one mole of water under standard conditions.

Standard enthalpy (or heat) of solution: The enthalpy change when one mole of a substance is dissolved in so much solvent that further dilution give no enthalpy change under standard conditions.

Standard state: The physical state of a substance at a pressure of 1 atm and a temperature of 25°C (298 K) that is the most stable state.

Standard temperature and pressure (STP): (Also known as standard conditions) A pressure of 1 atm and a temperature of 0°C (273 K).

State function: A quantity whose value depends only on the initial and final states of the system and not on the path followed by the system.

Stoichiometry: The relationships among the amounts of reactants and products involved in a balanced chemical equation.

Strong acid: An acid that is completely ionized in solution.

Strong base: A base that is completely ionized in solution.

Strong electrolyte: A substance (strong acids, strong bases, and most salts) that is completely ionized in the solution. Its aqueous solutions are good conductors of electricity.

Sublimation: The direct conversion of a solid into a vapour without changing into a liquid.

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Substance: A pure matter that has uniform properties. It may be element or compound.
Surface tension (γ): The amount of energy required to stretch or increase the surface of liquid by a unit area.
Surrounding: Everything in the universe that is not part of the system.
System: Anything that is under study, observation or experiment (in the laboratory).

T

Temperature: The measure of average kinetic energy of the particles in an object.
Theoretical yield: (Also known as expected yield or stoichiometric yield). The amount of product calculated from balanced chemical equation.
Thermochemistry: The branch of chemistry that is the study of heat changes of chemical reactions.
Thermodynamics: The study of energy and its transformation.
Third order reaction: A reaction whose rate depends on reactant concentration raised to the third power or to the first power of molar concentration of one reactant and square of the other reactant.
Triple covalent bond: A covalent bond formed by sharing of three electron pairs. It has one sigma and two pi bonds.

U

Unit cell: The basic repeating unit of the arrangement of particles in a crystal.
Unsaturated solution: The solution that contains less amount of solute than that of a saturated solution at a given temperature. It can dissolve further solute on addition.

V

Valence electrons: The outermost shell electrons of an atom.
Valence shell: The outermost shell of an atom.
Van der Waal's equation: A modified equation that is used to calculate the pressure and volume of real gases (non-ideal gases).
Van der Waal's forces: Attractive forces between molecules. The dipole-dipole, dipole-induced dipole, and London dispersion forces are van der Waal's forces. Ion-ion and ion-dipole forces are not van der Waal's forces.
Vapour pressure: The pressure exerted by a vapour in equilibrium with its pure liquid at a given temperature.
Viscosity: The measure of the resistance to flow of a liquid.
Volatile: A substance that vaporize easily; has a measureable vapour pressure.
Voltaic cell: See galvanic cell.
Volume (V): The space occupied by a substance or an object.

W

Weak acid: An acid that is not completely ionized in solution.
Weak base: A base that is not completely ionized in solution.
Weak electrolytes: A substance (weak acids, weak bases, and some salts) that is partly ionized in the solution. Its aqueous solutions are poor conductors of electricity.
Work (w): The energy required to move an object through a given distance against some force.

$$\text{Work} = \text{force} \times \text{distance}$$

X

X-rays: Electromagnetic radiations with wavelengths from about 0.1 nm to about 10 nm.

Y

Yield: The amount of product obtained during a chemical reaction.

Z

Zero-order reaction: A reaction whose rate is independent of the concentration of the reactant.

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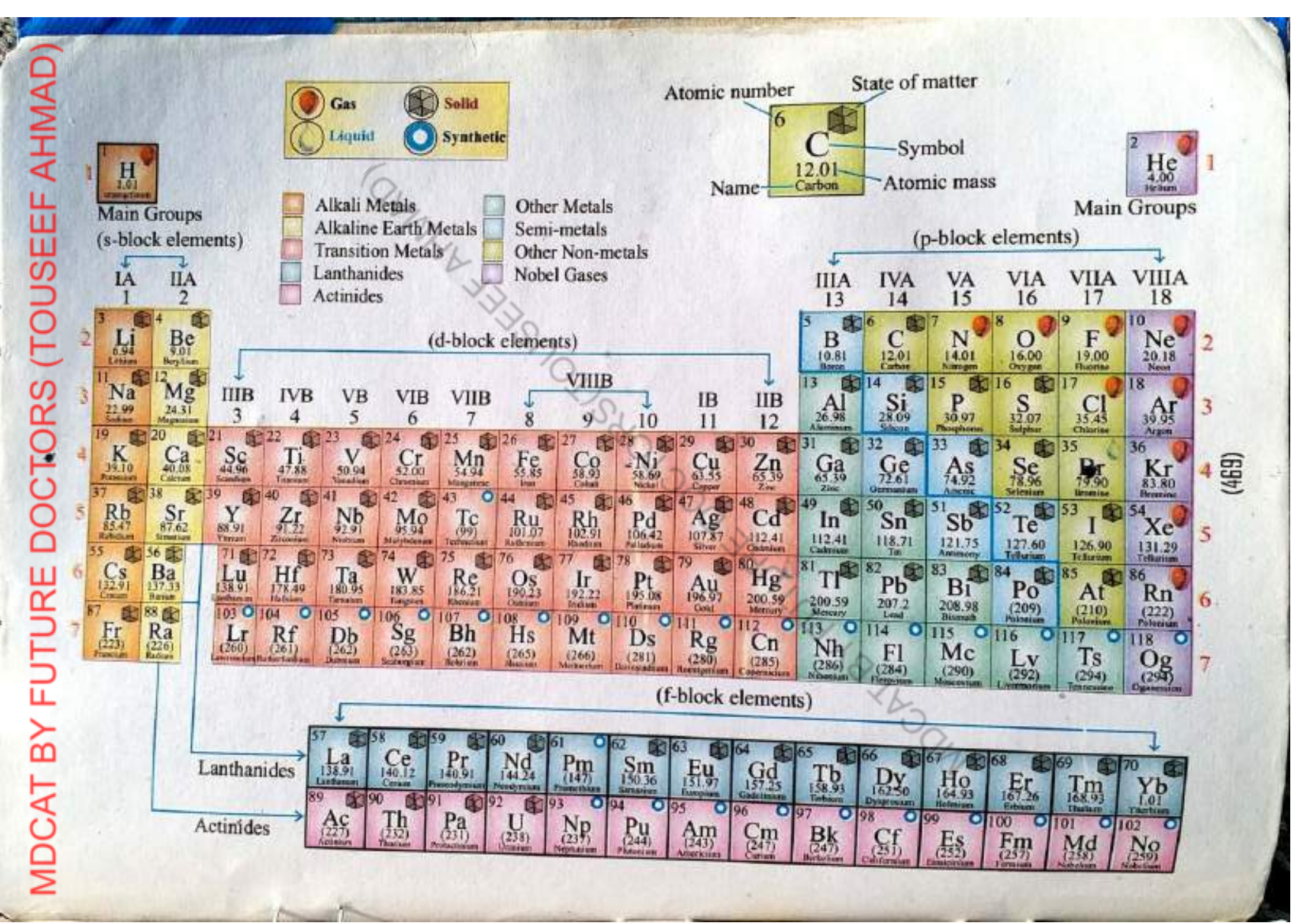

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Developed by New College Publication. According to the National Curriculum. 2005 under the National Textbooks and Learning Materials Policy 2007. N.O.C. No. 337-40/CB Dated: 01/04/2017, Office of the Director Bureau of Curriculum & Extension Centre, Balochistan, Quetta.

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تُرجمانِ ماضی، شانِ حال جانِ اِستقبال
سایۂ خدائے ذُوالجلال

Serial No.

Code No. CHM-XI/432(NP-2007)2017

Year	Edition	Copies	Price
2017	First	15,000	238/-