TEST EDITION

THE TEXTBOOK OF CHEMISTRY

For Class 11

Sindh Textbook Board Jamshoro

Sindh Textbook Board

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PREFACE

The era we are living in, is the era of science and technology wherein chemistry along with its connected disciplines play a pivotal role for the development of society in general and technology in particular, in order to guarantee continuous progress of humankind.

To keep the students abreast of the fundamental knowledge of chemistry in a very enlightened manner, this latest edition of *The Textbook of Chemistry for XI* is being unveiled and is expected to serve for the cause.

This Text Book is the result of countless endeavors put in by the author that fundamentally emphasizes on improving the learning skills of students. The book is designed according to the national curriculum and precisely focuses on the concepts of chemistry in a student-friendly language and a well-organized manner.

At the beginning of each chapter, readers will find study targets of all the fundamental topics involved. The text is presented with numerous illustrations, information tables, the relation of topics with science & technology and their significance in everyday life. Various solved examples along with self-assessment questions have also been included wherever necessary. Also, at the end of each chapter there are several numerical problems, multiple choice and reasoning questions provided to test the learned concepts.

The study material presented in this book covers the subject in accordance with the revised curriculum prepared by the Ministry of Education, Govt of Pakistan, Islamabad and is reviewed by independent team of Bureau of Curriculum, Jamshoro Sindh. Every topic is covered in the same level of detail that is considered prerequisites for the professional studies at undergraduate level.

Last but not the least, I am grateful to the respect worthy authors, reviewers and editors of this text book especially Prof. Dr. Moazzam Haider who contributed to the major part of this book with his untiring efforts. I also admire Director Technical and subject specialists of sindh textbook board for sincerely showing great courage and nobility of purpose.

Chairman
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STOICHIOMETRY

Chapter 1

Teaching Periods	Assessment	Weightage
10	1	8

Students will be able to:

- **Describe** mole and Avogadro's number with examples.
- **Determine** Avogadro's number and describe the relationship between moles and Avogadro's number.
- **Define** rounding off data, exponential notation and their practical applications in solving numericals.
- **Perform** stoichiometric calculations with balanced equations using moles, representative particles, masses and volumes of gases (at STP).
- **Identify** the limiting reactant in a reaction.
- **Know** the limiting reactant in a reaction. Calculate the maximum amount of product(s) produced and the amount of any unreacted excess reactant.
- **Calculate** theoretical yield, actual yield and percent yield from the given information.
- **Calculate** theoretical yield and percent yield by using balance equation.

INTRODUCTION

The spirit of chemistry is recognized in its practical nature. Just imagine how useful it could be to determine the amount of products formed when some known quantities of reactants undergo a chemical change. Think about an automotive engineer studying flue gases: what amount of exhaust gases will be produced due to the combustion of gasoline in an internal combustion engine? Or suppose you are in your kitchen to make 12 cups of delightful coffee with adequate quantity of sugar and milk. You need to calculate the proportion of each ingredient to be added. You won't be able to conceive the answers to these questions without the knowledge of **stoichiometry**.

Stoichiometry (Greek Stoicheion; element, and metron; measurement) deals with the study of quantitative relationship between reactants and products in a chemical reaction by using balanced chemical equation. You know that oxygen gas and hydrogen gas chemically combines to form water but without the knowledge of stoichiometric amounts of hydrogen (H_2) and oxygen (O_2), you cannot estimate how much water (H_2O) will be formed.

Conclusively, stoichiometry tells us what amount of each reacting species we require to consume completely into desired amount of product(s). Although stoichiometry is an important tool for solving diverse problems in laboratory, chemical industries, engineering, food manufacturing, pharmaceuticals and many other fields of science but it is based on the assumption that reactant molecules are completely converted into product. In fact, many chemical reactions are reversible to some extent, further, in some chemical processes side reactions also occur.

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1.1 MOLE AND AVOGADRO'S NUMBER

In routine work, we generally measure things by weighing or by counting with the option based on our comfort. It is more convenient to buy gloves by pairs (two gloves), bananas by dozens (one dozen is equal to 12 bananas) tea sachets by gross (one gross is equal to 144 sachets) and paper by reams (one ream is equal to 500 sheets) but purchasing rice from a grocery shop is convenient by weighing instead of counting.

Similarly, if we prepare a solution or perform a reaction in chemistry laboratory or even in process industry we deal with the enormous numbers of ions, molecules or formula units that mix with one another in specific ratio. Since atom or molecule is so tiny, how can it be possible to count them? To solve this difficulty chemists have devised a unit called as **mole** as a convenient way to count the number particles in chemical substance by weighing them.

Mole (Latin: heap or pile) is the SI unit use for measuring the amount of substance of specific number of particles. **"A mole is defined as gram atomic mass or gram molecular mass or gram formula mass of any substance (atoms, molecules, ions) which contains 6.02×10^{23} particles".** Mole represents the number of chemical entities in a fixed mass.

Conversely, we can say that one mole of any of the substances always contains 6.02×10^{23} particles and known as Avogadro's number (N_A) in the honor of Italian physicist Amedeo Avogadro. **"The number of particles present in one mole of any substance is called Avogadro's number (N_A) and its numerical value is 6.02×10^{23}".**

One mole of any substance always contains 6.02×10^{23} particles and no matter what the chemical nature of a substance is? Thus, one mole of carbon and one mole of magnesium contain same number of atoms but one mole of magnesium has a mass twice (24g) as that of one mole of carbon (12g).

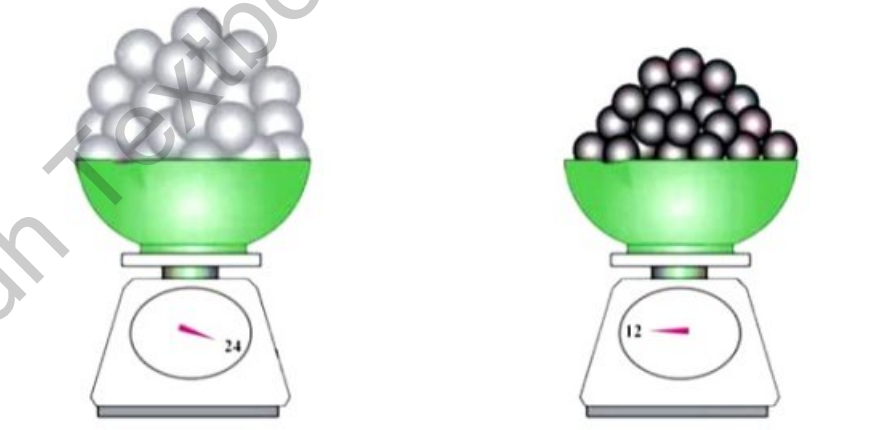

Fig. 1.1: one mole quantities of different substances contains equal number of particles

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While using the term mole for ionic compounds, we consider the number of formula units of that compound. For example one mole of $MgCl_2$ is a quantity which contains 6.02×10^{23} $MgCl_2$ units. However, in each $MgCl_2$ unit there is one Mg^{+2} ion and two Cl^- ions. This indicates that one mole of $MgCl_2$ contains 6.02×10^{23} Mg^{+2} ion and 12.04×10^{23} Cl^- ions.

$$MgCl_2 \rightarrow Mg^{+2} + 2Cl^-$$

Do You Know?

Avogadro's number (6.02×10^{23}) is such a huge value that if the number of atoms of an element is counted by a device at the rate of one million per second, it would take four billion years similarly if there is such number of basketballs it would make entirely a new planet like earth.

Comparing a dozen of bananas and a mole of carbon, it is important to note that bananas vary in mass but all carbon atoms have equal mass. Thus a fruit seller cannot sale one dozen bananas by weighing them however a chemist can deal with 1 mole carbon easily by weighing 12g of carbon. **"The mass in grams of one mole of any pure substance is known as molar mass"**. The unit for molar mass is grams per mole (g/mol).

The basic difference between the mass of one atom and the mass of 1 mole is that the atomic mass of one atom of an element is specified by a.m.u and the mass of one mole of an element is expressed in grams. Thus atomic mass of Fe is 55.85 a.m.u but its molar mass is 55.85 gram. A similar relationship holds for compounds for instance molecular mass of propane (C_3H_8) is 44 a.m.u but its molar mass is taken as 44 grams.

The volume of the given quantity of gas may be different at different temperatures and pressures. Chemists use standard conditions of temperature and pressure for taking the volume of gas. **"The volume of one mole of a gas at standard temperature (273K) and pressure (1 atm) is referred as molar volume"**. Molar volume of all ideal gases at STP is $22.4dm^3$ and can be determined by dividing molar mass with mass density. (molar volume = molar mass /density).

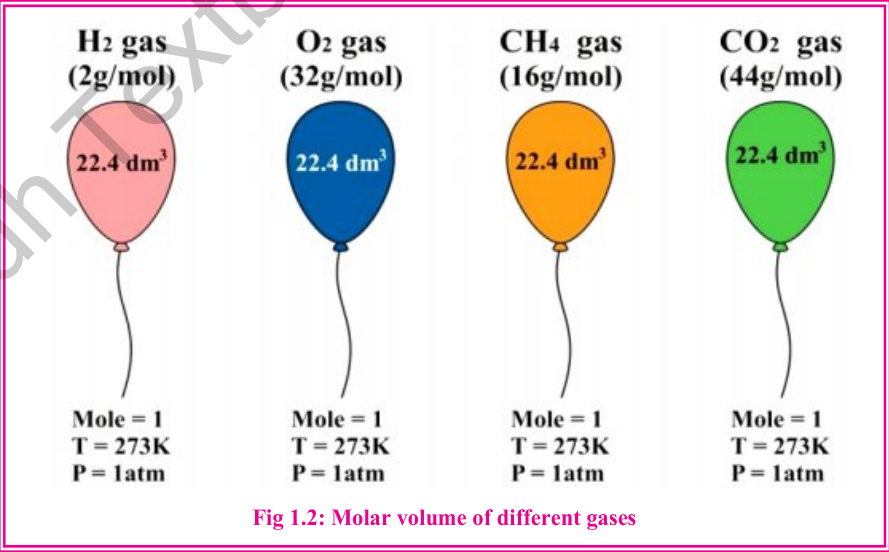

Fig 1.2: Molar volume of different gases

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Table 1.1 Relationship between Mole, Molar mass and Avogadro's Number

Name of substance	Symbol/ Formula	Molar Mass (g/mol)	Kind and number of particles in one mole
Sodium	Na	23.0	6.02×10^{23} Na atoms
Water	H_2O	18.0	6.02×10^{23} H_2O molecules 6.02×10^{23} O atoms $2(6.02 \times 10^{23})$ H atoms
Common Salt	NaCl	58.5	6.02×10^{23} NaCl Formula units 6.02×10^{23} Na^+ ions 6.02×10^{23} Cl^- ions
Calcium Chloride	$CaCl_2$	111	6.02×10^{23} $CaCl_2$ Formula units 6.02×10^{23} Ca^{2+} ions $2(6.02 \times 10^{23})$ Cl^- ions
Ferric Chloride	$FeCl_3$	162.35	6.02×10^{23} $FeCl_3$ Formula units 6.02×10^{23} Fe^{3+} ions $3(6.02 \times 10^{23})$ Cl^- ions

Inter conversion of Mole and Mass

While working on stoichiometric problems, we often need to interconvert mole and mass of reactants and products. For this purpose molar mass is used as conversion factor. To convert given mass of substance into mole, we divide it by molar mass. On the other hand if moles are needed to be converted into mass, we simply multiply it with molar mass. Conclusively, the following formula may be used for the inter conversion of mole and mass.

$$\text{No. of moles} = \frac{\text{Given mass (g)}}{\text{Molar mass of substance}}$$

Example 1.1

Calculate the number of moles in 25.5g of sodium metal.

Data:

Given mass of sodium metal =25.5 g

No. of moles of sodium metal=?

Solution:

Since the molar mass of sodium is 23g/mol, we use this molar mass as conversion factor to determine the number of moles of sodium.

$$\text{Moles of Na} = \frac{\text{Given mass of Na}}{\text{Molar mass of Na}} = \frac{25.5\text{g}}{23\text{g/mol}} = 1.11 \text{ moles}$$

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Example 1.2

Calculate the mass of 3.25 moles of water (H_2O).

Data:

Given No. of moles of water = 3.25

Mass of water (H_2O) = ?

Solution:

To convert mass of water into moles, we use the following relation

$$\text{Moles of water} = \frac{\text{mass of water}}{\text{molar mass of water}}$$

Mass of water = moles of water × molar mass of water

Mass of H_2O = 3.25 × 18 = 58.5g

Inter conversion of Mole and Number of Particles

If we need to convert moles into number of particles or vice versa, Avogadro's number is used as converting factor. This can be expressed in the following way.

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

Example 1.3

Calculate the number of molecules in 610g of Benzoic acid ($C_7H_6O_2$)

Data:

No. of molecules of Benzoic acid ($C_7H_6O_2$) = ?

Given Mass of Benzoic acid ($C_7H_6O_2$) = 610g

Solution:

Since molar mass of benzoic acid is 122 g/mol

122 g benzoic acid ($C_7H_6O_2$) contains = 6.02×10^{23} molecules of benzoic acid

$$1\text{g} \ldots\ldots = \frac{6.02\times10^{23}}{122}$$

$$610\text{g} \ldots\ldots = \frac{6.02\times10^{23}}{122}\times610$$

$$= 30.1 \times 10^{23} \text{ molecules of benzoic acid}$$

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Example 1.4

Calculate the mass of 4.39×10^{24} atoms of Gold(Au), molar mass of gold is 197 g/mol

Data:

Mass of Gold (Au) atoms =?

Given No. of atoms of Gold (Au) = 4.39×10^{24} atoms

Given Molar mass of Gold (Au) = 197 g/mol

Solution:

6.02×10^{23} atoms of Gold (Au) = 197 g of Gold

1 atom ..... $= \frac{197}{6.02 \times 10^{23}}$ g of Gold

4.39×10^{22} ..... $= \frac{197 \times 4.39 \times 10^{22}}{6.02 \times 10^{23}} = 14.365$ g of Gold

Example 1.5

Calculate the number of moles in 2.35×10^{25} atoms of Aluminum (Al).

Data:

No. of moles of Aluminum (Al) atoms = ?

Given No. of atoms of Aluminum (Al) = 2.35×10^{25} atoms

Solution:

Since one mole of any substance contains = 6.02×10^{23} particles.

Hence

6.02×10^{23} atoms of Al = 1 mole of Al

1 atom ..... $= \frac{1}{6.02 \times 10^{23}}$

2.35×10^{25} ..... $= \frac{1}{6.02 \times 10^{23}} \times 2.35 \times 10^{25} = 39$ moles of Al

Self Assessment

Graphite is one of the two crystalline forms of carbon which is a constituent component of lead pencils. How many atoms of carbon are there in 360 g of graphite? Also find the number of moles of carbon.

Inter conversion of Mole and Molar Volume

In certain stoichiometric calculations where gas evolves in the reaction, we are asked to determine the volume of gas released. In this situation we use molar volume as conversion factor.

$$\text{No. of moles} = \frac{\text{Volume of gas occupied at STP}}{\text{Molar Volume}}$$

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Example 1.6

What volume of oxygen gas (O_2) occupied by 1.5 moles at STP.

Data:

Volume of oxygen gas (O_2) = ?

Given No. of Moles of oxygen gas (O_2) at STP = 1.5 moles

Solution:

Since the volume of 1 mole of O_2 at STP is 22.4 dm^3

$$\text{No. of moles } O_2 = \frac{\text{Volume of } O_2}{22.4}$$

Volume of O_2 (STP) = $1.5 \times 22.4 = 33.6\ dm^3$

Calculations based on mass–mass relationship

In these types of problems, we determine the unknown mass of reactant or product from the given mass of substance in a chemical reaction with the help of balanced chemical equation.

Example 1.7

Calculate mass of carbon dioxide (CO_2) that can be obtained by complete thermal decomposition of 50g Lime stone ($CaCO_3$).

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

Data:

Mass of carbon dioxide (CO_2) =?

Given mass of Lime stone ($CaCO_3$) = 50g

Solution:

No. of moles in 50g $CaCO_3$ $= \frac{50}{100} = 0.5$ moles

1 mole of $CaCO_3$ gives ……. = 1 mole of CO_2

0.5 moles …… = 0.5 moles of CO_2

Now, mass of CO_2 …… = moles of CO_2 × molar mass of CO_2

Mass of $CO_2 = 0.5 \times 44$ = 22g

Calculation based on mass–volume relationship

Many chemical reactions are carried out with the production of gas from a solid substance. In this case the measurement of volume is more appropriate than mass. Stoichiometry of this type is known as mass-volume or volume-mass relationship.

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Example 1.8

Mass of 49g of solid potassium chlorate ($KClO_3$) on heating decomposes completely to potassium chloride (KCl) with the liberation of oxygen gas (O_2).

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

Determine volume of oxygen gas (O_2) liberated at STP

Data:

Given mass of potassium chlorate ($KClO_3$) = 49g

Volume of oxygen gas (O_2) =?

Solution:

No. of moles of $KClO_3 = \frac{49}{122.5} = 0.4$ moles

2 moles of $KClO_3$ gives = 3 moles of O_2

1 ..... $= \frac{3}{2}$ moles of O_2

0.4 ..... $= \frac{3}{2} \times 0.4 = 0.6$ moles of O_2

Now the volume of O_2 at STP can be determined by using Avogadro's concept.

Volume of 1 mole of a gas at STP = $22.4dm^3$

Volume of 0.6 mole of a oxygen gas (O_2) at STP = 22.4 x 0.6 dm^3

Volume of O_2 at STP = 13.44 dm^3

Self Assessment

On heating solid ammonium nitrate (NH_4NO_3), it decomposes to produce nitrous oxide (N_2O) and water

$$NH_4NO_{3\,(s)} \rightarrow N_2O_{\,(g)} + 2H_2O_{\,(l)}$$

If 200g of ammonium nitrate is completely consumed in the reaction calculate the:

(i) Mass of water formed (ii) Volume of N_2O gas liberated at STP

Calculations based on volume–volume relationship

In these types of problems, we determine the unknown volume of a reactant or product from the given volume of substance in a chemical reaction with the help of balanced chemical equation.

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Example 1.9

Calculate the volume of carbon dioxide at STP that can be produced by the complete burning of 50 dm^3 of butane gas (C_4H_{10}) in the excess supply of oxygen gas (O_2).

$$2C_4H_{10(g)} + 13O_{2(g)} \xrightarrow{\text{Heat}} 8CO_{2\,(g)} + 10H_2O_{(g)}$$

Data:

Volume of carbon dioxide (CO_2) at STP =?

Given volume of Butane (C_4H_{10}) = 50 dm^3

Solution:

According to balanced chemical equation:

2 dm^3 of butane produces = 8 dm^3 of carbon dioxide

1 dm^3..... $= \frac{8}{2}$

50 dm^3 ..... $= \frac{8}{2} \times 50 = 200\ dm^3$ of CO_2

1.2 ROUNDING OFF DATA

In chemical calculations our result is often consist of too many figures and for convenience we often round off the answer into proper numbers by dropping last digit(s). **"To reduce a number upto desired significant figures and adjust the last reported digit is known as rounding off data"**. The right most digits is generally considered as uncertain therefore, we conveniently drop it and round off the figure into smaller numbers to ensures the maximum removal of errors from the final result.

Generally, numbers are rounded to the nearest ten, hundred, thousand, million and so on.

Do You Know?

The digits in a number which show reliability in measurement are known as significant figures.

- All non-zero digits are significant figures.
- Zeros lying in between non-zero digits are significant figures.
- Zeros locating right after the decimal point in number less than one are not significant.
- Final zeros to the right of the decimal point are significant.
- Zeros that locate before the decimal point in number less then one are not significant.

Rules for rounding off data:

(i) If digit to be dropped is greater than 5, then add 1 to the digit to be retained.

For example: 5.768 is rounded up to 5.77 if three significant figures are needed to be retained.

(ii) If digit to be dropped is less than 5, then simply drop it without changing preceding number.

For example: if 5.734 is rounded up to three significant figures, we get 5.73

(iii) If digit to be dropped is exactly 5, there are two conditions:

* If the digit to be retained is even, then just drop the 5.

For example: when 7.865 is rounded up to three figures we get 7.86

* If the digit to be retained is odd, then add 1 to it

For example: 23.35 is rounded to 23.4

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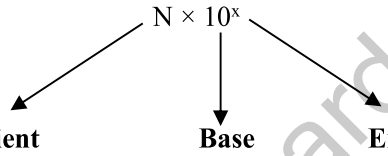
1.3 EXPONENTIAL NOTATIONS

While dealing scientific work we often face difficulties in the calculations of very small or very large numbers. Often we found wrong results due to the mistake in writing digits of too small and too large numbers. These numbers are much more conveniently expressed as multiple of 10.

For example, the mass of electrons is 0.0000000000,0000000000,0000000 911g which is written conveniently as 9.11×10^{-28}g. Similarly value of Avogadro's number is 602,300,000,000,000,000,000,000 which is written in exponential notation as 6.023×10^{23}.

Exponential notation not only helps in the simplification of calculations but also save space and time. Due to convenience, it is frequently used in different fields like engineering, physics, geology, astronomy, etc.

Exponential notation is represented as the product of two numbers $N \times 10^x$.



Where N (coefficient) may be the number between 1 to 9.999…

x (exponent) is an integer raised to base 10. Exponent may be positive or negative.

If the number to be expressed in exponential notation is greater than 1, the exponent is positive integer ($x > 1$) but if it is less than 1 ($x < 1$), the exponent is negative integer.

Inter Converting Standard and scientific notation

In order to tackle various mathematical calculations in chemistry you must aware how to convert standard notation into exponential notation or vice versa.

Consider the following two rules

(i) If we need to convert a numerical value from standard notation to exponential notation, decimal point should move to the left if the value is greater than 10 and move to right if the value is in between 0 to 1.

For example:

- 4600,000 change to 4.6×10^6 (decimal point moves six place to the left)
- 0.00038 change to 3.8×10^{-4} (decimal point moves four place to the right)

(ii) If we want to change an exponential value into standard notation, the decimal point should move to the right for the positive exponent and move to the left for negative exponent.

For example:

- 7.53×10^4 can convert into 75300 (decimal point moves four place to the right)
- 48.7×10^{-5} can convert into 0.000487 (decimal point moves five place to the left)

Applications of exponential notations

(i) Addition and subtraction

Before addition or subtraction, convert all numbers into the same exponents of 10. Then add or subtract the digit terms (coefficients).

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Example 1.10

Add 1.31×10^3 and 3.15×10^2 by using the rule of exponential notation.

Solution:

The value 3.15×10^2 is initially converted into 0.315×10^3 by placing decimal point to the left. Then add the coefficients of both values.

$$\begin{array}{r} 1.31 \times 10^3 \\ +\ 0.315 \times 10^3 \\ \hline 1.625 \times 10^3 \end{array}$$

(ii) Multiplication

Multiply all digit terms (coefficients) and add all exponents algebraically. The final result may be adjusted by placing the decimal to the left or right.

Example 1.11

Multiply 7.0×10^{12} and 2.0×10^{-3} by using the rule of exponential notation.

Solution:

Coefficients 7.0 and 2.0 will be multiplied while exponents 10^{12} and 10^{-3} will be algebraically added.

$$= (7.0)\,(2.0) \times 10^{12-3}$$
$$= 14 \times 10^9$$
$$= 1.4 \times 10^{10}$$

(iii) Division

Divide all digit terms (coefficients) and subtract all exponents algebraically. The final result may be adjusted by placing the decimal to the left or right.

Example 1.12

Divide 6.60×10^8 with 3.20×10^3 by using the rule of exponential notation.

Solution:

Coefficient 6.60 and 3.20 will be divided while exponents 10^8 and 10^3 will be algebraically subtracted.

$$= \frac{6.60 \times 10^8}{3.20 \times 10^3}$$
$$= \frac{6.60 \times 10^{8-3}}{3.20}$$
$$= 2.60 \times 10^5$$

(iv) Powers

Multiply the digit terms as well as exponent with a number which indicates the power. The final result may be adjusted by placing the decimal to the left or right.

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Example 1.13

Simplify $(3.25 \times 10^4)^2$ by using rules of exponential notation.

Solution:

Here digit term is 3.25 and exponent term is 10^4. Both are multiplied by whole power of the figure to get the answer.

$$= (3.25)^2 \times 10^{4x2}$$
$$= 10.56 \times 10^8$$
$$= 1.056 \times 10^9$$

(v) Roots

Adjust the exponent by shifting the decimal to the right or left in digit term in such a way that exponent must exactly be divided by the root. Then simplify the root of digit term and divide the exponent by a desired root.

Example 1.14

Simplify $\sqrt{2.5\times10^7}$ by using rules of exponential notation.

Solution:

Digit term is 2.5. It is adjusted to 25 by placing the decimal to the right.

$$= \sqrt{25\times10^6}$$

Now root of both digit term and exponent can be taken to get the answer.

$$= 5.0 \times 10^3$$

1.4 LIMITING REACTANT AND ITS CALCULATIONS

We know that a sandwich is made of two slices of bread and one shami. Suppose we have 20 slices of bread and 8 shamies. From this quantity we will be able to make only 8 sandwiches. Thus, 4 slices of bread will be left over. The available quantity of shamies limit the number of sandwiches.

The similar situation is occurred in many irreversible chemical reactions where one reactant is often completely used while some amount of other reactant remains unreacted. **"The reactant which is entirely consumed first during chemical reaction is called Limiting reactant or Limiting reagent".**

The reactant that is not completely consumed is often referred as excess reactant. Mathematically, limiting reactant is that which gives least number of moles of product in the chemical reaction because once, one of the reactants is consumed completely, the reaction stops. Consider the formation of water from hydrogen gas (H_2) and oxygen gas (O_2) in the following balance equation.

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

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If we start the reaction by taking 2 moles of hydrogen and 2 mole of oxygen it will be noted that hydrogen is consumed earlier and stops the reaction while O_2 left behind. Thus, H_2 is considered as "Limiting reactant" and O_2 is identified as "excess reactant".

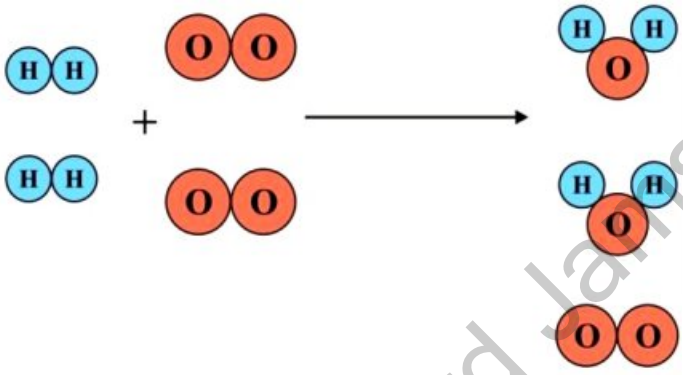

Fig 1.3: Reaction of two moles of H_2 and two moles of O_2 to give H_2O shows that hydrogen is limiting reactant while O_2 is excess reactant.

To find out a limiting reactant in a chemical reaction we must focus on following four steps.
(i) Write a balanced chemical equation of the given chemical process.
(ii) Determine the number of moles of reactants from their given amount.
(iii) Find out the number of moles of product with the help of a balanced chemical equation.
(iv) Identify the reactant which produces the least moles of product as limiting reactant.

Example 1.15

Combustion of Ethene in air to form CO_2 and H_2O is given in the following equation.

$$C_2H_{4(g)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 2H_2O_{(l)}$$

If a mixture containing 2.8g C_2H_4 and 6.4g O_2 is allowed to ignite, identify the Limiting reactant and determine the mass of CO_2 gas will be formed.

Data:

Mass of Ethene (C_2H_4) = 2.8g
Mass of Oxygen gas (O_2) = 6.4g
Mass of carbon dioxide (CO_2) =?
Limiting reactant =?

Solution:

To solve this problem you first convert the given masses of both reactants into their moles.

$$\text{Mole of } C_2H_4 = \frac{2.8}{28} = 0.1$$

$$\text{Mole of } O_2 = \frac{6.4}{32} = 0.2$$

To find out whether C_2H_4 or O_2 consumed earlier, we should go for the following calculations.

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Mole comparison of C_2H_4 and CO_2

According to balanced chemical equation

1 mole of C_2H_4 gives = 2 moles of CO_2

0.1 mole ……. = 0.2 moles of CO_2

Mole comparison of O_2 and CO_2

According to balance chemical equation

3 moles of O_2 gives = 2 moles of CO_2

$1 \ldots\ldots = \frac{2}{3}$ moles of CO_2

$0.2 \ldots\ldots = \frac{2}{3} \times 0.2 = 0.133$ moles of CO_2

Since the number of moles of CO_2 produced by O_2 is less, therefore O_2 is Limiting reactant.

Now: Amount of CO_2 produce will be calculated as

Amount of CO_2 = moles of CO_2 x molar mass of CO_2

Amount of $CO_2 = 0.133 \times 44 = 5.852$g

Example 1.16

When Aluminum is heated with Nitrogen gas at 700 °C, it gives Aluminum nitride.

$$2Al_{(s)} + N_{2(g)} \longrightarrow 2AlN_{(s)}$$

If 67.5 g of Aluminum and 140g of Nitrogen gas are allowed to react, find out the:

(a) Limiting reactant?

(b) Mass of Aluminum nitride (AlN) produced?

(c) Mass of excess reactant?

(Atomic mass of Al is 27 a.m.u and N is 14 a.m.u)

Solution:

We first convert the given amount of reactants into moles.

$$Al = \frac{62.5}{27} = 2.5 \text{ moles}$$

$$N_2 = \frac{140}{28} = 5 \text{ moles}$$

Mole comparison of Al and AlN

According to balanced chemical equation

2 moles of Al gives = 2 moles of AlN

$1 \ldots\ldots = \frac{2}{2}$

$2.5 \ldots\ldots = \frac{2}{2} \times 2.5 = 2.5$ moles

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Mole comparison of N_2 and AlN

1 mole of N_2 gives = 2 moles of AlN

5 moles ..... = 2 × 5 = 10 moles

Since number of moles of AlN produced by Aluminum is less, therefore Limiting reactant is Aluminum

Amount of AlN is calculated by multiplying its moles with molar mass

Mass of AlN = 2.5 × 41 = 102.5g

Now, mass of excess reactant is determined as

2 moles of Al combine with = 1 mole of N_2

1 ..... $= \frac{1}{2}$ mole of N_2

2.5 ..... $= \frac{1}{2} \times 2.5 = 1.25$ moles of N_2

Excess moles of N_2 = 5 – 1.25 = 3.75moles

Excess amount of N_2 = 3.75 × 28 = 105g

Self Assessment

Hydrogen gas is commercially prepared by steam methane process.

$$CH_4 + H_2O \xrightarrow{\text{Heat}} CO + 3H_2$$

If a mixture of 28.8g methane and 14.4g steam is heated in a furnace at elevated temperature to liberate carbon monoxide and hydrogen gases. Determine the Limiting reactant and the mass of hydrogen gas produced.

1.5 THEORITICAL YIELD, PRACTICAL YIELD AND PERCENT YIELD

After getting a proper knowledge about the concept of stoichiometry and Limiting reactant, we now focus on another aspect of calculation in chemical process, this is known as reaction yield. There are three types of yields:

(i) Theoretical yield
(ii) Actual yield
(iii) Percentage yield

The maximum amount of product obtained by a balanced chemical reaction by using its Limiting reactant is known as **Theoretical Yield**.

No matter how much you have expertise in chemical reactions or you use highly efficient techniques; you will lose some amount of product during the course of reaction in laboratory or chemical plant. Thus what we actually obtain is less than what we calculate (theoretical yield). The actual amount of product which is formed in experiment is called **Practical or Actual yield**. This difference between theoretical and practical yield is due to various causes.

(i) Either some amount of reactant may not react
(ii) The reactants may form any side product.

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(iii) There may occur reversible reaction.

(iv) There may loss certain amount of product due to physical processes like distillation, filtration, crystallization and washing etc.

The efficiency of a chemical process is judged by calculating the ratio of practical yield to theoretical yield. This ratio is known as **percent yield**.

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

Example 1.17

The reaction of calcium carbonate ($CaCO_3$) with hydrochloric acid is given as

$$CaCO_{3(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(s)} + CO_{2(g)} + H_2O_{(l)}$$

If during an experiment 50 g of $CaCO_3$ is reacted with excess of hydrochloric acid, 14.52 g of CO_2 gas is liberated, calculate the theoretical and percentage yield of CO_2 gas.

Solution:

We first determine the number of moles of $CaCO_3$

$$\text{Moles of } CaCO_3 = \frac{50}{100} = 0.5 \text{ moles}$$

According to balanced chemical equation

1 mole of $CaCO_3$ gives = 1 mole of CO_2

0.5..... = 0.5 moles of CO_2

Theoretical yield of CO_2 is now determined by multiplying its number of moles with molar mass

Theoretical yield of $CO_2 = 0.5 \times 44 = 22g$

Percentage yield can be determined by using the formula.

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

$$\text{Percentage yield of } CO_2 = \frac{14.52}{22} \times 100 = 66\%$$

Self Assessment

Under high pressure Magnesium (Mg) reacts with oxygen (O_2) to form Magnesium oxide (MgO).

$$2Mg + O_2 \longrightarrow 2MgO$$

If 4 grams of Mg reacts with excess of O_2 to produce 4.24 g of MgO. Calculate the percentage yield of MgO.

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Society, Technology and Science

Limiting Reactants in the preparation of bakery items

Preparing bakery items is a suitable analogy to comprehend the fundamental concept of stoichiometry.

For example, a recipe for making sixteen pancakes required for two cups of pancake powder, one and a half cup of milk, and two eggs. The equation expressing the preparation of sixteen pancakes is

2 cup pancake powder + 1.5 cup milk + 2 eggs → 16 pancakes

If four dozen pancakes are needed for family breakfast when large number of family members gets together, the ingredient quantity must be increased proportionally according to the amounts stated in the recipe. For example, the number of eggs required to make 48 pancakes is (2 eggs / 16 pancakes) × (48 pancakes) = 6 eggs

Activity

This activity is aimed to calculate the number of molecules of a substance in common use. You may take one or two teaspoons of sugar ($C_{12}H_{22}O_{11}$) when you have a cup of tea. Suppose you take 2 teaspoons of sugar, can you estimate the number of sugar molecules that you drink along with the tea?

In order to find out the number of molecules of sugar, first of all weigh the sugar on a digital balance of your kitchen, then find out the number of moles of sugar by dividing the weighed mass by the molar mass of sugar (342 g/mol). Now you can estimate the number of sugar molecules by multiplying the number of moles with Avogadro's number (6.02×10^{23}).

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SUMMARY with Key Terms

- **Stoichiometry** is the study of quantitative relationship between reactants and products in a chemical reaction by using balanced chemical equation.
- **Mole** is the gram atomic mass or gram molecular mass or gram formula mass of any substance (atoms, molecules, ions) which contains 6.02×10^{23} particles.
- **Avogadro's Number** is the number of particles (atoms, ions, molecules) present in one mole of any substance. It is denoted by N_A and its value is 6.02×10^{23}.
- **Molar Volume** is the volume occupied by one mole of any gas at 273K temperature and 1 atmospheric pressure. Molar volume of all ideal gases at STP is $22.4 dm^3$ and can be determined by dividing molar mass with density.
- **Molar Mass** is the mass of one mole of any substance; it is measured in g/mol.
- **Rounding off data** is a method of reducing the figures from the given numerical value. It defines as "to reduce a number to the desired significant figures and adjust the last reported digit".
- **Exponential Notations** is a shorthand mathematical form and written as X^n where x is multiplied itself by n time.
- **Limiting Reactant** is the reactant which is consumed entirely when the chemical reaction is completed is called Limiting reactant or Limiting reagent.
- **Reactant in excess** is the reactant which does not completely consume in the reaction and some of its amount remains unused at the end of reaction.
- **Theoretical yield** is the maximum amount of product obtained by a balanced chemical reaction.
- **Practical yield** is the amount of product formed during the experiment. This amount is usually less than theoretical yield.
- **Percent yield** is the percent ratio of practical yield and theoretical yield.

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EXERCISE

Multiple Choice Questions

1. Choose the correct answer

(i) If the volume occupied by oxygen gas (O_2) at STP is 44.8dm^3, the number of molecules of O_2 in the vessels are:

(a) 3.01×10^{23} (b) 6.02×10^{23}

(c) 12.04×10^{23} (d) 24.08×10^{23}

(ii) The number of carbon atoms in 1 mole of sugar ($C_{12}H_{22}O_{11}$) are approximately:

(a) 6×10^{23} (b) 24×10^{23}

(b) (c) 60×10^{23} (d) 72×10^{23}

(iii) In the reaction $2Na + 2H_2O \rightarrow 2NaOH + H_2$, if 23g of Na reacts with excess of water, the volume of hydrogen gas (H_2) liberated at STP should be:

(a) 11.2dm^3 (b) 22.4dm^3 (c) 33.6dm^3 (d) 44.8dm^3

(iv) Which of the following sample of substances contains the same number of atoms as that of 20g calcium:

(a) 16g S (b) 20g C (c) 19g K (d) 24g Mg

(v) Which of the following statement is incorrect?

(a) The mass of 1 mole Cl_2 gas is 35.5g

(b) One mole of H_2 gas contains 6.02×10^{23} molecules of H_2

(c) Number of atoms in 23g Na and 24g Mg are equal

(d) One moles of O_2 at S.T.P occupy 22.4 dm^3 volume

(vi) For Avogadro's number, this statement is incorrect:

(a) It is the no. of particles in one moles of any substances

(b) Its numerical value is 6.02×10^{23}

(c) Its value change if temperature increases

(d) Its value change if number of moles increases

(vii) The minimum number of moles are present in:

(a) 1 dm^3 of methane gas at STP (b) 5 dm^3 of helium gas at STP

(c) 10 dm^3 of hydrogen gas at STP (d) 22.4 dm^3 of chlorine gas at STP

(viii) Number of atoms in 60g carbon are:

(a) 3.01×10^{23} (b) 3.01×10^{24}

(c) 6.02×10^{23} (d) 6.02×10^{24}

(ix) Maximum number of molecules present in the following sample of gas:

(a) 100g O_2 (b) 100g CH_4

(c) 100g CO_2 (d) 100g Cl_2

(x) Generally actual yield is:

(a) Greater than theoretical yield

(b) Less than theoretical yield

(c) Equal to the theoretical yield

(d) Some times greater and some times less than theoretical yield

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Short Questions

1. Define the following:
   (i) Stoichiometry (ii) Exponential Notation (iii) Molar Volume
2. Express the following numbers in exponential notation:
   (i) 3652 (ii) 0.0231 (iii) 0.000072
3. Express the following in simple numbers.
   (i) 3.26×10^{-3} (ii) 1.921×10^{2} (iii) 1.02×10^{5}
4. Define rounding of data. Give various rules of rounding of data.

Descriptive Questions

1. Define theoretical yield, actual yield and percent yield. Why the practical yield is often less than theoretical yield?
2. What is meant by mole and Avogadro's number? How are they inter related to each other?
3. What is meant by Avogadro's number? Explain concept of mole with the help of Avogadro's number.
4. What is a Limiting reactant? How does it control the amount of product formed in a chemical reaction.

Numerical Questions

1. Calculate the number of moles and molecules in:
   (i) 38g of carbon disulphide (CS_2) (ii) 68.4g of sucrose ($C_{12}H_{22}O_{11}$)
   [Ans: (i) 0.499moles and 3.0×10^{23} molecules (ii) 0.199moles and 1.19×10^{23} molecules]
2. Ammonia gas can be produced by heating together the solid NH_4Cl and $Ca(OH)_2$.
   $$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + 2H_2O$$
   If a mixture containing 100g of each of these solids is heated, determine the limiting reactant and the mass of NH_3 gas produced.
   [Ans: Mass of NH_3 is 31.7g & Limiting reactant is NH_4Cl]
3. Aluminum chloride is used in the manufacturing of rubber. It is produced by allowing Aluminum to react with Cl_2 gas at 650°C.
   $$2Al_{(s)} + 3Cl_{2(g)} \longrightarrow 2AlCl_{3(l)}$$
   When 160g Aluminum reacts with excess of chlorine, 650g of $AlCl_3$ is produced. What is the percentage yield of $AlCl_3$?
   [Ans: 82.17%]
4. 1.6g of a sample of gas occupies a volume of 1.12 dm^3 at STP. Determine the molar mass of the substance.
   [Ans: 32g/mol]

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5. Silver sulphide (Ag_2S) is an anti microbial agent. In an experiment 24.8g Ag_2S is reacted with the excess of hydrochloric acid as given in the following reaction.

$$Ag_2S_{(s)} + 2HCl_{(aq)} \longrightarrow 2AgCl_{(s)} + H_2S_{(g)}$$

Calculate the

(i) Mass of AgCl formed

(ii) Volume of H_2S produced at STP

(At. Mass of Ag is 108 g/mol and S is 32 g/mol)

[Ans: 28.7g and 2.24dm^3]

6. Calculate each of the following quantities.

(i) Number of moles in 6.4g of SO_2.

[Ans: 0.1 mol]

(ii) Mass in gram of 4.5 moles of ethyne (C_2H_2)

[Ans: 117g]

(iv) Volume in cm^3 of 38.4g O_2 gas at STP

[Ans: 26880 cm^3]

(v) Number of molecules of 126g water

[Ans: 42.14×10^{23}]

(vi) Mass in gram of 4.8×10^{24} atoms of sodium

[Ans: 183.39g]

(vi) Number of formula units in 333g of $CaCl_2$

[Ans: 18.06×10^{23}]

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ATOMIC STRUCTURE

Chapter 2

Teaching Periods	Assessment	Weightage
10	1	8

Students will be able to:

- **Describe** properties of sub atomic particles.
- **Summarize** Bohr's atomic theory.
- **Understand** to use Bohr's atomic model for calculating radii of orbit energy, frequency and wave Number of radiations emitted or absorbed by an electron.
- **Describe** spectrum and relate discrete line spectrum of hydrogen to energy levels of electrons in the hydrogen atom.
- **Explain** production, properties, types and uses of X-rays.
- **Explain** the uses of nuclear radiation in health, agricultural etc.
- **Define** photon as a unit of radiation energy.
- **Describe** the concept of orbitals.
- **Explain** the significance of quantized energies of electrons.
- **Distinguish** among principal energy levels, energy sub levels, and atomic orbitals.
- **Describe** the general shapes of s, p, and d orbitals.
- **Describe** the hydrogen atom using the Quantum Theory.
- **Understand** to use the Aufbau Principle, the Pauli Exclusion Principle, and Hund's Rule to write the electronic configuration of the elements.
- **Describe** the orbits of hydrogen atom in order of increasing energy.
- **Explain** the sequence of filling of electrons in atoms.
- **Describe** radioactivity and uses of nuclear radiation in daily life.

INTRODUCTION

In history, first time two Greek philosophers Leucippus and Democritus (440 B.C) gave the idea that matter is composed of invisible, indivisible and infinite number of building blocks called atomos (Greek a ; non, tom ; break). This ancient theory of atom was based on philosophical reasoning rather than scientific basis. They said that different atoms and their different combinations produce different types of matters (solids, liquids and gases). Most philosophers of that time did not give weightage to their concepts about matter and composition but favoured the Aristotelian concept that "Matter is composed of four elements- earth, water, air and fire".

The idea of atom was revisited and studied upon many scientist and philosophers, however it was John Dalton (1803) who recognized as the introducer of modern atomic theory.

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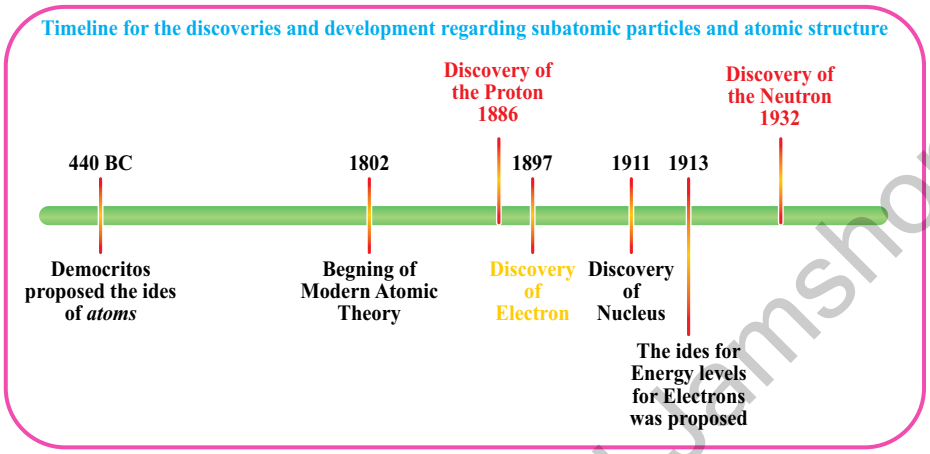

After 12 years of discovery of electron as a fundamental entity that dwell in an atom, Robert Andrews Millikan, in 1909 performed an ingenious oil drop experiment with charged oil drop getting suspended in electric field having its weight balanced by the electrostatic force, he found out that the charge on every oil drop was an integral multiple of 1.6×10^{-19} Coulomb which encouraged him to deduce that this must be the charge of Thomson's electrons.

In 1911, Ernest Rutherford laid the foundation that the atom consists of an extremely charged region which he called nucleus wherein the most of the mass of an atom is concentrated while electrons revolve in the extra-nuclear part.

By 1920, scientists knew and believed that most of the mass of atom was located in the central nuclear core and in 1932, English chemist James Chadwick informed the world about the third subatomic particle that was neutral and a part of nucleus which he named neutron.

2.1 SUBATOMIC PARTICLES AND THEIR CHARACTERISTICS

More than hundred subatomic particles have been discovered in an atom such as electron, proton, neutron, positron, mesons, hyperons, neutrino antineutrino etc, however, only electron, proton and neutron are considered to be the fundamental particles of an atom which play an important role for the determination of physical and chemical properties of elements. Almost all of the mass of an atom exists in nucleus and nucleus was discovered by Rutherford in (1911 A.D). Except protium (isotope of hydrogen), nuclei of all other atoms contain neutrons.

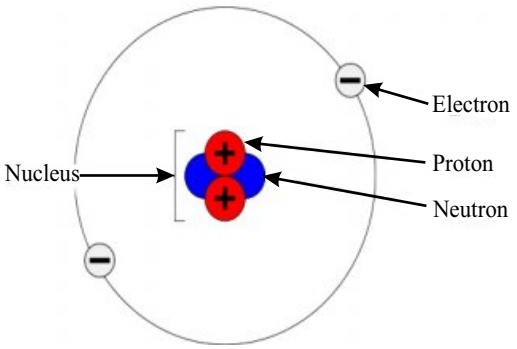

Fig 2.1: Electrons, protons and neutrons of Helium atom

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Electrons:

The subatomic particle electron was discovered by J.J. Thomson in 1897 A.D, while studying on cathode rays experiment. He called the cathode rays beam as electrons Thereafter, Millikan with his "Oil Drop Experiment" calculated the charge on an electron.

Electrons revolve in orbits and occupy about 100,000 times greater volume than nucleus but form less than one percent total mass of an atom. They carry negative charge whose magnitude is equal to positive charge of protons. Electrons are attracted by protons and this attractive force (electrostatic force) keeps electrons constantly moving around nucleus. The mass of electron is nearly 1836 times less than proton and 1839 times less than neutron.

J.J Thomson (1897 A.D)

Electronic configuration refers to the presence of electrons in various shells and sub-shells. This arrangement of electrons affects the atomic stability, melting points, boiling points, density etc. They are also involved in chemical bond formation.

Protons:

Protons are positively charged subatomic particles which are located in the nuclei of all elements. They were discovered by Goldstein (1886 A.D), a German Physicist, by using perforated cathode in Crook's discharge tube. He observed that positive ions were formed when cathode rays hit the gaseous atoms in discharge tube. Rutherford called these positively charged particles as 'PROTONS'. With respect to mass and charge, the protons of all elements are identical to each other. Atomic number of elements is related only to protons while mass number is the sum of protons and neutrons (About 99.94% mass of an atom exists in nucleus). Protons and electrons have same magnitude of charge but have different masses. All elements have different number of protons.

Goldstein (1886 A.D)

Neutrons:

The discovery of neutrons was made by James Chadwick (1932 A.D), in an artificial radioactivity experiment. He bombarded alpha particles from Polonium on Beryllium, a stable element and noted that some highly penetrating neutral particles were produced. These particles were named as neutrons.

$$_4Be^9 + {}_2He^4 \rightarrow {}_6C^{12} + {}_0n^1 \text{ [neutron]}$$

Like protons, neutrons are also the part of atomic mass but neutron has no charge. Neutrons of all elements have same nature and mass. They are bounded with each other and protons by the nuclear forces. Under certain circumstances, when electrostatic force (between protons) overcomes the nuclear force, nucleus becomes unstable and fission reaction is occurred.

James Chadwick
(1932 A.D)

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Neutrons are slightly heavier than protons. They are not deflected by electric or magnetic fields. However, the isotopes of same element always have the same number of protons but different number of neutrons. Further, the stability of nucleus depends upon the neutrons. The number of neutrons is determined by subtracting the number of protons from the mass number.

Number of neutrons = Mass number – Number of protons

Table 2.1 Properties of subatomic particles

Particles	Mass (a.m.u)	Mass (g)	Relative charge	Electric charge (coulomb)
Electron (e)	0.00055	9.11×10^{-28}	-1	-1.602×10^{-19}
Proton (p)	1.0073	1.673×10^{-24}	+1	$+1.602 \times 10^{-19}$
Neutron (n)	1.0086	1.674×10^{-24}	0	0

Self Assessment

(i) How many electrons protons and neutrons are present in $^{65}_{30}Zn$?
(ii) How many time the mass of electron is lesser than the mass of proton and neutron?

2.2 INTRODUCTION AND APPLICATION OF BOHR'S ATOMIC THEORY

Neil Bohr (1913 A.D)

Rutherford became successful in presenting that atoms have tiny positive nucleus and negatively charged electrons revolve around it. He compared the movement of electrons around nucleus like planets around sun. His comparison of atomic model with solar system was defective because electrons are charged bodies while planets are charge less. If electrons revolve like planets they should lose energy continuously. As a result, electrons become closer and closer to nucleus and finally fall into it. Further, if electron continuously emits energy it should form continuous spectrum. Actually, both phenomenons did not happen. Neither electrons fall into nucleus nor continuous spectrum is formed. Contrary, line spectrum is formed. These complications were explained by Danish Physicist Neil Bohr (1913 A.D). His atomic Model was based on Planck's quantum theory.

Postulates of Bohr's theory are given below.

(i) Electrons revolve around the nucleus in circular orbits situated at fixed distance from nucleus with definite energy.

(ii) As long as electron remains in an appropriate orbit, it neither loses, nor gains energy. Hence each orbit has a fixed energy level, however the energy of orbits increases with the increased distance from nuclei.

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(iii) During excitation, electron absorbs some quantized energy and jump from a lower energy orbit to an appropriate higher energy orbit but when it returns back to lower energy orbit it emits quantized energy.

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

Here '**υ**' is frequency of radiation and **"h"** is plank constant.

(iv) Electron can move only in those orbits in which the angular momentum of electron (mvr) is integral multiple of $nh/2\pi$.

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

Here '**m**' and '**v**' are the mass and velocity of electron and '**r**' is the radius of orbit.

2.2.1 Calculation of Radius, Energy, Frequency and Wave Number

The truth of the basic assumption of Bohr's theory was established when applied to the single electron system like Hydrogen and ions like He^{+1}, Li^{+2} etc.

Hydrogen atom consists of a single electron revolving around the nucleus.

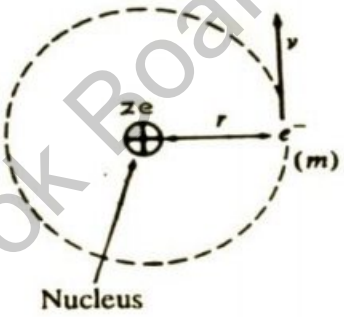

Fig 2.2: Hydrogen atom

Let '**e**' and '**m**' are the charge and the mass of electron, '**Ze**' is the charge on nucleus and '**r**' is the radius of an orbit in which electron is moving with a velocity '**v**'. According to Coulomb's law, the electrostatic force between the nucleus and electron is written as:

$$F = K\frac{Ze^{+}e^{-}}{r^2}$$

Where K is proportionality constant. It is equal to $\frac{1}{4\pi\varepsilon_o}$

Hence attractive force between nucleus and electron can be written as

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

But at the same time the centrifugal force on electron will be $\frac{mv^2}{r}$.

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As far as electron remains in the same orbit, the two opposite forces are equal.

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

$$mv^2 = \frac{Ze^2}{4\pi\varepsilon_o r} \text{ ---------- (i)}$$

$$r = \frac{Ze^2}{4\pi\varepsilon_o mv^2} \text{ --------- (ii)}$$

According to Bohr's thoery

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

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

Taking square on both sides,

$$v^2 = \frac{n^2h^2}{4\pi^2m^2r^2}$$

Now put the value of v^2 in equation (ii)

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

By rearranging, we get

$$r = \frac{\varepsilon_o n^2h^2}{Z\pi me^2} \text{ ---------- (iii)}$$

Where ε_o = Vacuum permittivity constant = 8.84×10^{-12} $C^2/J.m$

h = plank constant = 6.625×10^{-34} J.S

m = mass of electron = 9.11×10^{-31}kg

e = charge of electron = 1.602×10^{-19} C

Assembling all constants in equation (iii) we get

$$r = \frac{a^o n^2}{z} \text{ --------- (iv)}$$

and $$a^o = \frac{\varepsilon_o h^2}{Z\pi me^2}$$

a^o is Bohr's constant and its value is 0.529×10^{-8} cm or 0.529

Equation (iv) is used for the determination of radius of nth orbit of hydrogen atom and hydrogen like ions viz He^+, Li^{+2} etc.

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Example 2.1

Find the radius of 4th orbit of electron in Hydrogen atom.

Solution:

The radius of n = 4 for hydrogen atom can be determined by using Bohr's equation.

$$r = \frac{a^{o} n^{2}}{Z}$$

But for hydrogen Z = 1 hence

$$r = \frac{0.529 \times (4)^{2}}{1}$$

$$r = 8.46 \text{Å}$$

Calculation of Energy of electron in n^{th} orbit:

In any orbit of an atom, the total energy of an electron is the sum of potential energy (P.E) and kinetic energy (K.E).

$$E_{total} = K.E + P.E$$

P.E is the work done in bringing the electron from infinity to a point at a distance **r** from the nucleus and can be calculated as.

$$P \cdot E = \text{work done} = - \text{ force} \times \text{ displacement}$$

$$P \cdot E = \frac{-Ze^{2}}{4\pi\varepsilon_{o} r^{2}} \times r$$

$$P \cdot E = \frac{-Ze^{2}}{4\pi\varepsilon_{o} r}$$

Here negative sign indicates that P.E decreases when electron is brought from infinity to a point at a distance **r**.

Now total energy of electron is written as

$$E_{total} = \left(\frac{1}{2} mv^{2}\right) + \left(-\frac{Ze^{2}}{4\pi\varepsilon_{o} r}\right)$$

$$E = \left[\frac{1}{2} mv^{2}\right] - \left[\frac{Ze^{2}}{4\pi\varepsilon_{o} r}\right] \text{ ---------- } (v)$$

The value of mv^2 is taken from eq(i) and insert in eq(v)

$$E = \frac{1}{2}\left[\frac{Ze^{2}}{4\pi\varepsilon_{o} r}\right] - \left[\frac{Ze^{2}}{4\pi\varepsilon_{o} r}\right]$$

$$E = \frac{-Ze^{2}}{8\pi\varepsilon_{o} r} \text{ ---------- (vi)}$$

Taking the value of **r** from equation (iii) and put in equation (vi)

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

$$E = \frac{-mZ^2e^4}{8\pi\varepsilon_o^2 n^2 h^2} \text{ ---------- (vii)}$$

But for hydrogen atom, Z = 1, thus

$$E = \frac{-me^4}{8\varepsilon_o^2 h^2}\left(\frac{1}{n^2}\right) \text{ ---------- (viii)}$$

$$E = -K\left(\frac{1}{n^2}\right) \text{ ---------- (ix)}$$

Here K is a factor assembled by various constants present in equation (viii). Its value is 2.18×10^{-18} J/atom or 1312.8 KJ/mol

Example 2.2

Calculate the energy of an electron in L-shell of hydrogen atom (the value of K is 2.178×10^{-18} J/atom)

Solution:

L-shell correspond to second energy level (n = 2), Bohr's formula for energy of electron is given as

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

$$E = \frac{-2.18\times10^{-18}}{(2)^2}$$

$$E = -5.43\times10^{-19} \text{ joule}$$

Calculation of Frequency of radiations emitted from an electron:

When an electron jumps from higher energy to lower energy orbit, a definite amount of energy is emitted. Let E_1 be the energy of n_1 orbit and E_2 is for n_2 orbit, the emitted energy is written as

$$\Delta E = E_2 - E_1$$

Considering eq. (viii), the energies of electron in n_1 and n_2 orbit of hydrogen atom are written as

$$E_1 = \frac{-me^4}{8\varepsilon_o^2 h^2}\left(\frac{1}{n_1^2}\right) \text{ and } E_2 = \frac{-me^4}{8\varepsilon_o^2 h^2}\left(\frac{1}{n_2^2}\right)$$

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Where ε_o (the vaccume permittivity constant)

Now

$$\Delta E = \left[\frac{-me^4}{8\varepsilon_o^2 h^2}\left(\frac{1}{n_2^2}\right)\right] - \left[\frac{-me^4}{8\varepsilon_o^2 h^2}\left(\frac{1}{n_1^2}\right)\right]$$

$$\Delta E = \left[\frac{-me^4}{8\varepsilon_o^2 h^2}\left(\frac{1}{n_1^2}\right)\right] - \left[\frac{-me^4}{8\varepsilon_o^2 h^2}\left(\frac{1}{n_2^2}\right)\right]$$

$$\Delta E = \frac{-me^4}{8\varepsilon_o^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{----------} (x)$$

$$\Delta E = 2.18 \times 10^{-18}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{joule/atom} \text{---} (xi)$$

This equation is used for determining the emission or absorption of energy when electron jumps from one orbit to another.

If in equation (x), 'ΔE' is the energy difference appears as photon, it would have a frequency 'υ' and thus according to plank quantum theory it should be $\Delta E = h\upsilon$.

Now equation (x) is written as

$$h\upsilon = \frac{me^4}{8\varepsilon_o^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

And

$$\upsilon = \frac{me^4}{8\varepsilon_o^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ Hertz} \text{---------} (xii)$$

Self Assessment

Using Bohr model, determine the energy in Joule of a photon produced when an electron in hydrogen atom jump from an orbit n = 5 to n = 2.

Calculation of wave numbers of photons:

The wave numbers of absorbed or emitted photons are calculated by following equation.

$$\upsilon = \overline{V}C$$

By substituting in equation (xii) we get

$$\overline{V}C = \frac{me^4}{8\varepsilon_o^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

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$$\bar{V} = \frac{me^4}{8\varepsilon_o^2 h^3 C}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\text{But } \frac{me^4}{8\varepsilon_o^2 h^3 C} = R_H$$

$$\bar{V} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Where R_H is Rydberg constant and its value is 109678 cm^{-1}
It may also be written as
$R_H = 10967800\ m^{-1}$
$R_H = 1.09678 \times 10^7\ m^{-1}$

Example 2.3

Calculate the wave numbers of photon when electron of a hydrogen atom jumps from 4th orbit to 2nd orbit (value of $R_H = 1.09678 \times 10^7\ m^{-1}$).

Solution:

$n_1 = 2$

$n_2 = 4$

$Z = 1$

$\bar{V} = ?$

Bohr's equation for wave number of photon is given as

$$\bar{V} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\bar{V} = \left(1.09678 \times 10^7\right)\left[\frac{1}{(2)^2} - \frac{1}{(4)^2}\right]$$

$$\bar{V} = \left(1.09678 \times 10^7\right) \times 0.187$$

$$\bar{V} = 2.051 \times 10^6\ m^{-1}$$

Self Assessment

What is the wave number of a photon produced when an electron falls from n = 5 level to n = 3 level in hydrogen atom.

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2.2.2 The defects of Bohr's theory or Bohr's atomic Model

Confusions arose in Rutherford atomic model were explained in Bohr's atomic theory comprehensively but there were also some deficiencies in his proposed model.

(i) Bohr's model is only applicable to Hydrogen and those species which have single revolving electron around the nucleus (He^{+}, Li^{2+}, Be^{3+}). It could not explain the spectra of multi electrons systems like He, Li, Be, B etc.

(ii) According to Bohr's concept, electron revolves around nucleus in circular orbits. Later on, it was proved that electron did not move in single plane but in three dimensional spaces.

(iii) According to Bohr's concept, the electron in an atom is located at a definite distance from the nucleus and revolves with a definite velocity which is against the Heisenberg uncertainty principle.

(iv) Bohr's theory explain only the particle nature of electron and did not explain the wave nature of electron (de Broglie's hypothesis).

2.2.3 Spectrum and Hydrogen spectrum

A light which is composed of one kind of rays or wavelengths is known as monochromatic light. However, lights like sunlight, bulb light etc are composed of more than one type of rays. These are known as Poly chromatic lights. When a beam of any poly chromatic light is passed through a glass prism (placed in spectrometer), it splits (disperse) into several colors in order of increasing or decreasing wavelengths. The band of colors is called spectrum.

Continuous Spectrum

The spectrum which contains a continuous band of different colors is known as continuous spectrum. In this spectrum all colors are diffused into each other and the boundary line between the colours is not marked. When sun light passes through prism, it deviates and splits into continuous band of seven colors (VIBGYOR). Red color is least deviated and has high wavelength (7000Å) while violet color has maximum deviation and low wavelength (4000 Å). In rainy season, rainbow in sky is common example of continuous spectrum.

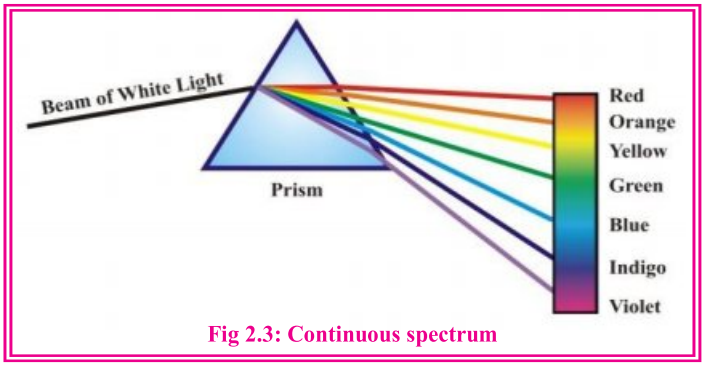

Fig 2.3: Continuous spectrum

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Line Spectrum

When light emitted from electrically or thermally excited atoms is passed through prism, certain distinct lines separated by dark space are obtained, this is known as line spectrum.

A gas is excited by strongly heating or passing through electric discharge tube at low pressure. Each element emit light of specific wavelength therefore the number of lines and the distance between them depends upon the nature of element, so line spectra is used as 'Finger Print' for the identification of elements.

Do You Know?

The word spectroscopy is derived from Latin word spectrum, which means image and Greek word skopia, which means observation. It is the study of the absorbtion and emission of light by matter.

For example, line spectrum of sodium contains two yellow colored lines separated by a definite distance.

Line spectra of the elements give the information that electrons around nucleus have definite amount of energy and are arranged in definite energy levels E_1. After absorbing energy, they jump to an appropriate energy level E_2 and then return back. The difference in emitted energy of electrons, E_2-E_1 is equal to the energy absorbed.

Line spectrum can be seen by the following two ways.

(i) Absorption line spectrum

(ii) Emission line spectrum

Absorption Line Spectrum

When a beam of light is passed through an absorbing material like gaseous sample of an element, the element absorbs certain wavelengths while rest of wavelengths pass through it. The spectrum obtained consists of a series of dark lines with a bright background and known as absorption line spectrum.

Emission Line Spectrum

Sodium vapours lamp (street light), mercury vapours lamp, electrical discharge tube, hot solids or elements emits radiations of certain wavelengths. The spectrum which is formed from such radiations is called emission line spectrum.

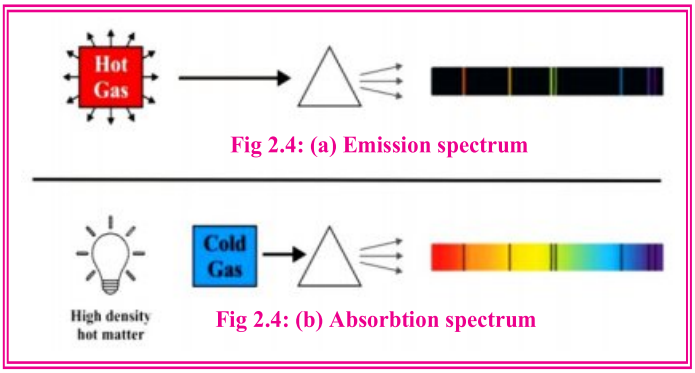

Fig 2.4: (a) Emission spectrum

Fig 2.4: (b) Absorbtion spectrum

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Hydrogen Spectrum

Hydrogen is a simplest atom. It has one electron revolving around mono positively charged nucleus. According to Bohr's theory, at ordinary temperature the electron in hydrogen atom resides in lowest energy level i.e in first orbit (ground state). When electric discharge is passed through hydrogen (Crook's tube) molecular hydrogen breaks up into atomic state. These atoms absorb energy from electric spark and come into excited state. Different electrons of different hydrogen atoms absorb different amount of energy and migrate to an appropriate different high energy levels (excited states). When electrons begin to revolve in higher energy level, hydrogen atoms become unstable. Then, electrons fall back to the original first orbit directly or to some other level by the emission of energies (photons). The emitted energies are equal to the difference of energies between the two levels. These radiations when pass through prism, a line emission spectrum of hydrogen is obtained. When hydrogen spectrum is viewed through high resolution spectrometer, several sharp fine lines are seen in the spectrum. The wavelengths of these lines lie into the ultraviolet, visible and infrared regions. These spectral lines are classified into five spectral series and named after their discoverers.

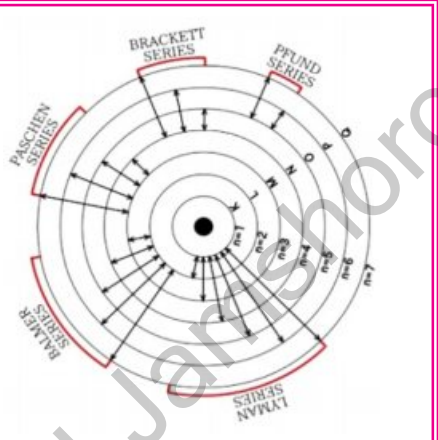

Fig 2.5: Transition of electron for five spectral lines of hydrogen spectrum

The wave numbers of each series of spectral lines is determined by the following equation.

$$\bar{V} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

Here R_H is Rydberg constant

$R_H = 1.09678 \times 10^7\ m^{-1}$

n_1 = lower energy level

n_2 = higher energy level

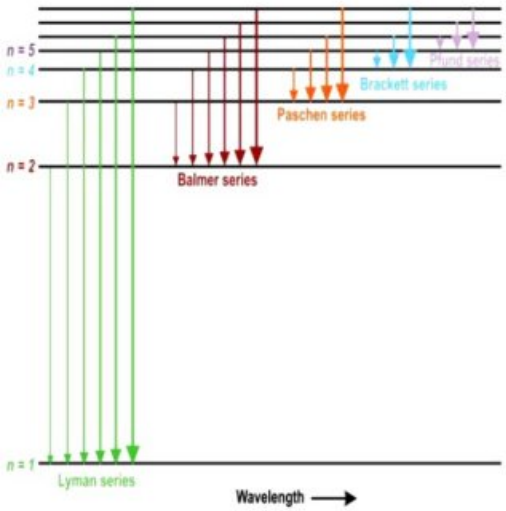

Fig 2.6: Origin of spectral lines of hydrogen spectrum as described by Bohr

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Lyman Series: These spectral lines are produced when electrons fall back from $n_2 = 2,3,4,5,6,7\cdots \infty$ to $n_1 = 1$ level. The range of wave number of this series lie in the ultraviolet region of the hydrogen spectrum (wave length less than 4000 Å).

Balmer Series: This series includes the spectral lines emitted by the transition of electrons occur from $n_2 = 3,4,5,6,7\cdots \infty$ to $n_1 = 2$ level. All the wave numbers of this series are in the visible region (wave length 4000-7000 Å).

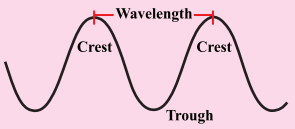
Paschen Series: In this series, transition of electron takes place from $n_2 = 4, 5, 6, 7\ldots\infty$ to $n_1=3$ level. The wave number values of these spectral lines lie in near infrared region (wave length above 7000 Å).

Bracket Series: If the migration of electrons occur from $n_2= 5, 6, 7, 8 \ldots\infty$ to $n_1=4$ level Bracket series is obtained. The wave number values of these spectral lines lie in mid infrared region.

P-fund Series: These spectral lines are produced when electrons fall back from $n_2= 6, 7\ldots\infty$ to $n_1=5$ level. The wave number values of these spectral lines lie in far infrared region.

Do You Know?

Wavelength is the distance between two identical points (Crest to crest or Trough to trough) in a wave. Its unit is cm, mm, m etc



2.3 PLANCK'S QUANTUM THEORY

This theory was given by German physicist Max Plank in 1900 A.D. to describe the emission and absorption of radiations. For this quantum theory, he was awarded Nobel Prize in 1918 A.D.

Postulates of plank's quantum theory

1) Atoms cannot absorb or emit energy continuously.
2) The absorption or emission of energy takes place in specified amounts called quanta (packets of energy). Quantum is a smallest unit of radiation energy, which can exist independently. A quantum of light energy is often called photon.
3) The energy of quantum (photon) is not fixed.
4) The amount of energy of quantum is directly proportional to the frequency of the radiations emitted or absorbed by the body.

$$E \propto \upsilon \quad \text{or} \quad E = h\upsilon$$

This is called as plank equation where h is called Planck's constant. Its value in SI units is 6.625×10^{-34} Js.

2.4 X-RAYS

In 1895 A.D, W. Roentgen accidently observed that when fast moving electrons (cathode rays) collide with metal anode in discharge tube, highly penetrating short wavelength

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radiations are produced. Initially, these rays were named as Roentgen rays but later on, these were called X-rays. These rays can penetrate through paper, glass, rubber, metal and human flesh.

2.4.1 Types of X-rays

Moseley used different anodes and analyzed the intensity of X-rays. On the basis of wavelengths there are two main types of spectral line of X-rays.

(a) K-series: These are produced by the elements (anodes) having large atomic number. These spectral lines have short wavelengths and high energy because transition of electrons occur from high energy level to low energy level (means there is big difference between two energy levels)

(b) L-series: Anodes having small atomic number produce these long wavelength spectral lines. These rays have low energy because there is small difference between two energy levels.

2.4.2 Production, Properties and Uses of X-rays

Production of X-rays

X-rays can be produced in a special type of discharge tube in which cathode is a heated filament. Under high voltage (5000 volt) and very low pressure (0.001mm) cathode rays are emitted from cathode and travel towards anode where they strike with high speed. The transition of electron occurs in the anode atoms which cause the production of X-rays photon.

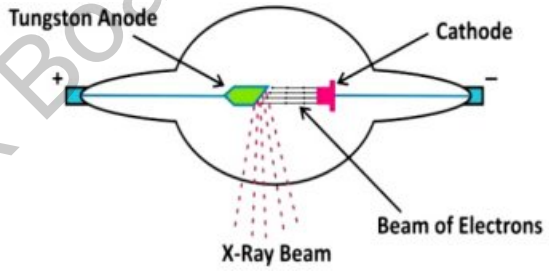

Fig 2.7: Production of X-rays in a discharge tube

Properties of X-rays

1. These are short wave length and high energy invisible electromagnetic radiations.
2. The range of wavelength lies between 0.1-10Å.
3. They travel with the speed of light.
4. Penetration power increases as energy of x-rays increases.
5. Like cathode rays, X-rays travel in straight line.
6. These rays are unaffected by electric or magnetic field.
7. They affect the photographic film.
8. X-rays possess enough energy to ionize gases, they damage and destroy the living cells.

Uses of X-rays

Initially, X-rays were used to assist in the setting of broken arm of a person. Then, uses of X-rays are increased with the passage of time.

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1. These are used for the analysis of metallic substance or bullets in flesh.
2. Dentists use them to examine the defective or damaged teeth.
3. These are used for destroying the cancer cells.
4. At air ports, these are used for checking the baggage containing metallic knife, blade or weapons, transport of illegal goods etc.
5. In crystallography, these are used for the determination of structures of crystals. Thus, x-ray diffraction technique was developed.

2.4.3 Moseley's Law and Atomic Number

Moseley in 1913 A.D., comprehensively studied the different wavelengths of x-rays produced from the anodes of thirty eight (38) different elements from Aluminum to Gold. During his work he noticed that the wavelengths of x-rays decreased regularly with the increase of atomic masses of anode metals. He further observed that the frequencies of these radiations are directly proportional to the number of proton in the nucleus. Mosely law states that the square root of the frequency $\left(\sqrt{\upsilon}\right)$ is directly proportional to the atomic number (Z) of an element.

$$\sqrt{\upsilon} \propto (Z-b)$$

$$\sqrt{\upsilon} = a(Z-b)$$

Where a and b are constant

2.5 RADIOACTIVITY

The phenomenon of radioactivity was given by French scientist Henry Becquerel in 1896 A.D. while working on uranium mineral called pitchblende. It was observed that there was continuous emission of some invisible rays. These rays were producing bright spots on photographic plates, ionizing gases, penetrating through thin metal sheets and producing fluorescence on zinc sulphide screen. Further, it was also observed that cooling, heating and compression did not affect these radiations. However, wrapping of pitchblende in lead sheet could stop the emission of these rays. Initially, these rays were named as Becquerel rays but later on, Marrie Curie coined the term radioactive rays. The elements, which emit these radiations spontaneously, are known as natural radioactive elements and the phenomenon is termed as natural radioactivity.

Do You Know?

Radiocarbon dating is a method for determining the age of an object containing organic material by using the properties of radiocarbon, a radioactive isotope of carbon. It is usually used to predict date ancient objects.

Marrie Curie and her husband, Pierre Curie isolated the radioactive components of the pitchblende mineral and separated two new radioactive elements Polonium and Radium.

Natural radioactive elements after spontaneous emission of rays, break down to more stable elements. This emission of radiations continues till the stable element lead (Pb-82) is formed.

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$$_{92}U^{238} \rightarrow {}_{90}Th^{234} + {}_{2}He^{4}$$
(Uranium) (Thronium) (α–rays)

Nuclear radiations are also produced when a stable element is bombarded or struck by a nuclear particle, this is known as artificial radioactivity.

Types of radiations:

Rutherford placed radioactive material in lead box and the radiations emitted from it were passed through an electric field. He observed three types of radiations- (α, β and γ). The separation of radioactive rays was also made by magnetic field. In magnetic field, alpha rays are deflected towards south pole and beta towards north pole.

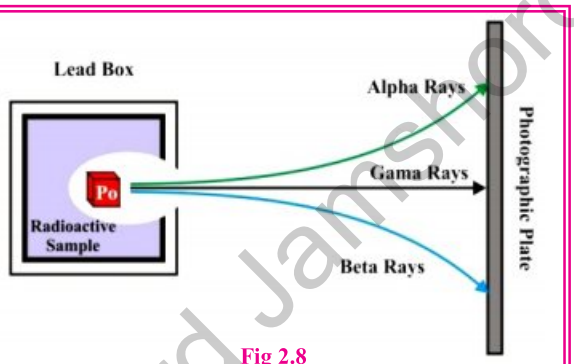

Fig 2.8
The production and separation of radioactive rays.

Table 2.2 **Comparison between the properties of alpha, beta and gamma rays.**

Property	Alpha, (∝)	Beta, (β)	Gamma, (γ)
Mass	4 amu	1/1836 amu	Zero
Composition	∝ particle is composed of two proton and two neutron like the composition of Helium nuclei	Beta particle is composed of electrons	These are electromagnetic radiations.
Deflection	They are deflected by electric and magnetic fields.	They are deflected by electric and magnetic fields but to the opposite direction of α-rays	They pass without any deflection in electric and magnetic field
Charge	+2 charge.	–1 charge.	Neutral
Ionization power	They have ionization power 100 times greater than β-rays and 10,000 times greater than γ-rays	They have lower ionization power than α- rays.	They have lower ionization power than α- rays and β-rays.
Penetration power	They have least penetration power.	They have moderate penetration power.	They have highest penetration power.
Speed	They travel 1/10 to $1/20^{th}$ of light velocity.	They travel $9/10^{th}$ of light velocity.	They travel as fast as velocity of light.

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Self Assessment

(i) What is an ∝ particle? What is its approximate molar mass?

(ii) Compare the penetrating power and ionization power of ∝, β and γ rays.

2.5.1 Uses of Nuclear Radiations

Following are the important uses of nuclear radiations.

1. In medical field, nuclear radiations are used to diagnose, monitor and treat various diseases. These radiations are used to study the bone formation in mammals. Radiotherapy is most commonly used for the treatment of cancer. Radioisotopes has immense role in the growing field called nuclear medicine.
2. In agriculture field, radioisotopes are used to treat the seeds in the production of new varieties of crops.
3. They are used for the production of energy. Nuclear power stations like Karachi Nuclear Power Plant produce electrical energy.
4. In industries they are used to monitor the quality of products. Radioisotopes are also used to measure the density of metals and thickness of plastics.
5. In the field of geology, these are used to study the rocks.
6. Carbon-14 isotope is used to measure the age of fossils and artifacts (archeology).

2.6 QUANTUM NUMBERS AND ORBITALS

According to Bohr, an electron is a particle and form circular path around the nucleus. de Broglie considered the motion of electron as wave. Schrodinger described the movement of an electron as wave in three dimensional space around the nucleus. A region of three dimensional space around the nucleus where maximum probability of finding of electrons take place is known as orbital.

Schrodinger through his wave equation calculated some mathematical integers which are called quantum numbers. Quantum numbers describe energy levels, sub-levels and orbitals available for electron.

There are four quantum numbers.

2.6.1 Principal quantum number:

It is represented by (n). It has any positive value: 1,2,3 ….∞. The energy of an electron in an atom depends on this quantum number. Principal quantum number describes the size and energy of orbit and the distance of electron from the nucleus. Larger the value of **n**, the greater is the distance between electron and nucleus.

For n = 1, 2, 3……., shells are indicated by K, L, M……..

The maximum number of orbitals in an orbit can be calculated by the formula $\mathbf{n^2}$ and the maximum number of electrons in an orbit are determined by using the formula $2n^2$.

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2.6.2 Azimuthal quantum number:

It is also known as subsidiary quantum number. It is denoted by (ℓ). It governs the shape of orbitals. This can have values $\ell = 0$ to (n – 1). When value of $\ell = 0$, the orbitals is called **s** orbital, when $\ell = 1$, it is **p** orbitals, when $\ell = 2$, **d** orbitals and $\ell = 3$, it is **f** orbital.

The maximum number of orbitals in an orbit are determined by the formula **$(2\ell + 1)$** whereas maximum number of electrons in a given sub-shell are calculated by **$2(2\ell + 1)$.**

2.6.3 Magnetic quantum number:

It is denoted by (m). It tells about the different orientations or directions of an orbital in space when subjected to magnetic field. Orbitals of same sub-shell have different orientation but same energy (degenerated orbitals) and same shapes.

The value of **m** depends upon the values of (ℓ).

Sub-shell	(2 ℓ +1) value	Orientations.(m = - ℓ to 0 to + ℓ)
S	One	1
P	Three	(–1, 0, +1)
d	Five	(–2, –1, 0, +1, +2)
f	Seven	(–3, –2, –1, 0, +1, +2, +3)

2.6.4 Spin quantum number:

It is denoted by (s). An electron while moving in an orbital around the nucleus also rotates or spins about its own axis. The spinning of an electron is either in clock-wise or anti clock wise. This spinning of electron is associated with magnetic field. In the same orbital one electron may spin clockwise (-1/2) or anti clockwise (+1/2), but in the same orbital, two electrons cannot have same spin quantum numbers.

Table 2.3 **A summary of quantum numbers, energy level, sub energy level and maximum number of electrons in sub energy level.**

Energy level (n)	Sub Energy levels (l)			Orientation of orbitals (m)
n	ℓ	Orbitals	Maximum electrons $2(2\ell + 1)$	$-\ell, 0, +\ell$
1	0	s	2	0
2	0	s	2	0
	1	p	6	-1, 0, +1
3	0	s	2	0
	1	p	6	-1, 0, +1
	2	d	10	-2, -1, 0, +1, +2
4	0	s	2	0
	1	p	6	-1, 0, +1
	2	d	10	-2, -1, 0, +1, +2
	3	f	14	-3, -2, -1, 0, +1, +2, +3

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Self Assessment

In the following sets of quantum number, state which set is permissible? Explain why the other is not permissible?

(a) $n = 0, \ell = 0, m = 0, s = s = +\frac{1}{2}$ (b) $n = 1, \ell = 0, m = 0, s = -\frac{1}{2}$

2.6.5 Shapes of orbitals:

The regions of space around the nucleus where likelihood of finding an electron is maximum are called orbitals. Each orbital is associated with a particular size, shape and oriented around the nucleus.

s- orbital:

s-orbital has spherical shape in which the probability of finding the electron is uniformly distributed around the nucleus. It has only one possible orientation in space in the magnetic field because it spread over all the three axes uniformly. It has no nodel plane. Its size increases with the increase in value of **n**.

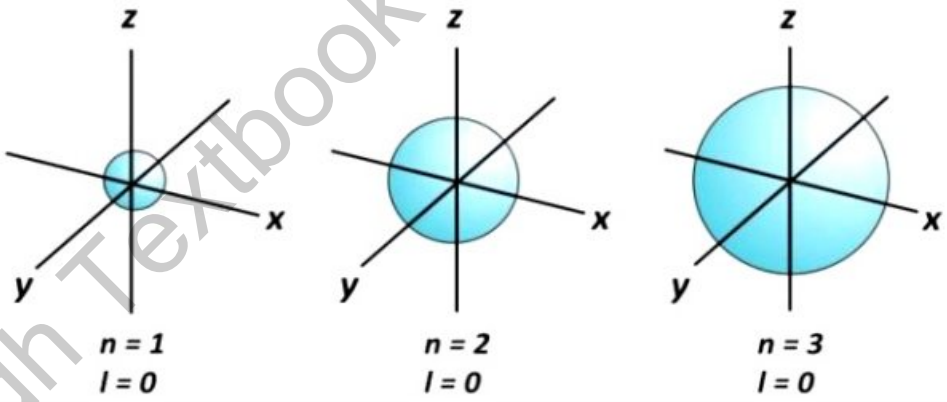

Fig 2.9 Shape of s-orbital

p-orbital:

The p orbitals are dumb-bell-shaped and they are oriented in space along the three mutually perpendicular axes (x, y, z), and are called $\mathbf{p_x}$, $\mathbf{p_y}$ and $\mathbf{p_z}$ orbitals. All the three **p** orbitals are perpendicular to each other. These are degenerate orbitals that are of equal energy.

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Each **p** orbital has two lobes. One of which is labeled (+) and the other (-). Each lobe is like a pear. The point when the two lobes meet each other is usually referred to as the nodal plane along which the probability of finding the electron is zero.

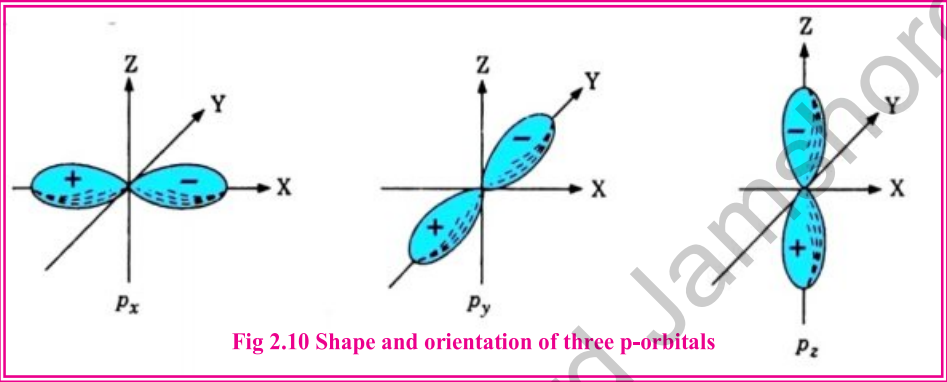

Fig 2.10 Shape and orientation of three p-orbitals

d-orbital:

d sub-shell is divided into five orbitals. Under the influence of magnetic field they have five directions dxy, dyz, dxz, dx^2y^2,dz^2 in space.

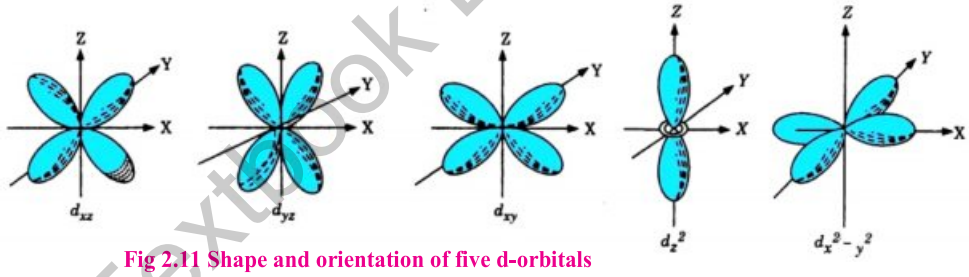

Fig 2.11 Shape and orientation of five d-orbitals

f-orbital:

These orbitals have seven directions when place in magnetic field.

2.7 ELECTRONIC CONFIGURATIONS

The distribution of electrons in the available sub-shells and orbitals (s, p, d, and f) is called electronic configuration. The superscript on sub-shells indicates the number of electrons and coefficient specifies the number of shell to which it belongs to. For example, the configuration of oxygen is O = $1s^2$, $2s^2$, $2p^4$. In $2p^4$, 2 is shell number and 4 number of electrons. Configuration of electrons in orbitals is indicated by a single arrow for one and double arrow for two electrons. Upward direction of an arrow (↿) shows the clock wise spin while downward direction (⇂) specify anti-clock wise spin of an electron.

Following are the rules for the electronic configuration.

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(1) Pauli's Exclusion Principle

This principle was given by Wolfgang Pauli (1925 A.D.) and based on experimental observations. This principle states that, **"In an orbital of an atom, no two electrons can have the same set of four quantum numbers, at least one quantum number must be different"**.

According to this principle, two electrons in an orbital may have same values of three quantum numbers (n, ℓ , m) but the value of fourth quantum number (s) must be different. It means that if one electron of same orbital has clockwise spin then second electron must have anti-clockwise spin. Consider two electrons of helium which are lying in s-orbital of first shell ($1s^2$). The set of four quantum numbers will be written as:

Helium Atom	Quantum numbers			
	n	ℓ	m	s
First electron	1	0	0	$+\frac{1}{2}$
Second electron	1	0	0	$-\frac{1}{2}$

From the Pauli's principle, it is concluded that an orbital can accommodates only two electrons and these two electrons must have opposite spins (↿⇂).

(2) Aufbau principle

Aufbau is a German word, which means "building-up". Pauli named this principle as Aufbau Principle. **"According to this principle, electrons are filled progressively to the various sub-shells in the order of increasing energy, starting with the 1s sub-shell having lowest energy".**

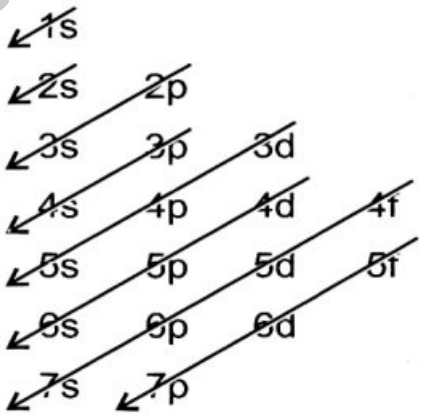

Fig 2.12: Systematic scheme of subshells in order of increasing energy.

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Example 2.4

Write the electronic configuration of the following.

(a) S (Z=16) (b) Na^+ (Z=11) (c) Cl^- (Z=17)

Solution:

(a) S (Z=16) = $1s^2, 2s^2, 2p^6, 3s^2, 3p^4$

(b) Na^+ ion contains one electron less than Na atom, so its electronic configuration will be as:

Na^+ (Z=11) = $1s^2, 2s^2, 2p^6$

(c) Cl^- ion contains one electron greater than Cl atom, so its electronic configuration will be as:

Cl^- (Z=17) = $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$

(3) (n + ℓ) Wiswesser rule:

This rule reminds us that the energy of an orbital depends upon the principal quantum number (n) and azimuthal quantum number (ℓ).

According to this rule, electrons are filled in various orbitals in the order of increasing (n + ℓ) value. **"Those orbitals which have lower (n+ ℓ) value are filled first. In case, if two orbitals which have same (n + ℓ) value, then orbital having lower 'n' value will be filled first".**

Do You Know?

The term iso electronic refers to those atoms or ions which have the same number of electrons and same electronic configuration.

For example Ne (Z = 10), Na^+(z = 11) and F^-(Z=9) have the same number of electrons (10) and same electronic configuration ($1s^2 2s^2 2p^6$).

To understand n + ℓ rule, let us consider the filling of electron in 3d and 4s orbitals. The n + ℓ value of 3d orbital (n = 3; ℓ = 2) is 5 but for 4s orbital (n = 4; ℓ = 0) is 4. Hence 4s orbital which has lower value of (n + ℓ) will fill first. Likewise, 4p orbital fills before 5s although the (n + ℓ) value for both is same, but 4p orbital has the lower value of the principal quantum number 'n'.

Self Assessment

Identify the orbital of higher energy in the following pairs.

(i) 4s and 3d (ii) 4f and 6p (iii) 5p, 6s (iv) 4s, 3d

(4) Hund's rule of Maximum Multiplicity:

Orbitals of same sub-shell possess same energy and are known as degenerated orbitals. For example:

p-sub shell consists of three orbitals (p_x, p_y and p_z), all have same energy. Similarly, five orbitals of d-sub shell are also degenerated orbitals.

3p = 3px, 3py, 3pz

3d = 3dxy, 3dxz, 3dyz, $3dx^2$-y^2, $3dz^2$

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In 1927 German Physicist Friedrich Hund gave his rule for filling of electrons in degenerated orbitals known as "Hund's rule of Maximum Multiplicity". According to this rule, **"In available degenerated orbitals (p, d and f), electrons are distributed in such a way that maximum number of half filled orbitals (single electron in orbital) are obtained".** For example, if we have three electrons to fill the 2px, 2py, 2pz orbitals, we will fill single electron in each orbital $2px^1$, $2py^1$, $2pz^1$ rather than double electrons $2px^{1\downarrow}$, $2py^1$, 2pz. Unpaired electrons are more stable than paired electrons because paired electrons create repulsion. Electronic configurations of some elements considering Hund's rule are given below:

$$C = 6 = 1s^{1\downarrow}\ 2s^{1\downarrow}\ 2px^1\ 2py^1\ 2pz$$

$$N = 7 = 1s^{1\downarrow}\ 2s^{1\downarrow}\ 2px^1\ 2py^1\ 2pz^1$$

$$O = 8 = 1s^{1\downarrow}\ 2s^{1\downarrow}\ 2px^{1\downarrow}\ 2py^1\ 2pz^1$$

$$F = 9 = 1s^{1\downarrow}\ 2s^{1\downarrow}\ 2px^{1\downarrow}\ 2py^{1\downarrow}\ 2pz^1$$

$$Ne = 10 = 1s^{1\downarrow}\ 2s^{1\downarrow}\ 2px^{1\downarrow}\ 2py^{1\downarrow}\ 2pz^{1\downarrow}$$

Society, Technology and Science

Firework Displays

We specially, see the colorful fascinating display of fireworks on the occasions of wedding ceremony, happy New Year, birth day parties, winning the elections or religious special days etc. These different colors of fireworks are due to the presence of different metallic compounds in burning material. The compounds of Copper give bluish green, Barium green and Strontium deep red colors.

In eighteenth century, scientists began to study these colors displayed during fireworks and used flame tests. From the light of flames line spectra were formed and analyzed the elements. These flame tests and spectra helped in the study elements and structures of atoms.

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Activity

The purpose of this activity is to comprehend the phenomenon of line spectrum. You definitely have a table salt (NaCl) in your kitchen. Sodium, being an alkali metal, gives distinct line spectrum when the salt is strongly heated over the flame. You can perform this activity quite easily.

Paste a small amount of table salt on a glass rod and put it over the flame. When it gets sufficient heat, the electron (of sodium) in the lower energy level jumps to higher energy level thus becomes excited and when it gets back to lower energy level, it consequently produces yellow spectrum which can be observed easily.

SUMMARY with Key Terms

- **Atom** is a complex organization of matter and energy. It is the smallest particle of matter which may or may not exist free in nature and takes part in chemical reactions.
- **Bohr Atomic Theory** describes that an atom has fixed number of circular orbits in which electrons revolve. An electron requires energy when it jumps from lower orbit to higher orbit and loses energy when it returns to lower orbit.
- **Continuous spectrum** is produced when a beam of white light is passed through a prism. This spectrum consists of a band of seven colours (VIBGYOR). The colours are diffused into each other and have no distinct boundary line.
- **Absorbtion Line spectrum** consists of a series of dark lines with bright background. It is obtained when a beam of light is passed through an absorbing material.
- **Emission Line spectrum** consists of a series of bright lines with dark background. It is obtained when light emitted from a hot solid or discharge tube.
- **Lyman series** is formed when electrons fall back from $n_2 = 2, 3, 4, 5, 6, 7 \ldots \infty$ to $n_1 = 1$ level. This series lie in UV region.
- **Balmer series** is formed when electrons fall back from $n_2 = 3, 4, 5, 6, 7 \ldots \infty$ to $n_1 = 2$ level. This series lie in visible region.
- **Paschen series** is formed when electrons transition takes place from $n_2 = 4, 5, 6, 7 \ldots \infty$ to $n_1 = 3$ level. This series lie in near IR region.
- **Bracket series** is formed when electrons jump down from $n_2 = 5, 6, 7, 8 \ldots \infty$ to $n_1 = 4$ level. This series lie in mid IR region.

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- **Pfund series** is produced when electrons jump back from $n_2 = 6, 7 \ldots \infty$ to $n_1 = 5$ level. This series lie in far IR region.
- **X-rays** are short wavelength and high penetrating electromagnetic radiations. These are produced when fast moving electrons hit metal anode in a discharge tube.
- **Radioactivity** is a phenomenon in which nucleus of an atom is splitted and emission of rays takes place. Henry Becquerel gave the concept of radioactivity.
- **Alpha rays** consist of positive charge particles. They deflect toward negative pole in an electric field.
- **Beta rays** consist of negative charge particles. They deflect toward positive pole in an electric field.
- **Gamma rays** are shortest wave length rays which pass through electric and magnetic field without any deflection.
- **Principle quantum number** is indicated by 'n'. It describes the size and energy of an orbital.
- **Azimuthal quantum number** is indicated by 'ℓ'. It describes the shape of orbitals.
- **Magnetic quantum number** is indicated by 'm'. It describes the orientation of orbitals in space in an applied magnetic field.
- **Spin quantum number** is indicated by 's'. This quantum number describes the spin of electron in an orbital. Spin of electron may be clock wise $\left(-\frac{1}{2}\right)$ or anti clock wise $\left(+\frac{1}{2}\right)$.
- **Orbital** is a space around the nucleus where maximum (95%) finding of an electron takes place.
- **Electronic configuration** is the distribution of electrons in the available sub-shells and orbitals (s, p, d, and f).
- **Pauli Exclusion Principle** states that "In an atom no two electrons can have same set of four quantum numbers. At least one quantum number must be different".
- **Aufbau Principle** tells that electrons are filled progressively to various sub-shells in the order of increasing energy, starting with the 1s sub-shell having lowest energy.
- **$n + \ell$ rule** tells that, those orbitals are filled first which have lowest $(n + \ell)$ value. When two orbitals have same $(n + \ell)$ value, the orbitals having lower (n) value will be filled first.
- **Hund's rule** states that when degenerated orbitals are available and more than one electron are to be filled in them, they should be filled in separate orbitals in such a way so as to give maximum number of unpaired electron and have the same direction of spin.

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EXERCISE

Multiple Choice Questions

1. Choose the correct answer

(i) Bohr's theory is not applicable to which of the following species.

(a) H (b) H^+

(c) He^{+1} (d) Li^{+2}

(ii) Nitrogen has the electronic configuration $1s^2\,2s^2\,2p_x^1\,2p_y^1\,2p_z^1$ and not $1s^2\,2s^2\,2p_x^2\,2p_y^1$

This is determined by.

(a) Aufbau principle (b) Pauli's rule

(c) Hund's rule (d) $n + \ell$ rule

(iii) Quantum number values for 3s orbital are

(a) $n = 0, \ell = 1$ (b) $n = 1, \ell = 0$

(c) $n = 3, \ell = 1$ (d) $n = 3, \ell = 0$

(iv) The radius of first orbit of hydrogen atom is …..

(a) 529 Å (b) 52.9 Å

(c) 5.29 Å (d) 0.529 Å

(v) Line spectrum is used as a tool for the identification of ….

(a) Colors (b) Electrons

(c) Elements (d) Molecules

(vi) In 1935 A.D. James Chadwick was awarded Nobel Prize because …

(a) He discovered proton

(b) He discovered neutron

(c) He determined the radius of hydrogen atom

(d) He gave the rules for electronic configuration

(vii) When 4d orbital is filled, the next electron enter into

(a) 5s (b) 5p

(c) 5d (d) 6s

(viii) Which of the following is not an iso electronic pair

(a) Na^+ and Ne (b) Na^+ and F^-

(c) Na and Ca (d) Na^+ and Mg^{+2}

(ix) Balmer series appears in the hydrogen spectrum if electron jump from any appropriate higher energy orbit to

(a) Second orbit (b) Third orbit

(c) Fourth orbit (d) Fifth orbit

(x) The shape of orbital for which $\ell = 0$ is

(a) Spherical (b) Dumbbell

(c) Double dumbbell (d) Complicated

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Short Questions

1. Differentiate between Continuous and Line spectrum.
2. Give three properties of each $\propto$, β and γ rays.
3. What is the shape of orbitals for which $\ell = 0$ and $\ell = 1$.
4. How does an orbital different from orbit?
5. Explain why the filling of electron in 4s orbital takes place prior to 3d?
6. Mention the defects of Bohr's atomic model.
7. Write down the electronic configuration of the following.
   (i) Fe (Z= 26), (ii) Br^- (Z= 35), (iii) Ca^{+2} (Z= 20)

Descriptive Questions

1. (a) State the postulates of Bohr atomic theory.
   (b) Drive an expression for the frequency of radiation emitted from an electron. Given that

$$E = \frac{-me^4}{8\varepsilon_o^2 h^2 n^2}$$

2. What are X-rays? How are they produced? Give their properties and uses.
3. State and illustrate the following rules of electronic configuration.
   a) Pauli's exclusion rule b) Hund's rule of maximum multiplicity
4. Explain hydrogen spectrum in term of Bohr's theory.
5. Describe four quantum numbers needed to specify an electron in an atom. Write all possible values of ℓ, m and s for n = 2.

Numerical Questions

1. Calculate the radius of hydrogen in 3rd orbit (Bohr constant for hydrogen is 0.529Å).
2. A photon of wave number $23 \times 10^5\ m^{-1}$ is emitted when electron undergoes a transition from a higher energy orbit to n = 2. Determine the orbit from which electron fall and also the spectral line appears in this transition of electron.
   (The value of Rydberg constant is $1.09678 \times 10^7\ m^{-1}$).

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THEORIES OF COVALENT BONDING AND SHAPES OF MOLECULES

Chapter 3

Teaching Periods	Assessment	Weightage
10	1	10

Students will be able to:

- **Describe** the features of sigma and pi bonds.
- **Use** VSEPR and VBT theories to describe the shapes of simple covalent molecules.
- **Describe** the shapes of simple molecules using orbital hybridization.
- **Determine** the shapes of some molecules from the number of bonded pairs and lone pairs of electrons around the central atom.
- **Define** bond energies and explain how they can be used to compare bond strengths of different chemical bonds.
- **Predict** the molecular polarity from the shapes of molecules.
- **Describe** how knowledge of molecular polarity can be used to explain some physical and chemical properties of molecules.
- **Describe** the change in bond lengths of hetero-nuclear molecules due to difference in Electronegativity values of bonded atoms.
- **Explain** what is meant by the term ionic character of a covalent bond.

INTRODUCTION

After getting detailed study about the structure of an atom in the previous chapter, the next investigation is why and how atoms combine to produce a molecule?

A molecule as compared to the atoms from which it is formed is more stable because it possesses energy lower than the energy of the uncombined atoms. This difference in energy is due to the fact that when atoms combine to form molecule, the attractive forces are created which result in the release of energy. **"The attractive force that holds atoms together in a compound is known as the chemical bond"**.

Studies on chemical bond formation came to materialize during early 20th century, after the electron had been discovered. Lewis (1916) gave the concept of valency and said that electrons in atoms are responsible for chemical bonding. Electronic theory of chemical bonding which is proposed independently by Kossel and Lewis tells that a chemical bond is formed between two atoms to acquire noble gas configuration. Atoms of almost all elements have incomplete outer shell and tend to complete their outer shell by the chemical combination with other atoms. It can be done either by sharing or transfer of electrons. Atoms of noble gases are extremely stable due to the completion of duplet/octet therefore they do not form any type of chemical bond and remains exist in atomic state (mono atomic molecule). The concept of ionic bond formation is quite simple and understandable. However, the way a covalent bond forms as well as the shape of molecules can be understood on the basis of various theories.

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3.1 THEORIES OF COVALENT BOND

Lewis concept for covalent bond formation provides us a guideline for writing the structural formula of various covalent compounds but neither describes the nature of bonding forces, nor about the shape of molecules and many other properties such as bond energies, bond strength and the para magnetic behavior of molecule.

There are two modern theories which describes the behavior of electron in molecule

(i) Valence Bond Theory (VBT)

(ii) Molecular Orbital Theory (MOT)

3.1.1 Valence Bond Theory

This theory was introduced by London and Heitler in 1927. This theory tells how the bonding in covalent molecule takes place by the overlapping of atomic orbitals. It not only provides basic information for analyzing the structure and the bonding in the molecule but also the strength of covalent bond as well as molecular shape on the basis of atomic orbital interaction. The main postulates of this theory are given below.

(i) A covalent bond is formed due to the overlap of half filled orbital of combining atoms. (The term overlap represents sharing of some common region in space).

(ii) As a result of overlapping there is a maximum electron cloud somewhere between the two overlapped orbital.

(iii) The electrons present in both overlapped orbital should be in opposite spin.

(iv) The strength of bond is determined by the extent of overlap. The greater the overlap, the stronger is the bond.

(v) Each atom involves in the overlapping keep its own atomic orbital but electron pair is shared up by both atoms which take part in the overlapping.

Valance bond theory describes two ways of overlapping of atomic orbital which results in the formation of following two types of covalent bonds.

(i) sigma (σ) bond

(ii) pi(π) bond

Sigma (σ) Bond:

This bond is established when the two atomic orbital overlap linearly in such a way that both orbital lie along the line joining the two nuclei. It defines as **"the bond formed by head to head overlapping of half filled atomic orbitals"**. The electron density in sigma bonded atoms found highest between the two bonded nuclei.

The formation of sigma bond results due to the following types of head to head overlapping.

s–s overlapping:

It is the overlap of half filled **s** orbital of two combining atoms. This type of overlapping exist in H_2 molecule.

Hydrogen atom contains just one electron in 1s-orbital. When the two hydrogen atoms come closer to each other, their half filled s-orbital overlap and form H–H sigma bond in which the electron cloud is rich along the axis between two nuclei.

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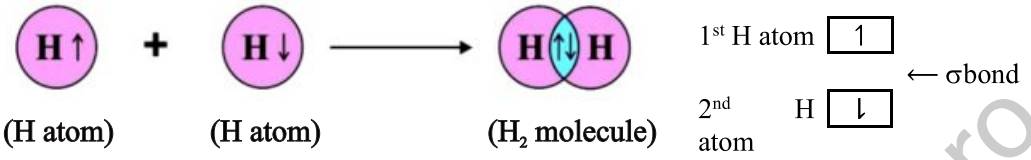
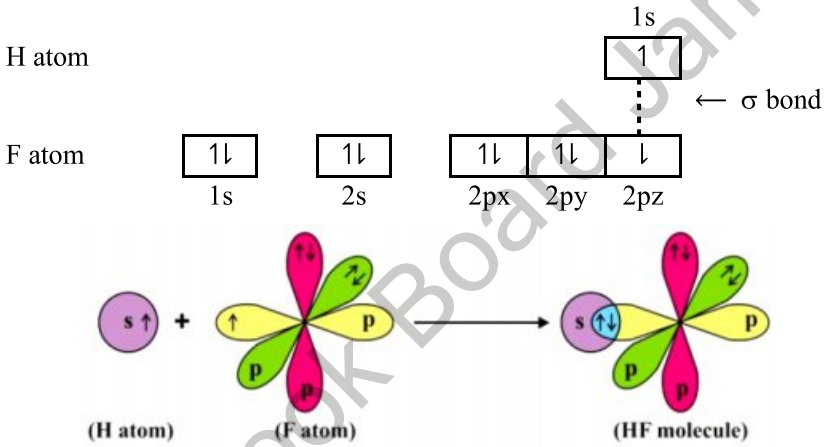


s–p overlapping:

It is the overlap of half filled **s** and half filled **p** orbital of two combining atoms. Example of molecule in which sigma bond is formed due to s-p overlapping are HF, HCl etc.

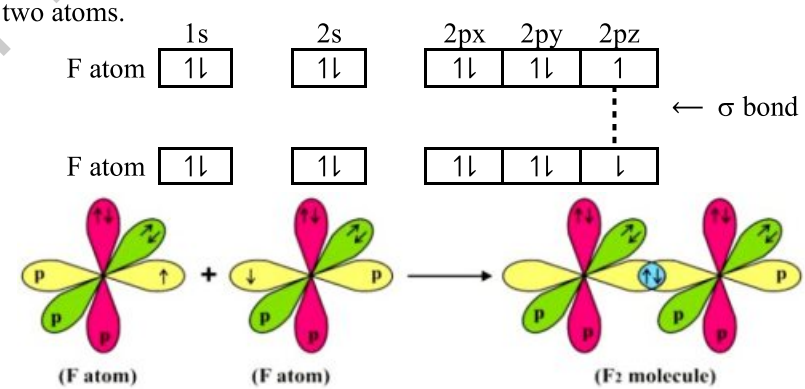
HF molecule is formed by overlap of half filled 1s orbital of hydrogen atom and half filled 2pz orbital of fluorine.



p–p overlapping:

It is the overlap of half filled **p** orbital of two combining atoms. The example of this type of overlapping is F_2 molecule.

The electronic configuration of fluorine is $1s^2\ 2s^2\ 2px^2\ 2py^2\ 2pz^1$, it means only pz orbital is occupied by single electron and available for overlap. VBT tells that, half filled pz orbital of both fluorine atoms undergo overlapping in which the electron pair is shared up between the two atoms.



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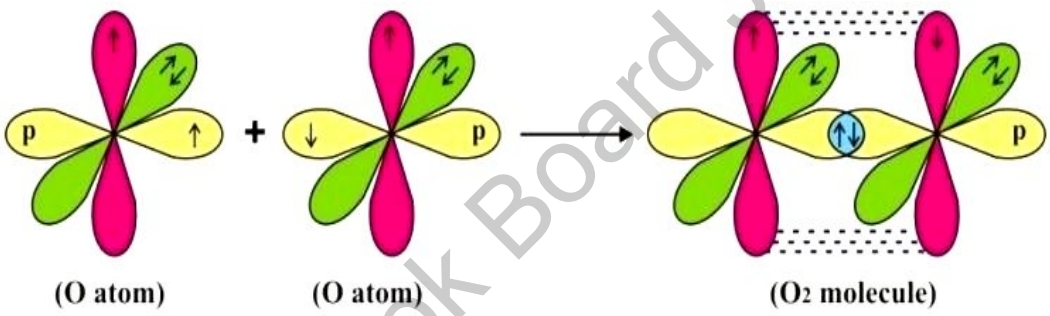
Pi(π) Bond:

This bond is formed by the lateral or side way overlap of the p-orbital between the two atoms which already bonded through sigma bond. The condition for the formation of pi bond is that the two p-orbital should be parallel to each other. The electron cloud of pi bond in unsymmetrical and is concentrated above and below the plane of sigma bond. In this situation the rotation of p-orbital become restricted between the two atoms. Since the region of overlapping of p-orbitals in the formation of pi bond is small (minimum), it is relatively weaker than sigma bond.

Example of molecules which possess pi bond are O_2 and N_2 etc.

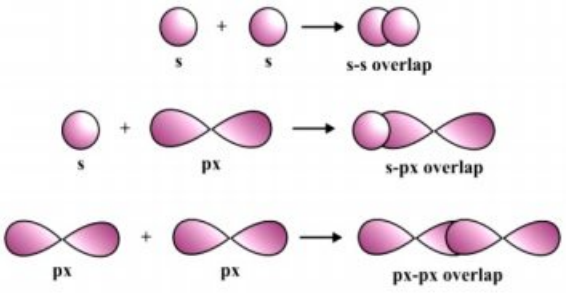
The electronic configuration of oxygen is $1s^2$, $2s^2$, $2px^2$, $2py^1$, $2pz^1$; since there are two half filled p orbital on each oxygen atom, one of them undergoes head to head overlapping to form sigma bond while the overlapping of other p-orbital takes place laterally which lead to the formation of pi bond.



Strength of bond in term of valence bond theory

An important feature of valence bond theory is that the strength of covalent bond is proportional to extent of overlapping of atomic orbital. The greater the overlapping the stronger the bond between the atoms and the higher the energy require to break the bond.

Due to spherical charge distribution in s–orbital, generally **s–s** overlap is not so effective as **s–p** and **p–p** overlap. Since p–orbital have directional charge distribution and longer lobes which cause more effective overlap. Thus **s–s** sigma bond is relatively weak than **s–p** and **p–p** sigma bond.



In pi (π) bond the orbital has two regions of electronic density, one is above the nuclear axis and other is below the nuclear axis. This type of overlapping of atomic orbitals is not maximum that is why pi bond is weaker than sigma bond.

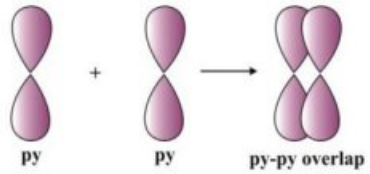


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Table 3.1 Some essential features of sigma and pi bond

Sigma Bond	Pi Bond
It is formed by head to head overlapping of half filled atomic orbital.	It is formed by lateral/parallel overlapping of half filled atomic orbital.
Only one sigma bond can exist between the bonded atoms.	Maximum two pi bonds can form between the two atoms.
Orbital free rotation can be possible between the two atoms if only sigma bond is present.	Orbital free rotation is not possible between the two atoms if pi bond is present.
Electron cloud is denser at the plane of bond axis.	Electron cloud is denser at above and below the plane of bond axis.

Limitation of Valance bond theory

Although VBT furnishes a good picture of bonding in molecules, however it has some short coming.

- It fails to describe the valencies in Carbon, Boron and Beryllium.
- It does not tell about para magnetic behavior of oxygen.
- It fails to describe the delocalization of electrons in the molecule.

Self Assessment

(i) Why sigma bond is stronger than pi bond?
(ii) Why p-p sigma bond is stronger than s-s and s-p?

3.1.2 Molecular Orbital Theory

Mullikan, Hund and Huckel (1927) developed an alternate theory known as molecular orbital theory to overcome the short comings of VBT. Assumptions of molecular orbital theory are given as:

(i) Atomic orbitals of similar energies linearly combine together to produce molecular orbitals.
(ii) Combination of two atomic orbitals (A.O) gives two molecular orbitals (MO) one of them has lower energy and other has higher energy than any of the atomic orbital from which they formed.
(iii) The molecular orbital with lower energy is called as bonding molecular orbital (BMO) and the orbital with higher energy is called as anti bonding molecular orbital (ABMO).
(iv) The movement of electrons in M.O is influenced by both nuclei of combining atoms.
(v) The filling of electrons into the molecular orbital is followed by fundamental rules of electronic configuration i.e. Aufbau principle, Hund's rule and Pauli rule.

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Characteristic of Bonding and Anti Bonding M.O

Bonding molecular orbital has lower energy than atomic orbital from which it is formed. Electrons in the bonding molecular orbitals favour bonding because combining orbital interact constructively thus the probability of electron density is maximum between the two nuclei.

Anti bonding molecular orbital has higher energy than the two combining atomic orbital. It is produced due to destructive interaction and hence electron density in the region between two nuclei is zero since the nodal plane bisecting the inter nucleus axis.

Molecular orbital theory (MOT) is best to predict the bond order and the magnetic properties of molecules. The formula used in determining the bond order is given as.

$$\text{Bond order} = \frac{N(b) - N(a)}{2}$$

Where

N(b) = Electrons in bonding M.O

N(a) = Electrons in anti bonding M.O

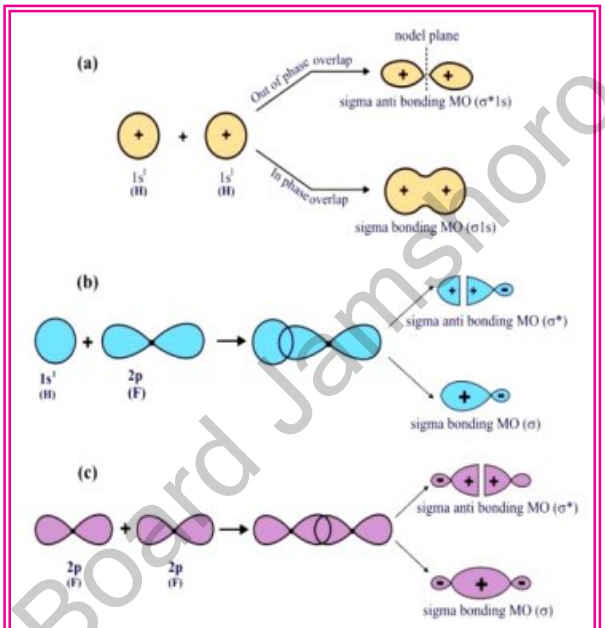

Fig 3.1: Description of the formation of molecular orbital in (a) H_2 molecule (b) HF molecule (c) F_2 molecule

Molecular orbital diagram for some homonuclear diatomic molecules are describe below.

H_2 – molecule

Hydrogen atom contains one electron in 1s orbital. The atomic orbital of both hydrogen atom linearly combine to form two molecular orbitals. According to the rule of electronic configuration, electrons accommodate in bonding MO since it possess low energy hence anti bonding MO remains vacant. This can be illustrated in the molecular orbital diagram.

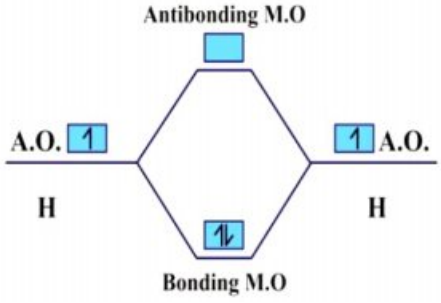

Fig 3.2: Molecular orbital energy diagram of H_2 molecule

Bond order of H_2 molecule is determine as

$$\text{Bond order of } H_2 = \frac{N(b) - N(a)}{2} = \frac{2 - 0}{2} = 1$$

Since there is no unpaired electron in any molecular orbital, hydrogen is diamagnetic in nature.

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O_2 – molecule

The electronic configuration of oxygen (z = 8) is $1s^2$, $2s^2$, $2p^4$. Thus there are five atomic orbitals with eight electrons in each oxygen atom. These five atomic orbitals of both oxygen atoms combine to form ten molecular orbitals as shows in molecular orbital energy diagram.

Bond order of O_2 molecule is determine as

$$\text{Bond order of } O_2 = \frac{N(b) - N(a)}{2} = \frac{10 - 6}{2} = 2$$

Since there are two unpaired electrons in anti bonding MO, O_2 is paramagnetic.

The molecular orbital configuration with increasing energy order is given as

$\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < \pi 2py = \pi 2pz < \sigma 2px < \pi^*2py = \pi^*2pz < \sigma^*2px$

Do You Know?

Substance that have unpaired electrons in their orbital are attracted by external magnetic field are said to be paramagnetic. For example O_2 Molecule.
Substance that have paired electrons in their orbital are repelled by external magnetic field are said to be diamagnetic. For example H_2, N_2, He etc.

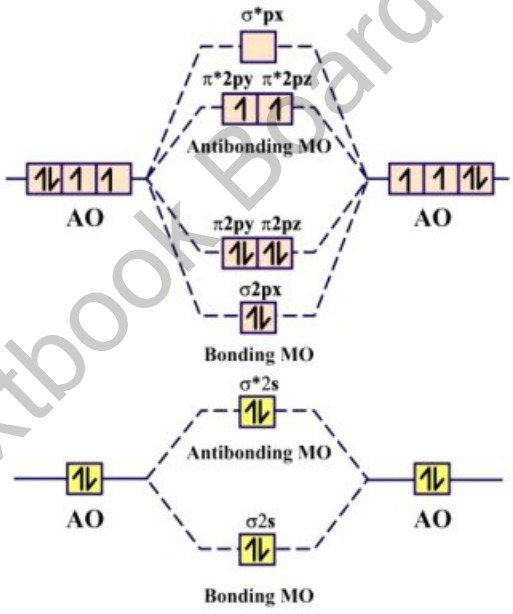

Fig 3.3: Molecular orbital energy diagram of O_2 molecule

Self Assessment

Write the molecular orbital energy diagram of N_2 molecule and determine its bond order. Also predict whether it is paramagnetic or diamagnetic?

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Valence Bond Theory	Molecule Orbital Theory
Valence Bond theory tells that only some valence electrons are involved in the bond formation.	Molecular orbital theory tells that bond formation occurs due to the involvement of all the valence electrons of interacting atoms.
According to valence bond theory, both the concerned atomic orbitals possess their individual identity.	According to the molecular orbital theory, both the concerned atomic orbitals donot possess their individual identity.
VBT doesn't introduce any adequate idea about the bond order.	MOT gives adequate idea about the bond order by virtue of which, the bond can be identified as single, double or triple bond.
The paramagnetic behavior of molecules such as oxygen molecule (O_2) cannot be explained by valence bond theory.	The paramagnetic behavior of molecules are very well explained using molecular orbital theory.

3.2 SHAPE OF THE MOLECULES

Simple poly atomic molecules and ions generally acquire linear, tetrahedral, pyramidal and angular shapes etc. These shapes can be determined experimentally, however also predicted on theoretical basis. Beside VBT there are two more significant theories which describe the shape of molecule.

(i) Valence shell electron pair repulsion theory (VSEPR)
(ii) Hybridization

3.2.1 Valence Shell Electron Pair Repulsion Theory (VSEPR)

This approach to the structure of a covalent molecule is due to sidgwick and powell (1940). They pointed out that the shapes of molecules can be determined by the repulsion between the electron pairs present in valence shell of central atom.

The main postulates of this theory are:

1. There may be two types of electron pairs surrounding the central atom.
   (a) Bond Pairs: These are the result of the sharing of unpaired electrons of central atom with unpaired electrons of surrounding atoms. These are also called active set of electrons.
   (b) Lone Pairs: These are the paired electrons of central atom which do not take part in sharing. They are also called non-bonding pairs. They are also considered to be active set of electrons.
2. Being similarly charged (i.e. negative) the bond pairs as well as the lone pairs repel each other.
3. Due to repulsion, the electron pairs of central atom try to be as far apart as possible; hence they orient themselves in space in such a manner that force of repulsion between them is minimized.

Do You Know?

Multiple bond (double and triple) is treated as single bond in VSEPR because π bonds do not alter the basic idealized geometry of a molecule.

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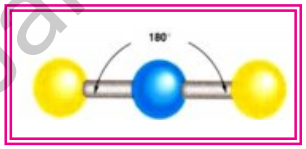
4. The force of repulsion between lone pairs and bond pairs is not the same. The order of repulsion is as follow.
   Lone pair-Lone pair repulsion > Lone pair-Bond pair repulsion > Bond pair-Bond pair repulsion.
5. In case of molecules with double and triple bonds, the π electron pairs are not considered to be an active set of electrons, hence not included in the count of total electron pairs.
6. The shape of molecule depends upon total number of electron pairs (bonding and lone pairs).

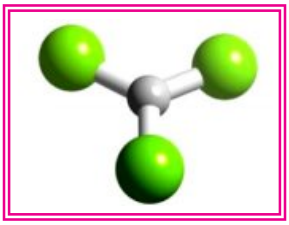
Prediction of Five Basic Shapes by VSEPR

Linear Shape



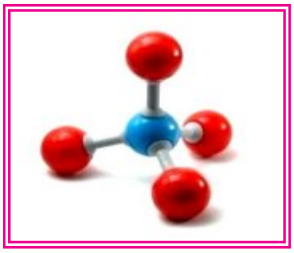
This shape is found in AX_2 type molecules in which the central atom (A) contains two bond pairs only. The equal repulsion of these two bond pairs of electrons extend the corner atoms (X) at 180° angle and makes linear shape.
Example of molecules having linear geometry are $BeCl_2$, C_2H_2, CO_2 etc.

Trigonal Planer Shape



This shape is found in AX_3 type molecules where the central atom (A) possesses only three bond pairs of electrons. The equal repulsion of these bond pair electrons orient the three corner atoms (X) at 120° and the geometry thus developed is trigonal planar.
Examples of some molecules which acquire trigonal planar geometry are BF_3, C_2H_4, $AlCl_3$ etc.

Tetrahedral Shape



Molecules which have tetrahedral shape are categorized into AX_4 type. Here the central atom (A) contains four paired electrons. The repulsion of these four electron pairs directed the four X atoms towards the corner of a tetrahedron. The angle settled in this type of repulsion is 109.5°.
Examples are CH_4, C_2H_6 etc.

Trigonal Pyramidal Shape

This is a cone like shape with a tetrahedral base and found in the molecules of AX_3E type where A is the central atom, X are the corner atoms and E is lone pair of electron in central atom.

The central atom in this type of molecules is surrounded by three bond pairs and one lone pair of electron of its own. Since the repulsion of lone pair of electrons is more effective than bond pair electrons, a

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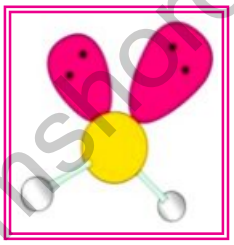
slight distortion in the tetrahedral shape occur by narrowing the angle at one side from 109.5° to 107°. It makes a pyramidal shape.
Examples are NH_3, PH_3 etc.

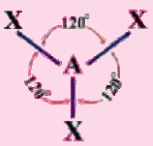
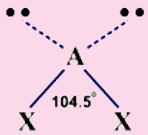
Angular Shape



Common examples of molecules having angular shape are H_2O, H_2S etc. This is an AX_2E_2 type shape in which A is central atom, X are two corner atoms and E_2 are two lone pair of electrons present in central atom.

There are two bond pair and two lone pair electrons around the central atom which initially makes a tetrahedral geometry in which two ends of tetrahedron are filled with two lone pairs and the other two corners occupied by bond pairs. Since the lone pair repulsion is greater than bond pair repulsion, the two bond pairs deviate from the lone pair and come near to each other at 104.5°. This makes a distortion in the tetrahedral geometry and develops an angular shape.

Table 3.2 Shape of molecule according to VSEPR theory

Type	Active Electron pair	Bond Pairs	Lone Pairs	Molecular Geometry	Shape	Examples
AX_2	2	2	0	Linear		$BeCl_2$ CO_2
AX_3	3	3	0	Trigonal Planar		BF_3 $AlCl_3$ BH_3
AX_4	4	4	0	Tetrahedral		CH_4 $SiCl_4$ CCl_4
AX_3E	4	3	1	Trigonal Pyramidal		NH_3 NF_3 PH_3
AX_2E_2	4	2	2	Angular or Bent		H_2O H_2S

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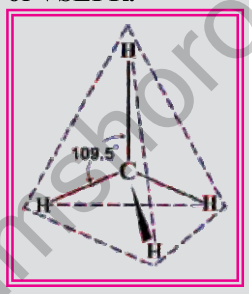
Example 3.1

Predict the shape of CH_4, NH_3, H_2O and CO_2 molecules on the basis of VSEPR.

CH_4 – molecule

We begin by drawing a Lewis structure to determine the number of electron pairs around the central atom.

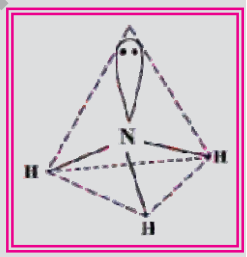
No. of Bond pair electrons = 4
No. of Lone pair electrons = 0
According to VSEPR, these four electron pairs repel to each other and directed towards the corner of tetrahedron at an angle of 109.5° hence the geometry of molecule is **tetrahedral.**



NH_3 – Molecules

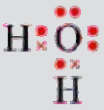
Lewis structure of NH_3 molecule is drawn as

This shows the following information
About central atom
Bond pair of electrons = 3
Lone pair of electrons = 1
According to VSEPR, the repulsion of lone pair is stronger which reduce the bond angle from 109.5° to 107°.
Hence the predicted shape of NH_3 molecule is trigonal pyramidal

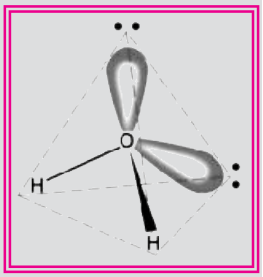


H_2O – Molecule

Lewis structure of H_2O molecule is drawn as

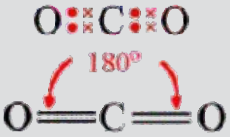


Electronic information around the centre atom is given as
No. of Bond pair electrons = 2
No. of Lone pair electrons = 2
The repulsion of two lone pair electrons reduces the bond angle from 109.5° to 104.5°.
Hence the shape of H_2O molecule is Angular



CO_2 – Molecule

The Lewis structure of CO_2 molecule is drawn as



This shows that two sigma and two pi bond exists in the molecule. According to VSEPR theory pi bond are not involved in the repulsion and geometry because these are inactive electron pairs. Since only two active electron pairs are found around the carbon atom, its shape is Linear.

Do You Know?

In many molecules, there are more than one central atoms. In these molecules we analyze one central atom at a time to determine the active sets of electron and to predict the geometry of molecule.
For example: in ethene molecule we first considered the left hand carbon atom to analyze the geometry of molecule then we carry out a similar analysis for right hand carbon atom.

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Self Assessment

According to VSEPR model, what molecular shape would you predict for
(i) BF_3 (ii) CS_2 (iii) CBr_4

3.2.2 Hybridization

Valency is generally regarded as the number of unpaired electrons in the valence shell of an atom. However, this rule is disregarded in some cases such as Beryllium, Boron, Carbon etc.

In terms of unpaired electrons beryllium would be expected to behave as an inert gas (valency = 0), boron might be expected to be mono valent (valency = 1) and carbon would be divalent (valency = 2). In actual practice, however, Be, B and C are divalent, trivalent and tetravalent respectively.

To account for the valency of such elements, it is assumed that some of the paired electrons are uncoupled and promoted to the orbital of slightly higher energy within the same orbit before the atoms form chemical bonds. The promotion will require an input of energy but such energy will be available from the heat of reaction when additional covalent bonds are formed. The arrangement of electrons after promotion is referred to as an excited state.

Table 3.3 Ground state and excited state configuration of Beryllium, Boron & Carbon

Elements	Atomic No.	Ground state	Excited state
Be	4	$1s^{1\downarrow}\ 2s^{1\downarrow}\ 2px\ 2py\ 2pz$	$1s^{1\downarrow}\ 2s^{1}\ 2px^{1} 2py\ 2pz$
B	5	$1s^{1\downarrow}\ 2s^{1\downarrow}\ 2px^{1} 2py\ 2pz$	$1s^{1\downarrow}\ 2s^{1}\ 2px^{1}\ 2py^{1}\ 2pz$
C	6	$1s^{1\downarrow}\ 2s^{1\downarrow}\ 2px^{1}\ 2py^{1}\ 2pz$	$1s^{1\downarrow}\ 2s^{1}\ 2px^{1}\ 2py^{1}\ 2pz^{1}$

Linus pauling settled this disparity by suggesting the idea that the atomic orbital having nearly equal energies can be mixed in various ways within an atom to form equivalent hybrid orbital. **"The mixing of different atomic orbital to produce the same number of equivalent orbital, having same shape and energy is known as hybridization"**. The orbitals so formed are called hybrid orbital and are designated according to the number of mixing orbitals.

Table 3.4 Types of hybridization due to mixing of s and p orbitals

Mixing Orbital	No. and type of Hybrid orbital produced	Type of Hybridization	S Character %	P Character %
One **s** and three **p**	Four sp^3 orbitals	sp^3	25	75
One **s** and two **p**	Three sp^2 orbitals	sp^2	33.33	66.66
One **s** and one **p**	Two sp orbitals	sp	50	50

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sp^3 Hybridization:

"Combination of one s and three p orbitals to produce four sp^3 hybrid orbitals is known as sp^3 or tetrahedral hybridization". The hybrid orbitals are different than the pure **s** or **p** orbitals; they possess the character of both **s** and **p** orbital in the ratio of 1:3. These sp^3 orbitals are directed towards the four corners of regular tetrahedron in which each angle is 109.5°.

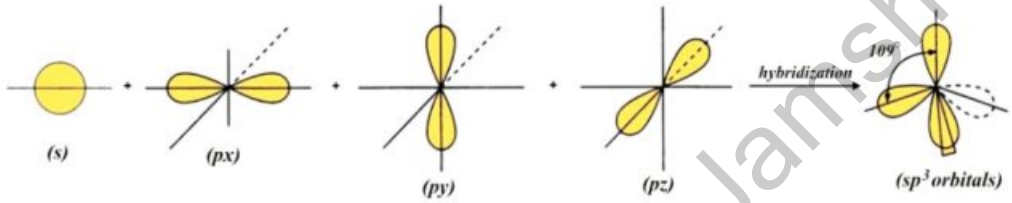
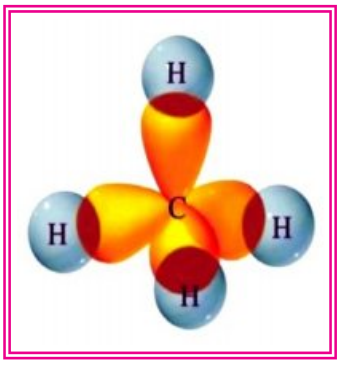


Fig 3.4: Mixing of 2s, 2px, 2py and 2pz orbital to produce four sp^3 hybrid orbitals

Methane Molecule (CH_4)



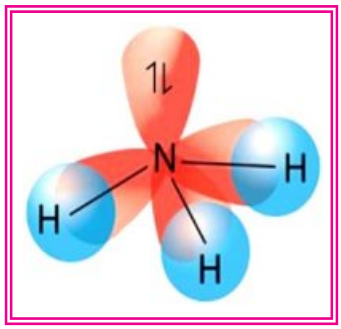
The electronic configuration of carbon is ($1s^2$, $2s^2$, $2px^1$, $2py^1$, $2px^0$) but it is assumed that one electron of 2s orbital get promoted to 2pz orbital to make it tetravalent.

C (z = 6) $1s^2$, $2s^1$, $2px^1$, $2py^1$, $2pz^1$ (tetravalent)

In methane, the four atomic orbital of carbon undergo a mixing process to produce four new orbital of equal energy and shape, each named as sp^3 hybrid orbital.

All four sp^3 hybrid orbital then directed towards the corner of a regular tetrahedron at an angle of 109.5°. Since each sp^3 hybrid orbital has one electron, it overlaps with 1s orbital of hydrogen atom. Thus four C–H sigma bonds are formed.

Ammonia Molecule (NH_3)



The electronic configuration of Nitrogen is $1s^2$, $2s^2$, $2px^1$, $2py^1$, $2pz^1$. Thus according to the concept of hybridization one **s** and three **p** orbital of the valence shell of nitrogen undergo the process of mixing to give four **sp^3** hybrid orbital which are directed towards the four corners of tetrahedron.

Out of four hybrids orbital three have single electrons hence they overlap with s-orbital of hydrogen and form three (N-H) sigma bonds. The fourth **sp^3** orbital which has lone pair of electron remains unbonded. The stronger repulsion of this orbital deviate the bond angle from 109.5° to 107° and give rise to a pyramidal geometry.

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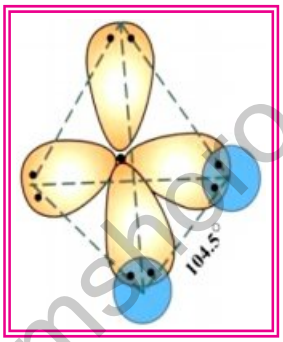
Water Molecule (H_2O)



The electronic configuration of oxygen is $1s^2$, $2s^2$, $2px^2$, $2py^1$, $2pz^1$. The four outer shells orbitals are assumed to be mixed together which results in the formation of four new sp^3 hybrid orbitals which are directed at the corner of tetrahedron.

Since only two sp^3 orbitals possess single electrons, they overlap with s-orbital of hydrogen to form two O–H sigma bonds. The remaining two sp^3 hybrid orbital contain lone pair of electrons.

Because the repulsion of lone pair is greater than bond pair, the shape of water molecule is not regular tetrahedron. The distortion of bond angle from 109.5° to 104° makes an angular geometry.

sp^2 – Hybridization:

"The mixing of one s and two p orbital to produce three sp^2 hybrid orbital is referred to as sp^2 (trigonal hybridization)". These orbitals are co-planar and directed towards the corners of an equilateral triangle (trigonal) at angle of 120° to each other. **sp^2** orbital are different than either **s** or **p** orbital and they are considered to have a character that is one third **s** and two thirds **p**. The fourth **p** atomic orbitals which is not involved in hybridization remains unhybridized at right angle to the plane of the **sp^2** orbitals.

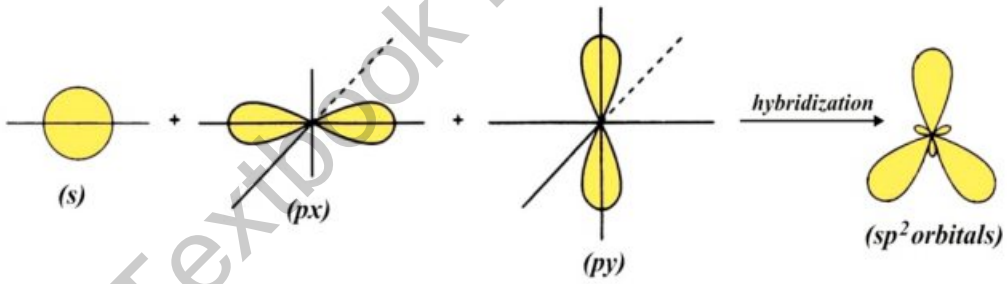


Fig 3.5: Mixing of s, px and py orbitals to produce three sp^2 hybrid orbitals

sp^2 hybridization provides a good model for describing the geometry of the molecules which contain carbon bonded to only three other atoms or groups, such as ethylene (C_2H_4) or Boron trifluoride (BF_3).

Boron Trifluoride Molecule (BF_3)

The electronic configuration of Boron in ground and excited state is given as

	1s	2s	2px	2py	2pz	
	1↓	1↓	1			(Ground state)
	1↓	1	1	1		(Excited state)

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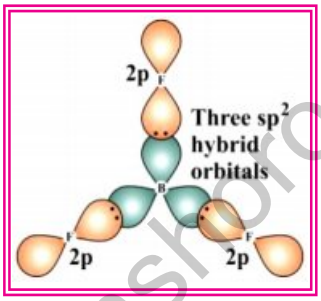
One half filled **s** orbital and two half filled **p** orbital undergo the process of hybridization to produce three sp^2 hybrid orbitals. These three sp^2 hybrid orbitals lie in the same plane (coplanar) with an angle of 120° and make a planer triangular geometry.

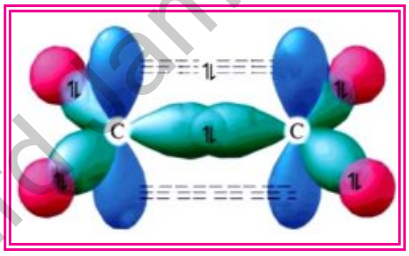
These three sp^2 orbitals of Boron then overlap with three **p** orbital of different fluorine atoms.



Ethene molecule (C_2H_4)

Ethene molecule consists of two central carbon atoms. Each carbon possesses three sp^2 hybrids orbital and one unhybrid pz orbital.

These three sp^2 hybrid orbital arrange themselves in triangular planar geometry at 120° angle. Two sp^2 orbitals of each carbon then overlap with s orbitals of two hydrogen atoms to form two C-H sigma bonds. The third sp^2 orbital of both carbon atoms overlap linearly with each other to form a C-C sigma bond. The unhybrid pz orbital of both carbon atoms which lie at right angle overlap side wise to form a pi bond.



sp Hybridization:

The hybridization of one **s** and one **p** atomic orbital leads to two hybrid orbitals known as **sp** hybrid orbital. These orbitals are co-linear at an angle of 180° which provides maximum separation and overlap. Each sp hybrid orbital has 50% s character and 50% **p** character (1:1 ratio). The other two **p** orbitals remain unhybridized and are oriented at the right angles to each other and to the plane of hybrid orbitals.

Do You Know?

s-character in sp^3, sp^2 and sp hybridization is 25%, 33% and 50% respectively. The greater the s-character the more close the electron to the nucleus and the stronger the bond. Thus sp hybridized orbital form relatively stronger bond.

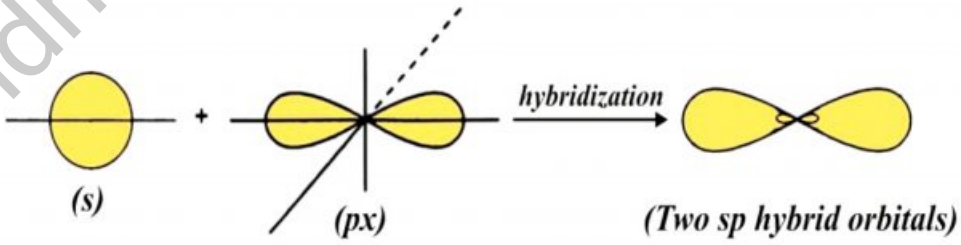


Fig 3.6: Mixing of one s and one px orbitals to produce two sp hybrid orbitals

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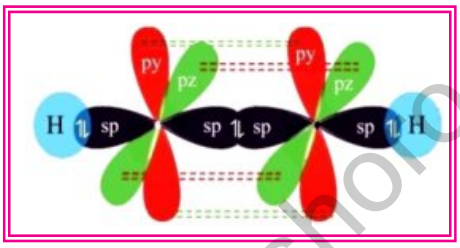
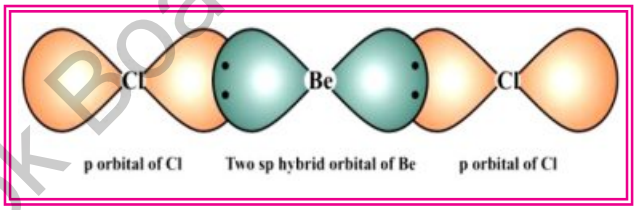
Ethyne Molecule (C_2H_2)



The type of hybridization in each carbon atom of ethyne is **sp** where as only **s** and **px** orbitals involve in the mixing process while the **py** and **pz** orbitals remain unhybridized. The two **sp** orbitals are inclined to each other at 180° angles where as the two unhybrid orbitals (**py** and **pz**) lie at right angle to the hybrid orbital as well as to each other. The two hybrid orbitals (**sp**, **sp**) and the two atomic orbitals (**py** and **pz**) contain single electron.

Each carbon utilizes its one **sp** orbital to overlap with **s** orbital of hydrogen while other **sp** orbital is involved in sigma bonding between the two carbon atoms. Thus overall three sigma bonds are formed at 180° angles which makes linear geometry. The unused **p** orbital lying parallel to each other undergoes side wise overlapping to form two pi bonds. One sigma and two pi bonds between the carbons atoms of ethyne molecule is identified as triple bond.

Beryllium Chloride ($BeCl_2$)



The excited state electronic configuration of Beryllium is $1s^2$, $2s^1$, $2px^1$, 2py, 2pz indicates that 2s and 2px orbitals of Beryllium should involve in the mixing process and hence the result is the production of two **sp** hybrid orbitals. Two **sp** hybrid orbitals of Beryllium overlap with p orbitals of two chlorine atoms in straight line at 180° angle. The linear geometry of molecule is due to the maximum repulsion of two electron pairs.

3.3 BOND CHARACTERISTICS

There are various characteristics of a chemical bond such as bond length, bond energy, bond order, dipole moment etc. All of these describe the strength and stability of bond.

3.3.1 Bond Energy

The formation and decomposition of chemical bond are two opposite processes, both associated with energy change. Bond formation is exothermic process and bond breaking is endothermic process. **"The energy involved for the breaking / formation of 1 mole of particular type of bonds in the molecule is known as bond energy"**. Alternatively the bond energy might be taken as energy released in the formation of a bond from its free atoms. It is important to note that the measurement of energy in bond dissociation is more accurate than the bond formation, thus the bond energy is generally considered as bond dissociation energy and written in term of positive sign. Since chemical reactions take place at constant pressure, the term enthalpy is often used. It is the energy required in KJ for the breaking of one mole bonds in the given sample of reactant.

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$$O_{2(g)} \longrightarrow O_{(g)} + O_{(g)} \ (\Delta H = +495 \text{ KJ/mol})$$
$$O_{(g)} + O_{(g)} \longrightarrow O_{2(g)} \ (\Delta H = -495 \text{ KJ/mol})$$

Comparison of bond energy with bond strength

Bond energy is very useful tool in determining the strength of a bond and hence help in understanding chemical reactivity. Bond energy and the strength of bond can be predicted on the basis of molecular polarity, radii of bonded atoms and the bond order.

(i) Polarity of molecule

The value of bond energy in diatomic molecule depends upon whether the molecule is homo diatomic or hetero diatomic. The bond energy of hetero diatomic molecule is relatively higher since atom lie closer due to the presence of ionic character on the bonded atom.

$$HCl_{(g)} \longrightarrow H_{(g)} + Cl_{(g)} \ (\Delta H = 431 \text{ KJ/mol})$$
$$Cl_{2(g)} \longrightarrow Cl_{(g)} + Cl_{(g)} \ (\Delta H = 242 \text{ KJ/mol})$$

In the above atomization processes, we noted that the bond energy of HCl is higher due to polarity in the molecules.

(ii) Size of the bonded atoms

The value of bond energy can be correlated with the size of atoms. Two atoms of smaller size are bonded more strongly due to short inter nuclear distance thus they can be broken if high energy is provided. For example,

$$H_{2(g)} \longrightarrow H_{(g)} + H_{(g)} \ (\Delta H = 436 \text{ KJ/mol})$$
$$Cl_{2(g)} \longrightarrow Cl_{(g)} + Cl_{(g)} \ (\Delta H = 242 \text{ KJ/mol})$$

The high bond energy is due to smaller size of hydrogen atoms. Thus not only the polarity but also the size of atoms in the molecule involve in bond energy.

(iii) Presence of multiple bonds

Generally molecules with multiple bonds require high bond energy for the dissociation. Consider the bond energies involve in carbon – carbon bond breaking.

C – C (348 KJ/mol)
C = C (614 KJ/mol)
C ≡ C (839 KJ/mol)

This shows that the greater the number of bonds between two atoms, the higher the bond energy. It may be noted that the bond energy of C = C is not exactly double to that of C – C and similarly the bond energy of C ≡ C is not exactly three times higher. The reason is that double bond between the two atoms express one sigma and one pi bond. Since the pi bond is relatively weak and requires less energy for the breaking, the same reason is for C ≡ C.

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Table 3.5 Average bond energies of some single and multiple bonds (KJ/mol)

Single Bond	Bond Energy (KJ/mol)	Multiple Bond	Bond Energy (KJ/mol)
H – H	436	C = C	614
Cl – Cl	242	C = N	615
C – C	348	C = O	799
C – H	413	O = O	495
H – Cl	431	S = O	523
H – F	567	C ≡ C	839
H – O	463	N ≡ N	941
H – N	391	C ≡ N	891

Self Assessment

(i) What are the various parameters which correlate bond energy with bond strength?
(ii) Why is the bond energy of multiple bond greater than single bond?

3.3.2 Bond Length

Molecule is the combination of atoms and formed by mutual sharing of electrons. Atoms in a molecule are located at a certain distance to balance the attractive and repulsive forces between nucleus and electrons. **"The distance between the nuclei of two bonded atoms in a molecule is known as bond length"**. Since the bonded atoms are always in vibrational motion due to their kinetic energy, precise bond length cannot be determined and hence we take the average of the bond length. Bond length is experimentally determined by x-ray diffraction technique. Bond length is a very small distance and the unit use for its measurement is Angstrom (Å) which is equal to 10^{-10}m.

Bond length is a characteristic of bond which describes the strength of bond. The shorter the bond length the stronger is the bond. We can mainly correlate the bond length with the following two parameters.

(i) Bond order: The greater the number of bonds between the two atoms, the shorter the bond length. For instance, the bond length in C ≡ C is shortest than C = C and C–C.

(ii) Bond polarity: The bond length between two different atoms is generally higher than similar atoms and its value depends upon the extent of polarity. For example bond length of H – Cl (1.27Å) is shorter than Cl – Cl (1.99Å).

Do You Know?

A covalent radius is the half of bond length between the nuclei of two identical atoms which are bonded through single covalent bond.

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Table 3.6 Bond length and bond energies of some bonds

Covalent Bond	Bond Length	Bond Energy
C – C	1.54 Å	348 KJ mol^{-1}
C = C	1.34 Å	614 KJ mol^{-1}
C ≡ C	1.20 Å	839 KJ mol^{-1}
Cl – Cl	1.99 Å	242 KJ mol^{-1}
O = O	1.21 Å	495 KJ mol^{-1}
N ≡ N	1.10 Å	941 KJ mol^{-1}

3.3.3 Ionic Character of Covalent Bond

When two different atoms having different electronegativities unite through covalent bond, a partially positive charge produced on less electronegative atom and a partially negative charge on high electronegative atom. The molecule now said to be polar bearing ionic character on its two oppositively charge poles and the bond exist between the two atoms is known as polar covalent bond.

Let consider the example of hydrogen chloride. The electronegativity of hydrogen (2.1) is less than chlorine (3.0), therefore shared electron pair is more shifted towards chlorine atom which results in appearing an ionic character on the covalent molecule.

Since ionic character of coval ent bond is mainly depends upon electronegativity difference between the two joined atoms, the strength of polar bond can be attributed by taking E.N difference as a primary tool. However size of the atom and bond length is also influencing factors for the bond strength. The electronegativities of some common elements in their relative order are given as.

H < I < C & S < Br < N & Cl < O < F
(2.1) (2.4) (2.5) (2.8) (3.0) (3.5) (4.0)

Do You Know?

Bond energy, bond length and bond order are three essential bond parameters which describe the strength of covalent bond.

When the difference of E.N of the two atoms is almost same then relative size of atoms decide the strength of ionic character.

Table 3.7 Percent polarity in some common bonds

Bond	EN Difference	Ionic Character
Cl – Cl	0	0
H – F	1.9	43%
H – Cl	0.9	17%
H – Br	0.7	12%
H – I	0.3	6%
C – H	0.4	4%
O – H	1.4	39%
C – Cl	0.5	10%

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Self Assessment

Compare the bond strengths of
(i) Sigma and pi bond (ii) Polar and Non polar molecule

3.3.4 Dipole Moment

We have learnt in previous section that when a molecule is assembled by two atoms of different electronegativities, a partially positive and negative charge create on the two ends. The net magnitude of this positive and negative charge in a diatomic molecule is equal and thus the molecule is electrically neutral and said to be dipole. Dipole moment is a measuring scale use for the degree of polarity of polar bond. It defines as **"The product of magnitude of charge and the distance between positive and negative centers"**. The net molecular moment is indicated by (→) since dipole moment is a vector quantity.

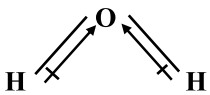
Dipole moment = q . d

It is noted experimentally that the charge (q) is of the order of 10^{-10}esu and the distance between positive and negative centre (d) is in the range of 10^{-8}cm. Therefore dipole moment of all polar molecules found in the limit of 10^{-18}esu.cm. This quantity is known as Debye (D) after the name of introducer (Peter Debye).

1 Debye = 1×10^{-18} esu.cm
The S.I unit of Dipole moment is Coulomb meter (Cm). The inter relation between Debye and columb meter is written as
1 D = 3.336×10^{-30}Cm

Molecular polarity and the shape of molecules

Dipole moment of a molecule depends not only upon the polarity of its bonds but it also depends upon the geometry of molecule. For example H_2O and CO_2 both contain polar bonds but the angular structure of H_2O results in a dipole moment of 1.85D and said to be polar molecule. CO_2 on the other hand has zero dipole moment. Although both (C = O) bond in CO_2 are polar but directed equally on the opposite side at 180° angle making a linear geometry thus the molecule is non polar.



(μ = 1.85D)

(μ = o)

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Table 3.8 Dipole moment of some common substances in Debye

Compound	Dipole moment (D)	Compound	Dipole moment (D)
H_2O	1.85	CH_3Cl	1.45
NH_3	1.49	C_2H_5OH	1.69
HCl	1.03	CO_2	0.00
HBr	0.78	CS_2	0.00
HI	0.38	CH_4	0.00
H_2S	0.95	H_2	0.00

Self Assessment

Which of the following molecules have dipole moment? In each case give a reason for your answer.

$CHCl_3$, SCl_2, H_2O, CO_2

3.4 EFFECT OF BONDING ON PHYSICAL AND CHEMICAL PROPERTIES

The nature and strength of bond affect on various physical and chemical properties of a substance such as solubility, melting point, boiling point, rate of reaction etc.

3.4.1 Solubility of Polar and Non Polar Covalent Compounds

It is well established that certain substances dissolve in liquid solvent while others are not. The criteria for deciding of solubility is to know whether they are polar or non polar. Many organic compounds are non polar in nature and cannot be dissolved in water however soluble in organic solvents. The solubility of covalent compound depends upon chemical nature of solvent and the substance to be dissolved.

(i) Solubility of polar substance in polar solvent

Polar covalent molecule is as a whole neutral but it possesses partially positive and negative charge on its two ends. Thus when it is added into a polar solvent a dipole–dipole interaction is developed among, solute-solvent and particles which makes it soluble.

We know that sugar is easily dissolved in water. This is due to the fact that several O – H bond in sugar molecule bear partially positive and negative charge on them. These polar areas of sugar molecule interact with positive and negative poles of water molecules to form hydrogen bonds. Due to this interaction sugar is soluble in water.

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(ii) Solubility of non polar substance in polar solvent

Non polar covalent molecules do not dissolve in polar solvent. For example when benzene put into water, it does not dissolve and form two layers. The reason is that benzene is non polar whereas water is polar in nature. Thus the positive and negative poles of water behave hydrophobically with benzene and not allow to dissolving it.

(iii) Solubility of non polar substance in non polar solvent

Non polar covalent molecules dissolve in non polar solvent on the basic principle that like dissolves like due to London forces. For example oil is dissolved in hexane because both are non polar. Since interaction among the particles of both oil and hexane are weak and comparable thus on dissolution, the attractive forces of solvent are enough for overcoming the attractive forces among oil molecules hence it dissolves.

3.4.2 Reactions of Polar and Non Polar Covalent Compounds

Chemical reactions take place by the breaking of existing bonds and the formation of some new bonds. Breaking of bond requires energy. The stronger the bond in the reactant molecule the higher the energy needed for their breaking. Since the atoms in the polar covalent molecule are held more firmly, so high bond dissociation energy is required to proceed the reaction. The feasibility of a chemical reaction is determined by having the information of bond energy required to break the total number of reactant molecules and the bond energy release in bond formation in total number of product molecules.

Society, Technology and Science

Disulphide bond and Hydrogen bond in straight and curly hairs

Hairs are composed of a type of protein known as keratin. In the structure of keratin many amino acids (cystein) link to each other by permanent disulphide bonds. The distance between sulphur atoms cause hairs to curl. The greater the distance among sulphur atoms, the more keratin molecule bend and more our hair curls.

Another type of connection among neighbors' amino acid chains is hydrogen bond which is much weaker and temporary. This hydrogen bond is affected by water. In humid day, moisture of atmosphere breaks hydrogen bond of hair and makes the hair ruin.

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Activity

This activity will enable you to understand the solubility of a liquid in another liquid. Take two test tubes and put few drops of cooking oil in both of them. Now add water in first test tube and petrol in the second one and shake both of them vigorously. You'll find that oil doesn't dissolve in water but in petrol it does. The reason is that oil is a non-polar organic liquid; it doesn't dissolve in water since it is polar in nature while it dissolves in petrol due to its non-polar nature.

SUMMARY with Key Terms

- **Valence Bond Theory** tells that covalent bond is formed by the overlapping of atomic orbital in which the shared pair of electron is localized between the two nuclei.
- **Molecular orbital theory** tells that when two atomic orbitals combine to form two molecular orbitals. One molecular orbital has lower energy than other orbital and known as bonding M.O. Other molecular orbital has higher energy than atomic orbital and known as anti bonding M.O.
- **Sigma bond** is formed by head to head overlapping of atomic orbital. It exists in s-s, s-p, p-p etc.
- **pi bond** is formed by the side way overlapping of atomic orbital (py-py and pz-pz). It is relatively weaker than sigma bond.
- **Hybridization** is the mixing of atomic orbital to produce equal number of same energy orbitals. It is of various type such as sp^3, sp^2, sp etc depending upon the number and type of orbital involved in the mixing.
- **Electron pair repulsion theory** describe the shape of simple covalent molecules on the basis of number of active electron pairs around the central atom.
- **Dipole moment** is the product of charge and the distance between positive and negative centers. It is measured in Debye, however its SI unit is coulomb meter.
- **Bond length** is the distance between the nuclei of two bonded atoms in a molecule. It is measured in Angstrom (Å).
- **Bond energy** is the amount of energy required to break 1 mole of a particular type of bond in the molecule. It is measured in KJ/mol.
- **Ionic character** of covalent bond is the polarity of molecule produced when the electron of two unlike atoms are shared up.

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EXERCISE

Multiple Choice Questions

1. Choose the correct answer

(i) If the bond angle in AB_2 type molecule is 104.5°, it geometry should be:
(a) Linear (b) Pyramidal (c) Bent (d) Planar Trigonal

(ii) The highest bond energy in the following is:
(a) Cl – Cl (b) H – F (c) H – O (d) H – N

(iii) The molecule which has zero dipole moment is:
(a) NH_3 (b) HCl (c) H_2O (d) CCl_4

(iv) The molecule which has maximum bond angle:
(a) CS_2 (b) H_2O (c) NH_3 (d) BF_3

(v) The shape and hybridization of BCl_3 molecule is:
(a) Tetrahedral and sp^3 (b) Linear and sp
(c) Planar trigonal and sp^2 (d) Angular and sp^3

(vi) Amongst the following molecules which one has trigonal pyramidal shape?
(a) SO_2 (b) CO_2 (c) NH_3 (d) C_2H_4

(vii) A simple covalent molecule possesses two bond pairs and two lone pairs around the central atom, its shape should be:
(a) Linear (b) Planar trigonal (c) Angular (d) Tetrahedral

(viii) The correct relation between Debye and coulomb meter is:
(a) $1D = 3.33 \times 10^{-30}Cm$ (b) $1D = 1.6 \times 10^{-19}Cm$
(c) $1D = 1.88 \times 10^{-12}Cm$ (d) $1D = 1.23 \times 10^{-8}Cm$

(ix) The bond order of N_2 molecule is:
(a) 0 (b) 1 (c) 2 (d) 3

(x) The number of sigma and pi bonds in C_2H_4 molecule are respectively:
(a) 3 and 1 (b) 2 and 2 (c) 5 and 1 (d) 4 and 2

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Short Questions

1. Define the following:
   (i) Bond Energy (ii) Bond length

2. The Dipole moment of water is 1.85D but CO_2 has zero dipole moment why?

3. Differentiate between the following:
   (i) VBT and MOT
   (ii) Sigma bond and pi bond
   (iii) Bonding M.O and Anti bonding M.O

4. Explain the following with scientific reasons.
   (i) Sigma bond is stronger than pi bond.
   (ii) HF has greater ionic character than HCl.
   (iii) Bond energy of molecules possessing multiple bonds is high.

5. Oil is insoluble in water but soluble in hexane explain why?

6. Which hybridization would you expect for the central atom in each of the following?
   $BeCl_2$, BF_3, CH_4, C_2H_2

Descriptive Questions

1. (a) Write down the postulate of VSEPR theory
   (b) Predict the shape of following molecules on the basis of VSEPR theory.
   $AlCl_3$, CCl_4, PH_3, H_2S

2. What do you mean by Hybridization? Explain sp^3 hybridization in CH_4 molecule and sp^2 hybridization in C_2H_4 molecule.

3. What are the basic postulates of valence bond theory? Explain various type of overlapping lead to sigma and pi bond.

4. Draw a molecular orbital diagram of O_2 molecule and
   (i) Write down MO electronic configuration
   (ii) Determine bond order
   (iii) Explain the paramagnetic behavior

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STATE OF MATTER I: GAS

Chapter 4

Teaching Periods	Assessment	Weightage
10	1	11

Students will be able to:

- **List** the postulates of Kinetic Molecular Theory.
- **Describe** the motion of particles of a gas according to kinetic theory.
- **State** the values of standard temperature and pressure (STP).
- **Relate** temperature to the average kinetic energy of the particles in a substance.
- **Use** kinetic theory to explain gas pressure.
- **Describe** the effect of change in atmospheric pressure on the weather.
- **Describe** the significance of absolute zero, giving its value in degree Celsius and Kelvin.
- **State** and explain the significance of Avogadro's Law.
- **Derive** Ideal Gas Equation using Boyle's, Charles' and Avogadro's law.
- **Explain** the significance and different units of ideal gas constant.
- **Distinguish** between real and ideal gases.
- **Explain** why real gases deviate from the gas laws.
- **Define** and describe the properties of Plasma.

INTRODUCTION

In previous classes we studied that anything which has mass and occupies space is called matter. In universe, there are four fundamental states of matters solid, liquid, gas and plasma. Among all the four states of matter, gas has quite different behaviour. The particles of gases are not orderly arranged and have very weak attractive forces as compared to solids and liquids.

The word gas is derived from Greek Khaos which means emptiness or gap. Due to the empty spaces, gas particles move in all directions. They move in straight lines until they collide with each other or the walls of the container. Based on elemental composition gases are classified into mono atomic, diatomic and polyatomic. Helium, Neon, Argon etc are mono atomic gases where as Nitrogen, Hydrogen, Oxygen, Fluorine, Chlorine are diatomic gases. There are many poly atomic gases found in the earth such as methane, ethane, carbon dioxide etc. Air is mainly the mixture of nitrogen and oxygen gases.

Gases play significant role in our daily life. The living things (animals and plants) need oxygen for breathing, plants make food using carbon dioxide, certain industries and power stations use natural gas for their production, different vehicles use compressed natural gas as an alternative to gasoline etc. Moreover, our kitchens also rely on natural gas to a greater extent.

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4.1 KINETIC MOLECULAR THEORY OF GASES

The general behaviour and properties of all gases are similar and well explained by Kinetic molecular theory. This theory was given by Swiss mathematician Daniel Bernoulli (1738) and then extended by Maxwell and Boltzmann. Thereafter, Rudolf Clausius in 1857 derived an equation on the basis of kinetic theory of gases which provided a base for gas laws. Basically, this theory was developed in reference to ideal gases but can reasonably be applied to real gases too.

This theory explains the macroscopic properties like temperature, pressure, volume etc and transport properties like diffusion, viscosity as well.

4.1.1 Postulates of Kinetic Molecular Theory

The basic postulates of kinetic theory of gases are as follows:

(i) Gases consist of a large number of tiny particles called molecules. Molecules may be mono-atomic (He, Ne, Ar), diatomic (O_2, N_2) or poly atomic (CH_4, C_4H_{10}).

(ii) Gas molecules are far away from each other and occupy negligible volume as compared to the total volume of the container

(iii) Gas molecules are in continuous random motion, traveling in a straight line until they collide with each other or with the walls of the container. The average distance covered by the gas between successive collisions is known as mean free path.

(iv) Gas particles undergo elastic collisions (a collision in which no loss or gain of energy takes place).

(v) Gas exerts pressure when molecules collide with the walls of container.

(vi) There is no force of attraction or repulsion found among ideal gas molecules, each molecule acts as quite independently.

(vii) The average kinetic energy of gas molecules depends upon absolute temperature. Thus when absolute temperature increases kinetic energy of the molecules increases.

$$KE \propto \text{Absolue temperature}$$

On the basis of above postulates, R. J. Clausius derived a kinetic equation.

$$PV=\frac{1}{3}mN\overline{C}^{\,2}$$

Where, P = pressure

V = volume

m = mass of a single molecule of a gas

N = number of moles of gas molecules

$\overline{C}^{\,2}$ = mean square velocity of the gas molecules

Under the given conditions, the gas molecules do not possess the same velocities, instead mean square velocity is taken for the molecules in the above equation. If n_1 molecules possess c_1, velocity, n_2 molecules with velocity c_2, and so on,

then mean square velocity can be calculated as.

$$\overline{C}^{\,2}=\frac{n_1C_1^2+n_2C_2^2+n_3C_3^2+\ldots}{n_1+n_2+n_3+\ldots}$$

Where, $\overline{C}^{\,2}$ is the average of the square of all the possible velocities.

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4.1.2 Pressure and its units

The atmosphere of our planet is mixture of gases. It exerts a measurable pressure on all living and non-living objects which have existence on the earth's crust. At 0 °C on sea level our body bears a pressure of 760 torr.

The pressure of air is measured by Barometer this device consists of long glass tube filling with mercury with upper end closed. A manometer is a type of Barometer that can be used to measure the pressure of a gas enclosed in a container.

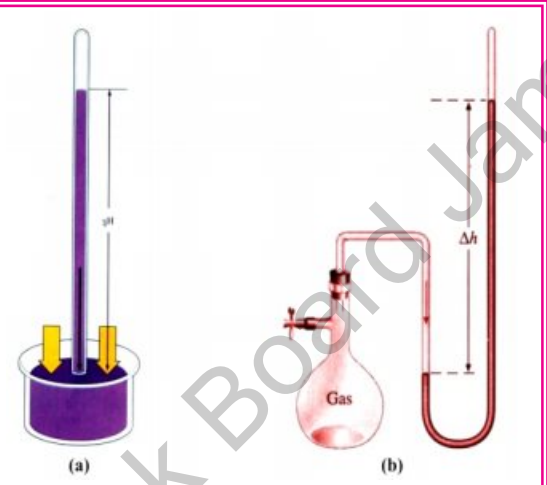

Fig 4.1: (a) Barometer (b) Manometer

We are quite familiar that when a gas is pumped into an automobile tire, it becomes hard which is due to the pressure of gas inside the tire. This pressure is due to the collision of gas molecules on the wall of tire. Blowing up a balloon provide clear evidence that gas exert pressure on the wall of its container. Thus, pressure is defined as, **"The magnitude of force that is applied on the surface of an object per unit area"**.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

According to the S.I system the unit of force is Newton and area is square meter.

Thus, the unit of pressure in SI measurement is N/m^2 which is known as pascal (Pa). Pascal is defined as, **"One Newton force that is distributed at an area of one square meter"**.

Although Pascal (Pa) is used in many scientific works but it is an in convenient size for most chemical measurements. Certain alternative units of pressure and their inter relation are given as.

101325 Pa = 1 atm = 760 mm Hg = 14.7 psi

Do You Know?

The air pressure decreases as altitude increases due to the following two facts.
(i) Gas particles of air are pulled down due to gravity and becomes more denser near earth surface.
(ii) Atmospheric depth is biggest at sea level and decreases at higher altitude.

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Example 4.1

The pressure of gas filled in automobile tire is generally measured in psi convert 32.8 psi into (i) atmosphere (ii) Kpa (iii) torr

Solution:

(i) Psi to atmosphere

Since 14.7 psi = 1 atm

$32.8 \text{ psi} = \frac{32.8}{14.7} = 2.23 \text{ atm}$

(ii) Psi to Kilo Pascal

Since 14.7 psi = 101.325 Kpa

$32.8 = \frac{101.325}{14.7} \times 32.8 = 226.085 \text{ KPa}$

(iii) Psi to torr

Since 14.7 psi = 760 torr

$32.8 \text{ psi} = \frac{760}{14.7} \times 32.8 = 1695.8 \text{ torr}$

4.1.3 Atmospheric pressure and its effect on weather

Gases such as oxygen, water vapors, nitrogen, ozone etc are very important for animals and plants and affect on Earth's atmosphere. Oxygen is used for breathing, nitrogen controls the oxidation reactions and ozone saves our atmosphere from the dangerous radiations of the sun. Similarly, the formation of clouds, temperature conditions, melting, boiling and vaporization processes are also directly related with weather conditions.

The atmospheric pressure is a thermodynamic property which is created by the mass of air molecules on the surface of earth. The size, number and nature of the molecules determine the density and temperature of the air. As the number and motion of the particles increases, atmospheric pressure increases and vice versa.

Low atmospheric pressure system is also called a depression. An area which has low pressure as compared to the surrounding is generally warmer where moist warm air rises up and cools down. This area has suffocating weather and invites winds, clouds and precipitation. Here the wind blows in anticlockwise direction. During day time there is comparatively moderate temperature while nights are warmer due to the trapping of solar radiations in cloudy weather.

The area which experiences a high air pressure as compared to surrounding is said to be in high pressure system. In such area, dry, cold and dense air moves downward to the ground. Here the wind blows in clockwise direction. Thus, clear sky and calm weather are developed.

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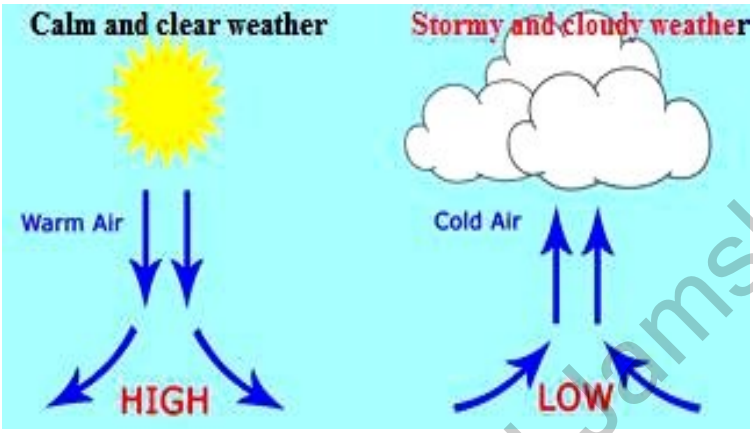

Fig 4.2: Effect of atmospheric pressure on weather

4.2 ABSOLUTE TEMPERATURE SCALE ON THE BASIS OF CHARLES LAW

Thermal energy is related to every form of matter, either matter is in condensed form or gaseous state. The measure of the hotness or coldness of a body is called temperature. Generally, temperature is measured with Celsius and Fahrenheit scales. However, there is also third scale which is known as Kelvin or Absolute scale which was introduced by Lord Kelvin (1824-1907). The temperature which is measured on this scale is known as Absolute temperature.

J. Charles showed a relationship between volume of a gas and absolute temperature while maintaining the pressure constant. According to him, when absolute temperature of a gas increases, its volume also increases because a rise of temperature increase the kinetic energy of gas molecules. This makes the molecules to move freely. As a result, the volume of a gas is increased.

4.2.1 Brief recall of Boyle's Law and Charles Law

Robert Boyle (1660 A. D) studied the effect of pressure changes on the volumes of ideal gases.

This law states as **"The volume of the given mass of a gas is inversely proportional to its pressure at constant temperature"**.

$V \propto \frac{1}{P}$ (At constant temperature)

This statement shows that if pressure of gas increases, its volume decreases with the same proportion provided that the temperature remains constant.

It is common observation that matter expands on heating and contracts on cooling. The change in volume due to expansion and contraction is very small in case of solids and liquids while gases exhibit enormous change due to the presence of large intermolecular spaces. The

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changes in volumes of gases due to the changes in temperature at constant pressure were studied by French Scientist Jacques Charles (1746-1823). He explained that the volume of given mass of a gas increases or decreases by 1/273 times of its original volume at 0°C for every degree rise and fall of temperature at given pressure. In nutshell it states that, **"The volume of given mass of a gas is directly proportional to the absolute temperature at a given pressure"**.

$V \propto T$ (At constant pressure)

4.2.2 Graphical Explantation of Absolute zero

When the graph is plotted between temperature (T) on x-axis and volume (V) on y-axis, a straight line is obtained. This straight line in upward direction shows that volume increases with the increase of temperature. If this straight line is further extended downward, it will intercept the temperature axis at –273.15°C.

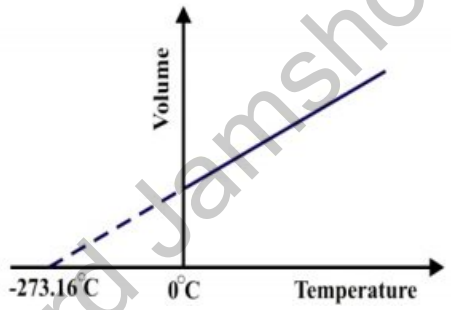

Fig 4.3: Graphical representation of the absolute zero.

According to Charles, at 0 K (-273.15°C) the volume of a gas should be zero. Actually no real gas can achieve this lowest possible temperature and before –273.15°C all gases are condensed in to liquids. Zero Kelvin is also known as Absolute zero. Absolute zero is a theoretical temperature and defines as, **"The temperature at which volume of an ideal gas becomes equal to zero"**. The concept of absolute zero cannot be applied to real gases. The inter-conversion between Celsius and Kelvin scale is given below:

$K = °C + 273$

Table 4.1: Conversion scale of Kelvin and Celsius temperature

Kelvin Scale	Celsius Scale
Kelvin = Celsius +273	
0	- 273.16
25	- 248.16
50	- 223.16
100	- 173.16
150	- 123.16
200	- 73.16
250	- 23.16
273 K	0°C

Self Assessment

Convert the following celsius temperatures into Kelvin temperatures.

(i) -12 °C (ii) 27 °C (iii) 43 °C (iv) 110 °C (v) 786 °C

4.3 AVOGADRO'S LAW

In 1811, Amedeo Avogadro, an Italian scientist, gave a relationship between volume and number of moles of gases at fixed temperature and pressure. This relationship is known as "Avogadro's Law" and defines as, **"Under the similar conditions of temperature and pressure equal volumes of all gases contain equal number of moles"**.

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Thus under similar conditions of temperature and pressure 1dm^3 any gas contains same number of molecules. We know that 1 mole of any gas at standard temperature (0 °C) and pressure (1 atm) occupies 22.4 dm^3 (**Molar Volume**) and contains 6.02 x 10^{23} molecules. It means that two or more gases having same volume must have same number of molecules and moles but different masses.

According to Avogadro's Law, **"the volume of a gas is directly proportional to the number of moles if the pressure and temperature are kept constant"**.

$V \propto n$ (At constant temperature and pressure)

Or $V = Kn$

$$\frac{V}{n} = k$$

It means that the ratio of volume to number of moles of a gas remains constant. Suppose a gas of n_1 moles is enclosed in a vessel of v_1 volume. If we insert more gas, the volume increases to v_2 hence.

$$\frac{V_1}{n_1} = k \; ; \; \frac{V_2}{n_2} = k$$

And

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Example 4.2

A cylinder contains 2.2 moles of oxygen gas at S.T.P. When more oxygen gas is pumped into the cylinder, the volume of a gas is changed from 2.0 dm^3 to 3.4 dm^3. Calculate how many moles of the oxygen gas are added to the cylinder?

Solution:

$V_1 = 2.0$ dm^3

$n_1 = 2.2$ moles

$V_2 = 3.4$ dm^3

$n_2 = ?$

Applying Avogadro's Law

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Substituting the values

$$\frac{2.0}{2.2} = \frac{3.4}{n_2}$$

$$n_2 = \frac{3.4 \times 2.2}{2.0}$$

$n_2 = 3.74$ moles

$\Delta n = n_2 - n_1$

$\Delta n = 3.74 - 2.2 = 1.54$ moles

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Self Assessment

At standard temperature and pressure 26.4 dm^3 of a gas contains 1.26 moles. If 0.25 moles are added to the gas, what will be the new volume of the gas?

4.4 IDEAL GAS EQUATION

Boyle's law, Charles's law and Avogardo's law can be combined into a single statement known as ideal gas laws or ideal gas equation This equation describes the behavior of a gas on the basis of relationship between volume and other variables like pressure, temperature and number of moles. When the values of any three of the variables **P,V,T** & **n** are known, the value of fourth can be calculated by using ideal gas equation.

4.4.1 Derivation of an ideal gas equation

According to Boyle's Law $V \propto \frac{1}{p}$ (At constant temperature)

According to Charle's Law $V \propto T$ (At constant pressure)

According to Avogadro's Law $V \propto n$ (At constant temperature and pressure)

By combining these laws we get:

$$V \propto \frac{n\,T}{P}$$

$$\text{or } V = \frac{RnT}{P}$$

And $PV = nRT$ - - - - (i)

Where, R is general gas constant.

For one mole of a gas this equation can be written as:

$PV = RT$

$$R = \frac{PV}{T} \text{ - - - - (ii)}$$

If we change the pressure from P_1 to P_2 and temperature from T_1 to T_2, then this equation can be written as:

$$R = \frac{P_1V_1}{T_1} \text{ and } R = \frac{P_2V_2}{T_2}$$

Therefore,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \frac{P_nV_n}{T_n} - - - \text{(iii)}$$

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Example 4.3

Laughing gas (N_2O) at 30°C and 820 torr pressure occupies a volume of 10.32 dm^3. Calculate the volume that it will occupy at standard temperature and pressure.

Solution:

$T_1 = 30°C = 30 + 273 = 303k$

$P_1 = 820$ torr

$V_1 = 10.32\ dm^3$

$V_2 = ?$

$T_2 = 273k$

$P_2 = 760$ torr

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_2 = \frac{P_1V_1T_2}{T_1P_2}$$

$$V_2 = \frac{820 \times 10.32 \times 273}{303 \times 760}$$

$V_2 = 10.03\ dm^3$

Self Assessment

An steal gas cylinder has a capacity of 15.8 dm^3 and filled with 785g of Helium gas at a temperature of 20°C. Calculate the pressure of Helium in the cylinder (mol. mass of Helium = 4 g/mol).

4.4.2 Gas constant and its units

Equation (ii) reveals that gas constant is the ratio of the product of pressure and volume to the absolute temperature. Its numerical value can be determined at STP.

(a) Value of R when pressure is in atmosphere and volume in dm^3.

We know that one mole of an ideal gas at S.T.P (one atmosphere pressure and 273 K) occupies 22.4 dm^3.

$$R = \frac{PV}{nT}$$

$$R = \frac{1 \text{ atmosphere} \times 22.4\ dm^3}{1 \text{ mole } 273k}$$

$R = 0.0821\ atm\ dm^3\ mole^{-1}\ K^{-1}$

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(b) Value of R when pressure is in N/m^2 and volume in m^3 (S.I unit):

According to the S.I system, pressure is measured in N/m^2 and volume in m^3:

since 1 atm = $101325 N/m^2$

And 1 dm^3 = 0.0224 m^3

$$R = \frac{PV}{nT}$$

$$R = \frac{101300 \times 0.0224}{1 \text{ mol} \times 273}$$

$R = 8.31 Nm\ mol^{-1}k^{-1}$

$R = 8.31\ J\ mol^{-1}\ k^{-1}$ (Because 1 Nm = 1 J)

Since 1 cal = 4.18 J, therefore the value of R may also be written as

$R = 1.99\ cal\ mol^{-1}\ K^{-1}$

Application of Ideal gas equation

Ideal gas equation is used to determine the molecular mass and density of gases.

(a) Molecular mass of the gas

As we know Moles = $\frac{\text{Given mass (m)}}{\text{molar mass (M)}}$

Now put this value of number of moles in equation (i)

$$PV = \frac{m}{M}RT \text{.....(iv)}$$

$$MPV = mRT$$

$$M = \frac{mRT}{PV} \text{.....(v)}$$

This equation is used to calculate the molecular mass of a gas.

(b) Density of the gas

By manipulating eq. (iv) we get

$$PM = \frac{m}{V}RT$$

Since d= m/V, therefore PM = dRT

Thus, $d = \frac{PM}{RT}$ .....(vi)

This equation is used for the determination of density of a gas. This equation indicates that density is directly proportional to pressure and molecular mass inversely proportional to absolute temperature.

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Example 4.4

Calculate the density of oxygen gas at 45 ºC when the gas is confined in cylinder at 1.54 atmospheric pressure.

Solution:

d = ?

T = 45°C = 45 + 273 = 318 K

P = 1.54 atm

R = 0.0821 atm dm^3 mol^{-1} K^{-1}

M_{O2} = 32 g mol^{-1}

The formula of density derived from general gas equation is given as

$$d = \frac{PM}{RT}$$

By substituting the values, we get

$$d = \frac{1.54 \times 32}{0.0821 \times 318}$$

$d = 1.889$ g/dm^3

Self Assessment

A chemist has synthesized a gas and find that its density is 1.88 g/dm^3 at 27°C and 1 atm pressure. Calculate its molar mass.

4.5 DEVIATION FROM IDEAL GAS BEHAVIOUR

A gas which strictly obeys gas laws (Boyle's law, Charles's law etc) or general gas equation (PV = nRT) under all conditions of temperature and pressure and behaves according to the kinetic molecular theory is known as an ideal gas. Actually none of the known gases exactly follow the ideal gas laws and called as real gases.

Real gas shows deviation from gas laws particularly at high pressure and low temperature. Therefore when the temperature of gas is lowered the attractive forces become significant, eventually the gas liquefies. This property of real gas causes deviate them from ideal behavior.

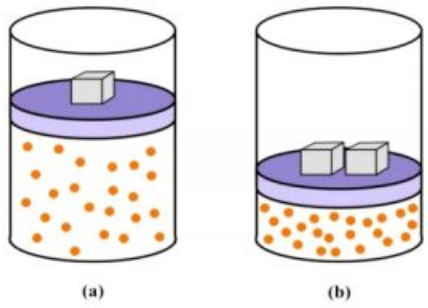

Fig 4.4: Effect of pressure on the volume of gas.

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4.5.1 Graphical explanation of deviation of real gases

To understand the attitude of real gases graphically, the general gas equation should be amended as.

$PV = Z(nRT)$ or $Z = \frac{PV}{nRT}$

Where Z is called as compressibility factor, its value is unity for an ideal gas, less than 1 for real gas showing negative deviation and more than unity for real gases showing positive deviation.

The graph plotted between Z and P for an ideal gas and various real gases provides the following information.

(i) All gases reaches a value z = 1, when the pressure approaches to zero. This reveals that all gases tend to act like ideal gas at very low pressure.

(ii) The extent of deviation of real gases from ideality is based on pressure, temperature and the nature of gases.

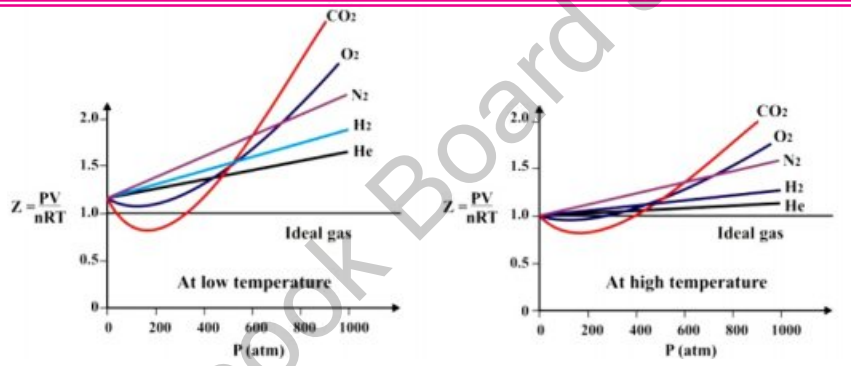

Fig 4.5: Deviation of real gases from ideality (a) at low temperature (b) at high temperature

4.5.2 Causes of deviation of real gases from ideal behaviour

To analyze why real gases deviate from ideal behavior, we should know the basics on which the ideal gas equation was formulated. The ideal gas equation was obtained from certain assumptions of kinetic molecular theory; two main assumptions are given below.

(i) The actual volume of the gas molecules is negligibly small as compared to the total space of the container.

This assumption remains valid at low pressure where the volume of gas is much larger due to large intermolecular spaces but at high pressure gas is in the compressed state and the volume of gas molecules becomes significant as compared to the volume of gas enclosed in the container.

(ii) Gas molecules have neither attractive nor repulsive forces.

This assumption is valid at low pressure and high temperature at which molecules tend to be far apart, because these forces diminish rapidly as the distance between molecules increases. But at high pressure and low temperature intermolecular forces becomes significant because molecules tend to be close together.

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4.6 VAN DER WAAL'S EQUATION

In order to modify the two conflicting postulates of the Kinetic Molecular theory regarding volumes and intermolecular attraction of gas molecules, a Dutch scientist, J.D. van der Waal (1873), gave a mathematical solution by the correction in molecular volume and intermolecular forces. This is known as van der Waal equation.

Do You Know?

Among all real gases Helium acts most likely as an ideal gas at room temperature.

4.6.1 Volume Correction

When pressure is applied to a gas, the molecules come closer to each other. By continuous increase in pressure a point is reached when molecules cannot further be compressed since repulsive forces are created. This indicates that gas molecules have definite volume. Although this is very small but not negligible. Keeping in view the definite volume of gas molecules, van der Waal calculated the actual volume of a gas as follows:

$V = V_{vessel} - nb$ …….. (i)

Where,

V = free volume

V_{vessel} = Volume of the vessel in which gas molecules are present.

n = number of moles

b = excluded volume of gas molecules per mole in highly compressed gaseous sate. It is theoretical volume.

The value of 'b' depends upon the size of gas molecules. Here it should be noted that '**b**' is not actual volume of a gas but it is assumed four times the actual volume of molecules.

$b = 4V_{molecule}$

Where, $V_{molecule}$ is actual volume of one mole of a gas.

4.6.2 Pressure Correction

van der Waal also corrected the pressure produced by the molecules of the real gases. As we have already discussed that the intermolecular attraction comes into play when the molecules are brought close together by squeezing the gas. Consider a molecule **A** in the interior of the gas, which is completely surrounded and attracted by the other gas molecules **B**. The resultant attractive force on the molecule **A** due to all the surrounding **B** molecules is zero as shown in figure 4.5b. However, as this molecule **A** approaches to strike the wall of vessel, it experience a net inward pull due to the attractive forces of molecules of **B**. It means that pressure produced on the wall would be little bit lesser than pressure of an ideal gas molecule.

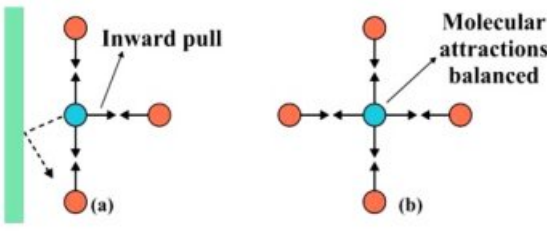

Fig 4.6: pressure of molecule which strike on the wall is less than ideal gas pressure

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Therefore,

$$P_{observed} = P_{ideal} - P_{less}$$

If observed pressure is simply indicated by P, ideal pressure P_i and less pressure P_L
Then equation will be:

$P = P_i - P_L$

Or

$P_i = P + P_L$ …….. (ii)

Since P_L is the pressure drop due to backward pull of striking molecules, it depends upon number of particles (A and B) per unit volume.

$$P_L \propto [A] . [B]$$

$$P_L \propto \frac{n}{v}\frac{n}{v} \quad \text{or} \quad P_L = \frac{an^2}{V^2}$$

Insert the value of P_L in equation (ii).

$$P_i = P + \frac{an^2}{V^2} \quad \text{…… (iii)}$$

The corrected pressure and volume is now put in general gas equation, we get.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

If n = 1 then equation will be:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \text{ …….. (v)}$$

This is van der Waal's equation. Here 'a' and 'b' are van der Waal's constants.

Table 4.2: van der Waal's constants for some common real gases

Gas	'a' (atm dm^6 $mole^{-2}$)	'b' (dm^3 $mole^{-1}$)
Hydrogen	0.0247	0.0266
Nitrogen	1.390	0.0391
Oxygen	1.360	0.0318
Methane	2.253	0.0428
Carbon dioxide	3.590	0.0428
Ammonia	4.170	0.0371
Sulphur dioxide	6.170	0.0564
Chlorine	6.493	0.0562

Units for van der Waal's constants 'a' and 'b':

Since $P = \frac{an^2}{V^2}$, hence $a = \frac{PV^2}{n^2}$

By substituting the units of P, V and n.

a = atm dm^6 $mole^{-2}$

Since "b", represents the volume per mol of gas, its unit dm^3/mol.

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Example 4.5

One mole of ammonia gas is kept in a cylinder of 5.5dm^3 at 27°C. Assuming ammonia gas as a real gas determine its pressure. The ven der Waal constant for ammonia are a = 4.17 atm dm^6 mol^{-2} and b = 0.0371 dm^3 mol^{-1}.

Solution:

n = 1 mole

T = 27°C = 27 + 273 = 300K

V = 5.5 dm^3

R = 0.0821 atm dm^3 mol^{-1} K^{-1})

P = ?

According to van der waal equation.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\left(P + \frac{4.17 \times 1}{(5.5)^2}\right)(5.5\text{-}0.0371) = (1)(0.082 \times 300)$$

$$(P + 0.138)(5.462) = 24.6$$

P = 4.365 atm

Example 4.6

Two moles of oxygen gas is kept in a vessel of 15.5dm^3 at a temperature of 37°C. Calculate the pressure exerted by the gas if

(a) gas behave as ideal (b) gas behave is non ideal

The ven der waal constant of O_2 gas are given as

a = 1.36dm^6 atm mol^{-2} and b = 0.0318 dm^3 mol^{-1}.

Solution:

n = 2 moles

T = 37 °C = 37+273 = 310 K

V = 15.5 dm^3

R = 0.0821 atm dm^3 mol^{-1} K^{-1})

P = ?

i) General gas equation is used if gas behave ideally,

PV=nRT

$$P = \frac{2 \times 0.0821 \times 310}{15.5} = 3.28 \text{ atm}$$

ii) van der Waal equation is used if it behaves as non ideal gas

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\left(P + \frac{1.36 \times 4}{(15.5)^2}\right)(15.5\text{-}2 \times 0.0318) = 2 \times 0.082 \times 310$$

P = 3.27 atm

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4.7 DALTON'S LAW OF PARTIAL PRESSURE

In 1801, an English chemist John Dalton gave a law dealing with the pressure exerted by non-reacting mixture of gases. This law states as **"The total pressure exerted by a mixture of non reacting gases in a closed vessel (fixed volume) is always equal to the sum of their individual pressures at a constant temperature"**.

If P_A, P_B, P_C etc are the individual pressures of gases in the mixture, the total pressure of the mixture is written as.

$$P_t = P_A + P_B + P_C + \text{------}$$

The pressure exerted by each individual gas in a mixture is called the partial pressure of that gas; this is the pressure that individual gas would exert if it were alone in the same container at the same temperature.

Do You Know?

Atmospheric pressure is due to weight of the blanket of air surrounding earth. With greater depth of atmosphere, more air is pressing down from above. Therefore, the atmospheric pressure is greatest at sea level and it decreases with increasing altitude. On the top of mount Everest atmospheric pressure falls to about one-third of the pressure at sea level.

Suppose we have three empty cylinders of equal capacity (1 dm^3), O_2 and N_2 gases are filled separately in first two cylinders at constant temperature. Let the pressure exerted by the O_2 gas and N_2 gas are 500 torr and 700 torr respectively. If now these gases are transferred into third empty cylinder under the condition of same temperature; the pressure exerted by the mixture gases is found to be 1200 torr which is exactly equal to the sum of partial pressure of O_2 and N_2.

According to Dalton's law

$P_t = P_{O2} + P_{N2} = 500 + 700 = 1200$ torr

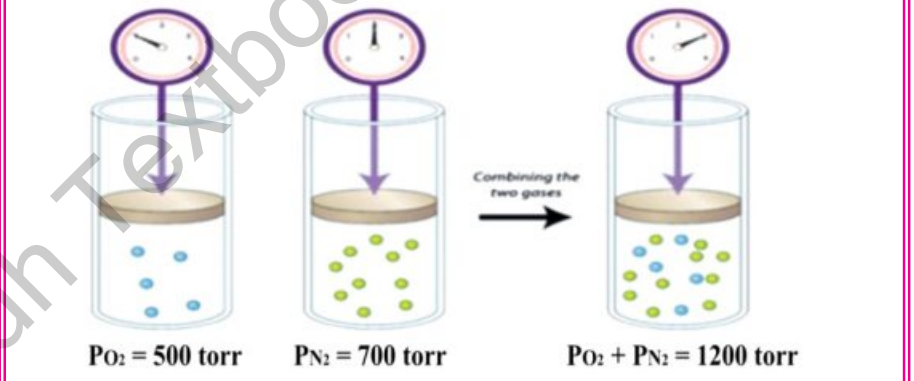

Fig 4.7: Pressure of individual gases and of their mixture

Since in the mixture, all non reacting gases behave independently, the molecules of each gas has equal opportunity to strike with the walls of cylinder and exert its own pressure without the involvement of pressure of other gases. Therefore general gas equation can be applied to individual gases in mixture and may be written as.

$$P_A V = n_A RT \qquad \text{or} \qquad P_A = \frac{RT}{V} n_A \ldots\ldots \text{(i)}$$

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$$P_B V = n_B RT \quad \text{or} \quad P_B = \frac{RT}{V} n_B \ldots\ldots \text{(ii)}$$

Since R, V and T are constant, therefore

$$P_A \propto n_A \quad \text{and} \quad P_B \propto n_B$$

Thus, at constant temperature and volume, the partial pressure of each individual gas in a mixture is proportional to its number of moles.

For the mixture of gases, the general gas equation may be written as

$$P_t V = n_t RT \quad \text{or} \quad P_t = \frac{RT}{V} n_t \ldots\ldots \text{(iii)}$$

Dividing equation (i) by (iii). we get

$$\frac{P_A}{P_t} = \frac{n_A}{n_t} \ldots\ldots \text{(iv)}$$

Similarly by dividing equation (ii) with (iii), we get

$$\frac{P_B}{P_t} = \frac{n_B}{n_t} \ldots\ldots \text{(v)}$$

Since mole fraction is the ratio of number of moles of individual gas and the total number of moles of all gases present in the mixture.

$$\frac{n_A}{n_t} = X_A \quad \text{and} \quad \frac{n_B}{n_t} = X_B, \text{ hence}$$

Equation (iv) and (v) are now reduced as

$$P_A = X_A P_t \ldots\ldots\ldots \text{(vi)}$$

$$P_B = X_B P_t \ldots\ldots\ldots\ldots \text{(vii)}$$

From the equation (vi) and (vii), it is concluded that partial pressure of any gas of the mixture is equal to the product of moles fraction of that gas and total pressure of the mixture. It should be noted that mole fraction of any gas in the mixture is less than one but sum of the mole fractions is always equal to one.

Applications of Daltons Law of partial pressure:

(i) Pressure of gases collected over water: When a gas is collected over water by downward displacement of water in a gas jar, the pressure of dry gas can be calculated by Daltons Law. When gas passes through water, it becomes moist and the total pressure will be equal to the sum of partial pressure of dry gas and water vapours (aqueous tension).

$$P_{total} = P_{dry\ gas} + P_{water\ vapours}$$

$$P_{dry\ gas} = P_{total} - P_{water\ vapours}$$

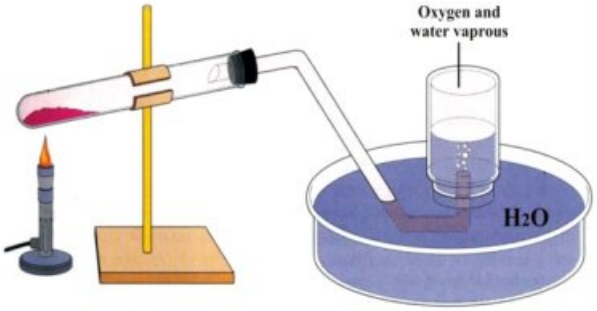

Fig 4.8: Pressure of gas collected over water is equal to the sum of pressure of dry gas and vapours

(ii) Maintenance of oxygen pressure at high altitudes: The pressure of air on high altitudes is lower than sea level due to decrease in number of molecules of gases. Normally, respiration depends upon the difference between the partial pressure of oxygen in the air (159 torr) and in the lungs (116

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torr). At higher altitudes, due to low partial pressure of oxygen causes the problem in the process of respiration.

(iii) Maintenance of oxygen pressure for deep sea divers: Opposite to altitude, as distance increases downward in the sea, partial pressure of oxygen increases. At the depth of 40 meters, pressure increases to five times. This increased pressure also causes problem in respiration. Therefore, deep sea divers use the SCUBA (Self Contained Underwater Breathing Apparatus), breathing tank for respiration. Scuba contains 96% helium gas and 4% oxygen gas.

Example 4.7

A 20 dm^3 cylinder is filled with 4.25 moles of oxygen gas and 12 moles of helium gas at 25 °C. Calculate the total pressure of gas mixture and partial pressures of oxygen and helium gases in the cylinder?

Solution:

$V = 20\ dm^3$

$n_{Oxygen} = 4.25$ moles

$n_{Helium} = 12$ moles

$n_t = n_{Oxygen} + n_{Helium}$

$n_t = 4.25 + 12 = 16.25$ moles

$T = 25\ ^oC = 25 + 273 = 298\ K$

$P_t = ?$

$P_{Oxygen} = ?$

$P_{helium} = ?$

According to general gas equation,

$$P_t = \frac{n_t\ RT}{V}$$

$$P_t = \frac{16.25 \times 0.0821 \times 298}{20}$$

$P_t = 19.88$ atm

Now the partial pressure of each gas in the mixture can be calculated by substituting the moles and total pressure in the given formula of Dalton's law.

$$P_{(oxygen)} = \frac{n_{O2}}{n_t} \times P_t$$

$$P_{oxygen} = \frac{4.25}{16.25} \times 19.88 = 5.19 atm$$

Similarly,

$$P_{helium} = \frac{12}{16.25} \times 19.88$$

$P_{helium} = 14.68$ atm

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Example 4.8

Oxygen gas is produced by heating potassium nitrate

$$2KNO_3 \longrightarrow 2KNO_2 + O_2$$

The gas is collected over water. If 225cm^3 of gas is collected at 25°C and 785mm Hg total pressure, what is the mass of O_2 gas collected? (Pressure of vapours at 25°C is 23.8 mm Hg)

Solution:

According to Dalton's law, the total pressure of mixture is equal to the sum of partial pressure of O_2 and vapours thus

$P_t = P_{(O2)} + P(\text{vapours})$

Hence

$P_{(O2)} = 785 - 23.8 = 761.2$ mmHg

Convert the units of pressure from mm Hg to atm & unit of volume from cm^3 to dm^3

$P = \frac{761.2}{760} = 1.001$ atm;

$V = 225cm^3 = \frac{225}{1000} = 0.225dm^3$

$T = 25°C = 25 + 273 = 298K$

We can use general gas equation to determine the number of moles of oxygen gas

$PV = nRT$

$n = \frac{1.001 \times 0.225}{0.082 \times 298} = 9.2 \times 10^{-3}$ moles

Now, mass of $O_2 = 9.2 \times 10^{-3} \times 32 = 0.294g$

Self Assessment

The mole fraction of oxygen in air is 0.2093, determine the partial pressure of oxygen in air if the atmospheric pressure is 760 torr.

4.8 GRAHAM'S LAW OF DIFFUSION AND EFFUSION

In the kinetic Molecular theory, we studied that gas molecules possess kinetic energy and move randomly. The movement of gas molecules through tiny hole into the region of low pressure is termed as **Effusion**. The diameter of tiny hole is considerably smaller than mean free path. Slow escaping of air from a tyre pinhole is an example of effusion. On the other hand, the process in which molecules of different gases homogenously intermix with each other is known as **Diffusion**. For example the spreading of fragrance of a rose flower or a perfume is because of diffusion. Lighter gases diffuse more rapidly than heavier gases.

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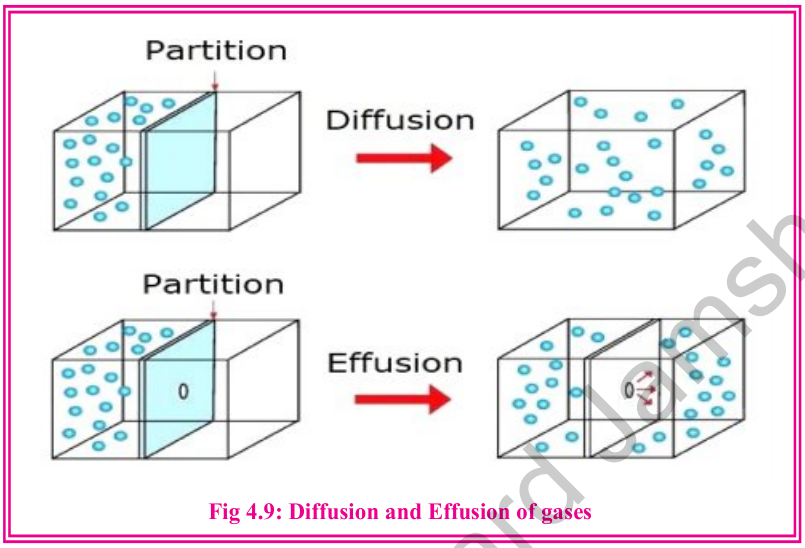

Fig 4.9: Diffusion and Effusion of gases

In 1831, Thomas Graham introduced a quantitative relationship between the rate of effusion or diffusion of gases and their densities by maintaining the temperature and pressure. After seventeen years in 1848, he modified his law by establishing the relation between rates of effusion or diffusion with molar masses in addition to densities of gases. This is known as Graham's law of diffusion which is stated as, **"At constant temperature and pressure, the rate of effusion or diffusion of a gas is inversely proportional to the square root of its density or molar mass"**.

If 'r' is rate of diffusion and 'd' is density of a gas then according to Graham's law:

$r \propto \frac{1}{\sqrt{d}}$ (At constant temperature and pressure)

$r = \frac{k}{\sqrt{d}}$ Where, k is constant for proportionality.

If we consider two gases 1 and 2, having rates of diffusion r_1 and r_2 and densities d_1 and d_2 respectively then:

$r_1 = \frac{k}{\sqrt{d_1}}$-----(i)

$r_2 = \frac{k}{\sqrt{d_2}}$-----(ii)

Now divide equation (i) with equation (ii) and we get:

$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}}$-----(iii)

The density of a given gas is directly proportional to its molecular mass, therefore,

$d_1 = \frac{M_1}{V}$ and $d_2 = \frac{M_2}{V}$

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We can write the equation (iii) as:

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \text{-----(iv)}$$

Where, M_1 and M_2 are the molar masses of gases.

Applications of Graham's Law:

(i) Densities and molar masses of different gases can be determined by using Graham's law.

(ii) The effect of toxic gases can be reduced by diffusing them into air.

(iii) Various isotopes of gases can be separated by applying Graham's law because isotopes posses different masses and have different rate of diffusion.

Example 4.9

Compare the rates of diffusion of helium (H_e) and methane (CH_4) gases.

Solution:

Mass of He = 4 a.m.u

Molecular mass of CH_4 = 12 + 4 = 16 a.m.u

$$\frac{rHe}{rCH_4} = \sqrt{\frac{MCH_4}{MHe}}$$

$$\frac{rHe}{rCH_4} = \sqrt{\frac{16}{4}} = \frac{4}{2} = \frac{2}{1} \text{ Ans}$$

Thus helium diffuses two times as fast as CH_4.

Example 4.10

The ratio of the rates of diffusion of two gases A and B is 1.5:1. If the relative molecular mass of gas A is 16, find out the relative molecular mass of gas B?

Solution:

According to Graham's Law

$$\frac{\gamma_A}{\gamma_B} = \sqrt{\frac{M_B}{M_A}}$$

$$\frac{1.5}{1} = \sqrt{\frac{M_B}{16}}$$

By applying the square root on both sides,

$$\left(\frac{1.5}{1}\right)^2 = \left(\sqrt{\frac{M_B}{16}}\right)^2$$

$$M_B = (1.5)^2 \times 16$$

$$M_B = 2.25 \times 16$$

$$M_B = 36$$

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Example 4.11

At a specific temperature and pressure, it takes 290s for a 1.5dm^3 sample of He to effuse through a porous membrane. Under similar conditions, if 1.5dm^3 of an unknown gas "X" takes 1085s to effuse, calculate the molar mass of gas "X".

Solution:

$$\frac{r_{He}}{r_x} = \sqrt{\frac{M_x}{M_{He}}}$$

$$\frac{V_{He}/t_{He}}{V_x/t_x} = \sqrt{\frac{M_x}{M_{He}}}$$

$$\frac{1.5/290}{1.5/1085} = \sqrt{\frac{M_x}{4}}$$

$$\frac{1085}{290} = \sqrt{\frac{M_x}{4}}$$

Squaring on both sides we get:

$$\left(\frac{1085}{290}\right)^2 = \frac{M_x}{4}$$

M_x=56g/mol

Self Assessment

If it takes 8.5 seconds for 5cm^3 of CO_2 gas to effuse through a porous material at a particular temperature and pressure. How long would it take for 5 cm^3 of SO_2 gas to effuse from the same container at the same temperature and pressure?

4.9 LIQUEFACTION OF GASES

Liquefaction is a physical process or technique in which gases are converted into liquids. Gas molecules at high pressure and low temperature come closer and attractive forces start operating. When the temperature is further lowered the attractive forces draw the molecules together to form a liquid.

Generally, it has been observed that, every gas has a specific temperature above which gas cannot be converted into liquid even at high pressure. The highest temperature, at which a gas can exist as a liquid, is called its **Critical Temperature**. While the pressure which is required at critical temperature to convert a gas into liquid is known as **Critical Pressure**. However, critical volume depends upon critical temperature and pressure. At critical temperature and pressure, the volume of one mole of a gas is called **Critical Volume**.

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It is important to note that critical temperature and critical pressure are the parameters which provide us the information about the liquefaction of gases. Each gas has the specific values of critical temperatures and pressures as mentioned in table 4.3. By maintaining these parameters gases are liquefied. There are various methods for liquefaction of gas.

Table 4.3: Critical temperature and critical pressure of some common gases.

Gas	Critical Temperature (°C)	Critical Pressure (atm)
Oxygen , O_2	-118.75	49.7
Ammonia, NH_3	132.44	111.5
Nitrogen, N_2	-147.06	33.5
Argon, Ar	-122.26	48
Freon-12, CCl_2F_2	111.54	39.6

4.9.1 Joule-Thomson effect

When a compressed gas is allowed to expand from a region of higher pressure to a lower pressure through a nozzle causes a fall in temperature. This is known as Joule Thomson effect. The fall in temperature is proportional to the pressure difference between compressed and expanded gas. The molecule of gas in low pressure area absorb energy from environment to reduce their attractive forces. The most common example of this effe ct is applied to liquefy Nitrogen and carbon dioxide (dry ice).

Do You Know?

Liquid natural gas (LNG) and liquid petroleum gas (LPG) are used as a fuel in automobile.
LPG and LNG are chemically different since LNG consists mainly of methane gas.

4.9.2 Linde's Method of Liquefaction of Gases

Hampson-Linde (1842-1934) introduced this method based on the principle of Joule-Thomson effect for the liquefaction of gases. According to this method, "when a gas is allowed to expand in a adiabatic closed system from a region of higher pressure to region of extremely lower pressure, the liquefaction of air or any gas takes place.

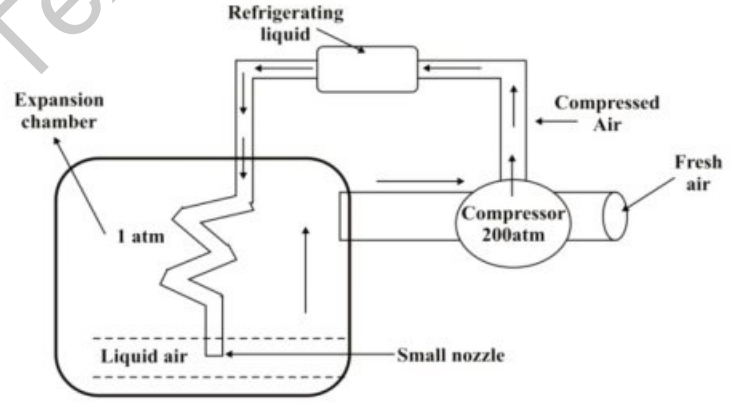

Fig 4.10: Liquification of gas by Linde's method

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In this method, first of all fresh air or any other gas is compressed to around 200 atmospheres in compressor. Then compressed air is allowed to pass through pipe which contains water. Here moisture present in air is condensed as water and removed. In this part, heat of compressed air is absorbed by the water and dry air moved through copper spiral coil having jet at the end. When dry air passes through it, expansion occurs pressure is reduced to one atmosphere. This causes the decrease in temperature of air. As a result, cooled air is formed in the expansion chamber which moves up and cools the incoming compressed air. Then uncondensed air from expansion chamber returns to the compression pump for recycling. This process of cooling and compression followed by expansion is repeated many times. Thus, liquid air is collected at the bottom of the expansion chamber and removed.

4.9.3 Liquid air and its uses

Ordinary air on compression and cooling to extremely low temperature becomes liquefies and known as liquid air. It is mainly used for the cooling purpose. It absorbs the heat very rapidly and helps to convert the gases (filled in containers) into liquids and liquids into the solids. It is the industrial source of various gases such as oxygen, argon, nitrogen etc through a process named as air separation. These liquefied gases have various applications in various fields and common life. Some important uses of liquefied gases are given below:

(i) Liquefied natural gas (L.N.G) is used as a fuel.
(ii) Liquefied petroleum gas (L.P.G) is a mixture of butane and other hydrocarbons, used as a fuel for portable heaters, gas cooktops and ovens. It is also used as fuel for engines.
(iii) Ammonia and liquid sulphur dioxide are used as refrigerants.
(iv) Liquid air is an important source of oxygen in rockets.
(v) Compressed oxygen is used for wielding purpose.
(vi) Nitrogen is used in medical science.

4.10 FOURTH STATE OF MATTER: PLASMA

Except solid, liquid and gas, the fourth state of matter is called "**Plasma**". This word is taken from the Greek "**plassein**" which means moldable substance. This state of matter was identified by William Crooks in 1879 while he was working on "Discharge Tube Experiment". He called it "radiant matter". But later on, in the 1920s, Irving Langmuir used the word "**Plasma**". Before solids, liquids and gases, plasma was existed in the universe. More than 99% of the visible universe is composed of plasma. Plasma occurs naturally in the sun, stars, nebulas and ionosphere, but rarely on our Earth. The shining of stars and the sun is due to the plasma. On Earth it is found in lightning bolts, flames, welding arcs, auroras and fluorescent lights.

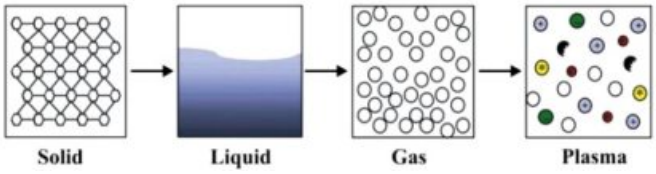

Fig 4.11: solid, liquid, gas and plasma states of matter.

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When a gas is heated at high temperature ($10^4 - 10^5$ K), most of the molecules are ionized along with formation of cloud of electrons. Despite high temperature, there still exist some un-ionized molecules and atoms. **"The mixture of positive ions, electrons and un-ionized molecules and atoms is known as plasma"**.

Natural plasma exists only at high temperature or low temperature vacuums. Natural plasma does not break down or react rapidly but it is extremely hot (over 20000°C). Its energy is so high that it can vaporize any matter. Plasma as a whole is neutral because it contains equal number of negatively charged electrons and positively charged ions. Plasma contains significant number of charged particles which affect its properties. The presence of charged particles enables it to respond to electrical and magnetic fields. Like gases, plasma has neither definite shape nor volume. Plasma shows characteristic glow in discharge tube depending upon the nature of the gas. For example hydrogen exhibits green, oxygen red and nitrogen purple glows.

Uses of plasma:

Plasma has enormous uses in various fields which are given below:

(i) When light of fluorescent bulb or neon signs is turned on, gas is excited and creates glowing plasma which lightens the surroundings.

(ii) It is used in television and computer chips.

(iii) Plasma is used in rocket propulsion, cleaning the environment, destroying biological hazards and healing wounds.

(iv) It is used in the processing of semiconductors and sterilization of some medical products.

(v) It is used in lasers, lamps, pulsed power switches and diamond coated films.

Society, Technology and Science

Deep sea diving is a dangerous task but with SCUBA (Self-Contained Underwater Breathing Apparatus) tank it becomes significantly safe and wonderful for experience. This breathing tank mainly contains oxygen along with nitrogen or helium and a small amount of carbon dioxide and it makes it quite possible to dive much deeper than 60 feet.

When anyone breathes through the SCUBA, the pressure of oxygen in lungs must be equal to the pressure exerted on the body. At the surface of water the partial pressure of oxygen in air is 0.21 atm. As we go down in the sea the partial pressure of oxygen increases continuously. At the depth of 33 feet, the partial pressure of oxygen becomes double. Therefore, SCUBA tank is maintained according to the required partial pressure of oxygen.

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Activity

In this activity, you can validate Charles' law at your home. Inflate two balloons up to the same size (volume) and then put either of them in your fridge and the other one in your room in normal ambient temperature for 1 hour. Can you guess what will happen an hour later?

The balloon that is kept inside the fridge will shrink as the air inside follows Charles law that at a constant pressure inside fridge, the decrease in the temperature of air (within balloon) causes the air inside to contract and eventually the balloon shrinks. Thus, it appears smaller in size as compared to the one kept in ambient temperature.

SUMMARY with Key Terms

- **Gas** is the state of a matter which has neither definite shape nor definite volume. Gas molecules are far away from each other and have weak attractive forces.
- **Kinetic Molecular Theory of gases** deals with the movement, arrangement, attractive force and pressure of gas particles (atoms or molecules).
- **Mean free path** is the average distance covered by a gas molecule before their collision.
- **Pressure of a gas** is the amount of force that applied to the surface of an object per unit area. The SI unit of pressure is pascal (N/m^2), however it is also measured in atmosphere and torr.
- **Atmospheric pressure** nearby sea level is taken as 1 atmosphere. It is measured by barometer. The pressure of air is lower than 1 atmosphere in hill sides.
- **Boyle's Law** describes the relationship between volume and pressure of an ideal gas and state as the volume of the given mass of a gas is inversely proportional to its pressure keeping the temperature constant.
- **Charles's Law** describes the relationship between volume and absolute temperature of an ideal gas and state as the volume of the given mass of a gas is directly proportional to its temperature keeping the pressure constant.
- **Absolute zero** is the minimum possible temperature at which gas occupies a theoretical zero volume. Actually before reaching this temperature all gases become liquefy.
- **Avogadro's Law** states that equal volume of all gases contains equal number of moles and the volume of a gas is directly proportional to its number of moles keeping the temperature and pressure constant.
- **Molar Volume** is the volume of one mole of any gas at standard temperature (0^oC) and pressure (1 atm). This volume is 22.4 dm^3.
- **Ideal gas** is that which obey general gas equation at all temperature and pressure.

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- **Real gas** is that which obey van der Waal equation. It reaches to ideal behavior at high temperature and low pressure.
- **Dalton law of partial pressure** tells that the total pressure of the mixture of two or more non reacting gases is equal to the sum of partial pressure of individual gases in a fixed volume enclosed container.
- **Graham's law of diffusion** tells that the rate of diffusion of a gas is inversely proportion to the square root of its density or molecular mass keeping the temperature and pressure constant.
- **Critical temperature** is the highest temperature at which a gas exists as liquid.
- **Critical pressure** is the pressure which is required at critical temperature to convert a gas into liquid.
- **Liquid air** Ordinary air on compression and cooling to extremely low temperature becomes liquefies and known as liquid air. It is mainly used for the cooling purpose.
- **Plasma** is the fourth state of matter. It is a mixture of ions and un ionized atoms and molecules.

EXERCISE

Multiple Choice Questions

1. Choose the correct answer

(i) According to Graham's Law of diffusion, the ratio of diffusion of H_2 and O_2 are respectively:

(a) 1:2 (b) 2:1 (c) 1:4 (d) 4:1

(ii) Collection of gas over water is an example of:

(a) Graham's law (b) Dalton's law
(c) Avogadro's law (d) Gaylussac law

(iii) The molar volume of oxygen gas is maximum at:

(a) 0°C and 1 atm (b) 0°C and 2 atm
(c) 25°C and 1 atm (d) 25°C and 2 atm

(iv) The diffusion rate of C_3H_8 and CO_2 are same because:

(a) Both are poly atomic gases (b) Both are denser than air
(c) Both have same molar mass (d) Both contains carbon atoms

(v) The volume of gas would be theoretically zero at:

(a) 0°C (b) 0 K (c) 273 K (d) 273°C

(vi) Real gas reaches the ideal behavior at:

(a) Low temperature and low pressure (b) High temperature and high pressure
(c) Low temperature and high pressure (d) High temperature and low pressure

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(vii) Which one of the following statement is incorrect about the gas molecules?

(a) They have large spaces
(b) They possess kinetic energy
(c) Their collision is elastic
(d) Their molar mass depends upon temperature

(viii) If the Kelvin temperature of ideal gas is increase to double and pressure is reduce to one half, the volume of gas will:

(a) Remains same (b) Double
(c) Reduced to half (d) Four time

(ix) The molar volume of oxygen gas is 22.4 dm^3 at:

(a) 0°C and 1 atm (b) 25°C and 0.5 atm
(c) 0 K and 1 atm (d) 25 K and 0.5 atm

(x) Under similar condition CH_4 gas diffuses..... times faster than SO_2 gas:

(a) 1.5 time (b) 2 times
(c) 4 times (d) 16 times

Short Questions

1. State the following gas laws.
   (i) Avogadro's law (ii) Charles law
2. State main postulates of kinetic molecular theory of gas.
3. Explain the following.
   (i) Pressure and its various units (ii) Absolute zero
4. What is liquid air? Mention its three uses.
5. What is plasma? Give its significance in daily life.

Descriptive Questions

1. State and explain Dalton's law of partial pressure. Give practical applications of Dalton's law.
2. Derive general gas equation. Also deduce the value of R in atm dm^3/mol.K and J/mol.K.
3. How an ideal gas is differentiated from real gas? What are the causes of deviation of real gas from ideal behavior? Explain this deviation at low temperature and high pressure.
4. What is meant by diffusion and effusion? Explain Graham's law of diffusion.

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Numerical Questions

1. Gorakh hill station is coldest area of Sindh province and has 83Kpa barometer pressure. What will be the pressure of this area in psi and atm units?

2. Calculate the volume occupied by 8g of methane gas at 40°C and 842 torr pressure? [Ans: V = 11.58 dm^3]

3. At 35°C, oxygen gas in a cylinder has 456 cm^3 volume and 0.85 atm pressure. Calculate the pressure when this oxygen gas is transferred to 10 dm^3 cylinder and cooled to 20°C. [Ans: 0.037 atm]

4. Compare the rates of diffusion of the following pairs of gases:
   (1) H_2 and D_2 (2) He and SO_2 (3) SF_6 and SO_2 [Ans: 1.41/1,4/1, 1.51/1]

5. Four containers of equal volume are filled as follows:
   (i) 2.0g of H_2 at 0°C (ii) 1.0g of H_2 at 273°C
   (iii) 24g of O_2 at 0°C (iv) 16g of CH_4 at 273°C
   (a) Which container is at the greatest pressure?
   (b) Which container is at the lowest pressure? [Ans: a = iv and b = iii]

6. A 500cm^3 vessel contains H_2 gas at 400 torr pressure and another 1dm^3 vessel contains O_2 gas at 600 torr pressure. If under the similar condition of temperature these gases are transferred to 2dm^3 empty vessel, calculate the pressure of the mixture of gases in new vessel.

7. If 16 cm^3 of hydrogen effuses in 30 sec, from a porous material, what volume of SO_2 will effuse in the same time (30 sec.) under similar conditions?

8. 40dm^3 of hydrogen gas was collected over water at 831 torr pressure at 23°C. What would be the volume of dry hydrogen gas at standard conditions? The vapour pressure of water at 23°C is 21 torr of Hg.

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STATE OF MATTER II: LIQUIDS

Chapter 5

Teaching Periods	Assessment	Weightage
12	1	7

Students 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.
- **Explain** applications of dipole-dipole forces, hydrogen bonding and London forces.
- **Explain** physical properties of liquids such as evaporation, vapour pressure, boiling point, viscosity and surface tension.
- **Use** the concept of Hydrogen bonding to explain the following properties of water: high surface tension, high specific heat, low vapor pressure, high heat of vaporization and high boiling point. and anomalous behavior of water when its density shows maximum at 4 degrees centigrade.
- **Define** molar heat of fusion and molar heat of vaporization.
- **Describe** how heat of fusion and heat of vaporization affect the particles that make up matter.
- **Relate** energy changes with changes in intermolecular forces.
- **Define** dynamic equilibrium between two physical states.
- **Describe** liquid crystals and give their uses in daily life.
- **Differentiate** liquid crystals from pure liquids and crystalline solids.

INTRODUCTION

Liquid state is the state of matter having definite volume, but no definite shape. This phase of matter is formed when particles come closer together due to the presence of short range attractive forces operating among them. However, the magnitudes of these forces vary from liquid to liquid. This is due to the great variations in their physical properties like boiling point, evaporation, viscosity etc.

A pure liquid is said to be a single phase substance composed of identical molecules. In the liquid state, though atoms and molecules remain close together in the form of clusters but acquire enough energy for moving around and can slip over each other. This freedom of liquid molecules to move easily makes them flow and to pour.

Water is the most abundant liquid compound present on the earth's crust. Water is used by human beings in many necessary processes for example agriculture, drinking, washing etc. It is a fact that almost 70% of our body consists of water. Oils are also liquids and play important roles in our daily life. We use oils for lubricating engines of automobiles, in the hydraulic machines, and also for cooking food (edible oils). Many fuels for example Gasoline, Kerosene oil and Diesel oil are liquids. Some elements are liquid at room temperature such as Mercury (a metal) and Bromine (a non-metal).

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5.1 KINETIC MOLECULAR INTERPRETATION OF LIQUIDS

The behavior of liquid in term of kinetic molecular theory is summarized below.
(i) Liquid molecules are close together having small spaces among them.
(ii) Liquid molecules are in constant motion but their movement is restricted.
(iii) There are weak attractive forces present among liquid molecules.
(iv) The collisions among liquid molecules are more frequent. Brownian motion is the result of unequal number of collision of liquid molecules with each other from different sides.
(v) Unlike gases, liquids do not show appreciable increase in their volumes by heating.

5.1.1 Simple properties of Liquids

Diffusion: Two miscible liquids diffuse into each other; however the process of diffusion in liquids is slower than gases due to small intermolecular gaps which cause difficulties in molecular movement. For example a drop of ink spreads in a glass full of water slowly.

Compression: Liquids are very less compressible as compared to the gases. In term of kinetic molecular theory liquid molecules are in constant random motion in small intermolecular spaces hence if we put a pressure on liquid its volume does not appreciably change.
An example of compression of liquid is hydraulic brakes system in automobile.

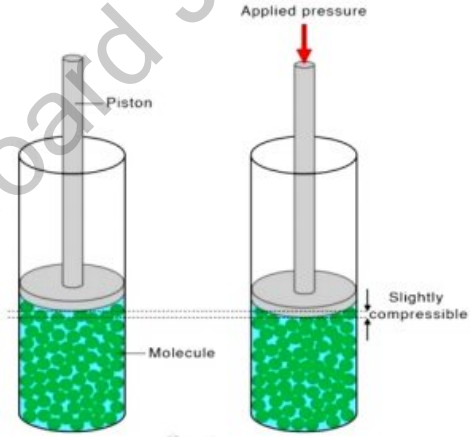

Fig. 5.1: Compression of liquid

Expansion and contraction: Liquids expand on heating. However they do not show appreciable increase in their volumes by heating like gases do. Expansion is due to high kinetic energy of molecules at the higher temperatures which result in the separation of molecules and creation of molecular gaps.

Contraction is opposite of expansion and it takes place by lowering the temperature. Molecules of liquid at low temperatures lose kinetic energies and come close together.

Molecular motion: Liquid molecules move randomly in all possible directions however due to small gaps and attractive forces speed of molecules is slower as compared to gas.

Kinetic energy: Molecules in liquid state are quite nearer to each other due to attractive forces hence collision among them is not as fast as in gases. Therefore kinetic energy of liquid molecules is relatively low. However, a rise in temperature breakdown the attractive forces and increases the molecular collision which results in increasing the kinetic energy.

5.2 INTER-MOLECULAR FORCES IN LIQUIDS (Van der Waal forces)

The forces of attraction among liquid molecules are collectively called intermolecular forces or secondary forces or more famously as Van der Waal forces. These attractive forces are actually physical bonds and are electro-static in nature.

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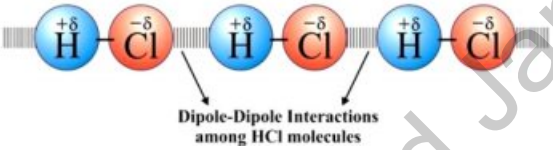
5.2.1 Dipole-Dipole Interaction

Liquid molecules are either polar or non-polar. Polar molecules bear partial positive and partial negative charges due to electronegativity differences on their opposite ends (dipoles). For example, HCl is a polar molecule and there is a partial positive charge on hydrogen atom at one end and partial negative charge on chlorine atom at the other end. These opposite poles attract each other in the liquid states. **"The electrostatic force of attraction between the positive end of one polar molecule and the negative end of other polar molecule are called dipole-dipole interaction"**. The strength of these forces depends upon difference of electronegativities of the two atoms in the polar molecule. As a rough comparison their strength is about 1% of a normal covalent bond.



An example of liquid in which dipole-dipole forces exists is iodine mono chloride (reddish brown oily liquid). The more electronegative chlorine atom possesses partially negative charge (-δ) where as less electronegative iodine atom bear partially positive charge (+δ). Thus partially negative chlorine terminal of one molecule is attracted to the partially positive terminal of iodine of another molecule.

5.2.2 Hydrogen Bonding

In certain molecules like H_2O, HF, NH_3 etc hydrogen atom is bonded to a electronegative smaller size atom. They are referred as highly polar molecules in which hydrogen bear a positive charge and other atom (N, O, F) bear negative charge. Molecules of these substances attract each other through a special type of dipole – dipole interaction known as hydrogen bond. **"The force of attraction between partially positive charged hydrogen atom of one molecule and lone pair of electron of highly electronegative atom of another molecule is called Hydrogen bonding"**.

Hydrogen bond is represented by the dotted lines (……). It is strongest among all inter-molecular forces however much weaker than ordinary covalent bond. The strength of hydrogen bond is about 5 to 10% of the strength of covalent bond.

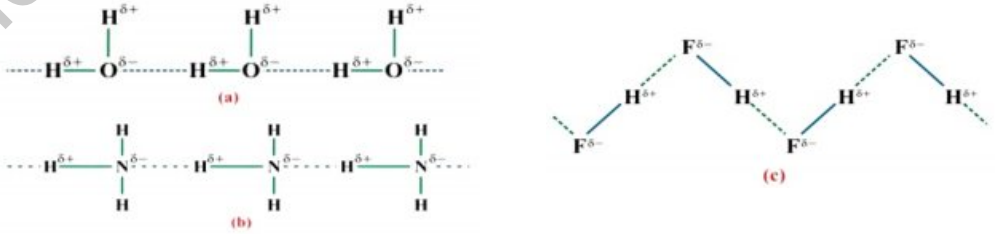


Fig. 5.2: Hydrogen bonding in (a) Water molecules (b) Ammonia molecules (c) Hydrogen fluoride

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Application of Hydrogen bonding

In many aspects, hydrogen bonds are important for life on earth and have a wide range of applications in many essential chemical and biochemical processes for example.

(i) Water is an essential need of human being. It is not only use for drinking but various other purposes. It exists in liquid state at ordinary temperature rather than gas due to the presence of hydrogen bonding. Hydrogen sulphide (H_2S) on the other hand is a hydride of same group but exist in gaseous state at room temperature since it does not have hydrogen bond.

(ii) Macro biomolecules such as protein, Deoxyribonucleic acid (DNA) etc play vital function for life. Hydrogen bonds hold their chain in particular sequence.

(iii) Cleaning action of soap and detergent is based on hydrogen bond formation between the polar part of detergent and soap with water molecules.

(iv) Paints are viscous material; they easily form a smooth layer on surface. The adhesive action of paints is developed due to hydrogen bonding.

(v) Fabric of cloths is made up of fibers such as silk, polyester, Nylon etc. The rigidity and tensile effect in threads is developed by hydrogen bonding.

Concept of hydrogen bonding to explain the properties of water

Water possesses some unique properties due to the presence of hydrogen bonding among its molecules.

High specific heat

Specific heat is the amount of heat energy required to raise the temperature of one gram of any substance by 1°C. Water does not warm or cool rapidly, this is due to high specific heat of water which is due to hydrogen bonding.

High specific heat of water has marked effect on the weather. It plays important role in moderating the temperature of earth's surface. Heat is absorbed and stored at day times while sun shines but released at nights. This is why the temperature of coastal areas usually remains moderate throughout day. On the other hand the temperature in desert areas usually shoots up at day time and falls steeply at nights because rocks and sand have lower specific heat.

High boiling point of water

Each water molecule consists of two polar hydrogen atoms and one oxygen atom with two non bonded pairs of electrons. Thus a water molecule can form a maximum four hydrogen bonds in three dimensional spaces hence extra energy is required for breaking hydrogen bonds that is why water boils at high temperature (100°C) as compared to most of other liquids. Hydrogen bonding among HF molecules is stronger due to high electronegative fluorine atom but boiling point of HF is quite lower than water because fluorine can make less number of hydrogen bond with electro positive hydrogen of neighboring molecule.

High density of water

Due to the presence of hydrogen bonds water molecules are strongly attracted and occupy less volume. Since density is inversely proportion to volume, the density of water is

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relatively high. At 20°C the density of water is 1 g/cm^3. Marine life survives under water due to high density of water.

High viscosity of water

Hydrogen bond is the strongest attractive force among other intermolecular attractions. Since water possess multiple hydrogen bonds in three dimensional space, its molecules are quite closer together. This led to its high viscosity as compared to other molecules of comparative size.

High surface tension of water

High surface tension of water molecules is due to the strong cohesive forces. These cohesive forces are conceptually hydrogen bonds.

Anomalous behavior of water:

Hydrogen bondings in water lead to some unusual and unique behavior which is seen in daily life. It shows highest density at 4°C and below this temperature its volume increases instead of decreasing. This anomalous behavior of water can be attributed by arrangement of hydrogen bonding among H_2O molecules.

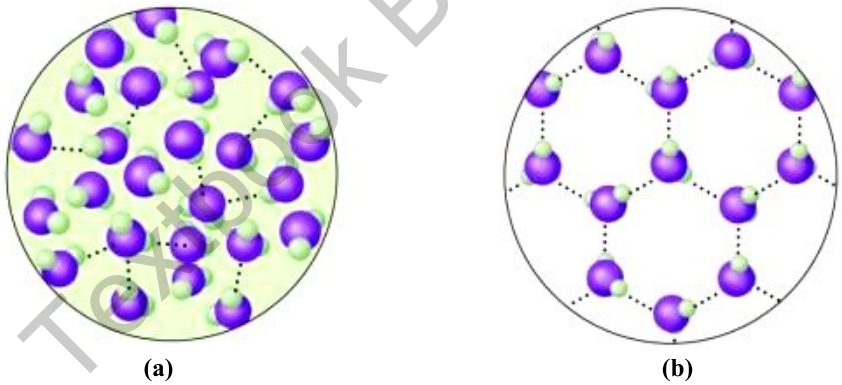

Fig. 5.3: Hydrogen bonding in (a) Ice (b) liquid water

Hydrogen bonding in water above 4°C is temporary due to the high thermal energies. Thus water molecules can easily break their hydrogen bond and quickly re-form new hydrogen bonding with some other molecules in the neighborhood.

When the temperature falls below 4°C, water molecules start arranging themselves by lining up in such a manner that each water molecule can form up to maximum number of four hydrogen bonds. The increased number of

Do You Know?

In the cold regions water supply pipelines burst if not properly insulated. The reason behind this is the anamolous expansion of H_2O below zero degree centigrade.

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hydrogen bonding results in the freezing of water into ice. In the form of ice water molecules are arranged in the more regular hexagonal patterns in the manner that empty spaces are created in the structure of ice and its volume expands up to 10%. The low density of ice can be seen when ice float on water.

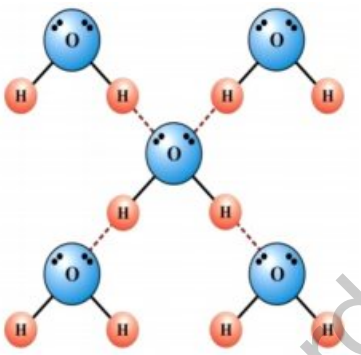

Fig. 5.4: Each water molecule form maximum four hydrogen bonds

Self Assessment

(i) Correlate the following behavior of water with hydrogen bonding among its molecules? ▪ High B.P ▪ High density

(ii) How the high specific heat of water effects on moderating the temperature of atmosphere?

5.2.3 London Dispersion Forces

Fritz London (1930)

These forces were first reported by German physicist Fritz London. These attractive forces exist among non- polar molecules which becomes polar temporarily. Never the less gasoline and benzene, are non-polar molecules but exist in liquid state at room temperature due to the presence of London dispersion forces.

When non polar substance such as H_2, Cl_2, F_2, CH_4, He, Ne, Ar etc are allowed to liquefy by lowering the temperature, a temporary interaction is developed among their molecules due to the distortion of electrons cloud of one atom by the electronic influence of other atom. This makes a short-lived polarization of molecule and it is said to be **instantaneous dipole**. This instantaneous dipole then distort the electron density of nearer atom and hence produce an **induce dipole** in the nearby atom. **"The attractive force which develop between an instantaneous dipole and an induce dipole is known as London dispersion force".**

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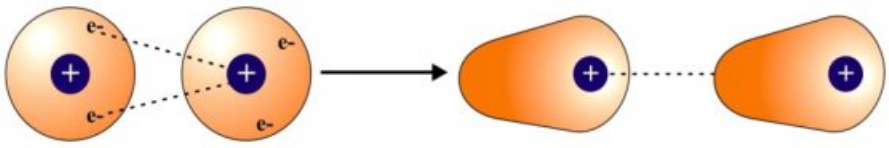

Fig. 5.5: London dispersion forces in two helium atoms

The strength of London dispersion forces depends mainly upon following two factors.

(i) Size of atom or molecule Large size atom or molecule possess greater number of electrons therefore more distortion of electrons is possible which increases the strength of London forces.

(ii) Atoms in the molecules The greater the number of atoms in a non polar molecule the more is the number of electrons hence the stronger the electronic distortion which results in enhancing the strength of London forces.

Self Assessment

Identify the intermolecular forces present in the given molecules.
(i) Hydrochloric acid (ii) Liquid helium (iii) Ice

5.3 PHYSICAL PROPERTIES OF LIQUIDS

`Depending upon the nature and strength of attractive forces among the molecules, liquids have following essential properties.

Evaporation:

We observe that moist clothes become dry while hanging outside in the sunshine, this is due to evaporation. **"At any given temperature, a certain number of the molecules in a liquid possess sufficient kinetic energy to escape from the surface. This process is called evaporation".** It is a surface phenomenon where change of state only takes place at the surface of liquids. Molecules at the surface start getting energy from surroundings and breaking away into gaseous phase.

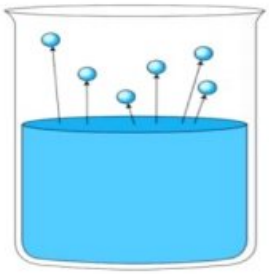

Fig. 5.6: Evaporation in a container

On the basis of the rates of evaporation, liquids can be divided into two types (i) volatile liquids and (ii) non-volatile liquids. The liquids which have higher vapor pressures and evaporate readily are called volatile liquids such as, ethanol, acetone and gasoline etc. and those which have low vapor pressures do not readily evaporate are called non-volatile liquids such as, mobil oil and mercury etc.

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Evaporation is an endothermic process. When it starts, the high energy molecules leave the liquid surface. Therefore the average kinetic energy of remaining molecules decreases. As a consequence the temperature of the liquid falls. For example, when we pour some ethanol on our palm, we feel coolness. This is because volatile liquids rapidly absorb heat from our skin and evaporate.

The rate of evaporation is affected by following three factors.

Surface Area

The larger the area of exposed surface the more is the tendency of molecule to transfer from liquid to air. This is due to the fact that greater surface area allows more molecules getting energy from surroundings and escape into air that is why water spilled on floor evaporates more readily as compared to the same amount of water in a container.

Do You Know?

Some water droplets are quickly formed at the outer surface of a cold bottle when it is taken out from refrigerator. This process is called condensation, which is exactly opposite to evaporation. Since it is exothermic process, it happens when gas molecules start losing kinetic energy by striking at cooler surfaces and change into liquid state.

Intermolecular Forces

Evaporation also depends upon the nature of intermolecular forces present among liquid molecules. For example, acetone evaporates quicker than water at the same temperature. This is because stronger intermolecular forces (Hydrogen bonds) are present among water molecules but weaker intermolecular forces (London dispersion forces) present among acetone molecules.

Temperature

Although, evaporation takes place at all temperature but a rise in temperature increases the rate of evaporation. It is in our observation that cloths dry more faster in summer, this is due to the fact that water molecules on wet cloths absorbs heat from atmosphere and becomes more energetic to overcome intermolecular forces and escape more readily.

Vapor pressure

When a liquid is enclose in a tightly covered container, and the air present above the surface of liquid is evacuated, the liquid starts to evaporate and enter into the enclosed space. Some of them will collide with the liquid surface and rejoin it. This process of rejoining the molecules from vapours phase back into liquid phase is known as condensation.

In the beginning the rate of evaporation is faster than the rate of condensation but when more liquid molecules escape out from the surface into the enclose space the rate of condensation increases

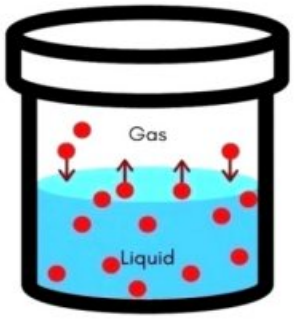

Fig. 5.7: Equilibrium between rate of evaporation and condensation

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gradually and a state of dynamic equilibrium is finally established when rate of evaporation and condensation becomes equal.

$$\text{Evaporation} \rightleftharpoons \text{Condensation}$$

The pressure of vapours at this stage becomes constant and known as vapours pressure of that liquid. **"The pressure exerted by the vapours when they are in equilibrium with liquid phase at that temperature is called as vapours pressure".**

Vapours pressure is independent upon the amount of liquid but depend upon temperature and intermolecular forces. Vapours pressure increase with increase in temperature due to increase in kinetic energy of molecules. For example vapours pressure of water at 20°C is 17.5 torr but at 100°C it is 760torr.

Another factor which affect on vapour pressure of liquid is the strength of existing intermolecular forces. The stronger the intermolecular forces the lesser the rate of evaporation and hence the lower the vapours pressure. For example the vapours pressure of diethyl ether at 20°C is 170 torr which is much higher than water (17.5 torr) at the same temperature. This is due to weak London dispersion forces among the molecules of ether.

Boiling point

When a liquid is heated, more molecules acquire high kinetic energy to escape into the air and the evaporation becomes more rapid. As a consequence, the vapour pressure of the liquid increases until it becomes equal to atmospheric pressure, the liquid is said to boil. **"Boiling point is the temperature at which the vapor pressure of liquid becomes equal to its atmosphere pressure"** when atmosphere pressure is one atmosphere; the boiling point is referred to as normal boiling point.

Boiling points of liquids depend upon the atmospheric pressure and it varies at the different regions on earth. At the sea level, where the atmospheric pressure is usually close to 760 torr, water boils at 100°C, whereas at mountainous regions such as Muree hills, atmospheric pressure is usually low (may be 700 torr), thus water boils at below 100°C.

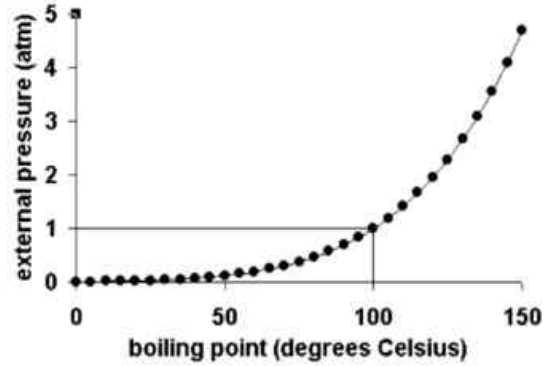

Fig. 5.8: Boiling point of water as a function of external pressure

At normal boiling point (100°C) of water, the food will be cooked easily. However at higher altitudes such as Gorakh Hills, Sindh, where air pressure is usually low, water boils at lower temperatures thus food will take longer time.

In pressure cooker which does not allow the steam to escape. Pressure cookers help to build greater pressures over the water surfaces inside the pot, and as a consequence boiling point of water rises that leads to the decrease in cooking time.

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For example glycerin boils at 290°C at 760 torr but it decomposes at this temperature. If it is heated under reduced pressure (50 torr), it boils at 210°C without decomposition.

Viscosity:

The decrease in flow of liquids is due to the internal resistance among the layers of molecules. Every layer offers some friction to the neighbouring layer which tends to flow over it. **"Viscosity is the measure of internal resistance of a liquid to flow"**.

Viscosity of a liquid is affected by following three factors.

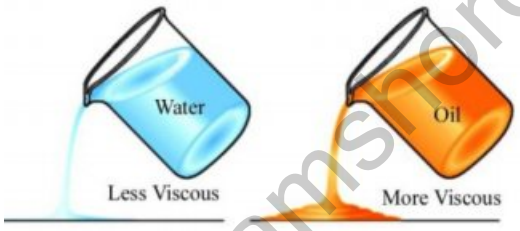

Fig. 5.9: Oil is more viscous than water

(i) Intermolecular forces:

Liquids like benzene, gasolines etc which consist of non polar molecules posses weak intermolecular forces and have relatively low viscosities. Contrarily, more polar liquid such as glycerol and methanol etc experience stronger intermolecular forces and possess high viscosity.

Water is more viscous than acetone because of stronger hydrogen bonding present in water molecules and weaker London dispersion forces present in acetone molecules.

(ii) Temperature:

It is our everyday experience that viscosity of liquids decreases with the rise of temperature due to increase in kinetic energy of molelcules. Honey is viscous at room temperature but can be made thin on heating, vegetable oil becomes less viscous while cooking.

Table 5.1: Viscosities of some liquids at different temperatures.

Liquid	Viscosity (centipoise)		
	0°C	20°C	50°C
Acetone	0.395	0.322	0.246
Water	1.789	1.005	0.55
Ethyl alcohol	1.78	1.19	0.701
Glycerin	12100	1499	--

(iii) Molecular Size:

Liquid of large molecular size are highly viscous because their molecular chains get tangled up in each other and create more friction to flow. For example paraffin oil and motor oil are viscous due to their large hydrocarbon chain. The high viscosity of honey is due to large molecular size as well as presence of hydrogen bond among the molecules.

Units of Viscosity:

The unit of viscosity is Poise and centi poise. The S.I unit of viscosity is $N.s.m^{-2}$.

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Surface Tension:

We have already discussed that liquid molecule attract each other but intermolecular forces are not uniform throughout the liquid body. Consider two molecules of liquid "A and B". Molecule" B" is nearly in the middle and molecule "A" is just on its surface. Molecule "B" is equally pulled from all sides by the neighboring molecules, however molecule "A" does not experience any pull from the above, as there is no any liquid layer above it due to surface position. Hence, there is net downward pull at the right angles which tends to contract the surface of a liquid. This shows that attractive forces on molecules at surface and inside liquid are unbalanced. Molecules at the surface of a liquid experience more attraction which works like a stretched membrane and it tends to compress the molecules below to the smallest possible area and create surface tension **"Surface tension is the force acting at right angle on the unit length of surface of liquid"**. Since work has to be done to lift the inner molecules to the surface of liquid, some energy is required to expand the surface area thus surface tension may also define as **"The amount of energy that cause to increase the unit area of liquid"**.
The unit of surface tension is dyne/cm or erg/cm^2.

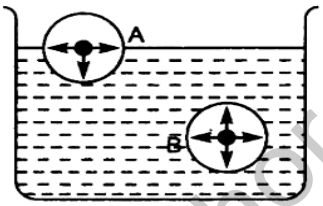

Fig. 5.10: Cohesive forces in the liquid molecules at surface and inner side

Fig. 5.11: Falling drop of a liquid is spherical in shape.

Liquids tend to minimize their surface area as much as possible to attain a spherical shape. You might have noticed spherical droplets of water coming out of tap for a while just after closing it. The reason behind is the presence of cohesive forces between the surface molecules and the molecules toward the interior side. Since the surface molecules are being pulled by the interior ones, as a consequence, the surface area is reduced as much as possible to acquire a spherical geometry since sphere has the least surface area for a given volume.

Do You Know?

Attractive forces between the molecules of same type are known as cohesive forces whereas the attractive forces between the molecules of different type are known as adhesive forces. For example Mercury when confined in a glass tube does not wet the wall due to its stronger cohesive forces as compared to adhesive forces that is why it is used in thermometer.

Table 5.2: Surface tensions of some common liquids at 20°C

Liquid	Surface tension (dynes/cm)	Liquid	Surface tension (dynes/cm)
Ethanol	22.03	Benzene	28.88
Acetone	23.7	Water	72.583
Chloroform	27.1	Mercury	471.6

An essential factor which affect on surface tension of liquids is the strength of intermolecular forces. The stronger the intermolecular forces the higher the surface tension.

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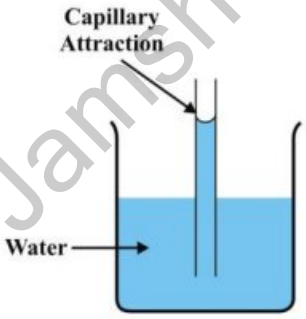
For example surface tension of water is stronger than many other liquids, due to the presence of stronger intermolecular forces (Hydrogen bonds). Mercury has much higher surface tension than water because its atoms are held together by strong metallic bond.

Surface tension is markedly affected by temperature. High temperature weakens the cohesive forces among the molecules which results in decreasing the surface tension.

Capillary action:

When you dip one end of a clean capillary tube in a liquid, you will observe the liquid rising to a certain height. **"The flow of liquid in a capillary tube is called as capillary action"**.

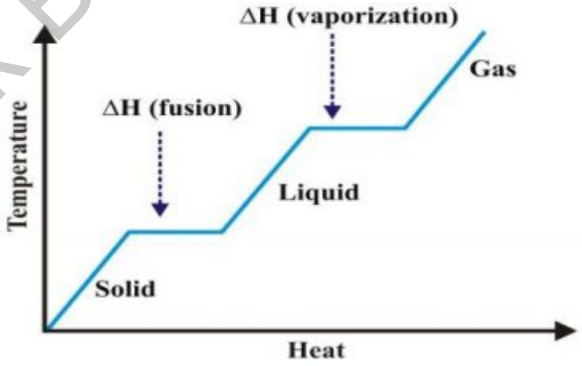


The flow of liquid in a capillary tube is due to a combine effect of cohesive forces among liquid molecules and adhesive forces between liquid molecules and the wall of tube. Water rises in the capillary tube because its adhesive forces become stronger in a tube of small diameter.

Other examples of capillary rise action are spreading of ink into blotting paper and rise of oil in the wicks of lamp.

5.4 ENERGETIC OF PHASE CHANGE

Transformation of substance from one physical state to another is accompanied by absorbtion or evolution of heat. This heat energy refers the strength of intermolecular forces and are of three types.



Molar heat of fusion (ΔH_{fusion}) It is the amount heat required to convert one mole of a solid completely into liquid at its melting point. The molar heat of fusion when ice is converted into water is given as.

$$Ice_{(s)} \longrightarrow Water_{(l)} \ (\Delta H_{fusion} = +\ 6.02 KJ/mol)$$

Even though heat is being supplied during melting but temperature remains constant because all of the energy is consumed by the molecules to over come the intermolecular forces.

Molar heat of vaporization (ΔH_v) The amount of heat required to convert one mole of a liquid into its vapours at boiling point is referred as molar heat of vaporization.

$$Water_{(l)} \longrightarrow Vapours_{(g)} \ (\Delta H_v = +\ 40.7 KJ/mol)$$

Heat of vaporization is much greater than the heat of fusion because while converting liquid into vapour, notable change in the intermolecular distance and potential energy of particles occur.

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Molar heat of sublimation (ΔH_s) the amount of heat absorbs when one mole of a solid is directly convert into vapours without going through a liquid state is known as molar heat of sublimation. For example dry ice (solid CO_2) changes directly from solid to gas at atmospheric pressure.

$$CO_{2(solid)} \longrightarrow CO_{2(gas)} \ (\Delta H \text{ sublimation}) = +25.2 \text{ KJ/mol}$$

5.5 LIQUID CRYSTALS

Fredrich Reintzer

A liquid crystal is a state of matter between liquid and solid. It was first discovered by Fredrich Reintzer (1888), while he was examining physico-chemical properties of different derivatives of cholesterol. He observed that cholesteryl –Benzoate did not melt the same way as other compounds, and it has two melting points. At 145.5°C it first melted into a cloudy liquid and then at 178.5°C it melted again and cloudy liquid became clear and this phenomenon was reversible. Liquid crystals are usually organic in nature or may be sometimes mixture of both organic and inorganic materials. Liquid crystals exist both naturally or they can be synthetically developed.

Liquid crystals can be differentiating from a pure liquid and crystalline solid with its certain characteristics. They have ability to flow like liquid but the molecular arrangement is similar to crystalline solids. Liquid crystal have optical properties as found in crystalline solid but exhibit anisotropy.

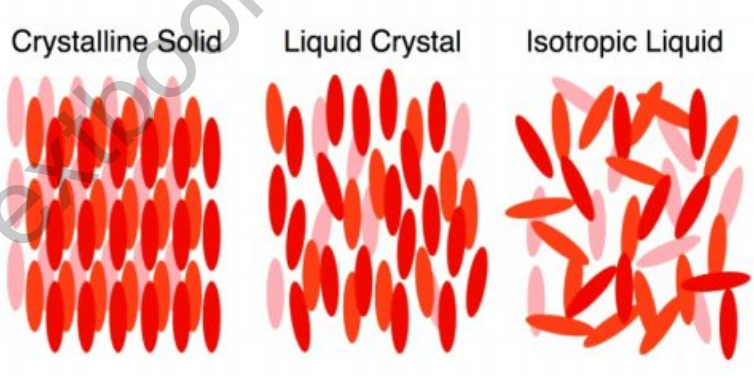

Fig. 5.12: Liquid Crystal

Uses of liquid crystals

- Liquid crystals are commonly used in our daily life. For example, liquid crystal displays (LCDs) are used in the screens of various devices like wrist watches, mobile phones, tablet computers, screens of computers, televisions, pH meters, ATM machine displays etc.
- Liquid crystals are used as temperature sensors in thermometers and other devices to measure the body temperatures.

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- Liquid crystals are used in many fields of science and engineering to detect faulty connections in microelectronic circuit boards.
- In the medical science liquid crystals help to detect blockage of veins, arteries and tumors etc.
- Liquid crystals are used in the chromatographic techniques as solvents for the separation of many components.
- Some of liquid crystals are also used in the hydraulic machines due to their high viscosities.

Society, Technology and Science

Use of liquid crystals in digital instruments

LCD is a great invention in modern technology due to its flat compact screen and excellent quality of picture.

Liquid crystal is sealed between the two glass sheets having a transparent conducting surface. When backlight is activated, the molecules of liquid crystal rearrange their direction to produce display.

Activity

This activity motivates you to study the effect of temperature on the viscosity of liquid. Just take one table spoon of honey at room temperature and pour it in an empty cup. You will observe that the honey will flow slowly due to dominant viscous forces between its different layers. Now take another table spoon of honey and heat it on a low flame for 1 minute. Then pour it in the same cup. Now you will observe a quick flow of honey into the cup. The reason is that heating honey increases its temperature, thereby causing its viscosity to decrease which in turn results in a faster flow.

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SUMMARY with Key Terms

- **Dipole-Dipole interactions** is the electrostatic force of attraction between the positive end of one polar molecule and the negative end of other polar molecule.
- **London dispersion forces** are weak intermolecular forces which develop among non polar molecules such as H_2, He, Ne, Ar, CH_4 etc. It is a short-lived polarization of molecule due to the distortion of electron of one atom by the electronic influence of other atom.
- **Hydrogen bonds** is the force of attraction between partially positive charged hydrogen atom in one molecule and lone pair of electron of highly electronegative atom in another molecule. It exist in the molecules which possess electro positive hydrogen atom and high electronegative atom.
- **Evaporation** is a surface phenomenon in which molecules from liquid surface starts escaping into gaseous state. It depends upon surface area of liquid and the forces which hold the molecules in liquid state.
- **Condensation** is the reverse process of evaporation in which gas molecules after losing their kinetic energy transform into liquid state.
- **Vapours pressure** is the pressure exerted by vapours when they are in equilibrium with liquid phase. It is dependent upon temperature and intermolecular forces.
- **Dynamic equilibrium** is established in a closed vessel when the rate of evaporation and rate of condensation of liquid becomes equal.
- **Boiling point** is the temperature at which vapours pressure of liquid becomes equal to the atmospheric pressure. The greater the atmospheric pressure, the higher the boiling point.
- **Viscosity** is the internal resistance to flow of a liquid. It is mainly depends upon intermolecular forces. The unit of viscosity in SI measurement in Nsm^{-2}.
- **Surface tension** is the force responsible for the tension at the surface of a liquid. It is the energy required to stretch the surface by unit area.
- **Capillary action** is the rise of water in a capillary tube. It occurs due to small surface area of capillary tube which causes weak surface tension.
- **Abnormal behavior of water** is found below 4°C when its volume increases due to the arrangement of hydrogen bonding. Ice has low density than liquid water that is why float on water.
- **Molar heat of fusion** is the heat required to convert one mole of solid completely into liquid at its melting point. Molar heat of fusion of water is + 6.02 KJ/mol.
- **Molar heat of vapourization** is the heat required to convert one mole of a liquid into its vapours at its boiling point. The molar heat of vapourization of water is 40.7KJ/mol.
- **Molar heat of sublimation** is the heat absorbs when one mole of a solid directly change into vapours without going through liquid state. It is the sum of molar heat of fusion and molar heat of vapourization.
- **Liquid crystals** is state between liquid and crystalline solids. They are used in making LCDs, ATM machines, computers etc.

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EXERCISE

Multiple Choice Questions

1. Choose the correct answer

(i) The boiling point of water (H_2O) is 100°C where as that of hydrogen sulphide (H_2S) is 42°C, This can be attributed to:
(a) Smaller bond angle of H_2S than H_2O
(b) Smaller radii of oxygen than sulphur
(c) High I.P of oxygen than sulphur
(d) Tendency of water to form hydrogen bond

(ii) Liquids can form convex meniscus in a narrow glass tube when:
(a) Cohesive forces are stronger than adhesive forces
(b) Adhesive forces are stronger than cohesive forces
(c) Cohesive and adhesive forces are equal in strength
(d) None of these

(iii) Which of the following statement is incorrect?
(a) Viscosity is the resistance against flow of liquid
(b) Liquid possess definite volume
(c) One feels sense of cooling after bath due to condensation
(d) Sublimation is endothermic process.

(iv) Which of the following possesses weakest London dispersion forces:
(a) Cl_2 (b) F_2 (c) Br_2 (d) I_2

(v) Hydrogen bond is not found in:
(a) H_2O (b) CH_4 (c) NH_3 (d) HF

(vi) The boiling points of different liquids may be different at the same external pressure due to:
(a) Amounts of liquids (b) Intermolecular forces
(c) Surface area (d) Viscosities

(vii) Which statement is incorrect about evaporation?
(a) It is an exothermic process
(b) It is a reverse process of condensation
(c) It occurs at all temperature and pressure
(d) It causes cooling effect

(viii) Which of the following liquids show maximum surface tension?
(a) Water (b) Mercury (c) Ethyl alcohol (d) Gasoline

(ix) (ix) A non-polar molecule with bigger size will experience:
(a) London forces (b) dipole-dipole interaction
(c) Hydrogen bonding (d) All of these

(x) Cooking time is reduced in a pressure cooker because:
(a) Boiling point of water increases (b) Boiling point of water decreases
(c) Vapor pressure of liquid is reduced (d) Heat is uniformly distributed

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Short Questions

1. Explain the following in terms of kinetic molecular interpretation of liquids:
   (a) Diffusion (b) Compression (c) Expansion (d)Molecular motion
2. Name three major kinds of intermolecular forces in liquids. Explain intermolecular forces in HCl.
3. Define the following:
   (a) Molar heat of fusion (b) Molar heat of vapourization (c) Molar heat of Sublimation
4. Describe hydrogen bonding in water and explain the anomalous behavior of water due to hydrogen bonding.
5. Water is more volatile than glycerin but petrol is more volatile than water at the same temperature. Explain in term of intermolecular force.
6. Give reasons for the following:
   i. Water spilled on floor evaporate faster than the same amount of water in a container.
   ii. A falling drop of a liquid is spherical.
   iii. Evaporation is a cooling process.
   iv. Boiling point of liquid remains constant although heat is continuously supplied to the liquid.
   v. Mercury has its meniscus upward.
   vi. Liquids cannot be compressed as gases do.
   vii. Density of water is highest at 4°C.
   viii. Honey is more viscous than water.

Descriptive Questions

1. What is Surface tension? Explain it with example. Give its unit and describe the factors that affect on surface tension of liquids?
2. Explain the factors why honey is more viscous than water?
3. What is hydrogen bond? How is it established? Give its application in industrial and biochemical process.
4. What is meant by liquid crystals? How is it differing from liquids and crystalline solids?

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STATE OF MATTER III: SOLIDS

Chapter 6

Teaching Periods	Assessment	Weightage
14	1	8

Students will be able to:

- **Describe** simple properties of solids e.g., diffusion, compression, expansion, motion of molecules, spaces between them, intermolecular forces and kinetic energy based on kinetic molecular theory.
- **Differentiate** between amorphous and crystalline solids.
- **Describe** properties of crystalline solids like geometrical shape, melting point, cleavage planes, crystal growth, anisotropy, symmetry, isomorphism, polymorphism, allotropy and transition temperature.
- **Explain** the significance of the unit cell to the shape of the crystal using NaCl as an example.
- **Name** three types of packing arrangements and draw or construct models of them.
- **Name** three factors that affect the shape of an ionic crystal.
- **Define** lattice energy.
- **Differentiate** between ionic, covalent, molecular and metallic crystalline solids.
- **Explain** the low density and high heat of fusion of ice.
- **Define** and explain molecular and metallic solids.

INTRODUCTION

Solid is a condense state of matter in which particles (atoms, ions or molecules) are closely arranged in fixed position and have very little freedom of movement due to strong inter ionic, inter atomic or inter molecular forces. Unlike liquids and gases, solids cannot flow and cannot take up the shape of container. Solids are identified by their rigid structure and mechanical strength. They tend to resist external pressure applied on them and are nearly incompressible. Solids have very high density as compared to liquids and gases, most of them melt on heating, and however some directly convert into gaseous state. Progress in science and technology leads to advancement in knowledge about solid state, hence we must endeavours to understand the nature and behavior of solids.

6.1 KINETIC MOLECULAR INTERPRETATION OF SOLIDS

Kinetic molecular theory tells us that particles in a solid have very little space due to strong attractive forces. These particles are tightly packed together about their mean position. Owing to the restricted movement of particles, solids have fixed shape and volume. However when a solid is heated, the vibrational energy of particles increases and when a particular temperature is reached the vibrational energy of solid particles overcome the attractive forces. As a result, particles of solid lose their mean position as well as specific arrangement and change into liquid state.

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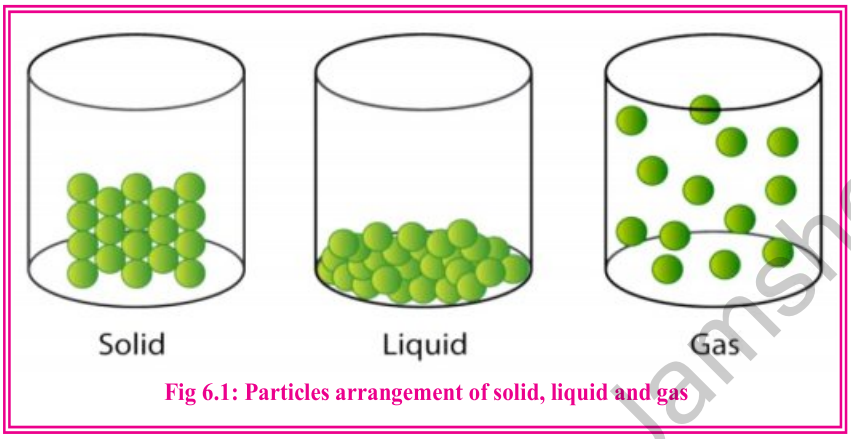

Fig 6.1: Particles arrangement of solid, liquid and gas

6.1.1 Simple Properties of Solids

Before going to deal with the concept of solid in broader aspect in the next sections, you need to understand some simple properties of solids related to their inter particles associations based on some limitations in the freedom of particles movement.

Kinetic energy and Molecular motion: Particles of solid can only vibrate about their mean position. They do not bear translational and rotational kinetic energy as liquid particles do.

Intermolecular forces: Particles in solid held together tightly in a fixed position due to some strong intermolecular forces.

Compression: Solids are nearly incompressible. In term of kinetic theory, particles are tightly bonded together due to strong attractive forces therefore only a very small empty space is left among them. It makes the solid denser, rigid and hard and can withstand considerable external pressure.

Diffusion: Solids diffuses very slowly as compared to liquids and gases. This is due to the close packing of particles and restriction against their free movement.

Expansion: Solids expand on heating but this ability is very little as compared to liquids and gases. Since particles of solids are arranged orderly in a fixed position, an increase in temperature weakens their attractive forces giving an increase in the volume.

Melting: Solids melt on heating at a particular temperature. In term of kinetic theory, vibrational energy of particles increases on heating until at melting temperature the vibrational energy of the solid particles overcome the energy of existing bonds among them thus solid melt and change into liquid state.

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Sublimation: Some solids directly change into vapours on heating without passing through liquid phase, which is known as sublimation. For example naphthalene, iodine, camphor and solid CO_2 are sublime.

In term of kinetic theory, the attractive forces in these solids are quite weaker compared with ordinary solids, thus on heating high energy surface particles of these solids directly pass into vapours.

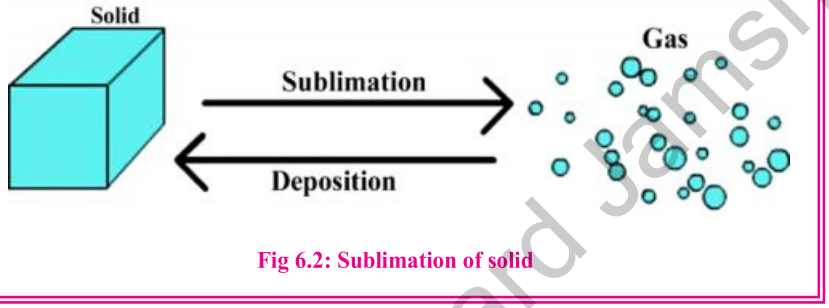

Fig 6.2: Sublimation of solid

6.2 TYPES OF SOLIDS

Most of the substances around us are solids rather than liquid or gases. Solids like sugar, salts, metals etc are hard and crystalline while some others such as rubber, plastic, etc are soft and amorphous. There are two main classes of solids named as crystalline solids and amorphous solids.

6.2.1 Crystalline Solids

Solids which comprise particles (atoms, molecules or ions) arranged in a well-defined three-dimensional order are known as crystalline solids. In these solids, the structural unit is an arranged in three dimensions. This regular pattern throughout the crystal is called crystal lattice and the smallest fundamental portion of crystal which repeats in all three dimensions to give the crystal structure is called unit cell. Crystalline solids are characterized by definite geometrical shape and sharp melting points. They are also known as true solids. Most of the solids in nature occur as crystalline solids. Some common example of crystalline solids are Sodium chloride, Diamond, Graphite, Sucrose, Ferrous sulphate, Magnesium chloride, Sodium carbonate etc.

6.2.2 Amorphous Solids

Solids which do not have a three dimensional regular arrangement of particles (atoms, molecules or ions) are known as amorphous solids. These solids do not have long range order of particles and assumed them closer to liquid. Thus, on continuous heating they gradually soften and finally convert into a flowing liquid. Glass for example is often called as super cooled liquid.

Do You Know?

Amorphous silica is one of the best material for converting sunlight into electricity (Photovoltaic cell).

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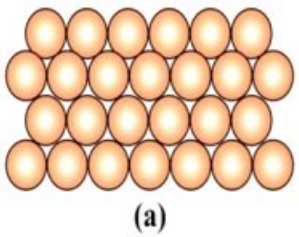
These solids do not have sharp melting point which means that they melt over a wide range of temperatures. Some common example of amorphous solids include rubber, glass, charcoal, plastics etc.



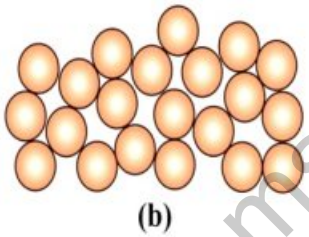


Fig 6.3: Arrangement of particles in (a) crystalline solids (b) amorphous solid

Table 6.1 Comparative Study of Crystalline and Amorphous Solids

Crystalline	Amorphous
They exist in definite geometrical shape	They don't have definite shape
They have sharp melting points	They melt over a wide range of temperatures
They show anisotropic behavior that is properties like mechanical strength, refractive index and electrical conductivity depend upon direction	They are isotropic in nature
They can be cut down at fixed cleavage plane	When they are cut or hammered cause in irregular fracture

6.3 PROPERTIES OF CRYSTALLINE SOLIDS

So far we have learnt that particles of crystalline solids vibrate about their allocated position in a well defined structure. Now we need to know about their fundamental properties on the basis of which a crystalline solid is distinguished from amorphous solid.

6.3.1 Symmetry

When a crystal is rotated to a certain angle, a regular repetition of edges and faces is observed, this is known as symmetry.

The symmetry of an individual crystal is determined by three elements known as plane of symmetry, axis of symmetry and centre of symmetry.

Plane of symmetry: It is an imaginary plane which divides the crystal into two equal parts in such a way that one is the image of other.

Axis of symmetry: It is an imaginary line on which the crystal can be rotated through 360°.

Centre of symmetry: It is a point in the crystal from which we can draw a line. This line intersects the surface of the crystal at equal distance on either side.

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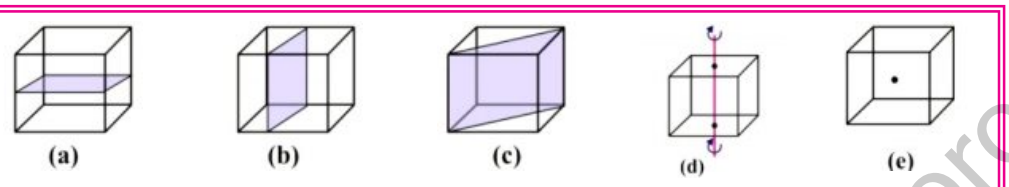

Fig 6.4: (a) (b) (c) planes of symmetry (d) axis of symmetry (e) Centre of symmetry of cubic crystal

6.3.2 Geometrical Shape of Crystals

Since the particles in crystalline solids are orderly organized in a repeating pattern in three dimensions, they possess definite geometrical shape. For example the shape of unit cell of diamond is cubic and graphite is hexagonal.

6.3.3 Sharp Melting Point

Crystalline solids have sharp melting point because attractive forces between the particles are long ranged and uniform.

6.3.4 Cleavage Plane

A big crystal can be cut or split into smaller crystals of identical shape, this process is called as cleavage and the line or point which have direction of cleavage is known as cleavage plane.

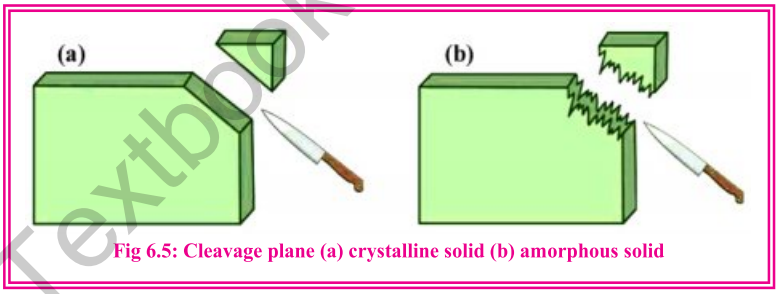

Fig 6.5: Cleavage plane (a) crystalline solid (b) amorphous solid

6.3.5 Crystal growth

When a hot saturated solution of salt or a molten solid is allowed to cool slowly, crystals are grown in various directions it is called crystal growth. For example a slow cooling of hot saturated solution of table salt gives cubic crystals.

6.3.6 Anisotropy

A very unique behavior of crystalline solid is the variation in certain physical properties (Refractive index, Coefficient of thermal expansion, Electrical and Thermal conductivity) along different directions in the crystal lattice. This phenomenon is known as anisotropy. The reason of anisotropic attitude is attributed to the fact that arrangement of particles is different in the different directions.

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For example graphite conduct electricity parallel to the layer because of electron movement is not allowed on perpendicular of the layer.

6.3.7 Isomorphism

The phenomenon in which different solid substances exist in the same crystalline structure is called isomorphism (iso; same and morphous; shape) and the substances which exhibit this behaviour are referred as isomorphous.

The constituent atoms of isomorphous substance are in the same atomic ratio but they have different physical and chemical properties.

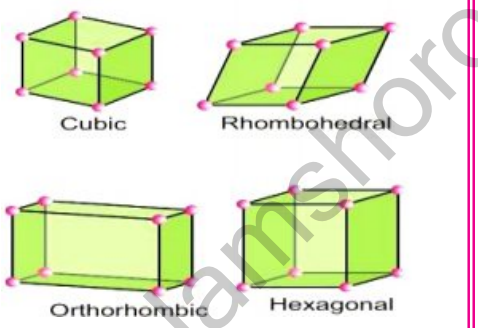

Fig 6.6: Geometry of crystals

Table 6.2 Isomorphism in different crystalline solids

Isomorphic Substance	Atomic Ratio	Geometry of Unit cell
NaCl and MgO	1 : 1	Cubic
$NaNO_3$ and $CaCO_3$	1 : 1 : 3	Rhombohedral
$ZnSO_4$ and $NiSO_4$	1 : 1 : 4	Orthorhombic
Ag_2SO_4 and Na_2SO_4	2 : 1 : 4	Hexagonal

6.3.8 Polymorphism

In the studies of crystallography, a unique feature of crystalline solid is the phenomena of exhibiting polymorphism. It refers to the existence of one chemical compound into two or more feasible geometry of unit cell. **"The phenomenon in which a substance under different conditions can exist in more than one crystalline structure is known as polymorphism"**. It is important to note that chemical nature of polymorphous substances remains the same but their physical properties like solubility, melting point, refractive index, hardness, thermal stability etc are different.

For example Lime ($CaCO_3$) exists in the following two crystalline form.

(i) Calcite ($CaCO_3$) which posses trigonal crystal structure

(ii) Aragonite ($CaCO_3$) which posses orthorhombic crystal structure

Both calcite and Aragonite have same chemical composition but different physical properties.

Self Assessment

(i) Crystalline substances are anisotropic in behavior, what does this statement means.

(ii) NaCl and MgO are isomeric substances how can you explain it?

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6.3.9 Allotropic Modification and Transition Temperature

Allotropy is limited to pure elements only. It defines as **"The existence of the same elements in two or more different crystal structures having the same chemical nature but different physical properties"**.

Carbon exists in two crystalline allotropic forms one is called Diamond which has a cubic geometry while other is Graphite in which the geometry of crystal is hexagonal.

The two important crystalline allotropic form of sulphure are:

* Rhombic sulphur ($\propto$ - sulphur)
* Monoclinic sulphur (β - sulphur)

Rhombic sulphur is a yellow octahedral crystalline form. It is stable at ordinary temperature but when heated gently above 95.5°C, it change into monoclinic sulphu

Transition temperature: The temperature at which two allotropic forms of the same element co exist in equilibrium with each other is known as transition temperature.

The transition temperature of Rhombic and monoclinic sulphur is 95.5°C.

$$\text{Rhombic Sulphur} \underset{}{\overset{95.5^{\circ}C}{\rightleftharpoons}} \text{Monoclinic Sulphur}$$

This means that just above and below of this specific temperature only one allotropic form can exist.

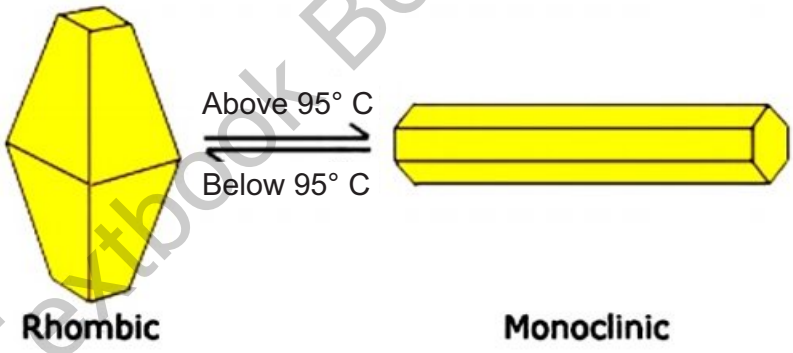

Fig 6.7: Rhombic and monoclinic sulphur at transition temperature

6.4 TYPES OF CRYSTALLINE SOLIDS

Crystalline solids are classified into following four main categories based on the nature of attractive forces.

6.4.1 Ionic Solids

These solids consist of positive and negative charged ions. The arrangement of these ions in three dimension network takes place in such a way that each ion is surrounded by fixed number of oppositively charged ions so that the strong and long range electrostatic attractions have developed among the ions in all directions.

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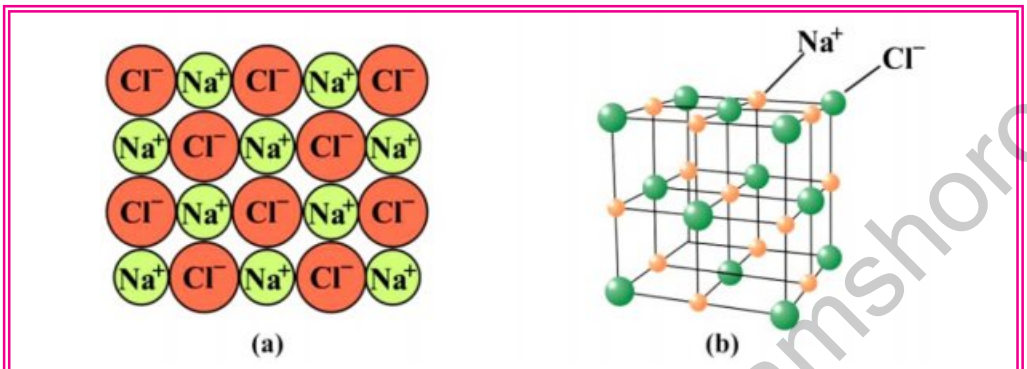

Fig 6.7: (a) Arrangement of ions in sodium chloride crystal (b) crystal lattice of sodium chloride

Some characteristics properties of ionic crystals are described here.

(i) They are hard at room temperature due to the presence of strong electrostatic forces of attraction.

(ii) They are brittle and can be shatter easily by hammering.

(iii) They possess high melting point.

(iv) They are soluble in water and similar polar solvent.

(v) They are unable to conduct electricity and heat in solid state because of restricted vibration of ions about their allocated position. In molten or aqueous state they conduct electricity since the ions move freely.

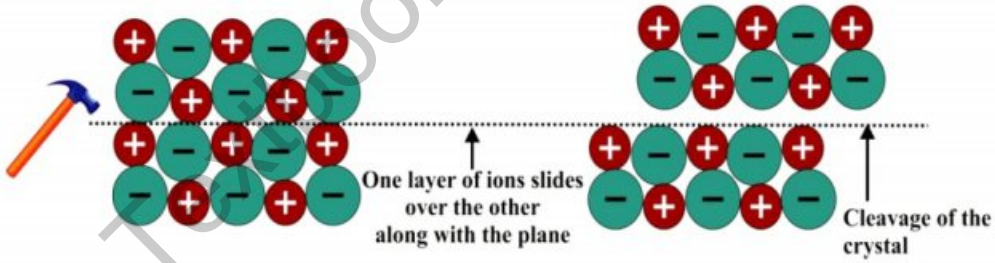

Fig 6.8: Ionic crystals are Brittle and break by hammering

Factors affecting the shape of an Ionic Crystal

Following factors affect the shape of ionic crystal.

i) Ionic Association:

Since the holding force in ionic solids is electrostatic type, the oppositively charge ions are closely packed in specific order to form a particular

Do You Know?

$CaCl_2$ an ionic solid has the ability to absorb moisture from air due to its hygroscopic and deliquescent nature. Its rate of moisture absorption is different from day to day depending upon air temperature and humidity. Therefore its serves as better dehumidifier than silica gel.

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shape. For example in the crystal of common salt, each Na^+ ion is covered up with six Cl^- ions. Similarly each Cl^- ion is surrounding by six Na^+ ion this arrangement give a cubic shape.

ii) Radius Ratio:

It is the ratio of radius of cation to that of radius of anion (r^+ / r^-) in the given ionic solid. It helps in predicting the shape of ionic solid.

$$\text{Radius ratio} = \frac{\text{radius of cation}}{\text{radius of anion}}$$

Table 6.3 Limiting radius ratio for predicting the shape of ionic solids

Limiting Radius ratio (r^+ / r^-)	Coordination No.	Geometry	Examples
0.15 to 0.22	3	Triangular planar	B_2O_3
0.225 to 0.414	4	Tetrahedral	ZnS, CuCl
0.414 to 0.732	6	Octahedral/Face Centered Cubic	NaCl, MgO
0.732 to 1.00	8	Body Centered Cubic	CsCl

iii) Poor Conductivity

Ionic compound are good conductor of electricity either in fused state or in aqueous solution due to the free movement of ions towards respective electrode when a potential difference is applied.

However, ionic compound exhibit poor conductivity in the solid state which indicates that ions are not free to move, rather they stay in a fixed position ensuring that the ionic crystal has a fixed shape.

Self Assessment

If the radius of Zn^{+2} ion is 0.74Å and S^{-2} ion is 1.84 Å, determine the radius ratio and predict the geometry of ZnS.

6.4.2 Covalent Solids

Covalent or atomic solids consist of atoms of the same or different elements which are bonded to each other by strong covalent bonds. A perfect single crystal of a covalent solid is considered as a single giant molecule as seen in diamond and silicon carbide etc.

Carbon exists in to common crystalline form known as diamond and graphite. Both are covalent solids but have different physical properties due to difference in the particles arrangement.

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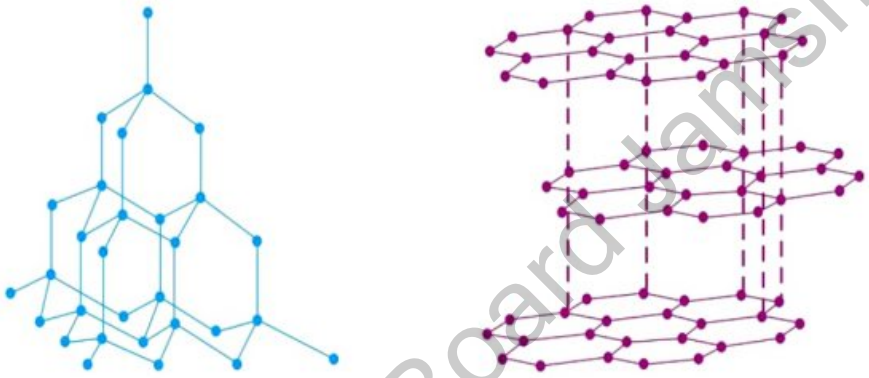
In diamond each carbon atom is covalently bonded with four other carbon atoms at an angle of 109.5° to form basic tetrahedral unit. This trend of covalent bond formation run continuously in the entire crystal three dimensionally and develop a network of covalent bonding which give rise to a giant structure.

Due to the close packing of atoms and large number of covalent bonds, diamond is hardest substance known having a very high melting point.



(a) (b)

Fig 6.9: structure of covalent solids (a) Diamond (b) Graphite

In graphite each carbon is bonded to three other carbon atoms at 120° forming layers of hexagons. These layers are held together by weak Vander Waal forces and are 3.35Å apart from each other. The greasy nature of graphite is due to inter layer space which allows one layer to glide over the other.

Some characteristics properties of covalent crystals are described below.

(i) Metallic solids are hard, high melting point and high density due to strong bonging among atoms.
(ii) They are bad conductor of electricity.
(iii) They are insoluble in water.
(iv) Graphite however, conducts electricity parallel to the layers due to the availability of delocalized electrons.

6.4.3 Metallic Solids

Particles of metallic crystals are metal atoms. According to electron sea theory, metal atoms lose their all valence electrons into the vacant spaces and become positively charged metal ions. These positive charged metal ions arranged themselves in a three dimensional crystal lattice and bonded with sea of electrons. This unique force of attraction between metal cations and sea of delocalized electrons is known as metallic bond.

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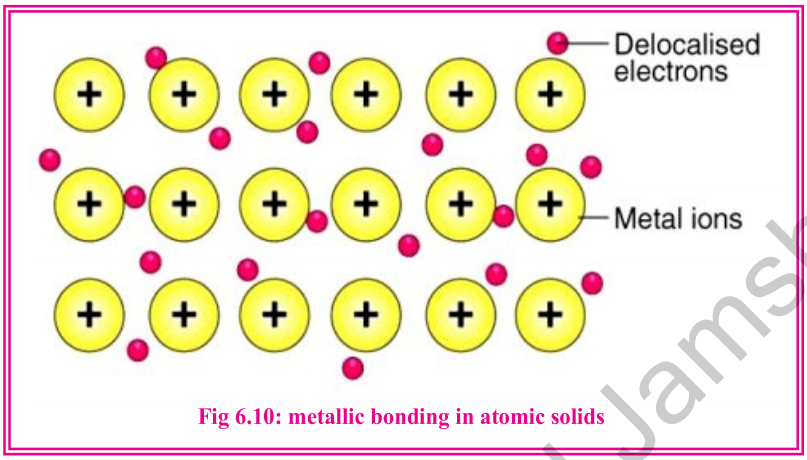

Fig 6.10: metallic bonding in atomic solids

Some characteristics properties of ionic crystals are described below.

(i) Metallic solids are identified by their malleability and ductility.

(ii) Metallic solids are looks like dull but when freshly cut, the inner layer appear shiny. This property is known as metallic luster.

(iii) The electrical conductivity of metallic solids is due to the free movement of delocalized electron in electric field.

(iv) Metals are good conductor of heat. Thus when a rod of metal is heated from one of its terminal, the free electrons of metal absorb heat and hence their kinetic energy increases. These free electrons then tends move towards the other end of the rod which is relatively cooler.

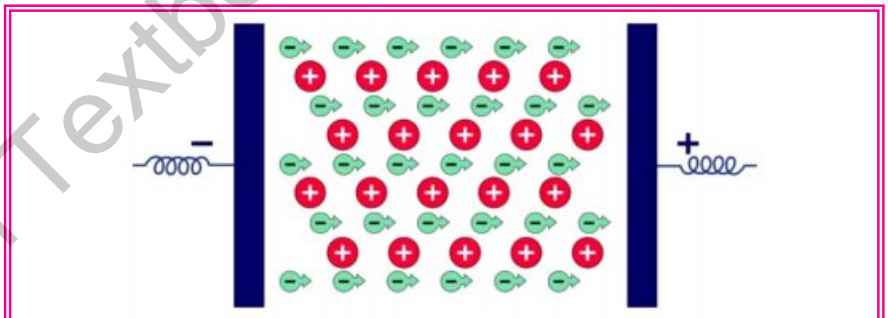

Fig 6.11: Flow of delocalized electrons in metal rod under electric conduction

Self Assessment

(i) How do metallic and ionic substance differ in conducting electricity.
(ii) How graphite conduct electricity?

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6.4.4 Molecular Solids

In these solids, constituent particles are molecules of the same substance.
The bonding in a particular molecular solid may be one of the following types.

(i) Dipole – dipole interaction
(ii) Hydrogen bonding
(iii) London forces

Since these intermolecular forces are much weaker than attractive forces found in ionic or covalent solids, that is why molecular crystals melt under relatively low temperature compared with ionic or covalent crystals. Molecular solid have low density, low melting point and serves as bad conductor of electricity.

Reason of low density and high heat of fusion of ice

Low density of ice is attributed to the tetrahedral arrangement of H_2O molecules through hydrogen bonding which create empty spaces and causes the structure of ice to expand. The expansion in the volume of ice decreases its density that is why ice float on liquid water. The high latent heat of fusion of ice (97.7 cal/g) is also related to the hydrogen bonding.

Table 6.4 Comparative study of four types of Crystalline Solids

Name of Crystalline Solid	Particles Type	Nature of Bond	General Properties	Examples
Ionic Crystals	Cat ion and an ions	Ionic bond	Hard, high m.p Conductor of electricity in molten and aqueous state	NaCl, KBr, $CaCl_2$
Covalent Crystals	Atoms	Network of covalent bond	Hard, high m.p Mostly bad conductor of electricity	Silicon carbide, Diamond
Metallic Crystals	Metal cat ion and electron sea	Metallic bond	Hard, high m.p malleable, ductile conductor of electricity	Na, Al, Fe, Cu etc
Molecualr Crystals	Molecules	London forces Hydrogen bond Dipole dipole interaction	Soft, low m.p bad conductor of electricity	Ice, Iodine, Dry ice

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6.5 CRYSTAL LATTICE

Atoms, ions or molecules in all solids are orderly placed on fixed positions or points in a most adequate manner. A crystal lattice or space lattice is a set of these infinite points representing the particles of crystals in three dimensional space. It is referred as "an array of points representing atoms, ion, or molecules of a crystal placed at three dimensional space.

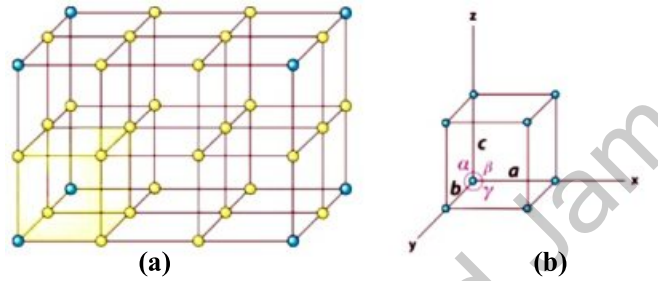

Fig 6.12: (a) structure of crystal lattice (b) dimensions of unit cell

6.5.1 Unit Cell

The smallest structural part of a crystal lattice is known as unit cell. It shows the 3D pattern of a specific crystal lattice in a least volume and provide us a detailed structural information of a crystalline solid. **"The smallest repeating pattern from which the lattice is built is known as unit cell".** The unit cells are repeated again and again to make the whole crystal lattice.

Do You Know?

There are seven crystal system based on axis (a, b, c) and angle ($\propto, \beta, \gamma$)

* Cubic → a = b = c and $\propto = \beta = \gamma = 90°$
* Tetragonal → a = b ≠ c and $\propto = \beta = \gamma = 90°$
* Orthorhombic → a ≠ b ≠ c and $\propto = \beta = \gamma = 90°$
* Rhombohedral → a = b = c and $\propto = \beta = \gamma \neq 90°$
* Hexagonal → a = b ≠ c and $\propto = \beta = 90°$ but $\gamma = 120°$
* Monoclinic → a ≠ b ≠ c and $\propto = \gamma = 90°$ but $\beta \neq 90°$
* Triclinic → a ≠ b ≠ c and $\propto \neq \beta \neq \gamma \neq 90°$

The shape of a unit cell is associated with three axial distance named as (a, b and c) and three axial angles named as ($\propto, \beta$ and γ). The axial distance (a, b, c) are the distances along three edges (x, y, z). The angle between **b** and **c** is $\propto$, the angle between **a** and **c** is β and the angle between **a** and **b** is γ.

6.5.2 Unit Cell of NaCl Crystal

The structure of sodium chloride crystal is built up by repeating face centered cubic unit cells. In crystallographic view point, each Na^+ ion is covered up with six Cl^- ions; similarly each Cl^- ion is surrounded by six Na^+ ions. This ionic arrangement suggests that the coordination number of sodium chloride crystal is 12.

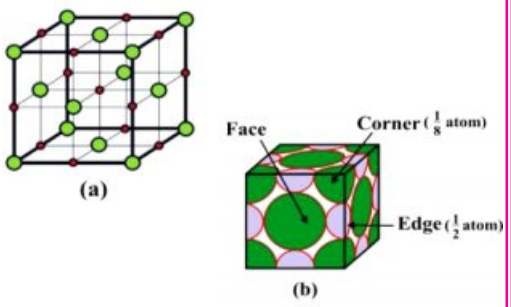

Fig 6.13: (a) cubic unit cell of sodium chloride (b) portion of atoms in the cubic unit cell

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Chloride (Cl^-) ion determination

Fig 6.10 reveals that eight (8) chloride ions are located at the eight corners of cube while six (6) chloride ions (Cl^-) at the centre of its six faces. On the basis of this information, one can determine the number of Cl^- ions in each unit cell of sodium chloride crystal.

Since each chloride ion (Cl^-) at the corner is shared between eight other unit cells thus, its share to each unit cell should be $\frac{1}{8}$ therefore,

No. of chloride (Cl^-) ions at the corner of one unit cell = $\frac{1}{8} \times 8 = 1$.

On the other hand six faces possess six chloride ions at their centre but each face share with two unit cells therefore.

No. of chloride (Cl^-) ions at face centre = $\frac{1}{2} \times 6 = 3$

Total No. of chloride ions in each unit cell = 1 + 3 = 4.

Sodium (Na^+) ion determination:

There are 12 edges of cube, each contains one sodium ion (Na^+). Also each Na^+ ion on the edge of cube is shared by four (4) unit cells therefore.

No. of Na^+ ions on each edge = $\frac{1}{4} \times 12 = 3$.

No. of Na^+ ion on the centre of unit cell = 1.

Total Na^+ ion in each unit cell = 3 + 1 = 4.

Close Packing in Metallic Solids

It is believed that metal atoms are arranged most likely in a tightly packed balls structure which minimize the empty space between them and justifying their high density. There are three types of close packing found in metals.

(i) Hexagonal Close Packing

In this type of packing the empty spaces create due to three neighboring sphere of the first layer is filled by the alignment of spheres of second layer. The spheres of third layer are directly parallel on the sphere of first layer so that an ABA type arrangement is developed which covers the 74% of empty space.

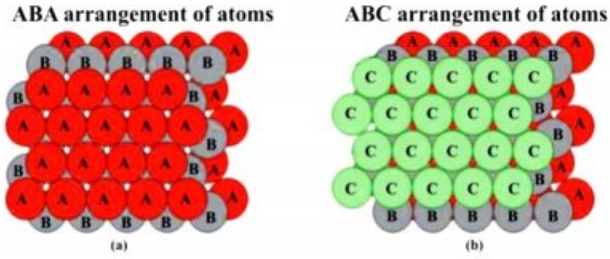

Fig 6.14: (a) Hexagonal close packing (b) face centered cubic close packing

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(ii) Face Centered Cubic Close Packing

In this type of packing the void spaces among the spheres of first layer is filled by spheres of second layer; however the spheres of third layer are displaced horizontally from first layer. This gives an ABCA arrangement which covers 74% of empty space.

(iii) Body Centered Cubic

This type of packing has relatively big void space. The arrangement of layer is ABAC type which covers up only 68% of empty space.

Table 6.5 **A brief summary of three kinds of packing in crystalline solids**

Type of close packing	Layer arrangement	Coordination number	Space Used
Hexagonal close packing	ABA	12	74
Face centered cubic close packing	ABCA	12	74
Body centered cubic	ABAC	8	68

6.5.3 Lattice Energy

In the formation of ionic solids, oppositively charged gaseous ions brought closer to each other and arranged three dimensionally in certain pattern. During this process a high amount of energy is released known as lattice energy. It is the energy associated with electrostatic interaction between the ions in a crystal and may be defined as **"the quantity of energy released when one mole of the Ionic crystal is formed from the gaseous Ions"**. It is also defined as the energy required to break one mole of crystalline solid into isolated ions in the gas phase. It is expressed in KJ $mole^{-1}$.

$$Na^{+}_{(g)} + Cl_{(g)} \longrightarrow NaCl_{(s)} \quad (\Delta H = -787 KJ/mol)$$

$$NaCl_{(s)} \longrightarrow Na^{+}_{(g)} + Cl^{-}_{(g)} \quad (\Delta H = +787 KJ/mol)$$

The lattice energy decreases with the increase in the size of cation or anions. The reason in both cases is the same. The smaller the size of cat ion or an ion the closer the packing of oppositively charged ions and thus require high energy to break the lattice and convert the solid into isolated ions. For example lattice energy of NaF (923 KJ/mol) is higher than KF (821 KJ/mol) because of smaller ionic radii of Na^{+} than K^{+} ion. The smaller ionic size of Na^{+} ion makes the packing more closely and thus need relatively high lattice energy for the separation of ions.

Lattice energy also affected by the charge of ion. The greater the charge of ion the higher is the lattice energy. For example lattice energy of BeF_2 (3505 KJ/mol) is much higher than LiF (1036) because Lithium possess +1 charge in LiF where as the charge of Beryllium is +2 in BeF_2.

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Table 6.6	Lattice energy values of some ionic solid in KJ/mole		
Ionic Solids	**Lattice energy KJ/mole**	**Ionic Solids**	**Lattice energy KJ/mole**
LiF	1036	BeF_2	3505
NaF	923	$BeCl_2$	3020
KF	821	$MgCl_2$	2524
LiCl	853	$MgBr_2$	440
NaCl	787	$CaCl_2$	2258
LiBr	807	$CaBr_2$	2176
NaBr	747	$AlCl_3$	5492

Lattice energy values are important in predicting the solubility of ionic solids in water. Ionic compounds with smaller Lattice energy and greater hydration energy are more soluble in water. Lattice energy is indirectly determined by the use of Born-Haber cycle. The procedure is based on Hess's Law (see section 11.4).

Society, Technology and Science

Specific use of crystalline and amorphous solid

Many crystalline and amorphous solids have diverse application in current technology and science. For example

- Sodium chloride is used in the manufacturing of various industrial chemicals such as Caustic Soda, Soda Ash, Sodium metal etc. It maintains the electrolyte balance in fluid of our body and also serves as food preservative.
- Graphite due to its slippery nature use as lubricant and in making pencils.
- Polystyrene is foam like amorphous solid. It is used in packaging of food, laboratory wares and sensitive electronic items.

Activity

This activity will let you verify that graphite conducts electricity.

Take a pencil and sharp it from both the sides. Take a metallic wire (of copper for instance) and then connect the two ends of pencil through wire with a battery or cell having a bulb in between as a part of circuit. What will you observe?

You will observe that the bulb will glow as soon as you have closed circuit, it means that the pencil is conducting charges since it contains lead and graphite. The former is a metal while the latter is a non-metal but it still conducts electricity due to the presence of a spare electron in its crystal lattice.

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SUMMARY with Key Terms

- **Solid** is a condense state of matter in which particles are tightly bonded together due to strong attractive forces.
- **Crystalline Solids** consists of numerous small building blocks called as crystals. They are identified by sharp melting point, anisotropic behavior and cleavage plane.
- **Crystal** of each solid has definite geometrical shapes, sharp edges and flat faces.
- **Amorphous Solids** are those in which particles are not organized in definite lattice pattern but are randomly arranged.
- **Sublimation** is the phenomena of direct conversion of solid into gases. This happens due to weak inter particles bonding in sublime solids.
- **Anisotropy** describes the behavior of crystalline solids in the variation of certain physical properties like electric conduction and refractive index.
- **Isomorphism** is the phenomena in which different solid substances exists in the same crystalline structure.
- **Polymorphism** is the phenomena in which a solid substance under different conditions can exist in more than one crystalline shape.
- **Allotropy** is the phenomena in which same element exist in two or more crystal structure.
- **Transition temperature** is the temperature at which both allotropic form of the same element co exist in equilibrium.
- **Ionic crystals** are hard and brittle because oppositively charged ions held up through strong attractive forces. Thus on applying external pressure similar ion come in front of each and create repulsive forces.
- **Diamond** is the hardest substance known because of close packing of atoms and large number of covalent bonds.
- **Graphite** is conductor of electricity parallel to the layer because in this direction flow of delocalize electrons is possible.
- **Metallic solids** are characterized by their malleability, ductility electrical and thermal conduction.
- **Crystal Lattice of sodium chloride** is made up of faced centered cubic cell in which eight Cl^- ions are located at eight corners and one Cl^- ion is located at the centre of each face. On the other hand 12 Na^+ ions are located at the edge and one Na^+ ion on the centre. However total number of Na^+ and Cl^- ions in each unit cell are ($Na^+ = 4$ and $Cl^- = 4$)
- **Lattice energy** is the energy release when one mole of ionic crystal is formed from isolated gaseous ions.

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EXERCISE

Multiple Choice Questions

1. Choose the correct answer

(i) Quantity of energy released when 1 mole of the ionic crystal is formed from the gaseous ions is called:
(a) Bond energy (b) Potential energy
(c) Ionization energy (d) Lattice energy

(ii) Graphite can conduct electricity in one direction only.With this behavior, it is said to be:
(a) Amorphous (b) Symmetrical
(c) Anisotropic (d) Polymorphous

(iii) NaCl and MgO are isomorphous solids because these have same:
(a) Melting point (b) Boiling point
(c) Geometrical shapes (d) Chemical Properties

(iv) The temperature at which two allotropic forms co-exist in equilibrium is called as:
(a) Melting temperature (b) Fusion temperature
(c) Transition temperature (d) Critical temperature

(v) Diamond is the example of:
(a) Ionic solid (b) Covalent solid
(c) Metallic solid (d) Molecular solid

(vi) Ice is a molecular solid, the intermolecular force of attraction among its molecules are:
(a) Ionic bond (b) Covalent bond
(c) Metallic bond (d) Hydrogen bond

(vii) If all three axes in unit cell are of different length but all angles are of 90° then it is identified as:
(a) Orthorhombic system (b) Cubic system
(c) Tetragonal system (d) Hexagonal system

(viii) In NaCl, each Na^+ ion is surrounded by Cl^- ions in the numbers:
(a) Four (b) Three
(c) Six (d)Seven

(ix) It is an example of crystalline solid:
(a) Alum (b) Glass
(c) Plastic (d) Rubber

(x) Each unit cell of sodium chloride consists of:
(a) Eight Na^+ and Eight Cl^- ions (b) Two Na^+ and Two Cl^- ions
(c) Four Na^+ and Four Cl^- ions (d) Four Na^+ and Six Cl^- ions

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Short Questions

1. Define the following terms:
   * Allotropy * Sublimation * Melting point * Unit cell
2. Define anisotropy. Which type of solids have this property?
3. What is Transition temperature? Explain with examples.
4. Explain why diamond is non-conductor of electricity and Graphite is a conductor?
5. Define lattice energy. Explain how it is effected by size and the charge of ion.
6. Differentiate between the following:
   (i) Crystalline and amorphous solids (ii) Isomorphism and polymorphism
7. Explain the following with scientific reason.
   (i) Why the compressibility of solids is nearly zero?
   (ii) Why some solids are sublime in nature?

Descriptive Questions

1. Define unit cell. Draw a diagram to show its axial distances and axial angles.
2. Give four properties of ionic solids. How can you determine the number of Na^+ and Cl^- ions in a unit cell of sodium chloride?
3. Give a brief account on metallic solids. Why they conduct heat and electricity?
4. What is meant by polymorphism? How it is related to allotropy. Give your answer with examples.
5. Molecular solids are soft and possess low melting point, how can you justify this statement?

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CHEMICAL EQUILIBRIUM

Chapter 7

Teaching Periods	Assessment	Weightage
9	1	7

Students will be able to:

- **Define** chemical equilibrium in term of a reversible reaction.
- **Write** both forward and reverse reactions an describe the macroscopic characteristics of each.
- **State** the necessary conditions for equilibrium and the ways that equilibrium can be recognized.
- **Write** the equilibrium expression for a given chemical reaction.
- **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.
- **Determine** the reactants or products are favored in a chemical reaction, given the equilibrium constant.
- **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.
- **Explain** industrial applications of Le Chatelier's Principle using Haber's process as an example.
- **Define** and explain solubility product.
- **Define** and explain common ion effect giving suitable examples.

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INTRODUCTION

Chemical reactions are generally treated as the conversion of entire stoichiometric amount of reactants into products. This is true for some reactions which carry out in an open vessel where the product once formed cannot be reversed. These are known as irreversible or unidirectional reactions and are shown by arrow (→) between reactants to products pointing towards products. One of the real life examples of these reactions is the combustion of methane while cooking in kitchen; it gives carbon dioxide and water.

$$CH_{4\,(g)} + 2O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2H_2O_{(l)}$$

However, it is a concerted fact that many reactions do not go to completion under a given set of conditions of temperature, pressure and concentration, especially when carried out in a closed vessel. These are known as reversible reactions. These reactions reached a stage where concentration of reactant and product becomes constant; this is known as chemical equilibrium.

7.1 REVERSIBLE REACTIONS AND DYNAMIC EQUILIBRIUM

Reversible reactions are those which produce only to a certain extent the products formed in these reactions may suddenly recombine and transform back into original reactants. Hence a two way reaction is established which occur simultaneously and continuously until the system reaches the state of equilibrium. We generally denote these type of reactions by a two half-headed arrows (⇌) pointing both directions in the chemical equation.

Some common examples of reversible reactions are mentioned below.

(i) Esterification of acid and alcohol

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \underset{\text{Heat}}{\overset{H_2SO_{4(conc.)}}{\rightleftharpoons}} CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$

(ii) Decomposition of N_2O_4 into NO_2

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

(iii) Formation of ammonia by Haber's process

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

(iv) Formation of Nitric oxide by elemental gases

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

7.1.1 Concept and Explanation of Chemical Equilibrium

Chemical equilibrium is a state of a reversible reaction in which all reacting species are present with no net change in their concentrations and this happens only if the two opposing reactions are occurring with the same rate. It means that reactants and products are continuously interconvert to each other with the same rate thus **"Chemical equilibrium is a state in a reversible reaction where no net change in the concentration of reactants and products occur with time"**.

Table 7.1 **Macroscopic characteristics of forward and reverse reaction.**

Forward reaction	Reverse Reaction
Forward reaction in a reversible reaction represents the transformation of reactants into products.	Backward reaction in a reversible reaction specify the conversion of products into reactants.
It takes place from left to right R ⟶ P	It takes place from right to left. R ⟵ P
At initial stage the rate of this reaction is found to be very fast.	At initial stage the rate of this reaction is noted to be almost negligible.
As the time going on, this reaction becomes slow down.	As the time passes, this reaction speed up gradually until the equilibrium is reached.

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Before going towards mathematical approach of chemical equilibrium, we need to know "when equilibrium is established in a chemical system?" To find the answer let us consider the reaction of Hydrogen and Iodine at an elevated temperature.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

(Purple) **(Colourless)**

Fig 7.1: (a) When the reaction of H_2 & I_2 starts (b) When equilibrium is reached

When certain amount of hydrogen and iodine are mixed in a sealed container at 500°C they start reacting and form some hydrogen iodide. Initially, only the forward reaction occurs because HI was not present in the vessel but as soon as some HI is formed, it readily decomposes back into H_2 and I_2. Although the rate of reverse reaction is quite slow in the beginning due to the low concentration of HI, but as the time goes on, the rate of forward reaction gradually decreases while the rate of reverse reaction increases in the same manner. Ultimately, the rate at which H_2 and I_2 react to form HI becomes equal to the rate at which HI breaks down back into H_2 and I_2 and thus the "equilibrium" is set up. This can be seen by the intensity of purple colour of Iodine which decreases gradually until a constant light purple colour is settled.

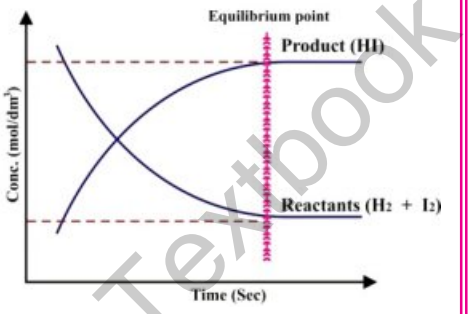

Fig. 7.2:(a) Variation in the molar conc. of H_2 + I_2(reactants) and HI(Products) with time indicating that at equilibrium point conc. of reactant and products become constant

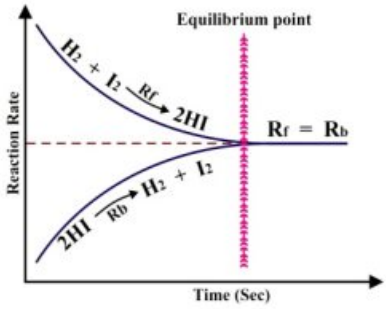

Fig. 7.2:(b) Variation in the rate of forward and backward reaction with time indicating that at equilibrium $R_f = R_b$

Necessary Conditions for equilibrium

For a reaction mixture to exist at equilibrium, it must achieve following conditions.

(i) Chemical equilibrium can only established if it is carried out in a closed vessel because in this system reactant or products particles cannot be escaped out.

(ii) Temperature, pressure and volume should be constant at equilibrium state. If any one of these variable is changed, the system will not remain in equilibrium.

(iii) The rate in the forward reaction and backword reaction should be the same that is the system attain a dynamic state.

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(iv) The concentration of both reactants and products should remain constant. The addition or removal of any one of them causes the equilibrium to be disturbed.

Ways to recognized chemical equilibrium

There are two ways to recognize the formation of a chemical equilibrium.

(i) Physical Method: In this method specific radiations (UV, IR or visible) pass through reaction mixture. Both reactants and products absorb radiations with respect to their equilibrium concentration noted by spectrometer. The % absorbance of these radiations determines the equilibrium concentration of reaction mixture.

Do You Know?

Concentration of a chemical solution is directly proportional to its absorption of light. There is a linear relationship between concentration and absorbance of the solution, which enables the concentration of a solution to be calculated by measuring its absorbance.

(ii) Chemical Method: For determining equilibrium constant by using chemical method let us consider the esterification of ethyl alcohol and acetic acid.

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$

Since the equation of esterification tells us that 1 mole of acetic acid and 1 mole of alcohol reacts to form 1 mole of ester and 1 mole of water therefore we conclude that the amount of acid used up in the reaction is equal to the amount of alcohol consumed and thus at equilibrium we have **(a – x)** mole of acetic acid,**(b – x)** moles of alcohol,**x** moles of ester and **x** moles of water. Reaction table now written as:

Conc.(mole/dm^3)	CH_3COOH +	C_2H_5OH	$\rightleftharpoons$	$CH_3COOC_2H_5$ +	H_2O
Initial	a	b		0	0
Change	-x	-x		x	x
Equilibrium	a – x	b – x		x	x

Now applying Law of mass action.

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$K_c = \frac{[x][x]}{[a\text{-}x][b\text{-}x]}$$

$$K_c = \frac{x^2}{[a\text{-}x][b\text{-}x]}$$

If we repeat the same experiment, by taking different amount of CH_3COOH and C_2H_5OH, we will observe that the value of K_c will be the same with the condition that temperature remains constant.

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Self Assessment

(i) Reversible reactions attain the position of equilibrium if they acquire certain necessary conditions. Can you mention these conditions?
(ii) It is said that chemical equilibrium is dynamic. How can you explain it?

7.1.2 Law of Mass Action and Expression for Equilibrium Constant

So far we have learned that whenever an equilibrium point is reached at a certain temperature in a closed chemical system:
(i) The active masses of both reactants and products stay constant.
(ii) The rate of forward and reverse reactions remains same.

Taking the above two necessary conditions of chemical equilibrium into their research two Norwegian scientists C.M Guldberg and Peter Wage (1864) found out that reversible reaction reaches a state where the ratio of its products concentration to that of reactants concentration becomes constant. On behalf of their research conclusions they derived a quantitative relationship between the rate of reaction and active masses of reacting substance known as law of mass action. It states that **"The rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is proportional to the product of the active masses of reactants"**. The term active mass refers to molar concentration that is the number of moles of reactants and products per dm^3.

To illustrate this law in a mathematical way let us consider a general reversible reaction in which reacting species A, B, C and D exists in equilibrium state at a certain temperature.

$$aA + bB \rightleftharpoons cC + dD$$

According to the law of mass action, the rate of forward reaction (R_f) is directly proportional to the product of active masses of A and B.

$$R_f \propto [A]^a [B]^b \quad \text{or} \quad R_f = K_f [A]^a [B]^b$$

Similarly the rate of backward reaction (R_b) is directly proportional to the active masses of C and D

$$R_b \propto [C]^c [D]^d \quad \text{or} \quad R_b = K_b [C]^c [D]^d$$

Since chemical equilibrium is dynamic in nature representing the equal rate in both direction (Rf = Rb), therefore $K_f [A]^a [B]^b = K_b [C]^c [D]^d$

By rearranging this relation we get

$$\frac{K_f}{K_b} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

At any given temperature both K_f and K_b are constant, the ratio K_f/K_b will also be constant and collectively termed as equilibrium constant symbolized by K_c.

$$\mathbf{K_c} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{---------- (i)}$$

This is known as equilibrium expression or equilibrium law. It reveals that 'when at a certain temperature a chemical reaction reaches to equilibrium state the ratio of active masses of products to reactants become constant'.

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Effect of change in temperature on the value of Kc

The value of equilibrium constant (K_c) varies with temperature. For example K_c for the synthesis of ammonia by Haber's process is 4.1×10^8 at 25°C but 0.5 at 400°C. Similarly Kc for the decomposition of N_2O_4 at 25°C is 4.64×10^{-3} but at 127°C it is 1.53.

Do You Know?

The unit of Kc depends on the form of equilibrium expression.
(i) If the number of moles of reactants are equal to the number of moles of products, Kc has no unit since conc. units (mol/dm^3) of all species are cancelled by each other.
(ii) If the number of moles of reactants are different from number of moles of product then the unit of Kc is determined by using the formula $(mol/dm^3)^{\Delta n}$.
(iii) In general practice the unit of Kc is not written.

Example 7.1

Write down the expressions of equilibrium constant (Kc) for the following reversible reactions.

$$\text{i) } 4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$$

$$\text{ii) } 2N_2O_{5(g)} \rightleftharpoons 4NO_{(g)} + 3O_{2(g)}$$

Solution:

To write an equilibrium expression, we should have the balanced chemical equation. All products given in the equation should be placed on numerator each separately in square bracket while reactants on denominator. Then finally raise the concentration of each substance to the power of its coefficient in the balance chemical equation.

(i) $K_c = \dfrac{[NO]^4\,[H_2O]^6}{[NH_3]^4\,[O_2]^5}$

(ii) $K_c = \dfrac{[NO]^4\,[O_2]^3}{[N_2O_5]^2}$

Example 7.2

An essential step in contact process is the oxidation of SO_2 to SO_3.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

If in an experiment, there are 5 moles of SO_2, 4 moles O_2 and 2.8 moles of SO_3 present at equilibrium state in a $2dm^3$ flask. Calculate Kc.

Solution:

Since equilibrium moles of all components in the reacting mixture are given, we first convert them into molar concentration and then put into equilibrium expression to find out Kc.

$[SO_2]_{eq} = \dfrac{5}{2} = 2.5\ mol/dm^3$

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$[O_2]_{eq} = \frac{4}{2} = 2\ mol/dm^3$

$[SO_3]_{eq} = \frac{2.8}{2} = 1.4\ mol/dm^3$

K_c expression for the given reaction may be written as

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\ [O_2]}$$

By substituting the equilibrium concentrations, we get.

$$K_c = \frac{[1.4]^2}{[2.5]^2\ [2.0]} = 0.157\ mol^{-1} \cdot dm^3$$

Example 7.3

Ethyl acetate is an ester of ethanol and acetic acid commonly use as an organic solvent.

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$

In an esterification process 180g of acetic acid and 138g ethanol were mixed at 298K and allowed to start reaction under necessary conditions. After equilibrium is established 60g of unused acetic acid were present in the reaction mixture. Calculate Kc.

Solution:

Moles of $CH_3COOH = \frac{180}{60} = 3$ moles

Moles of $C_2H_5OH = \frac{138}{46} = 3$ moles

	$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons$		$CH_3COOC_2H_{5(l)} + H_2O_{(l)}$	
Initial	3	3	0	0
Equilibrium conc.	3–x	3–x	x	x

But at equilibrium unused acetic acid is 60g which is equal to 1 mole.

Therefore

$3 - x = 1$

And

$x = 2$

Now substituting values of equilibrium mixture in Kc expression.

$$K_c = \frac{[CH_3COOC_2H_5]\ [H_2O]}{[CH_3COOH]\ [C_2H_5OH]}$$

$$K_c = \frac{[2]\ [2]}{[1]\ [1]} \qquad K_c = 4$$

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7.1.3 Relationship between Kc, Kp, Kx and Kn

Since equilibrium constant (Kc) has formulated from kinetic aspect of equilibrium law, it represents the molar concentrations of products and reactants. However, there are some other ways to express equilibrium constant for the same reaction. For a homogenous gaseous reaction in which all reacting species appear in gaseous state, the concentration of products and reactants can also be expressed in term of their partial pressure because it is easier for a gas to measure its pressure rather than concentration.

For the reaction $aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$

$$K_p = \frac{(P_C)^c \ (P_D)^d}{(P_A)^a \ (P_B)^b} \text{ ---------- (ii)}$$

P_A, P_B P_C P_D are the partial pressure of gases A, B, C, D and exponents a, b, c, d respectively are the coefficients of balanced equation.

Kp defines as **"the ratio of partial pressure of product gases to that of partial pressure of reactant gases each raised to the power equal to its own coefficient in the balanced chemical equation"**.

Equilibrium constant some time express in terms of K_n and K_x when the number of moles of reactants and products are given at equilibrium.

$$K_n = \frac{(n_C)^c \ (n_D)^d}{(n_A)^a \ (n_B)^b} \text{ ---------- (iii)}$$

$$K_X = \frac{(X_C)^c \ (X_D)^d}{(X_A)^a \ (X_B)^b} \text{ ---------- (iv)}$$

Here **n** specify the given number of moles and **X**, represents the mole fractions of A, B, C and D in the equilibrium reaction mixture.

Despite the fact that partial pressure of an ideal gas is directly proportional to its molar concentration at constant temperature, the numerical value of K_c is often not equal to K_p. Accordingly a quantitative relationship has been developed between these two equilibrium constants at a particular constant temperature.

$$Kp = Kc\ (RT)^{\Delta n} \text{ ---------- (v)}$$

Here,

R = Gas constant which is taken in 0.082 atm dm^3/mol. K.

T = Absolute temperature

Δn = [Sum of number of moles of products – sum of number of moles of reactants] in the given balance chemical equation.

The relationship between Kp, Kx, and Kn may be written as

$Kp = Kx\ (P)^{\Delta n}$ ---------- (vi)

$Kp = Kn \left(\frac{P}{n}\right)^{\Delta n}$ ---------- (vii)

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Example 7.4

Nitrosyl chloride is a yellow coloured gas prepared by the reaction of NO and Cl_2 gases.

$$2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl_{(g)}$$

If at certain temperature, the partial pressure of equilibrium mixture is NO = 0.17 atm, Cl_2 = 0.2 atm and NOCl = 1.4 atm, Calculate Kp

Solution:

The equilibrium expression of the given reaction is written as

$$K_p = \frac{(P_{NOCl})^2}{(P_{NO})^2\ (P_{Cl_2})}$$

Substituting the partial pressure in equilibrium expression, we get

$$K_p = \frac{(1.4)^2}{(0.17)^2\ (0.2)} \qquad K_p = \mathbf{339.1}$$

Self Assessment

The reaction of methane with hydrogen sulphide gives carbon disulphide.

$$CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)}$$

If Kc for this reaction at 727°C is 4.2×10^{-3}, Calculate its Kp. (Ans: 28.24)

7.1.4 Importance of K_C and Reaction Quotient

The reaction quotient (Qc) is an expression representing the ratio of molar concentration of products to that of reactants in a reversible reaction; Mathematically it has the same form as that of equilibrium constant expression (Kc), however, the concentration of reactants and products expressed in reaction quotient are not necessarily specify equilibrium state.

Consider a general reversible reaction.

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

The expression of reactant quotient may be written as

$$\mathbf{Qc = \frac{[C]_i^c\ [D]_i^d}{[A]_i^a\ [B]_i^b}}$$

The subscript 'i' attached with each square bracket represents the concentrations at any particular instant of time not necessarily be at equilibrium.

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It is important to note that the numerical value of Qc changes gradually during the course of reaction toward equilibrium state due to continuous change in the concentration of reactants and products. Finally, when reaction reaches the equilibrium, the concentration of reactants and products no longer change and at this moment Qc becomes equal to Kc.

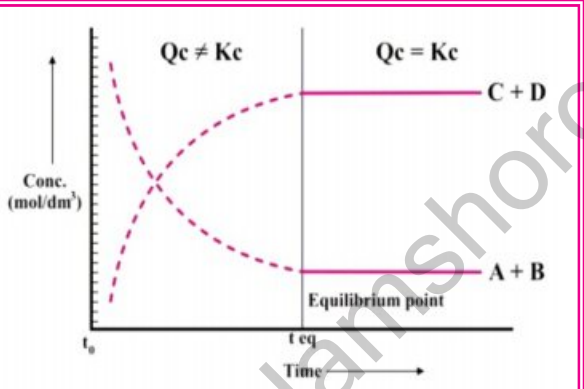

Figure 7.3 It shows that conc. of reactants (A and B) and products (C and D) both gradually change in the course of reaction till the equilibrium is reached where Qc will becomes equal to Kc

The distinction between Qc and Kc is important due to their usefulness in anticipating the direction of reaction. Reaction quotient (Qc) depends on the actual concentration of reactants and products at any time during the course of reaction and is changed with the time. On the other hand equilibrium constant (Kc) is a constant value which specify the equilibrium concentrations of reacting species at particular temperature.

Use of Kc in predicting the direction of reaction

Kc and reaction quotient are a very useful tool in determining whether the reaction has reached to equilibrium, if not, in which direction it proceed at that moment. A comparison of magnitude of Qc with Kc tells us the direction in which the reaction proceed to attain an equilibrium. The three possible cases are as follow.

Case-1:

If Qc < Kc, indicates that the system proceeds from left to right to a greater extent and the rate of formation of product is higher. The reason is that the conc. of reactants (denominator) is large relative to the conc. of products (numerator) in the reaction quotient expression.

Case-2:

If Qc > Kc, indicates that the system proceeds from right to left to a greater extent and the rate of formation of reactant is higher because the conc. of reactant (denominator) is smaller than conc. of product (numerator) in the reaction quotient expression.

Case-3:

If Qc = Kc, indicates that the system is in dynamic equilibrium and the rate of reaction in both the directions remains same.

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Example 7.5

Kc for the given reaction at certain temperature is 2.72.

$$A + 3B \rightleftharpoons 2C$$

If in a 5dm^3 reaction vessel the reaction mixture contains 8 moles A, 6 moles B, and 5 moles C. Predict whether the reaction is in equilibrium, if not what is the direction of net reaction?

Solution:

To find the answer, we first need to know what is the numerical value of Qc. It will be determined by substituting the values of conc. of A, B and C in reaction quotient expression then compare it with Kc. The relative values of Qc and Kc tells us whether the reaction is at equilibrium or proceed in a particular direction for getting equilibrium.

The molar concentrations of A, B and C can be calculated as

$[A] = \frac{8}{5} = 1.6 \text{ mol/dm}^3$

$[B] = \frac{6}{5} = 1.2 \text{ mol/dm}^3$

$[C] = \frac{5}{5} = 1 \text{ mol/dm}^3$

Qc expression of the reaction is written as

$$Qc = \frac{[C]^2}{[A]\,[B]^3}$$

Substituting these values in reaction quotient

$$Qc = \frac{(1)^2}{(1.6)\,(1.2)^3} = 0.36$$

Since Qc < Kc, the reaction mixture is not at equilibrium but proceed from left to right to increase the concentration of product.

Use of Kc in the prediction of extent of reaction

The value of K_c enables us to tell roughly, at a glance how far the reaction precedes before the equilibrium state is reached.

Since reactions have a long range of K_c values, the extent to which a chemical reaction proceeds is substantially discussed into three destinations in the reaction pathway.

Very large value of K_c Shows that ratio of products to reactants at equilibrium is very large and it infers that reaction is nearly to completion.

Very small value of K_c Shows that the ratio of products to reactants at equilibrium is very small and it infers that reaction proceeds hardly at all before reaching the equilibrium.

Intermediate value of K_c Shows that appreciable amount of both reactants and products are present in the equilibrium mixture.

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Table 7.2	Prediction of extent of reaction at particular temperature.	
Reactions	**Value of Kc at 25°C**	**Extent to which reaction proceed before equilibrium is reached**
$CH_{4(g)} + Cl_{2(g)} \rightleftharpoons CH_3Cl_{(g)} + HCl_{(g)}$	1.2×10^{18}	Almost go to completion
$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$	4.5×10^{-31}	Proceed negligibly
$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$	43.44	Proceed moderately

7.2 FACTORS AFFACTING EQUILBRIUM (Le-chatelier's principle)

Our area of study in this section is how an equilibrium system becomes temporarily unbalance by the change in experimental conditions such as temperature, pressure and concentration of reacting species and how the system restore its balance by speeding up either in forward or backward direction. These equilibrium constraints or reaction parameters may affect the position of equilibrium.

In 1884, Le-Chatelier, a French chemist introduced a general rule after a long research on how and why the balance of a chemical equilibrium is disturbed by some change of conditions, this is known as Le-Chatelier's principle. It states that **'If an external stress such as concentration pressure or temperature is applied to a system at equilibrium, the equilibrium is disturbed and tends to shift in a direction to offset the effect of stress imposed'**.

There are two parts in the statement of Le-Chatelier's Principle which need further explanation.

First part which refers to 'disturbance on equilibrium' means an altering in the experimental conditions push the system temporary out of equilibrium so that 'Qc' will no more equal to Kc. The second part which specifies the shifting of equilibrium position to left or right means system tends to repair its equilibrium by reducing the stress and tends to attain a new equilibrium where Qc = Kc.

We now study the effect of above mentioned factors on quantitative and descriptive view point.

7.2.1 Effect of Change in Concentration

When a system at equilibrium is disturbed by increasing or decreasing the concentrations of one or more species involved in the reaction, the equilibrium tends to shift towards left or right in order to reduce the effect of this stress and re adjust itself until Qc = Kc, thus

(i) The equilibrium position shifts towards the right if the amount of reactant is added or product is removed.

(ii) The equilibrium position shift to the left if reactant is removed or product is added.

In general whenever we add or remove some of the reacting species from a system at equilibrium, the system reacts in a particular direction to reduce the amount of added substance

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or to produce certain amount of removed substance so that the stress imposed on the system will be offset. To understand the guideline provided by Le-Chatelier's principle for the stress caused by change in the concentration considers the following system at equilibrium.

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$$

When certain amount of $CO_{(g)}$ or $H_{2(g)}$ is added to the system, the value of reaction Quotient (Q) is lowered than its K_c and the reaction is no longer at equilibrium. The stress caused by added $CO_{(g)}$ or $H_{2(g)}$ is alleviated by shifting the equilibrium to the right side. In doing so some amount of $CO_{(g)}$ and $H_{2(g)}$ has consumed and turning the value of Qc back to K_c. In kinetic aspect, it is simply said that the addition of $CO_{(g)}$ or $H_{2(g)}$ increases the rate in the forward direction by consuming more CO and H_2 and producing more CH_4 and H_2O until at a certain point a new equilibrium will be established. The effect of change in concentration on equilibrium position may be illustrated table 7.3.

Table 7.3 Effect of change in conc. of reacting mixture on equilibrium position

Stress type	Effect on equilibrium position $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	$Q_c = \frac{[CH_{4(g)}]\,[H_2O_{(g)}]}{[CO_{(g)}]\,[H_{2(g)}]^3}$
Adding more $CO_{(g)}$ or $H_{2(g)}$	Shift to the right	Qc < Kc
Removing some $CO_{(g)}$ or $H_{2(g)}$	Shift to the left	Qc > Kc
Adding more $CH_{4(g)}$ or $H_2O_{(g)}$	Shift to the left	Qc > Kc
Removing some $CH_{4(g)}$ or $H_2O_{(g)}$	Shift to the right	Qc < Kc

7.2.2 Effect of Change in Pressure or Volume

The effect of pressure change in altering the position of equilibrium is noticeably observed if all reacting species are in gaseous state where the numbers of moles of reactant gases are differ from number of moles of product gases ($\Delta n \neq 0$). The reason is that gases are highly compressible therefore referring to ideal gas laws (PV = nRT) the pressure applied to the system is directly proportional to the concentration of reacting species but inversely proportional to the volume at given constant temperature.

To understand the effect of pressure change on an equilibrium let us consider the following gaseous system in a cylinder fitted with a moveable piston.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

When the external pressure increases at constant temperature, the piston move downward causing a decrease in the volume which in general increases the concentration of all components of reacting mixture but since the number of moles of products are lesser than reactant, the denominator value exceed the numerator. Thus the system is no longer in equilibrium and to reduce this stress the reaction tends to shift on right side.

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In general, the effect of pressure on a homogenous gaseous equilibrium system may be summarizing in the guidance of Le-Chatelier's Principle as **"An increase of pressure shift the equilibrium in the direction of decrease volume where as a decrease pressure shift the equilibrium in the direction of increase volume"**.

Table 7.4 **Effect of change in pressure on some gaseous equilibria**

Equilibria	Effect of Increase pressure	Effect of decrease pressure
$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$	Equilibrium shift to the left	Equilibrium shift to the right
$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$	Equilibrium shift to the right	Equilibrium shift to left
$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$	Equilibrium remains unchanged	Equilibrium remains unchanged

7.2.3 Effect of Change in Temperature

Reactions in term of enthalpy change are classified into exothermic and endothermic (Sec-11.2) and if we are talking about reversible reactions, these are exothermic in one direction and endothermic in other direction. However, when the equilibrium is shown in an equation form, the sign of enthalpy term ($\Delta H°$) refer to the forward direction.

Consider the reaction

$$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)} \quad (\Delta H^{\circ} = -ve) \quad K_C = \frac{[PCl_5]}{[PCl_3][Cl_2]}$$

Sign of $\Delta H°$ shows that the reaction exothermic in the forward direction. If we increase the temperature of this equilibrium system by providing some heat, then according to Le-Chatelier's principle the system tends to speed up in the left side so that the added heat is absorbed and the stress of increased temperature is reduced. In doing so the rate of decomposition of PCl_5 becomes faster than its formation thus numerator value in the equilibrium constant expression becomes smaller than denominator. Finally, the system reaches to a new equilibrium state with lower value of Kc.

On the other hand, if we lower the temperature by removing heat from the system at constant pressure, it shifts to the right to produce more PCl_5. In this way the value of Kc to attain new equilibrium will be enhanced.

The effect of temperature may be summarized in Le-Chatelier's perspective as **"a decrease in temperature of a chemical system at equilibrium favours the reaction to proceed in the exothermic direction where as an increase in temperature favours the reaction to turn in the endothermic direction"**.

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Table 7.5	Effect of change in temperature on equilibria		
Chemical Systems		**Change of Temperature**	**Effect on equilibrium**
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $(\Delta H = -ve)$		Temperature Increases	Shift to the left
		Temperature Decreases	Shift to the right
$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ $(\Delta H = +ve)$		Temperature Increases	Shift to the right
		Temperature Decreases	Shift to the left

Self Assessment

For the reaction
$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ $(\Delta H = +ve)$
Predict the direction when following stresses are applied.
(a) Pressure increases (b) Temperature decreases (c) More PCl_5 is added

Effect of Catalyst

A catalyst minimizes the time to reach equilibrium but does not effect on change in equilibrium position of the system.

7.3 INDUSTRIAL APPLICATION OF LE CHATELIER'S PRINCIPLE (Haber's process)

The synthesis of ammonia by Haber's process is an industrial application of Le Chatelier's principle.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad (\Delta H = -ve)$$

The equation tells us that the reaction is exothermic and proceeds with decrease in number of moles of product. To get the maximum promising yield of ammonia following conditions of Le Chatelier's principle should be maintained.

(i) Effect of Pressure

In the given equation four moles of gases on the left side and two mole on the right side, an increase in the pressure shifts the reaction on the right side and favours the formation of ammonia gas. Since a very high pressure may be dangerous for the process, an optimum pressure should be settled. The optimum compromising pressure to a good yield of ammonia is 200 to 300 atm.

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(ii) Effect of Temperature

As the reaction is exothermic (ΔH° = -ve), a decrease in temperature shift the reaction to the right side and favours the formation of NH_3 gas. The lowering in temperature do favours the high yield of ammonia but on the other hand it slows down the rate of reaction. The optimum choice of temperature on operational level is 400-500°C.

(iii) Effect of Concentration Change

Increase in concentration of nitrogen (N_2) or hydrogen (H_2) or decrease in the concentration of Ammonia (NH_3) shift the reaction in the forward direction and yield the maximum amount of ammonia.

(iv) Addition of Catalyst

Catalyst speed up the reaction without effecting on equilibrium position.
Finely divided Iron is used as a catalyst in the synthesis of ammonia.

Example 7.6

In the synthesis of nitric acid by Ostwald process, one of the important reactions is the oxidation of nitric oxide to nitrogen dioxide.

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \quad (\Delta H^\circ = -114 \text{ KJ/mol})$$

Use Le Chatelier's principle to predict the direction of reaction when the equilibrium is disturbed by

(a) Increasing the pressure **(b) Increasing the temperature**
(c) Adding O_2 **(d) Removing NO**

Solution:

To predict the effect of each factor asking in the question we should apply Le Chatelier's principle individually.

(a) Since 3 moles of reactant gases reacts to form 2 moles of gaseous product, an increasing pressure shift the equilibrium to the right thus more NO_2 will form.
(b) The negative sign of ΔH° indicates that forward reaction is exothermic so increasing temperature shift the equilibrium to the left thus more NO and O_2 will form.
(c) Adding more O_2 gas in the reaction mixture shift the reaction to the right. Thus more NO_2 will produce.
(d) Removing NO gas from the reaction mixture shift the system to the left.

7.4 SOLUBILITY PRODUCT

Various ionic compounds such as $Ca_3(PO_4)_2$, AgCl, $BaSO_4$ etc are practically very slightly soluble in water and commonly known as sparingly soluble salts.

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$CaSO_4$ is a slightly soluble salt, when it is put into water, a very small part becomes ionized and certainly an equilibrium exists between its solid phase and ions in a saturated solution.

$$CaSO_{4(s)} \underset{}{\overset{H_2O}{\rightleftharpoons}} Ca^{+2}_{(aq)} + SO^{-2}_{4(aq)}$$

The equilibrium expression of this ionic equilibrium may be written as

$$K_C = \frac{[Ca^{+2}_{(aq)}]\,[SO^{-2}_{4(aq)}]}{CaSO_4}$$

Since concentration of solid $CaSO_4$ in solution is fixed therefore it is not included in the equilibrium expression and thus Kc is replaced by Ksp which is known as solubility product constant or if shortens the term called as solubility product.

$$Ksp = [Ca^{+2}]\,[SO^{-2}_4]$$

Do You Know?

In tropical regions NaCl is obtained by solar evaporation of sea water. The impurities of $CaCl_2$ and $MgCl_2$ are removed by treating the brine with sodium carbonate which gives insoluble precipitates of $CaCO_3$ and $MgCO_3$.

Solubility product (Ksp) of a sparingly soluble salt may define as **"the product of molar concentration of its positive and negative ions each raised to the power of its coefficient in ionized equilibrium equation"**.

Solubility product (Ksp) of a substance in saturated solution remains constant. Like other equilibrium constants it also changes with temperature.

Table 7.6 **Solubility product (Ksp) of some slightly soluble ionic compounds in aqueous medium at 25°C.**

Group of Compounds	Formula	Ksp	Group of Compounds	Formula	Ksp
Hydroxides	$Mg(OH)_2$	1.8×10^{-11}	Chlorides	AgCl	1.6×10^{-10}
	$Zn(OH)_2$	2.1×10^{-16}		$PbCl_2$	1.8×10^{-5}
Carbonates	$CaCO_3$	3.8×10^{-9}	Fluorides	CaF_2	3.9×10^{-11}
	$BaCO_3$	8.1×10^{-9}		MgF_2	6.6×10^{-9}
Sulphate	$CaSO_4$	2.4×10^{-5}	Sulphide	Pbs	8.5×10^{-28}
	$PbSO_4$	1.7×10^{-8}		CuS	8.7×10^{-36}

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Example 7.7

Write the solubility product expression for the following slightly soluble salts $CaSO_4$, $PbCl_2$, $Fe(OH)_3$.

Solution:

First we illustrate the balance equation of ionic equilibrium to find out coefficient of each ion and then write the Ksp expression.

$CaSO_{4(s)} \rightleftharpoons Ca^{+2}_{(aq)} + SO^{-2}_{4(aq)}$ $\quad Ksp = [Ca^{+2}]\,[SO^{-2}_4]$

$PbCl_{2(s)} \rightleftharpoons Pb^{+2}_{(aq)} + 2Cl^{-}_{(aq)}$ $\quad Ksp = [Pb^{+2}]\,[Cl^{-}]^2$

$Fe(OH)_{3(s)} \rightleftharpoons Fe^{+3}_{(aq)} + 3OH^{-}_{(aq)}$ $\quad Ksp = [Fe^{+3}]\,[OH]^3$

Example 7.8

Silver sulphate (Ag_2SO_4) is used for medicinal purpose to fill wounds. Its solubility in water at 25°C is 1.43×10^{-2} mol/dm^3. What will be its Ksp.

Solution:

First write a net ionic equation of Ag_2SO_4 to note the number of coefficient of each ion. Then put the values of ionic concentration in ksp expression.

$$Ag_2SO_{4(s)} \rightleftharpoons 2Ag^{+}_{(aq)} + SO^{-2}_{4(aq)}$$

The ionic concentrations of 2 moles Ag^+ and 1 mol SO^{-2}_4 are illustrated as

$[Ag^+] = 2 \times 1.43 \times 10^{-2} = 2.86 \times 10^{-2}$ mol/dm^3

$[SO^{-2}_4] = 1.43 \times 10^{-2}$ mol/dm^3

Now inserting these values in ksp expression

$Ksp = [Ag^+]^2\,[SO^{-2}_4]$

$Ksp = [2.86 \times 10^{-2}]^2\,[1.43 \times 10^{-2}]$

$Ksp = 1.17 \times 10^{-5}$ mol^3/dm^9

Example 7.9

The Ksp of $Zn(OH)_2$ is 2.1×10^{-16} mol^3/dm^9 at 25°C. Calculate its solubility in g/dm^3. (The atomic mass of Zn = 65.4)

Solution:

This problem is exactly reverse from previous one. Here we are given with the value of Ksp and the task is to find out solubility in g/dm^3. Making the strategy, first write the Ksp expression in which ionic concentration will be written in term of 'S' then calculate molar solubility from known Ksp value. Finally convert it into g/dm^3 by multiplying it with molecular mass of $Zn(OH)_2$.

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$$Zn(OH)_{2(s)} \rightleftharpoons Zn^{+2}_{(aq)} + 2OH^{-}_{(aq)}$$

$Ksp = [Zn^{+2}]\,[OH^{-}]^2$

Since there are two hydroxide ions for every zinc ion, we may rewrite the expression as

$Ksp = [X]\,[2X]^2$

$Ksp = 4x^3$

$2.1 \times 10^{-16} = 4x^3$

$\frac{2.1 \times 10^{-16}}{4} = X^3$

$X = 3.74 \times 10^{-6}$ mol/dm^3

To get the solubility in gram/dm^3, find the molecular mass of $Zn(OH)_2$ which is

$65.4 + 32 + 2 = 99.4$

$$\text{Solubility} = \frac{3.74 \times 10^{-6}\text{mol}}{\text{dm}^3} \times \frac{99.4\text{g}}{\text{mol}} = 3.717 \times 10^{-4}\text{g/dm}^3$$

Application of Ksp

Precipitation is a kind of double displacement reaction in which two solutions of different salts mixed together to form two products, one of these product is insoluble in solution and called as precipitate. For example when an aqueous solution of silver nitrate and potassium chloride mix together, the Ag^+ ions of $AgNO_3$ combine with Cl^- ions of KCl and form an insoluble silver chloride (AgCl) which can be precipitated out.

Do You Know?

Sparingly soluble salts play significant role in many aspects of our life including medicine, industry and even in several natural processes. For example $BaSO_4$ is opaque to X-rays and use to diagnose ulcer in food canal.

$$AgNO_{3(aq)} + KCl_{(aq)} \rightleftharpoons AgCl_{(s)} + KNO_{3(aq)}$$

The net ionic equation of the above precipitation reaction is shown as

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightleftharpoons AgCl_{(s)}$$

The Ksp of AgCl (Table-7.6) tells us about its limit of solubility in solution but the question is that whether or not a precipitate of AgCl forms when aqueous solutions of $AgNO_3$ and KCl of specific concentrations mixed together. To reach the answer we should know another term known as ionic product.

Ionic product or reaction quotient is **"the product of molar concentration of the ions each raised to the power by its coefficient mentioned in net ionic equation"**. Ionic product is relevant to both saturated and unsaturated solution while ksp is only applicable to saturated solution which involves a dynamic equilibrium between an insoluble salt and its aqueous ions.

Now by using the following three relationships between ionic product (Qsp) and solubility product (Ksp), one can predict even if the salt form precipitate by mixing two different salt solution.

Ksp > Qsp Solution is unsaturated in which no ppt is formed

Ksp = Qsp Solution is saturated

Ksp < Qsp Solution is supersated in which ppt is formed

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Example 7.10

A solution is prepared by mixing 600cm^3 of 7.5 × 10^{-4}M $BaCl_2$ into 300cm^3 of 2.4 × 10^{-3}M Na_2SO_4. Will a precipitate of $BaSO_4$ form when equilibrium is reached?
(Ksp of $BaSO_4$ = 1.1 × 10^{-10} mol^2/dm^6)

Solution:

To solve this problem, first we determine the concentration of Ba^{+2} ions and SO_4^{-2} ion in the total volume of the mixture i.e. in 900cm^3. Then determine ionic product (Q_{sp}) and finally compare it with ksp value of $BaSO_4$ to decide whether precipitate will form or not

$$[Ba^{+2}] = 7.5 \times 10^{-4}\text{M}\left(\frac{600}{900}\right) = 5 \times 10^{-4}\text{M}$$

$$[SO_4^{-2}] = 2.4 \times 10^{-3}\text{M}\left(\frac{300}{900}\right) = 8 \times 10^{-4}\text{M}$$

Now substitute these ionic concentrations into ionic product expression

$Q_{sp} = [Ba^{+2}]\,[SO_4^{-2}]$

$Q_{sp} = [5 \times 10^{-4}]\,[8 \times 10^{-4}] = 4 \times 10^{-7}$

But ksp of $BaSO_4$ is 1.1×10^{-10}.

Because Q_{sp} > ksp, precipitates of $BaSO_4$ will be formed in the solution.

7.5 COMMON ION EFFECT

In previous section we studied about precipitation of a sparingly soluble salt (AgCl) by the mixing of two highly soluble electrolytes such as $AgNO_3$ and KCl. We turn now to a different kind of process which involves the effect on solubility of a sparingly soluble salt when another salt having the same cation or an ion is added.

Do You Know?

Sink or wash basin pipes in our homes get chocked due to Mg^{+2} and Ca^{+2} ions of hard water which are precipitated as their oxides.

Consider the equilibrium settled when a saturated solution of silver chloride is prepared in water.

$$AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$

If now we add some amount of a soluble salt like sodium chloride (NaCl) which has Cl^- ion common to silver chloride. What will happen in Le Chatelier perspective? The increased Cl^- ions concentration in the solution produce a stress on AgCl equilibrium and to reduce this effect satisfactorily the excess Cl^- ions reacts with some Ag^+ ions and shift the equilibrium to the left and form precipitates of AgCl. Conclusively, solubility of silver chloride in the solution decreases if sodium chloride is added, thus **"to decrease the solubility of a sparingly soluble salt in solution by the addition of a highly soluble salt with one common ion refers as common ion effect"**.

Since common ion effect is related to the lowering in the solubility of slightly soluble salt in the precipitation formation, it plays versatile roles in many areas of analytical chemistry such as buffering of solutions, purification of salts, soap precipitation and other qualitative and quantitative analysis.

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Application of chemical equilibrium in industrial process

Obtaining the maximum amount of product in a concerned chemical reaction is the main task in many industrial processes and it depends on proper selection of reaction conditions as described by Lechatlier principle. It is a skill of a chemist to choose conditions that fovours the maximum yield of a commercially significant compound.

For example in the manufacturing of H_2SO_4 by contact process, oxidation of SO_2 is a reversible and exothermic reaction.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \ (\Delta H = -45 \text{ KJ/mol})$$

Since according to Lechatlier principle a low temperature and high pressure favour the maximum yield, but low temperature slow down the rate of reaction and high pressure dangerous for the equipment so an optimum temperature (450°C) and pressure (1 – 2 atmosphere) is opted for the process with a suitable catalyst (V_2O_5).

Activity

In this activity you will observe how the disturbance in the chemical equilibrium between gaseous CO_2 and carbonic acid of beverage bottle causes you to lose the appealing taste of a soft drink.

Take a bottle of a fizzy drink. The soft drink bottle, when sealed, contain the dissolved carbon dioxide (in the form of carbonic acid) and gaseous CO_2 (in the space between the liquid and the lid) which are in equilibrium with each other. Just open the lid and you get to hear the hissing sound of CO_2 escaping out and hence the equilibrium gets disturbed thereby causing carbonic acid to produce CO_2 that comes out and takes the place of escaped gas. Now keep the bottle opened for an hour and then taste it. You'll find it less fizzy or mild since it would have lost much of its dissolved CO_2.

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SUMMARY with Key Terms

- **Chemical Equilibrium** is a state in a reversible reaction where rate in both directions are equal and no net change in the conc. of reactants and products occur with time.
- **Equilibrium Constant (Kc)** is a quantity that represents the ratio of molar concentration of product to that of reactant at equilibrium state. It is independent upon concentration of reaction mixture, however change with the temperature.
- **Equilibrium Expression** reveals that when at certain temperature a chemical reaction reaches to equilibrium state the ratio of active mass of products to reactants become constant.
- **Reaction Quotient (Qc)** represents the ratio of molar conc. of products to reactants in a reversible reaction, its value however not necessarily equal to Kc.
- **Equilibrium Constant (Kp)** represents the ratio of partial pressure of products gases to that of reacting gases at equilibrium state of a homogenous gaseous reaction.
- **$Kp = Kc\ (RT)^{\Delta n}$** is a relationship between Kp and Kc of a gas phase reaction at specific temperature. If one is known, other can be determined at given temperature.
- **Law of mass action** tells that the rate in the forward and backward directions of a reversible reaction is proportional to the active masses of reacting species at constant temperature.
- **Direction of reversible Reaction** can be predicted at particular instant of time by comparing the value of Qc and Kc. If Qc = Kc then it is said to be at equilibrium.
- **Extent of reversible reaction** can be predicted by knowing the value of Kc. Hence if Kc is very large, the reaction is expected to proceed to maximum extent. Likewise a very small value of Kc tells us that the reaction proceed hardly at all.

- **Lechatlier Principle** tells that if a stress is imposed on a system at equilibrium, the equilibrium is unbalanced and it tends to turn in forward or backward direction to reduce the effect of this applied stress.
- **Change in Concentration** of any reacting substance make the system unbalance and for reducing the effect of this stress, system turns toward the direction of decreased concentration.
- **Change of Pressure** Increase pressure shift the equilibrium point in the direction of less volume where as decrease pressure shifts it in the direction of greater volume.
- **Change of Temperature** In endothermic reactions, an increase in temperature shift the equilibrium to the right where as in exothermic reactions an increase in temperature shift the reaction to the left.
- **Solubility Product (Ksp)** is the product of molar concentration of ions of a sparingly soluble salt and related to saturated solution which involves dynamic equilibrium between insoluble salt and its aqueous ions.
- **Ionic Product (Qsp)** is also the product of molar conc. of ions of a salt. It is relevant to both saturated and unsaturated solution.
- **Common Ion Effect** tells that the solubility of a sparingly soluble salt in a solution can be decreased by a adding a highly soluble salt with one ion common to it.

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EXERCISE

Multiple Choice Questions

1. Choose the correct answer

(i) In the equilibrium system of $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$, the correct relationship between Kc and Kp is:

(a) Kp> Kc (b) Kp< Kc (c) Kp = Kc (d) $\frac{K_p}{K_c} = 1$

(ii) The equilibrium of which of the following reaction would not be affected by an increase in pressure:

(a) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ (b) $2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl_{(g)}$

(c) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ (d) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

(iii) What happens to the value of Kc when a catalyst is added to a chemical system at equilibrium?

(a) It decreases (b) It increases

(c) It becomes zero (d) It remains unchanged

(iv) The correct Ksp expression of a sparingly soluble salt $Li_2C_2O_4$ among the following is:

(a) $Ksp=[Li^+][C_2O_4^{-2}]$ (b) $Ksp=[Li^+]^2[C_2O_4^{-2}]$

(c) $Ksp=[2Li^+][C_2O_4^{-2}]$ (d) $Ksp=[2Li^+]^2[C_2O_4^{-2}]^2$

(v) If the equilibrium expression of a reversible reaction is

$$Kc = \frac{[C]^2}{[A][B]}$$

The balanced equilibrium equation should be:

(a) $C \rightleftharpoons A + B$ (b) $A + B \rightleftharpoons C$

(c) $2C \rightleftharpoons A + B$ (d) $A + B \rightleftharpoons 2C$

(vi) The equilibrium of $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ (ΔH = +ve) is affected by change in:

(a) Temperature only (b) Pressure only

(c) Both temperature and pressure (d) Neither temperature nor pressure

(vii) In the reaction $A_{(g)} + B_{(g)} \rightleftharpoons 2C_{(g)}$, the equilibrium constants Kp = Kc because:

(a) $\Delta n > 1$ (b) $\Delta n < 1$ (c) $\Delta n = 1$ (d) $\Delta n = 0$

(viii) The term active mass use in law of mass action means:

(a) No. of mole (b) No. of molecules

(c) mole per dm^3 (d) gram per dm^3

(ix) NaCl when added to an aqueous silver chloride solution:

(a) Decreases the solubility of AgCl (b) Increases the solubility of AgCl

(c) Forms a clear solution (d) Does not effect

(x) Some reactions are nearly to completion in the forward direction and identified by their:

(a) Very high value of Kc (b) Very low value of Kc

(c) Very high value of ΔH (d) Very low value of ΔH

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Short Questions

1. Define the following:
   (i) Reversible reaction (ii) Chemical equilibrium
2. Write expression of Kc and Kp for the following reversible reactions.
   (i) $2NO_{2(g)} + 7H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 4H_2O_{(g)}$
   (ii) $2H_2S_{(g)} + 3O_{2(g)} \rightleftharpoons 2H_2O_{(g)} + 2SO_{2(g)}$
3. (a) Define solubility product.
   (b) Write the solubility product expression of the following salts.
   BaF_2, $Li_2C_2O_4$, $MgCO_3$, Ag_3PO_4
4. Using Le-Chatelier's principle, explain three ways in which yield of SO_3 can be increase in Contact process.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad (\Delta H^\circ = -ve)$$

Descriptive Questions

1. State Law of mass action and derive Kc expression of a general reversible reaction.
2. State Le-Chatelier's principle. Explain the industrial application of Le-Chatelier's principle using Haber's process.
3. Give brief account on Common ion effect.
4. Define equilibrium constant (Kc). How it helps in predicting the
   (i) Direction of reaction (ii) Extent of reaction.

Numerical Questions

1. At 444°C reaction of hydrogen and iodine is performed in a sealed $1dm^3$ steel vessel.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

   If equilibrium mixture contains 1 mole of H_2, 1 mole of I_2 and 7 moles of HI. Calculate
   (a) Equilibrium constant (Kc) (b) Initial concentration of H_2 and I_2
   [Ans: Kc = 49, initial conc. of $H_2 = I_2 = 4.5$ moles]
2. Lead fluoride (PbF_2) is a high melting white solid used in glass coating to reflect IR rays. Its solubility in water at 25°C is $0.58g/dm^3$. Calculate its Ksp.
   (At. mass of Pb = 207 and F = 19) [Ans: 5.3×10^{-8} mol^3/dm^9]
3. 3. A solution of $CaCO_3$ is prepared by mixing $200cm^3$ of 2.4×10^{-4}M $Ca(NO_3)_2$ and $300cm^3$ of 4.5×10^{-2}M K_2CO_3. Will $CaCO_3$ precipitate upon cooling to 25°C if Ksp of $CaCO_3$ at 25°C is 3.8×10^{-9}. [Ans: $CaCO_3$ precipitate]
4. Hydrogen iodide is a colourless gas prepared by reacting H_2 and I_2.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

   In an equilibrium study of above reaction, 1.2 mole of H_2 and 1.2 moles of I_2 were injected in an evacuated $1000cm^3$ sealed flask and start the reaction to occur at 440°C until the equilibrium is formed. If Kc for this reaction is 49, calculate the equilibrium concentration of H_2, I_2 and HI.
   [Ans: $[H_2] = 0.267$ mol/dm^3, $[I_2] = 0.267$ mol/dm^3, $[HI] = 1.866$ mol/dm^3]

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ACIDS, BASES AND SALTS

Chapter 8

Teaching Periods	Assessment	Weightage
10	1	7

Students will be able to:

- **Define** Bronsted and Lowery concepts for acids and bases.
- **Identify** conjugate acid-base pairs of Bronsted-Lowery acid and base.
- **Explain** ionization constant of water.
- **Calculate** pH, pOH in aqueous medium using Kw values.
- **Define** and explain leveling effect.
- **Define** Lewis acid and base with suitable examples.
- **Define** a buffer and make buffer solutions.
- **Show** with equations how a buffer system works.
- **Applications** of salts like NaCl, KCl, KI, $NaHCO_3$, $MgSO_4$, etc.
- **Use** the concept of hydrolysis to explain why aqueous solutions of some salts are acidic or basic.
- **Use** concept of hydrolysis to explain why the solution of a salt is not necessarily neutral.

INTRODUCTION

For centuries, acids and bases have been employed as laboratory chemicals and also used in homes. Acetic acid (CH_3COOH) can be found in our kitchens as vinegar, citric acid ($H_3C_6H_5O_7$) is found in citrus fruits like orange, lemon, etc., and phosphoric acid (H_3PO_4) serves as a flavouring agent in many carbonated beverages. Some common household bases are sodium hydroxide (NaOH) which is used as a drain cleaner, ammonia (NH_3) is used as a glass cleaner and sodium hydrogen carbonate ($NaHCO_3$) serves as baking soda in our cooking items.

An acid is any species that has a sour taste, produces hydrogen gas when it reacts with active metals like aluminium and zinc. On the other hand, a base is any species with a bitter taste and a slippery texture (Avoid tasting or touching laboratory chemicals; instead, use acetic acid in the form of vinegar in salad.) Furthermore, it was well understood that when acids and bases react, each cancels out the other's qualities in a process known as neutralisation.

Fig. 8.1: Common uses of acids, bases and salts

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8.1 ACIDIC, BASIC AND AMPHOTERIC SUBSTANCES

Oxides of metals and non metals are not themselves acid or base but when dissolves in water, they form acidic or alkaline solution. On the basis of this fact, oxides are classified into three main groups.

Do You Know?

A wide range of organic acids such as acetic acid, citric acid, ascorbic acid, oxalic acid, tartaric acid and amino acid etc are found in our food. They serve as flavorant, antioxidant, energy producer and microbial inactivitor etc.

(i) Metal oxides such as Na_2O, K_2O, CaO etc readily mixed in water to produce alkaline solution.

$$K_2O_{(s)} + H_2O_{(l)} \longrightarrow 2KOH_{(aq)}$$
$$Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)}$$
$$CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)}$$

(ii) Non metal oxides such as CO_2, SO_2, P_2O_5 etc when mixed in water, they produce acidic solution.

$$CO_{2(g)} + H_2O_{(l)} \longrightarrow H_2CO_{3(aq)}$$
$$SO_{2(g)} + H_2O_{(l)} \longrightarrow H_2SO_{3(aq)}$$
$$P_2O_{5(s)} + 3H_2O_{(l)} \longrightarrow 2H_3PO_{4(aq)}$$

(iii) Certain metal oxides such as ZnO, Al_2O_3 etc are not water soluble. However, they have ability to react with both acid and base. These are on the borderline of both acid and base and known as amphoteric substances.

$$Al_2O_{3(s)} + 2NaOH_{(aq)} \longrightarrow 2NaAlO_{2(aq)} + H_2O_{(l)}$$
$$Al_2O_{3(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(aq)} + 3H_2O_{(l)}$$

Beside oxides, certain other substances are also acidic and basic in nature for example Na_2CO_3 gives alkaline solution in water and NH_4Cl gives acidic solution.

Self Assessment

Identify acidic, basic and amphoteric substance in the following:
SO_2, NH_4Cl, Na_2CO_3, ZnO, Na_2O

8.2 THE BRONSTED-LOWRY THEORY OF ACIDS AND BASES

In 1923 J.N Bronsted (Danish Chemist) and J.M Lowry (British Chemist) individually propose this general approach to explain acids and bases as an extension of Arrhenious concept.

J.N Bronsted J.M Lowry

According to this theory **"Acid is a species which tends to donate proton (protogenic) whereas base is a species that accept proton (protophillic). Further, an acid base reaction is the transfer of proton from acid to base"**.

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In the light of this definition all hydrogen containing substances (either molecules or ions) which are capable of giving up proton (HCl, HNO_3, H_2SO_4, H_2O, H_3O^+, NH_4^+etc) are gathered in the list of acids where as all those substances which have ability to accept proton (NH_3, H_2O, OH^-, Cl^-, CO_3^{-2}, HSO_4^-) are categorized as bases.

8.2.1 Proton Donors and Acceptors

According to Bronsted Lowry concept, the necessary need for an acid base reaction is that one substance can donate a proton while other substance is able to accept it. In this proton transfer process both acid and base work together. This means if one species is an acid the other always be a base.

Let us consider what happens when a strong acid (HCl) dissolves in water and undergo ionization.

$$\underset{\text{(acid)}}{HCl_{(l)}} + \underset{\text{(base)}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{(conjugate acid)}}{H_3O^+_{(aq)}} + \underset{\text{(conjugate base)}}{Cl^-_{(aq)}} \text{------ (i)}$$

Since HCl donate a proton, it acts as an acid on the other hand water (H_2O) accept a proton and serve as base.

Look at the reverse of this acid base reaction where hydroxonium ion (H_3O^+) reacts with chloride ion (Cl^-). In the reverse reaction, H_3O^+ act as conjugate acid while Cl^- ion serves as conjugate base. Thus the equilibrium of the above reaction represents two acids and two bases, one on either side of the reaction arrow.

Now see the ionization of ammonia in to water in the given equilibrium.

$$\underset{\text{(base)}}{NH_{3(g)}} + \underset{\text{(acid)}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{(conjugate acid)}}{NH^+_{4(aq)}} + \underset{\text{(conjugate base)}}{OH^-_{(aq)}} \text{------ (ii)}$$

Reaction in the forward direction shows that water gives up a proton (acid) and ammonia accept it (base). In reverse phase of this reaction ammonium ion (NH_4^+) acts as conjugate acid and hydroxide ion (OH^-) as conjugate base.

While studying above two acid base reactions it is interesting to note that water serves as base when HCl is dissolved into it but acts as acid when ammonia is added.

8.2.2 Relative Strength of Bronsted Acid and Base

The direction of an acid base reaction depends on the relative strengths of concerned acid and base and the reaction is generally goes towards the direction of weaker acid or base. According to Bronsted-Lowry perception, the strongest acid has the weakest conjugate base and the strongest base has weakest conjugate acid.

Look at again the acid base reaction mentioned in equation (i). Since HCl is a strong acid, it donates proton to water molecules completely and forms a conjugate base of HCl which is Cl^- and conjugate acid of H_2O which is H_3O^+.

$$\underset{\textbf{(Stronger acid)}}{HCl_{(l)}} + H_2O_{(l)} \rightleftharpoons Cl^-_{(aq)} + \underset{\textbf{(Stronger acid)}}{H_3O^+_{(aq)}}$$

In term of relative strength of two acids (HCl and H_3O^+), HCl is stronger than H_3O^+ because it lose proton more readily than H_3O^+.

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CH_3COOH on the other hand is a weak acid since it is only 1.4% ionize when dissolve in water therefore it is weaker acid than H_3O^+.

$$\underset{\text{(Weak acid)}}{CH_3COOH_{(l)}} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + \underset{\text{(Strong acid)}}{H_3O^+_{(aq)}}$$

The relative order of the three acids discussed above is now written as

$$HCl > H_3O^+ > CH_3COOH$$

The relative order of strength of bases can be determined in the same way.

$$NaOH > NH_3 > NH_4OH$$

8.3 CONJUGATE ACID BASE PAIRS

In Bronsted-Lowry acid base reaction both reactants and products serves as acid and base.

A conjugate acid base pair represents two species, one on the left side and other on the right side of equation with the difference of one proton. It is important to note that strong acid has weak conjugate base and weak base has strong conjugate acid.

How to identify conjugate acid base pair

Consider the reaction of H_2S and NH_3.

$$H_2S_{(g)} + NH_{3(aq)} \rightleftharpoons HS^-_{(aq)} + NH_4^+{}_{(aq)}$$

To identify a conjugate acid base pair, it should be in our mind that the only difference between the two species is a proton (H^+). Here we see that H_2S change into HS^- by losing a proton. Thus H_2S and HS^- represents a conjugate acid base pair. NH_3 on the other hand accept a proton and change into NH_4^+ therefore it is another conjugate acid base pair.

$$\underset{\text{(Bronsted acid)}}{H_2S} + \underset{\text{(Bronsted base)}}{NH_3} \rightleftharpoons \underset{\text{(Conjugate acid)}}{NH_4^+} + \underset{\text{(Conjugate base)}}{HS^-}$$

Some common acid base pairs are listed below

Bronsted Acid		Bronsted Base		Conjugate Acid		Conjugate Base
HCN	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CN^-
CH_3COOH	+	NH_3	$\rightleftharpoons$	NH_4^+	+	CH_3COO^-
H_2O	+	H_2O	$\rightleftharpoons$	H_3O^+	+	OH^-
HBr	+	F^-	$\rightleftharpoons$	HF	+	Br^-
H_2O	+	CO_3^{-2}	$\rightleftharpoons$	HCO_3^-	+	$O\bar{H}$
HSO_4^-	+	CO_3^{-2}	$\rightleftharpoons$	HCO_3^-	+	SO_4^{-2}

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Self Assessment

Identify the acid and base on the right hand side of the following equilibria.

(i) $H_2S + H_2O \rightleftharpoons HS^- + H_3O^+$ (ii) $NH_4^+ + S^{-2} \rightleftharpoons HS^- + NH_3$

Limitations of Bronsted-Lowry Theory

(i) This theory cannot explain the reaction between acidic oxides (CO_2, SO_2, SO_3) and the basic oxides like (CaO, BaO, MgO) in which no involvement of proton transfer.

(ii) Certain substances like $AlCl_3$, BF_3 etc do not involve in the proton transfer but they function as acid.

8.4 STRENGTHS OF ACIDS AND BASES

Consider Bronsted Lowry theory, all acids have ability to donate proton in aqueous medium, however some acids release their proton faster than others. The relative strength of acids and bases can be measured by their degree of ionization in water.

The degree of ionization (α) is the ratio of the number of molecules ionized to the total number of the dissolved molecules. This ratio when multiplied by hundred(100), we can get ionization in percentages.

$$\%\text{age of ionization } (\alpha) = \frac{\text{Number of molecules split into ions}}{\text{Total number of molecules dissolved}} \times 100$$

The %age of ionization of strong acids or bases is up to 90-95%, which means that out of every 100 molecules, 90 to 95 molecules get ionized in aqueous solution. Many acids ionizes only to a limited extent in water, these are called weak acids. The aqueous equilibrium mixture of these acids possess unionized molecules of acid (HA), conjugate base and H_3O^+ ions.

Table 8.1 The percentage ionization of some acids and bases.

Acids	Degree of Ionization	Bases	Degree of Ionization
HCl	90 – 95%	NaOH	90 – 95%
HNO_3	90 – 95%	KOH	90 – 95%
H_2SO_4	60% (1st step)	$Ba(OH)_2$	77% (1st step)
CH_3COOH	1.4%	NH_4OH	1.4%

The ionization of an acid in its aqueous solution is a reversible process. We can write the equilibrium reaction of ionization of an acid as under:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

By applying the law of mass action to the acid ionization equilibrium:

$$K_c = \frac{[H_3O^+]\,[A^-]}{[HA]\,[H_2O]}$$

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In the dilute solution of an acid (HA) we assume that the concentration of liquid water remains constant.

Therefore

$$Ka = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

The ionization of a base (B) in water, at equilibrium is shown below.

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

Base ionization constant expression may be written in the same way as:

$$Kb = \frac{[BH^+]\,[OH^-]}{[B]}$$

The higher the value of Ka and Kb the stronger is the acid and base.

Table 8.2 Ionization constant values of some weak acids and weak bases at 25°C

Acids	Formula	Ka	Bases	Formula	Kb
Oxalic acid	$H_2C_2O_4$	5.6×10^{-2}	Ethylamine	$C_2H_5NH_2$	4.7×10^{-4}
Formic acid	HCOOH	1.7×10^{-4}	Ammonia	NH_3	1.8×10^{-5}
Acetic acid	CH_3COOH	1.7×10^{-5}	Hydrazine	N_2H_4	1.7×10^{-6}
Carbonic acid	H_2CO_3	4.3×10^{-7}	Hydroxylamine	NH_2OH	1.1×10^{-8}
Boric acid	H_3BO_3	5.9×10^{-10}	Pyridine	C_5H_5N	1.4×10^{-9}

8.4.1 Ionization Constant of Water (Kw)

Although water is chemically non electrolytic substance, however it conducts electricity to a very small extent due to its self ionization ability. During the reaction proton from one water molecule is transferred to another water molecule as given in the following reaction.

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+(aq) + O\bar{H}\,(aq)$$

The equilibrium constant may be written as

$$K = \frac{[H_3O^+][O\bar{H}]}{[H_2O][H_2O]}$$

$$K\,[H_2O]^2 = [H_3O^+][O\bar{H}] \quad \text{(Hence concentration of water is constant)}$$

$$K_W = [H_3O^+][O\bar{H}]$$

At 25°C, the value of Kw is 1.0×10^{-14}. This very small value of Kw shows that self ionization of water occurs to a very small extent. Since the number of $[H^+]$ and $[OH^-]$ in pure water are equal, we can determine the concentration of these ions by using above equation of Kw. Thus in pure water the conc. of each $[H^+]$ and $[OH^-]$ at 25°C is 1×10^{-7} M.

The value of Kw varies with temperature and a rise of temperature increases the value of Kw.

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8.4.2 pH, pOH and pKw

Soren Sorensen

The measurement of the concentration of aqueous H^+ and OH^- ions is a task to estimate the strength of acids and bases because the conc. of H^+ and OH^- ions are very low in aqueous solution specifically when a weak acid or base is dissolved. To cope up this difficulty Sorenson (1909) introduced a logarithmic scale since logarithm is very useful way in representing very small and very large quantities. **"pH is the negative logarithm of molar concentration of H^+ ions and pOH is the negative logarithm of molar concentration of OH^- ions in aqueous solution at given temperature".** Since pH is a logarithmic value, it has no unit.

$$pH = -\log [H^+] = \log \frac{1}{[H^+]}$$

$$pOH = -\log [OH^-] = \log \frac{1}{[O\bar{H}]}$$

pH scale represents numbers between zero (very acidic) to 14 (very alkaline) and specify the acidity or basicity of aqueous solution. A solution having pH = 7, represents the point of neutrality and it evident that solution contains equal conc. of H^+ ions and OH^- ions. The behavior of different solutions with respect to pH concept is summarized below.

Table 8.4 PH of acidic, basic and neutral solution at 25°C

Aqueous Solution	Conc. of H^+ and $O\bar{H}$ ions	pH
Neutral	$[H^+] = [O\bar{H}]$	7
Acidic	$[H^+] > [O\bar{H}]$	Less than 7
Alkaline	$[H^+] < [O\bar{H}]$	More than 7

Although, the pH of distilled water is 7 at 25°C, however it increases with the rise of temperature since temperature increases the extent of ionization.

The dissociation constant of water is represented as

$K_W = [H^+] [O\bar{H}]$

By taking negative logarithm on both sides

$(-\log K_W) = (-\log [H^+]) + (-\log [O\bar{H}])$

Since K_W at 25°C is 1×10^{-14}

Therefore

$pH + pOH = 14$

Do You Know?

Honey bee when stings a person, it injects a painful and irritating acid (formic acid) into the skin. It can give a relief if a mild base like backing soda is rubbed on the stung area of skin.

pH of a solution is mostly determined by using universal indicator. It is mixture of dyes usually pasted on a paper. It shows a change in the colour with the change of PH and helps us for measuring the strength of acids and bases. Several other indicators are known and each undergoes a colour change over a particular pH range.

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Table 8.5	Colour of some indicators in acid, base and neutral conditions.		
Indicator	**Colour in acid**	**Colour in Base**	**Colour when Neutral**
Litmus	Red	Blue	Purple
Methyl orange	Red	Yellow	Orange
Phenolphthalein	Colourless	Pink	Colourless
Universal Indicator	Red	Purple	Green

pH play a vital role in many biological and industrial process. Following is the list of pH of some common substances at 25°C.

Table 8.6	pH values of some common known substances		
Items	**pH**	**Items**	**pH**
Urine	6.0	Tomato	4-4.1
Human blood	7.35-7.45	Lemon juice	2.3
Milk	6.6	Soft drinks	3
Sea water	7.9-8.4	Milk of magnesia	10.5
Pure water	7.0	Stomach	1.6-1.7
Vinegar	2.8-3	Egg white	8.0-8.1
Orange juice	3.5-3.7	Wash soda	12.0

Example 8.1

Calculate the pH of 0.0025M aqueous solution of HCl at 25°C

Solution:

Since HCl is a strong acid, it is assumed to be completely ionized in aqueous solution.

$$\underset{(0.0025M)}{HCl_{(l)}} \rightleftharpoons \underset{(0.0025M)}{H^+_{(aq)}} + Cl^-_{(aq)}$$

Therefore for every molecule of HCl, there is one H^+ ion, hence

$$[H^+] = [HCl]$$

or $$[H^+] = 0.0025M$$

Now using the formula of pH

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

$$pH = -\log [0.0025]$$

$$pH = 2.6$$

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Example 8.2

Determine the pH of 0.1M NaOH solution at 25°C.

Solution:

NaOH is a strong base and it is assumed to be completely ionized in aqueous solution.

$$\underset{(0.1M)}{NaOH} \rightleftharpoons Na^{+} + \underset{(0.1M)}{OH^{-}}$$

Therefore the concentration of hydroxide ions (OH^-) is equal to the concentration of dissociated NaOH.

$$[OH^-] = [NaOH] = 0.1M$$

Now applying the relation

$pOH = -\log [OH^-]$

$pOH = -\log [0.1]$

$pOH = 1$

Since $pH + pOH = 14$

$pH = 14 - 1$

$pH = 13$

Example 8.3

The pH of a solution 25°C is 4.82, calculate its hydrogen ion concentration.

Solution:

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

Taking antilog of this equation, we get the following relationship

$[H^+] = 10^{-PH}$

$[H^+] = 10^{-4.82}$ (Take antilog of $10^{-4.82}$)

$[H^+] = 1.51 \times 10^{-5}M$

Self Assessment

The pH of a sample of urine is noted to be 5.3. Calculate $[H^+]$ and $[OH^-]$ ions in the solution.

8.4.3 Leveling Effect

Strong acids like HCl, HBr, HI etc when dissolve in water, they all exhibit apparently equal strength due to the fact that water play basic medium to get them ionized completely hence water serves as leveling solvent for these acids and the phenomena is called leveling effect.

Therefore, any acid stronger than hydroxonium ion (H_3O^+) completely reacts with water to form H_3O^+ ion and the corresponding conjugate base. This can be attributed to the fact that H_3O^+ is the strongest acid that can possibly exist in an aqueous solution.

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For example HCl completely react with water to form H_3O^+ and Cl^-.

$$HCl_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$$

The similar concept goes for bases as well. Any base stronger than hydroxide ion (OH^-) completely react with water to form OH^- ion and respective conjugate acid. The reason is similar to our former understanding that OH^- ion is strongest base that can possibly exist in any aqueous solution.

For example when sodium amide ($NaNH_2$) is placed in water then amide ion (NH_2^-) reacts completely with H_2O.

$$NH^-_{2(g)} + H_2O_{(l)} \longrightarrow NH_{3(aq)} + OH^-_{(aq)}$$

8.5 LEWIS DEFINITION OF ACIDS AND BASES

According to G.N Lewis (1923) **"Acid is a substance that accepts an electron pair whereas base is a substance that can donates electron pair"**. Lewis acid and base is commonly known as electrophillic (electron loving) and nucleophillic (nucleus loving) reagents since they have capability to accept and donate electron pair respectively.

Considering Lewis concept, hydrogen ion (H^+) is an acid because it accepts electron pair. Similarly hydroxide ion (OH^-) is base since it donate lone pair of electron.

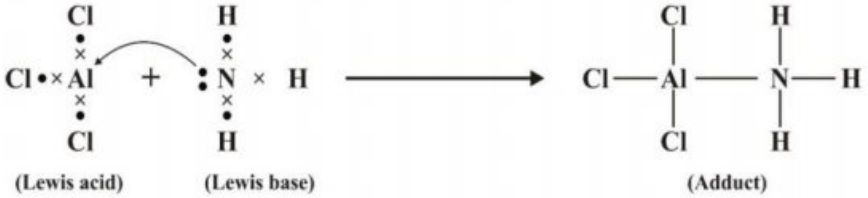
Do You Know?

Lewis acids are not only limited to $AlCl_3$ and BF_3 type molecules but molecules with polar multiple bonds as well as metal cations also function as lewis acids.

Lewis theory does not explain about the transfer of proton from one specie to another however it indicates sharing of electron pair between a donor and accepter reagent. Generally species (compounds or cations) having less than a full octet of electrons behave like Lewis acids and all species (compounds or anions), having lone pair of electrons behave like Lewis base. The product formed in a lewis acid base reaction possesses a coordinate covalent bond between lewis acid and base and known as adduct.

$$A + :B \longrightarrow A - B$$

Several neutral molecules such as $AlCl_3$, BF_3, $FeCl_3$ etc serves as Lewis acids due to electron deficiency on the central atom (fewer than eight valence electrons). On the other hand ammonia (NH_3), Phosphene (PH_3), Water (H_2O) etc although have their complete octet but possess lone pair of electron that is available to donate hence they serves as Lewis base.



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8.6 BUFFER SOLUTIONS AND THEIR APPLICATIONS

It is often necessary to maintain the pH of certain solutions in the laboratory and industrial processes. This can be achieved by the help of buffer solutions. **"A buffer solution is one whose pH is not changed significantly on dilution or even if the small amount of acid or base is added at constant temperature".** Buffer solution is a mixture of a weak acid and its conjugate base, or a weak base and its conjugate acid. It resists the change in pH and can keep it for long time.

There are two types of buffer solution.

Do You Know?

Buffering in blood is crucial to our survival. The pH of blood must be kept constant for normal body functions to work. If blood becomes too acidic, or too basic, then enzymes and proteins are unable to function.

Acidic Buffers: It contains weak acid and its salt with strong base, its PH is less than 7. For example: CH_3COOH and CH_3COONa.

Basic Buffers: It contains weak base and its salt with strong acid, its PH is more than 7. For example: NH_4OH and NH_4Cl.

Buffer Action

To understand how a buffer works, let us consider the ionization of acetic acid-sodium acetate solution.

$$CH_3COOH_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$
$$CH_3COONa_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

Both acetic acid and sodium acetate provides CH_3COO^- ions, however CH_3COO^- ions comes from CH_3COONa (strong basic salt) are in high concentration.

When small amount of an acid is added to this buffer solution, the most of the H^+ ions of acid combine with excess acetate ions (CH_3COO^-) of the solution to form acetic acid.

$$CH_3COO^-_{(aq)} + H^+_{(aq)} \longrightarrow CH_3COOH_{(l)}$$

Thus a very slightly change in the PH is observed and we say that PH remains practically unchanged.

When small amount of a base in added to this buffer solution the additional OH^- ions combine with H^+ ions of the buffer to form water molecules. As a result the equilibrium shifts to the right to produce more H^+ ions till practically all the excess of OH^- ions are neutralized and the original buffer pH is restored.

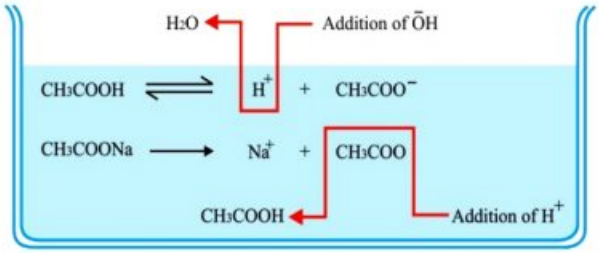

Fig 8.2: Buffer action of an acidic buffer

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Buffer Capacity

It is important to realize that buffer solution cannot keep the PH constant if enough acid or base is added into it. The quantity of substance (acid or base) that can be mixed into buffer solution before its PH change is known as buffer capacity.

Application of Buffer solutions:

1. Buffer solution plays a very significant role in biochemical system. For example pH of our blood is maintained at 7.3 to 7.4 due to bicarbonate and carbonic acid buffer.
2. Buffer solutions are widely used in industrial processes such as fermentation, dye processes and manufacturing of pharmaceuticals.
3. Buffer solution is used in agriculture to maintain the pH of soil for proper crop yield.
4. Buffer solution is extensively used in analytical chemistry and pathological laboratories.
5. Buffers are also used in foods industries to maintain the pH of various food items in order to preserve their flavor, appearance and micro-biological stability.

8.7 SALTS THEIR TYPES AND APPLICATIONS

"Salt is a substance produce by the reaction of acid and base. It consists of positive ion of base and negative ion of acid".

Salts may be neutral, acidic or basic, depending upon the number and types of ions present.

Table 8.7 Types of salts formed by neutralization reaction

Acid	Base	Types of Salts	Neutralization Reaction
Strong	Strong	Neutral	$NaOH + HCl \rightarrow NaCl + H_2O$
Strong	Weak	Acidic	$HCl + NH_4OH \rightarrow NH_4Cl + H_2O$
Weak	Strong	Basic	$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$
Weak	Weak	Neutral	$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$

Hydrolysis

When a salt (AB) dissolves in water, it breaks up into A^+ and B^- ions. These positive and negative ions may or may not react with water. If any one of these ions reacts with water, the solution becomes either acidic or alkaline.

$$A^+ + H_2O \longrightarrow AOH + H^+$$
$$B^- + H_2O \longrightarrow BH + O\overline{H}$$

Thus, the reaction of cation or anion of the salt with water to produce hydrogen ions (H^+) or hydroxyl ions (OH^-) and change the pH of solution is known as hydrolysis (hydro; water and lysis; to break).

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8.7.1 Salt and types of Salt

After getting the concept of hydrolysis we shift towards four possible types of salts.

Type-1: (Salt of Strong acid and Strong base)

These salts are formed by neutralization of strong acid and strong base. Since both cation and anion comes from strong base and strong acid respectively, they do not undergo hydrolysis and hence the pH of their aqueous solution remains 7.

For example: NaCl, K_2SO_4, $NaNO_3$ etc

Type-2: (Salt of Strong acid and Weak base)

These salts are formed by neutralization of strong acid and weak base. The an ion of these salts comes from strong acid and hence does not react with water, however cat ion which comes from weak base interact with water to give acid solution having pH less than 7.

For example: When NH_4Cl dissolves in water, it gives acidic solution

$$NH_4Cl_{(s)} \rightleftharpoons NH_4^+ + Cl^-_{(aq)}$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

Other examples of this type of salts are $(NH_4)_2SO_4$, $CuCl_2$ etc

Type-3: (Salt of weak acid and strong base)

These salts are formed by neutralization of weak acid and strong base. The cat ion which comes from strong base does not react further with water. The an ion which comes from weak acid reacts with water and undergo hydrolysis to give alkaline solution having pH more than 7. For example sodium carbonate when dissolve in water it gives basic solution.

$$Na_2CO_{3(s)} \rightleftharpoons 2Na^+_{(aq)} + CO^{-2}_{3\,(aq)}$$

$$CO_3^{-2} + 2H_2O \rightleftharpoons H_2CO_3 + 2OH^-$$

Other examples of this type of salt are CH_3COONa, $NaHCO_3$ etc

Do You Know?

The digestion of food is an example of hydrolysis. The water helps to break down the compounds you have eaten. This allows the larger compounds to be broken down into smaller compounds, so they are more easily absorbed.

Type-4: (Salt of Weak acid and weak base)

These salts are formed by neutralization of weak acid and weak base. Cation and anion of these salts come from weak base and weak acid respectively therefore they both have ability to undergo hydrolysis in aqueous solution. pH of aqueous solution of these salts may either be more than 7, less than 7 or exactly 7 depending upon the relative extent of hydrolysis of cat ion and anion.

For example: NH_4CN, CH_3COONH_4

8.7.2 Application of some salts

Salts play significant role in the synthesis of a variety of industrial products as well as many of them directly use in our daily life. Some applications of salts are mentioned in the following table.

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Table 8.8 Applications of some typical salts

Chemical Name	Common Name	Formula	Common Applications
Table salt	Sodium chloride	NaCl	Essential part of Human diet
Epsom salt	Magnesium sulphate	$MgSO_4$	Use to produce laxative effect to treat constipation
Gypsom salt	Calcium sulphate	$CaSO_4$	In making plaster of paris
Baking soda	Sodium bicarbonate	$NaHCO_3$	Use as antacid to relieve heart burn and acid indigestion
Washing soda	Sodium carbonate	Na_2CO_3	Use to remove rigid stains from Laundry
Salammoniac	Ammonium chloride	NH_4Cl	Use as expectorant in cough syrup
Muriate of potash	Potassium chloride	KCl	Use in making fertilizers

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Curdling of Milk

Fresh milk is an example of a colloid. It consists of fats and protein particles floating in water. This colloidal suspension scatters light and causes milk to appear white. The protein molecules (mainly casein) repel each other due to the presence of negative charges on them and help them naturally distribute evenly throughout liquid.

Milk is slightly acidic, and its pH is further lowered by milk bacteria which converts lactose into lactic acid or by the addition of some other acidic ingredients like lemon juice, vinegar etc. The protons (H^+) of these acids attach with negatively charged colloidal particles of protein and neutralize them. They now stop repelling each other. This allows them to stick together and coagulate into the clumps known as curds. The watery liquid left behind is called "Whey".

Activity

This activity will enable you to understand how an indicator works in acidic and basic medium.

Place a few small pieces of red cabbage in a bowl of boiling water, stir well, and let aside for 5 minutes, or until a dark solution forms. Now filter it and divide it between two beakers. In one beaker, place the egg white, and in another, the vinegar. It will be observed that the cabbage juice acquires green color in egg white and red in vinegar exhibiting its basic and acidic nature respectively. This is due to the presence of anthrocyanin pigment in cabbage, which causes the colour to change and so acts as an indicator.

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SUMMARY with Key Terms

- **Bronsted-Lowry theory** tells us that acid is a specie which tends to donate proton where as base is a specie that accept proton. It also tells that strong acid has weak conjugate base and strong base has weak conjugate acid.
- **Conjugate acid base pair** represents two species, one on the left side and other on the right side of equation with the difference of one proton.
- **Ionization constant of water** is the ionic product of H^+ ion and OH^- ion of water. Its value is 1×10^{-14} at 25°C.
- **pH Scale** is a logarithmic scale use to estimate the strength of acids and bases. It represents number between 0 (very acidic) to 14 (very basic).
- **Universal Indicator** is a mixture of dyes usually paste on a paper. It shows the change in colour with the change of pH and helps us for measuring the strength of acid and base.
- **Leveling effect** is the effect of solvent on the properties of acid and base. All acids stronger than H_3O^+ are completely reacts with water to form H_3O^+ ion and the corresponding conjugate base.
- **Lewis theory of acid and base** tells us that acid is a substance that can accepts an electron pair where as base is a substance that can donates electron pair.
- **Buffer Solution** is a mixture of weak acid with its strong basic salt or a weak base with its strong acidic salt. It tends to resist the change of PH.
- **Buffer Capacity** is the quantity of acid or base added to buffer solution before changing its pH. Buffer capacity is maximum when acid to salt ratio or base to salt ratio is equal to 1.
- **Buffer Range** is the range of pH over which a buffer solution remains effective on addition of strong acid or base.
- **Acid Buffers** are solutions which contain large amount of a weak acid and its salt with strong base. Their pH is less than 7.
- **Basic Buffers** are solutions having large amount of weak base and its salt with strong acid. Their pH is more than 7.
- **Degree of Ionization** is the ratio of number of molecule ionized and the total number of molecules of an acid or base in aqueous solution.
- **Hydrolysis** is the reaction of cation or anion of the salt with water molecule to change the pH of solution cation hydrolysis gives acid solution where as an ion hydrolysis give basic solution.
- **Salts** are formed in the neutralization reaction of acids and bases. These are classified into acidic basic and neutral salts depending upon the number and the type of radicals present in them.

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EXERCISE

Multiple Choice Questions

1. Choose the correct answer

(i) H_2SO_4 is stronger acid than CH_3COOH because:

(a) It gives two H^+ ion per molecule (b) Its boiling point is high

(c) Its degree of ionization is high (d) It is highly corrosive

(ii) Al_2O_3 is amphoteric oxide because it reacts with:

(a) Acids (b) Base

(c) Both acids and base (d) neither acid nor base

(iii) Which of the following is not a Buffer solution:

(a) CH_3COOH/CH_3COONa (b) $Na_2CO_3/NaHCO_3$

(c) NH_4OH/NH_4Cl (d) NaOH/HCl

(iv) Which oxide is amphoteric in nature:

(a) K_2O (b) CO_2

(c) CaO (d) Al_2O_3

(v) Which of the following does not alter the pH of a solution?

(a) NH_4Cl (b) Na_2CO_3

(c) NaCl (d) Mg(OH)Cl

(vi) Conjugated acid of NH_3 is:

(a) NH_4^+ (b) NH_2^-

(c) NH_2 (d) NH

(vii) Salt which is formed by the neutralization of weak acid and strong base is:

(a) $NaNO_3$ (b) NH_4Cl

(c) Na_2CO_3 (d) NH_4CN

(viii) Which of the following statements is not correct about the bases?

(a) They have bitter tastes (b) They have high pH value

(c)They react with acids to form salts (d) They turn blue litmus red

(ix) A conjugate acid base pair has the difference of only:

(a) One electron (b) One proton

(c) One electron pair (d) One proton pair

(x) Salt formed by neutralization of weak acid and weak base is:

(a) NH_4Cl (b) Na_2CO_3

(c) NH_4CN (d) Na_2SO_4

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Short Questions

1. Define pH & pOH of a solution? Also show that pH + pOH = 14.
2. Why the aqueous solution of NH_4Cl is acidic and Na_2CO_3 is alkaline.
3. Write down conjugate base of each of the following acids.
   H_2SO_4, H_2S, NH_4^+, HCOOH
4. What is meant by self-ionization of water? Write the expression of Kw. What is its value at 25°C?
5. Write equation and indicate the conjugate acid-base pairs for the following:
   (i) Acetic acid & ammonia (ii) Hydrochloric acid & water

Descriptive Questions

1. Explain Bronsted-Lowry theory of acids and bases. What is meant by conjugate acid-base pair give examples?
2. Define the process of hydrolysis. Explain the behavior of each of the following salts in aqueous solution. (i) K_2CO_3 (ii) $(NH_4)_2SO_4$ (iii) $NaNO_3$
3. What is Buffer solution? Explain how it resists the change of pH by adding small amount of acid and base. Give the applications of buffer solution.
4. Describe Lewis theory of acids and bases. What are the advantages of this theory over Lowry Bronsted theory?
5. What is salt? Explain Acidic, Basic and Neutral salts?

Numerical Questions

1. A solution is made by dissolving 14.8g HCl in water at 25°C. If the volume of solution is 750cm^3 and HCl is assumed to be completely ionized, calculate its pH.
   [Ans: pH = 1.2]
2. 2. The hydroxide ion concentration in an antiseptic solution at 25°C is 3.5×10^{-4}M. Calculate its pH. [Ans: pH = 8]

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CHEMICAL KINETICS

Chapter 9

Teaching Periods	Assessment	Weightage
8	1	7

Students will be able to:

- **Define** chemical kinetics.
- **Explain** the terms rate of reaction, rate equation, order of reaction, rate constant and rate determining step.
- **Determine** the order of reaction.
- **Calculate** units of rate constant.
- **Explain** effects of concentration, temperature and surface area on reaction rates.
- **Explain** why powdered zinc reacts faster.
- **Explain** what is meant by the terms activation energy and activated complex.
- **Relate** the ideas of activation energy and the activated complex to the rate of a reaction.
- **Illustrate** the collision theory to explain how the rate of a chemical reaction is influenced by the temperature, concentration, size of molecules.
- **Illustrate** a potential energy diagram for a reaction, discuss the reaction mechanism for the reaction.
- **Define** terms catalyst, catalysis, homogenous catalysis and heterogeneous catalysis.
- **Enlist** examples of catalyst in tabular form.
- **Explain** that a catalyst provides a reaction pathway that has low activation energy.
- **Describe** enzymes as biological catalysts.

INTRODUCTION

The knowledge of stoichiometry, enthalpy change and speed of reaction seeks the attention of chemists whenever they are concerned about a chemical reaction for its commercial use. The profitability of chemical process can be measured by the speed at which reactants convert into products. Speed of reaction means how fast reactants are consumed and products are formed. In our routine life we see that different chemical reactions occur at different rates for example combustion of coal proceeds rapidly while rusting of iron slowly.

If you need to proceed a chemical reaction at a convenient rate, it is necessary to have knowledge about the factors which control the rate of this particular reaction. The subject which deals with this aspect of chemical reaction is called as Chemical Kinetics.

9.1 CHEMICAL KINETICS

Chemical kinetic is the specific area of chemistry that deals with the rate of a chemical reaction. The word kinetic refers to the rate in term of change in the concentration of reactants and products with time. Consider the chemical reaction involves in the hydrogenation of ethyne.

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

Now think, how is the rate of this reaction measured? What happens at molecular level when reactants change into product? What factors makes the process faster? How many steps involves in reaction completion? Answer of all these questions is associated with the study of chemical kinetics. **"The study of rate of chemical reaction, mechanism of reaction and the factors that influence on the rate of chemical reactions is known as chemical kinetics"**.

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9.2 RATE OF REACTION

Chemical reactions are often carried out in solution the amount of reactants and products is conveniently taken in term of molar concentration. The reaction rate is therefore defined as **"Increase in the molar concentration of products or decrease in the molar concentration of reactants per unit time".** It may express as the ratio of change in the concentration of product or reactant to the change in time.

$$\text{Rate of reaction} = \frac{\text{Change in concentration of product or reactant}}{\text{Change in time}}$$

$$\text{Rate} = \frac{\Delta x}{\Delta t}$$

Since in S.I system the concentration is taken in mol/dm^3 and time in second, the unit of rate of reaction is mole/dm^3.s.

Consider a simple hypothetical reaction.

$$A \longrightarrow B$$

Initially no product (B) is formed but as the time passes, the conc. of A decreases and concentration of B increases gradually. This trend of change in the concentration of reactant (A) and product (B) is illustrated in figure 9.1.

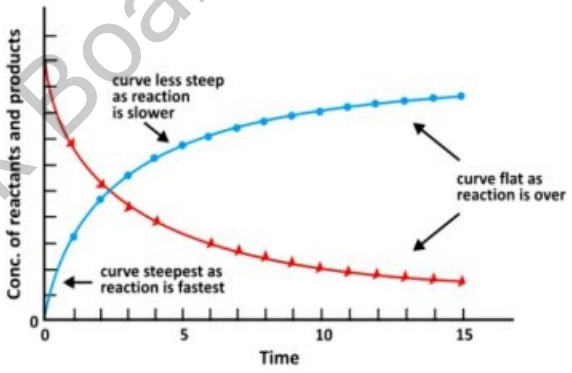

Fig. 9.1 Plot of conc. of reactant (A) and product (B) versus time

Reaction rate is expressed in the following two specific ways.

* The rate of appearance of products which indicates that concentration of product increases with time.

$$R = \frac{\Delta B}{\Delta t}$$

* The rate of disappearance of reactants which means concentration of reactants decreases with time.

$$R = \frac{-\Delta A}{\Delta t}$$

The negative sign indicates that reactant concentration decreases with time.

9.2.1 Rate law and Rate expression

Concentration of a substance represents the number of moles and molecules per unit volume. The higher the concentration of reactants, the more is the chances of molecular collision and hence the more is the rate of reaction. Rate law is a mathematical expression that explains the quantitative relationship of molar concentration of reacting species with the rate of reaction.

For a general reaction

$$xA + yB \longrightarrow \text{Product}$$

The rate law may be written as

$$\text{Rate} = K [A]^x [B]^y$$

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"Rate law is an equation which specifies the rate in term of reactant concentration with each term raised to some power". Here "K" is proportionality constant called as rate constant. It relates the reaction rate to the concentration of the reacting substances.

If we take the concentration of each reactants unity that is 1 mol/dm^3, then rate law will be reduced to

Rate = K

Hence specific rate constant at a given temperature may be defined as **"the rate of reaction when the molar concentration of each reactant is unity"**.

Each reaction has a fixed value of specific rate constant (K) at a particular temperature. Its value changes with the temperature, however independent upon change in concentrations of reactant.

Example 9.1

Nitrogen dioxide is an air pollutant gas. The rate of the decomposition of NO_2 is shown in the following equation.

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

In an experiment the initial concentration of NO_2 was found to be 0.35 mol/dm^3. What was the initial rate of this reaction if the rate constant at experimental temperature was 1.8×10^3 mol/dm^3.s.

Solution:

Since decomposition of NO_2 is of second order reaction, the rate law is written as

Rate = K $[NO_2]^2$

Rate = 1.8×10^3 $[0.35]^2$

Rate = 2.2×10^2 mol/dm^3.s

Self Assessment

The reaction rate (R) for the reaction $2A + B \rightarrow A_2B$ was found experimentally is given by the expression. $R = K[A]^2 [B]$

(a) Will K increase, decrease or remain unchanged if the concentration of A is doubled? If the concentration of B is doubled?

(b) Will R increase, decrease or remain unchanged, if the concentration of A is doubled? If the concentration of B is doubled?

9.2.2 Order of Reaction and its Determination

From the study of rate law, it is clarified that the rate of reaction depends upon the concentration of reactant each raised to the power of some coefficients.

Rate = K $[A]^x$ $[B]^y$

The exponent **x** and **y** are obtained experimentally. They may be a whole number or in fraction. The numerical value of **x** and **y** are not necessarily same as shown by stoichiometrical coefficient of equation. The exponents **x** and **y** specify the number of reacting molecules which

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involves in chemical change as a result of their change in concentration and refers as order of reaction. The overall order of reaction defines as **"the sum of all the exponents of the concentration in terms of reactants involve in the rate law"**.

It is important to note that rate law, as well as order of reaction are experimental parameter and cannot be determined by looking at equation.

The order of reaction can be zero, a small whole number or even in a fraction depending upon the number of species whose concentration directly affects the rate of reaction.

By taking the algebraic sum of experimentally determined power of concentration of reactants in the rate equation, we may classify reactions into first order, second order, third order etc. However certain reactions are categorized into zero order. The rate of these reactions is entirely independent upon concentration of reactants. They most often occur on the surface of metals. Photochemical reactions are also zero order reactions because they proceed by absorbing light of certain wave length instead of collision of reactants molecules. Light provides necessary energy to the reactant molecules for their bond breaking process.

There are various methods to determine rate law and order of reaction. However, a simple and common method is "initial rate method".

Consider a hypothetical reaction

$$A + B \longrightarrow AB$$

Suppose we performed a series of three experiments with different initial concentrations of reactants A and B and estimate initial rate in each case. We then established a data of each experiment as given in the following table.

Experiment No.	Initial [A] (mol/dm^3)	Initial [B] (mol/dm^3)	Initial Rate ($mol/dm^3.s$)
1	0.100	0.0050	1.25×10^{-4}
2	0.200	0.0050	2.50×10^{-4}
3	0.100	0.010	5.0×10^{-4}

A thorough look into above table gives the following conclusions.

In the first two experiments the concentration of B is held constant. The concentration of A is doubled from 0.100 mol/dm^3 to 0.200 mol/dm^3 which cause an increase in the initial rate by a factor of 2 from 1.25 x 10^{-4} $mol/dm^3.s$ to 2.50 x 10^{-4} $mol/dm^3.s$. This indicates that the rate of reaction is directly proportional to concentration of A.

$Rate \propto [A]$

Comparing experiment 1 and 3, we noted that initial conc. of A is held constant. On the other hand conc. of B changes from 0.005M to 0.010M (two times). The effect of this change in conc. of B on its initial rate is found to be increase four times. This justifies that the reaction rate is directly proportion to the square of concentration of [B].

$Rate \propto [B]^2$

Now the overall rate law of the reaction is written as

$Rate = K [A]^1 [B]^2$

And thus the order of reaction is 1 + 2 = 3

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Example 9.2

The initial rate data obtained in a series of experiments while working on the oxidation of nitric oxide to give nitrogen dioxide is given in the following table. Determine its rate law and find the order of reaction.

$$NO + O_2 \longrightarrow NO_2$$

Experiment No.	Initial [NO]	Initial [O_2]	Initial Rate
1	0.10M	0.10M	8×10^{-4} Ms^{-1}
2	0.10M	0.20M	16×10^{-4} Ms^{-1}
3	0.20M	0.10M	16×10^{-4} Ms^{-1}

Solution:

(i) When the initial concentration of NO is doubled (experiment 1 and 3), the initial rate is also doubled. Thus rate law with respect to A is.

$R \propto [A]^1$

(ii) When the initial concentration of O_2 is doubled (experiment 1 and 2), the initial rate is also doubled. Thus rate law with respect to B is.

$R \propto [B]^1$

(iii) The overall rate law now written as

$R = K [A]^1 [B]^1$

(iv) Order of reaction is thus $1 + 1 = 2$

9.2.3 Elementary and Overall Rate Constant and its Units

Chemical reactions may occur in either a single step or in multiple steps. A single step reaction is known as elementary reaction while the reaction which completes in two or more steps is called complex reaction. A reaction mechanism consists of a set of elementary reactions and describes the feasible path followed by the reactant(s) in the formation of product(s). In the mechanism of a complex reaction, one of the steps is slowest; it determines the rate of overall reaction and known as rate determing step or rate controlling step.

Consider for example the reaction between Nitrogen dioxide and carbon monoxide

$$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$$

The mechanism of this reaction involves the following two elementary steps

$$NO_{2(g)} + NO_{2(g)} \xrightarrow{K1} NO_{3(g)} + NO_{(g)} \text{ (Slow Step)}$$

$$NO_{3(g)} + CO_{(g)} \xrightarrow{K2} NO_{2(g)} + CO_{2(g)} \text{ (Fast Step)}$$

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Above mechanism provides us basic information that is kinetics and molecularity of reaction which may be summarized as.

- K_1 and K_2 are the rate constant of elementary reactions and NO_3 is reaction intermediate.
- Step-1 is slow therefore it must govern the kinetics of reaction and considered as rate determining step.
- Two molecules are involved in slow step therefore it is bimolecular reaction.
- In rate determining step only NO_2 is involved therefore the rate of this reaction is independent on concentration of CO.
- As far as kinetics concerned, this is second order reaction with respect to NO_2 and zero order reaction with respect to CO.
- The overall rate law is now written as

$$\text{Overall rate} = K_1 [NO_2]^2$$

Do You Know?

Order of reaction and molecularity are two different terms.
(i) Order of reaction is an experimental parameter where as molecularity is determined by looking at the balance chemical equation.
(ii) Order of reaction may be zero but molecularity may not be zero.

Unit of Rate Constant

The unit of rate constant (k) of a particular reaction depends upon order of reaction and may be calculated by manipulating the rate law. For example the decomposition of NO_2 is of second order reaction and its rate law may be written as $R = K [NO_2]^2$.

$$\text{Thus } K = \frac{\text{Rate}}{[NO_2]^2}$$

Since the unit of rate of reaction is $mol/dm^3.s$ and unit of concentration is mol/dm^3, the unit of K may be obtained as,

$$K = \frac{mol/dm^3.s}{[mol/dm^3]^2}$$

$K = dm^3\ mol^{-1}.s^{-1}$.

Because the molarity is specified in mol/dm^3, we may express the unit of "**K**" in more simplified form as

$K = M^{-1}\ s^{-1}$

The unit of rate constant (K) for the zero order, first order, second order and third order can be determine by inserting the units of concentration and rate of reaction in their rate laws. A summary of units of rate constant is given below.

Do You Know?

When a wooden match stick is lighted in air, it will continue to glow for a periods of time. But if we insert this burning match stick into a cylinder of pure oxygen, it will glow five times faster. This is because air contains only 21% oxygen where as oxygen in the cylinder is five times more concentrated.

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Table 9.1	Rate law and units of rate constant of various order of reactions		
Order of Reaction	**Rate Law**	**Unit of K**	**Examples**
Zero Order	Rate = K	Ms^{-1}	$H_{2(g)} + Cl_{2(g)} \xrightarrow{hv} HCl_{(g)}$
1st Order	Rate = K [A]	s^{-1}	$NH_4NO_{2(aq)} \longrightarrow N_{2(g)} + 2H_2O_{(l)}$
2nd Order	Rate = K [A] [B] Rate = K $[A]^2$	$M^{-1} s^{-1}$	$2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$
3rd Order	Rate = K $[A]^2$ [B] or Rate = K [A] $[B]^2$	$M^{-2} s^{-1}$	$2NO + Cl_2 \longrightarrow 2NOCl$

Example 9.3

Decomposition of SO_2Cl_2 is of first order reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ write its rate law and deduce the unit of rate constant.

Solution:

Since decomposition of SO_2Cl_2 is governed by first order kinetics the rate law is written as Rate = K $[SO_2Cl_2]$

Now the unit of rate constant (K) is obtained if we put the units of concentration and unit of rate of reaction in the rate law.

$$K = \frac{mol/dm^3.s}{mol/dm^3}$$

$$K = s^{-1}$$

9.2.4 Factors Affecting the Rate of reaction

A very useful aspect of chemical kinetic is to control the speed of chemical reactions. Often we ambitious to speed up a chemical reaction for economical or industrial point of view, but in many cases we deliberately slow down the reaction for a careful control of some potentially explosive process. Various factors influence on the rate of chemical reactions.

(i) Nature of Reactants

Different reactants undergo with different rates in the chemical change. It can be attributed to their structure, nature of bonding and physical state. For example when a piece of sodium and iron exposed to air, sodium oxidizes completely much faster than iron. Similarly when metal sodium and calcium are put into water, sodium reacts rapidly where as calcium moderately. The reason is that sodium is highly electropositive and it readily loses its valence electron.

Generally substances having ionic bond reacts quickly as compared to the covalent substances.

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(ii) Concentration of Reactants

According to rate law, the rate of reaction increases with increasing the concentration of one or more reactants. More crowding of reactant, molecules allow more collision to happen. Thus chances of successful collision increases resulting in increase rate of formation of products.

Consider a reaction in which A and B react to form a product AB.

$$A + B \longrightarrow AB$$

Let suppose the reaction is obeyed by second order kinetics the rate law may be expressed as R = K [A][B]. If the concentration of A is doubled, the number of collision among particles of A and B per unit time would also be doubled. Consequently the rate of reaction increases by a factor of two fold. Now if we double the concentration of both A and B, the collision per unit time has therefore doubly doubled. It increases the rate of reaction four times.

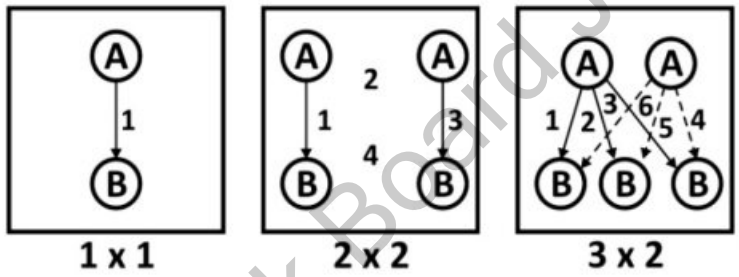

Fig 9.2: Effect of increase in concentration of A and B on the rate of reaction

Example 9.4

In the reaction $2SO_3 \rightarrow 2SO_2 + O_2$, the rate law of the decomposition of SO_3 is $R = K[SO_3]^2$. What will be the rate if concentration of SO_3 is (i) doubled (ii) halved

Solution:

By considering the rate law, the rate of reaction is determined as

(i) When the concentration of SO_3 is doubled, the rate will increase by $[2]^2 = 4$ times

(ii) When the concentration of SO_3 is halved, the rate will decrease by $\left[\frac{1}{2}\right]^2 = \frac{1}{4}$ time.

(iii) Surface Area

The surface area of solid is an important factor to enhance the rate of reaction. The greater the surface area, the more is the possibility of reactant particles to collide with each other and increases the reaction rate.

Fine powdered substances have greater surface area as compared to chunk. For example powdered zinc reacts more vigorously with dilute hydrochloric acid as compared to its chips because powder zinc offer greater surface area for HCl to act upon. This can be demonstrated by the intensity of bubbles produce by the liberation of hydrogen gas.

$$Zn_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(s)} + H_{2(g)}$$

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(iv) Radiations

A specific class of chemical reactions occurs due to the absorption of light of certain wavelength; these are known as photo chemical reactions. The absorbed light provides appropriate energy for breaking the chemical bonds of reactant molecules and initiates the reaction. These reactions can be speed up by increasing the intensity of appropriate light. An increase in the intensity of light means more energy is provided to the reacting molecules which facilitate the bond breaking process.

The reaction of H_2 and Cl_2 is a zero order reaction in which light radiation (photon) provide necessary activation energy to the reactant molecules. Other examples are photo synthesis and photography etc.

(v) Temperature:

As a rule of thumb, reaction rate is approximately double with the rise of temperature by 10°C. A rise of temperature increases the kinetic energy of reacting molecules which enhances the frequency of collision. Although the reactant molecules collide with one another billions times per second but every collision does not lead to a reaction. Only those molecules would react to form products which have energy equal to or greater than certain critical energy known as activation energy.

The distribution of kinetic energies in a chemical system at two different temperatures as given in fig 9.4 tells us what happens when the temperature rises.

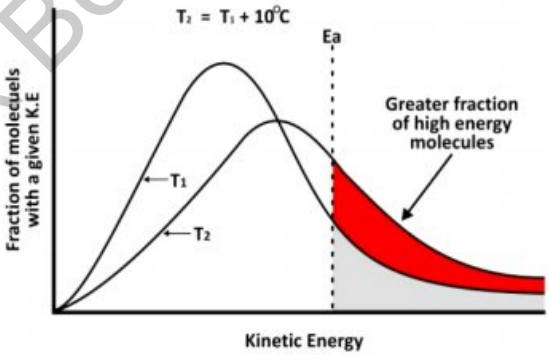

Fig. 9.3: Effect of temperature on the number of molecules having kinetic energy greater than Ea.

At temperature (T_1) large part of the molecules possess average kinetic energy however a small part of the total molecules found to possess kinetic energy equal or larger than activation energy. This small fraction of high energy molecules are illustrated in shaded area. As the temperature increases from T_1 to T_2 (T_1 + 10°C), a change in energy distribution occur and more molecules have acquired high kinetic energy and cross the energy barrier. This is indicated by flattening the curve at temperature T_2. Further, the shaded area which represents the molecules with energy equal or higher than activation becomes broader by roughly two folds.

Self Assessment

A rise of 10°C, increases the rate of reaction twice, explain it by the help of energy diagram.

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9.3 COLLISION THEORY, TRANSITION STATE AND ACTIVATION ENERGY

Chemical reaction initiate by bond breaking of reactants molecules and this happens only when they collide among each other. Collision theory postulated that the rate of chemical reaction increases with the increased number of collision per unit time. Many reactant molecules collide with each other under given set of conditions, however only a fraction of molecules undergo bond breaking process. The successful molecular collision depends not only upon their high kinetic energy but also the proper orientation of colliding molecules at the time of collision.

During movement when reactant molecules come closer together, they are repelled by their electron cloud and most of them bounce off without any chemical change but only those molecules which possess very high kinetic energy overcome this repulsive force and change into product since a part of their kinetic energy converts into vibrational energy. The vibration of colliding molecule results in bond breaking which is the first step towards product formation. Thus, in an energetic viewpoint, there is some minimum energy that must be needed by the reacting molecules and below which no effective collision occurs. This energy is known as threshold energy (E_t). In order to increase the energy content of reacting molecules up to the threshold level, energy is externally supplied (usually in the form of heat). This additional energy externally supplied is known as activation energy (Ea).

Activation Energy = Threshold Energy – Average Internal Energy of Molecules

If we have a look at fig 9.4(a) and 9.4(b), we can observe a potential energy hill. All those reactants molecules which possess energy equal to or greater than the energy barrier undergo effective collision.

Small value of activation energy indicates that a large number of reactant particles take part in effective collisions and the reaction is said to be fast. On the other hand, a large value of energy of activation illustrate that only a small fraction of reacting particles undergo effective collision, such reaction are identified as slow reactions.

The potential energy diagram depicted in fig. 9.4(a) of an exothermic reaction in which the reactants at the start of the reaction are at higher energy level then the products. Whereas the potential energy diagram depicted in fig 9.4(b) is of an endothermic reaction in which the reacts at the start of reaction are at lower energy level than the products.

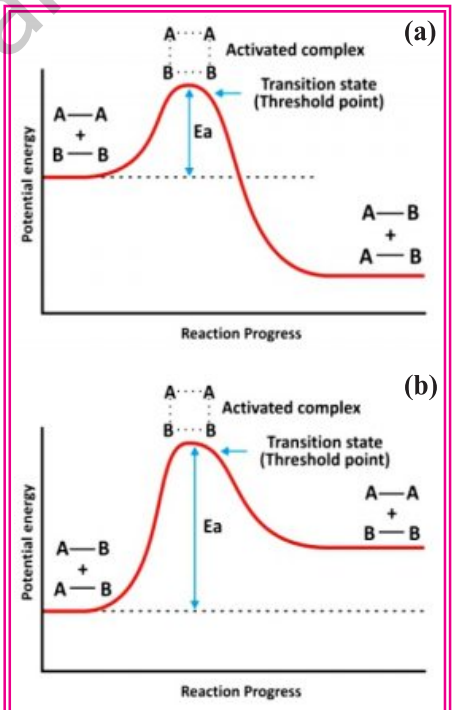

Fig. 9.4: Potential energy diagram of (a) exothermic reaction (b) endothermic reaction

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In both the figures 9.4(a) and 9.4(b), the peak of potential energy curve represents a transition state of molecules that are neither reactants nor products having partial bonds and is highly unstable with very short life span. The chemical species undergoing this transition state is known as activated complex shown as dotted lines in fig. 9.4.

Self Assessment

In term of collision theory how can you explain that all molecular collisions do not lead to formation of product.

9.4 CATALYSIS

In many synthetic processes, our concern is to get maximum yield of product in minimum period of time. We often avoid accelerating the reaction by elevating the temperature because of energy cost and also due to heat sensitivity of reacting chemicals. Alternatively we use catalyst, **"A substance which alters the rate of a chemical reaction without undergoing permanent changes in its chemical nature is called catalyst and the process involving the use of catalyst is referred as catalysis".** Catalyst can be separated after the completion of reaction and hence use over and over again.

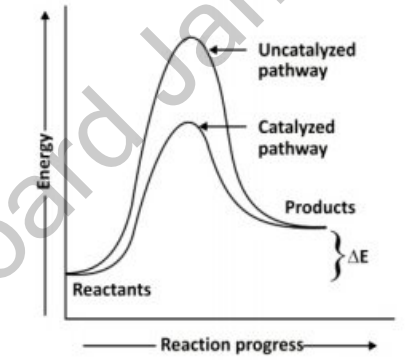

Fig. 9.5: shows that the energy of activation of catalyzed reaction is lower than uncatalyzed reaction.

9.4.1 Characteristics of Catalyst

Now we shift towards how does a catalyst works? How can we speed up the reaction without raising the temperature? Catalyst provides a new and more efficient pathway with a lower energy of activation so a relatively large fraction of reactant molecules cross the energy barrier and undergo effective collision. It must involves in early step of the reaction and then reproduce in equal amount in the later step that is why it not appeared as reactant in the equation of chemical reaction.

Consider an uncatalyzed bimolecular reaction.

$$A + B \xrightarrow{\text{slow}} AB$$

When catalyst is added, the reaction involves two step pathway during which catalyst first used and then reproduced.

$$A + \text{Catalyst} \xrightarrow{\text{fast}} \text{A-catalyst}$$

$$\text{A-catalyst} + B \xrightarrow{\text{slow}} AB + \text{Catalyst}$$

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A positive catalyst increases the rate of reaction by lowering the energy of activation where as negative catalyst retard the reaction rate by placing itself in between reacting molecules to decrease the number of effective collision. In many chemical processes our concern is to fasten the reaction therefore positive catalyst are simply called as catalyst on the other hand negative catalyst are known as retarding catalyst or inhibitors.

Table 9.2 **List of positive and negative catalyst of some industrially significant process**

Chemical Process	Catalyst	Nature
Synthesis of NH_3 by Haber Process $N_2 + 3H_2 \longrightarrow 2NH_3$	Iron Powder	Positive
Synthesis of H_2SO_4 by contact process $2SO_2 + O_2 \longrightarrow 2SO_3$	V_2O_5	Positive
Decomposition of Potassium Chlorate $2KClO_3 \longrightarrow 2KCl + 3O_2$	MnO_2	Positive
Oxidation of Chloroform $CHCl_3 + \frac{1}{2}O_2 \longrightarrow COCl_2 + HCl$	2% ethyl alcohol	Negative
Decomposition of H_2O_2 $H_2O_2 \longrightarrow H_2 + O_2$	Glycerin	Negative

Catalytic reactions are generally categorized into two groups depending upon catalyst physical state and its mode of action. These are named as homogenous catalysis and heterogeneous catalysis.

9.4.2 Homogenous Catalysis

All those catalytic reactions in which both catalyst and reactants are in the same phase refer as homogenous catalysis. Homogenous catalytic reactions are segregated into two classes.

(i) Acid Base Catalysis

A number of organic reactions proceed catalytically in the presence of H^+ or OH^- ions. In these reactions both catalyst and reactants are present in the same aqueous phase. For example hydrolysis of ethyl acetate can be speed up if strong mineral acid is added.

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$$CH_3COOC_2H_{5(aq)} + H_2O_{(aq)} \xrightarrow{H_2SO_{4(aq)}} CH_3COOH_{(aq)} + C_2H_5OH_{(aq)}$$

In this reaction both ethyl acetate (reactant) as well as H_2SO_4 (catalyst) exist in aqueous state.

(ii) Auto Catalysis

In some chemical reactions one of the products itself serves as catalyst, these are known as auto catalyzed reactions. Initial rate of this reaction is slow but as soon as the product formed, the rate of reaction increases. For example in redox titration between $KMnO_4$ and oxalic acid Mn^{+2} ion of $MnSO_4$ catalyzed the reaction.

$$2KMnO_{4(aq)} + 5H_2C_2O_{4(aq)} + 3H_2SO_{4(aq)} \longrightarrow 2MnSO_{4(aq)} + 10CO_{2(g)} + 8H_2O_{(l)} + K_2SO_{4(s)}$$

9.4.3 Heterogeneous Catalysis

In most of the catalytic process catalyst exist in different physical state than reactants. These are identified under the category of heterogeneous catalysis. For example

(i) In the manufacturing of sulphuric acid by contact process a solid catalyst vanadium penta oxide (V_2O_5) is used to convert gaseous sulphur dioxide to sulphur trioxide.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_{5(s)}} 2SO_{3(g)}$$

(ii) In the manufacturing of ammonia by Haber process solid iron powder is used to enhance the reaction rate between nitrogen and hydrogen gases.

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe(s)} 2NH_{3(g)}$$

In heterogeneous catalysis, solid catalyst adsorbs reactant molecules on its surface by lowering the energy of activation and enhances the reaction rate.

9.4.4 Enzyme Catalysis

Enzymes are special kind of the proteins which serve as biochemical catalysts in living system. They not only catalyze the reaction thousand time faster but also highly specific as compared to inorganic catalyst. Each enzyme acts only upon a specific substrate. The specificity of enzymes can be attributed to presumption that each enzyme has a specific shaped active site on its surface where molecule of substrate can attached when come in close contact through proper orientation in the same way as key fit into particular lock.

Enzymes kinetics for catalyzing biochemical process is quite complex, however a simple scheme is shown below.

$$A + B + E \rightleftharpoons ABE \longrightarrow AB + E$$

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Where A and B are reactants and E is enzyme while ABE represent substrate-enzyme intermediate in the transition state. The ABE complex provides a new pathway to product (AB) with a lower energy of activation.

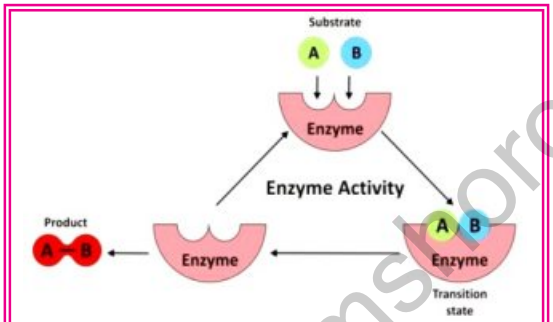

Fig. 9.6: Scheme showing enzyme kinetics for a biochemical process

Many biochemical processes occurring in living system are catalyzed by enzymes. For example digestion of food is catalyzed by various enzymes such as protease, amylase, lipase etc. They breakdown the bigger size carbohydrate, proteins and lipid molecules into smaller one which then easily be absorbed by cellular membrane of intestine.

Enzymes are also use to catalyze several industrial processes. For example in the fermentation of sugarcane into commercial alcohol two enzymes (zymase and invertase) are used which are found in yeast.

Society, Technology and Science

Use of enzyme in removing stain from fabric

Certain hydrolyses enzymes such as protease, amylase and lipase are used in modern laundry detergents for the removal of stains from fabric. Their presence increases the rate of cleaning action of detergent without damage of fabric thread.

Since stains on the fabric are of different types such as sweat, gravy, oil etc, a range of enzymes is added into detergents. For example: Protease removes egg or gravy stain, amylase eliminate starch stains, lipase take out oil and fat spots.

Enzymes break down protein, fats and starch molecules of stain to form water soluble substances which then washed away.

Activity

This activity enables you to understand how catalyst alters the rate of chemical reaction. Hydrogen per oxide decomposes as give in the following reaction.

$$H_2O_2 \rightarrow H_2 + O_2$$

Take equal volume of hydrogen peroxide in two different conical flask. Now put some black powder of manganese dioxide into first flask only.

Observe what happens in both flasks. You will see that oxygen gas evolves with effervescence in the first flask quickly. This indicates that rate of decomposition of H_2O_2 is faster in the presence of catalyst.

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SUMMARY with Key Terms

- **Chemical Kinetics** is the branch of chemistry which deals with the rate of chemical reaction, mechanism of reaction and the factors that influence the rate of chemical reaction.
- **Rate of reaction** is the increase in concentration of product or decrease in the concentration of reactants per unit time during a chemical reaction.
- **Average rate** is the change in concentration of reactants or products in a specified time period. It can be determined by dividing the difference in concentration with difference in measured time.
- **Rate law** is an equation which specifies the rate in term of reactant concentration with each term raised to some power.
- **Specific rate constant** is the rate of reaction when the molar concentration of each reactant is unity.
- **Order of reaction** is the sum of power of concentration of reactants as expressed in rate law. It may be a whole number, a fractional value or even zero.
- **Molecularity** is the total number of molecules taking part in a chemical reaction.
- **Reaction mechanism** is a set of elementary reactions which describes the feasible path followed by reactants to convert into products.
- **Rate determining step** is the slowest step in a complex reaction.
- **Factors that affect on the rate of chemical reactions** are nature of reactants, concentration of reactants, surface area of reactants, molecular size of reactants, temperature, radiations and catalysts.
- **Collision theory** tells that chemical reaction occur due to the effective collision among reacting molecules.
- **Activation energy** is the additional energy which the reacting molecules must achieve above their average kinetic energy for their effective collision.
- **Activated complex** is a high energy, unstable and short live time state exists during the transformation of reactants into products.
- **Catalyst** is substance that alters the rate of chemical reaction without itself being permanently changed.
- **Homogenous catalyst** is one which exist in the same phase as that of reactant species.
- **Heterogenous catalyst** is those which exist in different phase from reacting species.
- **Enzymes** are biochemical catalyst. They enhance the rate of chemical reactions in much biochemical process.

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EXERCISE

Multiple Choice Questions

1. Choose the correct answer

(i) For a hypothetical reaction x + y → z, if the conc. of x is double, the rate increases by square and if the conc. of y is doubled the rate increases by twice. The experimental rate law of this reaction is:

(a) $R = K [x]^1 [y]^1$ (b) $R = K [x]^1 [y]^2$
(c) $R = K [x]^2 [y]^1$ (d) $R = K [x]^2 [y]^2$

(ii) The unit of rate constant (K) for the first order reaction is:

(a) s^{-1} (b) conc. s^{-1}
(c) $conc^{-1}$. s (d) $conc.^{-1} s^{-1}$

(iii) Rate constant of a reaction is affected by:

(a)Conc. of reactants (b) Conc. of products
(c) Temperature (d) Reaction time

(iv) The purpose of using of catalyst in a chemical reaction is to change:

(a) Equilibrium constant (b) Enthalpy of reaction
(c) Activation energy (d) Nature of reaction

(v) The overall order of reaction to which the rate law is R = K:

(a) Zero order (b) First order
(c) Second order (d) Third order

(vi) Ionic reactions are classified into:

(a) Slow reaction (b) Moderate reactions
(c) Fast reactions (d) Reversible reaction

(vii) The decomposition of H_2O_2 is inhibited by:

(a) 2% ethanol (b) Glycerin
(c) MnO_2 (d) V_2O_5

(viii) The best alternative term for the velocity of reaction is:

(a) Rate of appearance (b) Rate of disappearance
(c) Average rate (d) Instantaneous rate

(ix) Order of reaction is the power to which concentration of reactant is:

(a) Lowered (b) Raised
(c) Stopped (d) Constant

(x) In the reaction A → B, the rate of disappearance is written as:

(a) $\frac{dA}{dt}$ (b) $\frac{-dA}{dt}$
(c) $\frac{dB}{dt}$ (d) $\frac{-dB}{dt}$

Short Questions

1. Define the following:

(a) Rate of reaction (b) Velocity of reaction
(c) Order of reaction (d) Rate constant

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2. The rate law of the reaction $2NO + Br_2 \rightarrow 2NOBr$ is given as
Rate = $K[NO]^2 [Br_2]$, What is the order of reaction?
(i) With respect to each reactant (ii) Overall reaction
3. How can you define order of reaction? What are the units for the rate constants of zero order, first order and second order reactions?
4. Explains the following:
(i) Powdered marble ($CaCO_3$) reacts quickly with hydrochloric acid than solid lump of marble.
(ii) Milk sour more rapidly in summer than in winter.
(iii) Reactants in solution reacts faster at high concentration.
(iv) Raising the temperature causes an increase in the rate of reaction.
5. Differentiate between the following:
(i) Rate of reaction and rate constant (ii) Homogenous and Heterogeneous catalyst
(iii) Positive catalyst and inhibitor (iv) Elementary and overall reaction

Descriptive Questions

1. Enlist various factors which influence on the rate of chemical reactions and describe the effect of concentration and surface area of reactants on the reaction rate.
2. Explain in terms of collision theory how the reaction rate increases with the rise of temperature.
3. What is meant by energy of activation and activated complex? Explain with the help of potential energy diagram.

Numerical Questions

1. Decomposition of NO_2 into NO and O_2 is of second order reaction.

$$2NO_2 \longrightarrow 2NO + O_2$$

If the rate constant at certain temperature is 3.8×10^{-4} dm^3 mol^{-1} s^{-1} and the initial concentration of NO_2 is 0.38M, calculate the initial rate of the reaction.
[Ans: 5.48×10^{-5} $mol/dm^3.s$]

2. The overall rate law for the reaction

$$A + B \longrightarrow C \text{ is } R = K[A][B]$$

If in an experiment the initial concentration of A and B was found to be 0.43M and 0.78M respectively while the initial rate was $3.8 \times 10^{-3} Ms^{-1}$. Determine rate constant and mention its unit. [Ans: 1.13×10^{-2} $dm^3/mol.s$]

3. The reaction $2NO + Cl_2 \rightarrow 2NOCl$ was studied at 25°C. the following results were obtained

Experiment No.	Initial concentration (mol/dm^3)		Initial rate ($mol/dm^3.s$)
	NO	Cl_2	
1	0.1	0.1	2.52×10^{-3}
2	0.1	0.2	5.04×10^{-3}
3	0.2	0.1	10.05×10^{-3}

Illustrate the rate law and find the order of reaction. [Ans: Order of reaction = 3]

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SOLUTION AND COLLOIDS

Chapter 10

Teaching Periods	Assessment	Weightage
8	1	10

Students will be able to:

- **List** the characteristics of colloids and suspension that distinguish them from solutions.
- **Define** hydrophilic and hydrophobic molecules.
- **Explain** the nature of solutions in liquid phase giving examples of completely miscible, partially miscible and immiscible liquid-liquid solutions.
- **Explain** the effect of temperature on solubility.
- **Express** solution concentration in terms of mass percent, molality, molarity, parts per million, billion and trillion and mole fraction.
- **Define** Raoult's law with suitable examples.
- **Define** the term colligative property.
- **List** some colligative properties of liquids.
- **Describe** on a particle basis why a solution has a lower vapor pressure than the pure solvent.
- **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.
- **Explain** osmotic pressure, reverse osmosis and give their daily life applications.
- **Describe** types of colloids and their properties.

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INTRODUCTION

Let's consider a spoonful sugar is put into water, it dispersed uniformly so that we cannot see the particles of sugar. In chemistry **"Solution is a type of homogenous mixture in which individual components cannot be distinguished"**. The term solution is not restricted to the mixture of solid into liquid but broadly cover up the uniform mixing of solids liquids and gases. A solution consists of a solvent along with one or more solutes. Solvent is the medium in which solute is dissolved. Generally, the component present in larger amount is called solvent and the other which is in smaller amount is called solute. The components of solution may be more than two. For example sea water is solution of many components such as NaCl, $CaCl_2$, $MgCl_2$ etc. A solution which consists of only two components is known as binary solution. There are various reasons of preparing solution, some time we prepare them for specific reaction and some time for particular analytical or domestic purpose.

10.1 GENERAL PROPERTIES OF SOLUTION

Solution is a single phase mixture with no boundaries separating its components. Substances in a solution are physically mixed but no chemical change occurs during their mixing. Particles of solute and solvent in a solution (atoms, ions or molecules) are extremely small having a diameter of approximately less than 1 nm, this indicates that.

- Solution is a transparent mixture of its components.
- Component of solution cannot be separated by filtration.
- Light cannot be scattered though the solutions (Tyndall effect).

Whenever a solute dissolves in a solvent, there should be three types of intermolecular attractions involved, the solute-solute, solvent-solvent and solute-solvent. The basic rule in the formation of a solution is that the attraction between solute-solvent molecules becomes equal or greater than solute-solute and solvent-solvent molecules. The process of solution preparation is known as dissolution during which solute-solute interactions is broken down and solvent particles surrounds them from all sides to establish new stronger solute-solvent associations.

Generally, dissolution process is either endothermic or exothermic. This can be realized by studying two energies involve in the process. Lattice energy is the energy required to separate solute particles from solid crystal into solution and the solvation energy which released when interaction of solute and solvent particles takes place. Ions with greater charge and smaller size have high solvation energy hence their dissolution in exothermic. On the other hand many solid substances have strong particle binding in their crystal lattice. They must absorb energy from the solution and make the process endothermic. The energy difference of the above two processes is recognized as heat of solution. It is the change in enthalpy when a substance dissolves in solvent to make a solution at constant pressure.

10.1.1 Solution, Suspension and Colloids

Have you ever seen muddy water in a pond or even in your domestic water connection? This is a heterogeneous mixture of mud in water. If you fill a glass with muddy water you will observed that mud will be settled down after few minutes. Why this happens? This is due to the large size of solute particles, usually more than 1000nm. This muddy water is not a solution but we use another term suspension.

"Suspension is a cloudy, heterogeneous mixture whose dispersed particles are settled down eventually". The components of suspension may be identified as dispersed phase and dispersion medium. Another terminology use in this connection is colloid which can be placed in between solution and suspension. The particle size of colloids is neither too much large nor so small. It is in the range of 1 nm to 1000 nm. Colloids refer as the translucent heterogeneous mixture of microscopically dispersed particles into a dispersion medium which cannot be settled out.

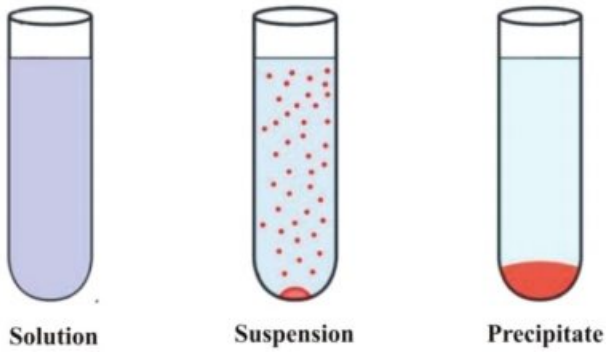

Fig 10.1: Illustration of solution, suspension & precipitates

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Table 10.1	Comparative study of true solution, suspension and colloids				
Types	**Physical Appearance**	**Particle Size**	**Visibility**	**Settling**	**Example**
True Solution	Transparent	Less than 1 nm	Invisible to nacked eye	Particles do not settle down	Glucose Solution
Colloidal Solution	Translucent	Between 1 nm to 1000nm	Visible under powerful microscope	Particles do not settle down to their own but can be made by coagulation	Milk
Suspension	Opaque	Above 1000nm	Easily visible	Particles settle down to their own	Mud in water

10.1.2 Hydrophillic and Hydrophobic Molecules

Many solutions in daily life are water based that means water is used as solvent. Did you work on acid and base solution in your chemistry laboratory? Have you ever think about the composition of salt solution, glucose solution, rain water, cola bottle etc, these all are aqueous solutions. It is a well known fact that water is a polar molecule therefore when an ionic or polar covalent substance is mixed into water; an interaction of positive and negative terminal of water molecules with the particles of dissolving substance (ions or molecules) develops which makes the molecules evenly distributed throughout the water in a homogenous pattern. Thus **"solute substances whose particles (ions or molecules) strongly associated with water are categorized into hydrophilic molecules"**. The term hydrophilic is derived from hydro mean water and phillic means to attract. Ethanol, acetic acid, amino acid, acetone etc are polar covalent molecules. They on dissolving in water form hydrogen bonding and thus form a solution.

On the other hand there are some substance which do not mix into water consist of hydrophobic molecules. These molecules are structurally non polar in nature therefore they do not have ability to attract water molecules (hydro; water and phobic; to dislike). Many organic molecules are structurally non polar when mix into water they do not attract with solvent molecules and show their hydrophobic behavior thus do not form a solution and said to be hydrophobic. For example Petrol, Benzene, Toluene etc.

10.1.3 The nature of Solution in Liquid Phase

On the basis of solids, liquids or gaseous state, there are nine types of solution. Whenever a solution of two liquids is needed to be prepared, we should have some know how about their chemical nature. Miscibility refers to the ability of two liquids to mix into each other in all proportion. Depending upon relative miscibility of two liquids we can develop three possibilities.

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(i) Completely miscible liquids:

When two liquids are mixed into each other in all proportion to form a homogenous mixture, they are said to be completely miscible.

While studying on molecular level, the intermolecular attractions of the two completely miscible liquids found to be of similar order. For example methanol and water both are polar molecules and on mixing they completely soluble into each other. The reason is that both water and methanol molecules possess same extent of hydrogen bonding in their pure liquid states as well as in mixture form.

Benzene and toluene both are non polar liquids. Referring the rule of thumb "likes dissolves likes they are categorized into completely miscible liquid pair. Again switch your mind towards their molecular attraction; the molecules of benzene and toluene in their pure liquid states as well as in mixture form interact through London dispersion forces.

(ii) Partially Miscible Liquids

Some liquids dissolve into each other to a limited extent up to a certain concentration. When such liquids mix into each other, they form two separate phases. Each phase is the saturated solution of the two liquids in-which one serves as solute and other is solvent.

For example when phenol is mixed into water at 25°C, a two phase solution is formed in which upper layer represents 5% phenol in 95% water while lower layer consists of 70% phenol in 30% water.

(iii) Completely Immiscible Liquids

When two liquids do not mix into each other and do not form solution are called immiscible liquids. For example water is polar liquid and benzene is non polar. These two liquid are totally immiscible in all proportion and form two separate layers on mixing.

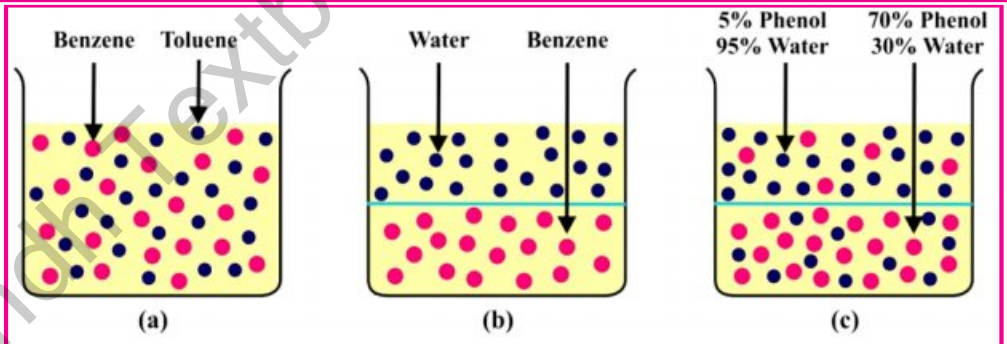

Fig 10.2: Illustration of (a) immiscible liquids (b) miscible liquids (c) Partially miscible liquids

Self Assessment

If you have water in one container and petrol in another container, which solvent is suitable for dissolving (i) grease (ii) common salt? Explain why?

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10.1.4 Effect of Temperature and Pressure on solubility of solution

Saturated solution is generally prepared by mixing maximum amount of solute that should be dissolved in fixed amount of solvent. **"Solubility is the amount of solute (in grams) that can be dissolved in a fixed quantity (volume) of a particular solvent to prepare a saturated solution at a specific temperature"**. Solubility of a substance is fundamentally depends on chemical nature of solute and solvent particles. However, it notably changes with temperature and pressure.

Effect of Temperature:

Solubility of many solids in liquid increases with the rise of temperature. This is attributed with the fact that rise of temperature increases the kinetic energy and randomness of particles and create more spaces among solvent molecules in which solid solute particles accommodate. However, some solids show a decrease trend in solubility with the rise of temperature. This dual behavior in the solubility of solids with the temperature can be predicted by whether heat absorb or evolve in the formation of solution. Many solids dissolve into solvent with the absorption of heat, solubility of these substances increases with the rise in temperature.

The dissolution of some solids ($AlCl_3$, Na_2SO_4 etc) and many liquids as well as gases in liquid solvent is carried out by exothermic process. Solubility of these substances decreases with the rise of temperature.

Effect of Pressure:

Solubility of solids and liquids in a liquid solvent is not appreciably change by altering the pressure. However the solubility of gases into liquid is significantly affected by pressure. In theoretical aspect the dissolution of gases into liquid is an equilibrium process. This means that a simultaneous entrance and exist of gas molecules from solution occur. Thus an increases in pressure increases the number of gas molecule so the rate of entrance of gas molecules into solution becomes higher than its exit. Conclusively solubility of gas into liquid increases with the rise of pressure.

Do You Know?

Carbonated water is a solution of CO_2 in water under high pressure. When cork of the bottle is opened, pressure reduces to atmospheric pressure due to which solubility of CO_2 in water decreases which can be observed in the form of bubbles on the surface.

10.2 CONCENTRATION UNITS

The term concentration expresses the amount of solute dissolved in fixed amount of solvent or solution. While performing chemistry practical, it is usually necessary to know what amount of solute is present in the given solution. There are several ways to express the concentration of solution each has its own significance for particular work.

10.2.1 Percentage Composition

This unit is frequently used in chemistry. It may be studied in term of w/w, w/v, v/w and v/v. The mass percent (w/w %) may be define as the mass of solute in gram per 100 gram of solution mathematically it may written as

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$$\text{Mass percent} = \left(\frac{\text{mass of solute}}{\text{mass of solution}}\right) \times 100$$

For example a 12% (w/w) aqueous sugar solution means 12g of sugar dissolves in 100g solution or 88g of water.

10.2.2 Molarity (M)

It is the number of moles of solute dissolved per dm^3 of solution.

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{volume of solution in } dm^3}$$

For example the molarity of 20g NaOH in $1dm^3$ aqueous solution is 0.5M.
Molarity is temperature dependent because the volume of solution decreases or increase with temperature.

10.2.3 Molality (m)

It is the number of moles of solute per kilogram of solvent.

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kilogram of solvent}}$$

For example the molality of 18g glucose in 1kg water is 0.1 mol/kg.
Molality does not change with temperature because masses remain unchanged by heating or cooling.

10.2.4 Mole Fraction (X)

This unit is used when two or more components are present in the solution. It is the ratio of number of moles of one component to that of all components of solution.

$$X_A = \frac{\text{moles of substance A}}{\text{total moles of solution}} \qquad X_B = \frac{\text{moles of substance B}}{\text{total moles of solution}}$$

The sum of mole fractions of all the components of a solution is always a unity

$$X_A + X_B = 1$$

For example if a solution is made up of 1 mole methanol in 4 moles water, the mole fraction of methanol will be 0.2 and water will be 0.8. Now if we add the mole fraction of both methanol and water we get unity.

$$X_{methanol} + X_{water} = 0.2 + 0.8 = 1$$

10.2.5 Parts Per million, Billion and Trillion

These units are used in analytical or biochemical research works when solute is present in very small quantity.

(i) Parts per million (ppm) is the number of parts or amount (mass or volume) of solute per million parts (10^6) of the amount (mass or volume) of solution.

$$\text{ppm} = \frac{\text{Amount of solute (mass or volume)}}{\text{Amount of solution (mass or volume)}} \times 10^6$$

For example when 1 mg of a solid present in $1dm^3$ of solution the concentration is said to be 1 parts per million (ppm).

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(ii) Parts per billion (ppb) is the number of parts or amount (mass or volume) of solute per billion parts (10^9) of the amount (mass or volume) of solution.

$$\text{ppb} = \frac{\text{Amount of solute (mass or volume)}}{\text{Amount of solution (mass or volume)}} \times 10^9$$

For example if 1 milligram of a substance present in 1000 dm^3 of solution, its concentration is marked as 1 ppb.

(iii) Parts per trillion (ppt) is the number of parts or amount (mass or volume) of solute per trillion parts (10^{12}) of the amount (mass or volume) of solution.

$$\text{ppt} = \frac{\text{Amount of solute (mass or volume)}}{\text{Amount of solution (mass or volume)}} \times 10^{12}$$

For example if 1 microgram of a substance present in 1000 dm^3 of solution.

Example 10.1

6.24g caustic soda (NaOH) is dissolved in water and the solution is made to 100cm^3 in a volumetric flask. Determine the concentration of this solution in term of molarity.

Solution:

$$\text{Molarity of Solution} = \frac{\text{Moles of NaOH}}{\text{Volume of Solution } (dm^3)}$$

$$\text{Molarity of Solution} = \frac{6.24 / 40}{100 / 1000}$$

$$\text{Molarity of Solution} = 1.56 \text{ mol/dm}^3$$

Example 10.2

An aqueous solution of 1.2 molality is prepared by dissolving some amount of oxalic acid into 475g water. Determine the mass of oxalic acid in the solution. (molecular mass of oxalic acid is 126 g/mol)

Solution:

$$\text{Molality} = \frac{\text{moles of solute (oxalic acid)}}{\text{mass of solvent in kg (water)}}$$

$$1.2 = \frac{\text{mass of oxalic acid}}{126 \times 0.475}$$

$$\text{mass of oxalic acid} = 1.2 \times 126 \times 0.475 = 71.82\text{g}$$

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Example 10.3

45g glucose dissolves in 72g water to make a solution. Calculate the mole fraction of glucose and water in the solution.

Solution:

First we determine the number of moles of glucose and water from their given masses

$$\text{Moles of glucose} = \frac{45}{180} = 0.25$$

$$\text{Moles of water} = \frac{72}{18} = 4$$

Now

$$\text{Mole fraction of glucose} = X_2 = \frac{n_2}{n_1 + n_2} = \frac{0.25}{4 + 0.25} = 0.0588$$

$$\text{Mole fraction of glucose} = X_1 = \frac{n_1}{n_1 + n_2} = \frac{4}{4 + 0.25} = 0.941$$

Example 10.4

Calculate the molality of a 12% urea solution (molar mass of urea is 60g/mol)

Solution:

(i) 12% urea solution represents 12g urea in 100g solution thus the mass of water is calculated as

Mass of water in gram = 100 – 12 = 88g

$$\text{Mass of water in kg} = \frac{88}{1000} = 0.088\text{kg}$$

$$\text{(ii) No. of moles of urea} = \frac{\text{mass of urea}}{\text{molar mass of urea}}$$

$$\text{No. of moles of urea} = \frac{12}{60} = 0.2 \text{ moles}$$

$$\text{(iii) Molality of urea} = \frac{\text{moles of urea}}{\text{mass of water (kg)}}$$

$$\text{Molality of urea} = \frac{0.2}{0.088} = 2.27 \text{ mol/kg}$$

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Example 10.5

In the analysis of water sample, it was reported that 1g of water contains 6.34×10^{-3} mg magnesium ions. Calculate the concentration of magnesium ions in ppm.

Solution:

We know that

$$ppm = \frac{\text{amount of solute}}{\text{amount of solvent}} \times 10^6$$

$$ppm = \frac{6.34 \times 10^{-3} mg}{1g} \times 10^6$$

$$ppm = \frac{6.34 \times 10^{-3} mg}{10^3 mg} \times 10^6 = 6.34$$

Thus concentration of magnesium ions in water = 6.34ppm

10.3 RAOULT'S LAW

It has been learnt in chapter-5 that when a liquid is put in a close vessel it maintains equilibrium with its vapours and the pressure of vapours above the surface of a liquid at equilibrium is known as vapours pressure. If now we prepare a solution of volatile solvent with non volatile solute and correlate the vapour pressure of pure solvent with that of solution we find that the vapours pressure of solution is lowered than that of pure solvent. Indeed the escaping of pure volatile solvent is much faster since all surface molecules belongs to solvent molecules but in a solution a part of surface is also occupied by non volatile solute particles. This decreases the number of solvent molecules on the surface and reduces the escaping tendency of the solvent molecules which results in lowering of vapours pressure of solution as compared to pure solvent.

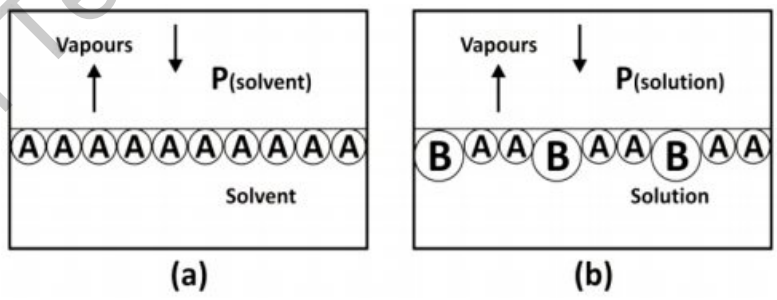

Fig 10.3: Vapours pressure of (a) pure solvent (b) solution

A French chemist F.M. Raout studied these phenomena of lowering of vapours pressure by the effect of solute particles in a solution and formulated a law (1887) known as

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Raoult law. For a non volatile solute system it states as **"the vapours pressure of a solution which is a made up of non volatile solute with volatile solvent is directly proportion to the mole fraction of solvent"**.

$P \propto X_1$

$P = P^\circ X_1$ - - - - - - - - - - - - - - (i)

Here **P** specifies the vapours pressure of solution, **P°** represents vapours pressure of solvent and $\mathbf{X_1}$ is the mole fraction of solvent.

Since in a binary solution $X_1 + X_2 = 1$, hence $X_1 = 1 - X_2$

Putting the value of X_1 in eq. (i) we get

$P = P^\circ (1 - X_2)$

$P = P^\circ - P^\circ X_2$

$P^\circ - P = P^\circ X_2$

$\Delta P = P^\circ X_2$ - - - - - - - - - - - - - - (ii)

Equation (ii) represents the second form of Raoult's law which states as the lowering of vapour pressure is directly proportional to the mole fraction of solute.

$$\frac{\Delta P}{P^\circ} = X_2 \text{ - - - - - - - - - - - - - - (iii)}$$

Here $\frac{\Delta P}{P^\circ}$ is referred as relative lowering in vapours pressure.

Eq. (iii) represents third form of Raoult law which states as the relative lowering of vapours pressure is equal to the mole fraction of solute.

Raoult's law is also applicable on a binary solution made up of two miscible volalite liquids having similar order of polarity and molecular size. The partial pressure of each liquid in the mixture is equal to the vapours pressure of pure component multiplied by its mole fraction and may be written as

$$P_A = P^\circ_A X_A \quad \text{and} \quad P_B = P^\circ_B X_B$$

Thus the total pressure of solution is equal to the sum of partial pressure of both liquid in the mixture.

$P_t = P^\circ_A X_A + P^\circ_B X_B$ - - - - - - - - - - - - - - (iv)

Self Assessment

(i) Why is the vapours pressure of an aqueous solution is lowered than pure water?
(ii) Under what conditions does Rault law is applicable?

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Example 10.6

Glucose is a non volatile solute in water. A glucose solution contains 0.15 moles glucose and 5.8 moles water at 20°C. Determine the lowering in the vapour pressure if the vapour pressure of pure water at 20°C is 17.5 torr. (Assume solution is an ideal)

Solution:

First we determine the mole fraction of glucose.

$$X_2 = \frac{n_2}{n_1 + n_2}$$

$$X_2 = \frac{0.15}{5.8 + 0.15} = 0.0252$$

Now applying second form of Raoult law

$\Delta P = P^\circ X_2$

$\Delta P = 17.5 \times 0.0252$

$\Delta P = 0.441$ torr

Example 10.7

The vapour pressure of a pure liquid A is 37mm Hg at 27°C. It is mixed into another liquid B to make a solution. The vapour pressure of A in the solution is found to be 33mm Hg. Calculate the mole fraction of A (Assume it obeys Raoult's law)

Solution:

$P_A^\circ = 37$mm Hg

$P_A = 33$mm Hg

$X_A = ?$

Applying the relationship of Rauolt law

$P_A = P_A^\circ X_A$

$$X_A = \frac{P_A}{P_A^\circ} = \frac{33}{37} = 0.89$$

Ideal and Non Ideal Solution

Binary solutions of two miscible liquids are categorized into ideal and non ideal solutions. The solution which perfectly obey the Raoult's law or obey the relationship mentioned in equation (iv) are referred as ideal solutions, however many solutions do not satisfy Raoult law due to the difference in the attractive forces and molecular size of solute and solvent particles. These solutions are formed by the change in volume and enthalpy and known as non ideal solution.

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There are four distinct characteristic of an ideal solution.

(i) It obeys Raoult law at all temperature and concentration.

(ii) The molecular interaction of liquid A-A, B-B and A-B remains almost same.

(iii) No heat absorbs or evolve in the formation of ideal solution ($\Delta H = 0$).

(iv) No change in the volume takes place in the formation of ideal solution ($\Delta V = 0$).

Example of liquid pair which form ideal solution on mixing are methanol ethanol, benzene-toluene etc.

Self Assessment

(i) What does an ideal solution means?

(i) Which of the mixture containing the following pairs Obey's Rault law.

- Methanol and Ethanol
- Toluene and xylene
- Methnol and water

10.4 COLLIGATIVE PROPERTIES OF SOLUTION

Certain physical properties of solutions depends upon the number of solute particles rather than its chemical nature, these are referred as colligative properties. (Colligative means collective). Examples are lowering of vapours pressure, elevation of boiling point, depression of freezing point and osmotic pressure. We specifically focus on the colligative properties of solutions of non volalite and non electrolyte solutes.

10.4.1 Lowering of Vapours Pressure

In previous section, we have studied about how the vapours pressure of a solution containing a non volatile and non electrolyte solute is lowered as compared to its pure solvent. Recall the second statement of Raoult's law which tells that the lowering in vapours pressure of solution is directly proportional to the mole fraction of solute.

$\Delta P = P^\circ X_2$

Thus the greater the number of non volalite solute particle, the more lowering in vapours pressure (ΔP) of solution.

10.4.2 Elevation of Boiling Point and Depression of freezing point

The temperature at which vapours pressure of a liquid becomes equal to atmospheric pressure (1 atm) is known as normal boiling point. If a non volatile and non electrolyte solute (solid) is dissolved into volatile solvent, its vapours pressure found to be lowered than 1 atmosphere. Since liquid boil only when its vapours pressure becomes equal to atmospheric pressure, some more heat is needed to the solution to reach its vapours pressure 1 atmosphere. This concluded that the boiling point of solution is greater than the boiling of pure solvent. **"Boiling point of a solution of non volatile solute is higher than pure solvent, this is a colligative property and known as elevation of boiling point (ΔT_b)".**

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To understand how is the elevation in boiling point of solution occur by adding non volatile solute let us consider graph of vapours pressure v/s temperature of pure solvent (curve AB) and solution (curve CD) in fig 10.5. Both curves meet the line of atmospheric pressure at point A and C respectively. It is specified from the graph that the boiling point of solution (Tb) is higher than pure solvent (Tb°) for equalization of vapours pressure to the atmospheric level.

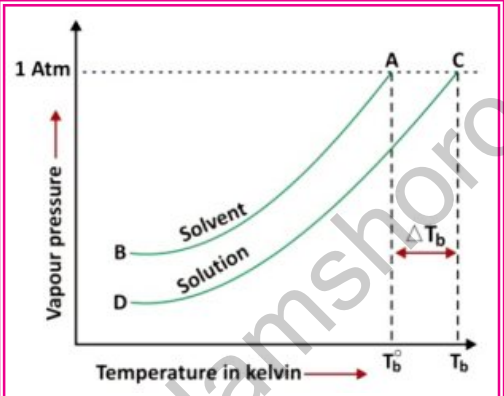

Fig. 10.4: Boiling point elevation of solution

Depression of freezing point

We know that kinetic energy of liquid molecules decreases on cooling and molecules approaches one another more closely and liquid finally turns into solid. **"Freezing point of a liquid is the temperature at which liquid and solid phases co exists in equilibrium with the same vapours pressure"**.

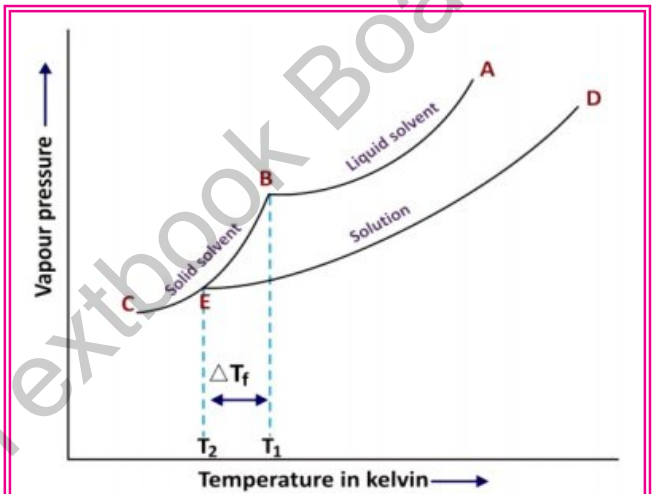

Fig. 10.5: Freezing point depression of solution

The presence of a non volatile solute lowers the freezing point of solvent. These phenomena can be explained in term of vapours pressure. Since at freezing point the vapours pressure of both liquid and solid phases must be same, the addition of solute causes a fall in vapours pressure. Thus in order to re-establish the equilibrium of two phases, temperature of solution is consequently lowered below the freezing point of pure solvent.

Do You Know?

While boiling an egg we often mix a small amount of table salt into water. This elevated the boiling point of solution and thus more heat is provided to the egg for its quick preparation.

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10.4.3 Osmotic Pressure

Surface of certain materials permit water and other smaller size particles to pass through but do not allow large solute particles. These serves as semi permeable membrane for example cellophane, animal bladder etc. Although the passage of solvent particles takes place in both directions of semi permeable membrane but their movement is faster from dilute solution to concentrated solution. This spontaneous process is commonly known as osmosis. It is important to note that the process of osmosis remains continue until the concentration both solution become same.

Do You Know?

When two solutions have equal osmotic pressure across a semi permeable membrane at the same temperature is referred as isotonic solution. Isotonic saline solution keep cell from shrinking and swelling in our body.

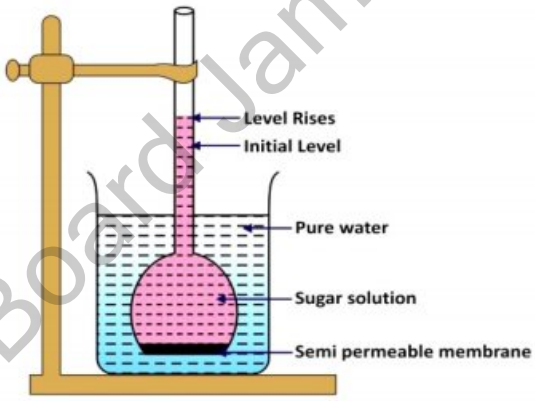

Fig. 10.6 Osmotic pressure

To demonstrate the process of osmosis, let us consider a sugar solution is filled into an inverted thistle funnel whose mouth is covered with semi permeable membrane. The funnel is dipped into a beaker of pure water. As the time going on, water from the beaker migrate to the sugar solution through semi permeable membrane and hence rises up the level of solution in the funnel tube until the descending pressure exerted by the solution stops the passage of solvent particles from beaker to funnel, this is known as osmotic pressure and define as **"the hydrostatic pressure exerted by the solution which stops the process of osmosis"**.

Do You Know?

To relief sore throat, we are often advised salt water gargling by doctors. Salt water contains high conc. of salt than fluid of the throat cells. Therefore on gargling, the excess fluid passes out through osmosis and reduces the irritation or discomfort.

Osmotic pressure is a colligative property since it depends upon the number of solute particles in the solution. It is represented by π and measured in atmosphere.

Daily life examples of Osmosis

(i) Due to bacterial infection or certain other reasons, swelling and bursting of RBCs takes place in blood stream. This biochemical process is known as heamolysis. Literally, heamolysis is endo osmosis during which water pass through semi permeable membrane of RBCs and destroy them.

(ii) Fresh water fish absorb water through their semi permeable skin because their body fluid is much saltier than the water in which they swim.

(iii) Although plant absorbs water through their entire surface including root, leaves and stem, however it mainly occur by root hairs through the process of osmosis.

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(iv) Jam is prepared by adding high amount of sugar, while pickles are prepared by adding sufficient salt, oils, vinegar etc. These additives make the solution of Jam and pickles highly concentrated. Therefore water pass out from the semi permeable membrane of bacteria and other microorganism through the process of osmosis causing bacteria killing and avoid the chances of spoilage.

(v) Food after digestion in various region of alimentary canal change into chyme which then absorb into body tissues through the semi permeable wall of small intestine.

10.5 COLLOIDS

Milk is a homogenous mixture of tiny particles of casein and some other ingredients in aqueous phase. These particles neither settle down like in suspension nor serves as solute of a solution. In chemistry they are known as colloidal dispersion or simply colloids. **"Colloids is a mixture in which one substance consisting of microscopically dispersed insoluble particles in suspended"** The size of colloidal particles is smaller than floating particles of suspension but larger than solute particles of solution. The size range of colloidal particle is from 1 to 1000nm. They cannot be seen by necked eye, never settle down in the container. However unlike solution they have ability to scatter light and this property is known as Tyndall effect.

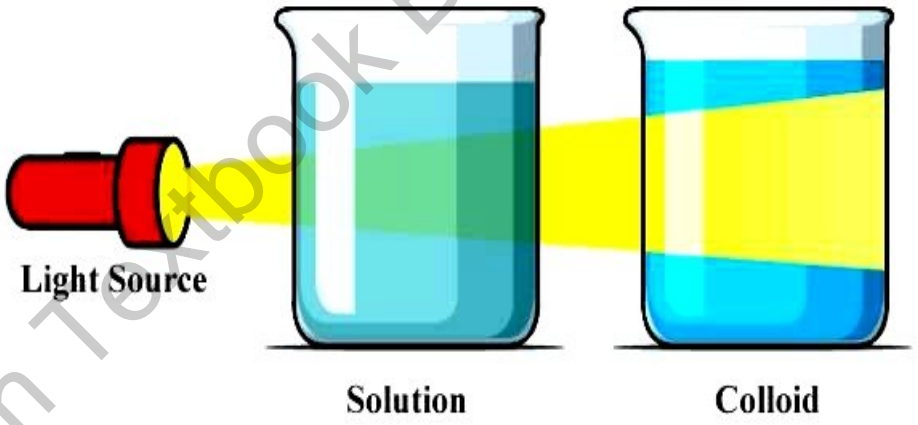

Fig. 10.7: Tyndall effect in colloidal solution

All those colloids in which water serves as dispersion medium are either hydrophilic or hydrophobic in nature. A hydrophilic colloid is that in which dispersed particles are strongly attracted by dispersion medium where as hydrophobic colloids shows lack of association of above type.

Colloids have a significant role in chemical industries, biochemical processes, agriculture and even in our daily life. Many of our food stuff are colloidal solution.

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10.5.1 Types of Colloids

Colloids are classified into following eight types depending upon the physical state of dispersed phase and dispersion medium.

Dispersion Medium	Dispersed Material	Type of Colloid	Suitable Examples
Gas	Liquid	Aerosol	Fog, Spray
Gas	Solid	Aerosol	Smoke
Liquid	Gas	Foam	Shaving Cream
Liquid	Liquid	Emulsion	Milk
Liquid	Solid	Sol	Paint
Solid	Gas	Solid Foam	Foam Rubber
Solid	Liquid	Gel	Jelly
Solid	Solid	Solid Sol	Ruby Glass

10.5.2 Properties of Colloids

(i) Colloidal solutions are heterogeneous in nature since they consist of two phases, the dispersed particles and dispersion medium. However they appear like a homogenous solution because of invisibility of suspended particles.

(ii) Most of the colloidal solution exists in cloudy or translucent appearance.

(iii) Colloidal particles can be seen under ultra microscope. The movement of colloidal particles is continuous, rapid and random like (Brownian motion). The reason of this type of motion is the unequal collision of colloidal particles with the particles of dispersion medium.

(iv) Colloidal particles can pass through filter paper but semi permeable material block their movement across the membrane.

(v) When a beam of visible light passes through a colloidal solution, it scattered by the colloidal particles and hence the whole path of the light beam becomes illuminates. This phenomenon is known as Tyndall effect.

(vi) Coagulation is the process of precipitation of colloidal particles which can be accomplished by heating or by adding electrolyte. On heating, colloidal particles strike to each other many times with high energy and aggregate into each other to form large particle and thus settle out.

(vii) Dispersed particles of colloidal solution possesses either positive or negative charge. However the charge of all dispersed particles remain the same that is why they repel each other and keep them self suspended in the dispersion medium instead of combining of form a large molecule. Electrophoresis the movement of colloidal particles towards particular electrode in an applied electric field

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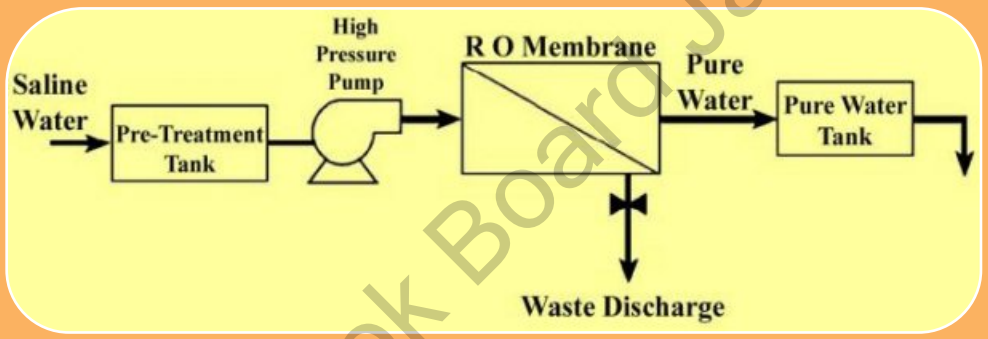
Society, Technology and Science

Concept of reverse osmosis in R.O plant

Reverse osmosis is a well known water purification technique in which sediments and contaminants of water are removed through semi permeable membrane and make the water drinkable. Reverse osmosis works on the basis of passage of water molecules across a semi permeable membrane from impure water to pure water by applying a high pressure which overcomes the osmotic pressure. In other words flow of water molecules takes places in reverse direction as carried out by natural osmosis. About 95 to 99 percent of the dissolved contaminant like salts, metal ions, protozoa etc are removed if water is processed by reverse osmosis.



Activity

The purpose of this activity is to enable you to prepare a solution of known strength (say one molar concentration of NaCl).

In order to prepare one molar solution of sodium chloride, you need to dissolve one mole of NaCl in one liter solution. Since the molar mass of NaCl is 58.5g/mol. First of all you need to weigh one mole of NaCl on a digital balance of your kitchen by putting on salt bit by bit till the stage the digital balance exactly indicates its mass equal to 58.5g. Now take a volumetric flask filled with some water and start dissolving the salt in it. Then gently pour water to make the solution up to 1 liter mark. One molar NaCl solution is ready at your home.

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SUMMARY with Key Terms

- **Solution** is a homogenous mixture of two or more substances. The component present in the larger amount is called solvent where as the component which is in smaller amount is solute.
- **Dissolution** is the process of formation of a solution. This process is accompanied by heat absorption or evolution. This heat is called as heat of solution.
- **Hydrophillic molecules** are those which evenly distributed though out the water and form a homogenous mixture. This is due to their ability to attract with positive and negative terminals of water molecules.
- **Hydrophobic molecules** do not mix into water and do not form aqueous solution since they are non polar in nature.
- **Miscibility** is the ability of a liquid to mix into another liquid.
- **Concentration** is the amount of solute dissolved in a fixed amount of solvent or solution. It expresses in term of percentage composition, molarity, molality, mole fraction etc.
- **Raoult's Law** states as the vapours pressure of solution of non volatile solute is directly proportional to the mole fraction of solvent.
- **Ideal solution** is that which perfectly obey Raoult's law at all temperature and concentration. In the formation of Ideal solution no heat absorbs or evolves and no change in the volume takes place.
- **Colligative properties** are certain physical properties of solution which depends upon the number of solute particles. These are lowering vapours pressure, elevation of boiling point, depression of freezing point and osmotic pressure.
- **Molal elevation of boiling point (Kb)** is a constant and defines as the elevation of boiling point of one molal solution.
- **Osmosis** is the spontaneous process of flow of solvent particles from higher concentration to lower concentration through a semi permeable membrane.
- **Osmotic pressure** is the hydrostatic pressure exerted by solution which stops the further passage of solvent particles across the semi permeable membrane.
- **Reverse Osmosis** is a water purification process through a membrane of tiny pores. It involves the flow of water molecules across the semi permeable membrane in the opposite direction under high pressure. The purpose is to filterate out salts and other large size particles from drinking water.
- **Colloids solution** is a translucent solution of the particles of 1 nm to 1000 nm size. Its particles can only be seen by powerful microscope however coagulate on heating or adding an electrolyte.
- **Suspension** is an opaque, heterogeneous mixture of the particles of above 1000 nm size which settle down to their own.

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EXERCISE

Multiple Choice Questions

1. Choose the correct answer

(i) Only one pair of liquid in the following set does not obey Roault law, identify it:

(a) Methanol and Ethanol (b) Benzene and toluene
(c) n-Hexane and n-heptane (d) Ethanol and Acetone

(ii) Identify the incorrect statement about colloidal solution:

(a) It showsTyndall effect (b) Its particles movement is Brownian type
(c) Its particle size is less than 1 nm (d) Its physical appearance is translucent

(iii) Effect of pressure change play significant role in the solubility of:

(a) Solid into liquid (b) Liquid into liquid
(c) Gas into liquid (d) All of them

(iv) Which is not a colligative property:

(a) Lowering in vapours pressure (b) Elevation in boiling point
(c) Depression in freezing point (d) Atmospheric pressure

(v) According to Raoult law the relative lowering of vapour pressure is equal to:

(a) Mole fraction of solvent (b) Mole fraction of solute
(c) Molality (d) Molarity

(vi) The sum of mole fractions of components of a solution is equal to:

(a) 0.0 (b) 1.0
(c) 10 (d) 100

(vii) How many moles of NaOH are present in a $2dm^3$ of 1 molar aqueous solution of it.

(a) 0.5 mole (b) 1 mole
(c) 1.5 mole (d) 2 mole

(viii) A colloidal solution of liquid into liquid is known as:

(a) Gel (b) Foam
(c) Sol (d) Emulsion

(ix) An example of completely immiscible liquid pair is:

(a) Benzene to toluene (b) Water and phenol
(c) Water and Benzene (d) Water and methanol

(x) A 15% W/W KOH solution can be prepared by mixing 15g KOH in:

(a) 15g water (b) 85g water
(c) 100g water (d) 115g water

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Short Questions

1. Name various units of concentration and explain mole fraction.
2. Define Molarity and molality. Which of these depends on temperature?
3. Explain on particles bases how the vapours pressure of solution is lowered by adding non volatile solute.
4. What are miscible and immiscible liquids? Why n-hexane (petrol) is immiscible in water?
5. Solubility of oxygen in water increases with pressure but solubility of glucose in water has negligible effect of pressure why?

Descriptive Questions

1. State Raoult's law and derive its mathematical expression.
2. What does an Ideal solution means? Give four characteristics to distinguish between ideal and non ideal solution.
3. Define osmosis and osmotic pressure. Give four daily life examples of osmosis.
4. What are colligative properties? Why does the boiling point of a liquid get raised when a non volatile solute is added?
5. Differentiate among true solution, colloidal solution and suspension on the bases of.
   (i) Particle size (ii) Visibility

Numerical Questions

1. Automotive antifreeze is a 60% (w/w) aqueous solution of ethylene glycol ($C_2H_6O_2$). Determine (a) molality of solution (b) mole fraction of ethylene glycol in the solution.
   [Ans: molality = 24.19mol/kg, X = 0.3]
2. A solution is prepared by mixing 46g ethanol (C_2H_5OH) and 180g water. Calculate the mole fraction of both components. [Ans: $X_2 = 0.090$, $X_1 = 0.909$]

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THERMOCHEMISTRY

Chapter 11

Teaching Periods	Assessment	Weightage
8	1	9

Students will be able to:

- **Define** thermodynamics.
- **Define** the terms system, surrounding, boundary, state of system, state function, internal energy, enthalpy, entropy, heat of formation, standard heat of formation.
- **Classify** reactions as exothermic and endotermic.
- **Relate** change in enthalpy to the heat of reaction and heat of combustion of a reaction.
- **Relate** change in internal energy of a system with thermal energy at constant volume and constant pressure.
- **Explain** Hess's law with examples.
- **Apply** Hess's law to construct simple energy cycles.
- **Explain** reaction pathway diagram in terms of enthalpy changes of the reaction.

INTRODUCTION

Energy changes are the most important feature of a chemical process. When gasoline is ignited with air in a car engine, a certain amount of energy is released which some works in moving the piston due to which the wheels of the car rotate. Similarly, food can provide us with energy as it is burned up with oxygen in every cell of our body.

Heat and temperature are two different terms. Temperature describes the random movement of particles of a substance where as heat is associated with transfer of energy between two bodies with a temperature change. Chemical reactions are generally carried out with the transfer of heat to or from environment. **"The study of energy transference as heat during a chemical process is known as thermochemistry"**.

11.1 THERMODYNAMICS

Thermodynamics is a Greek word, its first part 'Thermo' represents heat and the second part 'dynamic' which epitomizes flow or movement. **"Thermodynamics is an essential branch of science which deals with the study of inter transformation of heat, work, and other forms of energies"**. Thermodynamics applies to a variety of science such as physics, chemistry, engineering, etc and plays an imperative role in our daily life.

Thermodynamics is a macroscopic science and concerns with the initial and final states of a physical or chemical process but does not tell anything about the molecular constitution of matter. Hence, it helps to predict whether the thermochemical process can occur at particular conditions. However, it is incapable of assessing the rate of reaction.

11.1.1 Thermodynamics Terms

System:

A thermodynamic system is a quantity of matter of fixed identity, around which we can draw a boundary. **"It is a distinct part of our universe which is under particular experimental debate and separated from surrounding by an imaginary or real surface and can change its shape or size is called a system"**. It may be some water contained in a

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beaker, some gas enclosed in a cylinder, or some solution filled in a calorimeter or the whole of the universe. All systems contain a certain quantity of matter and are characterized by particular macroscopic properties.

Surroundings:

Everything outside the arbitrarily selected boundaries of the system that affects the system or is affected by it is called surrounding. It is referred to as the remaining part of the universe other than a system from which energy or matter can be exchanged with the system. The system and surrounding together constitute the thermodynamic universe of that specific process.

Boundary:

It is a physical (real) or conceptual (imaginary) closed surface that separates a system from its surroundings.

For example if a reaction between zinc dust and dilute hydrochloric acid is carried out in a container.

- The contents of the container, (zinc and HCl) constitute the system because they are characterized by specific factors, like mass, volume, temperature, etc.
- The entire remaining part of the universe including the wall and empty part of the container specifies its surrounding.
- The surface of the reacting material which separates the system from its surrounding is said to be a physical boundary.

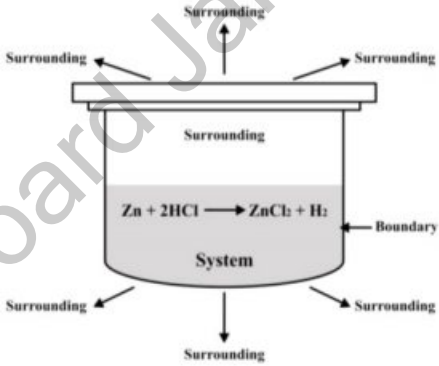

Fig 11.1: System, Surrounding & Boundary of Thermodynamic System

Thermodynamic systems are categorized into three main types on the basis of their ability to allow an interchange of mass and energy into environment thorugh their boundires.

Open System:

All such thermodynamic systems which communicate with the surrounding in term of both mass transfer and energy transfer are known as an open systems. The boundary of this type of system is open and non-insulated.

A boiling tea kettle is an open system because it transfers heat and matter (steam) to the surrounding.

Closed System:

All such thermodynamic systems which do not allow the exchange of mass but permit energy to be transferred with the environment are known as closed system. The boundary of a closed system is sealed but not insulated hence it is impermeable to mass only.

A pressure cooker is a good approximation to a close system where only heat transfers (except a little steam escapes through the top valved to prevent explosion).

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Think of any other close systems around you!

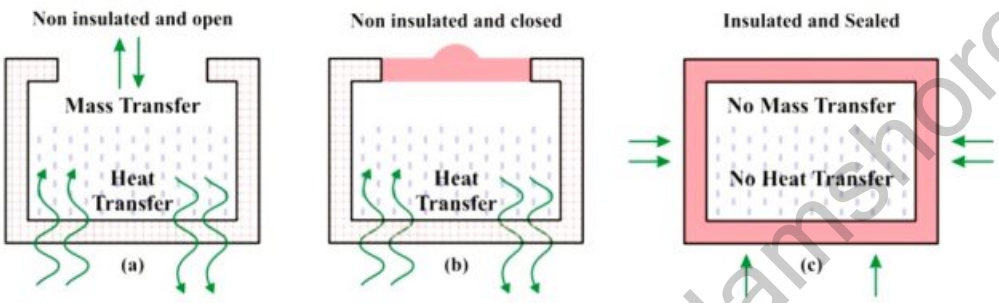

Fig 11.2: Three types of thermodynamic systems (a) open system (b) closed system (c) isolated system

Isolated System:

All such thermodynamic systems which neither exchange matter nor energy with the surrounding and hence totally independent of their surrounding are known as an isolated systems. The boundary of an isolated system is sealed and insulated.

A perfect isolated system does not exist as energy interaction in the form of heat radiation will always occur. However, some conceptually true isolated systems are thermo flask and insulated drink cooler.

Macroscopic Properties:

The description of a thermodynamic system is associated with some macroscopic quantities. These quantities can be measured if the system has large number of particles, thus macroscopic properties refers to the system having bulk amount. These are further classified into extensive and intensive properties depending upon whether they are proportional to the size of the system or not.

Entropy (S):

It is a measure of the disorder of the system. For example the arrangement of particles are more disordered in liquid and gases than solids. It is directly proportional to temperature.

State of System:

A thermodynamic system is said to be in a certain state if some macroscopic properties such as temperature pressure, volume, and moles are known. With the change of one or more of these macroscopic properties, the system changes its state.

Do You Know?

Intensive properties are those whose values are not dependent on quantity of matter in the given system. For example Pressure, density, Refractive index, surface tension, Melting point etc. Extensive Properties are those whose values for the entire system depend on the quantity of matter. For example Mass, Volume, Energy, Enthalpy, Moles etc.

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The description of a system before the change occur is known as an initial state whereas it is said to be a final state when the change has occurred. The change in any macroscopic properties of the system is determined by taking the difference of their values at the final and initial state.

For example in a chemical reaction, the enthalpy of reactant is represented by H_1 (initial state), and the enthalpy of product is shown by H_2 (final state) hence ($\Delta H° = H_2 - H_1$) is considered as the change in enthalpy in this chemical process.

State Function:

A state function is thermodynamic parameter which is dependent on initial and final state of the system and is independent of how the change is occurred. Examples of state function are internal energy, enthalpy, temperature, volume etc.

Enthalpy of a System:

Heat transfer in almost all physical and chemical process happens at constant volume. In the laboratory, for example, the reaction is usually carried out in open test tube, beakers or flask etc and hence the heat flow into or out of the reaction generally takes place under the condition of the constant pressure of air (approximately 1 atmosphere). In thios situation heat associated with the system may utilize both in altering the internal energy as well as performing work which may be seen by changing the volume of the reaction mixture in the reaction container.

To quantify the total heat contents of a system, chemists use a quantity named enthalpy (H). It defines as **"The sum of internal energy and algebraic product of its pressure and volume".**

$H = E + PV$ ---------- (i)

Equation (i) specify that enthalpy of a system depends on the quantity of internal energy, pressure and volume. Since P, V and E are all state functions, we must say that enthalpy is also a state function.

Enthalpy change (ΔH) of a reaction is measured in Calorie (metric unit system) as well as Joule (S. I unit system). The interrelation between Joule and calorie is given as

1 Cal = 4.18 Joules

Experience shows that in many chemical reaction amounts of heat evolves or absorbs in thousands of joules per mol. Hence for convenient it is measured in KJ/mol.

Self Assessment

(i) What is meant by enthalpy of system? Mention its units.
(ii) Which of the following are not classified into state function.
Work (W), Enthalpy change (ΔH), Volume change (ΔV), Internal energy change (ΔE).

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11.2 THERMOCHEMICAL REACTIONS

The progress of a chemical reaction i.e. the conversion of reactants into products involves the breaking of existing bonds of reactant particles for which energy has to be supplied and the formation of new bonds in which energy is released. Indeed, different bonds have different energy requirements for their breaking and re-forming thus to decide whether a chemical reaction takes place with the absorption or evolution of heat, we must know the energy difference of reactants and products. Since chemical reactions are usually taking place at constant pressure and the enthalpy of a system is stored in the chemical bond, the energy change in the formation of products from reactants is represented by ΔH.

Do You Know?

Gas welding is a combustion reaction between acetylene and oxygen. When the two gases contact to each other in a hand-held torch a relatively hot flame is produced having a temperature of 3000°C.

11.2.1 Exothermic Reactions

Exothermic reactions (Exo; out) are those in which heat is given out making the surrounding warmer. In the course of exothermic reactions, energy stored in the chemical bond of products is less than reactant hence these reactions are energetically favorable and often occur spontaneously but sometimes we need extra energy to get them started. The overall energy released in these reactions is represented by ΔH with a negative sign.

(a) (b)

Fig 11.3: Evolution and absorption of heat in thermochemical reaction (a) exothermic reaction (b) endothermic reaction

All combustion reactions including the burning of fuel and coal, oxidation of Sui gas, etc are exothermic reactions and can easily be noted by a rise of the surrounding temperature.

$$C + O_2 \longrightarrow CO_2 \ (\Delta H = -ve)$$

$$CH_4 + 2O_2 \longrightarrow 2CO_2 + 2H_2O \ (\Delta H = -ve)$$

11.2.2 Endothermic Reactions

Endothermic reactions (endo; taking in) are those in which heat is put into the system making the surrounding colder. In these reactions more energy is needed to break the bonds in the reactants than is released when new bonds are formed in the products. Since heat is used

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for the reaction to occur, these are referred to as non-spontaneous reactions. The net energy absorbed in these reactions is represented by ΔH with a positive sign.

An appropriate endothermic reaction is photosynthesis during which plants absorb solar heat through their chlorophyll parts and this heat is utilized for the conversion of CO_2 and H_2O into glucose.

$$2CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 \ (\Delta H = +ve)$$

$$CH_4 \rightarrow C + 2H_2 \quad (\Delta H = +ve)$$

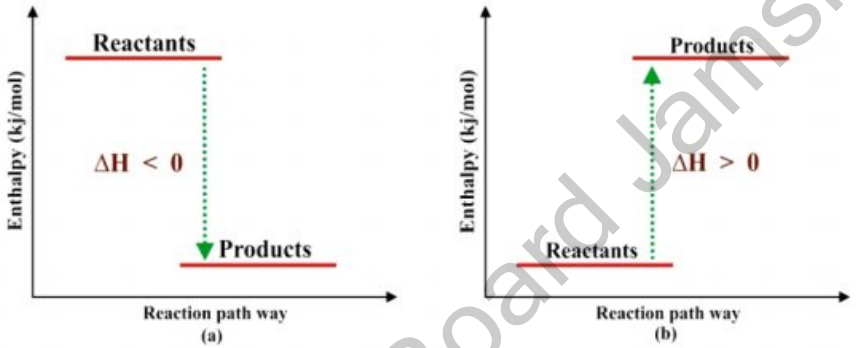

Fig 11.4: Energy diagram of thermochemical reaction (a) exothermic reaction (b) endothermic reaction

Self Assessment

Classify each of the following processes as exothermic or endothermic.

(i) Synthesis of Ammonia
(ii) Decomposition of Lime
(iii) Oxidation of Coal
(iv) Neutralization of NaOH and HCl
(v) Combustion of Hexane
(vi) Burning of Sui gas

11.3 FIRST LAW OF THERMODYNAMICS

The first law of thermodynamic is an adaptation of the law of conservation of energy that governs the transference of energy between the system and surrounding in the form of heat and work. This concept was enunciated by J.R. Mayer (1841) and formulated by Helmholtz (1847).

11.3.1 Statement and Mathematical Derivation

This law may be stated as; **"In any physical or chemical process, the net energy of a system and its surroundings must remain constant".** Or **"a system can not create or destroy energy, however, it can exchange energy with its surrounding in the form of heat and work"**. This law describes us that heat and work are mutually convertible but since energy can neither be created nor be destroyed, the total energy conversion remains constant.

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To develop the mathematical approach of the law let us consider a system in its initial state having internal energy $\mathbf{E_1}$. If "**q**" be the heat supplied to the system while **W** be the work done on the system, the internal energy increases to $\mathbf{E_2}$. Then according to the law, the internal energy change ($E_2 - E_1$) may be formulated as

$$\Delta E = q + w \quad \text{---------- (iii)}$$

Where

q = heat transfer across the system

W = work done

ΔE = change in the total energy of the system ($E_2 - E_1$)

The sign of '**q**' is taken positive if thermochemical process is concerned with heat absorbtion but in case of heat release it is taken as negative sign. The sign of **W** should be taken negative for thermochemical expansion and positive if it undergoes compression.

Equation (iii) may take the form $\Delta E = q$ if the heat is transferred to the system without work is being done but if work is done on the system without heat transfer it may change to $\Delta E = W$.

11.3.2 Derivation of Pressure-Volume Work Equation

Mechanical work due to expanding or squeezing of a system at constant external pressure is known as pressure-volume work.

Consider a gas confined in a cylinder fitted by a negligible weight, fraction less and movable piston of cross-section area **A** at a constant external pressure. If the force exerted by the gas on the inner wall of the piston is greater than external pressure, the piston move upward from a height $\mathbf{h_1}$ to $\mathbf{h_2}$ and hence does some work which may be formulated as

$$W = - F (h_2 - h_1)$$

Insertion of a negative sign indicates that external pressure opposes the expansion of gas. Since pressure is the force exerted on unit area ($P = F/A$) and thus the force is ($F = PA$), the work may be written as

$$W = - P A (\Delta h)$$

But $A.\Delta h$ represents volume change (ΔV) of the system so work done on thermodynamics system is deduced as

$$W = - P \Delta V \quad \text{---------- (iv)}$$

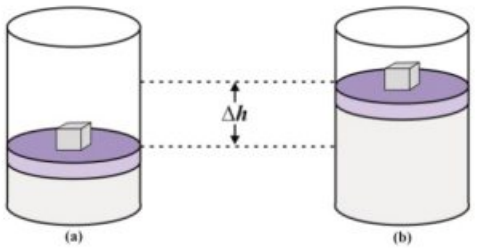

Fig 11.5: pressure-volume work in thermodynamic expansion process (a) volume at initial state (b) volume at the final state

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As far as the unit of pressure-volume work is concerned, we may have two options; either it takes in Joules (J) or in atm.dm^3. In S.I measurement pressure is taken in Pascal (N/m^2) and volume in cubic meter (m^3), their product will be in Joules. However, it is more agreeable to express pressure in atmosphere and volume in dm^3, it makes the unit of work is atm.dm^3. The two work units are co-related as

$$1 \text{ atm.dm}^3 = 101.325 \text{ Joules}$$

Example 11.1

A gaseous chemical reaction is carried out in a cylinder under a constant external pressure of 1 atm. If during the reaction volume increases from 3dm^3 to 5dm^3 by moving the piston upward. Calculate the workdone and express in kJ.

Solution:

Since the work done in an expansion process has negative sign, the equation of pressure volume work should be $W = -P\Delta V$.

Work $= -P\Delta V$

Work $= -1$ atm $(5\text{dm}^3 - 3\text{dm}^3)$

Work $= -2$ atm dm^3

But 1 atm dm^3 = 101.325J, hence

Work $= -202.65\text{J} = -0.20265\text{KJ}$

Self Assessment

Convert the values of following quantities.

(i) 20 calories energy into Joule

(ii) 3.5 atm dm^3 work into KJ.

Internal Energy

Every system is made of particles (atoms, ions, or molecules) and has a specific amount of energy. This energy is associated with the sum of all microscopic energies of the particles of the system and mainly categorised as kinetic and potential energies. The kinetic energy comprises of particles motion such as translational, vibrational, rotational motions etc. potential energy includes attractive and repulsive interaction between particles and other chemical energies stored in the chemical bond. **"The total energy content of a thermodynamic system under a given set of conditions is known as internal energy"**.

Change in internal energy (ΔE) can be measured experimentally ($\Delta E = E_2 - E_1$). Internal energy change (ΔE) is a state function because it depends only upon the initial and final state and not by a path to which change occurs.

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Example 11.2

Burning of petrol in an automobile engine gives carbondioxide and water vapours. If the gases do 675J work in pushing the piston outward and the system lose 435J heat to the surrounding, calculate the internal energy change in kJ.

Solution:

Since heat is given out, the value of **q** is taken with negative sign. Likewise sign of **W** is also taken negative because work is done by the system.

$q = -435J$

$W = -675J$

$\Delta E = ?$

$\Delta E = q + w$

$\Delta E = (-435) + (-675)$

$\Delta E = -1110J$

$\Delta E = -1.11KJ$

11.3.3 Applications at Constant Volume and Constant Pressure

So far we have learned categorically that heat absorb or evolve in a chemical process is related to its internal energy and PV work done. Now we will see that how the equation of First law of thermodynamics is applicable to the process that occur under constant pressure and constant volume.

The process at Constant Volume

When a reaction is carried out at constant volume ($\Delta V = 0$) no work is done on or by the system. In this situation internal energy change must equal to heat change of the reaction. The equation of the First law of thermodynamics may be reformed as $q_v = \Delta E$ (the subscript "**v**" specify constant volume process).

$q_v = \Delta E$ ---------- (v)

The process at Constant Pressure

It is a matter of fact that many chemical reactions in labs or workshops are carried out in open vessels. This means they carried out at constant pressure in a manner of thermochemical expansion. Thus according to the first law of thermodynamics, this constant pressure process may be illustrated as

$\Delta E = q_p - P\Delta V$

or $q_p = \Delta E + P\Delta V$ ---------- (vi)

Where q_p is the heat flow to or from the system at constant pressure, **ΔE** is internal energy change, and $P\Delta V$ is work done with changing the volume.

$q_p = (E_2 - E_1) + P(V_2 - V_1)$

$q_p = (E_2 + PV_2) - (E_1 + PV_1)$

$q_p = H_2 - H_1$

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And $q_p = \Delta H$ ---------- (vii)

Equation (vii) tells that, if a chemical process is occurred at constant pressure where only PV work is allowed due to compression of expansion the enthalpy change (ΔH) of system is equal to energy flow (q).

Substituting this value in equation (vi) we get

$\Delta H = \Delta E + P\Delta V$ ---------- (viii)

Equation (viii) represents gaseous reaction. However, for the reaction in which one or more solids or liquids are involved, the value of PΔV becomes almost zero because solids and liquids undergo very small volume change. Thus in this case enthalpy change (ΔH) will be equal to internal energy change (ΔE) and the equation of First law of thermodynamics is reformed as

$\Delta H = \Delta E$ ---------- (ix)

11.4 HESS'S LAW: (Enthalpy change calculations)

The change in enthalpy of some reactions are measured by calorimetric method. However, experimentally it is difficult to determine change in enthalpy of very slow and very fast reaction.

For example, combustion of carbon (graphite) to give carbon dioxide can be worked in a calorimeter, and ΔH° for this reaction can be conveniently measured.

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad (\Delta H° = -393.5 \text{ KJ/mol}) \quad \text{(i)}$$

Further, the same is true for the oxidation of carbon monoxide to carbon dioxide.

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \quad (\Delta H° = -283.5 \text{ KJ/mol}) \quad \text{(ii)}$$

Contradictorily, the measurement of ΔH° in the combustion of carbon to carbon monoxide is quite difficult because some of the carbon monoxides is further oxidized to carbon dioxide. (Subracting equation ii from i)

$$C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \qquad (\Delta H° = ?)$$

Enthalpy change of a reaction is a state function and it depends only on where the chemical process begins and finishes, but not on the route it takes from. Hence considering the energy cycle of the above three reactions (illustrated in fig 11.6), ΔH° of carbon monoxide can be measured indirectly.

G.H. Hess (1840) introduced a law of thermochemistry based on his observations on cyclic thermochemical changes which involve two or more different routes. This is known as Hess's law of enthalpy summation.

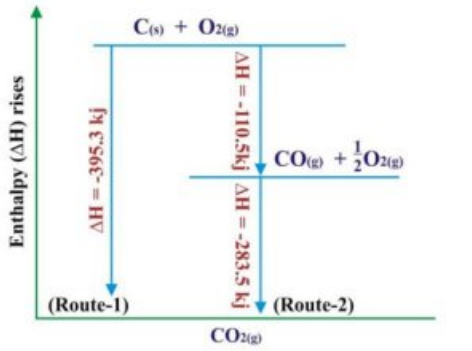

Fig 11.6: Energy cycle diagram for the formation $CO_2(g)$ (a) route-1 (b) route-2

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This law states as **"if a chemical reaction can be brought about in more than one path way, the net enthalpy change is the same provided that the initial and final states are the same"**.

11.4.1 Explanation of Hess's Law

Let us suppose a substance A is converted to Z by two different paths (illustrated in fig 11.7). It may either change directly to **Z** in one step or by involving some intermediate steps in which **X** and **Y** are formed. In both cases the total enthalpy change remains the same.

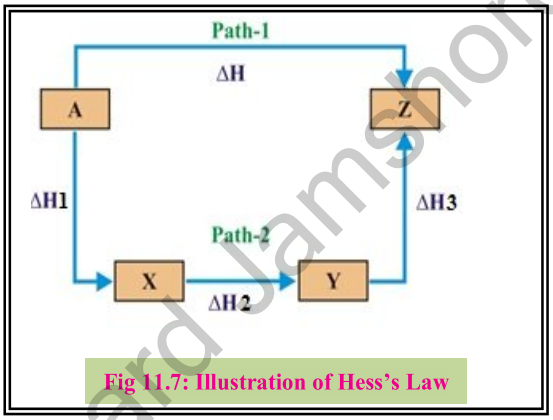

Fig 11.7: Illustration of Hess's Law

Path-1 = A $\xrightarrow{\Delta H}$ Z

Path-2 = A $\xrightarrow{\Delta H_1}$ X $\xrightarrow{\Delta H_2}$ Y $\xrightarrow{\Delta H_3}$ Z

Thus $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

Standard Enthalpies of Formation

It defines as **"the enthalpy change of a chemical reaction in which one mole of a pure substance is formed from its elements with all substance in their standard state"**.

The standard enthalpy of formation is represented by the symbol ΔH_f° in which superscript zero signifies standard conditions of 1 atmospheric pressure and 25°C, whereas subscript "f" stands for formation.

Conventionally ΔH_f° of most of the elements (H_2, O_2, N_2, Na, etc) are taken as zero because no further change is needed to bring them to standard state condition, However, for those elements which exists in more than one allotropic forms, the most stable allotropic form is conventionally assumed to have $\Delta H_f = 0$. For example, graphite is a thermodynamically more stable allotropic form of carbon than diamond at 25°C and 1 atm pressure hence ΔH_f of graphite is taken as zero. Similarly, O_2 (oxygen) is a more stable allotropic form than O_3 (ozone), and therefore ΔH_f of O_2 is assumed to be zero. The same case in for Rhombic sulfur ($\Delta H_f = 0$)

Table 11.1 The Standard States of various substances

Substances	Standard States
All pure solids & liquids	25°C
All gaseous compounds	25°C and 1 atm
All substances in the solution	25°C and 1 molar conc.
All elements	25°C and 1 atm

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Standard Enthalpy of Reaction

It is the enthalpy absorbed or evolved when fixed number of moles of reactants as represented in a balance chemical equation are completely reacted to form product with the condition that all reactants and products are in their standard states. It is represented by ΔH°. In general ΔH° in a balanced thermochemical equation is the sum of ΔH_f° of products minus the sum of ΔH_f° of reactants.

$$\Delta H^\circ_{reaction} = \left(\left(\Sigma \text{ np } \Delta H^\circ_{f\,(products)}\right) - \left(\Sigma \text{ nr } \Delta H^\circ_{f\,(\text{reactants})}\right)\right)$$

Where np and nr represent total number of moles of reactants and products take part in the reaction.

Table 11.2 **Standard Molar Enthalpy of Formation of some organic and inorganic substances at 25°C (In KJ/mol)**

Organic substances	ΔH_f° (KJ/mol)	Inorganic substances	ΔH_f° (KJ/mol)
$CH_{4(g)}$	– 74.85	$CO_{(g)}$	– 110.5
$C_2H_{6(g)}$	– 83.8	$CO_{2(g)}$	– 393.5
$C_3H_{8(g)}$	– 103.9	$SO_{2(g)}$	– 296.8
$C_2H_{4(g)}$	+ 52.30	$SO_{3(g)}$	– 396
$C_2H_{2(g)}$	+ 226.7	$H_2S_{(g)}$	– 20.17
$C_6H_{6(l)}$	+ 49.03	$NH_{3(g)}$	– 46.19
$CH_3OH_{(l)}$	– 239	$H_2O_{(l)}$	– 285.8
$C_2H_5OH_{(l)}$	– 277.7	$Fe_2O_{3(s)}$	– 824.2
$CH_3COOH_{(l)}$	– 484.2	$NaCl_{(s)}$	– 411

Use of Hess's Law in the determination of heat of reaction

There are two ways to calculate ΔH° of a reaction. It either determined calorimetrically or calculate from known values of ΔH_f° of all the susbstances involve in the reaction. Hess's law provides us a convenient way to find out the heat change involves in a chemical reaction by subtracting the sum of heat of formation of all reactants from the sum of heat of formation of all products.

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Example 11.3

Calculate the enthalpy of combustion of propane at 25°C by the given informations.

$$C_3H_{8(g)} + 5O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O_{(g)} \qquad (\Delta H^\circ = ?)$$

ΔH_f° **of** $C_3H_{8(g)} = -103.9 KJ/mol$

ΔH_f° **of** $CO_{2(g)} = -393.5 KJ/mol$

ΔH_f° **of** $H_2O_{(\ell)} = -285.8 KJ/mol$

Solution:

The mathematical form of heat of reaction ΔH° is given as.

$$\Delta H^\circ_{reaction} = \left[\left(\Sigma \text{ np } \Delta H^\circ_{f\,(products)}\right) - \left(\Sigma \text{ nr } \Delta H^\circ_{f\,(\text{reactants})}\right) \right]$$

Substituting the values.

$$\Delta H^\circ_{reaction} = \left[(-393.5 \times 3) + (-285.8 \times 4)\right] - \left[(-103.9 \times 1)\right]$$

$$\Delta H^\circ_{reaction} = -2219.8\, KJ/mol$$

Use of Hess Law in the determination of Heat of formation

Realizing the fact that thermochemical equations can be added subtracted or multiplied like ordinary algebraic equations, Hess's law is useful to calculate the heat of formation of many compounds where an experimental determination is not possible.

To understand how is Hess's Law useful in thermochemistry, look at the oxidation of sulphur to sulphur trioxide.

$$S_{(s)} + \tfrac{3}{2}O_{2(g)} \longrightarrow SO_{3(g)}$$

Analyzing the reaction, we find that sulphur can not be directly oxidized into SO_3, therefore ΔH_f° of SO_3 can not be determined if we put sulphur and oxygen in a calorimeter. The only option is to go for an alternative route which consists of following two steps.

Step-1: $S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)} \quad (\Delta H_1 = -296.8 KJ/mol)$

Step-2: $SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow SO_{3(g)} \quad (\Delta H_2 = -99.2 KJ/mol)$

Thus the ΔH_f° of $SO_{3(g)}$ is indirectly determined by adding enthalpy change of step 1 and step 2.

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)} \quad (\Delta H_1 = -296.8 KJ/mol)$$

$$SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow SO_{3(g)} \quad (\Delta H_2 = -99.2 KJ/mol)$$

$$S_{(s)} + \tfrac{3}{2}O_{2(g)} \longrightarrow SO_{3(g)} \quad (\Delta H_f^\circ = -396 KJ/mol)$$

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Example 11.4

Calculate the standard heat of formation of acetylene (C_2H_2) by using the data of the following thermochemical equations.

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ **(ΔH = – 393.5 KJ) -------- (i)**

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(\ell)}$ **(ΔH = – 285.8 KJ) -------- (ii)**

$C_2H_{2(g)} + \frac{5}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + H_2O_{(\ell)}$ **(ΔH = – 1299.5 KJ) -------- (iii)**

The desired equation is

$2C_{(s)} + H_{2(g)} \longrightarrow C_2H_{2(g)}$ **(ΔH_f° = ?) -------- (iv)**

Solution:

To determine ΔH_f value of C_2H_2, we have to generate the desired equation by manipulating and adding eq. (i), (ii) and (iii) together in such a way that all unwanted substances should be canceled.

In the desired equation (iv) we see that 2 moles of carbon and 1 mole of H_2 are needed as a reactant, this can be obtained by multiplying equation (i) by 2, which means that ΔH° will also be multiplied by 2.

$2C_{(s)} + 2O_{2(g)} \longrightarrow 2CO_{2(g)}$ (ΔH° = – 787 KJ)

Next, we see that C_2H_2 is needed as a product. To do this, the equation (iii) must be reverse with changing the sign of ΔH°.

$2CO_{2(g)} + H_2O_{(\ell)} \longrightarrow C_2H_{2(g)} + \frac{5}{2}O_{2(g)}$ (ΔH = + 1299.6 KJ)

Now sum up these three manipulated equations to get the required reaction. Also, sum up the three modified ΔH° values to get ΔH_f° of the desired reaction.

$2C_{(s)} + 2\cancel{O_{2(g)}} \longrightarrow \cancel{2CO_{2(g)}}$ (ΔH = – 787 KJ)

$H_{2(g)} + \cancel{\frac{1}{2}O_{2(g)}} \longrightarrow \cancel{H_2O_{(\ell)}}$ (ΔH = – 285.8 KJ)

$\cancel{2CO_{2(g)}} + \cancel{H_2O_{(\ell)}} \longrightarrow C_2H_{2(g)} + \cancel{\frac{5}{2}O_{2(g)}}$ (ΔH = + 1299.6 KJ)

$2C_{(s)} + H_{2(g)} \longrightarrow C_2H_{2(g)}$ (ΔH = 226.7KJ/mol)

11.4.2 Born Haber Cycle

Born Haber cycle is developed by two German chemists Max Born and Fritz Haber (1919) to correlate the lattice energy of ionic solids with some other energies involved in their formation. **"It is a cycle of enthalpy change in which an ionic solid is theoretically formed from its elements in their standard states"**. It is a

Max Born

Fritz Haber

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specific application of Hess's law and generally use to determine lattice energy of ionic solids.

To understand, how the lattice energy of a binary ionic solid determines by using Born Haber cycle let's take solid Cesium fluoride (CsF) as an example. We start by writing a thermochemical equation for the formation of CsF from its elements at their standard states (25°C and 1 atm).

The standard enthalpy of formation of $CsF_{(s)}$ as mentioned in table 11.2 is -553.5 KJ/mol

$$Cs_{(s)} + \tfrac{1}{2}F_2 \longrightarrow CsF_{(s)} \qquad (\Delta H_f^\circ = -553.5\ KJ/mol)$$

Now various energies involved in the formation of $CsF_{(s)}$ are described in the following stepwise manner.

Step-1: Sublimation of Cesium It involves the vapourization of metallic cesium into gaseous atom. The process is endothermic because heat is always needed to sublime a solid.

$$Cs_{(s)} \longrightarrow Cs_{(g)} \qquad (\Delta H_{(sub)} = 76.5\ KJ/mol)$$

Step-2: Ionization of Cesium atom It involves the loss of electron from cesium gaseous atom. The enthalpy change corresponds to this process is always positive and known as ionization enthalpy.

$$Cs_{(g)} \longrightarrow Cs^+_{(g)} + \bar{e} \qquad (\Delta H_{(IE)} = 375.5\ KJ/mol)$$

Step-3: Dissociation of gaseous Fluorine It involves the breaking of F_2 molecule into fluorine gas atoms. The enthalpy related to this process is ever positive and labeled as enthalpy of dissociation or often known as enthalpy of atomization.

$$\tfrac{1}{2}F_{2(g)} \longrightarrow F_{(g)} \qquad (\Delta H_{(D)} = \tfrac{1}{2} \text{ x } 157\ KJ/mol)$$

Step-4: Formation of $\bar{F}$ ion It involves the absorbtion of electron into fluorine gas atom. The enthalpy change of this thermochemical process is negative and specify as electron affinity.

$$F_{(g)} \longrightarrow \bar{F}_{(g)} \qquad (\Delta H_{(EA)} = -328.2\ kJ/mol)$$

Step-5: Formation of Solid CsF It involves the electrostatic interaction of oppositely charged gaseous ions. The enthalpy change in this process is indeed negative and known as Lattice energy.

$$Cs^+_{(g)} + \bar{F}_{(g)} \longrightarrow CsF_{(s)} \qquad (\Delta H_{(LE)} = ?)$$

Intended with Hess's Law, the sum of enthalpy change of these five steps will be equal to the enthalpy of formation of $CsF_{(s)}$ being the overall enthalpy change of the energy cycle is zero. This may be set out in fig 11.10 and formulated as.

$$\Delta H_f^\circ = \Delta H_{sub} + \Delta H_{IE} + \tfrac{1}{2}\Delta H_D + \Delta H_{EA} + \Delta H_{LE}$$

Substituting the values of concerned energies, we get lattice energy.

$$(-553.5) = (76.5) + (375.5) + \left(\tfrac{1}{2} \times 157\right) + (-328.2) + (-\Delta H_{LE})$$

$$\Delta H_{LE} = -755.8\ KJ/mol$$

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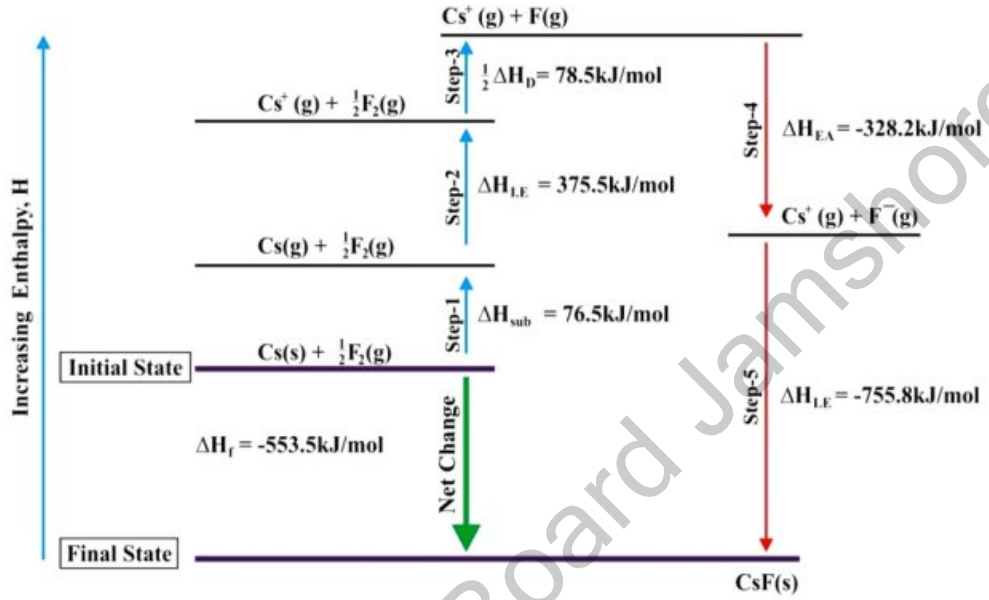

Fig 11.8: Born Haber cycle for the enthalpy change of formation of CsF(s)

Example 11.5

Use the data provided below for the formation of $RbCl_{(s)}$, write thermochemical equations for all the steps involved in the Born Haber cycle and determine the enthalpy of formation of $RbCl_{(s)}$.

Sublimation energy of $Rb_{(s)}$ = 82 KJ/mol

Ionization energy of $Rb_{(g)}$ = 403 KJ/mol

Dissociation energy of $Cl_{2(g)}$ = 242 KJ/mol

Electron affinity of $Cl_{(g)}$ = -348.5 KJ/mol
Lattice energy of RbCl = -689 KJ/mol

Solution:

Since, according to Hess's law overall enthalpy change of a cyclic thermochemical process is zero, the sum up of all five steps involved in the process will get heat of formation of RbCl. Thermochemical equations associated with Born Haber cycle in the formation of $RbCl_{(s)}$ maybe written as

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$Rb_{(s)} \longrightarrow Rb_{(g)}$ $(\Delta H^{\circ}_{(sub)} = 82KJ/mol)$

$Rb_{(g)} \longrightarrow Rb^{+}_{(g)}$ $(\Delta H^{\circ}_{(IE)} = 403KJ/mol)$

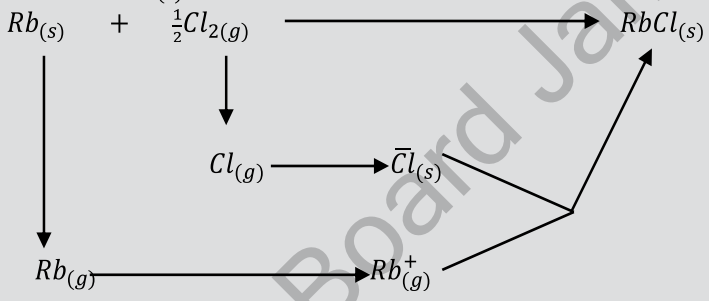
$\frac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)}$ $(\Delta H^{\circ}_{D} = \frac{1}{2} \times 242KJ/mol)$

$Cl_{(g)} \longrightarrow \bar{Cl}_{(g)}$ $(\Delta H^{\circ}_{EA} =$ -348.5KJ/mol)

$Rb^{+}_{(g)} + \bar{Cl}_{(g)} \longrightarrow RbCl_{(s)}$ $(\Delta H^{\circ}_{LE} = -689KJ/mol)$

$Rb_{(s)} + \frac{1}{2}Cl_{2(g)} \longrightarrow RbCl_{(s)}$ $(\Delta H^{\circ}_{f} = -431.5KJ/mol)$

The Born Haber cycle on $RbCl_{(s)}$ is presented below



Heat of formation of RbCl(s) may also be calculated by summing up the individual steps involved in the following simple way.

$$\Delta H^{\circ}_{f} = \Delta H_{sub} + \Delta H_{IE} + \frac{1}{2}\Delta H_{D} + \Delta H_{EA} + \Delta H_{LE}$$

$$\Delta H^{\circ}_{f(RbCl)} = (82) + (403) + \left(\tfrac{1}{2} \times 242\right) + (-348.5) + (-689)$$

$$\Delta H^{\circ}_{f(RbCl)} = -431.5\ Kj/mol$$

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Use of cold pouche for cooling

Endothermic reactions are all around us. You might have sprained on your wrist or swollen on the elbow, in these circumstances you often put an instant cold pack for quick relief. Let's imagine, what happens. The bag consists of ammonium nitrate and water in separate packing and when torn, they get mixed. The polar terminals of water molecules interact with ionic bond of ammonium nitrate and the energy needed for this process is absorbed from the surrounding which makes the water colder and thus bag feels chill.

$$4NH_4NO_{3(s)} \rightarrow NH^{+}_{4(aq)} + NO^{-}_{3(aq)}\ (\Delta H = +ve)$$

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Activity

You will always find a kitchen having usual cooking items such as vinegar (CH_3COOH) and baking soda ($NaHCO_3$). Can you deduce whether the chemical reaction between them is exothermic or it is an endothermic one?
For that, you need to have a glass tumbler and pour very little amount of acetic acid in it (1/5 of the volume). Check the temperature initially through a temperature probe (the one which you use to note the temperature of coffee). Let it be dipped in the tumbler. Now add a teaspoon of baking soda in it and keep yourself at a distance. You will observe bubbles forming rapidly. It appears as if something is boiling and your mind could misconceive it as an exothermic reaction but the temperature probe would show you a drop in temperature indicating that in actual it is an endothermic reaction.

SUMMARY with Key Terms

- **Thermodynamics** is the branch of physical science which deals with the study of intertransformation of heat work and other forms of energies.
- **Thermochemistry** is the study of energy change associated with a physical or chemical process.
- **Thermodynamic System** is a distinct part of the universe that is under experimental debate and separated from surrounding by a boundary.
- **Internal Energy, E** is mainly associated with the sum of all kinetic and potential energies of the particles of a system under study.
- **Enthalpy, H** is the heat contents of a system under constant pressure and describe as H = E + PV.
- **State Function** is a thermodynamic parameter on which description of a system is made, it depends on the initial and final state of the change but not on the path.
- **Exothermic Reactions** are those in which heat is given out making the surrounding warmer.
- **Endothermic Reactions** are those in which heat is put into the system making the surrounding colder.
- **The First Law of Thermodynamics** states that the total energy of a system and its surroundings must remain constant.
- **Pressure-Volume Work** is mechanical work associated with expansion or compression of a thermodynamic system, under a constant external pressure.
- **Standard Enthalpy of Formation**, ΔH_f° is the heat evolve or absorb when 1 mole of a substance is produced from its constitutent elements under their standard states i.e 25°C and 1 atm pressure.
- **Standard Enthalpy of combustion** ΔH_c° heat energy given out when one mole of a substance burn completely in air.

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- **Standard Enthalpy of Reaction, ΔH°** is the heat change of a chemical reaction and can be measured by subtracting the sum up values of ΔH_f° of products to the sum up values of ΔH_f° of reactants.
- **Hess's Law** tells that if a reaction is carried out through several steps then the enthalpy change for the overall reaction must be equal to the sum of enthalpy change of these individual steps.
- **Born Haber Cycle** is an application of Hess's Law and generally use to determine the Lattice of ionic compounds.

EXERCISE

Multiple Choice Questions

1. Choose the correct answer

(i) Least entropy found in which of the following state of water:

(a) Liquid water at 4°C (b) Liquid water at 25°C
(c) Steam at 100°C (d) Ice at 0°C

(ii) The energy corresponds to the given thermochemical process is labeled as:

$$Li^{+}_{(g)} + \bar{C}l_{(g)} \longrightarrow LiCl_{(s)}$$

(a) Ionization energy (b) Lattice energy
(c) Enthalpy of combustion (d) Enthalpy of atomization

(iii) Which of the following change is not an endothermic reaction:

(a) Decomposition of lime (b) Cracking of alkanes
(c) Combustion of butane (d) Photosynthesis

(iv) Heat transfer can not be feasible across the boundryof a:

(a) Open system (b) Close system
(c)Isolated system (d) Thermo permeable system

(v) Which of the following enthalpy change is always negative:

(a) Enthalpy of formation (b) Enthalpy of decomposition
(c) Enthalpy of combustion (d) Enthalpy of reaction

(vi) Standard enthalpy of formation of all of the following elements at 25°C and 1 atm pressure are zero except:

(a) $C_{(diamond)}$ (b) $C_{(graphite)}$
(c) O_2 (d) N_2

(vii) In the equation of First law of thermodynamics (ΔE = q + w), the property(s) which depends upon initial and final state is (are):

(a) ΔE (b) q
(c) W (d) Both q and W

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(viii) Which statement is incorrect:
(a) For constant pressure process, $\Delta H = \Delta E + P\Delta V$
(b) For constant volume process, $\Delta E = q$
(c) For exothermic reactions, $\Delta H \rangle 0$
(d) For Hess law $\sum \Delta H^\circ_{(cycle)} = 0$

(ix) In a thermochemical process, no work is done if the system is kept at:
(a) Constant temperature (b) Constant pressure
(c) Constant volume (d) Constant mass

(x) Volume is a:
(a) State function (b) Path function
(c) Intensive properties (d) Colligative property

Short Questions

1. State precisely the meaning of each of the following terms.
(i) System and surrounding (ii) State and state function
(iii) Internal energy and Enthalpy
2. What is meant by Internal energy change (ΔE) and Enthalpy change (ΔH)? Under what conditions are ΔE and ΔH equal?
3. How can you define standard enthalpy of formation and standard enthalpy of reaction.

Descriptive Questions

1. State and explain First law of Thermodynamics. Derive pressure-volume work of a system.
2. Discuss the applications of the First law of thermodynamics at constant pressure and constant volume.
3. State and explain Hess's Law of enthalpy summation. Discuss its applications.
4. Explain Exothermic and Endothermic reactions with the help of the energy diagram.

Numerical Questions

1. A thermochemical process is carried out at constant pressure of 8.52atm. If it absorbs 15.4KJ energy from the surrounding due to which an expansion in the volume of 4.7dm^3 is occurred. Calculate its change in internal energy. [Ans: 11.34KJ]
2. Using the data in table 11.2, calculate the standard enthalpy change for each of the following reactions.

$$2H_2S_{(g)} + 3O_{2(g)} \longrightarrow 2H_2O_{(\ell)} + 2SO_{2(g)}$$
$$Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + 3CO_{2(g)}$$

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3. In the manufacturing of HNO_3 by the Ostwald process, one of the most important exothermic reactions is the oxidation of ammonia.

$$4NH_{3(g)} + 5O_{2(g)} \longrightarrow 4NO_{(g)} + 6H_2O_{(\ell)}$$

Determine standard heat of reaction (ΔH°) from the following given data.

$$\Delta H_f^\circ \ of \ NH_{3(g)} = -46.19KJ/mol$$
$$\Delta H_f^\circ \ of \ NO_{(g)} = 90.25KJ/mol$$
$$\Delta H_f^\circ \ of \ H_2O_{(\ell)} = -285.8KJ/mol$$

[Ans: – 1169.04 KJ/mol]

4. Iso octane (C_8H_{18}) is an efficient fuel with a high octane rating. The combustion of C_8H_{18} in an internal combustion engine is represented in the following thermochemical equation. Find its standard heat of combustion.

$$C_8H_{18(\ell)} + 12\tfrac{1}{2}O_{2(g)} \longrightarrow 8CO_{2(g)} + 9H_2O_{(\ell)} \quad (\Delta H_f^\circ = \ ?)$$

Given that ΔH_f° of CO_2 = – 393.5 KJ/mol

ΔH_f° of H_2O = – 285.8 KJ/mol

ΔH_f° of C_8H_{18} = – 223.8 KJ/mol [Ans: – 5496.4 KJ/mol]

5. Glycerol ($C_3H_8O_3$) is a well known organic compound due to its versatile uses. Calculate the standard enthalpy of formation of Glycerol from the data given below.

$3C_{(s)} + 4H_{2(g)} + \frac{3}{2}O_{2(g)} \longrightarrow C_3H_8O_{3(\ell)}$ $(\Delta H_f^\circ = \ ?)$

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $(\Delta H^\circ$ = -393.5 KJ/mol)

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(\ell)}$ $(\Delta H^\circ$ = -285.8 KJ/mol)

$C_3H_8O_{3(\ell)} + 3\frac{1}{2}O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O_{(\ell)}$ $(\Delta H^\circ$ = -1654.1 KJ/mol)

[Ans: – 669.6 KJ/mol]

6. Draw a fully labeled Born Haber cycle for Rubidium chloride (RbCl) and determine the lattice energy by using the following values. (all in kJ/mol).

- $I.P_{1st}$ of Rb = 403
- Electron affinity of Cl = -349 KJ/mol
- Bond energy of Cl_2 = 242 KJ/mol
- Sublimation energy of Rb = 86.5 KJ/mol
- Heat of formation of $RbCl_{(s)}$ = -430.5 KJ/mol [Ans: -692 KJ/mol]

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ELECTROCHEMISTRY Chapter 12

Teaching Periods	Assessment	Weightage
12	1	8

Students will be able to:

- **Give** the characteristics of a Redox reaction.
- **Determine** oxidation and reduction in term of change in oxidation number.
- **Determine** oxidation number of atom of an element in a molecule or polyatomic ion on the basis of some assigned rules.
- **Enlist** oxidizing and reducing agents.
- **Balance** redox reaction that takes place in acid solutions.
- **Break** a redox reaction into oxidation and reduction half reactions.
- **Balance** the redox equation by using half-cell reaction method.
- **Define** cathode, anode, electrode potential and S.H.E.
- **Identify** the substance oxidized and the substance reduced in batteries.
- **Describe** the cell potential and how it is determined.
- **Describe** the reaction that occurs when a lead storage battery is recharged.
- **Illustrate** how a fuel cell produces electrical energy.
- **Explain** the types and uses of batteries in daily life.
- **Define** corrosion and describe simple methods like electroplating and galvanizing for its prevention.

INTRODUCTION

In our daily life many chemical reactions provide electrical energy. Have you ever think how portable radio, children's toys, or an automobile battery works? In fact in all these devices electrical energy generates due to chemical change. In reverse situation, we have a large list of chemical process in which electrical energy is used to bring about chemical changes. For example recharging of battery, extraction and purification of metals etc. Electro chemistry deals with the chemical change happen due to electric current as well as the generation of electric current by chemical change. It is best defined as **"the study of interchange of chemical and electrical energy"**. Electrochemistry is generally investigated by the usage of electrolytic and galvanic cells where electrical energy either produces or utilize by incorporating redox reactions.

12.1 OXIDATION-REDUCTION CONCEPTS

Reduction and oxidation reactions, collectively known as redox reactions, are associated with the electrons transfer from one species to another. If one species in a reaction loses electrons, it is said to be oxidized and acts as a reducing agent, at the same time the other specie gains electrons and gets reduced, therefore acts as oxidizing agent. The number of electrons lost and gained must be equal. Various natural processes that we observe in daily routine such as rusting of iron, photosynthesis, fading of cloth's color, generation of electric current in batteries are all concerned with simultaneous reduction and oxidation reactions.

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12.1.1 Oxidation and Reduction

Oxidation refers to the addition of oxygen or removal of hydrogen from a substance for example.

$$4Al + 3O_2 \longrightarrow 2Al_2O_3 \text{ (Al is oxidized to } Al_2O_3)$$

$$H_2S + Cl_2 \longrightarrow 2HCl + S \text{ } (H_2S \text{ is oxidized to elemental sulphur})$$

Reduction originally describes the addition of hydrogen or removal of oxygen from a compound. For example

$$2CuO \longrightarrow 2Cu + O_2 \text{ (Copper oxide is reduced to elemental copper)}$$

$$WO_3 + 3H_2 \longrightarrow W + 3H_2O \text{ (Tungsten oxide is reduced to elemental tungsten)}$$

According to modern electronic concept, **"oxidation is the chemical process in which electron are lost by an atom or ion where as reduction involves the gain of electrons"**. Thus oxidation may result in producing or increasing the positive charge on the species or decreasing its negative charge. Contrarily reduction involves in producing or increasing the negative charge on the species or decreasing its positive charge.

Oxidation Process	Reduction Process
$Fe \longrightarrow Fe^{+2} + 2\bar{e}$	$Cl_2 + 2\bar{e} \longrightarrow 2Cl^-$
$Hg^+ \longrightarrow Hg^{+2} + \bar{e}$	$O^{-1} + \bar{e} \longrightarrow O^{-2}$
$S^{-2} \longrightarrow S + 2\bar{e}$	$Cu^{+2} + 2\bar{e} \longrightarrow Cu$

According to oxidation number concept **"oxidation is a process in which the oxidation state of an element increases while reduction is a process in which the oxidation state of an element decreases"**.

Let us consider a redox reaction between zinc powder with dilute hydrochloric acid.

$$\overset{0}{Zn_{(s)}} + \overset{+1}{2HCl_{(aq)}} \longrightarrow \overset{+2}{ZnCl_{2(aq)}} + \overset{0}{H_{2(g)}}$$

Reduction

Oxidation

Characteristics of Redox Reactions

There are some general characteristics of redox reactions.

(i) All redox reactions may involve the transfer of electrons.

(ii) Oxidation and reduction process always occur side by side thus if one substance is oxidized the other is reduced at the same time.

(iii) Not all atoms in a redox reaction need to change their oxidation states but at least one atom should be oxidized and one should be reduced.

12.1.2 Oxidation Number

Oxidation number is an apparent charge on an atom in a compound or ion. Its value may be positive, negative or zero depending upon charge of combined atoms in the molecule or ion.

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Rules for Assigning Oxidation Number:

(i) Oxidation number of all elements in Free State (uncombined state) is taken as zero. For example: K°, Cl_2°, H_2° , O_2° , Cu° etc.

(ii) The oxidation number of a mono atomic ion is the same as the charge appear on it. For example: the oxidation number of Na^{+} ion is + 1 and Ca^{+} ion is +2.

(iii) The sum of oxidation numbers of all elements in a neutral compound is zero. For example: $H_2SO_4^{\circ}$ ($H_2^{+2}SO_4^{-2}$)

(iv) The oxidation number of oxygen in most of its compounds is -2. However in peroxides it is -1 (Na_2O_2 and H_2O_2), in super oxides is -1/2 (KO_2) and in oxy fluoride is +2 (OF_2).

(v) Oxidation of hydrogen in covalent compounds is assigned as +1. However in metal hydrides its oxidation number is taken as -1 (e.g. $Na^{+}H^{-}$, $K^{+}H^{-}$ etc).

(vi) The oxidation numbers of group IA and group IIA elements are generally assigned +1 and +2 respectively. Elements of group IA are Li, Na, K, Rb, Cs and group IIA are Be, Mg, Ca, Sr, Ba

(vii) The oxidation number of fluorine in all its compounds is always taken as -1 because it is most electronegative atom of all elements. The oxidation number of other halogen elements in binary compounds is also taken as -1 except when they are bonded to a more electronegative halogen or oxygen.

(viii) In polyatomic ion, the sum of oxidation numbers of all the atoms present in them is equal to the net ionic charge on the ion.

Example 12.1

Determine the oxidation number of (i) S in $Na_2S_2O_3$ (ii) Mn in MnO_4^{-}

Solution:

(i) $Na_2S_2O_3$ contains elements Na, S and O. From the rules given above, the oxidation number of Na is +1 and that of O is –2. Further the sum of oxidation number of all elements in a neutral compound is zero. Thus we may determine the oxidation number of sulphur in the following way.

$2(+1) + 2(S) + 3(-2) = 0$

$+2 + 2S - 6 = 0$

$2S = +4$

$S = +2$

(ii) Since sum of oxidation number of all the elements in a polyatomic ion is equal to its net ionic charge, we may determine oxidation number of Mn in MnO_4^{-} ion in the following way.

$Mn + 4(O) = -1$

$(Mn) + 4(-2) = -1$

$Mn - 8 = -1$

$Mn = +7$

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Self Assessment

Determine the oxidation number in the following species.
(i) Cl in ClO_3^- (ii) Cr in $Cr_2(SO_4)_3$ (iii) P in $Ca(H_2PO_4)_2$

12.1.3 Balancing oxidation reduction equation by ion electron method

Equations of redox reactions are often difficult to balance by simple inspection. There are two methods by virtue of which the redox reactions are balanced, namely; oxidation number method and ion electron method.

In ion electron method only those reactants and products of redox reaction are balanced that contain the elements undergoing a change in oxidation state. That is to say, only those reactants and products are balanced which are actually oxidized or reduced. Following steps are involved in balancing of chemical equation by ion electron method.

(1) Write a skeleton equation which includes those reactants and products that contain the elements undergoing a change in oxidation state.

(2) Transform the molecular skeleton equation into ionic form. If the given equation is already in the ionic form, then this step is omitted.

(3) Split the ionic equation into two partial equations i.e. the oxidation and reduction equation

(4) Balance each partial equation in terms of atoms. In neutral or acidic medium, H_2O and H^+ are added for balancing oxygen and hydrogen respectively. The oxygen atoms are balanced first. In case of basic medium, OH^- and H_2O are added to balance oxygen and hydrogen respectively.

(5) Balance the charge in each partial equation by adding electrons on either left or right side of the equation. It will be found that electrons are added to the left in the partial equation for the reduction equation and to the right in the partial equation for oxidation reaction.

(6) Multiply each partial equation by a number so that the electrons in both the partial equations become equal in number.

(7) Add the two partial equations after cancelling the electrons. In the sum equation, cancel out any species common to both sides.

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Example 12.2

Balance the following equation by ion electron method.

$$HNO_3 + H_2S \longrightarrow NO + S + H_2O$$

Solution:

The skeleton equation is given as

$$HNO_3 + H_2S \longrightarrow NO + S + H_2O$$

Step-1: Transform the molecular equation into ionic form:

$$H^+ + NO_3^- + H_2S \longrightarrow NO + S + H_2O$$

The oxidizing agent is the nitrate ion (NO_3^-) since its nitrogen atom undergoes a decrease in oxidation state. The reducing agent is H_2S since sulphur atom undergoes an increase in oxidation state. H_2S could have been written as sulphide ion (S^{-2}), but H_2S is preferable due to slight degree of ionization.

Step-2: Split the equation into oxidation and reduction half equations.

$NO_3^- \longrightarrow NO$ Reduction (Nitrogen from +5 to +2)

$H_2S \longrightarrow S$ Oxidation (Sulphur from -2 to 0)

Step-3: Since the medium is acidic, oxygen atoms are balanced by adding $2H_2O$ on right hand side and hydrogen atom are balance by $4H^+$ on left hand side in the first partial equation.

$$NO_3^- + 4H^+ \longrightarrow NO + 2H_2O$$

In the second partial equation two protons are added to the right to balance two hydrogen atoms on the left.

$$H_2S \longrightarrow S + 2H^+$$

Step-4: Balance the charge in the partial equations by adding electrons.

In first partial equation, the oxidation number of nitrogen decreases from +5 to +2, hence 3 electrons are added to the left side.

$$NO_3^- + 4H^+ + 3\bar{e} \longrightarrow NO + 2H_2O$$

In the second partial equation, the oxidation of sulphur increases from –2 to zero hence 2 electron are added to make it zero on the left

$$H_2S \longrightarrow S + 2H^+ + 2\bar{e}$$

Step-5: In order to equalize the electrons lost and gain, first partial equation is multiplied by 2 and second by 3.

$$2NO_3^- + 8H^+ + 6\bar{e} \longrightarrow 2NO + 4H_2O$$

$$3H_2S \longrightarrow 3S + 6H^+ + 6\bar{e}$$

Step-6: Cancel out the electron and add the partial equations.

$$2NO_3^- + 8H^+ + 6\bar{e} \longrightarrow 2NO + 4H_2O$$

$$3H_2S \longrightarrow 3S + 6H^+ + 6\bar{e}$$

$$2NO_3^- + 3H_2S + 2H^+ \longrightarrow 2NO + 3S + 4H_2O$$

This equation may be converted back to molecular form by combining NO_3^- and H^+

$$2HNO_3 + 3H_2S \longrightarrow 2NO + 3S + 4H_2O$$

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Example 12.3

Balance the following equation in basic aqueous solution by ion electron method.

$$Cr(OH)_3 + SO_4^{-2} \longrightarrow CrO_4^{-2} + SO_3^{-2}$$

Solution:

To balance a chemical equation, we first identify the elements which undergo change in their oxidation number. In the given equation Cr and S are undergoing oxidation number change.

Step-1: Split the given equation into two half reactions mentioning oxidation and reduction on the bases of either the oxidation number of Cr and S decreases or increases.

$$Cr(OH)_3 \longrightarrow CrO_4^{-2} \text{ (oxidation)}$$
$$SO_4^{-2} \longrightarrow SO_3^{-2} \text{ (reduction)}$$

Step-2: According to balancing rule in basic medium, we balance the oxygen atoms of first half equation by adding $5O\bar{H}$ on left hand side and hydrogen atoms are balanced by adding $4H_2O$ on right hand side.

$$Cr(OH)_3 + 5O\bar{H} \longrightarrow CrO_4^{-2} + 4H_2O$$

In second half equation, oxygen atoms are balanced by adding $2O\bar{H}$ on right hand side and hydrogen atoms are balanced by adding H_2O on left hand side.

$$SO_4^{-2} + H_2O \longrightarrow SO_3^{-2} + 2O\bar{H}$$

Step-3: Since the oxidation number of Cr increases from +3 to +6, the charges of first half equation are balanced by adding three electrons on right hand side.

$$Cr(OH)_3 + 5O\bar{H} \longrightarrow CrO_4^{-2} + 4H_2O + 3\bar{e}$$

On the other hand in second half equation the oxidation number of sulphur decreases from +6 to +4; this change must be balanced by adding two electrons on left hand side.

$$SO_4^{-2} + H_2O + 2\bar{e} \longrightarrow SO_3^{-2} + 2O\bar{H}$$

Step-4: For equalizing the number of electrons lost in first half equation and gain in second half equation, we must multiply first half equation by 2 and second half equation by 3.

$$2 \times [Cr(OH)_3 + 5O\bar{H} \longrightarrow CrO_4^{-2} + 4H_2O + 3\bar{e}]$$
$$3 \times [SO_4^{-2} + H_2O + 2\bar{e} \longrightarrow SO_3^{-2} + 2O\bar{H}]$$

Now add the two half equations and cancel out electrons as well as H_2O in both side to get the net balanced ionic equation.

$$2Cr(OH)_3 + 10\,O\bar{H} \longrightarrow 2CrO_4^{-2} + 8H_2O + 6\bar{e}$$
$$3SO_4^{-2} + 6\bar{e} + 3H_2O \longrightarrow 3SO_3^{-2} + 6O\bar{H}$$
$$2Cr(OH)_3 + 4O\bar{H} \longrightarrow 2CrO_4^{-2} + 3SO_3^{-2} + 5H_2O$$

Self Assessment

Balance the following equation by ion electron method.

(i) $Cr_2O_7^{-2} + Cl^- \rightarrow Cr^{+3} + Cl_2$ (acidic medium)

(ii) $MnO_4^- + SO_3^{-2} \rightarrow Mn^{+2} + SO_4^{-2}$ (basic medium)

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12.1.4 Chemistry of some important oxidizing and reducing agents

Electrons are neither created nor destroyed in a chemical reaction therefore oxidation and reduction always occurs simultaneously.

Consider the oxidation reduction process in the following reaction.

$$\overset{\overset{\text{(Oxidation)}}{\frown}}{Zn^{\circ}_{(s)}} + 2HCl^{-}_{(aq)} \longrightarrow \underset{\underset{\text{(Reduction)}}{\smile}}{ZnCl^{+2}_{2(aq)} + H^{\circ}_{2(g)}}$$

Zinc is one reactant that oxidizes to $ZnCl_2$ while HCl is other reactant which reduces to H_2. **"In any redox reaction the species that oxidizes the other substance and itself get reduced is known as oxidizing agent where as the species that reduces other substance but itself get oxidized is identified as reducing agent"**.

Do You Know?

Transmission of nerve impulse in biological system is an electrochemical process and was observed by an Italian scientist Luigi Galvani (1737-1798) during his investigation on frog.

Table 12.1 List of some redox reactions mentioning oxidizing and reducing agent

Redox Reaction	Oxidizing Agent	Reducing Agent
$Cl_2 + H_2S \xrightarrow{\text{Oxidation}} 2HCl + S$ (Reduction)	Cl_2	H_2S
$CuO + H_2 \xrightarrow{\text{Oxidation}} Cu + H_2O$ (Reduction)	CuO	H_2
$Fe_2O_3 + 3CO \xrightarrow{\text{Oxidation}} 2Fe + 3CO_2$ (Reduction)	Fe_2O_3	CO
$Al + H_2SO_4 \xrightarrow{\text{Oxidation}} Al_2(SO_4)_3 + SO_2 + H_2O$ (Reduction)	H_2SO_4	Al
$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \xrightarrow{\text{Oxidation}} Cr_2(SO_4)_3 + 4K_2SO_4 + 3I_2 + 7H_2O$ (Reduction)	$K_2Cr_2O_7$	KI
$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \xrightarrow{\text{Oxidation}} 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$ (Reduction)	$2KMnO_4$	$H_2C_2O_4$

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12.2 ELECTRODE, ELECTRODE POTENTIAL AND ELECTROCHEMICAL SERIES

The production or use of electric current through a chemical change is generally carried out in electrochemical cell which is a system consisting of electrodes that dips into an electrolytic solution.

Electrolytic Cell

An electrolytic cell is an apparatus containing two metallic rods or foils known as electrodes dipped in an electrolytic solution and connected to a battery wherein the electric current is used to derive a non-spontaneous redox reaction. The electrode connected to the negative terminal of battery is called cathode, through which electrons enter the solution whereas the electrode connected to the positive terminal of battery is called anode, through which electrons leave the cell. The electrodes are basically metallic plates, rods or foils through which the current enters or leaves the electrolyte. Cathode is the negative electrode (Reductions occurs) whereas anode is the positive electrode (Oxidation occurs). The electrolyte spontaneously dissociates to produce ions within the solution. The positive ions are known as cations while the negative ions are known as anions.

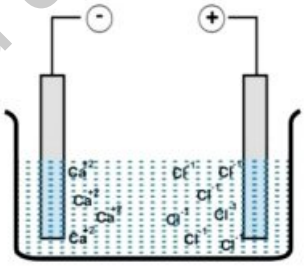

Fig 12.1: Process of electrolysis in an electrolytic cell

When the electric current is passed through the solution, anions move towards anode where they lose electrons to get oxidized. On the other hand, cations move towards cathode where they gain electrons to become reduced. By this we can say that oxidation occurs at anode while reduction occurs at cathode.

"The movement of cations and anions towards their respective electrodes accompanying all chemical changes in an electrolytic solution under the influence of electric current is known as electrolysis".

During the process of electrolysis, ions of electrolyte migrate towards their respective electrodes where they get oxidized or reduced. For example when aqueous calcium chloride is electrolyzed, the Ca^{+} ions move towards cathode and the Cl^{-} ions move towards anode.

$$Ca^{+2}_{(aq)} + 2\bar{e} \longrightarrow Ca_{(aq)} \text{ (Reduction at cathode)}$$

$$2Cl^{-}_{(aq)} \longrightarrow Cl_{2(g)} + 2\bar{e} \text{ (Oxidation at anode)}$$

Thus the reactions taking place in the electrolytic cell are redox reactions and the process of electrolysis remains continue in the electrolytic cell until all ions of the electrolyte change into neutral atoms.

Self Assessment

What is electrolysis? Describe the process of electrolysis for NaCl in an electrolytic cell.

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Galvanic Cell

A Galvanic or voltaic cell is type of electrochemical cell in which current is generated by a spontaneous redox reaction. Galvanic cell is typically consist of two half cells which are inter connected electrically. Each half cell is made up of a strip of metal immersed into a solution of its metal ions.

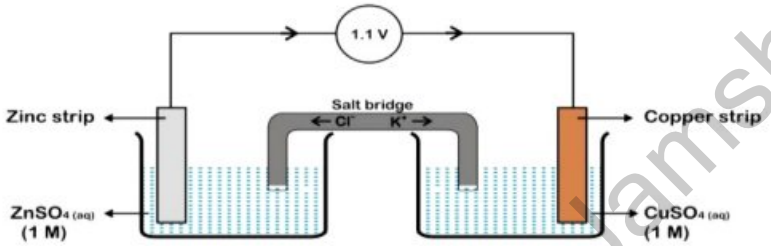

Fig 12.2: A Galvanic cell with zinc anode and copper cathode

"A salt bridge is a u-shaped glass tube in which an inert electrolyte is filled along with gel. It allows the flow of ions but prevent the mixing of solution". Thus maintain the electrical neutrality in each half cell.

The two half cell reactions and the net reaction can be written as

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2\bar{e} \text{ (Oxidation at zinc half cell)}$$

$$Cu^{+2}_{(s)} + 2\bar{e} \longrightarrow Cu_{(aq)} \text{ (Reduction at copper half cell)}$$

$$Zn_{(s)} + Cu^{+2}_{(s)} \longrightarrow Zn^{+2}_{(aq)} + Cu_{(aq)} \text{ (Net cell reaction)}$$

Galvanic cells are conveniently express in some short hand notations. For example Zinc-copper cell may be written as.

$$\underset{\text{(anode)}}{Zn_{(s)}} \,|\, Zn^{+2}_{(aq)} \,\underset{\text{salt bridge}}{||}\, Cu^{+2}_{(aq)} \,|\, \underset{\text{(cathode)}}{Cu_{(s)}}$$

Here single vertical line specifies the phase boundary between electrode and electrolytic solution where as double vertical lines indicate salt bridge.

Cell Potential

The electrical energy produce by voltaic cell is due to the electron flow from anode to cathode through an external wire. **"The driving force with which the electrons pushes out from anode into external circuit is known as electromotive force (emf) or cell potential or cell voltage"**.

Just as each half cell reaction is a part of overall reaction, the potential of each half cell make up the overall emf of the cell. Thus, knowing the emf of the cell and electrode potential of any one of the half cell, we could obtained the other. The standard electrode potential of a single half cell is defined as **"The difference of potential created between metal electrode and 1 molar solution of its ions at 25°C and 1 atmospheric pressure"**. It is abbreviated by E° and measured in volt.

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Electrode potential can be represented in term of oxidation potential or reduction potential. The capability of electrode to get oxidized in its electrolytic solution is known as oxidation potential where as the tendency of electrode to gain electrons and allows the positive ions of solution to deposit on it is called as reduction potential. IUPAC convention recommended that electrode potential is taken as reduction potential. Therefore while constructing a Galvanic cell, cathode should be of higher reduction potential and anode should be of lower reduction potential.

Do You Know?

Voltaic cell was first developed by Alessandro volta (1745-1827). He made it by fixing zinc and silver plates alternatively in a container and placed brine soaked card board between them. Since voltmeter was not invented at that time he checked the flow of current by hand shocked.

It is not possible to measure experimentally the electrode potential of a single electrode. The electrode potential of a single electrode can only be determine if it is coupled with another electrode having a known electrode potential. Chemists established an arbitrary standard known as reference electrode.

The most commonly used reference electrode is **standard hydrogen electrode (SHE)** which assigned as an electrode potential of 0.00 volt and thus the electrode potential of all other electrodes can be measured relative to it.

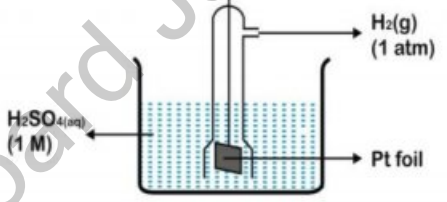

Fig. 12.3: Standard Hydrogen Electrode (SHE)

A standard hydrogen electrode (SHE) is a gas electrode and consists of a platinum rod coated with finely divided platinum which is immersed in 1M solution of H_2SO_4. Pure hydrogen gas is passed continuously through the solution under a pressure of 1 atm and 25°C. Platinum absorbs hydrogen gas on its surface. When it is connected to another half cell, the hydrogen gas at platinum electrode either pass into solution and form H^+ ions or the H^+ ions of solution reduced at platinum electrode to form hydrogen gas.

$$H_2 \longrightarrow 2H^+ + 2\bar{e} \text{ (Oxidation)}$$
$$2H^+ + 2\bar{e} \longrightarrow H_2 \text{ (Reduction)}$$

If oxidation takes place at platinum electrode, it serves as anode but if reduction occurs, it behaves as cathode.

Standard electrode potential of Galvanic cell (E°_{cell}) is the algebraic difference between the standard reduction potential of two half cells and can be expressed as

$$E^\circ_{cell} = E^\circ_{(cathode)} - E^\circ_{(anode)}$$

Experimental Determination of Electrode Potential of Zinc and Copper

Standard electrode potential of an electrode can be measured by using a reference electrode such as SHE. Let consider we want to determine the electrode potential of zinc. For this purpose we have to construct a voltaic cell made of Zinc–SHE electrodes. The first half cell consists of a strip of zinc immersed in 1M $ZnSO_4$ solution while the other half cell consists of platinum foil immersed in 1M H_2SO_4 solution at standard conditions.

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A salt bridge is made of KCl jelly which completes the circuit between the two half cells and prevent the mixing of solutions. Both electrodes are connected to each other through an external wire by means of a voltmeter.

Whenever the construction is completed and Galvanic cell is operational, the voltmeter shows emf of the cell which comes out to be 0.76 volt. Now note the flow of electrons in the external circuit. It should be from zinc electrode to SHE. Thus electrons must have originated at zinc and zinc is anode where oxidation takes place.

Half cell reactions on zinc and SHE electrode are written as

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2\bar{e} \text{ (Oxidation at anode)}$$

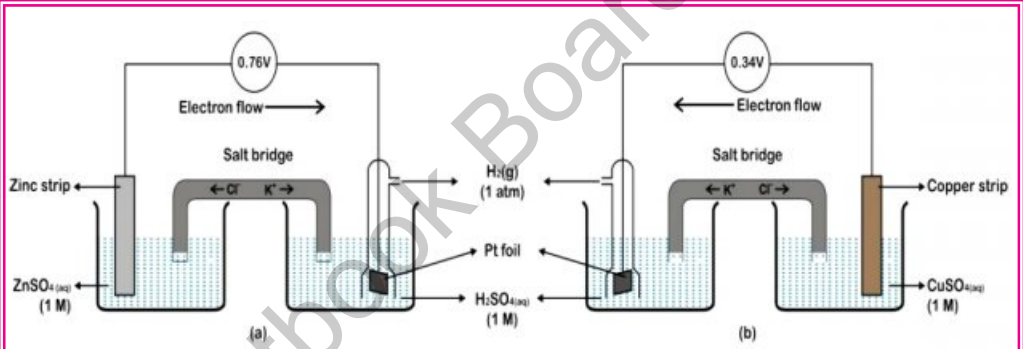
$$2H^{+} + 2\bar{e} \longrightarrow H_2 \text{ (Reduction at cathode)}$$

The electrode potential of zinc is now determined as

$$E^{\circ}_{(cell)} = E^{\circ}_{(cathode)} - E^{\circ}_{(anode)}$$

$$0.76 = (0.0) - E^{\circ}_{(Zn)}$$

$$E^{\circ}_{(Zn)} = -0.76 \text{ volt}$$



$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2\bar{e} \qquad H_{2(g)} \longrightarrow 2H^{+}_{(aq)} + 2\bar{e}$$

$$2H^{+} + 2\bar{e} \longrightarrow H_{2(g)} \qquad Cu^{+2} + 2\bar{e} \longrightarrow Cu_{(s)}$$

$$Zn \mid Zn^{+2}(1M) \,||2H^{+}(1M)|H_2\ (1\ atm); Pt \qquad H_2\ (1\ atm); Pt|\ 2H^{+}(1M)\ ||Cu^{+}(1M)|Cu$$

Fig 12.4: Galvanic cell of (a) zinc-SHE couple (b) copper-SHE couple

The electrode potential of copper and other substances can be determined in the same way.

Electrochemical Series

Taking SHE as a reference electrode, chemists determine the electrode potential of many substances and arranged in the order of increasing reduction potential, is known as electro chemical series.

The E° value of each electrode in ECS represents its relative tendency to undergo reduction as compared to the hydrogen ion at standard conditions.

Some important features of electrochemical series are given below:

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(i) Electrodes above hydrogen in ECS have negative electrode potential. They have stronger tendency to lose electron (oxidation) then hydrogen, these substance thus acts as reducing agent (anode).

(ii) Electrodes which are placed below hydrogen in ECS have positive electrode potential. They have greater ability to gain electrons (reduction) as compared to hydrogen and hence serve as oxidizing agent (cathode).

Table 12.2 Standard reduction potential at 25°C for some half reactions

Electrodes	Reduction Half – Reaction	E° (V)
Li^+/Li	$Li^+ + e^- \rightarrow Li$	-3.05
K^+/K	$K^+ + e^- \rightarrow K$	-2.93
Na^+/Na	$Na^+ + e^- \rightarrow Na$	-2.71
Mg^{2+}/Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
Zn^{2+}/Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
Fe^{2+}/Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
Cd^{2+}/Cd	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40
Ni^{2+}/Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.25
Pb^{2+}/Pb	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13
H^+/H_2	$2H^+ + 2e^- \rightarrow H_2$	0.000
Cu^{2+}/Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
Ag^+/Ag	$Ag^+ + e^- \rightarrow Ag$	+0.80
MnO_2/Mn^{2+}	$MnO_2 + 4H^+ + 4e^- \rightarrow Mn^{2+} + 2H_2O$	+1.28
$Cr_2O_7^{2-}/Cr^{3+}$	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+1.33
Cl_2/Cl^-	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
MnO_4/Mn^{2+}	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51
H_2O_2/H_2O	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	+1.78
$F_2/2F^-$	$F_2 + 2e^- \rightarrow 2F^-$	+2.87

Increasing strength of oxidizing agent ↓

Increasing strength of reducing agent ↑

12.3 BATTERIES

So far we have understood that how a Galvanic cell generate electricity. Indeed the current produce by it is not sufficient for commercial use, practically we combine two or more cells and make a battery.

"A battery consists of two or more Galvanic cells connected in series and is used to convert chemical energy into electrical energy by means of reduction-oxidation (redox) reactions".

Have you ever seen battery in your automobile car, or the devices like cellular phone, radio, torch, toys etc? You might note that these are light weight, compact in size and work at constant voltage, a commercial battery should fulfill all these criteria.

Batteries are classified into following two types.

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12.3.1 Primary Cells/Battery

In this type of batteries redox reaction takes place in only one direction and cannot be reversed. Thus these batteries cannot be recharged or reused. When all amount of electrolyte present in the cell is consumed, they become dead. The most inexpensive and commonly used primary cell is dry cell which we often use in remote control, transistors, flash lights and many other domestic works.

Do You Know?

Technologically, electrochemistry plays an imperative role in many ways in our lives. For example

(i) Batteries that power a variety of appliances vehicles and devices become more compact light weight and consumable day by day due to the research progress in electrochemistry.

(ii) Other domains of modern science in which electrochemistry is significantly involves are electro refining, electroplating, corrosion, protection, electrophoresis etc.

Dry Cell

The common dry cell was first invented by a French chemist Leclanche. The outer body of this cell is made up of zinc which serves as anode where as a graphite rod located at the centre works as cathode. The whole zinc container is lined with porous paper which works as a separator. The region between cathode and anode is filled with a paste of MnO_2, Carbon, NH_4Cl and $ZnCl_2$.

When the cell starts working Zn anode oxidizes to Zn^{+2} ions whereas at graphite cathode Mn^{+4} ions reduces to Mn^{+3} ions.

$$Zn \longrightarrow Zn^{+2} + 2\bar{e} \text{ (anode)}$$

$$2NH_4^+ + 2MnO_2 + 2\bar{e} \longrightarrow Mn_2O_3 + 2NH_3 + H_2O \text{ (cathode)}$$

The electrons generated at anode flow out to the external circuit. This cell produces 1.5 volt electric current and become dead after complete utilizing zinc electrode. 0

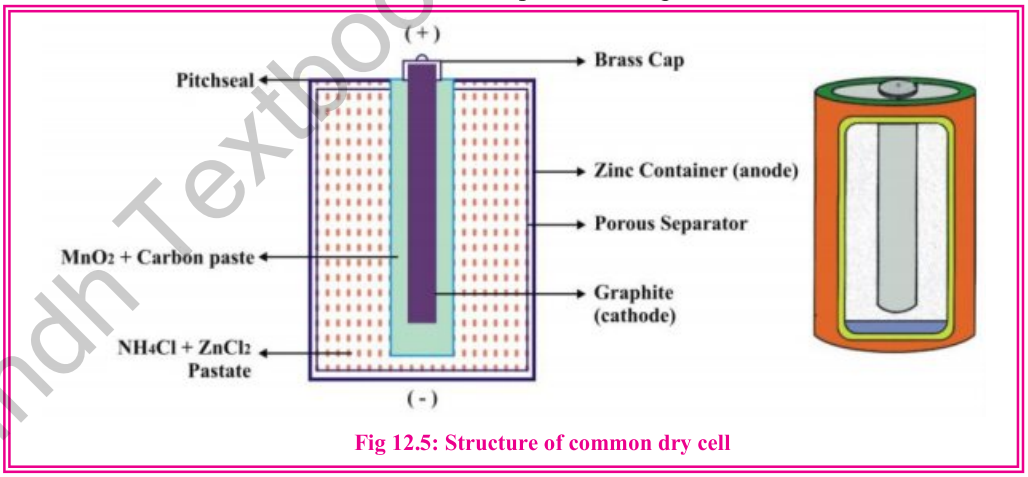

Fig 12.5: Structure of common dry cell

12.3.2 Secondary Battery

These batteries can be recharged by reversing the electricity flow through the cell by utilizing a source of external power supply after every use. Lead storage battery which is commonly known as car battery is an example of secondary battery.

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A 12 volt car battery is made up of six Galvanic cells connected in a series each of which has an emf of 2 volt. All anode plates are made up lead (Pb) while all cathode plates consists of lead coated with PbO_2. Both groups of plates are alternatively suspended into a dilute solution of H_2SO_4 of specific gravity 1.25.
When the battery starts working, lead atoms at anode oxidize to form lead ions.

$$Pb_{(s)} \longrightarrow Pb^{+2}_{(aq)} + 2\bar{e} \text{ (Oxidation at anode)}$$

The Pb^{+2} ions combine with SO_4^{-2} ions to form solid $PbSO_4$ which is deposited on anode.

$$Pb^{+2}_{(aq)} + SO^{-2}_{4(aq)} \longrightarrow PbSO_{4(s)}$$

The electrons generate at anode pushes out into external circuit and then re-enter into cell from cathode (PbO_2) where PbO_2 reduces to Pb^{+2} ions.

$$PbO_{2(s)} + 4H^{+}_{(aq)} + 2\bar{e} \longrightarrow Pb^{+2}_{(aq)} + 2H_2O_{(l)} \text{ (Reduction at cathode)}$$

The Pb^{+2} ions again combine with SO_4^{-2} ions of electrolyte and produce solid $PbSO_4$ which is deposited at cathode plates.
The net chemical change at anode and cathode during discharge may be written as.

$$Pb_{(s)} + SO^{-2}_{4(aq)} \longrightarrow PbSO_{4(s)} + 2\bar{e} \text{ (anode)}$$
$$PbO_{2(s)} + 4H^{+}_{(aq)} + SO^{-2}_{4(aq)} + 2\bar{e} \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)} \text{ (cathode)}$$

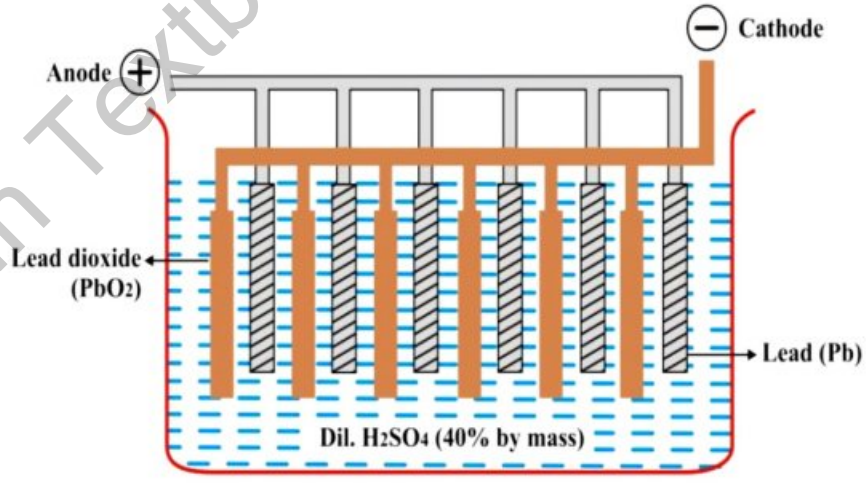

Fig 12.6: Structure of lead storage battery

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As long as lead battery works, its electrolyte (H_2SO_4) uses up gradually which results in covering the electrodes with $PbSO_4$. Thus it becomes unable to release electricity and said to be discharge. This can be checked by lowering in the specific gravity of acid as well as drop of voltage.

How is car battery recharged?

When the battery is needed to be recharged, its anode (Pb) is connected to negative terminal and cathode (PbO_2) is connected to positive terminal of external power supply. In doing so, the redox reaction becomes reverse and may be written as

$$PbSO_{4(s)} + 2\bar{e} \longrightarrow Pb_{(s)} + SO^{-2}_{4(aq)}$$

$$PbSO_{4(s)} + 2H_2O_{(l)} \longrightarrow PbO_{2(s)} + 4H^{+}_{(aq)} + SO^{-2}_{4(aq)} + 2\bar{e}$$

Thus H^+ ions conc. increases gradually in the electrolyte until the specific gravity again reaches the original value and the voltage of the battery is restored.

12.3.3 Fuel Cell

A hydrogen oxygen fuel cell is unique type of Galvanic cell which is based on the reaction between hydrogen and oxygen to produce water and the heat release in the reaction is use to produce electricity. Unlike other batteries, it cannot store reactants hence reactants are fed continuously which utilize in the reaction and the product thus formed remove out continuously. The most familiar Fuel cell is hydrogen oxygen fuel cell. It consists of two porous carbon electrodes having a thin platinum paste. Platinum serves as catalyst. The compartment between the two electrodes is filled with concentration solution of KOH which works as electrolyte. Hydrogen gas fed into the cell from anode side and oxygen from cathode side. These gases after bubbling through their concerned electrode enter into electrolytic solution.

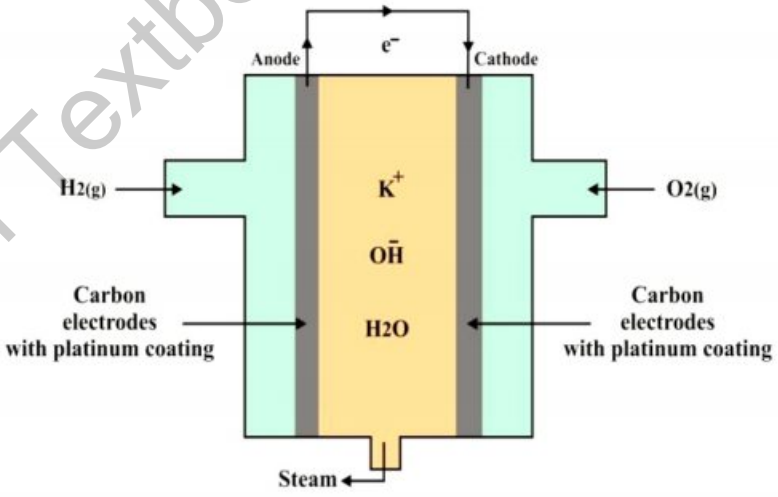

Fig 12.7: Structure of hydrogen oxygen fuel cell

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The reaction at cathode and anode are given below:

$$2H_{2(g)} + 4O\bar{H}_{(aq)} \longrightarrow 4H_2O_{(l)} + 4\bar{e} \text{ (anode)}$$
$$O_{2(g)} + 2H_2O_{(l)} + 4\bar{e} \longrightarrow 4O\bar{H}_{(aq)} \text{ (cathode)}$$
$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} \text{ (overall reaction)}$$

12.4 CORROSION AND ITS PREVENTION

We often noted that metals on exposure to air lose their luster and strength. A brown, green or grayish layer develops on their surface which makes them dull. It is due to chemical interaction between metal and the environment such as oxygen of air and moisture. **"A spontaneous process in which surface atoms of metals get oxidized (harmful oxides) due to the action of surrounding medium is known as corrosion"**. Generally, corrosion occurs on the surface of metal but when the upper surface gets corroded, the atoms in the inner layer get exposed to air and become corroded. This process remains continue up to a certain depth which makes the metal brittle, and weak. However some metals are self protective to corrosion since only the atoms of outer layer oxidize.

Fig 12.8: Corrosion of Iron

The most familiar type of corrosion which we see in daily life is the **"rusting of iron"**. Rust is a brown powderly material produce on the surface of iron appliances due to an oxidation reaction of iron atoms with moist air.

$$4Fe_{(s)} + 3O_{2(g)} \longrightarrow Fe_2O_{3(s)}$$

Various theories describes the phenomena of corrosion but the most adequate is the electrochemical theory which tells that metal atoms serves as cathode and anode and water containing O_2 and CO_2 works as electrolyte which involves in the flow of electrons. In the light of this theory **"corrosion is an electrochemical process"**.

Prevention against corrosion

We aware that iron, copper and various other metals are essentially used in many commercial as well as domestic purpose. To keep them for long period, they should be protected against corrosion by using certain temporary or permanent techniques. Iron Gate of our house is painted so that paint resists the contact of moist air with the metal atoms. Coating of grease or oil in machineries and tools are commonly seen for corrosion control. Often a thin layer of another metal such as zinc, tin or chromium is coated on the metal. For more permanent safety, alloying of metals is carried out.

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Galvanizing

"The process of coating a thin layer of zinc on a metal is known as galvanizing". Since zinc is placed above iron in ECS, it preferably oxidizes and consumes rather than iron and thus protects the iron against corrosion. Galvanizing is carried out either by spraying molten zinc on the surface of iron made material or by dipping the iron sheets into molten zinc.

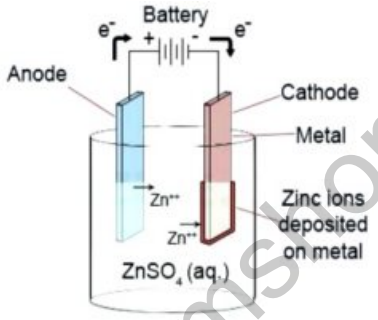

Fig 12.9: Galvanizing of metal sheet

Electroplating

We have studied in sec 12.2 that during the process of electrolysis metal cat ions of electrolytic solution deposited on cathode. Thus a thin layer of tin, chromium etc can be coated on given metal, this process is known as electroplating. Its most common use is electroplating of tin. **"Electroplating is the coating of one metal on the surface of another by involving electrolysis"**. Vegetable oil, food and juice containers are generally tin plated. Tin plating protects iron as long as it remains coated, if scratched then iron exposed to air and starts to get corrosion.

In the electrolytic process, the iron sheets after cleaning, washing and drying are suspended into a bath containing a mixture of stannous chloride and hydrochloric acid. Pure tin is made the anode and the iron sheet works as cathode. On passing the current through the bath, tin starts depositing on the iron sheet and thus iron sheets are tinned electrolytically.

Society, Technology and Science

Solar cell as a source of energy

Solar cell or photovoltaic cell is a device which converts solar energy into useable electricity. The material of most of the solar cell is silicon which serves as semiconductor. When exposed to sun light, it absorbs radiations and transfer energy of photons into electrons of silicons. The electrons after absorbing this energy jump out into the external circuit.

Solar technology provides us an opportunity to make saving in electricity bills. Although the cost of solar panels installation is high but it produces free electricity. Further, remote areas which are beyond electric power transmission, this method of renewable energy becomes popular day by day.

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Activity

The combination of copper and aluminum strips in the citric acid of the lemon serves as the source of electric energy in this activity.
Just insert aluminum foil and copper coin in the lemon such that they remain as far as possible from each other. Now connect these metals to a bulb with the help of wires. The lemon's citric acid serves as an electrolyte. Since aluminum is located in the upper side of ECS, so it oxidizes and releases electrons to the external circuit. Copper on the other hand, undergoes reduction by gaining the electrons and thus bulb is lit by an electric current.

SUMMARY with Key Terms

- **Oxidation** is a chemical process in which electrons are lost by an atom or ion. During this process oxidation number of an element increases.
- **Reduction** is a chemical process in which electrons are gained by an atom or ion. During this process oxidation number of an element decreases.
- **Oxidizing agent** is the specie which oxidizes the other substance and itself get reduced in a redox reaction. Stronger oxidizing agents found in the lower region of ECS. Thus strongest oxidizing agent is fluorine.
- **Reducing agent** is the specie which reduces the other substance but itself get oxidized in a redox reaction. Stronger reducing agent is located on upper region of ECS. Thus strongest reducing agent is Li.
- **Redox reactions** are associated with electron transfer from one species to another. Each redox reaction can be broken into two half reactions, one comprises with the loss of electron and other with the gain of electrons.
- **Electrochemical cell** is a system in which electric current is either producing or use through chemical change.
- **Electrolysis** is the process in which a non spontaneous reaction takes place at the expense of electric energy. During this process ions of electrolyte migrate towards their respective electrodes where they get oxidized or reduced.

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- **Galvanic cell** is a device in which electricity is generated by spontaneous redox reaction. It consists of two half cells and each is made up of a strip of metal immersed into a solution of its metal ions. Cathode in this cell is positive and anode is negative.

- **Salt bridge** is a U-shaped glass tube is which an inert electrolyte is filled along with gel. It allows the flow of ions but prevent the mixing of solution.

- **Cell Potential (E°_{cell})** of a Galvanic cell is the deriving force with which the electrons push out from anode into external circuit. It is measured by connecting two half cells through a voltmeter.

- **Standard electrode potential (E°)** is the difference of potential created between a metal electrode and one molar solution of its ions at 25°C and 1 atmospheric pressure.

- **Standard hydrogen electrode (SHE)** is a reference electrode which assigned as electrode potential of 0.0 volt. It consists of a platinum rod immersed in 1M acid solution where pure hydrogen gas at 1 atmospheric pressure and 25°C is passed.

- **Electrochemical series (ECS)** is an arrangement of various electrode potential in order of their increasing values. All the electrodes above hydrogen in ECS have negative values and they are reducing agent where as below hydrogen electrode potential values are positive indicating that they are oxidizing agent.

- **Corrosion** is electrochemical process in which atoms on the metal surface get oxidized due to environment oxygen and moisture.

- **Galvanizing** is the coating of thin layer of zinc on the metal to protect it form corrosion.

- **Electro tinning** is the coating of tin on metal sheet by using the process of electrolysis. It helps in preventing a metal from corrosion.

- **Battery** is the source of direct current and construct by connecting two or more galvanic cells.

- **Primary batteries/Cells** are not rechargeable; thus when their chemicals have been consumed, they stop doing chemical reactions.

- **Secondary batteries/Cells** are galvanic cells in which chemical reactions are easily being reversible. These cells can be recharged by flowing current in reverse direction.

- **Dry Cell** is a primary cell in which metallic zinc is oxidized to Zn^{+2} ions and liberates electrons which flow along the container to the external circuit.

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- **Lead storage battery** is a portable secondary battery use in automobile in which lead serves as anode and lead oxide (PbO_2) works as cathode.
- **Fuel Cell** is a special type of Galvanic cell which generates electricity by chemical reactions but a continuous supply of reactants and a continuous removal of product are required.

EXERCISE

Multiple Choice Questions

1. Choose the correct answer

(i) The outer body of dry cell serves as anode, it is made up of:
(a) Copper (b) Zinc
(c) Lead (d) Iron

(ii) The conduction of electricity through an electrolytic solution is due to the flow of:
(a) Electrons (b) Ions
(c) Atoms (d) Molecules

(iii) During electrolysis, the reaction that takes place at anode is:
(a) Oxidation (b) Reduction
(c) Hydrolysis (d) Simultaneous oxidation and reduction

(iv) This statement is not correct for lead storage battery:
(a) It can be recharged (b) It is a primary battery
(c) Anode is made up of lead (d) Cathode is made up of lead oxide

(v) In Zn-SHE voltaic cell, the half reaction occurs at anode is:
(a) $Zn^{+2} + 2\bar{e} \longrightarrow Zn$ (b) $Zn \longrightarrow Zn^{+2} + 2\bar{e}$
(c) $2H^{+} + 2\bar{e} \longrightarrow H_2$ (d) $H_2 \longrightarrow 2H^{+} + 2\bar{e}$

(vi) The strongest oxidizing agent in the electro chemical series is:
(a) Li (b) H_2
(c) Cu (d) F_2

(vii) Galvanized rode of iron is coated with:
(a) Nickel (b) Zinc
(c) Chromium (d) Carbon

(viii) Fuel cell is a typical Galvanic cell which is based on the reaction between:
(a) Nitrogen and oxygen (b) Hydrogen and oxygen
(c) Methane and oxygen (d) Hydrogen and zinc

(ix) Oxidation number of Cr in $Na_2Cr_2O_7$ is:
(a) + 3 (b) + 6
(c) + 8 (d) + 12

(x) Which of the following half cell reaction show oxidation:
(a) $Fe^{+3} \rightarrow Fe^{+2}$ (b) $Cl_2 \rightarrow 2Cl^{-}$
(c) $SO_4^{-2} \rightarrow SO_4^{-3}$ (d) $Zn \rightarrow Zn^{+2}$

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Short Questions

1. Define the following:
   - Primary and secondary cell
   - Oxidizing agent and reducing agent
   - Redox reactions
   - Oxidation and reduction
   - Oxidation number

2. What is meant by oxidation number? Determine the oxidation number in following.
   (i) Cr in H_2CrO_4 (ii) S in $K_2S_4O_6$
   (iii) Fe in Fe_3O_4 (iv) Cl in $HClO_4$

3. Define the term standard electrode potential and hydrogen electrode.

4. In the process of electroplating the item to be plated is made cathode, give reason?

5. What is corrosion? What causes it to form? What can be done to prevent its formation?

6. How can you define an electrochemical series? Give its properties.

Descriptive Questions

1. (a) What is meant by electrode potential and standard Hydrogen electrode (SHE).
   (b) Describe how the electrode potential of copper is determined.

2. Sketch a copper-zinc Galvanic cell, write the cell reaction and show the direction of electron flow.

3. What is the difference between a primary cell and secondary cell sketch a diagram of dry cell and explain its working.

4. Balance the following equations by ion electron method.
   (i) $Cr_2O_7^{-2} + I_2 \longrightarrow Cr^{+3} + IO_3^-$ (acidic medium)
   (ii) $MnO_4^- + SO_3^{-2} \longrightarrow Mn^{+2} + SO_4^{-2}$ (basic medium)
   (iii) $MnO_4^- + Cl^- \longrightarrow Mn^{+2} + Cl_2$ (acidic medium)
   (iv) $Cl_2 + O\bar{H} \longrightarrow Cl^- + ClO_3^- + H_2O$ (basic medium)
   (v) $MnO_4^- + C_2O_4^{-2} + H^+ \longrightarrow Mn^{+2} + CO_2 + H_2O$ (acidic medium)
   (vi) $Fe^{+2} + Cr_2O_7^{-2} + H^+ \longrightarrow Fe^{+3} + Cr^{+3} + H_2O$ (acidic medium)

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MCQS ANSWER KEYS

Chap #	MCQs No.									
	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	(ix)	(x)
1	c	d	a	a	a	c	a	b	b	b
2	b	c	d	d	c	b	b	c	a	a
3	c	b	d	a	c	c	c	a	d	c
4	d	b	c	c	b	d	d	d	a	c
5	d	a	c	b	d	b	a	b	a	a
6	d	c	c	c	b	d	a	c	a	c
7	a	c	d	b	d	a	d	c	a	a
8	c	c	d	d	c	a	c	d	b	c
9	c	a	c	c	a	c	b	d	b	b
10	d	c	c	d	b	b	d	d	c	b
11	d	b	c	c	c	a	a	c	c	a
12	b	b	a	b	b	d	b	b	b	d

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APPENDIX - 1

Multiples and Submultiples of SI Units

Prefixes	Symbols	Multiplying Factor	
tera	T	10^{12}	1 000 000 000 000
giga	G	10^{9}	1 000 000 000
mega	M	10^{6}	1 000 000
kilo	K	10^{3}	1 000
hecto	H	10^{2}	100
deca	Da	10	10
deci	D	10^{-1}	0.1
centi	C	10^{-2}	0.01
milli	M	10^{-3}	0.001
micro	U	10^{-6}	0.000 001
nano	n	10^{-9}	0.000 000 001
pico	p	10^{-12}	0.000 000 000 001

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APPENDIX - 2

Atomic Numbers & Atomic Weights

Element	Symbol	Atomic Number	Atomic Weight
Hydrogen	H	1	1.008
Helium	He	2	4.003
Lithium	Li	3	6.938
Beryllium	Be	4	9.0121
Boron	B	5	10.821
Carbon	C	6	12.0116
Nitrogen	N	7	14.007
Oxygen	O	8	15.999
Fluorine	F	9	18.998
Neon	Ne	10	20.179
Sodium	Na	11	22.989
Magnesium	Mg	12	24.307
Aluminum (aluminium)	Al	13	26.9815385
Silicon	Si	14	28.086
Phosphorus	P	15	30.973
Sulfur (sulphur)	S	16	32.059
Chlorine	Cl	17	35.446
Argon	Ar	18	39.948
Potassium	K	19	39.098
Calcium	Ca	20	40.078

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Element	Symbol	Atomic Number	Atomic Weight
Scandium	Sc	21	44.955
Titanium	Ti	22	47.867
Vanadium	V	23	50.941
Chromium	Cr	24	51.996
Manganese	Mn	25	54.938
Iron	Fe	26	55.845
Cobalt	Co	27	58.933
Nickel	Ni	28	58.693
Copper	Cu	29	63.546
Zinc	Zn	30	65.380
Gallium	Ga	31	69.723
Germanium	Ge	32	72.630
Arsenic	As	33	74.921
Selenium	Se	34	78.971
Bromine	Br	35	79.907
Krypton	Kr	36	83.798
Rubidium	Rb	37	85.467
Strontium	Sr	38	87.62
Yttrium	Y	39	88.905
Zirconium	Zr	40	91.224

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Element	Symbol	Atomic Number	Atomic Weight
Niobium	Nb	41	92.906
Molybdenum	Mo	42	95.950
Technetium	Tc	43	97
Ruthenium	Ru	44	101.07
Rhodium	Rh	45	102.905
Palladium	Pd	46	106.42
Silver	Ag	47	107.868
Cadmium	Cd	48	112.414
Indium	In	49	114.818
Tin	Sn	50	118.710
Antimony	Sb	51	121.760
Tellurium	Te	52	127.600
Iodine	I	53	126.904
Xenon	Xe	54	131.293
Cesium (caesium)	Cs	55	132.905
Barium	Ba	56	137.327
Lanthanum	La	57	138.905
Cerium	Ce	58	140.116
Praseodymium	Pr	59	140.907
Neodymium	Nd	60	144.242

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Element	Symbol	Atomic Number	Atomic Weight
Promethium	Pm	61	145
Samarium	Sm	62	150.36
Europium	Eu	63	151.964
Gadolinium	Gd	64	157.25
Terbium	Tb	65	158.925
Dysprosium	Dy	66	162.500
Holmium	Ho	67	164.930
Erbium	Er	68	167.259
Thulium	Tm	69	168.934
Ytterbium	Yb	70	173.045
Lutetium	Lu	71	174.966
Hafnium	Hf	72	178.49
Tantalum	Ta	73	180.947
Tungsten (wolfram)	W	74	183.84
Rhenium	Re	75	186.207
Osmium	Os	76	190.23
Iridium	Ir	77	192.217
Platinum	Pt	78	195.084
Gold	Au	79	196.966
Mercury	Hg	80	200.592

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Element	Symbol	Atomic Number	Atomic Weight
Thallium	Tl	81	204.385
Lead	Pb	82	207.2
Bismuth	Bi	83	208.980
Polonium	Po	84	209
Astatine	At	85	210
Radon	Rn	86	222
Francium	Fr	87	223
Radium	Ra	88	226
Actinium	Ac	89	227
Thorium	Th	90	232.037
Protactinium	Pa	91	231.035
Uranium	U	92	238.028
Neptunium	Np	93	237
Plutonium	Pu	94	244
Americium	Am	95	243
Curium	Cm	96	247
Berkelium	Bk	97	247
Californium	Cf	98	251
Einsteinium	Es	99	252
Fermium	Fm	100	257

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Element	Symbol	Atomic Number	Atomic Weight
Mendelevium	Md	101	258
Nobelium	No	102	259
Lawrencium	Lr	103	262
Rutherfordium	Rf	104	263
Dubnium	Db	105	268
Seaborgium	Sg	106	271
Bohrium	Bh	107	270
Hassium	Hs	108	270
Meitnerium	Mt	109	278
Darmstadtium	Ds	110	281
Roentgenium	Rg	111	281
Copernicium	Cn	112	285
Ununtrium	Uut	113	286
Flerovium	Fl	114	289
Ununpentium	Uup	115	289
Livermorium	Lv	116	293
Ununseptium	Uus	117	294
Ununoctium	Uuo	118	294

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APPENDIX - 3

Constant Values

Physical Constant	Symbols	Values
Speed of light	C	3×10^{8} m/s
Planck constant	H	6.625×10^{-34} J.S
Boltzmann constant	K	1.38×10^{-23} J/K
Universal gas constant	R	8.314 J/(mol.K) 0.082 atm dm^3/mol.K
Avogadro's number	N_A	6.023×10^{23}
Charge of electron	E	1.602×10^{-19} Coulomb
Permitivity of vacuum	$\in_0$	8.84×10^{-12} C^2/J.m
Mass of electron	m_e	9.1×10^{-31} kg
Mass of proton	m_p	1.6726×10^{-27} kg
Mass of neutron	m_n	1.6749×10^{-27} kg
Rydberg constant	R_h	1.09678×10^{7} m^{-1}
Bohr radius	a_0	0.529×10^{-10} m
Molar Volume	V(STP)	22.4dm^3
Standard Temperature	T (STP)	273 K = 0°C
Standard Pressure	P (STP)	101325 Pa = 1 atm
Standard Hydrogen Electrode	SHE	0 volt
Density of water at 4°C	ρ_{H2O}	1 g/cm^3
Specific heat of water	C_{H2O}	4200 J/Kg.K
Ionization constant of water	KW(125°C)	1×10^{-14}

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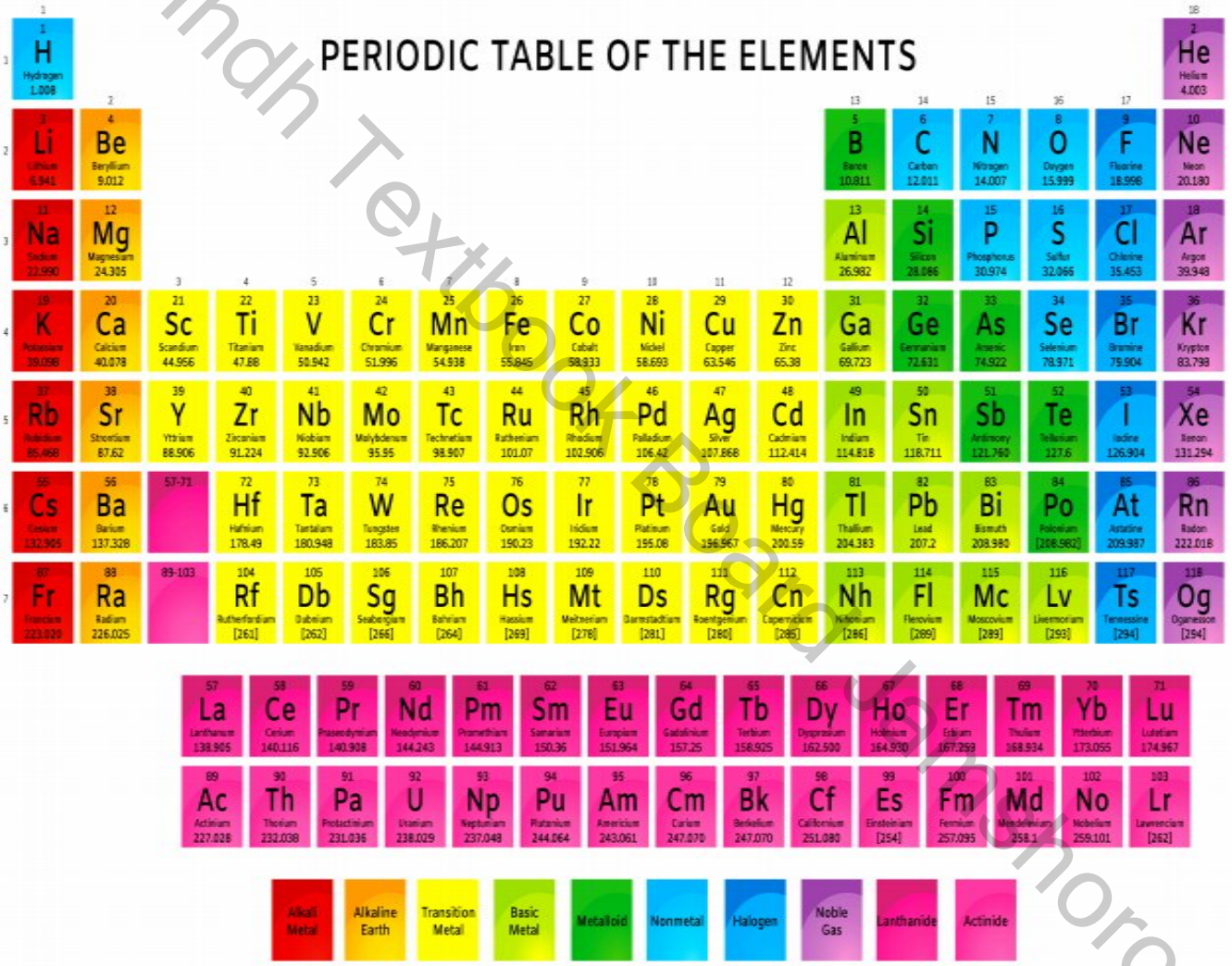
PERIODIC TABLE OF THE ELEMENTS



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