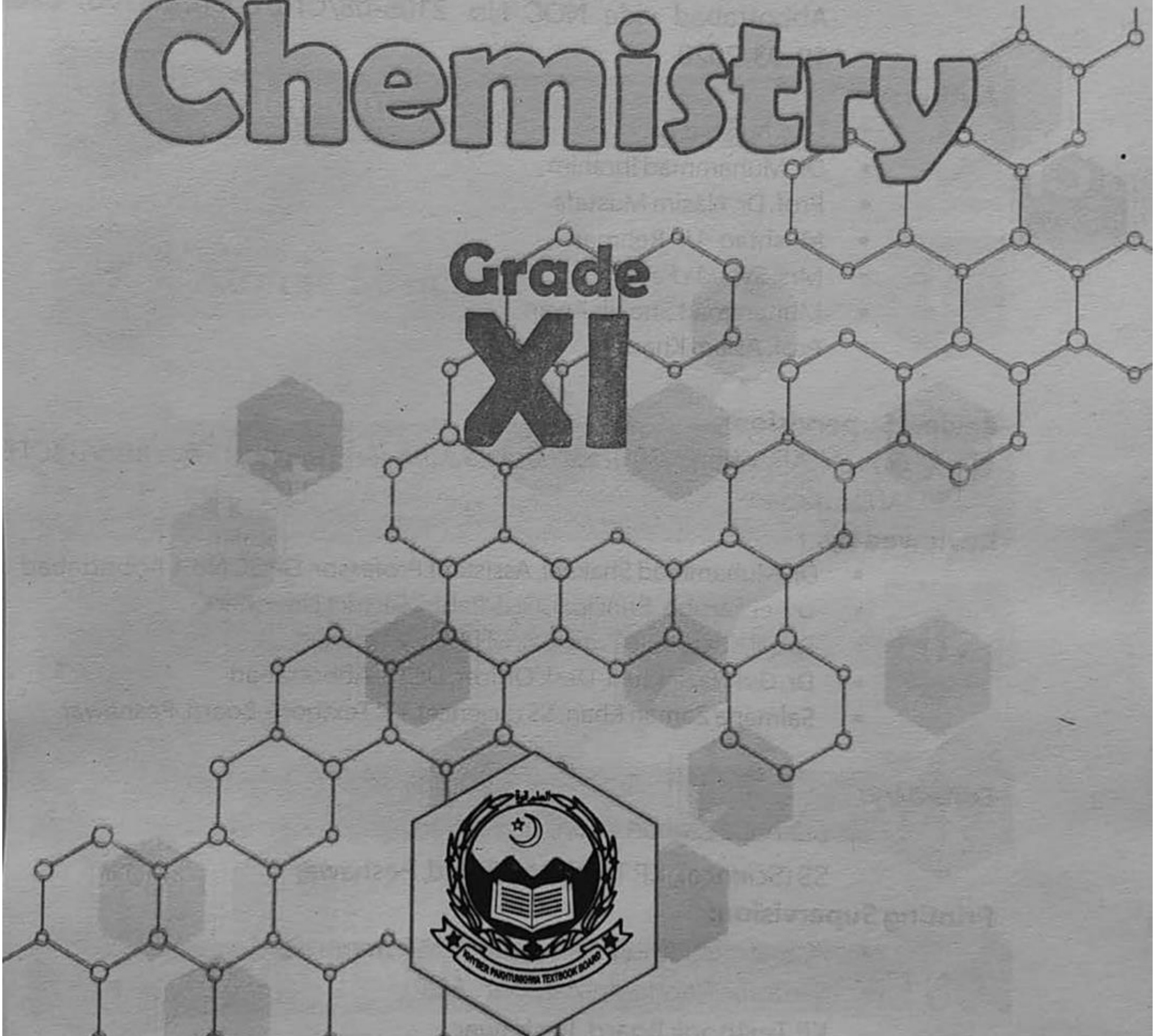
A Textbook of

Chemistry

Grade XI



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Unit - 01

Stoichiometry

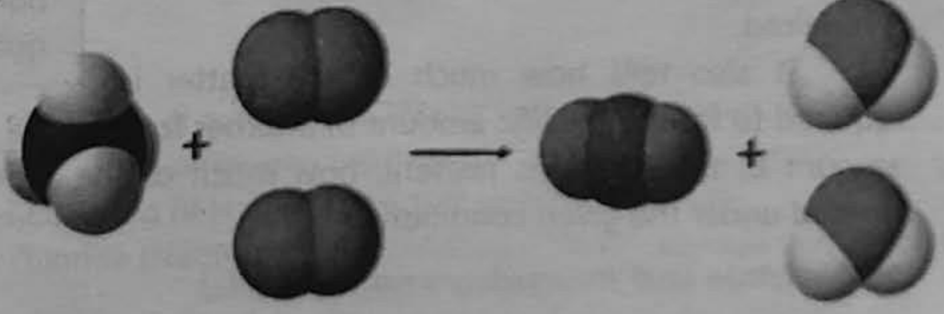
After studying this unit, the students will be able to:

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

Teaching
10

Assessment
01

Weightage %
08



$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

Introduction

Thousands of different reactions are going on in laboratories, factori kitchens, car engines, the atmosphere, the earth beneath you and within yo body. These chemical reactions have a great effect on your lives. There are ma examples of such reactions like conversion of food to energy in the human bod formation of ammonia (fertilizer) by combining nitrogen and hydroge preparation of starch by plants from carbon dioxide and water using energy fro sunlight etc. The main purpose of chemistry is to understand chemical change Chemist calculates the amount of product from the balanced chemical equatio A wrong calculation of amount would result many problems. Therefore, it required for a chemist to calculate the exact amount of reactants and products.

As you have learned in previous grades, chemistry involves in th measurements to find out what happens between atoms and molecules duri the chemical reaction. In this unit, you will learn how to interpret th balanced chemical equation in terms of interacting with moles, representat particles, masses and volumes of gases and their stoichiometric calculations.

Stoichiometry, (Greek words Stoicheion means elements and metron means measurement). Stoichiometry is quantitative chemistry. It is the study of the relationship between relative amounts of substances involved in a chemical reaction. The formula of a compound provides information about the relative amount of each element present.

Stoichiometry is essential when quantitative information about a chemical reaction is required.

It also tells how much of the matter is required to form a specific amount of another form of the matter or if a particu amount of the matter is present, how much of the product could possibly formed under the given conditions.

Tidbit

Analytical chemistry is the branch of chemistry, which deals with the study of analysis of obtaining, processing, characterizing the composition of matter and structure of matter, both qualitatively and quantitatively.

1.1 Mole and Avogadro's number (N_A)

The idea of atomic mass, relative to the mass of the carbon $^{12}_{6}C$ isoto taken as 12 units, has already been discussed in your previous grades. *Rela atomic mass is defined as the mass of one atom of an element compared w* *the mass of $\frac{1}{12}$ of carbon* (C-12).

One gram- atom of any element is the relative atomic mass of the element expressed in grams. For example, the relative atomic mass of chlorine (Cl) is 35.5 atomic mass units (amu) and that of sulphur (S) is 32 amu. Therefore, one gram-atom of chlorine would be 35.5g and one gram-atom of sulphur would be 32 g.

Mole can be defined as the atomic mass, molecular mass, formula mass or ionic mass of a substance expressed in grams.

The concept of the gram - atom is useful because it is impossible to see or weigh individual atoms or even a large number of atoms. We can actually weigh one gram- atom of an element.

One gram-atom of any element contains the same number of atoms. This quantity has been given the name "mole" (mol). It follows that one mole of any element contains the same number of atoms.

Generally speaking, mole is a counting unit just like a dozen (12 similar things) or a gross (144 similar things). Mole, however, is a very large counting unit. It is equal to 6.023×10^{23} similar things, i.e. atoms, molecules, ions, etc. This constant number, present in one mole of a substance, was experimentally determined by an Italian scientist, Amadeo Avogadro and is known as Avogadro's number, represented by N_A. The number of particles (atoms, molecules, ions) in one mole of any substance is called Avogadro's number and is numerically equal to 6.023×10^{23}.

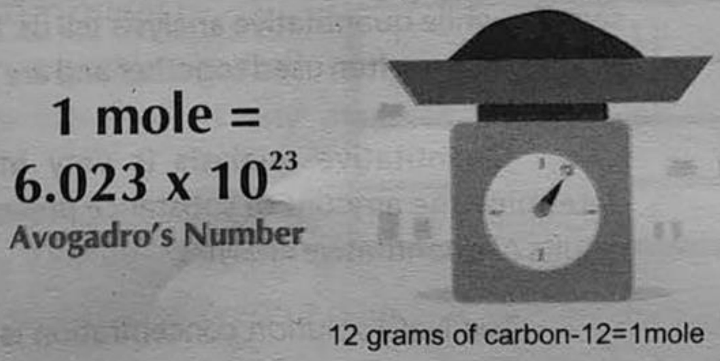


Figure 1.1 Mole and Avogadro's number (N_A)

For example,

1 mol of oxygen (O) = 16g of oxygen = 6.023×10^{23} atoms of oxygen

1 mol of oxygen (O_2) = 32g of oxygen = 6.023×10^{23} molecules of oxygen

1 mol of water (H_2O) = 18g of H_2O = 6.023×10^{23} molecules of H_2O

1 mol of sodium chloride (NaCl) = 58.5g of NaCl=6.023×10^{23} formula units of NaCl

So mole can also be defined as, *"the amount (mass) of a substance, which contains Avogadro's number (6.023×10^{23}) of particles (atoms, ions, molecules, formula units)." It establishes a link between mass of substance and number of particles.*

Table 1.1 Names of the First 20 Elements

Element	Symbol	Atomic Number	Atomic Mass	Element	Symbol	Atomic Number	Atomic Mass
Hydrogen	H	1	1.008	Helium	He	2	4.002
Lithium	Li	3	6.94	Beryllium	Be	4	9.012
Boron	B	5	10.81	Carbon	C	6	12.01
Nitrogen	N	7	14.00	Oxygen	O	8	15.99
Fluorine	F	9	18.99	Neon	Ne	10	20.18
Sodium	Na	11	22.99	Magnesium	Mg	12	24.30
Aluminium	Al	13	26.98	Silicon	Si	14	28.08
Phosphorus	P	15	30.97	Sulphur	S	16	32.06
Chlorine	Cl	17	35.45	Argon	Ar	18	39.94
Potassium	K	19	39.09	Calcium	Ca	20	40.07

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Several methods are used to find the sample. These may be broadly classified as qualitative analysis and quantitative analysis. Qualitative analysis tells us 'what' is in the sample, while quantitative analysis tell us 'how much' is in the sample. These two types of analysis are often used together and are considered in analytical chemistry.

Quantitative analysis is very important in chemistry. Chemists usually determine the amount of substance present in the compound. Here are a few sample results of quantitative analysis:

- The NaCl solution concentration is 0.1 M.
- The chemical reaction produces 5.50 moles.
- Ore contains 64.88% silver by mass.

Beside this, quantitative analysis is very important in medical science. Medical sciences use the result of chemical analysis for example, glucose is determined in blood and urine of diabetics. The cholesterol level in blood is determined by quantitative analysis.

1.2 Mole Calculation

Molar Mass

Molar mass is defined as the mass in grams of one mole of a substance. The term ***molar mass*** is also used to the mass of a mole of any substance (atoms, molecules, formula units or ions); it is the atomic mass of an atom or the sum of the atomic masses of all the atoms in a molecule, an ion or a formula unit (in grams).

You can find the molar mass (mass of one mole) of any substance using the following steps.

- Write down the formula of the substance; for example, formula of sulphuric acid is H_2SO_4
- Work out its molecular mass; sulphuric acid contains two hydrogen atoms (atomic mass 1 amu), one sulphur atom (atomic mass 32 amu) and four oxygen atoms (atomic mass 16 amu). So, formula mass for sulphuric acid

$$\begin{aligned}(H_2SO_4) &= 2H + S + 4O\\ &= (2 \times 1) + (1 \times 32) + (4 \times 16)\\ &= 2 + 32 + 64 = 98 \text{ amu}\end{aligned}$$

- Express this in grams per mole; the molar mass of sulphuric acid is 98 g/mol.

In experimental work, chemists work with varying masses. They cannot always use one mole of a substance. The equation that links the mass of a substance to the number of moles present is,

$$\text{Number of moles (n)} = \frac{\text{mass(in grams)}}{\text{molar mass(in grams per mol)}} \qquad (1.1)$$

Using the above equation, you can convert any mass of a particular substance into moles or vice versa.

As one mole of any substance contains 6.023×10^{23} (Avogadro's number) of atoms, molecules or formula units, one can also develop an equation between the number of moles and the number of particles present. This will lead to the following relationship.

$$\text{Number of moles(n)} = \frac{\text{Number of particles(atoms, molecules, formula units)}}{\text{Particles per mole or Avogadro's number (mol}^{-1})} \qquad (1.2)$$

Or

$$\text{Number of moles(n)} = \frac{\text{Number of particles(atoms, molecules, formula units)}}{6.023 \times 10^{23}\,(\text{mol}^{-1})} \qquad (1.3)$$

The following examples will illustrate the above equations.

Example 1.1

How many moles are there in 60g of sodium hydroxide (NaOH)?

Solution:

The relative formula mass of sodium hydroxide (NaOH) = Na + O + H

So,

Molar mass of NaOH = 23+ 16+ 1= 40 g/mol

$$\text{Number of moles}(n)=\frac{\text{Mass}(g)}{\text{Molar mass of NaOH}(g/mol)}$$

$$\text{number of moles}(n)=\frac{60g}{40g/mol}=1.5mol$$

Reading Check

1. Define relative atomic mass.
2. What is gram atom?

Practice Problem 1.1

1. Calculate the molecular masses (in amu) of the following compounds:
   (a) Sulphur dioxide (SO_2) and (b) Caffeine ($C_8H_{10}N_4O_2$).
   (Atomic mass of C= 12, S = 32, N = 14, H = 1, O = 16)
2. Calculate the No. of moles in 5.68g of iron. (Atomic mass of Fe=55.8)

Example 1.2

What is the mass of 0.5 moles of calcium carbonate ($CaCO_3$)?

Solution:

The relative formula mass of calcium carbonate ($CaCO_3$)= Ca + C + 3O

Molar mass of $CaCO_3$ = 40 + 12 + (16 x 3) = 100g/mol

$$\text{Number of moles}(n)=\frac{\text{Mass}(g)}{\text{Molar Massof } CaCO_3(g/mol)}$$

$$0.5=\frac{\text{mass}(g)}{100g/mol} \quad \text{or} \quad \text{Mass} = 0.5\times100 = 50g$$

Example 1.3

In a certain experiment, 8.50×10^{25} molecules of water were used. Calculate the number of moles of water.

Solution:

Number of H_2O molecules = 8.50×10^{25}

So, $$\text{Number of moles}(n)=\frac{\text{Number of } H_2O \text{ molecules}}{\text{Avogadro's number}}$$

$$\text{Number of moles}(n)=\frac{8.50\times10^{25}}{6.023\times10^{23}}=1.41\times10^2 mol$$

Thus, 1.41×10^2 moles of water would have reacted in this particular experiment.

Practice Problem 1.2

How many Cu atoms are present in 0.5 mol of copper?

Example 1.4

How many formula units are present in 125g of hydrated copper sulpahte ($CuSO_4.5H_2O$)?

Solution:

Mass of hydrated copper sulpahte ($CuSO_4.5H_2O$) = 125g

The relative formula mass of hydrated copper sulphate is,

Formula mass of $CuSO_4.5H_2O$ $= 64 + 32 + (4 \times 16) + [5\times(2\times1 + 16)]$

$= 64+32+64+5(18)=250\text{amu}$

Thus, Molar mass of $CuSO_4.5H_2O$ = 250g/mol

So,

$$\text{Number of moles}(n)=\frac{\text{Mass (g)}}{\text{Molar Mass of } CuSO_4.5H_2O\,(\text{g/mol})}$$

$$\text{Number of moles}(n)=\frac{125\text{g}}{250\text{g/mol}}=0.5\text{mol}$$

Calculate the number of formula units as,

$$\text{Number of moles}(n)=\frac{\text{number of formula units of } CuSO_4.5H_2O}{\text{Avogadro's number}}$$

$$0.5=\frac{\text{number of formula units of } CuSO_4.5H_2O}{6.023\times10^{23}}$$

Number of formula units of $CuSO_4.5H_2O$ $= 0.5 \times 6.023\times10^{23}$

$=3.011\times10^{23}$ formula units

Thus, there are 3.011×10^{23} formula units of $CuSO_4.5H_2O$ in 125g of the salt.

Practice Problem 1.3

What is the mass of 1.204×10^{22} atoms of lead? (Atomic mass of Pb= 207)

Self-Assessment

1. What is the number of moles in each of the following?
   a) 52g of silicon (atomic mass of Si =28)
   b) 1.42g of O_2 (oxygen gas)(atomic mass of O =16)
   c) $3.6\text{x}10^{24}$ atoms of lithium (atomic mass of Li = 7)
   d) $4\text{x}10^{22}$ formula units of potassium chloride (KCl). (atomic mass of K= 39, Cl= 35.5)
2. Which of the following contains the greatest number of particles?
   a) 4g of lithium (atomic mass of Li=7)
   b) 4g of chlorine gas (Cl_2). (atomic mass of Cl=35.5)
   c) 4g of hydrogen gas (H_2). (atomic mass of H=1)
   d) 4g of water (atomic mass of H=1, atomic mass of O =16)

1.2.1 The Mole and Chemical Equations

When iron reacts with sulphur, it produces Iron sulphide (FeS), the equation is,

$$Fe_{(s)} + S_{(s)} \xrightarrow{\text{Heat}} FeS_{(s)}$$

This indicates that equal number of atoms of iron and sulphur are needed to react. We know that 1 mole of iron (56g) and 1 mole of sulphur (32g) contain the same number of atoms. Reaction of these amounts would give 1 mole of iron sulphide (88g).

$$\begin{array}{ccccc} Fe_{(s)} & + & S_{(s)} & \xrightarrow{\text{Heat}} & FeS_{(s)} \\ 1\text{mol} & & 1\text{mol} & & 1\text{mol} \\ 56\text{g} & & 32\text{g} & & 88\text{g} \end{array}$$

The mass of the product is equal to the total mass of the reactants. This is in accordance with the law of conservation of mass (matter), which states *that matter (mass) can neither be created nor destroyed during a chemical reaction.*

In chemistry calculations, we frequently need to calculate the relationship between reactants or products in a chemical reaction. For example, if we know the mass of one reactant, we can find how much product will be formed if the reactant is fully converted into products. At the same time,we can know how much of a second reactant is required to fully react with the first reactant. A chemical equation must, therefore, be balanced because it indicates the number of moles of reactants and products involved in the reaction. There are various ways of doing these calculations because quantities can be expressed either in moles or in mass units.

The stoichiometric calculation can be carried out by the following steps.

1. Write correct and balanced chemical equation.
2. Convert the mass of given substance into moles by dividing with molar mass.
3. Calculate the moles of required substance using their coefficient in the balanced chemical equation.
4. Convert the moles of required substance into mass.

a. Mole – Mole Conversion

If you are given the mole of one substance, you can calculate the moles of the other substances.

Example 1.5

Oxygen can be prepared by the decomposition of potassium chlorate ($KClO_3$). How many moles of $O_{2(g)}$ can be formed by taking 10 moles of $KClO_{3(s)}$

according to the following equation?

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

Solution:

We have the conversion factor from the balanced chemical equation as:

$$2 \text{ mol of } KClO_3 \cong 3 \text{ mol of } O_2$$

$$1 \text{ mol of } KClO_3 \cong \frac{3}{2} \text{ mol of } O_2$$

$$10 \text{ mol of } KClO_3 \cong \frac{3}{2}\times 10 = 15 \text{ moles of oxygen}$$

Practice problem 1.4

How many moles of carbon dioxide will be produced by the complete combustion of 2.0mol of glucose ($C_6H_{12}O_6$) according to the following equation? $C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(g)}$

Self-Assessment

1. Define molar mass.
2. What is Avogadro's number?
3. What is balanced chemical equation?
4. What are stoichiometric calculations?
5. How many ways can you read the given equation?

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

b. Mole – Mass Conversion

If you are given the mole of one substance, you can calculate the mass of the other substances.

Example 1.6

How many grams of CO_2 can be produced by thermally decomposing 8.8 moles of $ZnCO_{3(s)}$?

Solution

$$ZnCO_{3(s)} \longrightarrow ZnO_{(s)} + CO_{2(g)}$$

First, we do a mole – mole ratio calculation and then convert the calculated moles into grams at the end. Thus from balanced equation:

$$1 \text{ mol of } ZnCO_{3(s)} \cong 1 \text{ mol of } CO_2$$

So, $$8.8 \text{ mol of } ZnCO_{3(s)} \cong \frac{1}{1}\times 8.8 \text{ mol of } CO_2 = 8.8 \text{ mol of } CO_{2(g)}$$

Now convert number of $CO_{2(g)}$ into grams, using the formula

$$\text{Number of moles} = \frac{\text{mass(in grams)}}{\text{molar mass(in grams per mol)}}$$

Molar mass of $CO_{2(g)} = C + 2O = 12 + (2 \times 16) = 44 g/mol$

So, mass of $CO_{2(g)}$ produced = moles × molar mass of $CO_{2(g)}$

$$= 8.8 \cancel{mol} \times 44 g/\cancel{mol} = 387.2 g$$

Example 1.7

How many moles of NaCl are produced from 15.5g of HCl, according to the neutralization reaction?

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

Solution

The molar mass of HCl = 1 + 35.5 = 36.5g/mol

$$\text{Number of moles of HCl}(n) = \frac{\text{mass(in grams)}}{\text{molar mass(in grams per mol)}}$$

$$= \frac{15.5 g}{36.5 g/mol} = 0.425 mol$$

By using the equivalency (conversion factor) from the balanced chemical equation, we see that,

1mol of HCl ≅ 1 mol of NaCl

Thus, 0.425 mol of HCl ≅ 0.425 mol of NaCl

Hence, 15.5 g of HCl will produce 0.425 mol of NaCl.

Practice Problem 1.5

- How many grams of $CO_{2(g)}$ can be produced by thermally decomposing 6.5moles of $CaCO_{3(s)}$?

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

- Calculate the mole of copper oxide obtained from 110 g of $CuSO_4$.

$$2CuSO_{4(s)} \longrightarrow 2CuO_{(s)} + 2SO_{2(g)} + O_{2(g)}$$

c. Mass – Mass Conversion

If you are given the mass of one substance, you can calculate the mass of the other substances.

Example 1.8

What mass of aluminium oxide (Al_2O_3) is produced from 14.5g of Al metal, when it reacts completely with oxygen gas according to the following equation?

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

Solution

Convert 14.5g of Al into moles,

Molar mass of Al = 27g/mol

$$\text{Number of moles of Al} = \frac{\text{mass(in grams)}}{\text{Molar mass of Al (in grams per mol)}}$$

$$\text{Number of moles of Al} = \frac{14.5\text{ g}}{27\text{g/mol}} = 0.54\text{mol of Al}$$

Use conversion factor (equivalency) from the balance chemical equation:

$$4\text{ mol of Al} \cong 2\text{ mol of } Al_2O_3$$

$$\text{Therefore, } 0.54\text{ mol of Al} \cong \frac{2}{4}\times 0.54 \cong 0.27\text{ mol of } Al_2O_3$$

Finally, we calculate the mass of Al_2O_3 produced, by converting 0.27 moles of Al_2O_3 into grams. For this, we need molar mass of Al_2O_3 which is,

Molar mass of Al_2O_3 = 2Al + 3O = $(2\times 27)+(3\times 16)$ = 54+48 =102g/mol

So, mass of Al_2O_3 produced = mole × molar mass

$$= 0.27\cancel{\text{mol}} \times 102\text{g}/\cancel{\text{mol}} = 27.54\text{g}$$

Practice problem 1.6

The oxidation of glucose ($C_6H_{12}O_6$) to carbon dioxide (CO_2) and water (H_2O) occurs as:

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

What is the mass of CO_2 produced, when 856g of $C_6H_{12}O_6$ are decomposed?

1.2.2 Calculations Involving Gases

Not all chemical reactions involve solids and liquids. For those reactions in which gases are involved, it is more convenient to measure volumes than masses. In gaseous reactions, weighing of gases as compared to solids and liquids is relatively difficult. It is much easier to measure the volume of a gas as gases weigh very little. But we need to know how the given volume of a gas is related to the number of atoms or molecules present. For this, we take help from the *Avogadro's law, which states that equal volumes of all gases, at the same temperature and pressure, contain equal numbers of particles (atoms or molecules).* (You will study this law in more detail in unit 4).

It has been found experimentally that one mole of any gas at standard temperature (0°C or 273K) and pressure (1 atmosphere) or STP (standard temperature and pressure), occupies a volume of $22.4dm^3$. This is

Tidbit

Units of Volume

1 litre = $1\ dm^3$

1 litre = 1000ml

$1dm^3 = 1000cm^3$

called the molar volume (volume of one mole) of the gas at STP.

Avogadro's law applies to all gases. So making use of this fact, it is easier to convert the volume of any gas into moles or moles into volume using the following relationship.

$$\text{Number of Moles of gas (n)} = \frac{\text{Volume}\left(dm^3\right)\text{at STP}}{\text{molar volume}\left(22.4\ dm^3/mol\right)\text{at STP}} \qquad (1.4)$$

Example 1.9

According to the following equation solid sulphur burns in oxygen and produces SO_2.

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

If 15g of sulphur is burnt, what volume of $SO_{2(g)}$ is produced, at STP?

Solution

Given equation for the reaction at STP

$$\begin{array}{lll} S_{(s)} \quad + & O_{2(g)} & \longrightarrow \quad SO_{2(g)} \\ 1mol & 1\ mol & \qquad\quad 1\ mol \\ 32g & 22.4dm^3 & \qquad\quad 22.4dm^3 \end{array}$$

$$\text{Number of moles of sulphur burnt} = \frac{\text{mass(in grams)}}{\text{molar mass(in grams per mol)}}$$

Atomic mass of S = 32

$$\text{Number of moles of sulphur burnt} = \frac{15g}{32\ g/mol}$$

Number of moles of sulphur = 0.469 mol

From the equation 1 mol of S ≅ 1 mol of $SO_{2(g)}$

Therefore, 0.469 of S ≅ 0.469 of $SO_{2(g)}$

To calculate the volume of $SO_{2(g)}$ produced, we have

$$\text{Number of Moles (n)} = \frac{\text{Volume}\left(dm^3\right)\text{at STP}}{\text{molar volume}\left(22.4\ dm^3/mol\right)}$$

$$0.469\ mol = \frac{\text{Volume}\left(dm^3\right)}{22.4\ dm^3/mol}$$

$$\text{Volume } (dm^3) = 0.469\ \cancel{mol} \times 22.4\ dm^3/\cancel{mol} = 10.51 dm^3$$

Thus, burning 15g of sulphur will produce $10.51 dm^3$ of $SO_{2(g)}$.

Example 1.10

What volume of chlorine gas would be needed at STP to produce 10d of hydrogen chloride (HCl) gas in presence of excess of $H_{2(g)}$, according to th following equation.

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

Given the chemical equation at STP

$$\begin{array}{llll} H_{2(g)} & + \; Cl_{2(g)} & \longrightarrow & 2HCl_{(g)} \\ 1\text{mol} & 1\text{mol} & & 2 \text{ mol} \\ 22.4\ dm^3 & 22.4\ dm^3 & & 2(22.4\ dm^3) = 44.8\ dm^3 \end{array}$$

Here, the volumes of the gases involved are in the same ratio, as the numbers of moles, given by the equation.

From equation,

$$2 \text{ mol of } HCl_{(g)} \cong 1 \text{ mol of } Cl_{2(g)}$$

$$44.8dm^3 \text{ of } HCl_{(g)} \cong 22.4\ dm^3 \text{ of } Cl_{2(g)}$$

Therefore, $$10dm^3 \text{ of } HCl_{(g)} = \frac{22.4\ dm^3}{44.8dm^3} \times 10dm^3Cl_2 = 5dm^3 \text{ of } Cl_{2(g)}$$

Tidbit

Equal volumes of different gases contain the same number of particles, whereas, equal mass of different gases do not contain the same number of particles.

Practice Problem 1.7

1. Calculate the No. of molecules present in 11.5 dm^3 of N_2 at STP.
2. What is the volume, in dm^3, of 3 moles of oxygen gas(O_2) at STP?
3. In an experiment, hydrochloric acid was reacted with calcium carbonate at STP and 80cm^3 of carbon dioxide was produced. Calculate the number of molecules of carbon dioxide given off.

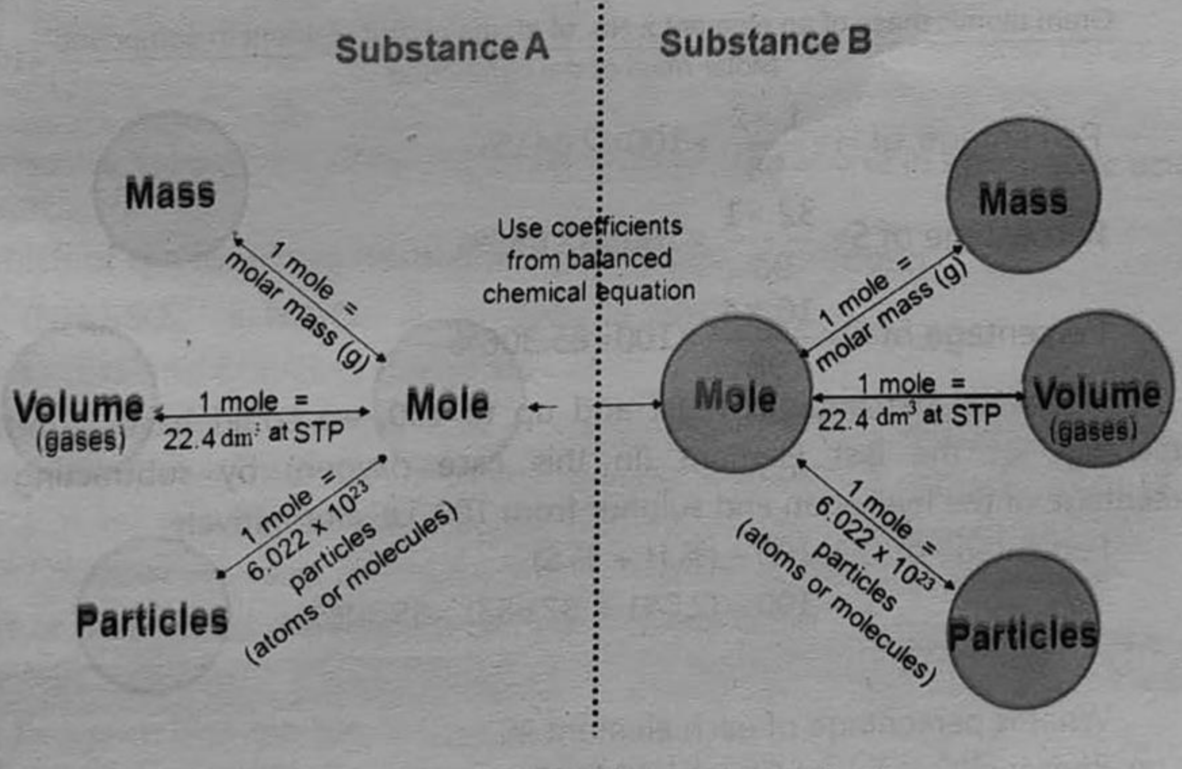


Figure 1.2 Representation of different Conversions

1.3 Percentage Composition

a. Determining Percent Composition from Mass Data

The percent by mass of each element in a compound is called percentage composition of a compound. Once the elements present in a compound are identified and the molecular mass or formula mass of the compound is determined, it is easy to calculate the percentage composition. The following mathematical relationship will help you in this connection.

$$\text{Percentage of an Element} = \frac{\text{Total mass of the element in compound}}{\text{Total mass of the compound}} \times 100 \quad (1.5)$$

Or

$$= \frac{\text{Gram atomic mass of an element x No. of atoms of that element in compound}}{\text{Molar mass of the compound}} \times 100 \quad (1.6)$$

Sum of the individual percentages of all the elements must be equal to 100.

Example 1.11

Calculate the percentage composition of sulphuric acid (H_2SO_4).

Solution

From the formula, we get:

$$\text{Molar mass of } H_2SO_4 = (2\text{x}1) + (1\text{x}32) + (4\text{x}16)$$
$$= 2 + 32 + 62 = 98\text{g/mol}$$

Thus, percentage of each element is calculated as follows,

$$\frac{\text{Gram atomic mass of an element x No. of atoms of that element in compound}}{\text{Molar mass of the compound}} \times 100$$

$$\text{Percentage of H} = \frac{1 \times 2}{98} \times 100 = 2.041\%$$

$$\text{Percentage of S} = \frac{32 \times 1}{98} \times 100 = 32.653\%$$

$$\text{Percentage of O} = \frac{16 \times 4}{98} \times 100 = 65.306\%$$

Since, the percentages must add up to 100, we could have found the percentage of the last element (in this case oxygen) by subtracting the percentage of the hydrogen and sulphur from 100. i.e. alternatively,

$$\text{Percentage of O} = 100 - (\%\ \text{H} + \%\ \text{S})$$
$$= 100 - (2.041 + 32.653) = 65.306\%$$

Practice Problem 1.8

What is percentage of each element in,

(a) Benzene (C_6H_6) (b) Glucose ($C_6H_{12}O_6$)

b. Determining Masses from Percent Composition Data

You can also perform the reverse calculation, determining the mass of an element in a given sample, if we know the total mass of the sample and its percent composition.

Example 1.12

You have a 10.0g sample of a metal alloy that contains only aluminium and zinc. If the sample is 36% aluminium by mass, what masses of Al and Zn are present?

Solution

You are told that the sample is 36 % Aluminium by mass. Because the only other component is zinc, it must make up the remaining 64% of the mass. You can multiply each of these percentages by 10.0 grams to find the masses of each element.

% of Aluminium = 36

% of Zn = 100 – 36 = 64%

Mass of sample = 10g

To find masses of Al and Zn,

$$\text{Mass of Al} = \frac{36}{10\cancel{0}} \times 1\cancel{0} = 3.6\text{g}$$

$$\text{Mass of Zn} = \frac{64}{10\cancel{0}} \times 1\cancel{0} = 6.4\text{g}$$

Practice problem 1.9

a. Calculate the percent composition by mass of H, P and O in Phosphoric acid (H_3PO_4).

b. Which of the following has highest percentage of nitrogen

i. $(NH_4)_2SO_4$ ii. NH_4Cl iii. NH_4NO_3 iv. $(NH_4)_3PO_4$

1.4 Excess and Limiting Reagents

Limiting Reagent: *A reactant that is consumed earlier during a chemical reaction is called limiting reagent.* It can also be defined as the reagent *which produces the least number of moles of products in a chemical reaction.* It limits or determines the amount of products formed in the reaction.

Reading Check

What is percentage composition?

Excess Reagent: *The reactant whose some amount remains unreacted or unused after the completion of the reaction is called excess reagent.*

Consider the reaction of hydrogen and oxygen to form water.

$$2H_{2(g)} + O_{2(g)} \xrightarrow{\text{Heat}} 2H_2O_{(l)}$$

Tidbit

In the chemical industry, you need to know the limiting reactant in order to get the maximum yield of product at minimum cost.

A brief inspection of this balanced chemical equation indicates that one mole of oxygen, (if it is completely consumed) requires two moles of hydrogen to form 2moles of water. If one carefully measures 1 mole of oxygen and 2 moles of hydrogen, ignites them, one would get 2 moles of water. When the stoichiometric amounts (as given in the balanced chemical equation) are reacted together, there will be no reactants left at the end of the reaction.

In actual practice, however, due to one reason or the other, one may n take the amount of the reactants in stoichiometric ratios, as demanded by t balanced chemical equation. For example, one may take 5 moles of oxygen fo moles of hydrogen to form water. Since the above balanced chemical equati indicates that,

$$2 \text{ moles of } H_2 \cong 1 \text{ mole of } O_2$$

$$\text{Therefore, } 4 \text{ moles of } H_2 \cong \frac{1}{2} \times 4 = 2 \text{ moles of } O_2$$

Thus, out of 5 moles of oxygen available, only 2 moles will react with moles of hydrogen and the remaining 3 moles of oxygen will be left unreact The unreacted oxygen is termed as "reactant (reagent) in excess" and hydrog which is consumed earlier, is termed as "limiting reagent". In a chemical reacti the maximum amount of the product formed is controlled by the amount of "limiting reagent" because as soon as the limiting reagent is consumed, reaction stops and no more products are formed.

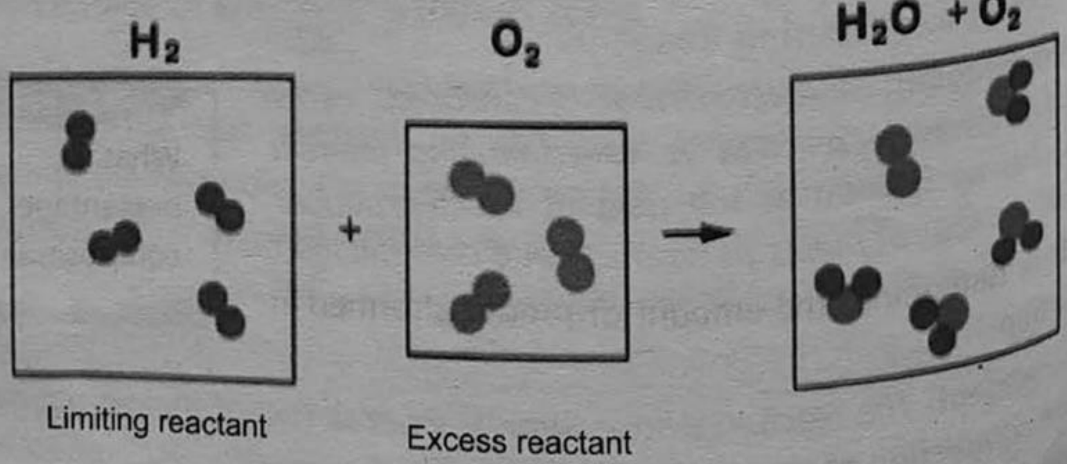


Figure 1.3 Limiting and excess reagent

In many situations, it is inconvenient, or time consuming to weigh the exact amounts of two or more reactants needed to produce a given amount of the product. Thus, almost, all reactions that go to completion have a limiting reagent. Sometimes, it is obvious while in other situation it needs calculation to identify it. Following are the steps that help in identifying the limiting reagent.

1. The amounts of the reactants (if given in mass units) are first converted into moles.
2. Using balanced chemical equations, the moles of the required product are calculated from the available moles of each reactant.
3. The reactant, which gives the least number of moles of the required product, will be the limiting reagent.
   Alternatively, comparison of the moles of reactants with help of balanced chemical equation also helps in identifying the limiting reagent.

Example 1.13

Carbonic acid (H_2CO_3) can be prepared according to the following reaction.

$$CO_{2(g)} + H_2O_{(l)} \longrightarrow H_2CO_{3(aq)}$$

If 120g of CO_2 is dissolved in 80g of water then,

(a) Identify the limiting reagent

(b) Calculate the maximum amount (in grams) of the product formed.

Solution

(a) Given the balanced chemical equation

$$CO_{2(g)} + H_2O_{(l)} \longrightarrow H_2CO_{3(aq)}$$

First we convert the amounts of both the reactants into moles,

Mass of CO_2 = 120g

Molar mass of CO_2 = (1 x 12) +(2x16) = 12+32 =44g/mol

$$\text{Moles of } CO_2 = \frac{120g}{44g/mol} = 2.72 \text{ moles}$$

And mass of H_2O = 80g

Molar mass of H_2O = (2x1) +(1x16) = 18g/mol

$$\text{Moles of } H_2O = \frac{80g}{18g/mol} = 4.44 \text{ moles}$$

Now calculate the number of moles of the product (H_2CO_3) from the number of moles of each of the reactants.

From balanced chemical equation, we have,

$$1 \text{ mol of } CO_2 \cong 1 \text{ mol of } H_2CO_3$$

Therefore, $2.72 \text{ mol of } CO_2 \cong 2.72 \text{ mol of } H_2CO_3$

Similarly, $1\text{mol of } H_2O \cong 1 \text{ mol of } H_2CO_3$

Therefore, $4.44 \text{ mol of } H_2O \cong 4.44 \text{ mol of } H_2CO_3$

Since 120g of CO_2 produces less number of moles (2.72 moles) of carbo acid, so CO_2 is the limiting regent and H_2O is the reagent in excess.

(b) The amount of product (H_2CO_3) is controlled by the amount of limitin reagent. Therefore, the maximum amount (in moles) of the product formed be 2.72 moles.

We have the molar mass of H_2CO_3=(2x1)+(1x12)+(3x16)= 62g/mol

$$\text{Therefore, moles of } H_2CO_3 = \frac{\text{Mass(g)}}{\text{Molar mass}}$$

$$2.727 \text{ mol}= \frac{\text{Mass(g)}}{62\text{g/mol}}$$

$$\text{Mass of } H_2CO_3 = 2.727\cancel{\text{mol}} \times 62\text{g/}\cancel{\text{mol}}$$

$$= 169.07\text{g}$$

Thus, the maximum amount of H_2CO_3 produced will be 169.07g.

Practice Problem 1.10

If 0.600 mol of chlorine gas is reacted with 0.500mol of aluminium me to produce aluminium chloride, which reactant is in excess? How many moles aluminium chloride can be produced during the reaction?

1.5 Theoretical Yield and Actual Yield as Percentage

Yield: *The yield of a chemical reaction is the amount of product th produced from given amount of reactants.*

When we perform stoichiometric calculations, we are trying to find out theoretical yield based on the amount of reactants available.

Theoretical yield: *The amount of the product calculated on the bas balanced chemical equation is called theoretical yield of the reaction.* Ac yields can only be determined by performing the experiment and measuring final mass of the product.

It is the calculated quantity of the product that we should get, using starting amounts of the reactants. However, in actual practice, you will often less amount of the yield (product) than the theoretical yield. This is called ac yield of the reaction.

Actual yield: *The actual yield is the amount of product that is actually produced during a chemical reaction by performing an experiment. Other names, used for actual yield, are experimental yield or practical yield.*

The actual yield of a reaction is always less than the theoretical yield. There are number of reasons. Few are given below.

- The reaction may have not gone to completion, i.e. all the amount of the reactants may not have converted into products due to reversibility of the reaction.
- Some of the amounts of the reactants may have converted into some other products by a side reaction or chain reaction.
- It may be difficult to recover all of the products from the reaction medium and some of the products might be lost during recovery. This is called mechanical loss of the product (Human error).
- Reaction conditions (like temperature, pressure, pH etc) might have been disturbed.

Example 1.14

When 1.92 g of magnesium was heated in excess of oxygen. Calculate the theoretical yield of magnesium oxide (MgO).

Solution:

$$2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO_{(s)}$$

Molar mass of Mg = 24g/mol

$$\text{Number of moles of Mg} = \frac{\text{Mass of Mg}}{\text{Molar mass of Mg}} = \frac{1.92}{24} = 0.08 \text{ mol}$$

According to above equation,

2 mol of Mg ≅ 2 mol of MgO

So, 0.08 moles of Mg ≅ 0.08 mol of MgO

Molar mass of MgO = 24 + 16 = 40 g/mol

Theoretical yield of MgO = Number of moles of MgO x molar mass of MgO

Theoretical yield of MgO = 0.08 x 40 = 3.2g

Percent Yield

The efficiency of a chemical reaction is determined with the help of percent yield, which is actually a comparison of actual yield and theoretical yield.

Percent yield can be calculated using the following expression:

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

Example 1.15

Heating 24.8g of copper carbonate ($CuCO_3$) in a crucible produced only 13.9g of copper oxide (CuO). What is the percentage yield of copper oxide?

Solution

The actual yield of CuO = 13.9g

Theoretical yield is calculated from the balanced chemical equation which is:

$$CuCO_{3(s} \xrightarrow{Heat} CuO_{(s)} + O_{2(g)}$$

1mol → 1mol 1mol

64+12+(16x3)=124 → 64+16=80

$$\text{Moles of } CuCO_3 = \frac{24.8}{124} = 0.2$$

According to balanced chemical equation,

1 mol of $CuCO_3$ ≅1 mol of CuO

0.2 mol of $CuCO_3$ ≅ 0.2 mol of CuO

So,

Mass of CuO = Theoretical yield = 0.2 x 80 = 16.0g

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

$$\text{Percentage Yield of Copper oxide} = \frac{13.9}{16.0} \times 100$$

Percentage Yield of copper oxide = 86.87%

Practice Problem 1.11

If 1.274 g of copper sulphate ($CuSO_4$) reacts with excess of zinc metal, 0.392 g copper metal was obtained during the chemical reaction. Calculate the percentage yield of Cu metal.

$$CuSO_{4(aq)} + Zn_{(s)} \longrightarrow Cu_{(s)} + ZnSO_{4(aq)}$$

Self-Assessment

1. Show the stepwise sequence that how mass (reactants) into mass (products) can be converted.
2. Define the molar volume of the gas. Convert $5dm^3$ into cubic centimetre (cm^3).
3. Define limiting reagent.
4. What steps are used for identifying the limiting reagent?
5. What is percentage yield?
6. Why actual yield of a reaction is always less than the theoretical yield?

KEY POINTS

- Stoichiometry is quantitative chemistry, which deals with the calculations based on balanced chemical equations.
- Mole is the atomic mass, molecular mass or formula mass of an element, molecule or ionic compound, respectively, expressed in grams.
- Avogadro's number is the number of particles in one mole of substance. It is a constant number, equal to 6.023×10^{23}.
- The idea of mole can be applied to chemical equations, to calculate the amounts of reactants consumed or that of the products formed.
- Stoichiometric problems can be solved, using mole- mole, mole – mass and mass – mass conversions.
- When gases are involved, the concept of molar volume of the gas at STP ($22.4 dm^3$) is helpful to calculate the number of moles and volumes.
- Percentage composition of a compound is the number of grams of each element per 100g of the compound.
- Limiting reagent in a chemical reaction is the one which is consumed earlier or which gives least amount of product from a balanced chemical equation.
- Excess reagent is the one, which is left behind unreacted, after the reaction is over.
- Theoretical yield is the amount of the product calculated on the basis of balanced chemical equation.
- Actual yield is the amount of product that is actually produced experimentally during a chemical reaction.
- The percent yield of a reaction tells us what percentage of the possible amount of product was actually obtained.
- Chemists use percentage yield to express the efficiency of a chemical reaction.

EXERCISE

Choose the Correct Option.

1. The mass of an atom(element) compared with the mass of one atom of C - 12 is called,
   a. One mole
   b. Gram atomic mass
   c. Atomic number
   d. Relative atomic mass
2. Which of the following is not true for a mole?
   a. It is a counting unit
   b. It is the gram atomic or gram formula mass of a substance
   c. It contains 6.023×10^{23} particles
   d. It contains different number of particles for different substances
3. What is the mass (in grams) of 5 moles of water (H_2O)?
   a. 90g
   b. 36g
   c. 18g
   d. 100g
4. The number of molecules in 22g of CO_2 is
   a. 6.023×10^{23}
   b. 3.011×10^{23}
   c. 6.023×10^{21}
   d. 6.023×10^{22}
5. What will be the values of temperature and pressure at standard condition (STP),
   a. 100°C, 1 atm
   b. 298K, 1atm
   c. 273K, 760mm Hg
   d. 0°C, 760cm Hg
6. The molar volume of SO_2 gas at STP is,
   a. $64dm^3$
   b. $24dm^3$
   c. $22.4dm^3$
   d. $22.4cm^3$
7. The percentage of Ca in $CaCO_3$ is,
   a. 12%
   b. 10%
   c. 48%
   d. 40%
8. Given the equation: $CO_{2(g)} + C_{(s)} \longrightarrow 2CO_{(g)}$
   Which of the following equivalences is not correct for the reaction,
   a. $1mol\ CO_2 \cong 2\ mol\ CO$
   b. $1mol\ C \cong 56g\ CO$
   c. $44g\ CO_2 \cong 28g\ CO$
   d. $44g\ CO_2 \cong 12g\ C$
9. A limiting reactant is one
   a. Which is present in maximum amount
   b. Which produces minimum No. of moles of product
   c. Which produces maximum No. of moles of product
   d. Does not affect the amount of product

10. Efficiency of chemical reaction can be checked by calculating
    a. Actual yield
    b. Theoretical Yield
    c. Percentage Yield
    d. Amount of the reactant unused
11. Actual yield will reach the ideal (theoretical) value if the % yield of the reaction is,
    a. 10%
    b. 50%
    c. 90%
    d. 100%
12. The maximum No. of moles are present in
    a. 11.2 dm^3 of H_2 gas at STP
    b. 44.8 dm^3 of N_2 gas at STP
    c. 67.2 dm^3 of CO_2 gas at STP
    d. 22.4 dm^3 of O_2 gas at STP

Short Questions

1. What is gram atom? Why the concept of gram atom is useful in chemistry?
2. Explain why balanced chemical equations are used in stoichiometric problems?
3. How will you identify the limiting reagent in a reaction and how it controls the amount of product formed?
4. Why the actual yield is always less than the theoretical yield of a reaction?
5. Can you make the distinction between limiting and excess reagent?

Numerical Questions

1. The mass of 5 moles of an element X is 60g. Calculate the molar mass of this element. Also, name the element. Ans: 12, Carbon (C).
2. Calculate the molecular/formula masses of the following compounds.
   (Atomic mass of C= 12, K = 39, Cr = 52, Al= 27, H = 1, O = 16)
   (a) C_2H_5OH (b) Al_2O_3 (c) $K_2Cr_2O_7$ Ans: (a). 46, (b). 102, (c). 294
3. Calculate the mass in grams of (a) 7.75 moles of Al_2O_3, (b) 15 moles of H_2SO_4 (c) 1.0 x 10^{25} molecules of H_2O. (Atomic mass of S= 32, Al= 27, H = 1, O = 16)
   Ans: (a). 790.5g, (b). 994g, (c). 16.60g
4. How many moles are present in each of the following samples? (Atomic mass of H= 1, C= 12, O =16, Na= 23, Mg= 24, S = 32, Cl = 35.5, Ca =40)
   a. 30g of MgS
   b. 75g of Ca
   c. 8.85kg of CO_2
   d. 40 dm^3 of O_2 gas at STP
   e. 7.5 x 10^{20} molecules of C_6H_6
   f. 40g of NaCl
   Ans.: (a) 0.5357mol, (b) 1.875 mol (c)201.1363mol, (d) 1.7857 mol (e) 1.2452 x10^{-3} mol (f) 0.6837 moles
5. Calculate the mass of Mg metal required to consume 2560g of CO_2 in the reaction. (Atomic mass of C =12, Mg = 24, O=16)
   $$2Mg_{(s)} + CO_{2(g)} \longrightarrow 2MgO_{(s)} + C_{(s)}$$
   Ans: 2.79g

Descriptive Questions

1. (a) Define and explain mole and Avogadro's number with examples.

   (b) Given the equation,

   $$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)} + \text{Heat}$$

   How can this equation be read in terms of particles, moles and masses?

   (c) Define molar volume of a gas. What will be the volume of 60g of NH_3 at STP? (Atomic mass of N= 14, H= 1) Ans: 79.05 dm^3

2. (a) What do you mean by percentage composition of a compound? How the percentage of an element is calculated in a compound.

   (b) Calculate the percentage composition of each element in the following compounds. (Atomic mass of Al= 27, K = 39, Mg=24, Mn=55, Na =23, O=16 S= 32)

   (i) $MgSO_4$ (ii) $KMnO_4$ (iii) $NaAl(SO_4)_2$

   Ans:
   (i) % Mg=20, % S=26.66, %O=53.33
   (ii) %K = 24.68, % Mn=34.81, %O = 40.50
   (iii) % Na=9.50, % Al=11.15, %S=26.44, %O=52.89

3. When steam is passed through red-hot carbon (a mixture of H_2 and CO gas) called water gas, is formed.

   $$C_{(s)} + H_2O_{(g)} \longrightarrow CO_{(g)} + H_{2(g)}$$

   (a) Which is the limiting reagent if 24.5g of carbon is mixed with 1.89 moles of water vapours?

   (b) Calculate the amount (in grams) of the excess reagent left unreacted. (Atomic mass of C=12, O=16, H= 1)

   Ans: (a) Water is the limiting reagent. (b).1.812g

4. (a) Calculate the percentage yield if 6.53g of hydrogen gas is produced when 5 mole of zinc is consumed in the reaction. (Atomic mass of Zn= 65.38, Cl= 35.5, H= 1)

   $$Zn_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_{2(g)}$$

   Ans: 65.3%

   (b) The percentage yield of the following reaction is 85%.

   $$2Al_{(s)} + 3Cl_{2(aq)} \longrightarrow 2AlCl_{3(s)}$$

   How many grams of $AlCl_{3(s)}$ will be actually obtained from 100g of aluminium metal? (Atomic mass of Al= 27, Cl= 35.5)

   Ans: 420.19g

(c) Given the equation,

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

at STP. How many moles of NH_3 would be formed if $6.3dm^3$ of N_2 gas react with an excess of H_2? (Atomic mass of N=14, H=1) Ans: 0.56 mol

5. Given the equation,

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

(a) How many moles of water will be obtained by burning 5.6 moles of O_2 in an excess of H_2?

(b) How many moles of O_2 would be needed to react with 58.5g of H_2 to form water?

(c) How many grams of H_2 would be needed to form 120g of H_2O?

(Atomic mass of O= 16, H= 1)

Ans: (a) 11.2 mol, (b) 14.625 mol, (c) 13.33g

Project

- Take a glass and add $250cm^3$ of water to it. Find out the number of water molecules present in it.
- Take another glass and add $250cm^3$ of water to it. Then add 200g of sugar into it. Now find out the number of sugar molecules in the given sample. Also, find out the total number of molecules present in sugar solution (water + sugar) in the glass.

Unit - 02

Atomic Structure

After studying this unit, the students will be able to:

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

Teaching	Assessment	Weightage %
10	01	08

Introduction

A Greek philosopher Democritus for the first time in the fifth century B.C, suggested that all kinds of matter is composed of small microscopic particles known as atoms that cannot be further divided. Later in 19th Century, after the development of John Dalton's atomic theory, several important discoveries were made that led to a new understanding of the atom. A number of experiments proved that the atom is divisible and consists of subatomic particles called electrons, neutrons and protons. Most of the mass of an atom is concentrated in a central unit called nucleus, which contains protons and neutrons. The nucleus is surrounded by orbits, which have the light particles electrons, which are responsible for most of the volume occupied by the atom. The electron was the first subatomic particle to be discovered, followed by discoveries of the proton and the neutron. These sub-atomic particles are of much significance for a chemist, since the arrangement of these particles within an atom determines its physical and chemical properties.

In the previous grades, you have learnt about the discoveries of the nucleus, Rutherford's atomic model, Bohr's atomic model and shell. In this unit, you will be able to calculate the atomic radii, energy, wavelength and frequency of radiations absorbed or emitted by electronic transitions. You will also learn about the production, properties and types of X – rays, hydrogen spectrum and quantum numbers which will improve your existing understanding of the atom.

Tidbit

Word atom is derived from the Greek word 'atomos' meaning indivisible.

2.1 Discharge Tube Experiments (The Discovery of Electron)

The development of John Dalton's atomic theory led towards the invention of new instruments. For example, the Crookes tube or gas discharge tube, developed by Sir William Crookes, opened the door to discover the subatomic particles of an atom. The discovery of electron is attributed to the knowledge derived from discharge tube experiments.

A gas discharge tube consists of a glass tube. Two metallic electrodes, acting as cathode and anode are sealed in the walls of a glass tube. The tube is attached to a vacuum pump by means of a small tube, so that the conduction of electricity through a gas may be studied at any desired value of low pressure. A high voltage source is connected to the electrodes.

William Crookes conducted a series of experiments in the late 19th century using a gas discharge tube to study the passage of electric current through gases. His apparatus was consisted of a glass tube with meal electrodes, anode and cathode, on the two ends of the tube. The tube can be connected to a vacuum pump so that the electrical conduction through the gas may be studies at any desired value of low pressure. A high voltage sources is connected to the electrodes.

It was observed by Crookes, that the gas inside the tube, at ordinary pressure, did not conduct electricity, even when the electrodes were connected to a source of very high potential, of reduced by means of the vacuum pump and the electrodes were connected to a high voltage of 5000 – 10,000 volts, an electric discharge was observed through the gas, producing a uniform glow inside the tube. This happened at a pressure of about 0.1mm Hg. When the pressure inside the tube was further reduced to about 0.01mm Hg, the original uniform glow disappeared and the whole tube was filled up by dark space and no luminous discharge was observed. At this stage, the electrical resistance between the two electrodes became very high and i became difficult to maintain the discharge, unless the potential difference betwee the electrodes was very high (approximately 10,000 volts). Under this conditio some rays (faint fluorescent light) was produced which created fluorescence on the glass wall opposite to the cathode. When different gases were used in the discharge tube, under similar conditions, with different metals used as electrodes, the same rays were produced. These rays were called cathode rays by Goldstein (1886), since these were originated from cathode.

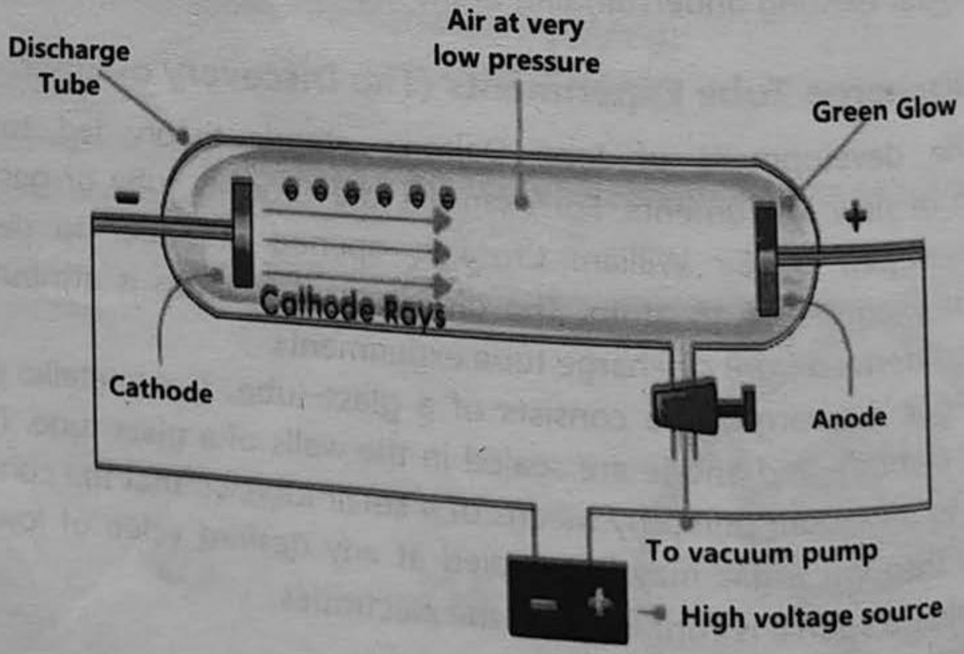


Figure 2.1 Cathode ray tube

Later J.J. Thomson and other scientists made further investigations on cathode rays and its properties which ultimately lead to the discovery of electron which were by then called cathode rays.

Note: Crookes used cold cathode at his time in this system. The gas particles inside the tube were ionized at anode and became positively charged particles which were attracted towards cathode due to its negative charge and collided with it with high speed which resulted in emission of electrons from cathode. These electrons then rushed towards anode. In modern cathode ray tube, hot cathode is used. Due to high temperature the electrons are energized and expelled from the cathode due to attraction of anode and move with high speed towards anode. However, in addition to thermionic effect, the phenomenon of ionization of gas (as in the case of cold cathode) cannot be ignored in this case.

2.1.1 Characteristics of Cathode Rays

Later on, a number of experiments, performed by various scientists, showed that the cathode rays have the following characteristics.

i. These rays travel in straight lines perpendicular to the cathode surface and away from the cathode.
ii. They produce a sharp shadow if an opaque object is placed in their path as shown in figure 2.2.
iii. These rays produce fluorescence (a glow) when they strike the wall of the discharge tube.
iv. These rays heat up the metal on which they fall.
v. These rays can move a small pin wheel placed in their path as shown in figure 2.3, as these rays are bunch of moving particles with definite mass and kinetic energy.
vi. These rays produce X-rays when they strike heavy metal anode.
vii. These rays can ionize the gases.
viii. These rays can cause a chemical change in a material on which they fall, as they have reducing effect.
ix. These rays can penetrate metallic sheets like Aluminum and Gold.
x. Cathode rays are negatively charged particles as when these rays are through an electric field, they are deflected towards positively charge plate/ electrode as shown in figure 2.4.
xi. These rays are also deflected by magnetic field as shown in figure 2.5.
xii. The charge to mass ratio (e/m) of cathode rays (electron) is 1.7588×10^{11}C/kg.
xiii. Charge (e) on cathode rays (electron) is 1.6022×10^{-19}C.

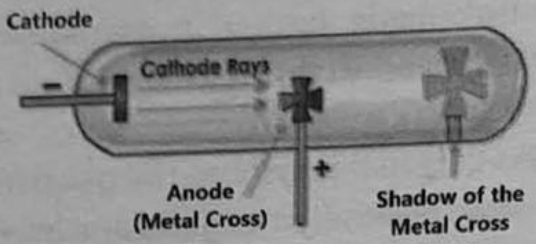


Fig 2.2 Cathode Rays Casting Shadows

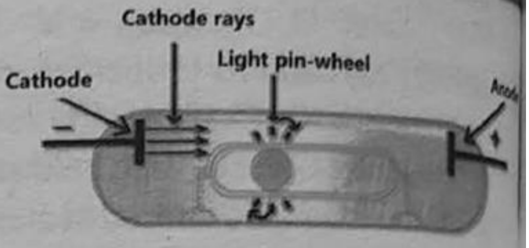
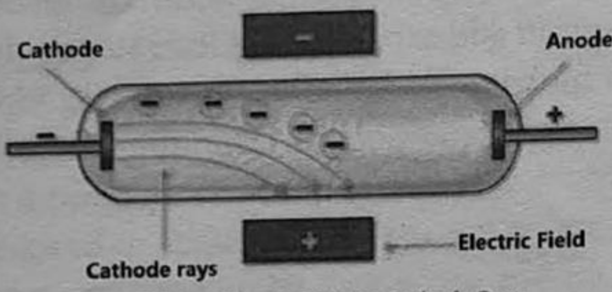


Fig 2.3 Cathode Rays, Rotating light Pin-Whe



Effect of Electric Field on Cathode Rays

Figure 2.4 Cathode rays, deflecting in an electric field

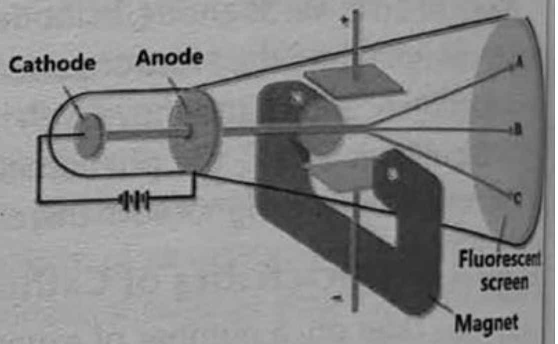


Figure 2.5 Cathode rays, deflecting magnetic field

On the basis of the above characteristics, it was concluded that th cathode rays were in fact negatively charged particles. G. J. Stoney gave the particles the name "electrons".

2.1.2 Mass of the Electron

The e/m ratio of electron is 1.7588x 10^{11}C/kg and the charge is 1.6022 x 10^{-19}C. Maki use of these two values the mass of electron "m" can be calculated as,

The charge to mass ratio, $\frac{e}{m}=1.7588\times10^{11}\text{C/kg}$ (2.1)

The charge on an electron, $e = 1.6022\text{x}10^{-19}\text{C}$

Putting the value of 'e', in equation (2.1), you get,

$$\frac{1.6022\times10^{-19}\text{C}}{m} = 1.7588\times10^{11}\text{C/kg}$$

By cross multiplication,

$$m \times 1.7588\times10^{11}\text{C/kg} = 1.6022\text{x}\times10^{-19}\text{C}$$

$$m=\frac{1.6022\times10^{-19}\text{C}}{1.7588\times10^{11}\text{C.kg}^{-1}}$$

or $m = 9.1069\times10^{-31}\text{kg}$

or $m= 9.1069\times10^{-28}\text{g}$

Reading Check

What is a gas discharge tube? Write the conditions that are necessary for the production of cathode rays.

2.1.3 Canal Rays or Positive Rays – The Discovery of Proton

From a number of experiments, it was concluded that beside cathode rays (electrons) which carry negative charge, there are some positively charged particles present in an atom because atom as a whole is an electrically neutral particle.

In 1886, Eugen Goldstein used a discharge tube with holes (perforation) in the cathode. He observed that while cathode rays were moving away from the cathode, there were some other rays (streams of dim luminous glow), produced at the same time, moving towards cathode and passed through the perforated cathode and caused a glow on the wall opposite to the anode. These were called the canal rays because they were coming from perforations (canals). It was concluded that these rays must be positively charged and hence named positive rays.

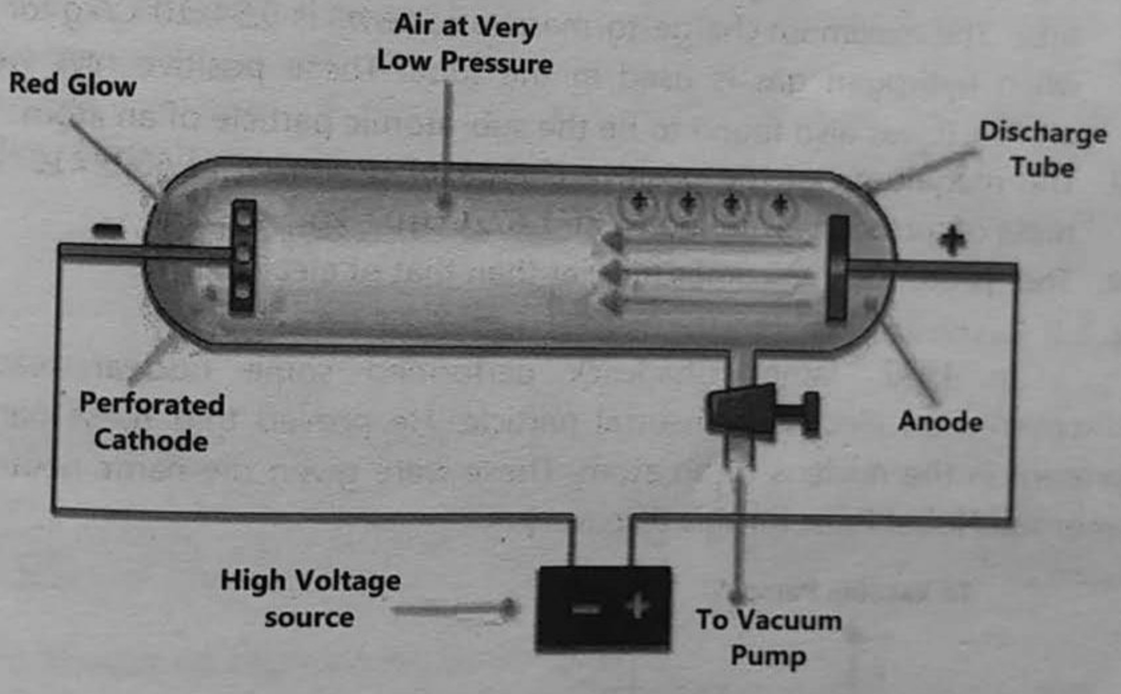


Figure 2.6 Canal ray tube

2.1.4 Positive Rays Production

When high-speed electrons (cathode rays) collide with the molecules of remaining gas in the discharge tube, they knock out one or more electrons from them. Thus, positive ions (cation) are produced.

$$M + e^- \longrightarrow M^+ + 2e^-$$

These ions are positively charged and attracted by the cathode, some of which pass through the perforated cathode and strike at the walls of the tube.

2.1.5 Characteristic of Canal Rays or Positive Rays

Some of the characteristics of canal rays or positive rays are,

i. These rays travel in straight lines perpendicular to the anode surface.

ii. These rays have particle nature because these rays can move a small wheel placed in their path.

iii. These rays are deflected by electric and magnetic field in opposite directio electron.

iv. Their attraction towards cathode shows that they are positively char particles.

v. They produce fluorescence when strike with zinc sulphide (ZnS) layer.

vi. The charge-to-mass ratio (*e/m*) of positive rays is always less than cath rays.

vii. The e/m ratio changes with the nature of the gas placed in the disch tube. The maximum charge-to-mass ratio (*e/m*) is $9.54x10^{7}$C/kg for these when hydrogen gas is used in the tube. These positive rays were na proton. It was also found to be the sub-atomic particle of an atom.

viii. The magnitude of the positive charge of proton is 1.6022×10^{-19}C and mass of proton was found to be 1.6726×10^{-27}kg.

ix. The proton is 1836 times heavier than that of electron.

2.1.6 Discovery of Neutron (Artificial Radioactivity)

In 1932, James Chadwick performed some nuclear reactions discovered an electrically neutral particle. He proved that these particles present in the nucleus of an atom. These were given the name neutron; he awarded Nobel Prize for this discovery.

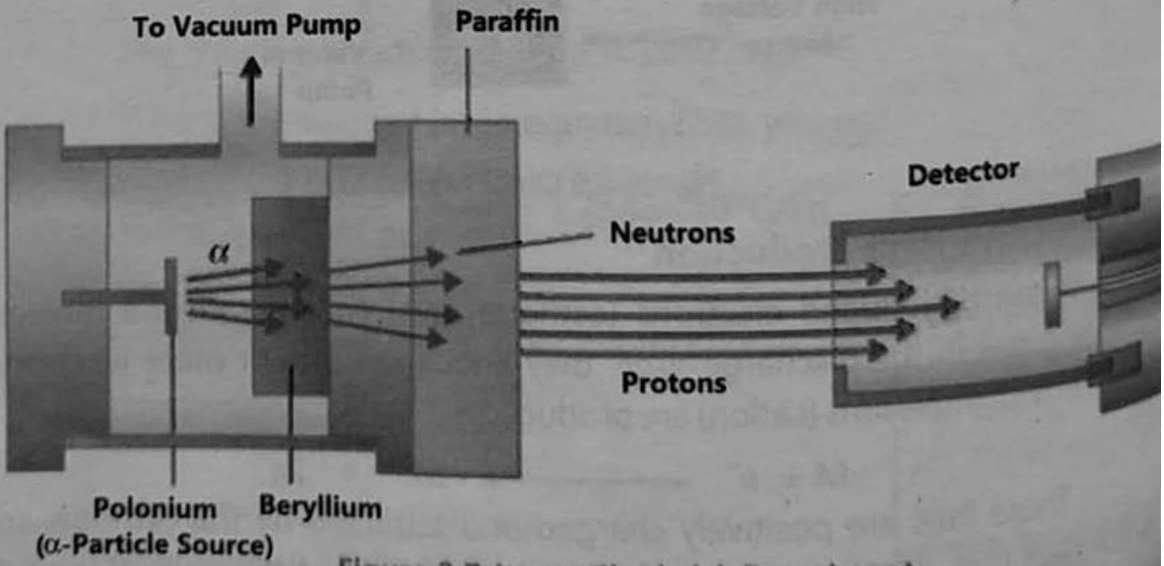


Figure 2.7 James Chadwick Experiment

He bombarded the nucleus of lighter atoms such as, Beryllium (Be) with α-particles produced from Polonium (Po). He observed that some highly penetrating radiations were produced. These radiations were neutral to the charge detector and were called neutrons. Examples of nuclear reactions (artificial Radioactivity) taking place are,

$$ {}^{9}_{4}\text{Be} + {}^{4}_{2}\text{He}\ (\alpha\text{- particle}) \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}\text{n}\ (\text{neutron}) $$

$$ {}^{27}_{13}\text{Al} + {}^{4}_{2}\text{He}\ (\alpha\text{- particle}) \longrightarrow {}^{30}_{15}\text{P} + {}^{1}_{0}\text{n}\ (\text{neutron}) $$

2.1.7 Characteristics of Neutron

Neutrons have the following characteristics.

i. Neutrons are highly penetrating particles.

ii. These particles carry no charge and are not deflected by electric or magnetic fields.

iii. These particles can knock out high-speed protons from substances like paraffin, water, cellulose etc.

iv. Neutron has mass 1.6749×10^{-27}kg and is 1842 times as heavy as electron.

Reading Check

Write an equation, which shows the production of neutron from the lighter atoms.

Table 2.1 Characteristics of the Three Fundamental Particles

Particles	Mass (kg)	Charge (C)	Unit Charge	Relative Atomic Mass (amu)
Electron	9.1069×10^{-31}	-1.6×10^{-19}	– 1	0.00055
Proton	1.6726×10^{-27}	$+1.6 \times 10^{-19}$	+ 1	1.0073
Neutron	1.6749×10^{-27}	0	0	1.0087

Bohr's Model of Hydrogen Atom

Rutherford atomic model set the foundation for the structure of an atom. According to the classical laws of Physics, an electron revolving around the nucleus, will lose energy continuously and will fall down into the nucleus. Thus, Rutherford model failed to explain why electrons did not do so.

In 1913, Neils Bohr proposed a new model of an atom based on the Quantum theory of energy and rectified the defects in Rutherford atomic model. With his model, he tried to explain why a revolving electron did not fall down into the nucleus.

The main postulates of the Bohr's model of an atom are,

1. Electrons are revolving around the nucleus in fixed circular paths called the orbits or shells. Each orbit is associated with a definite amount of energy. These orbits are also called energy levels.
2. The energy of the electron in an orbit is related to its distance from the nucleus. The farther the electron from the nucleus, the higher will be the energy.
3. As long as electrons are revolving around the nucleus in fixed circular orbit, they do not lose (radiate) or absorb energy.
4. When an electron jumps from a higher energy orbit to the lower energy orbit, it loses energy and when it jumps from lower energy orbit to higher energy orbit, it absorbs energy.

   The energy difference between two levels is given by,

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

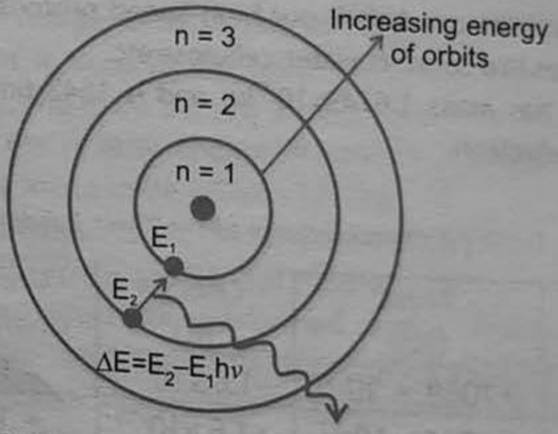


Figure 2.8 Energy Difference between Two Levels

Where, E_1 is the energy of lower orbit and E_2 is that of higher energy orbit. ΔE is the energy difference, h is the Planck's constant and ν is the frequency of radiation emitted or absorbed by the electron.

5. The angular momentum (mvr) of the electron in the hydrogen atom is quantized and can have values which are the whole number multiple of

$$mvr \propto \frac{h}{2\pi}$$

$$\text{that is; } mvr=\frac{nh}{2\pi}$$

Where, 'n' is the whole number say, 1, 2, 3, 4.... and represent the shell, 'm' is the mass of electron, 'v' is the velocity of electron, 'r' is the radius of the orbit in which electron are revolving and 'h' is the Planck's constant, its value is 6.6262×10^{-34} Js.

Based on these assumptions, Bohr presented a model for hydrogen atom that can best explain the spectrum of hydrogen atom.

2.2 Application of Bohr's Model

2.2.1 Derivation of Radius, Energy, Frequency, Wave Length and Wave Number

1. Derivation of Radius

Bohr had assumed that proton, being 1836 times heavier, remains stationary with respect to electron, which revolves around the nucleus in the hydrogen atom.

Consider an atom of hydrogen with atomic number 'Z'. It has 'Z' number of proton with nuclear charge 'Ze'. An electron of charge 'e' is revolving around the nucleus in circular path (orbit) of radius 'r', with velocity 'v'. According to Coulomb's law, the electrostatic force of attraction between the electron and the nucleus is given by,

$$F_{\text{Coulombic}} \propto \frac{q_1 q_2}{r^2}$$

$$F_{\text{Coulombic}} = k\frac{q_1 q_2}{r^2} \qquad (2.2)$$

As,

Charge on nucleus(proton), $q_1 = Ze$

Charge on electron, $q_2 = e$

$$F_{\text{Coulombic}} = k\frac{Ze.e}{r^2}$$

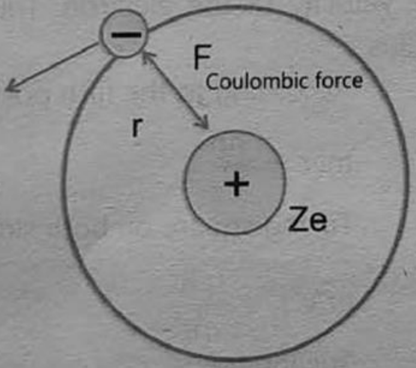


Figure 2.9: A hydrogen atom with atomic number 'Z'

Where the proportionality constant $k = \frac{1}{4\pi\varepsilon_o}$ and ε_o is the vacuum permittivity constant and is a measure of how easy it is for electrostatic force to pass through the vacuum (free space) and its value is $8.854 \times 10^{-12} C^2N^{-1}m^{-2}$. Putting the value of k in equation (2.2), you get

$$F_{\text{Coulombic}} = \frac{Ze^2}{4\pi\varepsilon_o r^2} \qquad (2.3)$$

This centripetal force, provided by the Columbic force of attraction is balanced by the centrifugal force, $\frac{mv^2}{r}$.

$$F_{Centrifugal} = \frac{mv^2}{r} \qquad (2.4)$$

As forces on both sides are equal, opposite and balance each other, so equating equation (2.3) and (2.4) you get,

For a stable orbit,

$$F_{Centrifugal} = F_{Coulombic}$$

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

Or $$mv^2 = \frac{Ze^2}{4\pi\varepsilon_o r} \qquad (2.5)$$

Rearranging $$r = \frac{Ze^2}{4\pi\varepsilon_o v^2 m} \qquad (2.6)$$

Equation (2.6) shows that radius is inversely proportional to the square of the velocity of the electron. Thus, electron moves faster in an orbit of smaller radius.

According to the fifth postulate of Bohr's atomic model, you have

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

Taking square on both sides, you have,

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

Solving for 'v^2'

$$v^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \qquad (2.7)$$

Activity No. 1

Looking into the values of r_1, r_2, r_3 and r_4 and $r_2 - r_1$, $r_3 - r_2$ and $r_4 - r_3$, etc. What do you conclude about the spacing between the orbits?

Substituting the value of v^2 from equation (2.7) into equation (2.6) and solving for 'r', you get,

$$r = \frac{n^2h^2\varepsilon_o}{Ze^2\pi m} \qquad (2.8)$$

For hydrogen Z = 1, so the equation (2.8), for radius of hydrogen atom is,

$$r = n^2\left[\frac{\varepsilon_o h^2}{\pi e^2 m}\right] \qquad (2.9)$$

Where the terms in brackets are constant quantities, and are equal to,

$$\left[\frac{\varepsilon_o h^2}{\pi e^2 m}\right] = \alpha_o$$

$$\alpha_o = 0.529\,\text{Å}$$

$$r = n^2 \times \alpha_o$$

$$r_n = n^2 \times 0.529\ \text{Å} \qquad (2.10)$$

For hydrogen the radius of 1st and 2nd Bohr's orbits will be,

When, $n = 1$

$$r_1 = (1)^2 \times 0.529\,\text{Å} = 1 \times 0.529\,\text{Å} = 0.529\,\text{Å}$$

When, $n = 2$

$$r_1 = (2)^2 \times 0.529\,\text{Å} = 4 \times 0.529\,\text{Å} = 2.116\,\text{Å}$$

Example 2.1

Calculate the radius of 3rd and 4th orbits of hydrogen atoms.

Solution:

You have to calculate r_3 (for n=3) and r_4 (n=4), using equation (2.9),

$n = 3$

$$r_3 = n^2\,(0.529\,\text{Å})$$

$$r_3 = (3)^2 \times 0.529\,\text{Å} = 9 \times 0.529\,\text{Å} = 4.761\,\text{Å}$$

$n = 4$

$$r_4 = (4)^2 \times 0.529\,\text{Å} = 16 \times 0.529\,\text{Å} = 8.464\,\text{Å}$$

Practice Problem 2.1

Calculate the radius of 5th and 6th orbits of hydrogen atom.

2. Derivation of Energy of the Electron in an Orbit

Electron in an atom possesses kinetic energy (K.E.) due to its motion and potential energy (P.E.) due to the attractive force between protons and electrons. The total energy of electron (E) in particular orbit is the sum of its K.E. and P.E.,

$$E = K.E. + P.E. \qquad (2.11)$$

Where $$K.E = \frac{1}{2}mv^2 \qquad (a)$$

And P.E. is equal to the work done in bringing the electron from infinity (where there is no interaction with the nucleus) to a point at a distance 'r' from the nucleus (where interaction exists). In doing so work must be done, this is given by, Work done = P.E. = - force x distance (r)

Here the force of attraction between the electron and the nucleus is as given by equation (2.3), therefore,

$$\text{P.E.} = -\frac{Ze^2}{4\pi\varepsilon_0 r^2} \times r$$

$$\text{P.E.} = -\frac{Ze^2}{4\pi\varepsilon_0 r} \qquad \text{(b)}$$

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

Putting values of K.E. and P.E. in equation (2.11), you get,

$$E = \frac{1}{2}mv^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} \qquad (2.12)$$

Now substituting the value of mv^2 from equation (2.5) into equation (2.12) you get,

$$E = \frac{1}{2}\left(\frac{Ze^2}{4\pi\varepsilon_0 r}\right) - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$E = -\frac{Ze^2}{8\pi\varepsilon_0 r} \qquad (2.13)$$

Now, putting the value of 'r' from equation (2.8), in equation (2.13) you get,

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

For nth orbit, the energy of electron will be,

$$E_n = -\frac{Z^2e^4m}{8\varepsilon_o^2n^2h^2}$$

$$E_n = -\frac{e^4m}{8\varepsilon_o^2h^2} \times \frac{Z^2}{n^2} \qquad (2.14)$$

For hydrogen atom, Z = 1, so,

$$E_n = -\frac{e^4m}{8\varepsilon_o^2h^2}\left(\frac{1}{n^2}\right) \qquad (2.15)$$

By inserting the values for various parameters it comes out to be,

$$\frac{me^4}{8\,\varepsilon_0^2 h^2} = 2.18 \times 10^{-18}\,\text{J/atom}$$

Thus, equation 2.15 becomes as,

$$E_n = -2.18 \times 10^{-18}\left(\frac{1}{n^2}\right) \text{ J/atom}$$

Or

$$E_n = -2.18 \times 10^{-18}\left(\frac{1}{n^2}\right) \times \frac{6.022 \times 10^{23}}{1000} \text{kJ/mol}$$

$$E_n = -\frac{1312.36}{n^2} \text{ kJ/mol} \qquad (2.17)$$

Equations (2.16) and (2.17) show that energy of the electron in an atom depends on the value of 'n', it is, therefore, called the principal quantum number. Further, the energy state associated with, n = 1 is called the ground state energy and represents the lowest energy state. All energy states higher than n=1 are called excited state for hydrogen atom.

Activity No. 2

You may also try for $E_2 - E_1$, $E_3 - E_2$, $E_4 - E_3$ and $E_5 - E_4$ etc. to check what happens to the difference in energies between two successive energy levels (orbits) as you move away from the nucleus?

The energy associated with the electron in various orbits (different 'n' values), can be calculated using equation (2.17).

When n= 1, $E_1 = -1312.36$kJ/mol

n=2, $E_2 = -328.32$kJ/mol

n=3, $E_3 = -145.92$kJ/mol

It is evident from the above calculations that the energy of electron increases as the value of 'n' increases.

Practice Problem 2.2

Calculate the energy of 4th and 5th levels of the hydrogen atom.

3. Energy Difference between Two Orbits

You have the energy equation 2.14,

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

Let E_1 be the energy of orbit n_1 and E_2 be the energy of the orbit n_2, then the above energy equation, for the two orbits

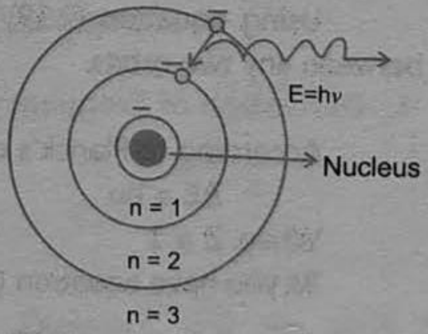


Fig 2.10 Energy Difference between Two Orbits

can be written as, $E_1 = -\frac{e^4 m}{8\varepsilon_o^2 h^2} \times \left(\frac{Z^2}{n_1^2}\right)$ for lower energy level,

and $E_2 = -\frac{e^4 m}{8\varepsilon_o^2 h^2} \times \left(\frac{Z^2}{n_2^2}\right)$ for higher energy level

Therefore, change in energy, $\Delta E = E_2 - E_1$

Then,

Putting the values in the above equation, you get,

$$\Delta E = \frac{Z^2 e^4 m}{8\varepsilon_o^2 h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

For hydrogen atom, Z = 1, so,

$$\Delta E = \frac{e^4 m}{8\varepsilon_o^2 h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad (2.18)$$

As you have,

$$\frac{me^4}{8\varepsilon_o^2 h^2} = 2.18 \times 10^{-18} \text{J/atom}$$

Thus, equation (2.18) becomes,

$$\Delta E = 2.18 \times 10^{-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{J/atom} \qquad (2.19)$$

Or

$$\Delta E = 1312.36 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{kJ/mol} \qquad (2.20)$$

Using equation (2.19) or (2.20), you can calculate the energy difference between any two orbits.

4. Derivation of Frequency, Wavelength and Wave Number

According to Planck's quantum theory,

$$\Delta E = h\upsilon$$

When, Z = 1

As you have equation (2.18)

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

Or

$$\Delta E = h\upsilon = \frac{e^4 m}{8\varepsilon_o^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad (2.21)$$

i. Frequency

For the calculation of frequency of radiation emitted or absorbed during electronic transitions between the orbits, the equation (2.21) becomes,

$$\upsilon = \frac{e^4 m}{8\varepsilon_o^2 h^2 \times h}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{Hz}$$

$$\upsilon = \frac{e^4 m}{8\varepsilon_o^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{Hz} \qquad (2.22)$$

ii. Wave number

The wave number of radiation can be calculated as,

The equation for velocity of radiation is,

$$c = \upsilon\lambda$$

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

As wave number $(\bar{\upsilon})$ is reciprocal of wavelength i.e.,

$$\bar{\upsilon} = \frac{1}{\lambda}$$

So, you can write,

$$\upsilon = \frac{1}{\lambda} \times c = c\bar{\upsilon}$$

$$\upsilon = c\bar{\upsilon}$$

or,

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

Putting the value of v from equation (2.22), you get,

$$\bar{\upsilon} = \frac{\upsilon}{c} = \frac{1}{\lambda} = \frac{e^4 m}{8\varepsilon_o^2 h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) m^{-1} \qquad (2.23)$$

As you have,

$$\frac{me^4}{8\,\varepsilon_o^2 h^3 c} = R = 1.09678 \times 10^7 m^{-1}$$

Where R is called Rydberg's constant. Therefore, you can write the equation (2.23) as,

$$\bar{u}=R\ \frac{æ1}{çèn_1^2}-\frac{1ö}{n_2^2÷ø}$$

$$\bar{\upsilon}=1.09678\times10^{7}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)m^{-1}\quad ....(2.24)$$

Equation (2.23) and equation (2.24) give the value for the wave number of the photon emitted or absorbed, when electron jumps between any two orbits.

Reading Check

1. Write the equation used for the determination of radius of hydrogen atom.
2. Write the energy equation for the n^{th} orbit.

Practice Problem 2.3

In a hydrogen atom, an electron jumps from 3rd orbit to 1st orbit. Find out th frequency and wavelength of the spectral line.

2.2.2 Spectrum of Hydrogen Atom

Spectrum

A band or series of radiations in order of increasing or decreasing order o wavelengths or frequencies when light is resolved into it constituent radiations i called spectrum.

For example, spectrum of sunlight, hydrogen, electric bulb light. Th instrument used to study the spectra (plural of spectrum) is calle spectrophotometer. The spectrum from an ordinary light or sunlight consists of tw main parts, visible and invisible.

Spectrum is of two types.

a. Continuous spectrum
b. Line spectrum

a. Continuous Spectrum

The spectrum, which has no dark or bright spaces between lines, mean n clear boundary can be seen between the lines (colours) is called continuo spectrum.

Different colours diffuse into each other, so that the boundaries of differe colours cannot be marked, for example, rainbow, the spectrum of sunlight an ordinary tungsten filament lamp. When the sunlight or ordinary electric light i passed through a prism, it is dispersed into seven colours; these colours form th continuous spectrum as shown in the figure 2.11.

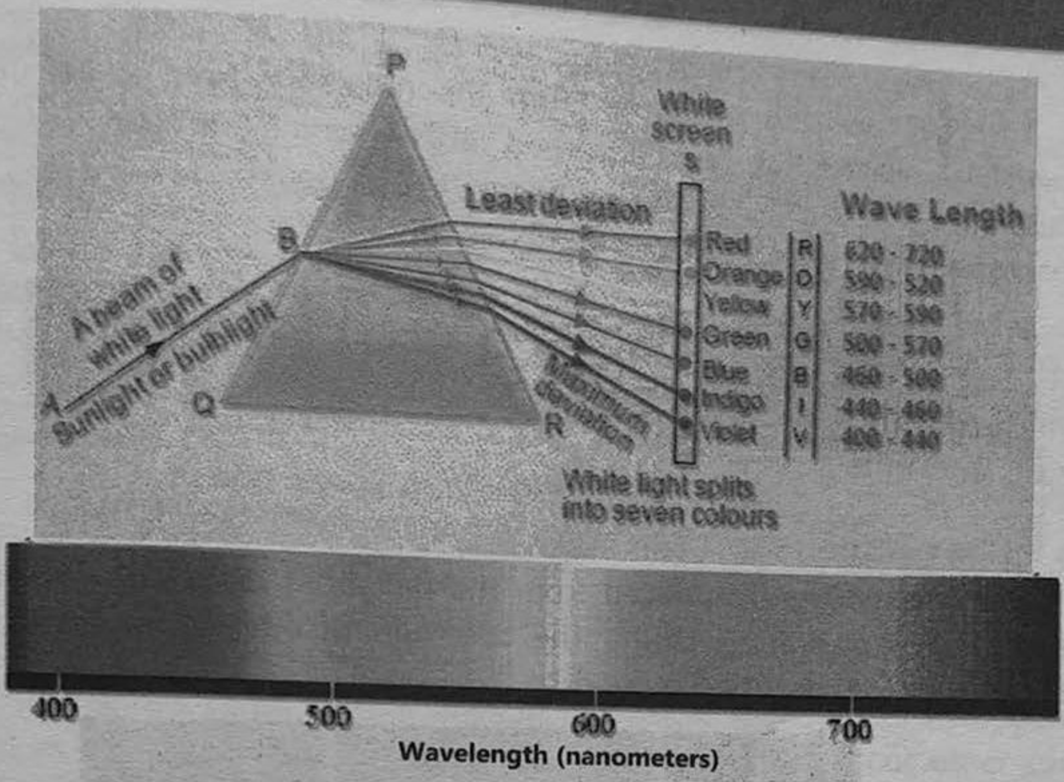


Figure 2.11 Continuous Spectrum of sun light

b. Line Spectrum

The spectrum, which consists of lines with dark or bright spaces between them, is called line spectrum. In this type of spectrum, there is a clear-cut boundary between the colour bands. Line spectrum is also called atomic spectrum. Each element emits light of definite wavelength. Therefore, various elements can be distinguished with the help of line spectrum as shown in the figure 2.12.

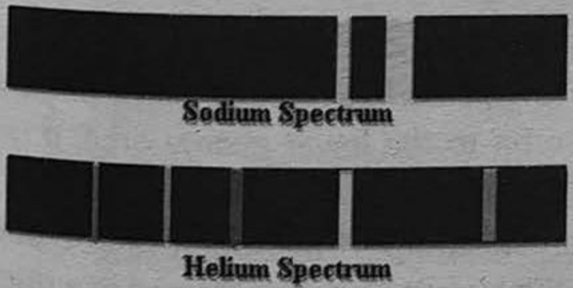


Fig.2.12 Line Spectrum

The line spectrum may be,

i. Line absorption spectrum
ii. Line emission spectrum

Tidbit

Sodium (Na$^+$) ion impart yellow colour to the Bunsen flame, indicating that it absorbs (and then emits) radiation in this region, strontium (Sr^{+2}) ion gives red colour and potassium (K$^+$) ion gives violet colour to the Bunsen flame.

i. Line Absorption Spectrum

The spectrum produced from the radiations from which the rays of particular wavelength are absorbed after passing through the absorbing substance. The spectrum obtained consists of a series of dark lines in a bright background, is called atomic absorption spectrum.

Figure 2.13 Hydrogen Absorption Spectrum

ii. Line Emission Spectrum

The line spectrum produced from the radiations emitted by a substance is called the emission spectrum. The spectrum of emitted radiations produces bright lines with dark background.

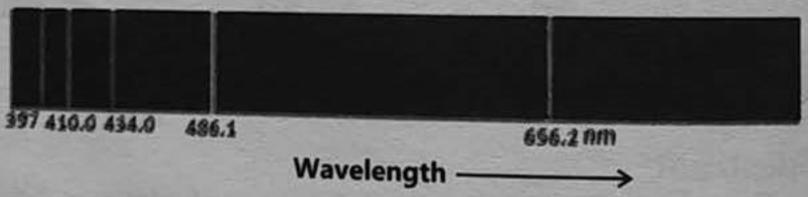


Figure 2.14 Hydrogen Line Emission Spectrum

Spectrum of Hydrogen Atom

Bohr proposed that the energy, which is emitted or absorbed by an atom, must have specific values. The change in energy when an electron moves to higher or lower energy levels is not continuous, rather, it is discrete (energy pulse).

When a hydrogen atom is excited and absorbs energy from surrounding, its electron is moved to higher energy level, a dark band is obtained but when an electron jumps from a higher energy orbit to the lower energy orbit, it radiates energy and bright band is formed in the line spectrum.

Experimentally the line emission spectrum of hydrogen can be obtained by passing electric discharge through the hydrogen gas contained in a discharge tube at low pressure. The light radiations emitted are then examined with the help of a **spectroscope.** The bright lines recorded on the photographic plate constitute the atomic spectrum of hydrogen as shown in figure 2.15.

In 1884, J. J. Balmer observed that there were four prominent coloured lines i.e. red, blue-green, blue-violet and violet in the visible hydrogen spectrum.

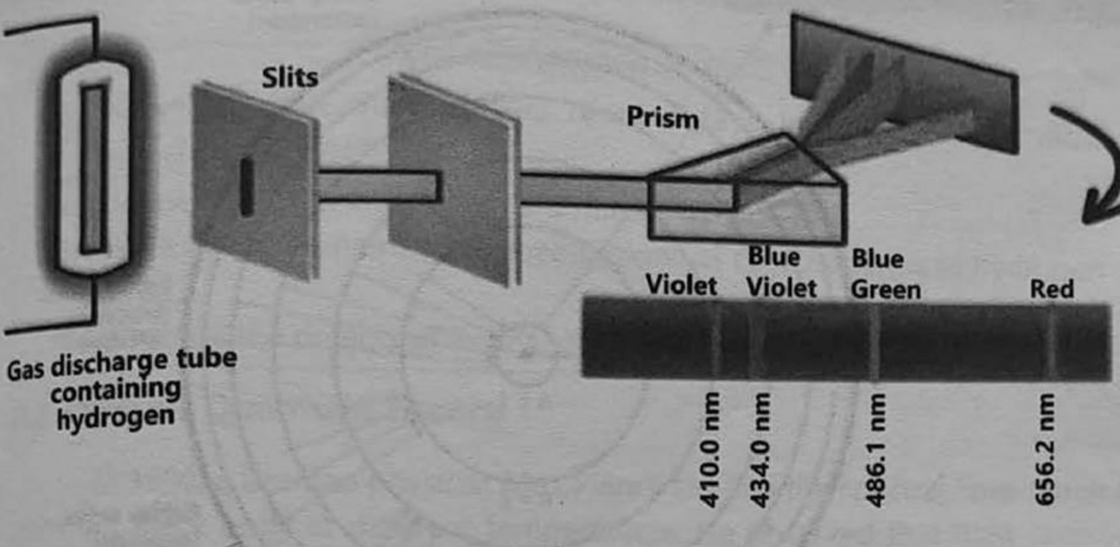


Figure 2.15 Atomic Spectrum of Hydrogen

The above series of four lines in the visible spectrum of hydrogen was named as the **Balmer Series.** In addition to Balmer Series, four other spectral series were discovered in the infrared and ultraviolet regions of the hydrogen spectrum. Thus, in all you have **Five Spectral Series** in the atomic spectrum of hydrogen and are named after the discoverer of these series. These are:

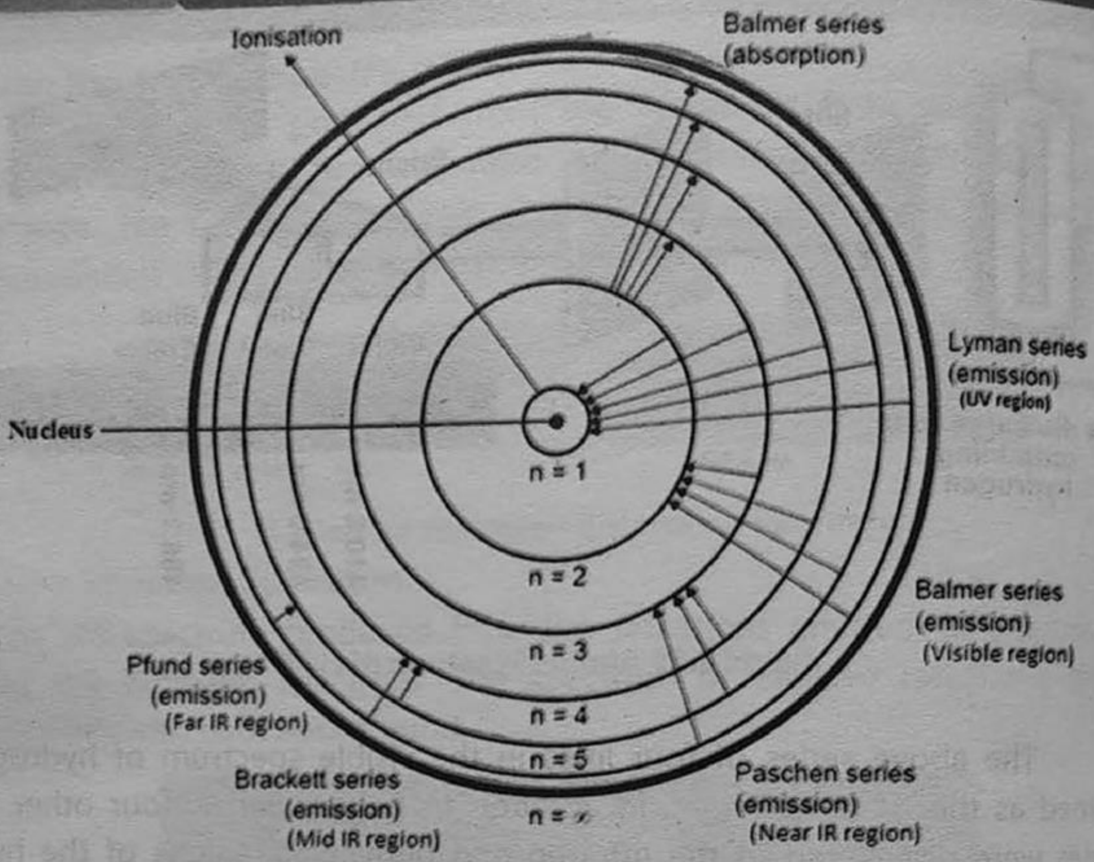
1. **Lyman Series** (Ultraviolet region), is obtained, when electron returns to its ground state, i.e. $n_1=1$ from higher energy levels, such as, $n_2= 2,3,4,5$. etc.

2. **Balmer Series** (Visible region), is obtained, when electron returns to the 2nd energy level, i.e. $n_1 = 2$ from higher energy levels, $n_2 = 3,4,5,6$ etc.

3. **Paschen Series** (Near Infrared region), is obtained, when electron returns to the 3rd energy level, i.e. $n_1 = 3$ from higher energy levels, $n_2 = 4, 5, 6$ etc.

4. **Brackett Series** (Mid Infrared region), is obtained, when electron returns to the 4th energy level, i.e. $n_1 = 4$ from higher energy levels, $n_2 = 5, 6, 7$ etc.

5. **Pfund Series** (Far Infrared region), is obtained, when electron returns to the 5th energy level, i.e. $n_1 = 5$ from higher energy levels, $n_2 = 6, 7$ etc.



Spectral series	Emission	Absorption	Frequency
Lyman series	Down to n =1	Up from n =1	Ultraviolet
Balmer series	Down to n =2	Up from n =2	visible light
Paschen series	Down to n =3	Up from n =3	Near infrared
Brackett series	Down to n =4	Up from n =4	Mid infrared
Pfund series	Down to n =5	Up from n =5	Far infrared

Figure 2.16 Hydrogen Spectral Series in Various Regions

2.2.3 Defects of Bohr's Model

The great success of Bohr's model of atom lies in its ability to predict lines in the hydrogen spectrum. It also explains spectra of other hydrogen like simple ions like He^+, Li^{++}, Be^{+++} but fails to explain the following.

1. It is unsuccessful to explain the spectrum of more complicated atoms (multi electron system).
2. It cannot explain the multiplicity of the spectral lines (fine structure) observed under a high resolving power spectrometer.
3. It cannot explain the effect of magnetic field (Zeeman effect) and electric field (Stark effect) on the spectra of hydrogen atom.
4. Modern research no longer believe in well- defined electron orbits as assumed in Bohr's model.

Self-Assessment

1. Name any four characteristics of canal rays, including charge, mass and charge to mass ratio.
2. Define spectrum and name its different types.
3. Write down the names and their regions of spectral series of hydrogen atom.
4. What are the defects of Bohr's atomic model?

2.3 Planck's Quantum Theory

In 1900, a German physicist Max Planck studied the spectral lines obtained from hot black body at different temperatures. He observed that light radiation was produced discontinuously by the particles of the hot body, which were vibrating with a specific frequency. These vibrations increased with an increase in temperature. Thus, Planck proposed a new theory called Planck's quantum theory.

The main postulates of this Planck's quantum theory are,

1. Energy emitted or absorbed by a hot body is not in a continuous form but in small units of waves. These 'unit waves' or 'wave packets' or 'pulses of energy' are called quanta (singular Quantum). In case of light energy, the quantum of energy is often called photon.

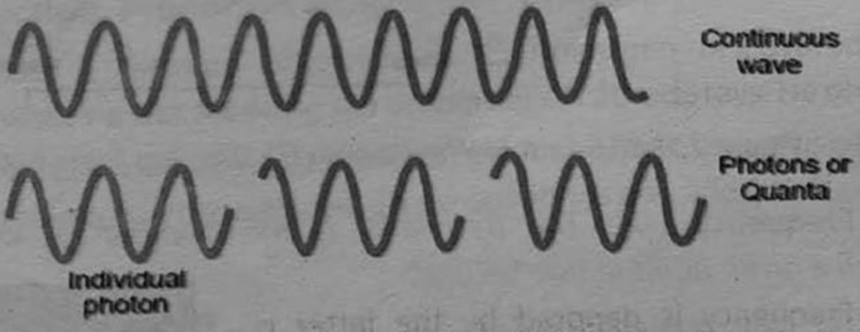


Figure 2.17 Continuous Wave and Photons or Quanta

2. The energy, E, associated with quantum or photon is directly proportional to frequency (υ) of the radiation.

$$E \propto \upsilon$$

Or $$E = h\upsilon \qquad (2.23)$$

This is called Planck's equation. Where 'υ' (nu) is the frequency of the emitted radiation and 'h' is the Planck's constant and its value is 6.6262×10^{-34}Js.

The frequency 'υ' is also related to wavelength and speed of radiation the equation,

$$c = \upsilon\lambda \qquad (2.24)$$

Where 'c' is the speed of light and 'λ' is the wavelength of any radiation.

3. A body can emit (or absorb) either one quantum (hυ) or any wh number multiple of this unit.
   $E = nh\upsilon$
   Where n = 1, 2, 3... etc. It means energy is quantized.

2.3.1 Postulates with Derivation of $E = hc\bar{\upsilon}$

Wavelength (λ): *The wavelength is defined as the distance between adjacent crests or troughs of a wave.*

Wavelength is denoted by the Greek letter λ (lambda). It is expressed centimeters or meters or in *angstrom* units. One angstrom, Å, is equal to 10^{-8} It is also expressed in nanometers ($1nm = 10^{-9}$ m).

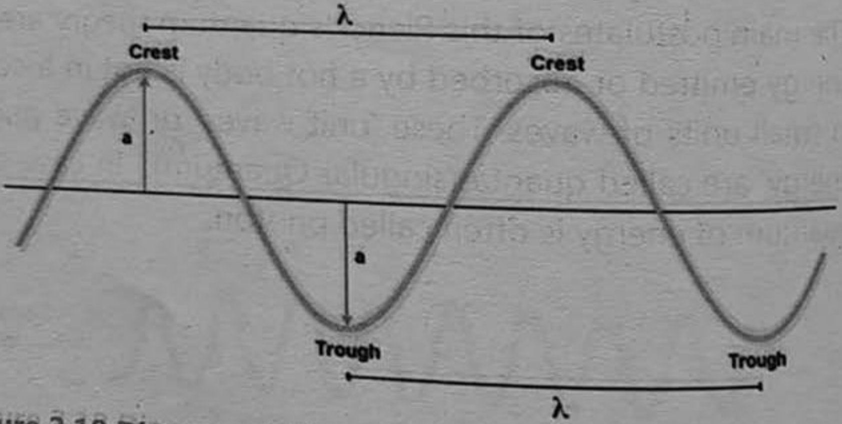


Figure 2.18 Diagram of Wavelength (λ) showing Crest and Trough

Frequency (υ): *The frequency is the number of waves, which through a given point in one second.*

Frequency is denoted by the letter υ (nu) and its unit is *hertz* (Hz)

Speed(c): *The speed (or velocity) of a wave is the distance through which a particular wave travels in one second.*

Speed is denoted by 'c' and it is expressed in meter per second (ms^{-1}). The velocity of light is $3 \times 10^{8} ms^{-1}$ in vacuum.

Tidbit

υ = f, both are use as symbol of frequency. chemistry, 'υ' is used as symbol of frequency and physics 'f' is used as symbol of frequency.

Wave number ($\bar{\upsilon}$): *It is the number of waves per unit length.* This is reciprocal of the wavelength and is given the symbol $\bar{\upsilon}$ (nu bar). That is,

$$\bar{\upsilon} = \frac{1}{\lambda} m^{-1} \text{ or } cm^{-1}$$

The frequency of a photon is inversely proportional to its wavelength,

$$\upsilon \propto \frac{1}{\lambda}$$

We have also,

$$c = \upsilon\lambda \text{ (where 'c' is the velocity of light)}$$

$$\upsilon = \frac{c}{\lambda} \qquad (2.25)$$

$$\text{As } E = h\upsilon \qquad (2.26)$$

Putting the value of υ in equation (2.26), you get,

$$E = \frac{hc}{\lambda} \qquad (2.27)$$

As you know $\bar{\upsilon} = \frac{1}{\lambda}$

Putting the value of $1/\lambda$ in equation (2.27), you get,

$$E = hc\bar{\upsilon} \qquad (2.28)$$

Thus, it can be concluded that the energy of photon is related to the frequency, wave length and wave number.

2.4 X – Rays

2.4.1 Production, Properties and Uses of X-Rays

In 1895, a German physicist, W. C. Roentgen discovered the X-rays accidentally while he was studying the properties of cathode rays. He observed that, *when high energy electrons (cathode rays) strike the heavy metal used as an anode, some sort of radiations are produced. These radiations are called X – rays.*

Production of X- Rays

X-Rays can be produced by a number of ways. The most important methods are

1. Roentgen method (Gas Tube)
2. Coolidge Method
3. By using betatron (an electron accelerating machine).

Roentgen Methods of X-Rays Production

It consists of special type of discharge tube as shown in the figure 2.19.

The pressure inside the tube is reduced to 0.001 mm of Hg. The voltage is kept 30,000 to 50,000 volts. The cathode is a heated filament and due to high potential difference between the cathode and anode, electrons are emitted from cathode and travel towards the anode where it strikes with high speed. Due to some electronic transition, high energy X-ray photons are emitted from the anode.

The cathode is concave shaped with its focus on the anode. The electrons emitted from cathode are focused on small portion of anode and X – rays are emitted from that small portion of anode.

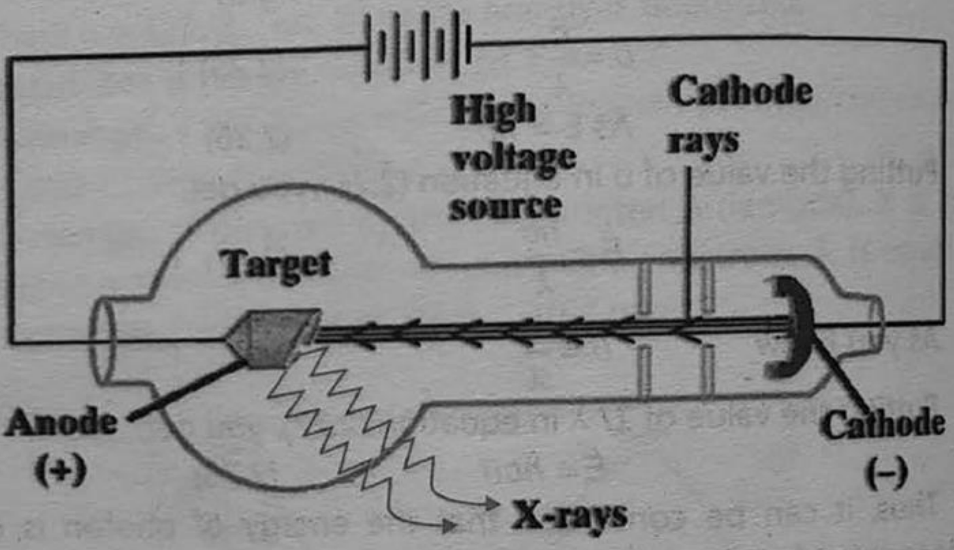


Figure 2.19 X – Rays Production by Roentgen Method

Properties of X-Rays

X–rays are electromagnetic radiations and have very high frequency (shorter wavelengths). The wavelength of the radiations constituting X-rays ranges from 10^{-2} Å to 10^{+2} Å (0.001 nm to 10nm). The following are the main properties of X –rays.

1. These rays travel in straight line.
2. These rays are not deflected by electric and magnetic field.
3. They are neutral in nature.
4. They have the ability to ionize the gases. The ionizing power depends on the intensity of the X – rays beam.
5. They can produce fluorescence in substances like NaCl, salts, glass etc.
6. These rays can be reflected and refracted.
7. These rays can be diffracted by crystalline substances.
8. These rays can penetrate through many substances. Their penetration

power is different in different substances.

9. These rays can blacken the photographic plate.

Uses of X-Rays

Following are the main uses of X-rays.

1. X-rays are used in the field of medicine due to different penetrating power through the flesh and bones of the body.
2. X-rays are used in the XRD analysis (X-rays diffraction analysis) for measuring space between the ionic layers of a crystalline substance.
3. X-rays are used for the ionization of gases.
4. X-rays were used by Watson and Crick to identify the double helix structure of DNA.

2.4.2 Types of X-Rays

There are two types of X-ray spectra

1. Continuous 2. Characteristic

1. Continuous X-rays

The continuous X-rays spectrum appears when an electron previously accelerated by a high potential difference is deflected by the nucleus of target atom of anode. This deflection results in loss of energy of the incoming electrons, which is released as X-ray photons. Thus, the maximum X-rays frequency possible emitted is equal to the maximum energy of the incoming electrons.

2. Characteristic X-rays

The second type of X-rays spectrum arises when an incoming electron has enough energy to remove an electron of target atom from its inner shell. The other electrons of atom will rearrange to fill the missing space and a set of X-rays lines will be emitted corresponding to these electron transitions from outer shells to inner shells.

This X-rays spectrum has definite series named as K-series, L-series etc. The production of these series is described as follow.

Supposes K–shell electron is knocked out from an atom creating a vacancy in the K–shell. Then electron from either, L, M, or N shell will quickly jump down in order to fill the vacancy in the K–shell, emitting the excess energy in the form of X-rays photon. An X-rays photon emitted due to transition of L–shell to the vacant space in the K-shell is called Kα characteristics X-rays. The transition from M and N-shells to K-shell gives rise to Kβ and Kγ characteristics X-rays, respectively. These X-rays are of high energy. Similarly L, M, and N series characteristics X-rays, relatively of low energy, are produced due to the ejection of electrons from L, M and N – shells, respectively, and produce Lα, Lβ, Mα, M etc. characteristics X –rays.

Inside the same group of lines, α denotes a transition between t consecutive levels, β denotes a transition skipping one level, etc.

Every metal has its own characteristic X-rays line spectrum. This li spectrum is the characteristic of target material used. This characteristic X-ray spectrum has discrete spectral lines.

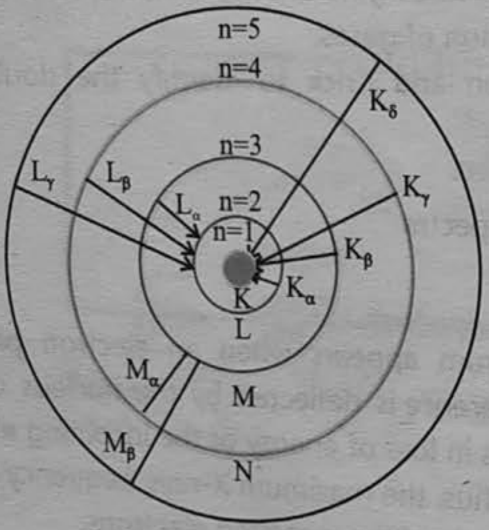


Figure 2.20 Inner - Shell transition

Tidbit

The spectral lines of x-rays could be classified into two different distinct groups, shorter wavelengths are identified by K- series and Longer wavelengths are identified by L-series and M-series etc.

2.4.3 X – Rays and Atomic Number (Z)

In 1913, Henry Moseley observed that the frequency of emitted X - ra depends upon on the material used as target element (anode). Greater th number of positive charge on the nuclei of the target element, greater will be th frequency of the emitted X –rays. Therefore, each element was assigned characteristic number equal to the positive charges on the nucleus of the ato The number of unit positive charges on the nucleus of an atom of an elemen termed as atomic number; it is represented by 'Z'. Since the positive charge on the nucleus is due to the presence of protons inside the nucleus, the number of unit positive charge will directly indicate the number of protons. Thus, the atomic number of an element is the number of protons present in its nucleus.

Reading Check

- What are X- rays? Write its different types.
- Define Planck's quantu theory and prove that $E = hc\bar{\upsilon}$

2.4.4 Moseley's Experiment

Mosley used the discharge tube used by Roentgen for the discovery of X – rays. He performed a number of experiments and proved that positive charge on the nucleus was the fundamental property of the element. Moseley used different X-rays tubes with anodes of different materials and took spectrum of X – rays in each case, by allowing them to fall on a photographic plate. It was observed that the wavelength of X – rays depends on the element used as anode and excitation voltage.

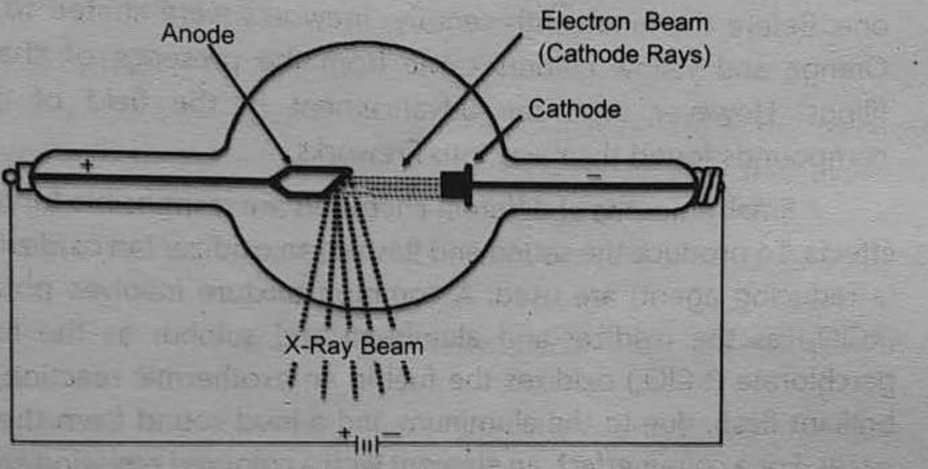


Figure 2.21 Moseley's Experiment (X- Rays tube)

2.4.5 Moseley's Law

Moseley showed that the square root of the frequency ($\sqrt{\upsilon}$) of a spectral line is directly related with the nuclear charge (Z), provided that the excitation potential is kept constant.

On the basis of results, he suggested that, "the square root of the frequency ($\sqrt{\upsilon}$) is directly proportional to the atomic number (Z) of an element."

Mathematically, it can be written as,

$$\sqrt{\upsilon} \propto Z$$

In order to get the accurate results, Mosley modified this relationship as,

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

Reading Check

Define Moseley's law.

Where 'b' is a constant and is known as screening constant. For spectral lines of K – series, b = 1. Thus,

$$\sqrt{\upsilon} = a\,(Z-b) \qquad (2.29)$$

Where "a" is the proportionality constant, equation (2.29) represents Moseley's law. It is used for the calculation of the atomic number Z, if the frequencies of the spectral lines are known.

STS Science, Technology and Society

Fireworks Display

The art of using mixtures of chemicals to produce fire is an ancient one. Before the nineteenth century, fireworks were limited to few chemicals. Orange and yellow colours came from the presence of charcoal and iron filings. However, with the advancement in the field of chemistry, new compounds found their way into fireworks.

Small amounts of different chemicals are responsible for most of the amazing effects. To produce the sound and flashes, an oxidizer (an oxidizing agent) and a fuel (a reducing agent) are used. A common mixture involves potassium perchlorate ($KClO_4$) as the oxidizer and aluminum and sulphur as the fuel. The potassium perchlorate ($KClO_4$) oxidizes the fuel in an exothermic reaction, which produces a brilliant flash, due to the aluminum and a loud sound from the rapidly expanding gases. For a colour effect, an element with a coloured emission spectrum is included. Recall that the electrons in atoms can be raised to higher-energy orbitals when the atoms absorb energy. The excited atoms then release this excess energy by emitting light of specific wavelengths, often in the visible region.

In fireworks, the energy to excite the electrons comes from the reaction between the oxidizer and fuel. Sodium imparts yellow colour in fireworks, red colour come from strontium salts. Barium salts give a green colour; copper salts give a blue colour in fireworks.

2.5 Quantum Numbers and Orbitals

Quantum numbers are certain numbers (which are a set of numerical values) that give information about the designation (energy, shape of orbital etc.) of an electron in an atom.

Quantum numbers are important because they can be used to determine the electronic configuration of an atom and the probable location of its electrons. There are four quantum numbers, three of which have been derived from the mathematical solution of the Schrödinger equation for the hydrogen atom. They are called the principle quantum number, the azimuthal quantum number and the magnetic quantum number. These quantum numbers will be used to describe atomic orbitals and to label electrons that reside in them. A fourth quantum number, called the spin quantum number was discovered independently and describes the behaviour of a specific electron and completes the description of electrons in atoms. These four quantum numbers are,

i. Principal quantum number (n)
ii. Azimuthal quantum number (l)
iii. Magnetic quantum number (m)
iv. Spin quantum number (s)

2.5.1 Principle Quantum Number (n)

This quantum number denotes the principal shell to which the electron belongs. This quantum number represents the main energy level or shell in which the electron is present. It represents the average distance of the electron from the nucleus. The principal quantum number 'n' can have non-zero, positive, integral values n = 1, 2, 3...

- An electron with $n = 1$, has the lowest energy and is bound most firmly to the nucleus.
- Higher the value of '*n*' means that the size of the energy level is larger, with a higher probability of finding an electron farther from the nucleus.
- Energy of the electron depends on the value of 'n', lower the value of 'n' lower will be the energy of the electron in that orbit and vice versa.

The letters K, L, M, N, O, P and Q are also used to designate the energy levels or shells of electrons with 'n' value of 1, 2, 3, 4, 5, 6, 7, respectively. The maximum number of electrons that is possible in any energy level of principal quantum number is calculated by the formula $2n^2$.

For example, if n = 1, maximum number of electrons possible = $2n^2 = 2\times(1)^2=2$ and so on.

2.5.2 Azimuthal Quantum Number (ℓ)

Chemists use a variety of names for the second quantum number. They are referred as angular momentum quantum number, the azimuthal quantum number, the secondary quantum number or the orbital-shape quantum number. Regardless of its name, the second quantum number refers to the energy sublevels within each principal energy level/shell.

Azimuthal Quantum Number defines the shape of the orbital occupied by the electron and the angular momentum of the electron. It also shows the number of sub-shell in a given shell. It also shows us the shape of orbital. Thi quantum number is represented by 'ℓ'.

For any given value of the principal quantum number, *n*, the azimutha quantum number ℓ may have all whole number values from 0 to $n-1$, each o which refers to an energy sublevel or sub-shell. *The total number of such possible sublevels in each principal energy level is numerically equal to the principa quantum number of the level under consideration.* These sublevels are also symbolized by letters s, p, d, f etc. The letters s, p, d and f have been taken from the old spectroscopic terms, *sharp, principal, diffused and fundamenta* respectively. The values of 'ℓ' for different values of n are given in table 2.2.

Table2.2 Principle Quantum Number and values of Azimuthal Quantum Number

n value	ℓ value	Sub-shell	Should be written as	No. of sub-shell
1	0	s	1s	1
2	0,1	s, p	2s,2p	2
3	0,1,2	s, p, d	3s, 3p,3d	3
4	0,1,2,3	s, p, d, f	4s,4p,4d,4f	4

The value of 'ℓ' also determines the shape of the sub-shell. The shapes o sub-shell are due to revolution of electron around the nucleus, e.g. when ℓ= then it is s-orbital (sub-shell) and is spherical, when $\ell=1$, the sub-shell i dumbbell shaped and is called p-sub-shell, when $\ell=2$, the sub-shell is sausag shaped (double dumbbell) and is called the d sub-shell, and when $\ell=3$, the sub shell is even more complicated and is called the f sub-shell.

2.5.3 Magnetic Quantum Number (m)

This quantum number has been based upon the splitting up of spectral line (Zeeman Effect). By applying a strong magnetic field to electrons with the sam values of principal quantum number 'n' and of azimuthal quantum number 'ℓ', electrons may differ in their behaviour. Therefore, a new quantum number, called th magnetic quantum number, is introduced.

- This quantum number is also called *Orientation Quantum Numbe* because this quantum number indicates the orientation of the orbital i the space around the nucleus. This quantum number is represented b 'm' as it explains the magnetic properties of an electron.
- The number allowed to m, depends on the 'ℓ' values and ranges from − through 0 to + ℓ, making a total of $(2\ell + 1)$ values. i.e. when $\ell=0$, m =

(sub-shell is 's'), when ℓ=1, m= −1, 0, +1 (sub-shell is p, which is oriented in three directions x, y, z in space). That is to say, the sub-shell 'p' has three degenerate orbitals p_x, p_y and p_z, arranged in space along x, y and z axes.

When ℓ =2, m = −2, −1, 0, +1, +2 (sub-shell is 'd', which implies that it has five space orientations due to five 'm' values and are designated as d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2}.

When ℓ=3, m= −3, −2, −1, 0, +1, +2, +3 (sub-shell is 'f', having orientations in seven different directions in space.

The table 2.3 shows the possible magnetic quantum number values (m) for the corresponding azimuthal quantum number (ℓ).

Table 2.3 Relationships among Values of n, ℓ and m

n value	Possible values of ℓ	No of sub-shell	Sub-shell designation	Possible values of m	Number of orbitals in sub-shell	Total number of orbitals in shell
1	0	1=s	1s	0	1	1
2	0 1	2=s, p	2s 2p	0 1, 0, -1	1 3	4
3	0 1 2	3=s, p, d	3s 3p 3d	0 1, 0, -1 2,1,0,-1,-2	1 3 5	9
4	0 1 2 3	4=s, p, d, f	4s 4p 4d 4f	0 1, 0, -1 2,1,0,-1,-2 3,2,1,0,-1,-2,-3	1 3 5 7	16

2.5.4 Spin Quantum Number (m_s or s)

The spin quantum number describes the spin for a given electron on its axis. An electron can have one of two possible spin values, either clockwise or anti-clockwise direction. The direction of the spin can be found out by the application of an external magnetic field. Since an electron has equal probability to spin clockwise and anticlockwise direction on its own axis around the nucleus, so the value for s may be $-\frac{1}{2}$ or $+\frac{1}{2}$. The clockwise motion is assigned $+\frac{1}{2}$

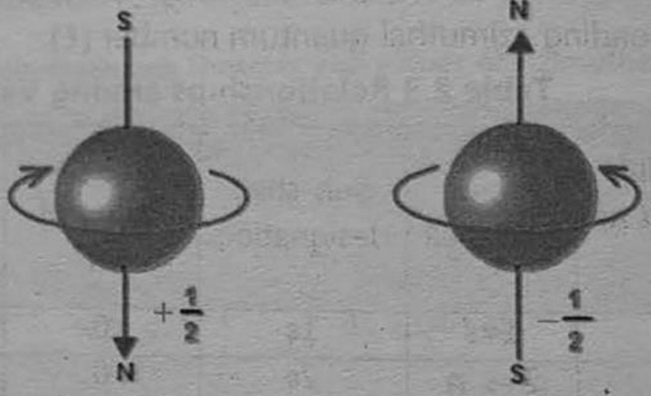
'value and downward arrow (↓).The anticlockwise motion is assigned '$-\frac{1}{2}$ 'val

and upward arrow (↑) i.e. s = $+\frac{1}{2}$ (↓) or s= $-\frac{1}{2}$ (↑) or

$$m_s = +\frac{1}{2}\ (\downarrow) \text{ or } -\frac{1}{2}\ (\uparrow) = \pm\frac{1}{2}$$

The probability of spin of electrons is supposed to be 50% clockwise an 50% anticlockwise.

A single orbital can hold a maximum of two electrons, with opposite spin



Clockwise Spin

Anticlockwise Spin

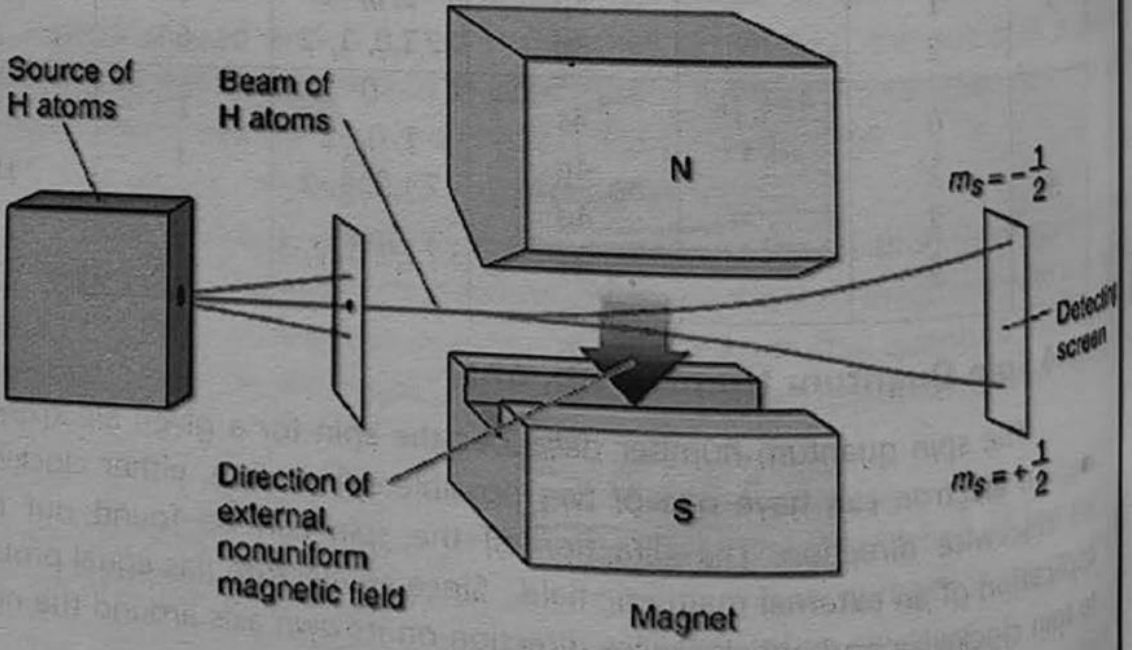


Figure 2.22 Discovery of Electron spins (Stern-Gerlach Experiment)

Two electrons, with the same spin, are said to have parallel spins and are represent by (↑↑) or (↓↓), while others are said to have anti-parallel or pair up spins and are represented by (↓↑) or (↑↓).

Reading Check

What are quantum numbers? Write the name of four quantum numbers.

2.5.5 Shapes of s, p and d Orbitals

Orbital have no physical existence. These are, in fact, regions of space around the nucleus; where there is maximum probability of finding an electron, with a definite amount of energy. These regions have no strict boundaries. An orbital is associated with a size, a three-dimensional shape and an orientation around the nucleus. Together, the size, shape and position of an orbital represent the probability of finding a specific electron around the nucleus of an atom. The overall shape of an atom is a combination of all its orbitals. Thus, the overall shape of an atom is spherical.

The type and shape of the orbital depend on the value of the azimuthal quantum number 'ℓ'.

i. s- Orbital

An electron for which $\ell = 0$ is located in an s orbital, regardless of the value of its principal quantum number n. This orbital is spherical in shape as shown in figure 2.23. It is found nearest to the nucleus. Its size increases with the increase in the value of 'n'. They are just like tennis ball.

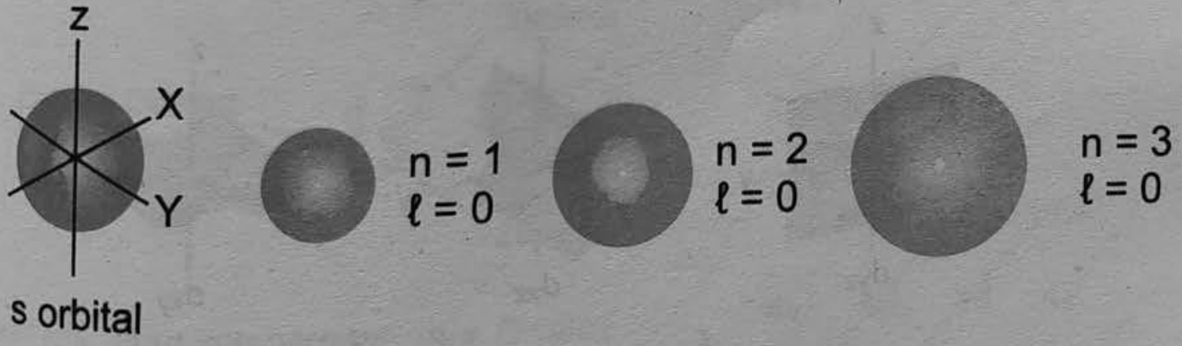
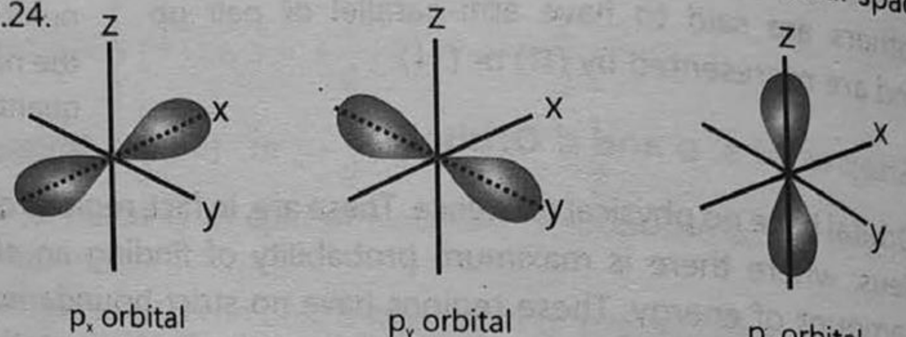


Figure 2.23 Shape of s orbital

ii. p- Orbital

Electrons for which $\ell = 1$, the value of 'm' include -1, 0, +1, which consist of three orbitals i.e. p-orbitals have three possible orientations. They are designated as p_x, p_y, p_z depending upon the axis of orientation. Each p-orbitals has two lobes one on each side of the nucleus. They are of dumbbell-shape, ead of which is perpendicular to the two others in three-dimensional space as show in figure 2.24.



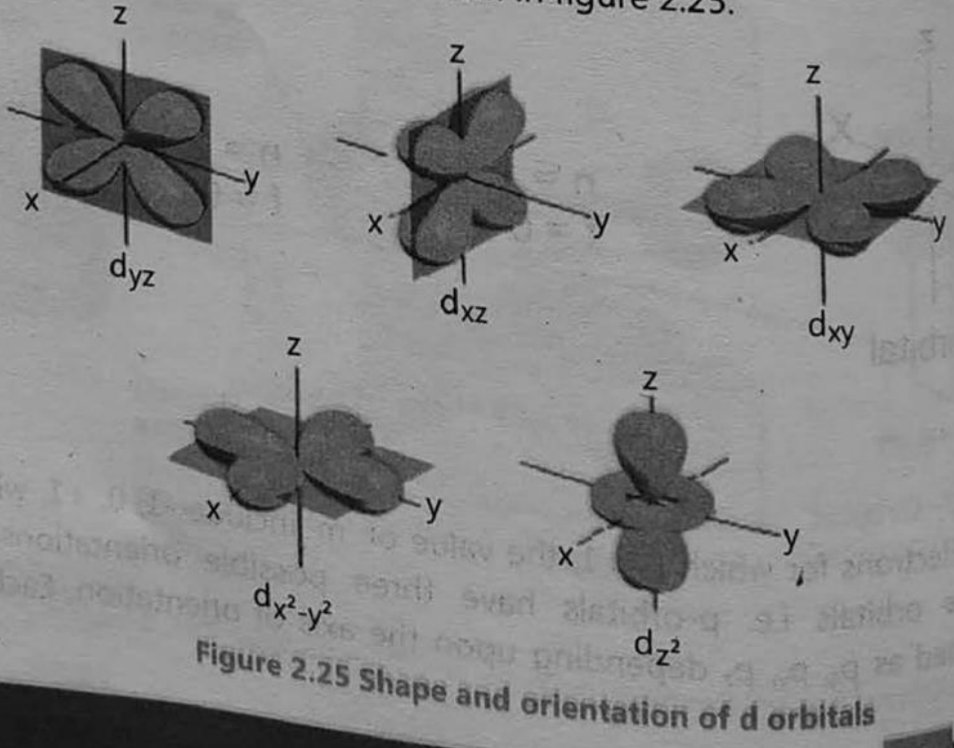
p_x orbital p_y orbital p_z orbital

Figure 2.24 Shape and orientation of p orbitals

iii. d- Orbital

When ℓ = 2, the values of 'm' include -2, -1, 0, +1, and +2, which consis of five d orbitals. The d-orbitals have five possible orientations. The five d-orbita are designated as d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2}. These orbitals have complex geometric shapes as compared to p-orbitals. The three d- orbitals d_{xy}, d_{yz}, d_{zx} have the lobes lying on the planes xy, yz, zx. The $d_{x^2-y^2}$ have somewhat similar structure t d_{xy}. The shape of the d_z^2 orbitals is different from others. The d_z^2 resembles p orbital with an additional doughnut shaped space in the centre.

Even though the d_z^2 appears to have a different shape than the others is still mathematically equivalent and exhibits the same properties (such as to energy) as the other d-orbitals as shown in figure 2.25.



d_{yz} d_{xz} d_{xy} $d_{x^2-y^2}$ d_{z^2}

Figure 2.25 Shape and orientation of d orbitals

2.6 Electronic Configuration

The distribution or filling of electrons in the various sub – shells and orbitals of an atom is called electronic configuration.

There are three rules used for the distribution of electrons in the sub – shells and orbitals. These rules are,

2.6.1 Aufbau Principle (The building up Principle)

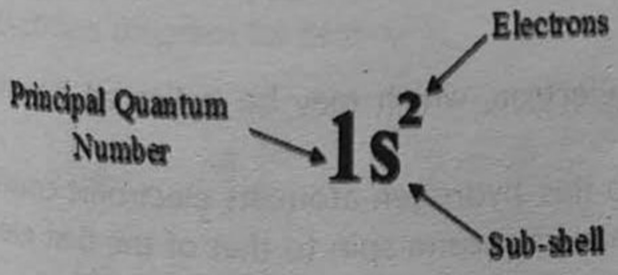
Aufbau is a German word meaning building up or construction. Aufbau principle states that electron fill orbitals that have the lowest-energy first. In other words, electrons are filled in different orbitals in the order of their increasing energies.

The energy of an orbital is determined by the sum of the principle quantum number (n) and the azimuthal quantum number (ℓ). This rule is also called $(n + \ell)$ rule. This rule consists of two parts.

i. The orbitals with the lower value $(n + \ell)$ have lower energy than the orbitals of higher $(n + \ell)$ value.

ii. When two orbitals have the same $(n + \ell)$ value, the orbitals with lower value of 'n' have lower energy and will be filled up first.

The notation for the electronic configuration includes the principal quantum number (n), the letter designation for azimuthal quantum number (s, p, d and f) and a superscript to indicate the number of electrons in the orbital or sub-shell e.g.



For example, let us compare the $(n + \ell)$ value of '3d' and '4s' orbitals,

For 3d orbitals $n = 3$, $\ell = 2$

$n + \ell = 3 + 2 = 5$

For 4s orbitals $n = 4$, $\ell = 0$

$n + \ell = 4 + 0 = 4$

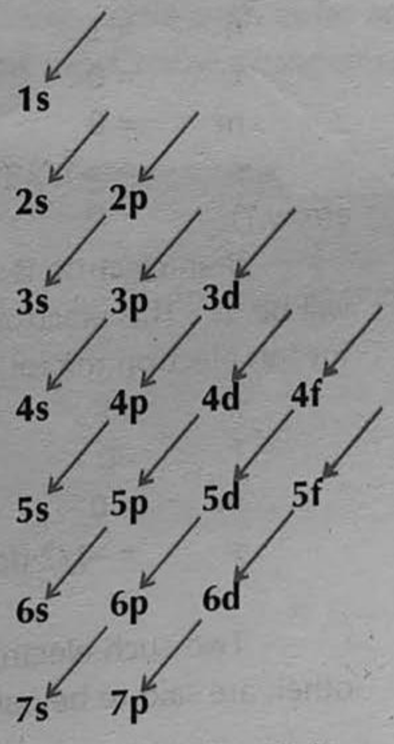


Figure 2.26 Order of filling atomic orbitals

Therefore, '4s' orbital is filled before '3d' orbital.

Similarly, for '4p' orbitals $n = 4$, $\ell = 1$

$$n + \ell = 4 + 1 = 5$$

and '5s' orbitals, $n = 5$, $\ell = 0$

$$n + \ell = 5 + 0 = 5$$

In this case, '4p' orbital has lesser value of 'n' and hence it has lower energ than '5s' orbital and is filled first. It is, therefore, clear that '4s' orbital would be fille before '3d' orbitals (belonging to a lower shell i.e. third) are filled because the latte have higher energy than the former.

Therefore, the order of filling various sub-shells(orbitals) according t '$n + \ell$' rule would be, $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$, ... etc.

2.6.2 Pauli's Exclusion Principle

In 1925, Austrian physicist Wolfgang Pauli put forward a principle for th distribution of electrons in the orbitals. According to this principle, *In a give atom no two electrons can have the same set of four quantum numbers (n, ℓ, m and s).* An orbital can accommodate a maximum of two electrons and that thes two electrons residing in the same orbital must have opposite spin.

For example, consider the hydrogen atom. Its electronic configuration i $1s^1$. Therefore, hydrogen atom has one electron. For this electron the fo quantum numbers (n, ℓ, m and s) are,

$n \quad = 1$
$\ell \quad = 0$
$m \quad = 0$
$s \quad = +1/2$ (for one electron, which may be indicated by an upwa arrow,↑)

If an electron is added to this hydrogen atom, its electronic configuratio will be $1s^2$. This electron must have opposite spin to that of the first electron, s for this electron the four quantum numbers (n, ℓ, m, and s) are,

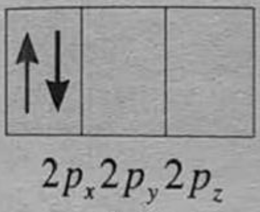
$n \quad =1$
$\ell \quad =0$
$m \quad = 0$
$s \quad = -1/2$ (for other electron, which may be by a downward arrow, ↓)

Two such electrons, in the same orbital, with their spins opposite to ea other, are said to be paired and are represented by (↓↑).

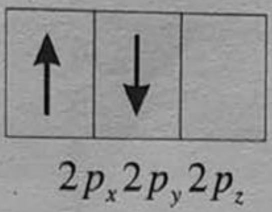
2.6.3 Hund's Rule

Hund's rule (named after the German physicist F. H. Hund), states that when a number of orbitals are available to the electrons and these orbitals have equal energies, the electrons will be arranged in these orbitals in such a way, so as to give maximum number of unpaired electrons and have the same direction of spin.

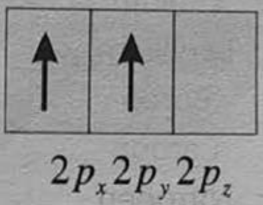
Carbon is an element, which has six electrons. The electron configuration of carbon ($Z = 6$) is $1s^2 2s^2 2p^2$. These three are the different ways of distributing two electrons among three *p* orbitals,



(a)

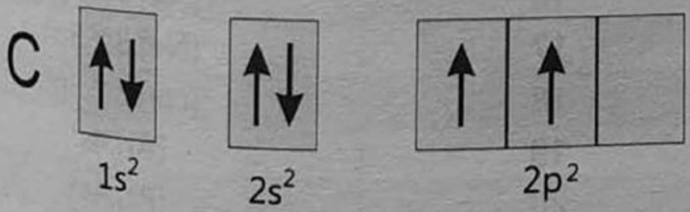


(b)



(c)

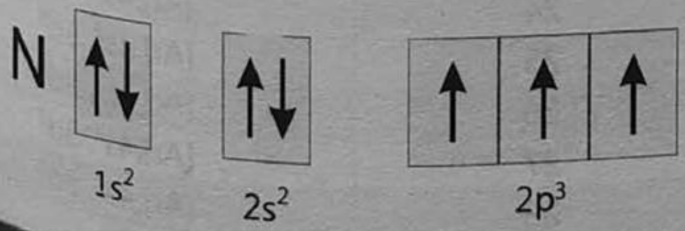
All the above three arrangements are according to the Pauli Exclusion Principle. Therefore, you must find out which one will give the greatest stability. This answer is provided by *Hund's rule,* which states *that the most stable arrangement of electrons in sub-shells is the one with the greatest number of parallel spins.* The (c) arrangement satisfies this condition, while both in (a) and (b) the two electrons spins cancel each other. Thus, the most stable arrangement of electrons diagram for carbon is,



The electronic configuration of nitrogen ($Z = 7$) is $1s^2 2s^2 2p^3$ and the electrons in orbitals are arranged as follow;

Tidbit

Different orbitals belonging to the same sub-shell are degenerate (same energy) e.g., $2p_x$, $2p_y$ and $2p_z$ are degenerate orbitals.



The Hund's rule describes that all three 2*p* electrons have parallel spins to one another; the nitrogen atom contains three unpaired electrons.

2.6.4 Electronic Configurations

Based on the rules above, the electronic configurations of first forty elements in the periodic table are given in table 2.4.

Table 2.4 Electronic Configurations of First forty Elements

Element	Symbol	Atomic Number (Z)	Electronic configuration
Hydrogen	H	1	$1s^1$
Helium	He	2	$1s^2$
Lithium	Li	3	$[He],2s^1$
Beryllium	Be	4	$[He],2s^2$
Boron	B	5	$[He],2s^2,2p^1$
Carbon	C	6	$[He],2s^2,2p^2$
Nitrogen	N	7	$[He],2s^2,2p^3$
Oxygen	O	8	$[He],2s^2,2p^4$
Fluorine	F	9	$[He],2s^2,2p^5$
Neon	Ne	10	$[He],2s^2,2p^6$
Sodium	Na	11	$[Ne],3s^1$
Magnesium	Mg	12	$[Ne],3s^2$
Aluminum	Al	13	$[Ne],3s^2,3p^1$
Silicon	Si	14	$[Ne],3s^2,3p^2$
Phosphorous	P	15	$[Ne],3s^2,3p^3$
Sulphur	S	16	$[Ne],3s^2,3p^4$
Chlorine	Cl	17	$[Ne],3s^2,3p^5$
Argon	Ar	18	$[Ne],3s^2,3p^6$
Potassium	K	19	$[Ar],4s^1$
Calcium	Ca	20	$[Ar],4s^2$
Scandium	Sc	21	$[Ar],4s^2,3d^1$
Titanium	Ti	22	$[Ar],4s^2, 3d^2$
Vanadium	V	23	$[Ar],4s^2, 3d^3$
Chromium	Cr	24	$[Ar],4s^1, 3d^5$ (more sta
Manganese	Mn	25	$[Ar],4s^2, 3d^5$
Iron	Fe	26	$[Ar],4s^2, 3d^6$
Cobalt	Co	27	$[Ar],4s^2, 3d^7$
Nickel	Ni	28	$[Ar],4s^2, 3d^8$

Copper	Cu	29	[Ar],4s^1, 3d$^{10}_{\text{(more stable)}}$
Zinc	Zn	30	[Ar],4s^2, 3d^{10}
Gallium	Ga	31	[Ar],4s^2, 3d^{10},4p^1
Germanium	Ge	32	[Ar],4s^2, 3d^{10},4p^2
Arsenic	As	33	[Ar,4s^2], 3d^{10},4p^3
Selenium	Se	34	[Ar],4s^2, 3d^{10},4p^4
Bromine	Br	35	[Ar],4s^2, 3d^{10},4p^5
Krypton	Kr	36	[Ar],4s^2, 3d^{10},4p^6
Rubidium	Rb	37	[Kr], 5s^1
Strontium	Sr	38	[Kr], 5s^2
Ytterbium	Y	39	[Kr],5s^2, 4d^1
Zirconium	Zr	40	[Kr],5s^2, 4d^2

Self-Assessment

1. Briefly write the Moseley experiment.
2. Explain the magnetic quantum number in detail.
3. What are the shapes of s, p and d orbitals?
4. Define Pauli's exclusion principle and Hund's rule.
5. What is mean by Aufbau principle?

KEY POINTS

- Electron, proton and neutron are the fundamental particles of all kind matter.
- In discharge tube experiment, cathode rays are in fact electrons and the ca rays (when hydrogen gas is in the discharge tube) are protons.
- Electron is 1836 times lighter than proton.
- According to Planck's quantum theory, energy emitted or absorbed by a body does not propagate in continuous form but in form of sm units/packets of energy. The 'unit wave' or 'pulse of energy' is called quant He proposed the equation E = $h\nu$, for the energy of quantum.
- Bohr rectified the Rutherford atomic model and developed an atomic mo for hydrogen on the basis of quantum theory in 1913.
- Bohr successfully gave equations for the calculation of radius and ene of orbits of electron and frequency, wavelength and wave number of radiatio released or absorbed during electronic transition between shells.
- Bohr explained the spectrum of hydrogen atom.
- X – rays are high frequency radiations, discovered by Roentgen. These ra are produced by hitting the metal surface by high-energy electron beam.
- According to Moseley, the number of positive charges in the nucleus is th fundamental property of an element.
- Moseley's law states that, the square root of the frequency ($\sqrt{\upsilon}$) of th emitted X – ray radiation is directly proportional to the atomic number (Z) o an element, $\sqrt{\upsilon} \propto Z$
- Quantum numbers are a set of numbers, which designate an electron in a atom. These are four in number i.e. principal quantum number (n), azimuth quantum number (ℓ), magnetic quantum number (m) and spin quantu number (m_s, or s)
- An orbital is a region of space around the nucleus where the probability finding electron is maximum.
- Aufbau principle, Pauli's exclusion principle, and Hund's rule are followed the distribution of electrons in different orbitals of multi electron atoms.

EXERCISE

Choose the Correct Option.

1. The e/m ratio of cathode rays is,
   - a. 1.76×10^{23} C/kg
   - b. 1.76×10^{11} C/kg
   - c. 1.76×10^{-31} C/kg
   - d. 1.76×10^{7} C/kg
2. The wave number ($\bar{\upsilon}$)of a radiation with $\lambda = 2\times10^{8}$nm will be,
   - a. 0.5×10^{-8} nm^{-1}
   - b. $10nm^{-1}$
   - c. $5nm^{-1}$
   - d. $100nm^{-1}$
3. For an electron in K-shell, the correct four quantum numbers are represented by,
   - a. $n=1,\ \ell=0,\ m=0,\ s=+\frac{1}{2}$
   - b. $n=2,\ \ell=0,\ m=0,\ s=+\frac{1}{2}$
   - c. $n=1,\ \ell=1,\ m=0,\ s=-\frac{1}{2}$
   - d. $n=2,\ \ell=2,\ m=+2,\ s=+\frac{1}{2}$
4. All are electromagnetic in nature except,
   - a. IR rays
   - b. X – Rays
   - c. UV- rays
   - d. cathode Rays
5. The energy associated with quantum of radiation is,
   - a. $h\upsilon$
   - b. $\frac{nh}{2\pi}$
   - c. $2h\upsilon$
   - d. $\frac{1}{2}h\upsilon$
6. Bohr's theory cannot be applied on,
   - a. H
   - b. H^{+}
   - c. He^{+1}
   - d. Li^{+2}
7. Which of the following sets of quantum numbers are not possible?
   - a. $n = 3,\ \ell = 2,\ m = 0,\ s=-\frac{1}{2}$
   - b. $n = 3,\ \ell = 3,\ m = -3,\ s=+\frac{1}{2}$
   - c. $n = 4,\ \ell = 3,\ m = -3,\ s=+\frac{1}{2}$
   - d. $n = 3,\ \ell = 1,\ m = 0,\ s=+\frac{1}{2}$

8. The frequency of a green light is 6×10^{14}Hz, its wavelength is,
   a. 5nm b. 500nm c. 5000nm d. 100nm
9. Which of the following sub-shell do not exist?
   a. 1p b. 5d c. 6f d. 1s
10. All quantum numbers are obtained from solution of Schrödinger equa except,
    a. Principal quantum number, n
    b. Magnetic quantum number, m
    c. Spin quantum number, s
    d. Azimuthal quantum number, ℓ
11. The maximum number of electrons in 3*s* orbital,
    a. 1 b. 2 c. 6 d. 10
12. The splitting of spectral lines in magnetic field is
    a. Stark effect
    b. Zeeman effect
    c. Aufbau principle
    d. Pauli exclusion principle
13. If the mass of electron is reduced to half, the Rydberg's constant,
    a. Becomes half
    b. Becomes double
    c. Remains unchanged
    d. Becomes one fourth
14. Which element has the electronic configuration of noble-gas notation [$5s^2, 4d^2$
    a. Se b. Sr c. Zr d. Mo
15. The mathematical form of Moseley's law is
    a. $\sqrt{v} = b(z-a)$
    b. $\sqrt{v} = a(z-b)$
    c. $\sqrt{v} = \frac{a}{b}\sqrt{z}$
    d. $\sqrt{v} = \frac{b}{a}z$

Short Questions

1. Name any four properties of cathode rays.
2. How will you differentiate between a continuous and a line spectrum?
3. How did Moseley discover that the atomic number (Z) is the fundamental property of an element?
4. What are the shortcomings of Bohr's atomic model?
5. Can you give the reason that 4s orbital are written first than the 3d orbital.

Numerial Questions

1. Calculate the distance (Å) between the nucleus and an electron in the 5th orbit of an excited hydrogen atom. Ans.: 13.225Å
2. What will be the wave number ($\bar{\upsilon}$) of the spectral line of an electron when it jumps from $n_2 = 4$ to $n_1 = 2$? Ans.: $20.58 \times 10^5 m^{-1}$
3. What is frequency of a radiation with wave number ($\bar{\upsilon}$) equal to $0.5 \times 10^8 m^{-1}$? Ans.: 1.5×10^{16} Hz
4. Calculate the wavelength of an electron when it moves with the velocity of light. Ans.: 2.424×10^{-12}m
5. What will be the energy (kJ/mol) of an electron residing in n=3 in hydrogen atom? Ans.: −145.817kJ/mol
6. How much energy is lost when an electron in hydrogen atom jumps from $n_2=3$ to $n_1=1$? Ans.: 1166.542kJ/mol

Descriptive Questions

1. (a) What is Planck's quantum theory? What are the postulates of this theory?
   (b) Prove that $E = hc\bar{\upsilon}$, where E = energy, h= Planck's constant, c = velocity of light, and $\bar{\upsilon}$ = wave number.
   (c) What will be energy of a radiation with $\lambda=2\times10^{-8}$m? Ans.: 9.939×10^{-18}J
2. (a) Write down the main postulates of Bohr's atomic model.
   (b) How can Bohr's model of atom be applied to hydrogen atom to calculate the radius of nth shell? Ans: $\bar{\upsilon}=1.028\times10^7 m^{-1}$, $\lambda=9.72\times10^{-8}$m
3. (a) Derive expression using Bohr's model, for the energy difference (ΔE), frequency (ν) and wave number ($\bar{\upsilon}$) in hydrogen atom.
   (b) How does Bohr's model explain the hydrogen spectrum?
4. (a) What are X-rays? How are these rays produced?
   (b) Enlist some characteristics of X – rays.

5. (a) Define quantum numbers. What information is given by the sp quantum number? What are the possible values for this quantu number?

   (b) What information is given by the magnetic quantum number?

6. (a) What is an orbital? How does it differ from an orbit?

   (b) Discuss the shapes of s, p and d orbitals.

   (c) Calculate the wave number and wavelength of a photon when th electron jumps from $n_2 = 4$ to $n_1 = 1$. Ans: $\bar{\upsilon}=1.028\times10^{7}m^{-1}$, $\lambda=9.72\times10$

   (d) Identify the series of spectral lines to which this photon belongs?

Project:

- Take three different salts and identify unknown metal ion in them by using flame test.
- Construct a simple gas discharge tube from low cost substances, showing th electrodes, vacuum pump, power supply etc.

Unit -03

Theories of Covalent Bonding and Shapes of Molecules

After reading this unit, the students will be able to:

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

Teaching
12

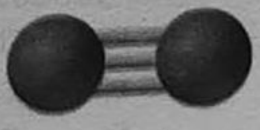
Assessment
01

Weightage %
11

H—H

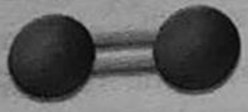
Single bond

N≡N



Triple bond

O=O



Double bond

Introduction

Dalton's atomic theory opened the ways for the scientists to think abou nature of forces that hold the atoms together. Earlier the scientists assumed chemical bond result from attraction between oppositely charged particles. S molecules like N_2, H_2 and other organic compounds were discovered which coul be explained on the basis of this concept.

In 1916, G.N. Lewis proposed that the sharing of electron was respons for the formations of bonds between molecules. He used electronic configurat to explain that how atoms join together to form molecules. He gave electronic theory of valence, according to this theory, *In chemical bond format atoms interact by sharing of electrons, to attain noble gas electr configuration.* This theory was called doublet or octet theory. This the described the sharing of electron, and covalent bond formation. This theory a identified the single, double and triple covalent bonds by sharing of one, two a three pairs of electrons respectively. The electronic theory of valence tells ab the number of electrons present in the valence shell of the central at However, this theory fails to explain geometry of molecules.

You have studied in the previous grades about the chemical bonding a its different types. In this unit, you will learn about the shapes of molecu physical and chemical properties of molecules, molecular polarity and bo energies.

3.1 Shapes of Molecules

The shape of molecules can be determined in the laboratory by mod methods such as X–rays diffraction and electron diffraction techniques. Molec shapes are important because they provide information about molecular pol and symmetry. The shape of molecule cannot be explained by the covalent bo etc. Various theories are used to understand the nature of bond and shap molecule. These theories are,

i. The valence shell electron pair repulsion theory (VSEPR)
ii. The valence bond theory
iii. The molecular orbital theory

3.1.1 Valence Shell Electron Pair Repulsion Theory (VSEPR)

In 1970, R. G. Gillespie and Nyholm proposed a theory known as Valence shell electron pair repulsion or VSEPR theory. This theory is based electron pair repulsion in valence shell of central atom. This theory states that *electron pairs (both lone pairs and shared pairs) surrounding the central ato* *be arranged in space as far apart as possible to minimize the electrostatic repulsion between them.* This theory helps in determining the geometries of the molecules. The main postulates are,

1. Pairs of electrons are arranged in space around the central atom in such a way that the distance between them is maximum and electron pair repulsion is minimum.
2. These electron pairs which form bonds are called bond pairs and those electron pairs, which do not form bonds, are called lone – pairs.
3. A lone pair of electrons is capable of occupying more space on the central atom than a bond pair. Hence, it will cause more repulsion as compared to bond pair. The electron pairs repulsion decrease in the following order,

   Lone pair – Lone pair > Lone pair – Bond pair > Bond pair – Bond pair
4. Forces of repulsion decrease with increasing bond angles.
5. As multiple covalent bonds and lone pair of electrons, occupy more space than the bond pairs, therefore, the ideal bond angles are changed.
6. Multiple bonds behave as a single electron pair bond in structural determination.
7. The effect of a bonding electron pair decreases with increasing electronegativity of an atom bonded to central atom forming in a molecule.
8. Shapes of molecules depend upon the number and nature of the electron pairs in space around the central atom.

Applications of VSEPR theory

Covalent bond is directional in nature. It explains the geometry of the molecules and tells about the possible structure of the molecule. Examples are,

Reading Check

Write down at least five postulates of the VSEPR theory.

1. Shapes of Molecules Containing Two Electron Pairs

Beryllium chloride ($BeCl_2$) is a typical example of molecules, which contain two electron pairs. It's Lewis structure is given below.

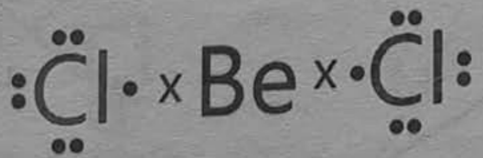


Figure 3.1 Lewis [illegible]re of $BeCl_2$

Two bond pairs are present in valence shell of the central beryllium atom, which are arranged in such a way that minimizes the repulsion between them.

The bonding pair will occupy the opposite side of the beryllium, forming an ang of 180°. This angle gives linear structure to $BeCl_2$ or a straight line arrangement the atoms. Therefore, $BeCl_2$ molecule is **linear**.

Linear Structure of $BeCl_2$ VSEPR model of $BeCl_2$

Figure 3.2

2. Shapes of Molecules Containing Three Electron Pairs

a) All three are Bond Pairs

Example is, Boron tri-fluoride (BF_3)

Boron, $B_5 = 1s^2, 2s^2, 2p_x^1, 2p_x^0, 2p_z^0$ has three valence electrons.

The boron has three valence electrons; all these three electrons form three bonds and no unshared electrons are left. The three bond pairs will be at maximum distance from each other. Therefore, the repulsion between them is minimum and the distance is maximum. The Lewis structure of BF_3 is shown in figure 3.3.

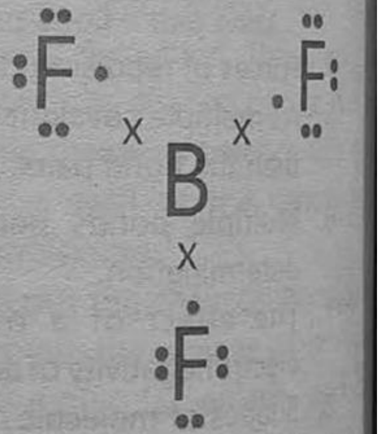
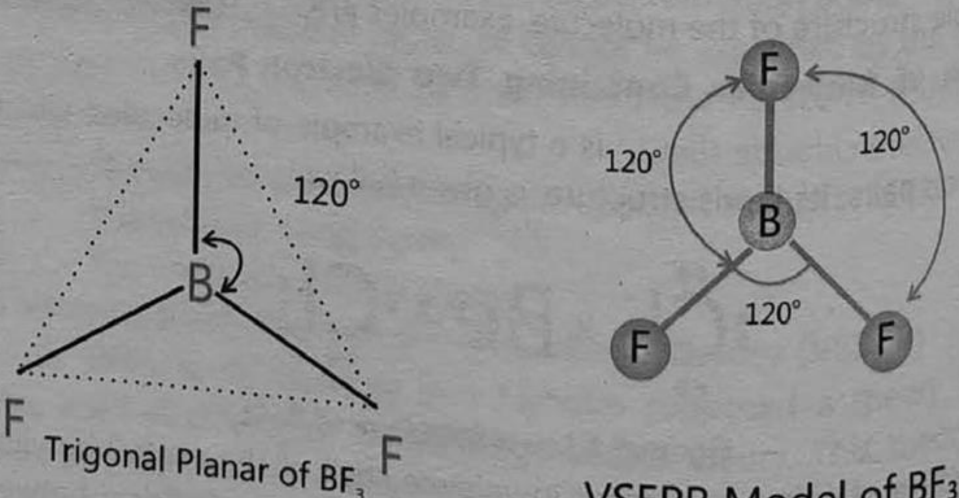


Figure 3.3 Lewis Structure of BF_3

The three F atoms will occupy the corners of an equilateral triangle. All th four atoms (three F and one B) lie in the same plane. The angle between them is 12 The shape of such molecule is **trigonal planar.**



Trigonal Planar of BF_3

VSEPR Model of BF_3

Figure 3.4

Tidbit

Many boron compounds are electron-deficient, meaning that they lack an octet of electrons (mostly have six electrons) around the central boron atom. This deficiency of electron is responsible for acidic nature of boron compounds.

b. Two Bond Pairs and One Lone Pair

Example of the molecules having two bond pairs and one lone pair is, **Stannous Chloride ($SnCl_2$)**

Stannom, Sn_{50} = [Kr] $4d^{10}5s^25p^2$ has four valence electrons. Two electrons present in 5s orbital remain non-bonding (lone pair) and two electrons of 5p orbitals form two covalent bonds with chlorine atoms. The Lewis structure of $SnCl_2$ is,

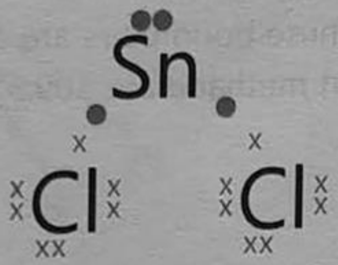
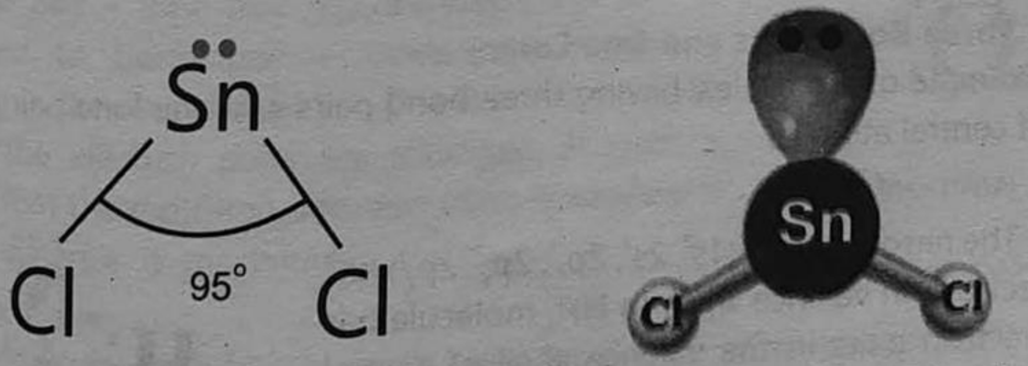


Figure 3.5 Lewis Structure of $SnCl_2$

Molecules with two bond pair electrons and one lone pair shall have the non – linear geometry. The lone pair occupies more space than the bond pair of electrons. Therefore, it pushes the bond pairs of electrons. The lone pair present in the stannous chloride occupies one corner of the triangle and the other two are occupied by two Cl atoms as shown in figure 3.6. Therefore, the bond angle is reduced than ideal angle of 120°. The effective molecular shape of $SnCl_2$ is angular (V-Shaped).



Angular structure of $SnCl_2$

VSEPR Model of $SnCl_2$

Figure 3.6

3. Shapes of Molecules Containing Four Electron Pairs

i. All the four are Bond Pairs

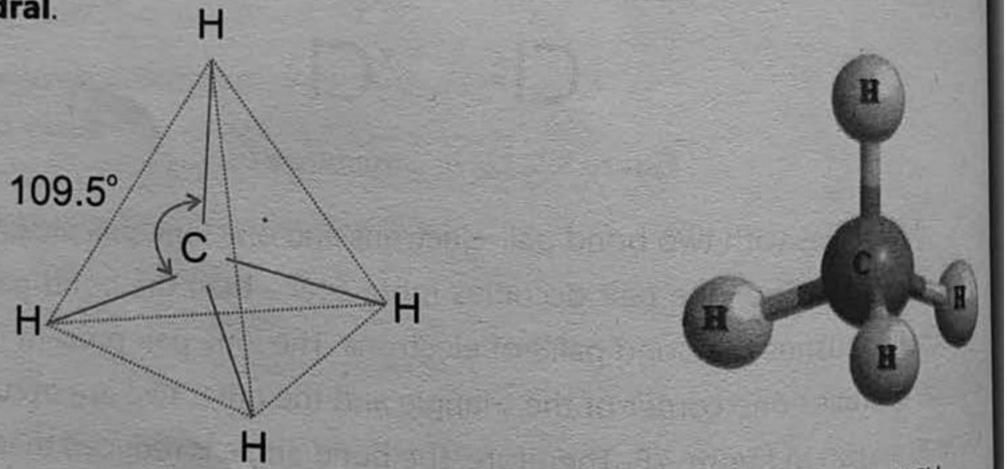
Example of molecules having four bond pairs in valence shell of central atom is,

Methane (CH_4)

Figure 3.7 Lewis Structure of C

Carbon has four electrons ($1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^0$) in the valence shell, which share with four electrons of four hydrogen atoms. All the four pairs are bond pairs.

The electron pairs are arranged in such a manner that the repulsion is minimum and the distance is maximum. These bond pairs are arranged in tetrahedral manne The H – C – H bond angles in methane are 109.5°and the shape of the molec is **tetrahedral**.



Tetrahedral Structure of CH_4 VSEPR Model of CH_4

Figure 3.8

ii. Three Bond Pairs and One Lone Pair

Example of molecules having three bond pairs and one lone pair in valen shell of central atom is,

Ammonia (NH_3)

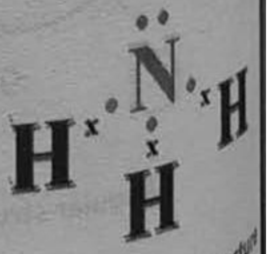
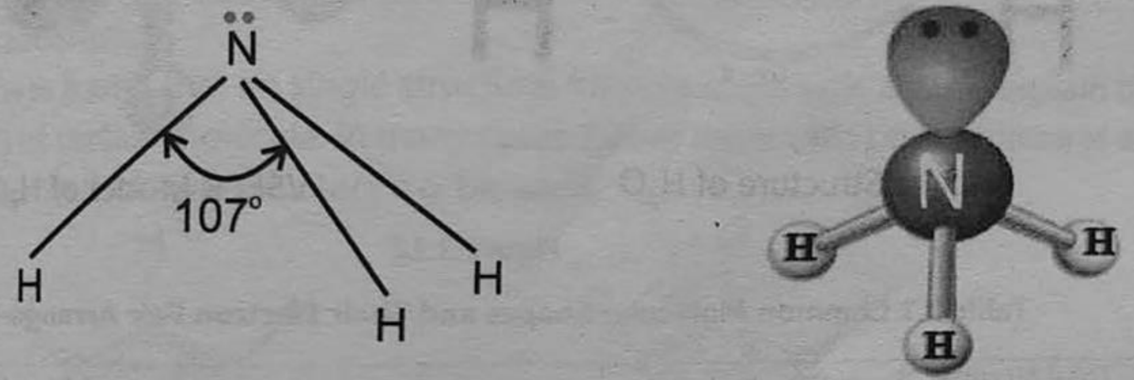


Figure 3.9 Lewis Structure of NH_3

The nitrogen, $N_7 = (1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1)$ has five electrons in valence shell. In NH_3 molecule has four electron pairs in the valence shell of central atom. Three of them are bond pairs and one is lone pair.

The electron pairs are arranged in such a manner that the repulsion between them is minimum and the distance is maximum.

According to VSEPR theory, lone pair – bond pair repulsion is greater than bond pair – bond pair repulsion. The lone pair occupies more space than the bond pair of electrons. Therefore, the three N – H bond pairs are pushed closer and bond angle decreases. Therefore, the ideal bond angle is changed and reduced to 107.5°. Moreover, due to absence of atom on lone pair, NH_3 does not show the expected tetrahedral arrangement but possesses a **trigonal pyramidal** structure with the observed angle 107.5°as shown in figure 3.10.



Trigonal Pyramidal Structure of NH_3 VESPR Model of NH_3

Figure 3.10

iii. Two Bond Pairs and Two Lone Pairs

Example of the molecules having two bond pairs and two lone pairs in the valence shell of central atom is water.

Water (H_2O)

The oxygen, O_8= ($1s^2$, $2s^2$, $2p_x^2$, $2p_y^1$, $2p_z^1$), in water molecule has four electron pairs; two bond pairs and the two lone pairs. The lone pair – lone pair repulsion is maximum as compared to bond pair – bond pair repulsion, resulting in the decrease of H – O – H bond angle to 104.5°. The electron pairs are arranged in such a manner that the repulsion between them is minimum and the distance is maximum.

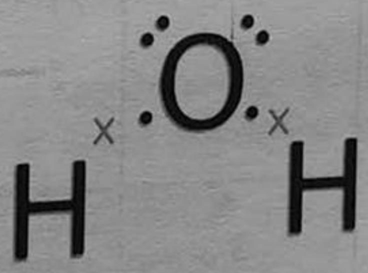
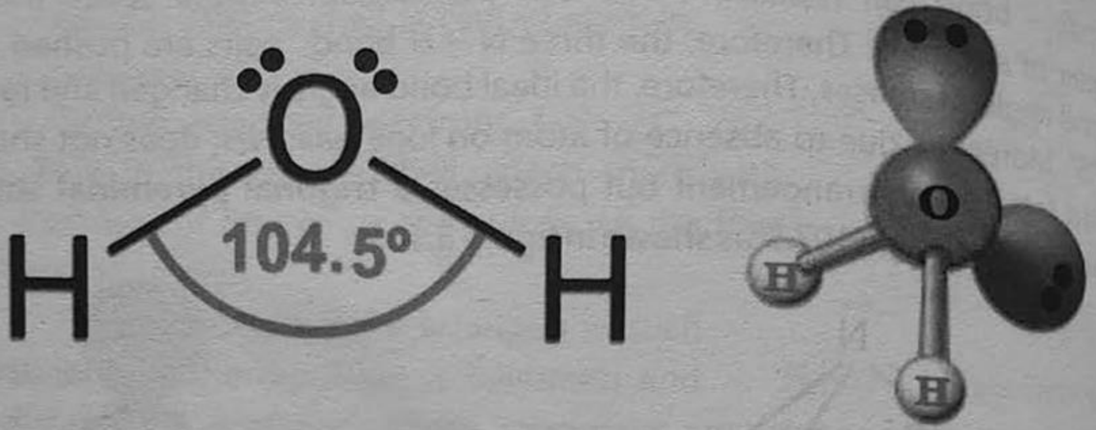


Fig: 3. 11 Lewis Structure of H_2O

Molecules with four electron pairs repel each other and thus are directed towards the four corners of a regular tetrahedron. However, the two lone pairs of electrons occupy more space than the bond pair of electrons. Therefore, they push the bond pairs of electrons to greater extent. Thus, the ideal bond angle is reduced. Moreover, due to absence of atoms on lone pair, the H_2O molecule is bent at an angle of 104.5°. Such a molecule is called a bent molecule (V – shaped) or angu molecule.

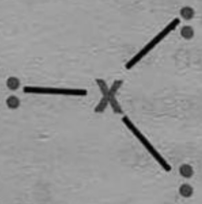
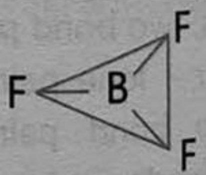
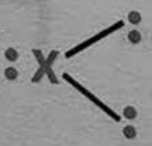
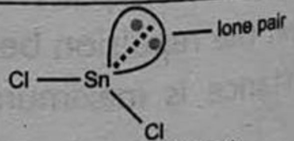
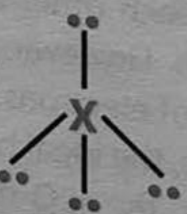
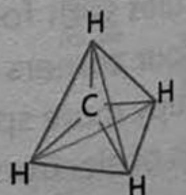


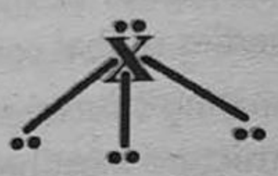
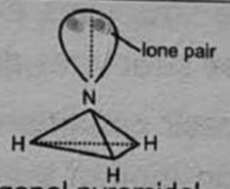
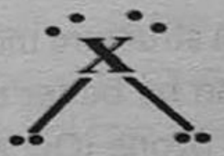
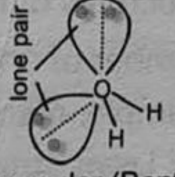
Angular Structure of H_2O

VSEPR Model of H_2O

Figure 3.12

Table 3.1 Common Molecular Shapes and Their Electron Pair Arrangements

Total Number of electron pairs Present in Valence Shell of Central Atom	Geometric arrangements of electron pairs	Type of electron pairs	Name of molecular shape	Example
2	:—X—:	2 bond pair 0 lone pair	Cl—Be—Cl linear	$BeCl_2$
3		3 bond pair 0 lone pair	 trigonal planar	BF_3
3		2 bond pair 1 lone pair	 angular (Bent)	$SnCl_2$
4		4 bond pair 0 lone pair	 tetrahedral	CH_4

4		3 bond pair 1 lone pair	 trigonal pyramidal	NH_3
4		2 bond pair 2 lone pair	 angular (Bent)	H_2O

3.1.2 Resonance

It was found that no single structural formula could satisfactorily explain the structures of certain molecule. In many cases, two or more valid Lewis structures are used to show a molecule structure e.g. benzene.

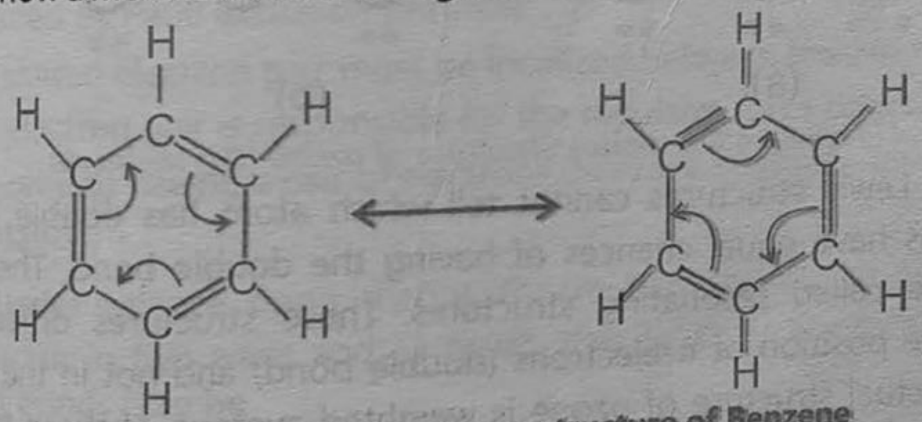


Figure 3.13 Resonance structure of Benzene

Even though these Lewis structures differ in the position of their electrons, they all represent the same molecule. It is important to know that none of these Lewis structures has a real physical existence, and the best representative is certainly the weighted average of these Lewis structures.

The phenomenon in which two or more structures can be written for a compound, which involves identical positions of atom, is called resonance. In other words, you can simply say that, a molecule or ion that has multiple correct Lewis structures shows resonance. Each of these Lewis structures is called a resonating structure. The actual structure of the molecule is said to be a resonance hybrid of all possible structures.

This led to the idea that such molecules exist in the state, which is combination of two or more electronic structures.

Tidbit

Resonance Hybrid

The weighted average of resonance contributors, which best represents, the reality. Demonstrating the molecule the way it is observed in lab.

These structures express some of the properties of the compounds b none of these structures describing all the properties of that compound.

a. The basic conditions for writing the resonating structures are,
b. The position of the nuclei (atom) in all structure must be the same.
c. The structures differ only in the position of pi(π)electrons
The number of unpaired electrons in each structure must be the same.

For example, many bonding situations can be better described with mo than one valid Lewis structure for ozone (O_3). In ozone (O_3), the central atom h a single bond with one oxygen atom and a double bond with other oxygen at as,

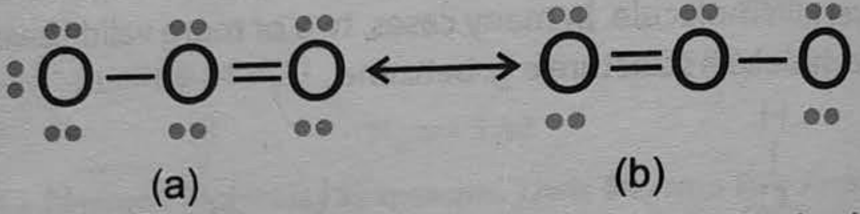

(a) (b)

Figure 3.14 Resonance Structure of ozone (O_3) Molecule

These Lewis structures cannot tell which atom has double bond. Bo oxygen atoms have equal chances of having the double bond. These possib structures are called resonating structures. These structures differ from o another in the position of π-electrons (double bond) and not in the position atoms. The actual structure of ozone is weighted average of these two possi Lewis structures.

The phenomenon of resonance explained a number of facts, which w not explained by the simple Lewis structures. The most important effect resonance is that it stabilizes the resonance hybrid. The energy of resonance hyb is lower than calculated value of resonating structures.

3 .2 Theories of Covalent Bonding

The following two theories are used to understand the nature of cova bond, in addition to VESPR and Resonance Theories.

1. The Valence Bond Theory (VBT) and Hybridization Theory
2. The Molecular Orbital Theory (MOT)

3.2.1 Valence Bond Theory (VBT) and Hybridization

For a theory to be accepted, it must explain experimental data and be abl predict behaviour of a substance. For example, VSEPR theory has gained widespr acceptance because it explains and predicts all dimensional molecular shapes (2D and 3D) that are consistent with experimental data collected for thousan different molecules. However, VSEPR theory does not provide an explanation of chemical bonding (sharing of electrons between atoms).

Valence bond theory is successful in explaining the sharing of electrons between atoms, bond lengths and shapes of covalent molecules. This theory was developed by W. Heitler and F. W. London in 1927.

The following are the assumptions of valence bond theory,

1. A covalent bond is formed by the overlap of half filled orbitals (have one electrons only) of two atoms.
2. If two half filled orbitals overlap, a single covalent bond is formed. If more than two half filled orbitals overlap, then multiple covalent bonds are formed.
3. The orbitals, which overlap, must have electrons with opposite spin as required by Pauli exclusion principle.
4. The shared electron pair must be localized between the atoms.
5. The electron pair is responsible for the repulsive force between atoms.
6. The orbitals having a pair of electrons (two) are unable to take part in the bond formation.

Under valence bond theory, the mutual sharing of electrons between atoms occur in two ways and as result, two types of bonds are formed. These covalent bonds may be

i. Sigma (σ) bond
ii. Pi (π) bond

i. Sigma (σ) Bond

It is formed by the linear overlap of half filled atomic orbitals. This type of overlap is maximum and hence forms a strong bond. In sigma bond, the electronic density is maximum in between the two bonded nuclei. The shared pair of electrons is attracted by two nuclei and, as a result, a decrease in energy occurs. *The bond, which is formed by the linear (head on) overlap is called sigma bond.* All single covalent bonds are sigma bonds.

The following types of overlapping result in sigma bond formation.

a) s – s overlap
b) s – p overlap
c) p – p overlap

a. s – s overlap

In this overlap, the 's–orbital' of one atom overlaps with the 's– orbital' of the other atom. For example, hydrogen molecule (H_2).

Hydrogen molecule is formed between two hydrogen atoms by over two 1s orbitals. When two half filled, $1s^1$ orbitals of hydrogen come close overlap each other, the energy decreases, reaches to a minimum and a sig covalent bond is formed as shown in figure 3.15.

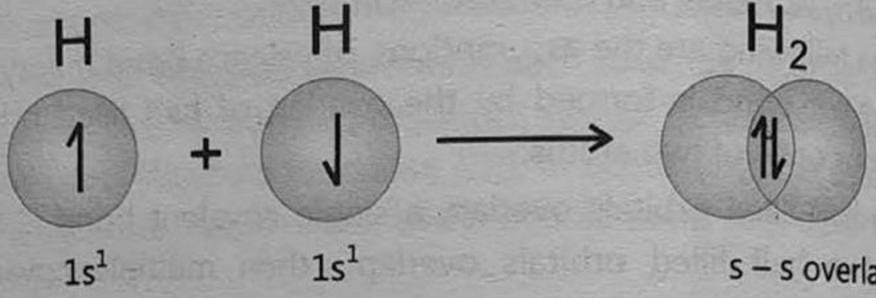


Figure 3.15 s – s Overlap in Hydrogen Orbitals

b. s – p overlap

In this overlap the 's – orbital' of one-atom overlaps with the 'p – orbital' other atom, for example, hydrogen chloride (HCl) molecule.

In HCl molecule, hydrogen contains one-half filled 1s atomic orbital there is one half filled p-atomic orbital in chlorine. When hydrogen and chl atoms come closer to one another, their '1s' and 3p orbitals overlap linearly energy decreases, reaches to a minimum and a sigma (σ) covalent bond is form shown in figure 3.16.

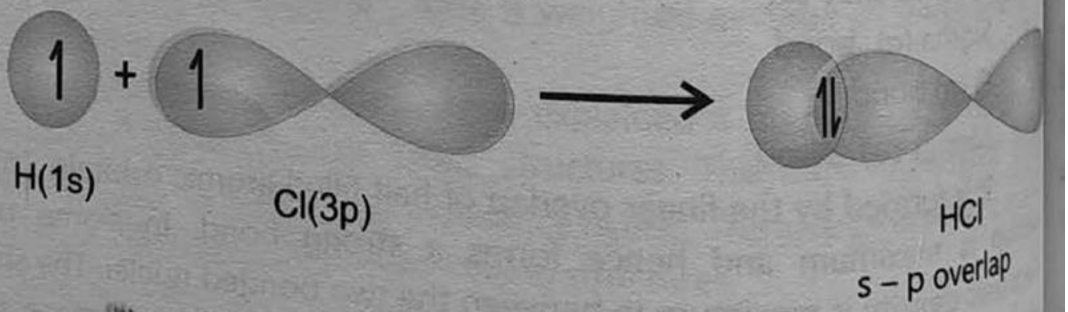


Figure 3.16 s – p Overlap in Hydrochloric Acid (HCl) Molecule

c. p – p Linear overlap

In this overlap, the 'p' orbital of one atom overlaps with another 'p' o of the other atom endwise, linearly or heads – on. In this overlapping, a s bond is formed. For example, F_2, Cl_2, Br_2

The formation of F_2 molecules is an example of p – p orbital overlap fluorine atom contains one-half filled p atomic orbital. These two half fille orbitals overlap linearly to form a sigma bond. The electronic density is ma along the bond axis as shown in figure 3.17.

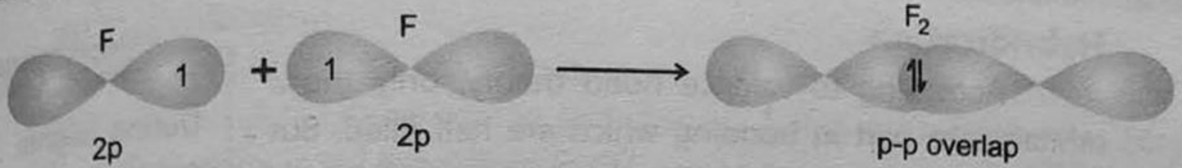


Figure 3.17 p – p Linear Overlapping in Fluorine Molecule

ii. Parallel overlap or Pi (π) Bond

The bond, which is formed by side wise or parallel overlap of the half filled p - orbitals of two already bonded atoms (through sigma bond), is called pi(π) Bond.

Pi – bond is always formed by the side wise or lateral overlap of half filled p - orbitals only. The pi – bond is weak bond. It cannot exist without the sigma bond. In pi (π) bond the orbital has two regions of electronic cloud density i.e. above and below the bond axis; unlike in sigma bond where electronic density has only one region around bond axis. Since this overlap is not maximum overlap therefore, pi bond is weaker than sigma bond.

For example, in O_2 molecule, each oxygen atom has electronic configuration $1s^2$, $2s^2$, $2p_x^2$, $2p_y^1$, $2p_z^1$. There are two half-filled p orbitals on each oxygen atom. The two oxygen atoms are joined by two bonds. One of them is formed by linear overlap of p orbitals, forming a sigma bond, while the other p – orbitals overlap side wise to form a Pi bond as shown in the figure 3.18.

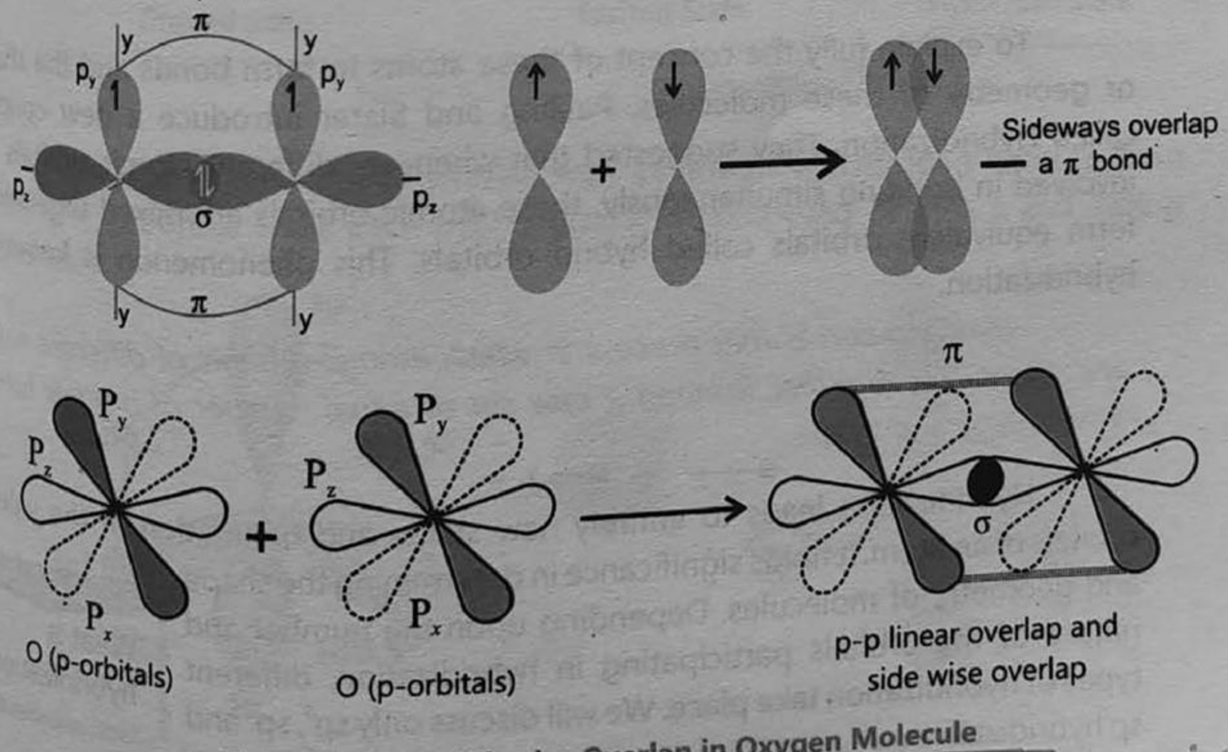


Figure 3.18 p-p Sidewise Overlap in Oxygen Molecule

Hybridization

According to valence bond theory, only those orbitals take part in bonding which are half filled. But there are molecules in which the number of bonds formed by an atom is more than their available half filled orbitals. Carbon has six electrons, $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^0$. Electro configuration shows that there are only two half-filled orbitals, it is expected t only two single bonds will be formed. However, carbon atom forms four bon with other atoms in most molecules such as in CH_4 molecule.

Reading Check

Define sigma and pi bonds.

It is assumed that one of the 2s electrons in ground state is promoted to t empty p orbital. This new state of carbon is called the excited state.

C (Ground state) = $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$

C (Excited state) = $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$

As there are four half-filled orbitals in the carbon atom in its excited state, i expected that four bonds will be formed. The three C–H bond would be formed b the overlap of the p-orbital and 1s orbital of each hydrogen atoms. The fourth C– bond will be formed by the overlap of 2s orbital of carbon with the 1s orbital of hydrogen atom. This implies that two different type of C–H bonds are involved in th formation of methane molecule. However, experimental data shows that all the C– bonds are identical.

To explain fully the concept of these atoms to form bonds and the shap or geometry of these molecules, Pauling and Slater introduce a new concep called Hybridization. They suggested that whenever different atomic orbitals ar involved in bonding simultaneously, these atomic orbitals are mixed together to form equivalent orbitals called hybrid orbitals. This phenomenon is known a hybridization.

Hybridization is that process in which atomic orbitals of different energ and shape mix together forming a new set of equal number of orbitals havin same energy and shape.

Hybridization leads to entirely new shape and orientation of the valen orbitals of an atom. It holds significance in determining the shape and geometry of molecules. Depending upon the number and nature of the orbitals participating in hybridization, different types of hybridization take place. We will discuss only sp^3, sp^2 and sp hybridization.

Reading Check

What is hybridization?

i. sp^3 Hybridization

The mixing of one s and three p orbitals to form four equivalents sp^3 hybrid orbitals of the same energy and shape is called sp^3 hybridization. For example, carbon atom is sp^3 hybridized in CH_4 molecule.

In methane (CH_4) molecule, carbon atom forms four identical bonds by using four equivalent hybrid orbitals. These orbitals are the result of sp^3 hybridization, one s and three p-orbitals of carbon are mixed to form four sp^3 hybrid orbitals. These sp^3 orbitals are similar in shape and energy and become oriented at an angle of 109.5°.

C (Ground state)= $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$

C (Excited state)= $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$

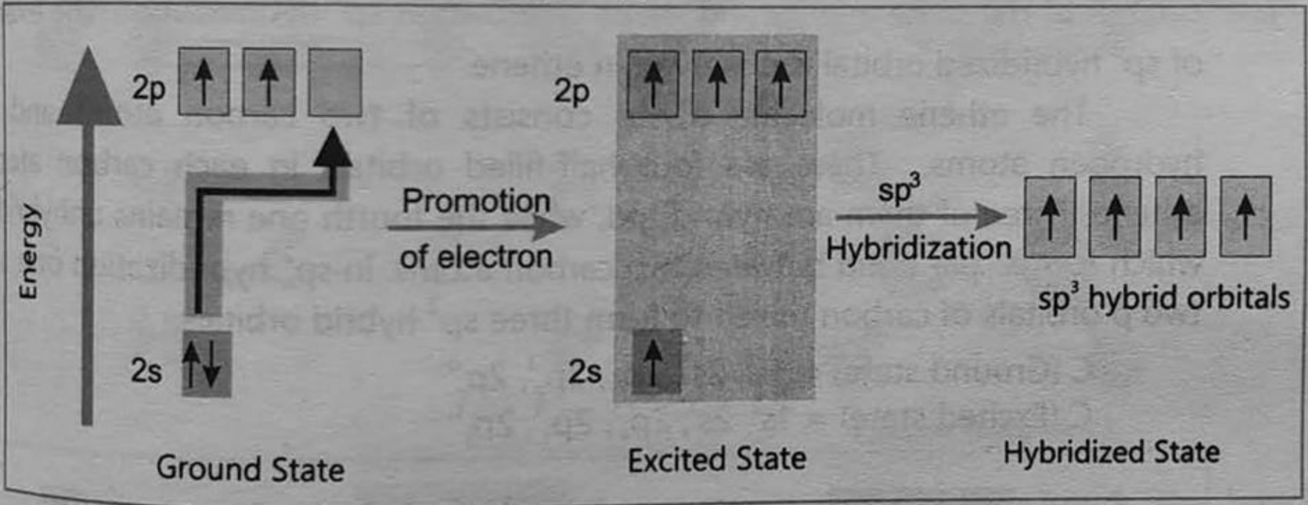


Figure 3.19 (a) sp^3 Hybridization

Each sp^3 hybrid orbital overlap with 1s orbital of hydrogen atom to form four C – H bonds. Thus, each hybrid orbital is composed of 25% s and 75% p character.

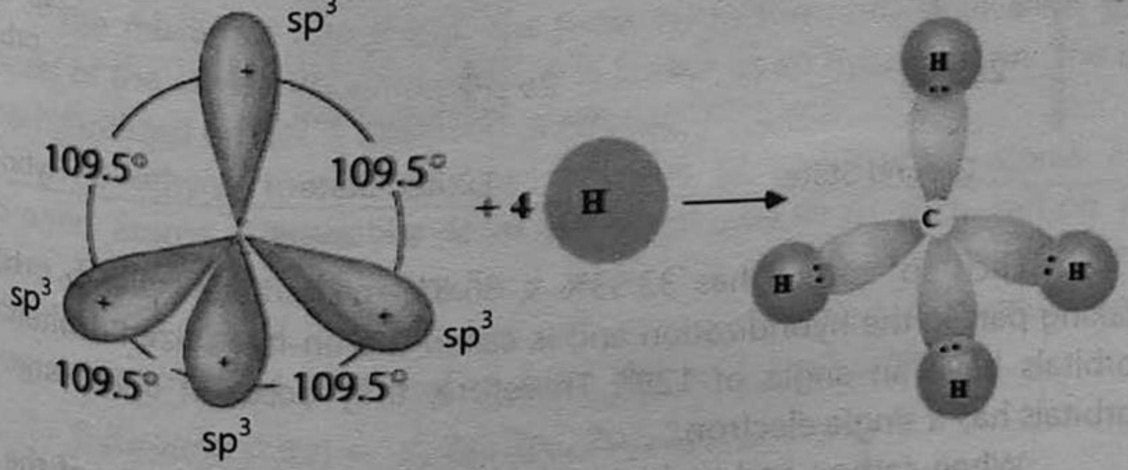
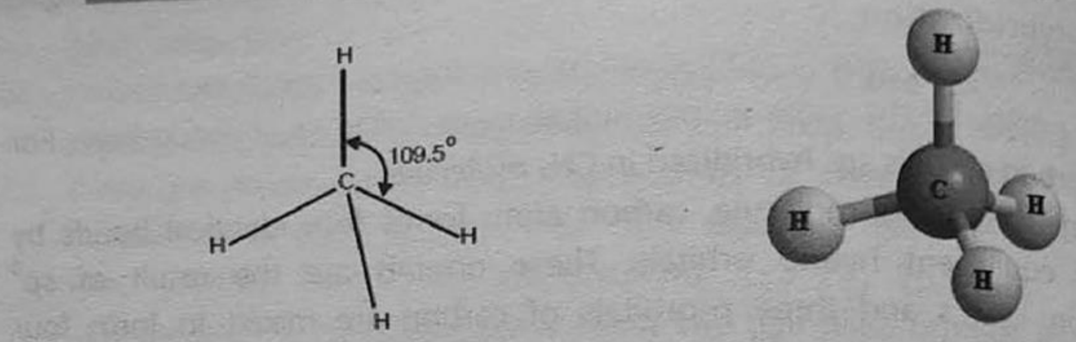


Figure 3.19 (b) sp^3 Hybrid Orbitals and Hydrogen Atoms



CH$_4$ Moleucle

Figure 3.20 Tetrahedral CH$_4$ Molecule

ii. sp^2 hybridization

The mixing of one s and two p-orbitals to form three equivalent sp^2 hy orbitals of the same energy and shape is known as sp^2 hybridization. The exa of sp^2 hybridized orbital is observed in ethene.

The ethene molecule (C_2H_4) consists of two carbon atoms and hydrogen atoms. There are four half-filled orbitals in each carbon ato ethene. Three of them are hybridized, while the fourth one remains unhybridi which forms pi– bond between two carbon atoms. In sp^2 hybridization one s two p orbitals of carbon mixed to form three sp^2 hybrid orbitals.

C (Ground state) = $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$
C (Excited state) = $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$

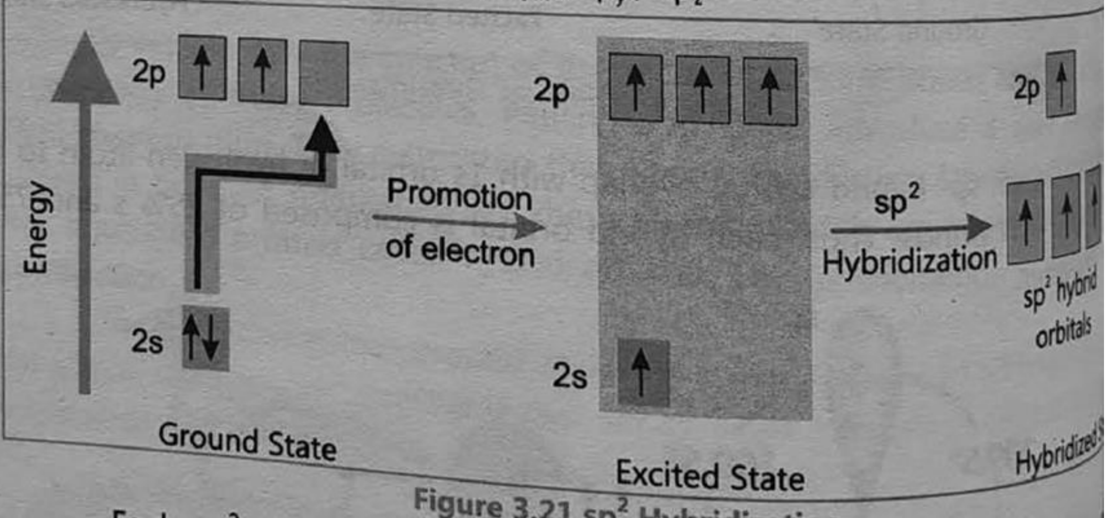


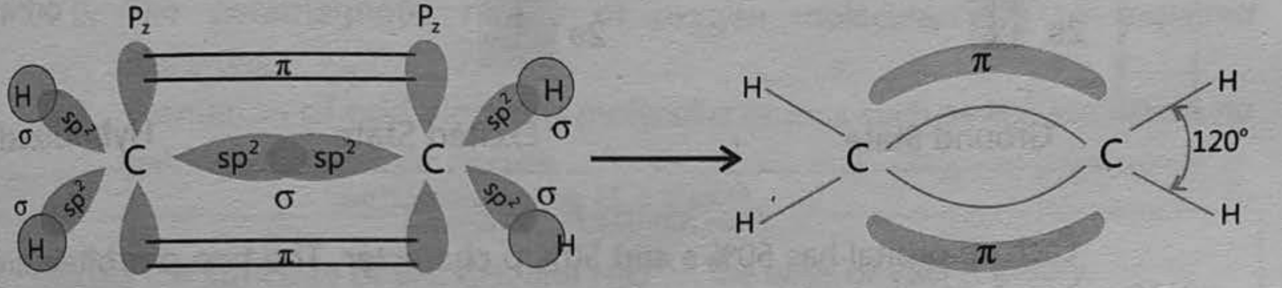
Figure 3.21 sp^2 Hybridization

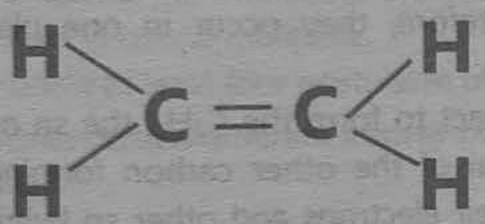
Each sp^2 orbital has 33.33% s, 66.67 % p character. One p orbital is taking part in the hybridization and is called the un-hybridized orbitals. These orbitals have an angle of 120°. Therefore, they occur in one plane. Each orbitals has a single electron.

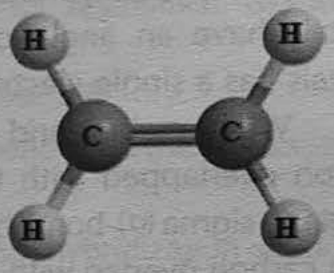
When carbon and hydrogen react to form the C_2H_4, one of the three orbitals of one carbon overlaps with sp^2 orbital of the other carbon, forming a C – C, covalent sigma (σ) bond by sharing their unpaired electron.

The remaining two sp^2 orbitals of each carbon overlap with two s orbitals of the two hydrogen atoms forming two more covalent (C – H) sigma bonds by the sharing of their unpaired electron.

As each carbon has one p un-hybridized, these orbitals also overlap sidewise with each other forming a weaker covalent bond called pi(π) bond.







Ethene (Ethylene)

Figure 3.22 Ethene Molecule

The double bond consists of one sigma and one π - bond. The bond length of C=C double bond is 1.34Å . The C – H bond length is 1.10Å. The bond angle is 120°. Thus, the structure of ethene is planer. There are five sigma bonds and one π - bond in ethene molecule.

iii. sp Hybridization

The mixing of one s and one p orbital to form two equivalent sp hybrid orbitals of the same energy and shape is known as sp hybridization. The example of sp hybridized orbital is observed in ethyne.

The ethyne molecule (C_2H_2) consists of two carbon atoms and two hydrogen atoms. There are four half-filled orbitals in each carbon atom in ethyne. Two of them are hybridized, while the other two remain unhybridized, which form pi – bond between two carbon atoms. In sp hybridization one s and one p orbitals of carbon mixed to form two sp hybrid orbitals.

C (Ground state) = $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$

C (Excited state) = $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$

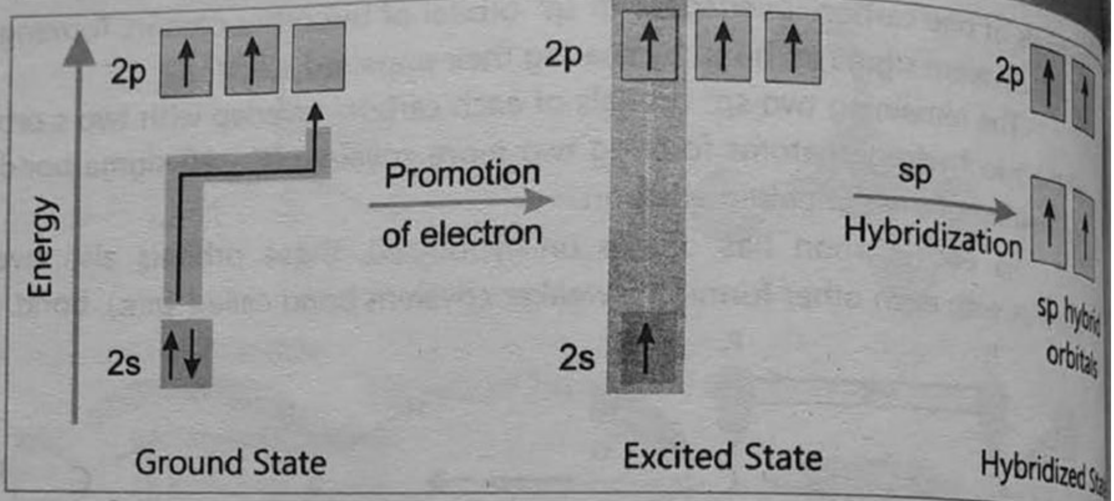


Figure 3.23 sp Hybridization

Each sp orbital has 50% s and 50% p character. The two p orbitals are n taking part in the hybridization and are called the un-hybridized orbitals. The s orbitals have an angle of 180°. Therefore, they occur in one plane. Each s orbitals has a single electron.

When carbon and hydrogen react to form the C_2H_2, the sp orbital of on carbon overlapped with the sp orbital of the other carbon forming a C- covalent sigma (σ) bond by sharing their electrons and other sp hybrid orbitals each carbon overlap with 1s orbital of hydrogen to form C – H sigma bond, whi the two unhybridized p orbitals overlap sidewise to form two pi (π) bonds.

As each carbon has two un-hybridized p orbitals, which are bi-lobe dumbbell shaped. Their one lobe is above the plane and other lobe is belo These orbitals also overlap with each other parallel or laterally forming pi-bond

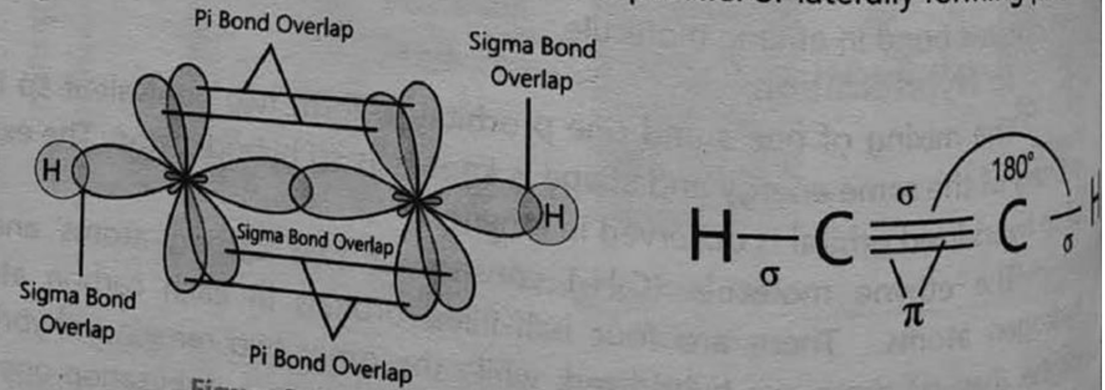


Figure 3.24 Overlapping of Orbitals and Ethyne Molecule

The ethyne (acetylene) molecules consists of triple bond between carb atoms (C≡C) i.e. one sigma and two pi-bonds having a length of 1.20Å. The C –H bond length is 1.09Å . The bond angle is 180° and the shape molecule is linear. Overall, there are three sigma and two pi-bonds (π – bonds) in the molecule of acetylene.

Shortcoming of Valence Bond Theory

Though the valence bond theory explains the bonding and geometry of many molecules and ions, but it failed to explain the,

1. Formation of coordinate covalent bond.
2. The paramagnetic nature of oxygen molecule, due to unpaired electrons.
3. Formation of odd electrons molecules or ions such as H_2^+ ion where no pairing of electrons occurs.

Self-Assessment

1. Discuss the structure of BF_3, CH_4 and H_2O on the basis of VSEPR theory.
2. Define resonance? What are the basic conditions for resonance? Discuss the resonance in ozone molecule.
3. Write down at least four postulates of the valence bond theory.
4. How sigma bond is different from pi-bond. Explain bonding in the molecules of HCl, Cl_2 and O_2.
5. What is hybridization? Discus the sp^3, sp^2 and sp hybridization in different molecules in detail.
6. What are the shortcomings of VBT?

STS Science, Technology and Society

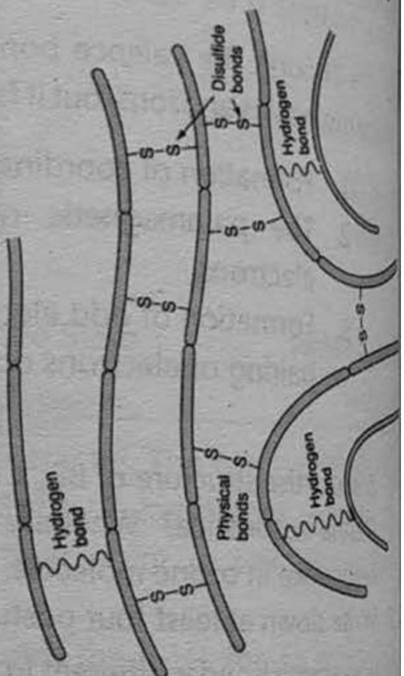
Hair is composed of keratin, a strong fibrous protein. The hydrogen bonds and disulfide bonds are responsible for straight and curly hairs.

Hydrogen bonds

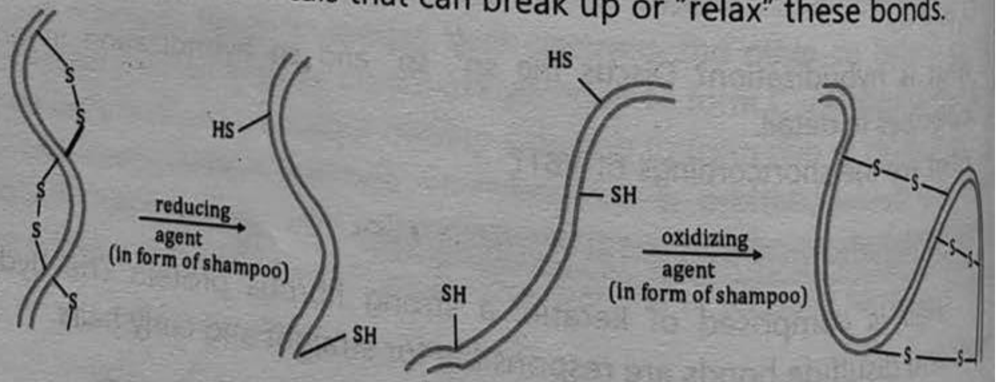
These bonds are the most flexible. Hydrogen bonds are easily broken in the presence of water and heat. They are the primary bonds responsible for changing our hair's overall shape. Hydrogen bonding allows our hair to change shape temporarily and produces a strong hold. When the hair is wet by either shampooing/conditioning or in the presence of humidity, the molecules enter the fibers, break up the hair's preset hydrogen bonds, and form new bonds. For example, hair is usually set in rollers while wet. The hair is then held in position until it dries. As the hair dries, hydrogen re-bonding occurs, but in the new "shape".

The hair will remain in the new "shape" until it is wetted with wate again and that can occur either through shampooing/conditioning or throug humidity.

Disulphide bonds



Disulphide bonds are also known as Cysteine bond, Sulphur bond or S-bond. There is a formation of α covalent bond called a disulphide bridge between the sulphur atoms on two cysteins on separate chains of keratin. These bonds are stronger than hydrogen bond. The more disulphide that occurs in the fiber, the curlier and kinkier the hair. These bonds cannot be broken by water or heat treatment. Only chemical agents can break these bonds. Therefore, if a person with curly hair wants straight hair, he/she would need to use chemicals that can break up or "relax" these bonds.



3.2.2 Molecular Orbital Theory (MOT)

In 1932, Hund and Mulliken put forward the molecular orbital theory. T theory explains the formation of covalent bond and paramagnetic propertie molecules in a better way. According to molecular orbital theory, all atomic or of the atoms take part in the formation of molecule. Mix with one another to giv to an equal number of new orbitals called molecular orbitals. The molecular or with lower energy are called bonding molecular orbitals and denoted by σ or π. other with higher energy are called anti-bonding molecular orbitals denoted by π*. The main features of molecular orbital theory are as under.

1. All the molecular orbitals have definite energy. Their relative energies are,

   $\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < \sigma 2p_x < \pi 2p_y = \pi 2p_z < \pi^* 2p_y = \pi^* 2p_z < \sigma^* 2p_x$

2. The arrangement of electrons in molecular orbitals occurs according to the Pauli's exclusion principle, Aufbau principle and Hund's rule.

3. The sigma (σ) and pi (π) notation are used in the same way as they are used in the valence bond theory but here the bonding molecular orbital (B.M.O) are σ and π, while the anti-bonding molecular orbitals (A.B.M.O) are σ* and π*.

The number of bonds in a molecule is one-half of the difference of the number of electrons in the bonding molecular orbital and the number of electrons in the anti-bonding molecular orbitals and is called bond order.

Mathematically,

$$\text{Bond order} = \frac{\left(\begin{array}{c}\text{No. of electrons in}\\ \text{bonding molecular orbitals}\end{array}\right) - \left(\begin{array}{c}\text{No. of electrons in}\\ \text{anti-bonding molecular orbitals}\end{array}\right)}{2}$$

Usually in practice, only molecular orbitals formed from the valence orbitals are considered for determining bond order.

ReadingCheck

Define bond order.

Applications of Molecular Orbital Theory

i. Hydrogen Molecule (H_2)

The atomic number of hydrogen is one. Its electronic configuration is '$1s^1$'. Hydrogen molecule (H_2) is formed by the overlap of two $1s^1$ atomic orbitals of two hydrogen atoms. They produce two molecular orbitals. One is bonding molecular orbital (B.M.O) σ(1s) and the other is anti-bonding molecular orbitals (A.B.M.O) σ*(1s). The molecule has two electrons to be filled in these molecular orbitals. According to Aufbau principle both these electrons will enter in the lower energy bonding molecular orbitals (B.M.O) and the anti-bonding molecular orbitals (A.B.M.O) remains vacant. The electronic configuration of the molecule is represented by the equation:

$$2H\,(1s^1) \longrightarrow H_2\,[\sigma(1s^2)\,\sigma^*(1s^0)]$$

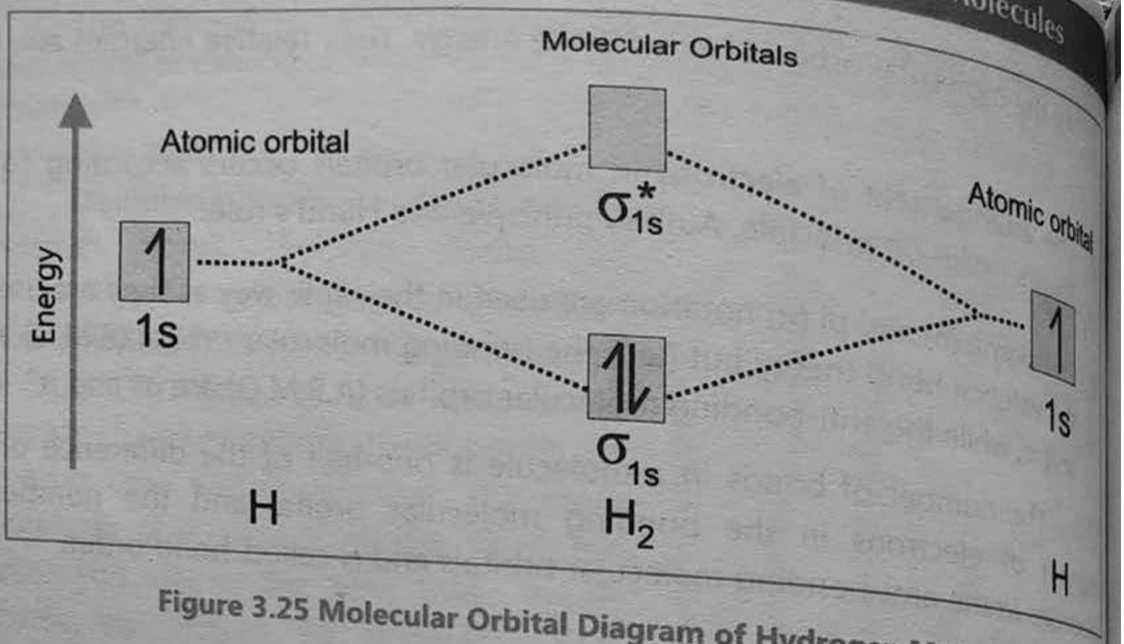


Figure 3.25 Molecular Orbital Diagram of Hydrogen Molecule

The number of bonds in the molecule is,

$$\text{Bond order} = \frac{(\text{No. of electrons in BMO's}) - (\text{No. of electrons in ABMO's})}{2}$$

$$\text{Bond order} = \frac{(2-0)}{2} = \frac{2}{2} = 1$$

Thus, the two hydrogen atoms are bonded through only one bond in th molecule.

ii. Helium Molecule (He_2)

The atomic number of 'He' is two. Its electronic configuration is $1s^2$. Tw atomic orbitals of two He atoms combine to produce two molecular orbitals. One bonding molecular orbital (B.M.O) σ(1s) and the other is anti-bonding molecu orbitals, (A.B.M.O) σ* (1s). The molecule has four electrons to be filled in the molecular orbitals. According to Aufbau principle two electrons enter in the low energy bonding molecular orbitals (B.M.O) σ(1s) and the other two electrons ent the anti-bonding orbitals (A.B.M.O) σ*(1s). The electronic configuration of th molecule is represented by the equation:

$$2He\,(1s^2) \longrightarrow He_2\,[\sigma(1s^2)\,\sigma^*(1s^2)]$$

Each one of these molecular orbitals would accommodate two elect as shown in the figure 3.26.

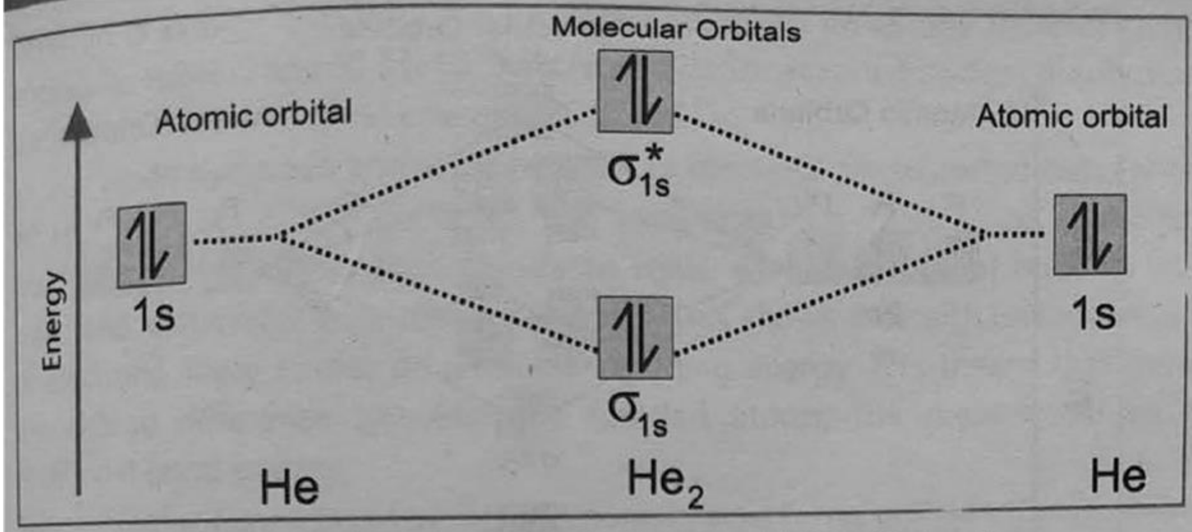


Figure 3.26 Molecular Orbital Diagram of Helium Molecule

The number of bonds in the molecule is,

$$\text{Bond order} = \frac{(\text{No. of electrons in BMO's}) - (\text{No. of electrons in ABMO's})}{2}$$

$$\text{Bond order} = \frac{(2-2)}{2} = 0$$

As bond order is zero so no bond is formed in He_2. It means that this molecule does not exist.

iii. Oxygen Molecule (O_2)

The atomic number of Oxygen is eight. Its electronic configuration is $1s^2$, $2s^2$, $2p_x^2$,$2p_y^1$,$2p_z^1$. Each oxygen atom contributes six electrons to O_2 molecule from its valence shell. The two participating oxygen atoms contribute a total of $2(2+2+1+1) = 12$ valence electrons, There are eight molecular orbitals and 12 electrons are accommodated in them as shown in Fig. 3.29.

The molecule of oxygen is represented by the equation.

$$2O(1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1) \longrightarrow O_2[\sigma(2s^2), \sigma^*(2s^2), \sigma 2p_x^2, \pi 2p_y^2 = \pi 2p_z^2, \pi^* 2p_y^1 = \pi^* 2p_z^1, \pi^* 2p_x^0]$$

The electronic configuration of the molecular orbitals and presence of the two unpaired electrons is responsible for the paramagnetic behaviour of oxygen molecule. The unpaired electrons create a magnetic field around them due to their spin.

The explanation of paramagnetic behaviour of O_2 molecule is the greatest success of the Molecular Orbital Theory. Both VSEPR theory and VBT fail to explain the paramagnetic property of oxygen molecule.

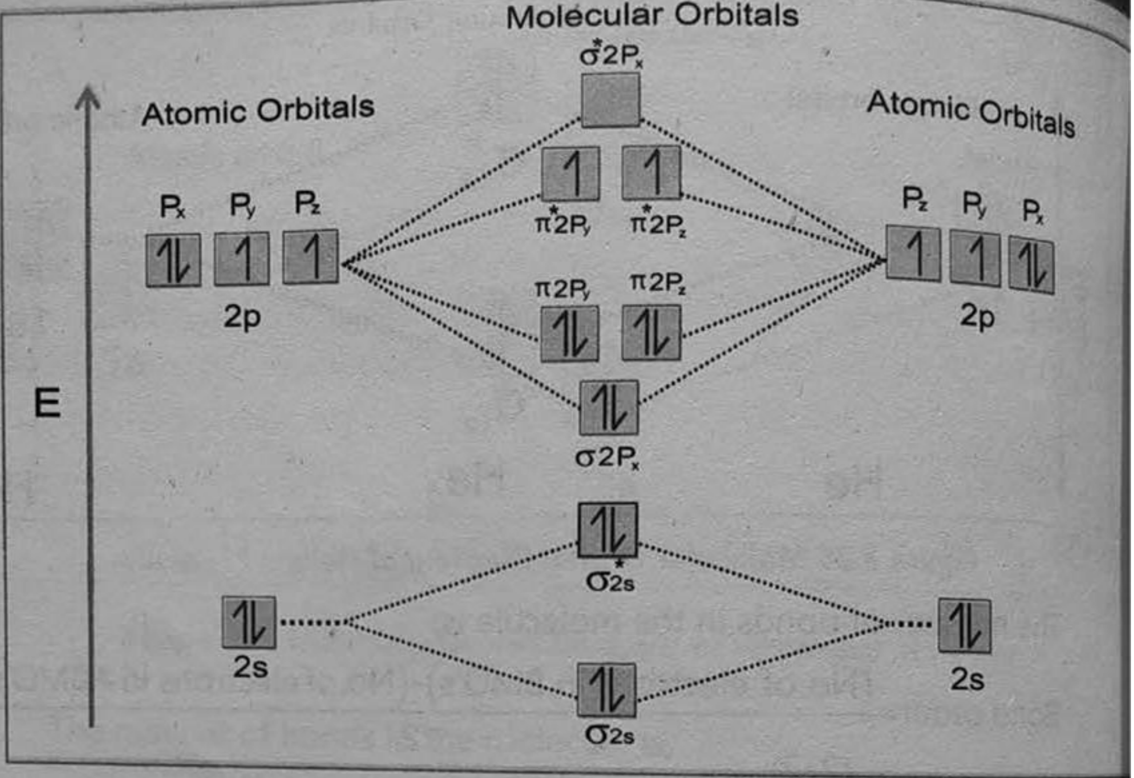


Figure 3.27 Molecular Orbitals Diagram of Oxygen Molecule

The number of bonds in the molecule is,

$$\text{Bond order} = \frac{(\text{No. of electrons in BMO's}) - (\text{No. of electrons in ABMO's})}{2}$$

$$\text{Bond order} = \frac{(8-4)}{2} = \frac{4}{2} = 2$$

There are two bonds in the oxygen molecule.

3.3 Bond Characteristics

3.3.1 Bond Energy

Bond energy is defined as *the amount of energy required to break mole of bonds in gaseous substance to form neutral atoms (also in gase state).*

Thus, bond energy is the measure of the strength of a bond: the larger bond energy, the stronger the chemical bond and vice versa. It depends up electro-negativity, size of the atoms and bond length. The S.I unit of bond ene is $kJ.mol^{-1}$.

The energy required to break one mole of hydrogen molecule $436kJ.mol^{-1}$ and $72.42 \times 10^{-23}kJ$ is required to break one bond. The sharing electrons between the two bonded hydrogen atoms is equal, so each bon hydrogen atom contributes $36.21 \times 10^{-23}kJ$ energy per atom, which is half of total bond energy. Similarly, the energy required to break one mole of chlorine molecules is 243kJ and 40.34×10^{-23}kJ is required to break one bond or contribution of each Cl atom towards bond energy is 20.17×10^{-23}kJ.

When hydrogen and chlorine react to form HCl the expected bond energy of HCl is 56.38×10^{-23} kJ / bond but experimentally 72.39×10^{-23}kJ/bond is produced. This is higher than calculated value, which shows that bond in HCl is polar and is stronger than non-polar bond. This shows that with unequal sharing of electrons, there comes an additional binding energy. This means that greater the charge difference between the bonded atoms, the greater will be the additional bond energy.

Table 3.2 Comparison of Experimental and Calculated Bond Energy of Hetero Nuclear Molecules

Bond	***Bond energies (KJ mole^{-1})***			
	$X=F$	$X=C\ell$	$X=Br$	$X=I$
H–X (calculated)	293	236	311	291
H–X (experimental)	567	436	366	299
Difference	274	200	55	9

The bond energies of carbon to carbon being in order of C≡C>C=C>C–C, the bond length is in reverse order C–C>C=C>C≡C. The bonds with higher bond energy values have shorter bond length.

3.3.2 Bond Length

Bond length is defined as the mean distance between the nuclei of two covalently bonded atoms in a molecule. Bond lengths are determined experimentally using X-ray diffraction or the analysis of molecular spectra. The length of a chemical bond is the result of an equilibrium between attractive and repulsive forces of the bonded atoms.

The bond length is measured in angstrom (Å), nanometer (nm) or picometer (pm). The bond length of identical diatomic molecules having identical atoms is the sum of the radii of these atoms. For example, the bond length of the C – C is 154pm and bond length of Cl – Cl is 198pm.

For hetero-nuclear diatomic molecules, bond length become shortened and deviates from the calculated sum of individual covalent radii, due to increase in difference of electronegativity. For example, experimentally calculated bond length of HCl is 127pm, whereas the calculated value for atomic radii of H= 37pm and Cl = 99pm gives H – Cl bond length equals to 136pm. The calculated values are always higher than experimental values for heteronuclear molecules. This is due to the difference in electronegativity, which produces polarity. This result in shortening of bond length due to the force of attraction between the polar ends. This can easily be observed in table 3.2.

Table 3.3 Comparison of Experimental and Calculated Bond Lengths of Heteronuclear Molecul

Bond	Bond length in pm(picometer)		
	Calculated value	Experimental value	Difference
H – F	108	92	16
H – Cl	136	127	09
H – Br	151	141	10
H – I	171	161	10

3.3.3 Ionic Character

The type of bond between any two atoms in a molecule can b determined from the difference of electronegativities values of the two bonde atoms. A molecule composed of two identical atoms, its electronegativi difference is zero, and hence is always non-polar and does not have any ioni character.

On other hand, when a molecule is formed between two different atom that have different electronegativity values, such a bond is polar in nature an has an ionic character. If the difference of electronegativity between two bonde atoms is less than 0.4, it is non-polar bond. If the difference of electronegativity from 0.4 – 1.7, bond will be polar with some ionic character. If the difference electronegativity is greater than 1.7, the bond will be ionic in character.

3.3.4 Dipole Moment

A quantitative measure of the polarity of a bond is its dipole moment which is the product of the charges 'q' and the distance 'r' between the centres charges.

Mathematically it can be expressed as,

$$\mu = q \times r \qquad (3.1)$$

Where 'q' is charge and 'r' is distance between centres of charges. T direction of the dipole is shown by the sign $+\!\!\!\longrightarrow$ .The arrow points to the parti negatively charged end of the dipole. For example,

$$\overset{+\delta}{\mathrm{H}} \;\overset{\mu}{+\!\!\!\longrightarrow}\; \overset{-\delta}{\mathrm{Cl}}$$

For complicated molecules, the net dipole moment is the vector sum o the individual bond moments. To keep the molecule electrically neutral, t charges on both ends of the diatomic molecule must be equal in magnitude opposite in sign. However, in equation (3.1), '*q*' refers only to the magnitude the charge and not to its sign, so 'μ' is always positive.

Dipole moments are usually expressed in Debye units (D). In SI syste charges are expressed in Coulombs (C) and distance in meters (m); thus, dipole moment is expressed in unit of coulomb meter (Cm) in SI system. The conversion factor is

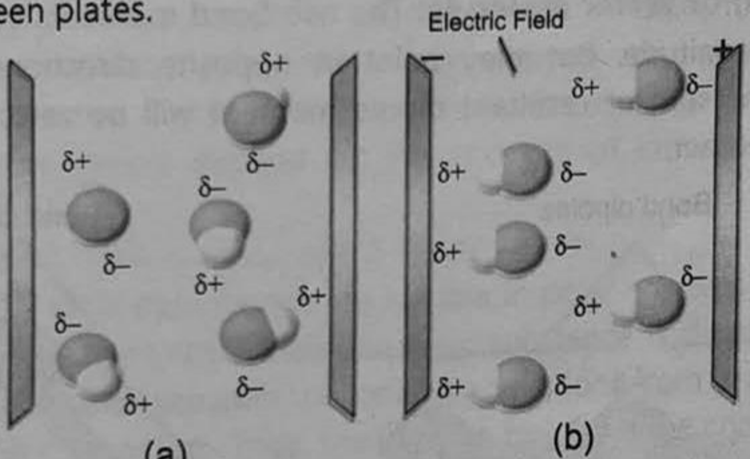
$$1\ \text{D} = 3.336 \times 10^{-30}\ \text{Cm}$$

Measurement of Dipole Moment

ReadingCheck

1. What is bond energy?
2. What is dipole moment?

The dipole moment of a substance can be experimentally measured with the help of an electric condenser. When condenser is charged by connecting to battery, electric field is set up with field strength equal to the applied voltage divided by distance between plates.



(a) (b)

Figure 3.28 (a) Molecules are always randomly distributed in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction

When polar molecules are placed between charged plates these molecules, align themselves with negative end toward positive plate and positive end toward negative plate. As a result, a decrease in strength of electric field is observed. From this decrease in strength of electric field, the dipole moment is determined.

Application of Dipole Moment

Dipole moment provides two types of information about the molecule's structure.

a. Percentage of ionic character of bond

From experimentally determined dipole moments, the percentage of ionic character of bond can be calculated by the following formula.

$$\text{Percentage of ionic character} = \frac{\mu_{\text{observed}}}{\mu_{\text{ionic}}} \times 100$$

μ_{observed} is experimental value of dipole moment of the molecule and

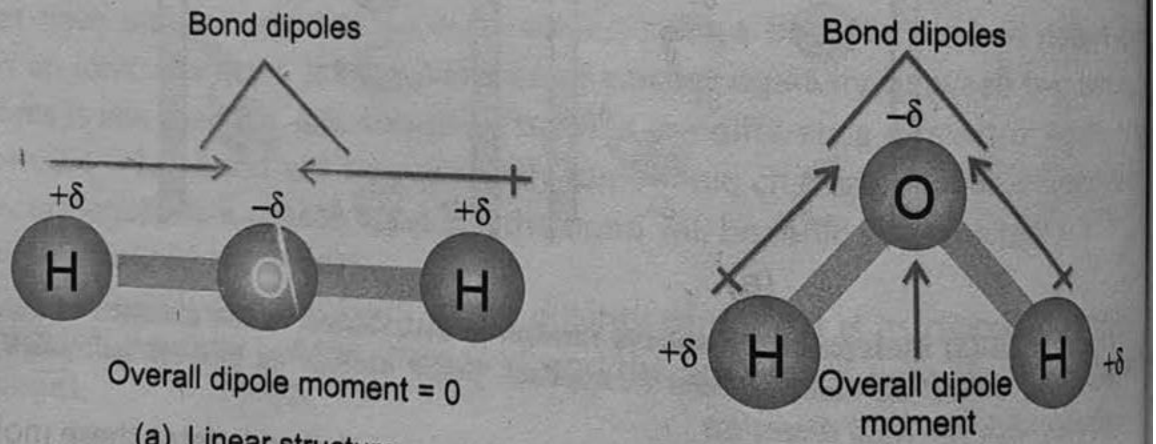
μ_{ionic} is dipole moment of molecule if it is 100% ionic. Greater the percent ionic character of a molecule higher will be its polarity.

b. Determining the Geometry of the Molecule

Dipole moment can provide important information about the geometry of the molecules. If two or more geometrical shapes for a molecule are possible then the correct structure can be identified from the study of its dipole moment. For example, Water has two possible structures, linear and angular as shown in figure 3.28.

The arrows show the shift of electron density from the less electronegative hydrogen atoms to the more electronegative oxygen atom.

Structure (a) of Water Molecule: The two bond moments of O – H bonds are equal in magnitude. But they point in opposite directions in a linear H_2O molecule, the sum or resultant dipole moment will be zero, because they will cancel each other.



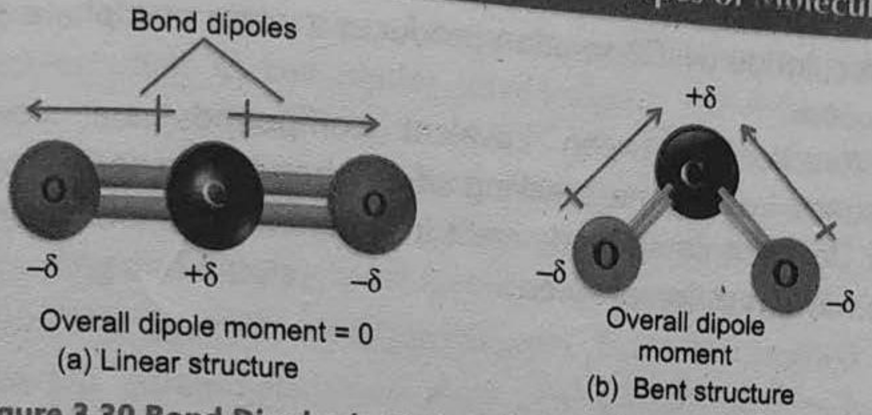
(a) Linear structure

(b) Angular structure

Figure 3.29 Bond Dipoles in Water Molecule

Structure (b) of Water Molecule: On the other hand, if the H_2O molecule was bent, the two bond moments would partially reinforce each other, so that the molecule would have a dipole moment. Experimentally it is found that water has 1.84D dipole moment. Therefore, we conclude that the water molecule has angular shape 3.31(b) and not a linear 3.31(a).

Carbon dioxide (CO_2) does not have any dipole moment as shown in figure 3.32(a). The reason is that CO_2 has linear structure. It has two polar C=O bonds acting in opposite directions. They cancel out the effect of each other, so the molecule as a whole is non-polar. *If the bonds dipoles in a molecule do not cancel out each other exactly, the molecule is polar.*



(a) Linear structure

(b) Bent structure

Figure 3.30 Bond Dipoles in Carbon dioxide (CO_2) molecules

3.4 Effect of Bonding on Physical and Chemical Properties

The type of bonding present in substances characterizes the properties in them. Physical properties of compounds depend on the strength of intermolecular attractive forces (Van der Waals forces). On the other hand, chemical properties mainly depend on the strength of intra-molecular forces (bond strength).

3.4.1 Solubility of Ionic and Covalent Compounds

Most of the ionic compounds are soluble in polar solvents like water but insoluble in non-polar solvents. When an ionic substance is dissolved in water, the polar water molecules separate the cations and anions from the crystal lattice by their electrostatic attraction. Thus, the ions are free from the crystal lattice and ionic compound dissolve in water. Non-polar solvents, like Benzene, do not dissolve ionic compounds because the attraction between solvent and solute molecules is negligible.

A Non-polar compound (solute) dissolves in a non-polar solvents. This is due to presence of weak Van der Waals forces are present in it. These weak attractive forces of solvent overcome attractive forces among solute molecules. From the above discussion, you can conclude that **"Like Dissolves Like"**.

3.4.2 Reactions of ionic and Covalent Compounds

Ionic compounds usually do not react in solid state because the ions are very tightly held together. When they are dissolved in water, the oppositely charged ions separate from one another and become ready for a chemical reaction.

When aqueous solutions of two ionic compounds are mixed together, very rapid reaction takes place and new product is formed. This is because, as there is no bond breaking is involved in solutions, on mixing solutions, ions combined and new bonds are formed, for example, mixing of silver nitrate ($AgNO_3$) and sodium chloride (NaCl) solution produces a white precipitate of silver chlorid milliseconds.

Reactions between covalent compounds are slow because th compounds involve the breaking of old bonds and formation of new cova bonds. Covalent compounds react in different ways and their reaction depe on the way a reaction proceeds.

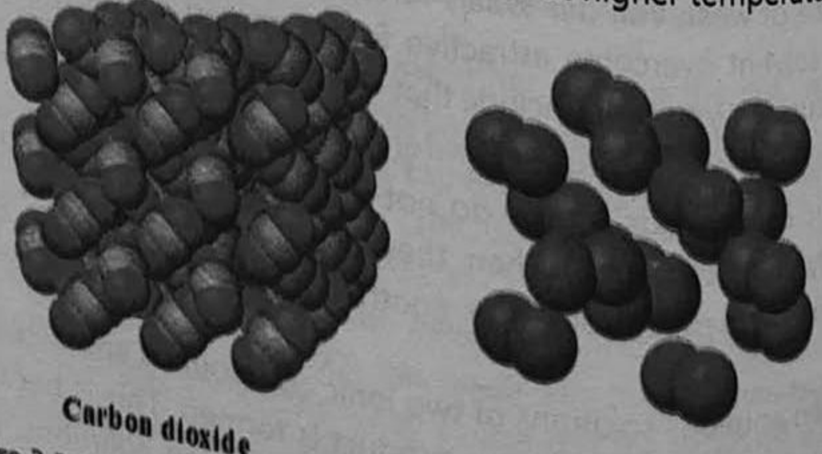
3.4.3 Directional and Non-Directional Nature of Ionic and Cova Compounds

There is a marked difference between ionic and covalent bonds. Ionic bo are non-directional whereas covalent bonds are directional in nature. That is why covalent molecules have definite geometry. This is due to the fact covalent bo are formed by overlapping of atomic orbitals, which have definite direction. Du covalent bond formation, these atomic orbitals overlap each other when they are proper direction. This gives definite geometric shape to the atoms in molecules. T covalent bonds are directional, for example, the covalent bond in methane (CH directional in nature. The four sp^3 hybridized orbitals of carbon make an angle 109.5° with each other. The hydrogen atom can only make bond with these orbita they approach at angle 109.5° to carbon atom.

3.4.4 Molecular, Network and Metallic Solid

a. Molecular Solids

Molecular solids are, made up of molecules. Like atomic solids, t molecules that make up molecular solids, such as ice, sugar and iodine a composed of neutral molecules. Substances consisting of larger, nonp molecules have larger attractive forces and melt at higher temperatures.



Carbon dioxide

Iodine

Figure 3.31 Molecular Solids of Carbon dioxide (CO_2) and Iodine (I_2)

Molecular solids composed of molecules with permanent dipole moments (polar molecules) melt at still higher temperatures. For example, the melting point of non-polar propane (C_3H_8) is −190°C. A molecule of polar formic acid (HCOOH), which has a similar number of electrons and the same molar mass as propane, melts at 8.4°C. The large difference in boiling point is due to the hydrogen bonding and dipole-dipole forces in formic acid.

b. Network Solids (Macro Molecules)

Unlike the intramolecular covalent bonds that hold atoms together in separate molecules, it is possible for atoms to bond covalently into continuous two or three-dimensional arrays, called *network solids*. A wide range of properties can be found among network solids. Diamond and graphite are examples of network solids.

In diamond, each carbon atom forms single covalent bonds to four other carbon atoms, which are at the corners of a tetrahedron. The four carbon atoms are, in turn, covalently bonded to four other carbon atoms and so on. This bonding exists throughout the entire crystal. When all the atoms in a crystal are covalently bonded to one another throughout the whole crystal, the solids are termed network solids.

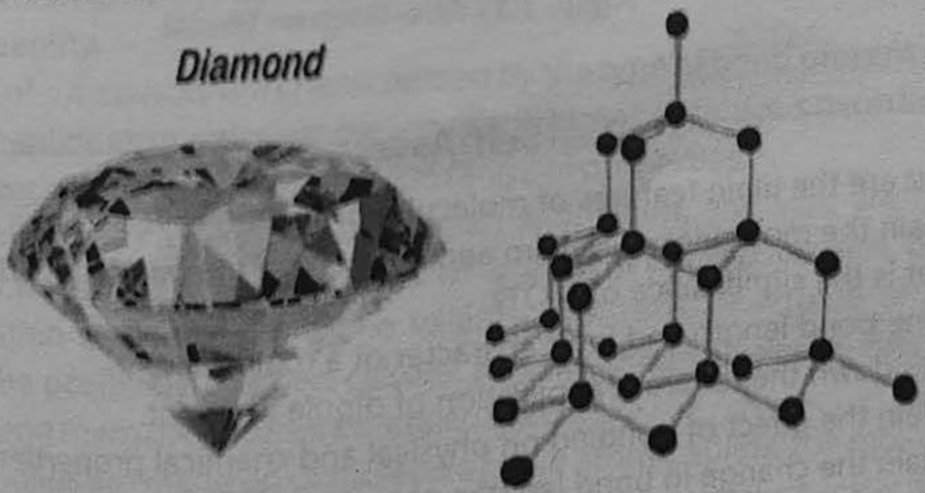


Figure 3.32 Diamond

c. Metallic Solids

Metallic solids such as crystals of copper, aluminium and iron are formed by metal atoms. Metals are composed of a closely packed centers of metallic cations, within delocalized, mobile valence electrons. The force of attraction between the positively charged cations and the pool of valence electrons that moves among them constitutes a metallic bond.

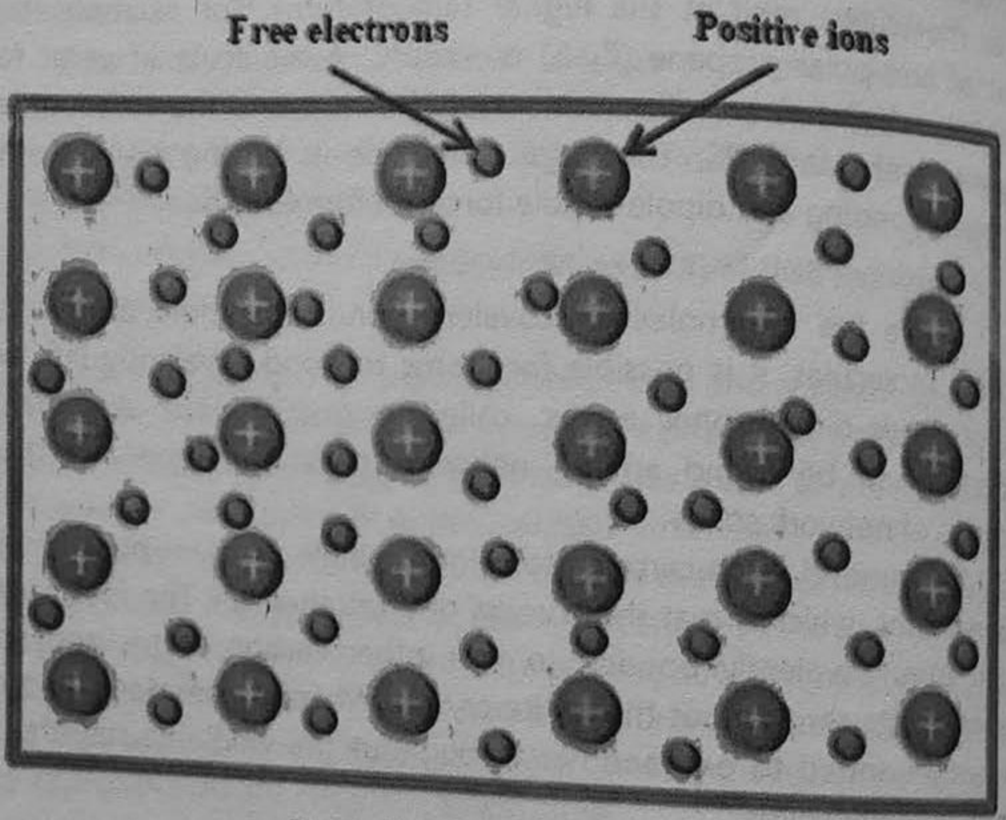


Figure 3.33 Free-Electron Model

Self-Assessment

1. What are the main features of molecular orbital theory?
2. Explain the molecules of Helium and Oxygen on the basis of MOT.
3. What is the significance of MOT?
4. Define bond length and ionic character of a molecule.
5. Write down the different application of dipole moment.
6. Explain the effect of bonding on physical and chemical properties.
7. Explain the change in bond lengths of hetero-nuclear molecules due to difference in electronegativity values of bonded atoms.
8. Explain the difference between molecular, network and metallic solid.

KEY POINTS

- Chemical bonds are forces that hold the atoms together in molecules.
- Covalent bonds are formed by the sharing of electrons.
- VSEPR theory tries to explain the geometry of the molecules.
- Resonance structures are models that give the same relative position of atoms as in Lewis structures but show different places for their bonding and lone pairs.
- In valance bond theory (VBT), the overlapping of atomic orbitals form a covalent bond.
- In molecular orbital theory (MOT), combination of atomic orbitals forms molecular orbitals.
- The intermixing of different atomic orbitals to form equivalent orbital called hybrid orbital is known as hybridization.
- Bond energy is the energy required to break the bonds per mole to form individual atoms.
- Bond length is the mean distance between the nuclei of the two bonded atoms.
- Dipole moment (μ) is a product of charge and distance between the charges. It is a vector quantity.
- Properties of substances are characterized by the type of bond present in them.
- In Network solids atoms are bonded covalently into continuous two-dimensional or three dimensional arrays with a wide range of properties.
- Metallic solids such as crystals of copper, aluminium, and iron are formed by metal atoms. Metals are composed of a closely packed centers of metallic cations, within delocalized, mobile valence electrons. The force of attraction between the positively charged cations and the pool of valence electrons that moves among them constitutes a metallic bond.
- Molecular solids are made up of molecules. Like atomic solids, the molecules that make up molecular solids, such as ice, sugar and iodine are electrically neutral.

EXEERCISE

Choose the correct option.

1. The head on overlap of p–orbitals of two atoms give rise to bond called,
   - a. Sigma bond b. Pi (π) bond
   - c. Ionic bond d. Metallic bond
2. Which one of the following molecules has a pyramidal structure?
   - a. CH_4 b. NH_3
   - c. H_2O d. C_2H_4
3. Specie in which the central atom uses sp^2 hybrid orbitals in its bonding is,
   - a. PH_3 b. NH_3
   - c. CH_3^+ d. SbH_3,
4. On the basis of VSEPR theory, a molecule with three bond pair and n lone pair of electrons will have a structure
   - a. Linear b. Trigonal planar
   - c. Tetrahedral d. Trigonal pyramidal
5. Which of the following is an example of a network solid?
   - a. Sugar, $C_{12}H_{22}O_{11(s)}$ b. Graphite , $C_{(s)}$
   - c. Carbon dioxide, $CO_{2(s)}$ d. Magnesium fluoride, $MgF_{2(s)}$
6. All are true for π-bond except
   - a. π-bond is formed from sp hybrid orbitals
   - b. π-bond is formed by the parallel overlap of half filled p-orbitals
   - c. π-bond is formed when a sigma bond is already present
   - d. π-bond is weaker than sigma bond
7. Which one of the following molecules has zero dipole moment
   - a. NH_3 b. NF_3
   - c. BF_3 d. H_2O
8. The bond angle in H_2O is
   - a. 90° b. 109.5°
   - c. 180° d. 104.5°
9. Which one of the following compounds has the highest ionic character
   - a. HF b. HCl c. HBr d. HI
10. Liquid oxygen is
    - a. Diamagnetic b. Paramagnetic
    - c. Antimagnetic d. Ferromagnetic

11. In Carbon dioxide (CO_2) molecule, the number of sigma covalent bond(s) is/are,
   a. 1 b. 2
   c. 3 d. 4

12. H_2S has a net dipole moment while BeF_2 has zero dipole moment, because
   a. H_2S molecule is linear while BeF_2 is angular
   b. H_2S molecule is angular, while BeF_2 molecule is linear
   c. Fluorine has more electronegativity than S
   d. Be is more electronegative than S

13. Which one has the least bond angle
   a. NH_3 b. H_2O
   c. CH_4 d. BF_3

14. The bond order in O_2 molecule is
   a. Zero b. 1
   c. 2 d. 3

15. The unhybridized "p" orbital in sp^2 hybridization is
   a. parallel to sp^2
   b. in the same plane
   c. perpendicular to sp^2 orbitals
   d. out of plane

Short Questions

1. What evidence can you find that the CO_2 molecule has linear but H_2O molecule has angular structure?
2. Give the reason that why O_2 molecule is paramagnetic.
3. What ideas justify that the bond angle in NH_3 is 107.5° but in H_2O, it is 104.5°?
4. Differentiate between atomic and molecular orbitals.
5. What data was used to make the conclusion that the calculated bond lengths of the heteronuclear molecules are always higher than experimental values?
6. How would you prove that the sigma (σ)-bond is stronger than pi (π)-bond?
7. What information would you use to support the view that the molecule of the He_2 does not exist?
8. Differentiate between bonding and anti-bonding orbitals.

9. Give reason that why the structure of BF_3 is trigonal planar and NH_3 is trigon pyramidal.
10. Why the bond energies of polar molecules are higher than the non-pola molecules?

Descriptive Questions

1. (a) Draw a Lewis structure for $AlCl_3$, PH_3 and H_2O. Use VSEPR theory to predict the molecular shape of these molecules.
   (b) What VSEPR notations correspond to molecules that have a bent shape?
   (c) Discuss the different types of overlapping that lead to sigma bond formation.
2. (a) Explain how σ and π bonds are similar and how they are different.
   (b) Define and explain resonance with suitable example.
   (c) Discuss the (i) Bond energies (ii) Bond length and (iii) Ionic character with suitable examples.
3. (a) Explain the HCl, H_2O and N_2 molecules on the basis of valance bond theory.
   (b) Define and explain hybridization with reference to sp mode of hybridization.
   (c). Describe how knowledge of molecular polarity can be used to explain some physical and chemical properties of molecules?
4. (a) Write down the main points of molecular orbital theory.
   (b) Draw the bonding in the molecule of oxygen with the help of molecular orbital theory.
   (c) Explain with the help of MO theory, the paramagnetic character of oxygen.
5. (a) How the geometry of the molecule can be determined by using the dipole moment.
   (b) How could you measure the dipole moment of a molecule?
   (c) Write down the difference among molecular, network and metallic solids.

Project:

Use ball and stick models to represent the molecules of BF_3 and NH_3 in front of your class.

Unit - 04

States of Matter I: Gases

After reading this unit, the students will be able to:

- List the postulates of Kinetic Molecular Theory. (Remembering)
- Describe the motion of particles of a gas according to Kinetic Theory. (Applying)
- State the values of standard temperature and pressure (STP). (Remembering)
- Relate temperature to the average kinetic energy of the particles in a substance. (Applying)
- Use Kinetic Molecular Theory to explain gas pressure. (Applying)
- Describe the effect of change in pressure on the volume of gas. (Applying)
- Describe the effect of change in temperature on the volume of gas. (Applying)
- Explain the significance of absolute zero, giving its value in degree Celsius and Kelvin. (Understanding)
- State and explain the significance of Avogadro's law. (Understanding)
- Derive Ideal Gas Equation using Boyle's, Charles' and Avogadro's law. (Understanding)
- Explain the significance and different units of ideal gas constant. (Understanding)
- Distinguish between real and ideal gases. (Understanding)

Teaching

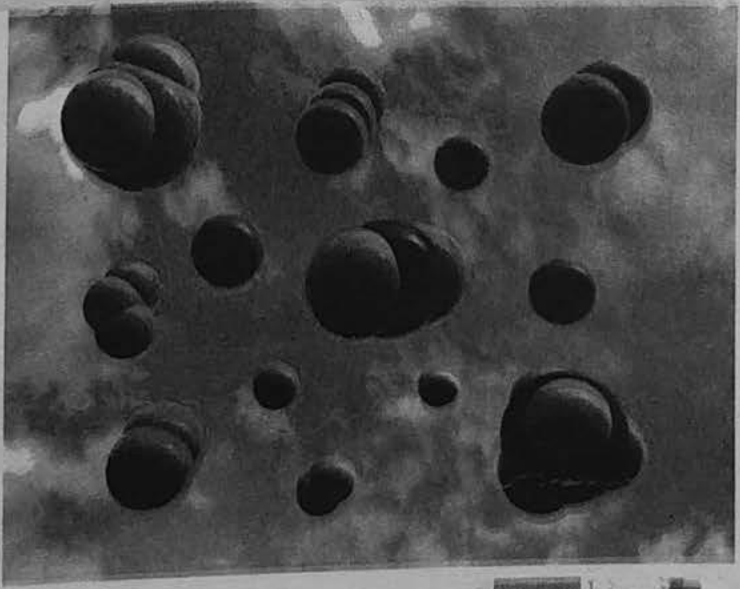
14

Assessment

01

Weightage %

12



- Explain why real gases deviate from the gas laws. (Analyzing)
- Define and describe the properties of Plasma. (Applying)
- Derive new form of Gas Equation with volume and pressure corrections for real gases. (Understanding)
- State and use Graham's Law of Diffusion. (Understanding)
- State and use Dalton's law of Partial Pressure. (Understanding)
- Describe some of the implications of the Kinetic Molecular Theory, such as the velocity of molecules and Graham's law. (Applying)
- Explain Linde's method for the liquefaction of gases. (Understanding)
- Define pressure and give its various units. (Remembering)
- Define and explain plasma formation. (Understanding)

Introduction

Gases, liquids and solids constitute the three principal states of matter. The gaseous state is characterized by its simplicity and uniformity of behaviour. Gases have no fixed shape or volume, because of the lack of particle intermolecular attractions. They spread out and fill the container in which it may be kept. Gases are easily compressed because of the large spaces between the particles. The rapid and random movement of the particles in all directions means that gas molecules enjoy greater freedom of motion. The overall movements of the particles in the direction from higher concentration to lower concentration make it possible to smell perfume or food when the source is at some distance from us. When the external conditions such as temperature and pressure are changed, the volume of all gases is affected to nearly the same extent, irrespective of the nature of a gas.

In the previous grades, you have learnt the gas laws but here in this unit, you will study the motion of particles of a gas according to kinetic molecular theory, use of kinetic molecular theory to explain gas pressure, the relationship between gas temperature, pressure, amount and volume. You will also study the effect of change in pressure and temperature on the volume of gas, the significance of absolute zero, real and ideal gases. You will be able to define, describe and explain the fourth state of matter, plasma.

Gases

The state of matter, which has neither definite volume nor definite shape, is called gas. It can also be defined as matter with the highest energy state due to the weak intermolecular forces present in them.

4.1 Kinetic Molecular Theory of Gases

Kinetic molecular theory of gases is based on the fundamental concept that molecules in gases are in constant movement. The kinetic molecular theory was first postulated by, Daniel Bernoulli, which was further developed by James Maxwell and Boltzmann to explain the various properties of gases.

4.1.1 Postulates of Kinetic Molecular Theory

The main postulates of this theory are,

1. All gases consist of small particles called molecules.
2. The molecules of the gas have higher kinetic energy than those of liquids and solids.
3. The molecules are far away from each other and have larger distances at ordinary conditions. That is why volume of the gas consists of mostly empty spaces.
4. The volume of a gas molecule is negligibly small as compared to the total volume occupied by the gas.
5. The attractive or repulsive forces among the gas molecules are negligible. Therefore, every gas molecule behaves independently.
6. The molecules of a gas are in constant random motion. They collide with each other as well as with the walls of the container. The pressure of gas molecules is due to the collision of molecules.
7. All the collisions of a gas molecule are elastic, because the total energy of the molecule remains constant.
8. The average kinetic energy of gas molecules is directly proportional to the absolute temperature.
9. The molecules of different gases have the same average kinetic energy at the same temperature.
10. The force of gravity has almost no effect on the gas molecules.

4.1.2 Pressure and its Units

The molecules of the gas are in constant random motion. They collide with each other as well as with any other surface, or with the walls of the container in which they are stored. Therefore, gas molecules exert pressure on any surface with which they collide. The pressure exerted by a gas depends on volume, temperature and the number of molecules present. Gases can be compressed or expanded.

Tidbit

The apparatus used for measuring gas pressure is called a manometer.

Pressure is defined as *force per unit area.* It is represented by "P". Mathematically it can be written as,

$$\text{Pressure (P)} = \frac{\text{Force (F)}}{\text{Area (A)}}$$

The atmosphere is the thick blanket of air (gases) surrounding earth, whi exerts pressure on the surface of earth. The atoms and molecules of the air (gase in the atmosphere are attracted towards earth by a force called gravitational forc The force experienced by any area exposed to earth's atmosphere is equal to th weight of the column of air above it.

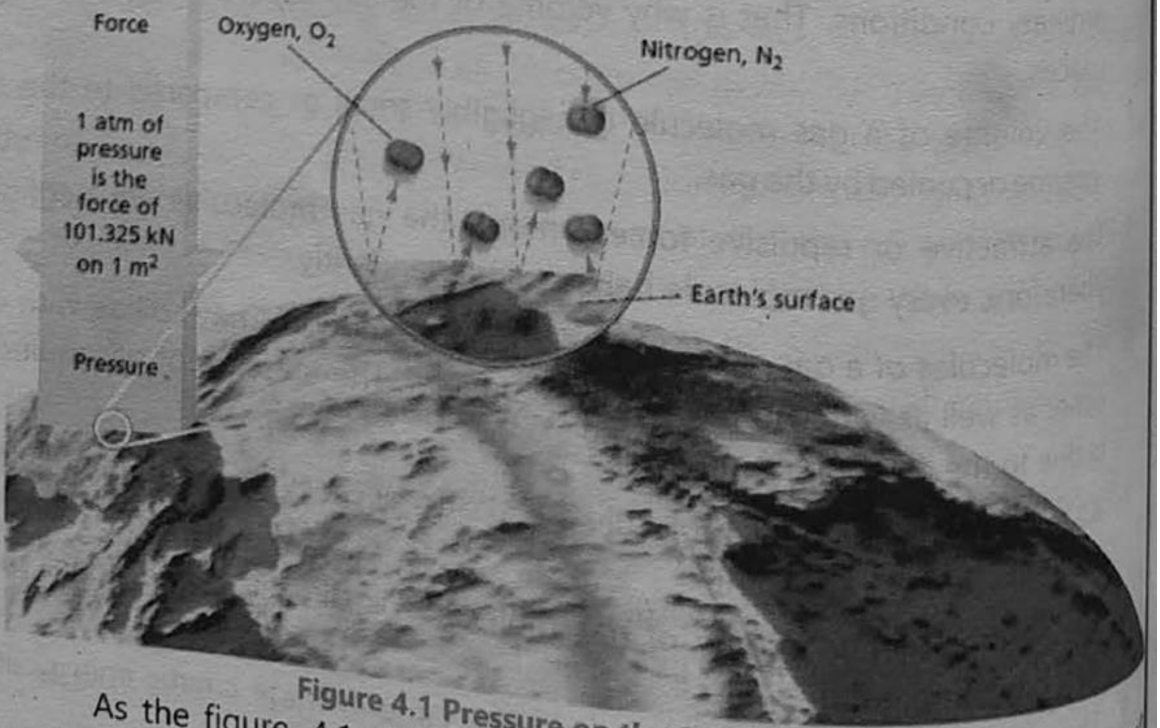


Figure 4.1 Pressure on the Surface of Earth

As the figure, 4.1 shows that atmospheric pressure at sea level is abo equal to the weight of a 1.03kg mass per square centimetre of surface, 101.325kN/m^2.The pressure of the atmosphere is the weight of the gases th compose the atmosphere. Atmospheric pressure is the sum of the individual pressures of the various gases (78% nitrogen, 21% oxygen and 1% other gases, including argon and carbon dioxide) in the atmosphere. Atmospheric pressure is the pressure exerted by earth's atmosphere. The actual value of atmospheric pressure depends on location, temperature, and weather conditions.

Units of Pressure

The SI unit of force is the Newton (N), whereas the unit of area is m^2.

$$\text{Pressure (P)} = \frac{\text{Force}}{\text{Area}} = \frac{N}{m^2} = Nm^{-2}$$

At sea level, the atmosphere exerts a pressure of 760mm Hg. This is used to define another pressure unit called atmosphere (atm). *One atmosphere is the force exerted by 76cm (760mmHg) long column of mercury on an area of $1cm^2$ at 273.15K.* It is the average pressure of atmosphere at the sea level. Thus, one atmosphere can support 760mm Hg at sea level. The mm Hg unit is also called the *torr*, after the Italian scientist Evangelista Torricelli, who invented the barometer. Thus, 1 atm pressure at 273K (called the standard pressure) equals to 76 cm Hg or 760 mm Hg or 760 torr.

In SI, pressure is expressed in derived units called Pascals. One Pascal (Pa) is defined as *the pressure exerted by a force of one Newton (1N) acting on an area of one square meter.*

$1\ Pa = 1\ N/m^2$ or Nm^{-2}

In many cases, it is more convenient to express pressure in kilopascals (kPa). The standard atmosphere (1 atm) is equal to $1.013\ 25 \times 10^5$ Pa, or 101.325 kPa.

Example 4.1

The pressure of a gas is 49torr. Convert this pressure into both atmospheres and Pascal.

Solution

Pressure in torr = 49 torr

1 atm = 760torr

So,

$$49\ \text{torr} \times \frac{1\,\text{atm}}{760\,\text{torr}} = 0.06447 = 6.447 \times 10^{-2}\ \text{atm}$$

Pressure in atm = 6.447×10^{-2} atm

1 atm = 101325 pascal

Reading Check
Define pressure and atmospheric pressure and give the common units of pressure.

So, $6.447 \times 10^{-2} \text{ atm} \times \frac{101325 \text{ Pa}}{1 \text{ atm}} = 6.5327 \times 10^{3} \text{ Pa}$

4.1 Practice problem

Reading on barometer is 2.21 atm. Calculate the corresponding pressure in (a) torr and (b) Pascal.

Table 4.1 Units of Pressure

Unit	Symbol	Definition/relationship
Pascal (Newton per square meter)	Pa	SI pressure unit, $1 \text{Pa} = 1 \text{Nm}^{-2}$
Millimetre of mercury	mm Hg	pressure that supports a 1 mm mercury column in a Barometer
Torr	torr	1 torr = 1 mm Hg
Atmosphere	atm	average atmospheric pressure at sea level at 273.15K 1 atm = 760 mm Hg 1 atm = 760 torr 1 atm = 101325 Pa 1 atm = $1.013\,25 \times 10^5$ Pa 1 atm = 101.325 kPa

1atm=760mm Hg=760 torr=101325Pa

4.2 Absolute Temperature Scale on the Basis of Charle's law

4.2.1 Brief Recall of Boyle's and Charles' law

Boyle's Law

According to Boyle's law, at constant temperature, volume of a fixed mass a gas is inversely proportional to the pressure applied on it.

Mathematically it can be written as,

$V \propto \frac{1}{P}$ (at constant temperature and mass)

$V = k \times \frac{1}{P}$

$$PV = k \qquad (4.1)$$

(Where 'k' is called constant for Boyle's law.)

When the volume of a given mass of gas is changed from V_1 to V_2 and pressure is changed from P_1 to P_2, then Boyle's law equation can be written as.

$$P_1V_1 = P_2V_2 \qquad (4.2)$$

According to the above equation, the Boyle's law can also be defined as, *the product of pressure and volume of given mass of gas remains constant at constant temperature.*

Graphical Verification

If a graph is plotted between various pressures, P and the respective volume, V of fixed mass of a gas at constant temperature, a curve called isotherm is obtained as shown in figure 4.2. It indicates that V is inversely proportional to the applied P as shown.

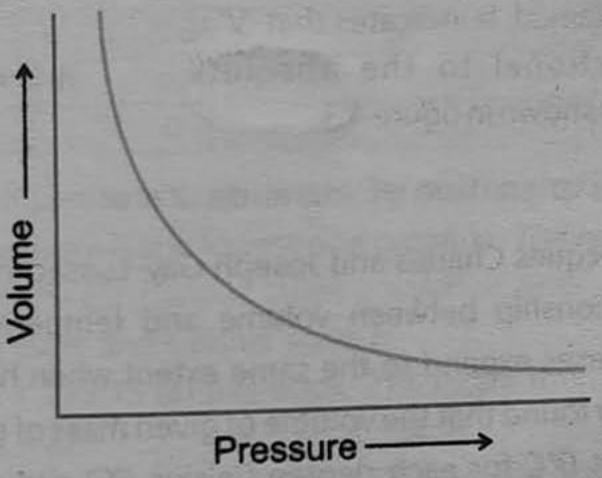


Figure 4.2 Graphical Representation of Boyle's Law

Charles' Law

This law states that, *the volume of a fixed mass of gas is directly proportional to the absolute temperature at constant pressure.*

Mathematically, it can be written as,

$V \propto T$ (at constant pressure and mass)

$V = kT$

$$k = \frac{V}{T} \qquad (4.3)$$

(Where 'k' is called constant of Charles' law.)

When the volume of the fixed mass of a gas is changed from 'V_1' to 'V_2', by changing the temperature from 'T_1' to 'T_2', then the above equation will take the following form,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad (4.4)$$

Not For Sale

From the above equation, the Charles' law can be defined as, *the ratio of volume and absolute temperature of the given mass of a gas is constant at constant pressure.*

Graphical Representation of Charles' law

If a graph is plotted between various temperature and the respective volumes of a fixed mass of a gas at constant pressure a straight line is obtained. It indicates that 'V' is directly proportional to the absolute temperature 'T' as shown in figure 4.3.

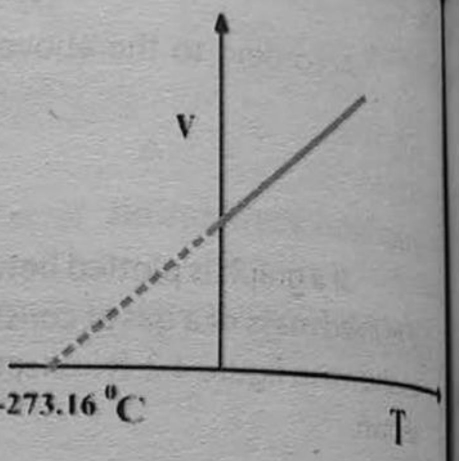


Figure 4.3 Graphical Representation of Charles' law

4.2.2 Graphical Explanation of Absolute Zero

In 1787, Jacques Charle's and Joseph Gay-Lussac independently discovered quantitative relationship between volume and temperature. Their experiments showed that all gases expand to the same extent when heated through the same temperature. They found that the volume of given mass of gas changes by $\frac{1}{273}$ of the original volume at 0°C for each degree Celsius (°C) rise or fall in temperature at constant pressure.

For example, raising the temperature to 1°C causes the gas volume to increase by 1/273 of the volume it had at 0°C. A 2°C temperature increase causes the volume to expand by 2/273 of the original volume at 0°C; 100°C temperature increase causes the volume to expand by 100/273 of the original volume at 0°C. I the temperature is increased by 273°C, the volume increases by 273/273 of the original, that is, the volume of the gas became doubles.

The same regularity of volume change occurs if a gas is cooled at constant pressure. At 0°C, a 1°C decrease in temperature will decreases the original volume by 1/273. At this rate of decrease in volume, a gas cooled from 0°C to − 273°C would be decreased by 273/273. In other words, it would have zero volume, which is not actually possible. In fact, gases cannot be cooled to − 273°C. Before they reach that temperature, intermolecular forces exceed the kinetic energy of the molecules, and the gases condense to form liquids or solids.

Table 4.2 Temperature - Volume Data for a Gas Sample (at Constant Mass and Pressure)

Celsius temperature (°C)	Temperature (K) °C + 273	Volume (cm^3)	$\frac{V}{T}$ or $k\left(cm^3K^{-1}\right)$
273	546	1092	2
100	373	746	2
10	283	566	2
1	274	548	2
0	273	546	2
-1	272	544	2
-73	200	400	2
-173	100	200	2
-223	50	100	2
-273	0	0	

The Kelvin temperature scale is a scale that starts at a temperature of -273.15°C. That temperature is the lowest one possible. *The temperature – 273.15°C is referred to as* absolute zero *and is given a value of zero in the Kelvin scale.* The relation of the Kelvin scale and Celsius scale is,

K = °C + 273.15 (In this book, 273.15 are rounded off to 273)

T= t°C + 273 (4.5)

It is represented by K, after Lord Kelvin who discovered it and 't°C' is the temperature on Celsius scale and 'T" the Kelvin temperature.

Graphical Explanation

A graph is plotted between temperature 'T' on x-axis and volume 'V' for a given mass of a gas according to table 4.4 at constant pressure, you get a straight line. When you extrapolate the graph upto 0 Kelvin (–273°C), this line cuts the temperature axis at – 273°C, which is lowest possible temperature. The line breaks before reaching the temperature of a gas to –273°C. It means that at this temperature all the gases have zero volume or not in the gaseous state.

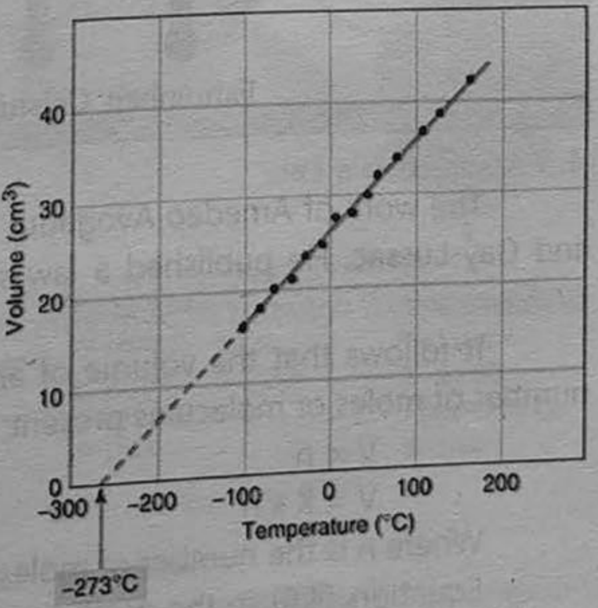


Figure 4.4 Graph between Volume and Temperature for a Gas

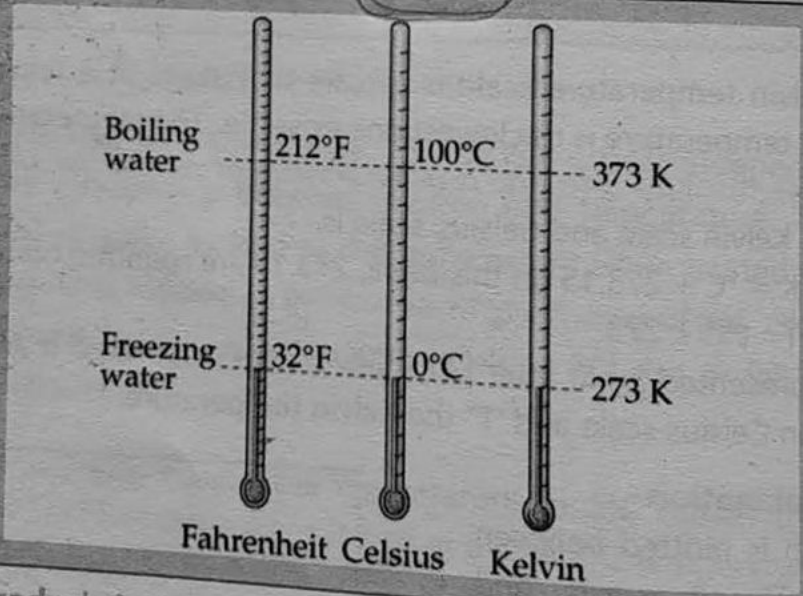
The gases are condensed and converted into the liquid or solid. Therefore, the ga laws cannot be applied on them. Actually, all the gases are converted into liqui before this temperature.

Tidbit

Absolute temperature must be used in all gas law problems involving temperature.

The boiling point, freezing point of water and absolute zero on Fahrenhei Celsius and Kelvin are,

	Fahrenheit	Celsius	Kelvin
Boiling point of water	212°F	100°C	373K
Freezing point of water	32°F	0°C	273K
Absolute Zero	- 459 °F	-273 °C	0K



4.3 Avogadro's Law

The work of Amedeo Avogadro supplements the studies of Boyle, Charle and Gay-Lussac. He published a law stating that *at the same temperature a pressure, equal volumes of different gases contain the same number of molecule*

It follows that the volume of any given gas must be proportional to th number of moles or molecules present; that is,

$V \propto n$

$V = K \times n$ (4.6) (at constant 'P' and 'T')

Where n is the number of moles of gas and K is proportionality constant (4.7)

Equation (4.6) is the mathematical expression of *Avogadro's law*, whi states that *at constant pressure and temperature, the volume of a gas is direc proportional to the number of moles of the gas present.*

As one mole of a gas has Avogadro's number of particles, so 22.414dm^3 of various ideal gases at STP will have Avogadro's number i.e. 6.023 x 10^{23} molecules. One dm^3 of H_2 at STP weighs approximately 0.0899 grams and one dm^3 of O_2 at STP weighs 1.4384 grams, but their number of molecules is the same. Although oxygen molecules is 16 times heavier than hydrogen but this does not disturb the volume occupied because molecules of the gases are widely separated from each other at STP. One molecule is approximately at a distance of 300 times its own diameter from its immediate neighbour at room temperature.

Mole–Mass–Volume Relationships of Gases

One mole of any gas contains 6.022 x10^{23} molecules (Avogadro's number). It has been experimentally determined that the volume occupied by a mole of any gas is 22.4 dm^3 at STP. This volume, 22.4 dm^3, is known as the *molar volume* of a gas. *One mole of a gas occupies 22.4 dm^3 at STP.*

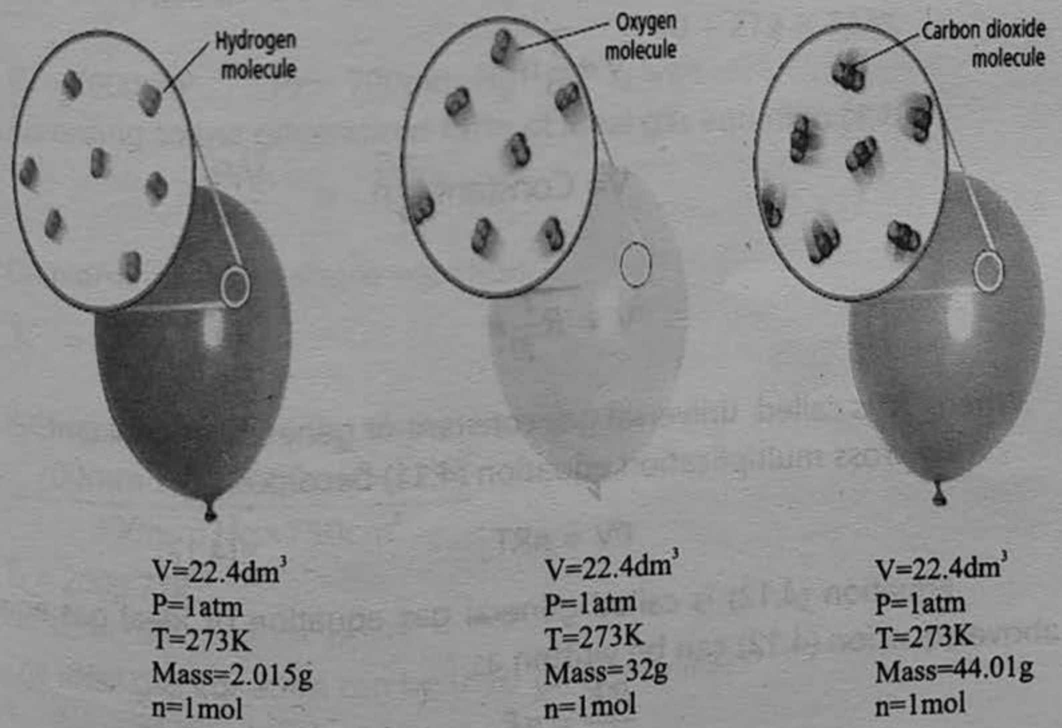


Figure 4.5 One mole of Different Gases at STP

4.4 Ideal Gas Equation *or General Gas Equation*

An ideal gas is a gas that behaves exactly as outlined by the assumptions of the kinetic molecular theory.

The equation that relates the pressure, volume, number of moles a temperature of an ideal gas is called ideal gas equation.

4.4.1 Derivation of Ideal Gas Equation

It is derived by combining the Boyle's law, Charles law and Avogadro's la

According to Boyle's law, volume of the fixed mass of a gas is invers proportional to the applied pressure at constant temperature.

$$V \propto \frac{1}{P} \text{ (at constant temperature)} \quad (4.8)$$

According to Charles law, volume of the fixed mass of a gas is direc proportional to the absolute temperature at constant pressure.

$$V \propto T \text{ (at constant pressure)} \quad (4.9)$$

According to Avogadro's law, volume of a fixed mass of a gas is direc proportional to its number of moles at constant temperature and pressure.

$$V \propto n \text{ (at constant temperature and pressure)} \quad (4.10)$$

Combining these three proportionalities equations (4.8), (4.9) and (4.10), we get,

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

$$V = \text{Constant } \frac{T}{P}n$$

$$V = R\frac{T}{P}n \quad (4.11)$$

Where 'R' is called universal gas constant or general gas constant.

By cross multiplication equation (4.11) becomes,

$$PV = nRT \quad (4.12)$$

Equation (4.12) is called general gas equation or ideal gas equation. The above equation (4.12) can be written as,

$$\frac{PV}{T} = nR$$

Since standard moles for any gas is taken one i.e., n = 1, then the equatio (4.12) becomes,

$$\frac{PV}{T} = R \quad (4.13)$$

For initial state: when the Pressure (P_1), Volume (V_1) and Temperature (T_1), then

$$\frac{P_1V_1}{T_1} = R \qquad (4.14)$$

For final state: Pressure (P_2), Volume (V_2) and Temperature (T_2), then

$$\frac{P_2V_2}{T_2} = R \qquad (4.15)$$

Then combining equation (4.14) and (4.15) we get,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \qquad (4.16)$$

This is the generalized form of ideal gas equation.

Example 4.2

750cm^3 of a gas at 300mm Hg and 50°C is heated until the volume of gas is 2000cm^3 at a pressure of 700mm Hg. What is the final temperature of the gas?

Solution

$V_1 = 750cm^3$, $P_1 = 300mm\ Hg$, $T_1 = 50°C$

$= 50 + 273 = 323K$

$V_2 = 2000cm^3$, $P_2 = 700mm\ Hg$, $T_2 = ?$

According to the generalized form of ideal gas equation (4.16),

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

On rearranging the above equation,

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

Putting the values in the above equation,

$$T_2 = \frac{700mm\ Hg \times 2000cm^3 \times 323K}{300mm\ Hg \times 750cm^3}$$

$T_2 = 2009.77K$

4.4.2 Gas Constant and its Units

The ideal gas equation can be used to determine,

1. Value of "R" at STP
2. Value of "R" in SI unit
3. Mass of gas (m)
4. Density of gas (d)
5. Concentration of gas (c)

i. Calculation of Value of "R" at STP

According to the general gas equation (4.12), we have,

$PV = nRT$

On rearrangement, the above equation becomes,

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

At 0°C (273.15 K) and 1 atm pressure, many real gases behave like an ide gas. Experiments show that under these conditions, 1 mole of an idealgas occupie 22.414 dm^3. At STP, it is known that:

Standard temperature (T) = 0°C
= 0°C + 273 = 273K
Pressure (P) = 1 atm
Amount (n) = 1 mol
Volume (V) = 22.4 dm^3

Putting these values in equation (4.17), we get,

$$R = \frac{1atm \times 22.4dm^3}{1mol \times 273K}$$

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

ii. Calculation of Value of "R" in SI Units

If the pressure is expressed in Newton's per meter square (Nm^{-2}) and the Volume (V), in cubic meter (m^3), so we have,

Amount (n) = 1 mol
Standard temperature (T) = 0°C = 0°C + 273 = 273K
Pressure (P) = 1 atm = 101325Nm^{-2}
Volume (V) = 22.4 dm^3 = $\frac{22.4dm^3}{1000}$ = 0.024m^3 (As 1 $dm^3 = 10^{-3}m^3$)

As we have equation (4.17),

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

Putting these values in equation (4.17), we get,

$$R = \frac{101325Nm^{-2} \times 0.0224m^3}{1mol \times 273K}$$

$R = 8.313Nm^{-2}.\ m^3.\ mol^{-1}.\ K^{-1}$

Or, we get,

$R = 8.313Nm.mol^{-1}.\ K^{-1}$

As, we also know that, *Newton meter (Nm) = Joule (J)*

So, we can write as,

$$R = 8.313\ JK^{-1}.mol^{-1}$$

As, we also know that, 1 calorie = 4.184 Joule

Then, the above values for R can be written as,

$$R = \frac{8.3143}{4.184} = 1.987\ cal.K^{-1}.mol^{-1}$$

4.2 Practice Problems

1. What pressure will be exerted by 0.400mol of a gas in a $5.00dm^3$ containers at 17°C?
2. Find the values of 'R' in $dm^3.mm\ Hg.\ mol^{-1}.K^{-1}$
3. Find the values of 'R' in $dm^3.torr.\ mol^{-1}.\ K^{-1}$
4. Find the values of 'R' in $cm^3.torr.\ mol^{-1}.K^{-1}$

iii. Calculation of Value of Mass (m) of gas

The molecular mass of the gas can be determined with the help of ideal gas equation.

According to the ideal gas equation (4.12), we have,

$$PV = nRT \qquad (4.18)$$

As we know that,

$$\text{Mole (n)} = \frac{\text{Mass of the gas}}{\text{Molecular mass of the gas}} = \frac{m}{M}$$

Putting the value of n in equation (4.18), we get,

$$PV = \frac{m}{M} RT$$

By cross multiplication,

$$PV \times M = mRT$$

By rearranging, we get,

$$m = \frac{PVM}{RT} \qquad (4.19)$$

If the molecular mass of the gas (M), temperatures (T), pressure (P) and volume (V) of the gas are known then the mass of the gas can be determined by using the equation (4.19).

Example 4.3

Calculate the mass of $1dm^3$ of NH_3 gas at 30°C and 1000 mm Hg pressure, considering that NH_3 is behaving ideally?

Solution

Mass of NH_3 (m) =?

Volume (V) = $1\ dm^3$

Temperature (T) = 30°C

$$= 30 + 273 = 303\text{K}$$

Pressure (P) = 1000 mm Hg

$$= \frac{1000}{760} = 1.316 \text{ atm}$$

General gas constant (R) $= 0.0821\text{dm}^3.\text{atm. mol}^{-1}.\text{K}^{-1}$

Molecular mass of NH_3 (M) = 17 g.mol^{-1}

According to the equation(4.19)

$$m = \frac{PVM}{RT}$$

Putting the values in the above equation,

$$m = \frac{1.316\text{atm} \times 1\text{dm}^3 \times 17\text{g.mol}^{-1}}{0.0821\text{dm}^3.\text{atm.mol}^{-1}.\text{K}^{-1} \times 303\text{K}}$$

$$m = 0.8993\text{g}$$

4.3 Practice Problem

Calculate the molecular mass of butane gas if 3.69g occupy 1.53 dm^3 at 20.0°C a
1.00 atm.

iv. Calculation of Value of Density (d) of gas

The density of a gas can be determined with the help of ideal gas equatio

According to the general gas equation (4.12), we have,

$$PV = nRT \qquad (4.20)$$

As we know that,

$$\text{Mole (n)} = \frac{\text{Mass of the gass}}{\text{Molecualr mass of the gas}} = \frac{m}{M}$$

Putting the value of 'n' in equation (4.20) we get,

$$PV = \frac{m}{M} RT \qquad (4.21)$$

By rearranging equation (4.21) becomes,

$$PM = \frac{m}{V} RT \qquad (4.22)$$

Since we have,

$$\text{Density(d)} = \frac{\text{mass}}{\text{Volume}} = \frac{m}{V}$$

Putting the value of '$\frac{m}{V}$' in equation (4.22) we get,

$$PM = d \times RT$$

Or $$d=\frac{PM}{RT} \tag{4.23}$$

The density of the gas can be determined if the pressure (P), molecular mass (M), temperature (T) and universal gas constant (R) are known.

Example 4.4

What is the density in $g.dm^{-3}$ of SO_2 at 20°C and 750mm Hg pressure?

Solution:

$P = 750mm\ Hg$

$= \frac{750}{760} = 0.98atm$

$T = 20^\circ C$

$= 20 + 273 = 293K$

Molecular mass of SO_2 =64g/mol

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

$d=?$

According to the general gas equation,

$PV = nRT$

On solving for 'd' we get,

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

Putting the values in the equation we get,

$$d=\frac{0.98atm\times64g.mol^{-1}}{0.0821dm^3atm.K^{-1}.mol^{-1}\times293K}$$

$d= 2.60g.dm^{-3}$

4.4 Practice Problem

Calculate the density in $g.dm^{-3}$ of NH_3 at 25°C and 1.2atm.

v. Calculation of Concentration (c) of Gas

The concentration of a gas can be determined with the help of ideal gas equation.

According to the general gas equation (4.12), we have,

$$PV = nRT \tag{4.24}$$

As we know that,

$$\text{Concentration}(c)=\frac{\text{mole}}{\text{volume}}=\frac{n}{v}$$

Rearranging the equation (4.24), we get,

$$P=\frac{n}{V}RT \qquad (4.25)$$

Putting the value of $\frac{n}{V}$ we get,

$$P= cRT \qquad (4.26)$$

On rearranging equation (4.26), we get,

$$c=\frac{P}{RT}$$

The concentration of the gas can be determined if the pressure temperature (T), and universal gas constant (R) are known.

Self-Assessment

1. List the physical characteristics of gases.
2. What are standard temperature and pressure (STP)?
3. Derive the ideal gas equation. Give its different units for each term in the equation.
4. Why the density of a gas is much lower than that of a liquid or solid?
5. What are the basic assumptions of the kinetic molecular theory of gases?

4.5 Deviation from Ideal Gas Behaviour

All the gas laws are based on the behaviour of an ideal gas, that is, a gas with a behaviour that is described exactly by the gas laws for all possible values of *Pressure, Volume*, and *Temperature*. Most real gases actually do behave very nearly like an ideal gas over a wide range of temperatures and pressures. However, when conditions are such that the gas molecules come close together (under high pressure and/or temperature), they show deviation from ideal behaviour. Actually, all gases de from gas laws to an extent that depends on the pressure, temperature, and nature of the gas. Such gases are called non-ideal or real gases.

Tidbit

A **Real gas** is a gas that does not behave completely according to the assumptions of the kinetic molecular theory.

4.5.1 Graphical Explanation

We will examine the experimentally observed behaviour of real gases measuring the pressure, volume, temperature, and number of moles for a gas noting how the quantity $\frac{PV}{nRT}$ depends on pressure. Plots of $\frac{PV}{nRT}$ versus P shown for several gases in figure 4.6. For an ideal gas, $\frac{PV}{nRT}$ equals to 1 under all conditions. This ratio is called the compressibility factor (Z),

$$Z=\left(\frac{PV}{RT}\right) \qquad (4.27)$$

Compressibility factor (Z)

The extent to which a real gas departs from the ideal behaviour may be depicted in terms of a new function called the Compressibility factor, denoted by Z It is mathematically written for 1mole of a gas as,

$$Z=\frac{PV}{RT}$$

The deviations from ideality may be shown by plotting compressibility factor $\left(\frac{PV}{RT}\right)$ versus pressure (P atm), as shown in the figure 4.6.

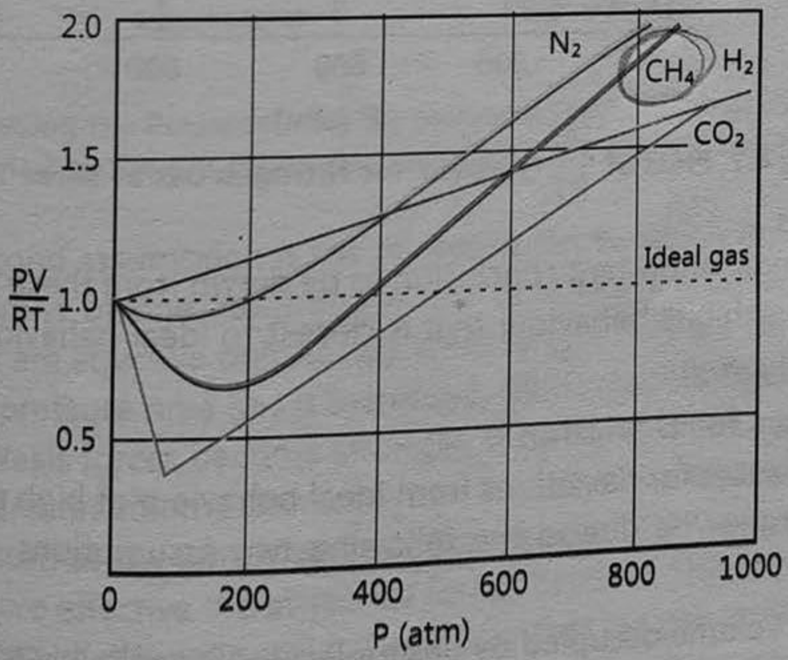


Figure 4.6 **Plots of** PV/RT **versus** P **for Several Gases at 313K**

For an ideal gas, Z=1 and it is independent of temperature and pressure. The deviations from ideal behaviour of a real gas will be determined by the value of Z being greater or less than 1. *The difference between unity and the value of the compressibility factor of a gas is a measure of the degree of non-ideality of the gas.*

To show the effect of temperature, $\frac{PV}{RT}$ is plotted versus *P* for nitrogen at several temperatures in figure 4.7. Note that the behaviour of the gas appe to become more nearly ideal as the temperature is increased.

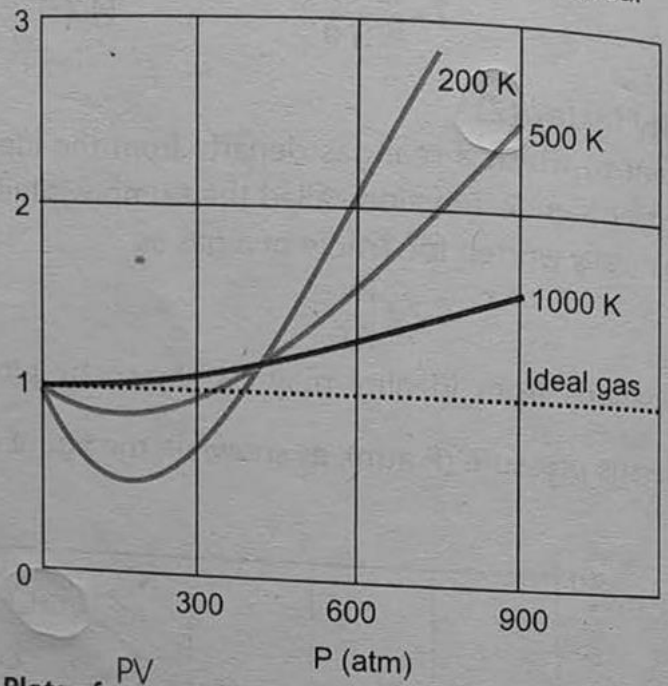


Figure 4.7 Plots of $\frac{PV}{RT}$ versus *P* for Nitrogen Gas at Three Temperatures

Conclusions

The most important conclusion to be drawn from these figures is that a gas typically exhibits behaviour that is closest to ideal behaviour at *low pres and high temperatures.*

4.5.2 Causes for Deviation

The causes for deviations from ideal behaviour at high pressure or ver temperature may be due to the following two assumptions of kinetic theo gases.

1. The volume occupied by gas molecules is negligibly small as compare the volume occupied by the gas.
2. The forces of attraction between gas molecules are negligible.

The first assumption is valid only at low pressures and high tempera when the volume occupied by the single gas molecule is negligible as comp to the total volume of the gas. However, at high pressure, the molecules of a come closer together, and the amount of empty space between the molecul reduced.

At these higher pressures, the volume of the gas molecules themselves becomes considerable relative to the total volume occupied by the gas as shown in figure 4.8. The gas, therefore, becomes less compressible at these high pressures; the volumes of molecules are no more negligible as compared to the total volume of the gas.

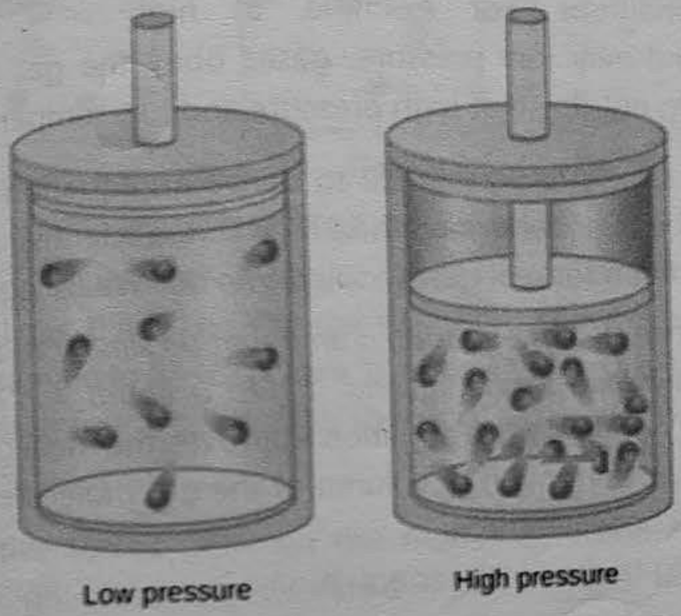


Figure 4.8 Raising the Pressure of a Gas Increases the fraction of its volume that is occupied by the gas molecules and makes the gas less compressible

The second assumption is the attractive forces, which result from attraction between electrons of one atom and nuclei of adjacent atoms, exist between all molecules, but are effective only at very short range. They are called Van der Waals forces. As the pressure on a gas is increased, molecules are forced closer together and Van der Waals forces become stronger, drawing the molecules still closer and resulting in a greater volume decrease than Boyle's law predicts. This effect is even more pronounced at low temperatures because the more slowly the molecules are moving the more effective the attractive forces become. This explanation suggests that the assumption of kinetic molecular theory that the gas molecules do not have attractive forces between them is one reason of deviation of gases from ideal behaviour. Molecules of real gases do exert force on each other, the condensation of every gas on cooling shows that attractive forces are always there among the molecules. These forces are not very important when the molecules are far apart (i.e. at low pressure and high temperature) but they become noticeable at higher pressure and low temperature.

4.6 Van der Waals Equation

Reading Check

Define compressibi factor.

An ideal gas would obey the gas laws strictly but all real gases more or less deviate from these laws. The nature and extent of deviation depend upon the conditions. For example, at high temperature and very low pressure, gases obey the gas laws almost perfe whereas they do not do so at high pressure and low temperature.

Various attempts were made to derive an equation for non-ideal i.e. gases to describe their behaviour. In 1873, a Dutch scientist, J.D. Van der Waals forward an equation for real gases, called Van der Waals equation.

The Van der Waals equation is an equation similar to the ideal gas equat but includes two constants, 'a' and 'b', to account for deviations from i behaviour. The Van der Waals equation improves the ideal gas law by adding t terms, one for the correction of volume of the gas molecules and another for t attractive forces between them.

According to the ideal gas equation,

$$PV = nRT$$

This equation explains the behaviour of an ideal gas consisting of volu less entities that do not interact with each other. In contrast, a real gas consists atoms or molecules that have finite volumes. Therefore, the volume available t given particle in a real gas is less than the volume of the container because the g particles themselves occupy some of the space. Van der Waals pointed out t both the pressure (P) and volume (V) factors in the ideal gas equation nee correction in order to make it applicable to real gases.

4.6.1 Volume Correction

When a gas is compressed, the molecules become so close together t further increase in pressure will be opposed by the molecules themselves. This is o possible when the molecules of the gas have a finite volume. The volume, V in t ideal gas equation, PV = nRT, is the free volume, V in which the molecules a effectively free to move about. But when the molecules do occupy an apprecia part of the total volume, V then compressible volume V_{free} should be set equal to t difference between V and $V_{molecules}$ or b

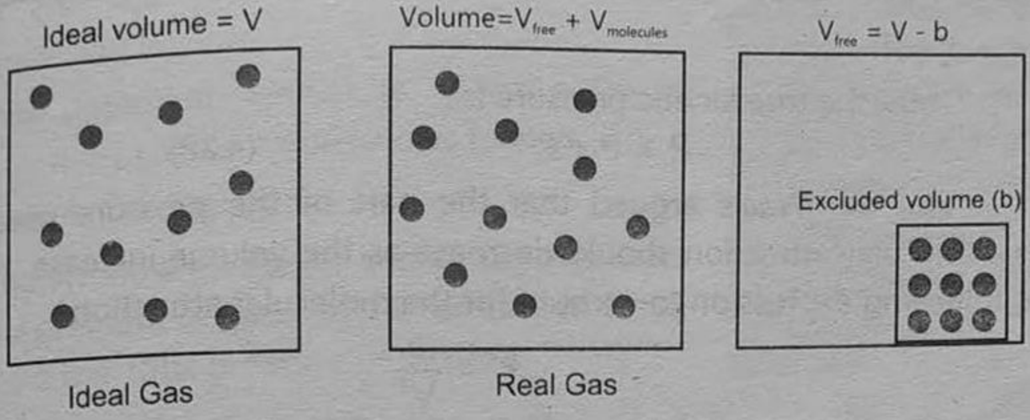


Figure 4.9 Volume of a Real Gas

For an ideal gas, b = 0 and Van der Waals, therefore, proposed that V in the gas equation be changed to (V – b), where 'b' is the effective molar volume of the real gas and approximately four times greater than $V_{molecules}$.

4.6.2 Pressure Correction

The attractive forces between the molecules come into play when the molecules are brought closer together by compressing the gas and become slow down by decreasing temperature. Consider a molecule A in the interior of the gas, which is completely surrounded by other gas molecules. The resultant attractive force experienced by the molecules A due to all the other molecules is zero. However, as this molecule approaches the wall of the container, it is subjected to an inward pull due to unbalanced molecular attraction. Thus, when the molecule is about to strike the wall and contribute its share to the total pressure of the gas, the other molecules in the gas exert an attractive force tending to prevent it from doing so. The observed pressure P consequently will be less than the ideal pressure, P_i by P',

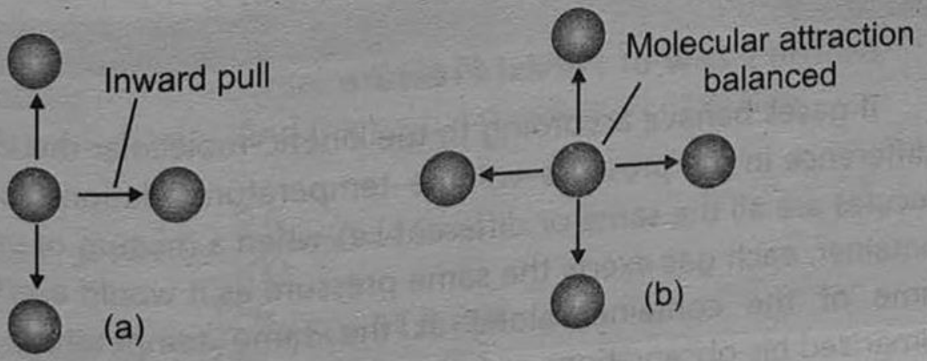


Figure 4.10
(a) A molecule about to strike the wall has a net inward pull;
(b) A molecule in the interior of gas has balanced attractions.

$P = P_i - P'$

Thus, the true kinetic pressure is,

$$P_i = P + P' \qquad (4.28)$$

Van der Waals argued that the part of the pressure used up agai intermolecular attraction should decrease as the volume increase. He sugges the following expression to account for the molecular attraction.

$$P' = \frac{a}{V^2}$$

Where 'a' is co-efficient of attraction i.e., attraction per unit volume and constant for a particular real gas. Thus, the effective kinetic pressure is given by,

$$P_i = P + \frac{a}{V^2}$$

Now, making correction for both the pressure and volume, the ideal gas equation for one mole of a real gas becomes,

$$\underbrace{\left(P+\frac{a}{V^2}\right)}_{\text{Kinetic pressure of a real gas}}\ \underbrace{(V-b)}_{\text{free volume of of a real gas}}=RT \qquad (4.29)$$

It represents the behaviour of real gases (non-ideal) over wide ranges of temperature and pressure more accurately than the ideal gas equation. The Van der Waals equati for 'n' moles of gas may be written as below.

$$\left(P+\frac{an^2}{V^2}\right)(V-nb)= nRT \qquad (4.30)$$

Reading Check

1. Write down two evidences to show that gases do not behave ideally under all conditions of temperatu and pressure.
2. Write the Van der Waals equation for a rea gas.

4.7 Dalton's Law of Partial Pressure

If gases behave according to the kinetic-molecular theory, there should no difference in the pressure–volume–temperature relationships whether the g molecules are all the same or different i.e., when a mixture of gases is enclosed a container, each gas exerts the same pressure as it would exert if it occupied th volume of the container alone at the same temperature. In 1803, Dalt summarized his observations as follows,

"The total pressure exerted by a mixture of gases in a container is equal the sum of the partial pressures of all the gases present in the mixture provi

that no chemical reaction occurs at constant temperature and volume."

This statement, known as *Dalton's law of partial pressures,* can be expressed as follows,

$$P_{TOTAL} = P_A + P_B + P_C + \ldots$$

The symbols P_A, P_B, P_C, and so on, represent the partial pressure of gases in the mixture, whereas, P_{TOTAL} (P_T) is the total pressure of mixture.

Tidbit

Partial Pressure

The pressure exerted by a particular gas is hypothetical pressure of a gas when it alone occupies the same volume as the mixture.

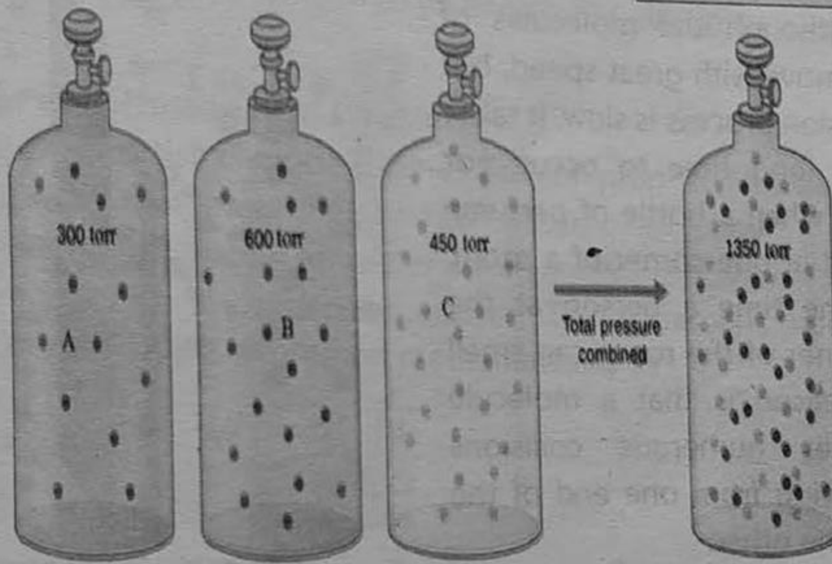


Figure 4.11 The individual Pressures of gases A, B, C and their Total Pressure

Thus, if we have a mixture of three non-reacting gases, *A, B,* and *C,* exerting partial pressures of 300 torr, 600 torr, and 450 torr, respectively, the total pressure will be 1350 torr.

$$P_{total} = P_A + P_B + P_C$$

$$P_{total} = 300\text{ torr} + 600\text{ torr} + 450\text{ torr} = 1350\text{torr}$$

Example 4.5

A gaseous mixture contains 9.6% NH_3 and 22.6% N_2 and 67.8% H_2 gases. If its total pressure is 50atm, find the partial pressure of each gas.

Solution

$$\text{Pressure of } NH_3 = \frac{9.6}{100} \times 50 = 4.8\text{ atm}$$

$$\text{Pressure of } N_2 = \frac{22.6}{100} \times 50 = 11.3\text{ atm}$$

$$\text{Pressure of } H_2 = \frac{67.8}{100} \times 50 = 33.9\text{ atm}$$

4.8 Graham's law of Diffusion and Effusion

Gas Diffusion

Diffusion is the term used to describe the mixing of gases. *Diffusion c be defined as the ability of two or more gases to mix spontaneously until they fo a uniform mixture by random motion and collision (by virtue of their kine properties). Or*

The spontaneous mixing of different non-reacting gases to form homogenous mixture.

Although the molecules of the gas move with great speed, but the diffusion process is slow. It takes relatively long time to occur. For example, when a bottle of perfume is opened at one corner of a room, after some time a person at the other corner of the room can smell it. The reason is that a molecule experiences numerous collisions while moving from one end of the room to the other.

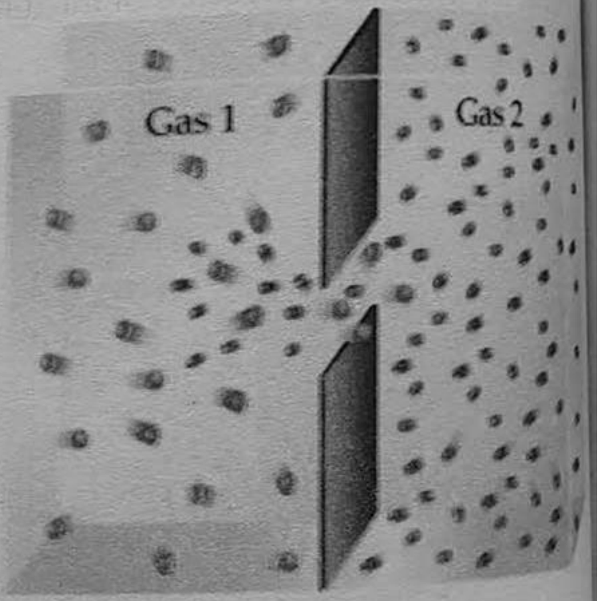


Figure 4.12 Diffusion of two Gases

Gas Effusion

Effusion is the term used to describe the passage of a gas through a tin hole of molecular dimension, as shown in figure. 4.13. *Effusion* is *the process b which gas molecules escapes from one compartment of a container to another by passing through a small opening of molecular dimension without collision.* In this process, gas molecules spread one by one without collisions to form a homogenous mixture.

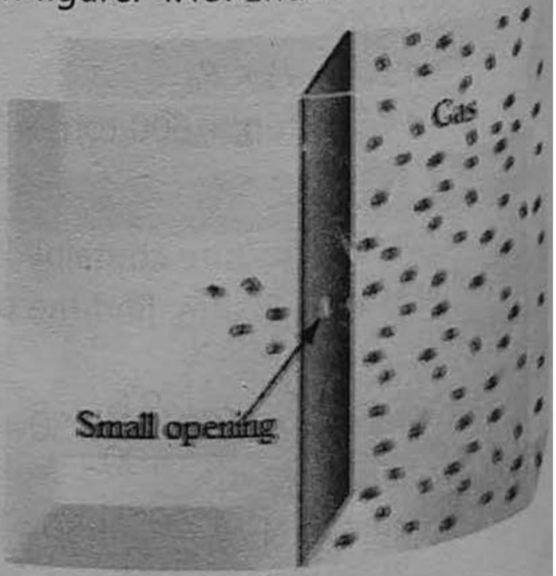


Figure 4.13 Gas Effusion

A general example to differentiate between diffusion and effusion is the 'bursting' and 'puncturing' of a vehicle tyre. During bursting, gas molecules spread suddenly. This phenomenon is called diffusion, while during puncturing, gas molecules spread by escaping through a small hole. This phenomenon is called effusion.

Rate of Diffusion or Effusion of a Gas

The distance travelled by gas molecules per unit time is called rate of diffusion or effusion of gas. Rate of diffusion of a lighter gas is greater than a heavier gas, even at the same temperature because rate of diffusion or effusion of a gas is not only directly proportional to its energy but also inversely proportional to its mass.

Graham's Law of Diffusion and Effusion

In 1832, the Scottish chemist Thomas Graham proposed his law of diffusion of gases, which states that *under the same conditions of temperature and pressure, the rates of diffusion or effusion for gases are inversely proportional to the square roots of their densities, or molecular masses.* This statement, now known as *Graham's law of diffusion,* is expressed mathematically as

$$\frac{r_A}{r_B}=\sqrt{\frac{d_B}{d_A}} \qquad (4.31)$$

Or $$\frac{r_A}{r_B}=\sqrt{\frac{M_B}{M_A}} \qquad (4.32)$$

Where, r_A and r_B are the rate of diffusion or effusion, d_A and d_B are their densities, and M_A and M_B are molecular masses of gases A and B, respectively.

Experimental Verification of Graham's Law of Diffusion

Take a 100cm long glass tube. Plug a cotton swab soaked in hydrochloric acid $(HCl)_{(aq)}$ at one end and another cotton swab soaked in ammonia solution $(NH_3)_{(aq)}$ at the other end simultaneously. The two gases diffuse from their solutions into air of tube and after some time react to form a white ring of ammonium chloride (NH_4Cl). This white smoke of ammonium chloride (NH_4Cl) is 60cm from the NH_3 plug and 40cm from the HCl plug.

Let 'r_{NH_3}' 'M_{NH_3}' and 'V_{NH_3}' represent rate of diffusion, molecular mass and velocity of NH_3 respectively, while 'r_{HCl}' 'M_{HCl}' and 'v_{HCl}' represent the rate of diffusion, molecular mass and velocity of HCl respectively.

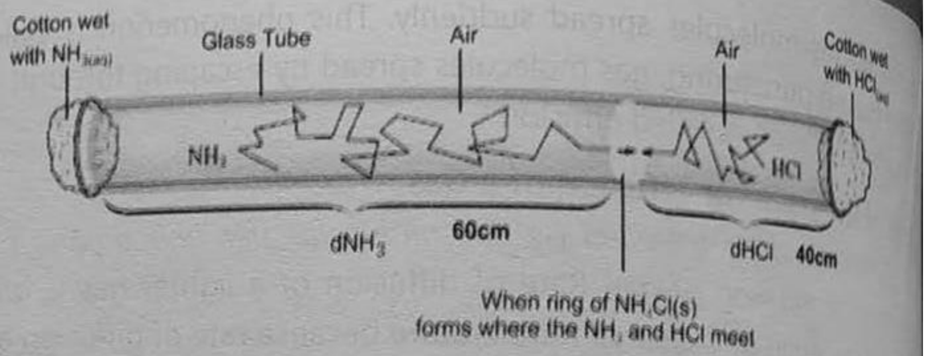


Figure 4.14 $HCl_{(aq)}$ and $NH_{3(aq)}$ meet in the tube, a white ring of $NH_4Cl_{(s)}$ forms

$$NH_{3(aq)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(s)}$$

Since, we know that,

$$S = vT \quad (S = \text{distance travelled by gas})$$

Or

$$v = \frac{S}{T}$$

Distance covered by NH_3 = 60cm

Distance covered by HCl = 40cm

Putting the values in the above equation,

$$\text{Velocity of } NH_3 = v_{NH3} = \frac{60}{t} \tag{4.33}$$

and

$$\text{Velocity of HCl} = v_{HCl} = \frac{40}{t} \tag{4.34}$$

Dividing equation (4.33) by equation (4.34), we get

The ratio of velocities of two gases depends on their distance travelled the respective gases.

$$\frac{\text{Velocity of } NH_3}{\text{Velocity of HCl}} = \frac{v_{NH_3}}{v_{HCl}} = \frac{60}{t} \div \frac{40}{t}$$

$$\frac{v_{NH_3}}{v_{HCl}} = 1.5$$

But,

$$\frac{v_{NH_3}}{v_{HCl}} = \frac{r_{NH_3}}{r_{HCl}}$$

So, $\frac{r_{NH_3}}{r_{HCl}} = 1.5$ (Experimental results)

This ratio show the relative rate of diffusion of two gases, which may be calculated on the bases of Graham's law of Diffusion.

As we have the equation,

$$\frac{\text{Rate of Diffusion of } NH_3}{\text{Rate of Diffusion of HCl}} = \sqrt{\frac{\text{Density of HCl}}{\text{Density of } NH_3}} \qquad (4.35)$$

Density of HCl is 1.66 $g.dm^{-3}$ and that of NH_3 is 0.76 $g.dm^{-3}$ putting the values in equation (4.35) we get,

$$\frac{r_{NH_3}}{r_{HCl}} = \sqrt{\frac{1.66}{0.76}}$$

$$\frac{r_{NH_3}}{r_{HCl}} = \sqrt{2.184}$$

$$\frac{r_{NH_3}}{r_{HCl}} = 1.477 \cong 1.5 \text{ (Theoretical result)}$$

It shows that rate of diffusion of NH_3 is 1.5 times faster than the rate of diffusion of HCl.

As

$$\frac{r_{NH_3}}{r_{HCl}} = \sqrt{\frac{M_{HCl}}{M_{NH_3}}} \qquad (4.32)$$

Similarly, we know that,

Molecular mass of HCl = M_{HCl} = 36.5

and Molecular mass of NH_3 = M_{NH3} = 17

Putting the values in the equation, (4.32)

$$\frac{r_{NH_3}}{r_{HCl}} = \sqrt{\frac{36.5}{17}} = 1.465 \cong 1.5 \text{ (Theoretical result)}$$

As experimental and theoretical results are the same. Therefore, it verifies Graham's law of diffusion.

Example 4.6

Determine the relative rates of diffusion of equal volumes of H_2 and CO_2 under the same conditions of temperature and pressure.

Solution

Molecular mass of H_2 = 2

Molecular mass of CO_2= 44

According to Graham's law of diffusion,

$$\frac{r_{H_2}}{r_{CO_2}} = \sqrt{\frac{M_{CO_2}}{M_{H_2}}}$$

Putting the values in the above equation,

$$\frac{r_{H_2}}{r_{CO_2}} = \sqrt{\frac{44}{2}} = \sqrt{\frac{22}{1}} = \frac{4.7}{1}$$

$$r_{H_2} = 4.7\, r_{CO_2}$$

This means that hydrogen (H_2) molecules diffuse 4.7 times faster tha carbon dioxide (CO_2) under identical conditions.

4.5 Practice problem

Calculate the relative rates of effusion of carbon dioxide (CO_2) and sulphu dioxide (SO_2), from the same container and at same temperature and pressure.

Application of Kinetic Molecular Theory of Gases

Velocity of molecules

There are different types of molecular velocities of gases. Here we will deal with root mean square velocity. It is square root of average of square velocities of gas molecules and is represented by u_{rms}.

Reading Chec
Differentiate between effusion and diffusion gases.

$$u_{rms} = \sqrt{\bar{u}^2}$$

$$u_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 ... + v_n^2}{N}}$$

Where $v_1, v_2, v_3,$ -------- v_n are velocities of N molecules of gas.

The value of the RMS of velocity, u_{rms} at a given temperature can be calculated from the kinetic gas equation given below.

$$PV = \frac{1}{3} mN\bar{u}^2 \qquad (4.36)$$

Where P, V = pressure and volume of the gas
N = number of molecules
m = mass of each molecule
$\bar{u}^2$ = *average* (or mean) of the *squares* of all individual molecular velocities

Solving the equation (4.36) for $\bar{u}^2$ you will get,

$$\overline{u^2} = \frac{3PV}{mN} \qquad (4.37)$$

For one mole of gas,

$$PV = RT$$

If N= Avogadro's number, then $mN = M$, where 'M' which is molar mass, and putting the value of PV in equation (4.37), so you get,

$$\overline{u^2} = \frac{3RT}{M}$$

Taking the square root

$$\sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}} \qquad \text{As } u_{rms} = \sqrt{\overline{u^2}}$$

$$u_{rms} = \sqrt{\frac{3RT}{M}} \qquad (4.38)$$

Putting the values of R, T and M, the value of u_{rms} can be determined.

Graham's Law of Diffusion of gases

According to kinetic molecular theory *at the same temperature and pressure, the molecules of different gases have the same average kinetic energy.*

Therefore, the average kinetic energies of gas molecules 'a' and 'b' at the same temperature should be equal.

Average kinetic energy of gas 'a' = Average Kinetic energy of gas 'b'

$$\frac{1}{2}m_a\overline{v_a^2} = \frac{1}{2}m_b\overline{v_b^2}$$

$$m_a\overline{v_a^2} = m_b\overline{v_b^2}$$

Divide the above equation by 'm_a'

$$\frac{m_a\overline{v_a^2}}{m_a} = \frac{m_b\overline{v_b^2}}{m_a}$$

$$\overline{v_a^2} = \frac{m_b\overline{v_b^2}}{m_a}$$

Divide the above equation by '$\overline{V}_b^{2}$'

$$\frac{\overline{v_a^2}}{\overline{v_b^2}} = \frac{m_b\overline{v_b^2}}{m_a\overline{v_b^2}}$$

$$\frac{\overline{v_a^2}}{\overline{v_b^2}} = \frac{m_b}{m_a} \qquad (4.39)$$

Taking square root of equation (4.39)

$$\frac{\overline{v}_a}{\overline{v}_b} = \sqrt{\frac{m_b}{m_a}} \quad Or \quad \frac{\overline{v}_a}{\overline{v}_b} = \sqrt{\frac{m_bN}{m_aN}}$$

Where N = No. of molecules of a gas

As for one mole,mass of a gas is

Nm = M

So

$$\frac{\bar{v}_a}{\bar{v}_b} = \sqrt{\frac{M_b}{M_a}} \qquad (4.40)$$

It is known that,

$$\bar{v}_a \propto r_a$$

$$\bar{v}_b \propto r_b$$

Where,

r_a = rate of diffusion of gas 'a'

r_b = rate of diffusion of gas 'b'

Putting the values of '$\bar{v}_a$' and '$\bar{v}_b$' in equation (4.40), we get,

$$\frac{r_a}{r_b} = \sqrt{\frac{M_b}{M_a}}$$

$$\frac{r_a}{r_b} = \sqrt{\frac{M_b}{M_a}}$$

Or

$$\frac{r_a}{r_b} = \sqrt{\frac{d_b}{d_a}}$$

This is Graham's law of diffusion, which is explained by the Kinetic Molecula Theory.

4.9 Liquefaction of Gases

The process in which the gases are converted to their liquid states by lowe temperature and increasing pressure is called liquefaction of gases.

Increase in pressure on a gas causes the gas molecules to come closer t each other, while decrease in temperature decreases the kinetic energy of g molecules. This results in development of attractive forces between molecu resulting in liquefaction of gases.

It is observed that,it is impossible to liquefy a gas by pressure alone if th required temperature is not obtained. Above this required temperature, t attractive forces are not strong enough to condense a gas into liquid. *Th temperature above which a gas cannot be liquefied no matter how great t* *pressure is applied is called critical temperature (Tc).*

The critical pressure (Pc), is the minimum pressure that is required to liquefy a gas at its critical temperature.

The critical volume (Vc), is the volume occupied by one mole of the gas at critical temperature (T_c) and critical pressure (P_c).

At critical temperature and critical pressure, the gas is in a state which is intermediate between gaseous and liquid state called **critical state.**

Table 4.3 Critical Temperature and Critical Pressure of Various Gases

S. No	Gas	T_c in °C	P_c in atmosphere
1	Oxygen (O_2)	- 118.8	49.7
2	Nitrogen(N_2)	-147.1	33.5
3	Hydrogen (H_2)	-239.9	12.8

4.9.1 Joule – Thomson effect

Various methods are used for the liquefaction of gases. These methods are generally based upon Joule – Thomson effect.

Joule-Thomson effect is based on the principle that when a compressed gas is forced through a porous plug into a region of low pressure, there is appreciable cooling.

When a compressed gas is allowed to enter from region of high pressure into a region of low pressure, it expands. This sudden expansion causes cooling. This phenomenon is known as Joule-Thomson Effect.

In compressed gas, molecules are very close to each other and have attractive forces. When a gas is expanded suddenly molecules move away from each other. This process requires energy, which is obtained from the gas itself, hence it is cooled.

4.9.2 Linde's Method of Liquefaction of Gases

Linde's Method is based on Joule-Thomson effect in order to liquefy gases or air. The apparatus used for the liquefaction of gas by this method is shown in figure 4.15.

i. Pure air or gas is first compressed to 200 atm by passing through a compressor.
ii. The water in air or gas is condensed and removed.
iii. The heat generated as a result of compression is removed by passing the gas through spiral coils C.
iv. The dry gas is then passed through a copper spiral coil E having a jet J at the lower end.

v. It is then expanded to almost 1 atm when it comes out of jet J.

vi. When the air comes out of the jet, expansion takes place from 200 atm to atm. In this way fall of temperature occurs due to Joule-Thomson Effect. Th cooled air goes up and cools the incoming compressed air.

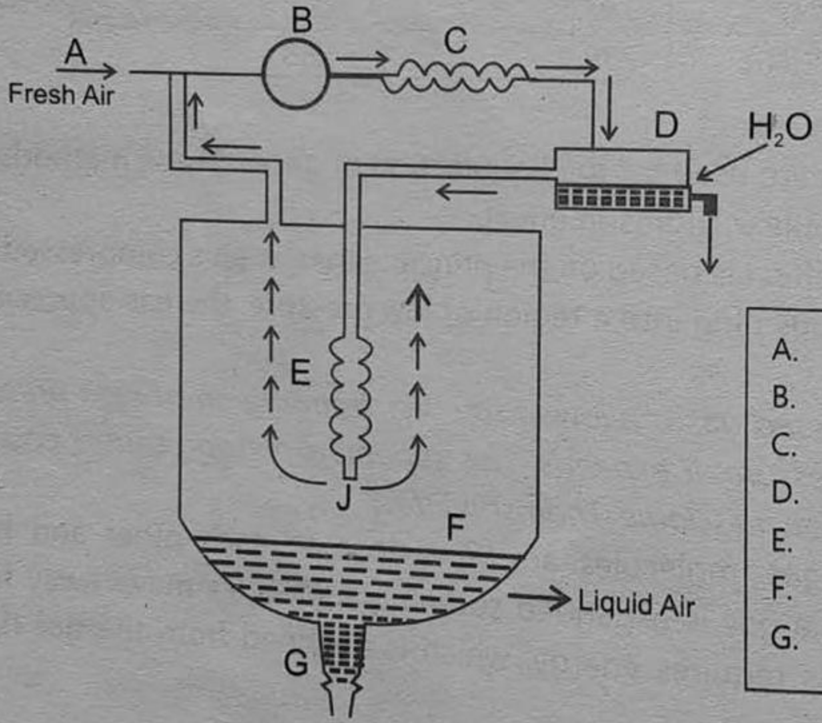
vii. The cycle is repeated several times.

viii. The temperature of the expanding gas finally drops and the remaining ai liquefied.

ix. The liquid air is collected in chamber F and can be drawn off at regular interva through outlet G.

Reading Check

What is liquefaction of gases?



A. Inlet of Air
B. Compressor
C. Condensing Coils
D. Receiver for Water
E. Copper Spiral with a Jet J
F. Liquefied Air Chamber
G. Outlet for Liquefied Air

Figure 4.15 Linde Apparatus

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The advantage of liquefying gases is that they can then be stored and transported in much more compact form than in the gaseous state. Liquefied gases are used for a number of purposes. Some of the most important uses are,

- Liquid natural gas is used as a fuel in vehicles in the form of liquefied natural gas (LNG).
- Liquid oxygen is used in hospitals for patients suffering from breathing problems.
- Liquid oxygen and liquid hydrogen are used in rocket engines.
- Liquid nitrogen is used by dermatologists. It is also used for low temperature

and freezing purposes.

- Liquid oxygen and liquid acetylene can be used in welding operations.
- Liquid chlorine is used for killing the pathogens in drinking water, purification of swimming pools, sanitation of industrial waste and sewage water. It is also used for bleaching of pulp and textiles and in the preparation of different chemicals such as carbon tetra chloride (CCl_4) etc.
- Liquid air is distilled and used to obtain nitrogen, oxygen and argon.
- Liquefaction of gases is also important in the field of research known as cryogenics.
- Liquid helium is widely used for the study of behavior of matter at temperatures close to absolute zero, 0K .

4.10 Fourth State of Matter: Plasma

Solid, liquid and gas are the three fundamental states of matter. Plasma is considered the fourth state of matter.

Plasma is a Greek word which means, that *'which is diffused' that is, 'unclear or semi transparent'. Plasma is a state of matter in which it exists as a mixture of neutral particles, positive ions and negative electrons. For example, our sun is composed of plasma.*

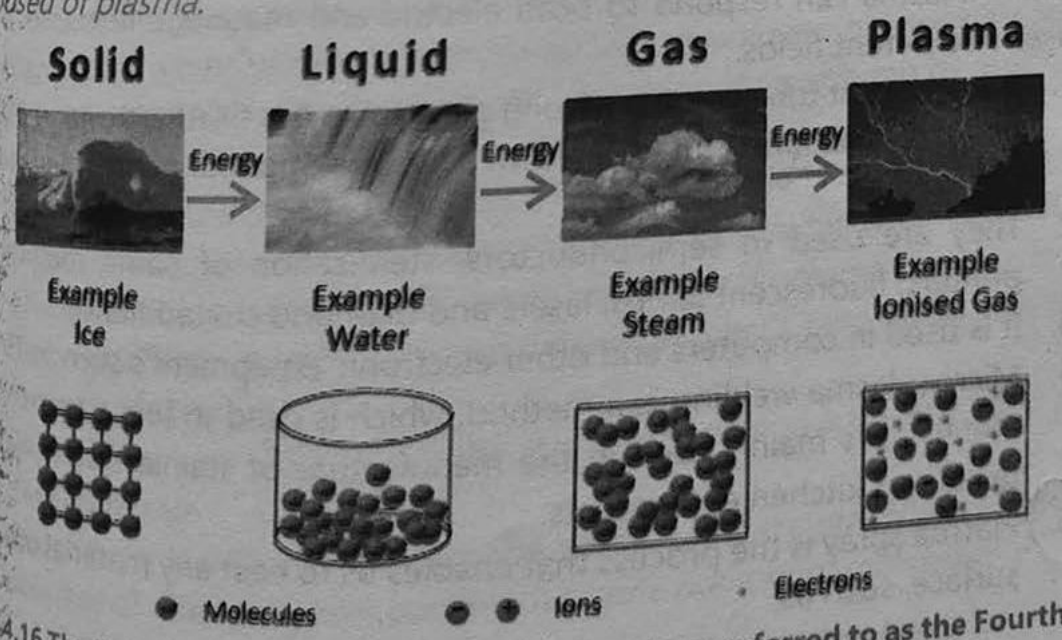


Figure 4.16 The Four States of Matter; Plasma is sometimes referred to as the Fourth State

Origin of Plasma

This term was originally applied by Irving Langmuire in 1928 to an gas. Since an ionized gas cannot exist at room temperature, that is why, observed for the first time in an electrical discharge at high temperature.

Plasma Formation

On heating a solid, it is converted into liquid. On further heating, the li is converted into vapours. Now if vapours are further heated, some of them lo electrons and positive ions are formed.

Plasma is a mixture of neutral particles, positive ions and free electro Plasma is considered a unique fourth state of matter. The properties of plas clearly distinguish it from an ordinary gas such as it conducts electricity and responds to magnetic fields.

Occurrence of Plasma

Plasma is found in the region around sun and stars. Since sun and stars ha far more matter, therefore, it is said that more matter (about 99% of the univers is made up of plasma. On earth, plasma is limited to lightning bolts, flames an fluorescent lights, neon signs etc. when an electric current is passed through neo gas; it produces both plasma and light.

Although it contains positive ions and negative electrons but their charge are equal and hence plasma is neutral.

Applications

Plasma can respond to both electric and magnetic fields, so it has ma uses in different fields.

1. A fluorescent tube consists of long glass tube. It is filled with neon gas. The ne gas in plasma form is used for lightening. The colour of plasma depends upon t gas used.
2. They are used in semiconductors, sterilization of some medical produ printers, fluorescent lamps, lasers and diamond coated films.
3. It is used in computers and other electronic equipment's such as TV etc.
4. Micro–plasma welding is a method, which is used to join paper-thin sheets metals. It is mainly used in the manufacture of stainless steel, water stora tanks and kitchen equipments.
5. Plasma spray is the process that enables us to coat any material onto any o surface, such as,
   - Metal onto metal: Titanium onto steel, to prevent corrosion
   - Metal onto non-metal: Copper onto porcelain, used in capacitors
   - Non-metal onto metal: Alumina onto stainless steel, to reduce wear and on stainless steel
   - Non-metal onto non-metal: Teflon onto ceramics, to prevent corrosio acids.

Self-Assessment

1. State Dalton's law of partial pressures.
2. How the pressure and volume correction is made in the ideal gas equation.
3. Define Joule–Thomson effect.
4. Derive Graham's law of diffusion and effusion for molecular masses of gases.
5. Write down the experimental verification of Graham's of diffusion and effusion.
6. Differentiate between ideal and real gas.
7. What is plasma, Write down its applications?
8. Why real gases deviate from the gas laws?
9. Discuss briefly in points the Linde's method for the liquefaction of gases.
10. Define critical temperature, critical pressure and critical volume.

KEY POINTS

- Gas is the state of matter, which has neither definite volume nor definite shape. In other words, gas is the matter with the highest energy state.
- Kinetic molecular theory of gases is based on the fundamental concept that molecules in gases are in constant movement.
- Barometer, a type of manometer, is used to measure atmospheric pressure.
- One atmosphere is the force exerted by 76cm long column of mercury on an area of 1cm^2 at 273.15K
- One Pascal is the pressure exerted by a force of one Newton (1N) acting on an area of one square meter. SI unit of pressure is N/m^2, which is one Pascal.
- Charles' and Gay-Lussac experiments showed that volume changes by 1/273 of the original volume at 0°C for each Celsius degree (°C) rise or fall in temperature at constant pressure.
- The temperature – 273.15°C is the absolute zero, and is given a value of zero in the Kelvin scale.
- Avogadro's law states that at the same temperature and pressure, equal volumes of different gases contain the same number of molecules.
- One mole of any gas contains 6.022 x10^{23} molecules (Avogadro's number).One mole of a gas occupies 22.4 dm^3 at STP.
- An ideal gas is a gas that behaves exactly as outlined by the assumptions of the kinetic molecular theory.

- The conditions 0°C and 1 atm are called standard temperature and pressur (abbreviated as STP).
- Compressibility factor shows the extent to which a real gas deviate from th ideal behaviour. Real gases are non-ideal gases.
- Dalton's law states that the total pressure exerted by a mixture of gases in a container is equal to the sum of the partial pressures of all the gases present in the mixture provided that no chemical reaction occurs at constant temperature and volume.
- Diffusion is the ability of two or more gases to mix spontaneously until they form a uniform mixture by random motion and collision (by virtue of their kinetic properties). Lighter gases diffuse at higher rates than heavier gases.
- Effusion is the process by which gas molecules escape from one compartment of a container to another by passing through a small opening without collision.
- Graham's law of diffusion states that under the same conditions of temperature and pressure, rates of diffusion for gases are inversely proportional to the square roots of their densities or molecular masses.
- Liquefaction of gases is the process in which the gases are converted to the liquid state by lowering temperature and increasing pressure.
- When a compressed gas is allowed to enter from region of high pressure into a region of low pressure, it expands. This sudden expansion causes cooling. This phenomenon is known as Joule-Thomson Effect.
- Plasma is considered as the fourth state of matter. About 99% of the universe is made up of plasma.

EXERCISE

Choose the Correct Option.

1. If absolute temperature of a gas is doubled and the pressure is reduced to, one-half the volume of gas will,
   a. remain unchanged b. double
   c. reduce to half d. increase four times
2. One dm^3 of Hydrogen at STP weighs approximately
   a. 0.0789g b. 0.0799g
   c. 0.0987g d. 0.0899g
3. In a factory producing liquid air, one of the pipes carrying dry air at -80°C is blocked with a white solid. This white solid is,
   a. Argon b. Ice
   c. Nitrogen d. Carbon dioxide
4. The spreading of perfume or scent in air is due to
   a. Diffusion
   b. Effusion
   c. Attraction with air
   d. Low density
5. A gas has certain volume at 10°C. How much temperature should be raised to double its volume,
   a. 566K b. 283K
   c. 293K d. 283°C
6. The rate of diffusion of hydrogen (H_2) compared with helium (He) is,
   a. 0.5 times b. 1.4 times
   c. 2 times d. 4 times
7. The non-ideal behaviour results chiefly from
   a. Intermolecular attraction and infinite volume
   b. Elastic collisions and finite volume
   c. Intermolecular attractions and finite volume
   d. Intermolecular attraction only
8. The molar volume of helium (He) is $44.8dm^3$ at,
   a. 100 °C and 1atm
   b. b. 25 °C and 0.25atm
   c. 0 °C and 0.5atm
   d. 40 °C and 0.5atm

9. Which statement about the behaviour of the particles in a gas is not correct
   a. They are able to move at great speeds
   b. The forces of attraction between the particles are negligible
   c. There is large space among the particles
   d. They are arranged in regular patterns
10. At the same temperature and pressure which of the following gases has th greatest density,
   a. CO_2 b. SO_2
   c. Cl_2 d. H_2O
11. Weight of one dm^3 of O_2 at STP is
   a. 1.4384 g b. 1.5394 g
   c. 1.6384 g d. 1.3384 g
12. The value of ideal gas constant in $dm^3.torr.k^{-1}.mol^{-1}$
   a. 0.0821 b. 1.98722
   c. 62.364 d. 8.3143
13. 760 torr is equal to,
   a. 760 Pascal b. 76 Pascal
   c. 101325 Pascal d. 1.01325 Pascal
14. At 50°C a gas has 1atm pressure, and $20dm^3$ volume, its volume at STP wou be
   a. $16.94dm^3$ b. $10.92dm^3$
   c. $3.66dm^3$ d. $42.2\ dm^3$
15. Which of the following gases will have the fastest effusion rate?
   a. CH_4 b. NH_3 c. CO_2 d. O_2

Short Questions

1. Justify that $1cm^3$ of hydrogen (H_2) and $1cm^3$ of methane (CH_4) at STP will ha same number of molecules although one molecules of methane (CH_4) is 8 tim heavier than that of hydrogen (H_2).
2. Do you think that some of the postulates of kinetic molecular theory of gas are faulty? Write down these postulates.
3. Why high pressure and low temperature make the gases non-ideal?
4. What is your opinion about rapid expansion of gases causes cooling?
5. Why do you think that lighter gases can diffuse more rapidly than heavier on

Numerical Questions

1. A mass of gas is under a pressure of 760 torr and occupies volume of 525cm^3. If the pressure is doubled, what volume would the gas now occupy? Assume the temperature is constant. (Answer: 262.5cm^3)
2. Hydrogen gas diffuses through a porous plate at a rate of 500cm per minute at 0°C. What is the rate of diffusion of oxygen gas through the same porous plate at 0°C? (Answer: 125cm)
3. It was desired to obtain a volume of 1000cm^3 of oxygen at 100°C and 640 mm Hg. How many moles of oxygen would be required? (Answer: 0.0275mol)
4. Calculate the density of CH_4 at 0°C and 1 atmosphere . (Answer: 0.7139gdm^{-3})
5. A sample of Krypton with a volume of 6.25 dm^3 and a pressure of 765 torr and a temperature of 20°C is expanded to a volume of 9.55 dm^3 and a pressure of 375 torr. What will be its final temperature? (Answer: 219.64K)

Descriptive Questions

1. (a) Explain the concept of diffusion and effusion of gases.
   (b) Apply the knowledge of the kinetic theory of gases and derive an expression of Graham's law of diffusion.
   (c) The rate of effusion of an unknown gas through a pinhole is found to be 0.279 times the rate of effusion of H_2 through the same pinhole. Calculate the molecular mass of the unknown gas at STP. (Answer: 25.7g)
2. (a) State Dalton's law of partial pressure. Write down its mathematical form.
   (b) Explain the significance of absolute zero, giving its value in degree Celsius and Kelvin.
   (c) What pressure is exerted by a mixture of 2g of helium (He), 16g of oxygen (O_2) and 10g of carbon dioxide (CO_2) at 10°C in a 5dm^3 vessel? (Answer: 5.703atm)
3. (a) How would you relate temperature to the average kinetic energy of the particles in a substance?
   (b) Explain Linde's method for the liquefaction of gases.
   (c) Give two points of evidence to show that gases do not behave ideally under all conditions of temperature and pressure.
4. (a) Write the Van der Waals equation for a real gas. Clearly explain the meaning of the corrective terms for pressure and volume.
   (b) The temperature of a real gas usually drops when it is allowed to enter into a low pressure (vacuum). Explain.
   (c) Define and describe the properties of plasma.

5. (a) State basic postulates of kinetic molecular theory of gases.
   (b) Explain how Graham's law of diffusion can be derived from the Kine Molecular Theory.
   (c) Explain the absolute zero on the basis of Charles' law.

PROJECT:

1. Use the daily weather reports in the newspapers or news and conduct a meteorological research to study the interrelationships among atmospheric pressure (air pressure), temperature, humidity, and other weather variables. Prepare a report of a week explaining your results and present it in the class.
2. The pressure of air in car tyres is checked regularly for safety and to prevent uneven tyre wear and tear. What units of measurement are used on a typical tyre gauge? Also, find out that how gauge pressure relates to atmospheric pressure.

Unit - 05

States of Matter II: Liquids

After studying this unit, the 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. (Understanding)
- Explain applications of dipole – dipole forces, hydrogen bonding and London forces. (Applying)
- Explain physical properties of liquids such as evaporation, vapour pressure, boiling point, viscosity and surface tension. (Understanding)
- Use the concept of Hydrogen bonding to explain the following properties of water: high surface tension, high specific heat, low vapour pressure, high heat of vaporization and high boiling point. Anomalous behaviour of water when its density shows maximum at 4 degree centigrade. (Applying)
- Define molar heat of fusion and molar heat of vaporization. (Remembering)
- Describe how heat of fusion and heat of vaporization affect the particles that make up matter. (Understanding)
- Relate energy changes with changes in intermolecular forces. (Applying)
- Define dynamic equilibrium between two physical states. (Remembering)
- Describe liquid crystals and give their uses in daily life. (Applying)
- Differentiate liquid crystals from pure liquids and crystalline solids. (Applying)

Teaching

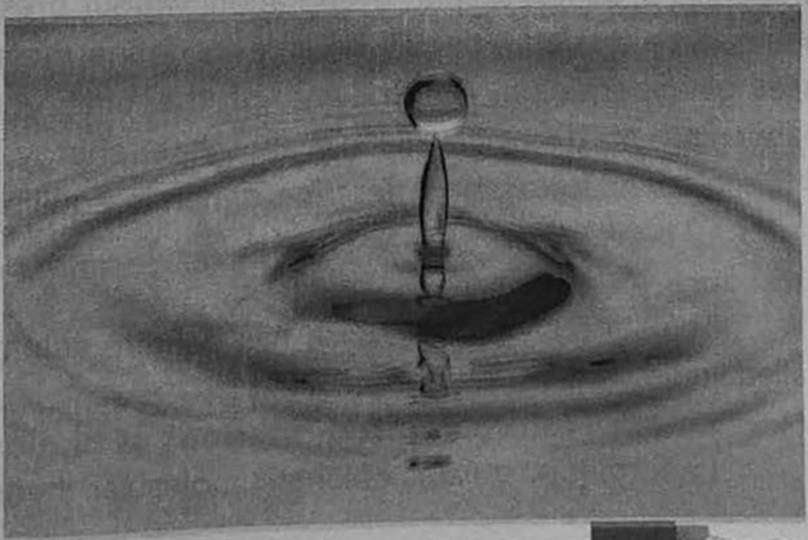
09

Assessment

01

Weightage %

11



Introduction

It is well known that there is a complete absence of order in gases, a complete regularity in the structure of perfectly crystalline solids, while some of the properties of the liquids resemble those of the gases at one extreme and solids at the other.

Both gases and liquids are fluids and offer no resistance to deformation. They adopt the shape of the container. The similarities in density and compressibility of the liquids and solids suggest some sort of resemblance in arrangement of the molecules in the liquid and the solid states of the matter near the melting point.

The cohesion in a liquid may be due to ionic forces in molten electrolytes, metallic forces in molten metal's, hydrogen bonding in water or Van der Waal's forces in organic liquids and in some cases more than one of these forces may operate.

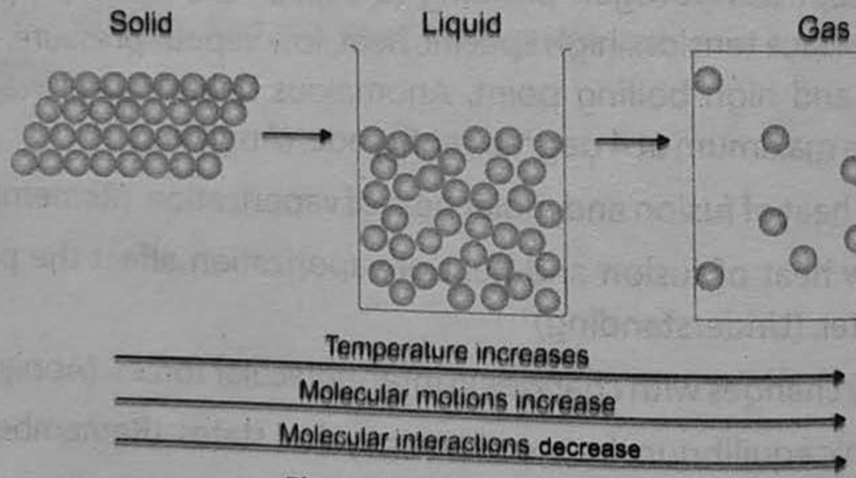


Figure 5.1 States of Matter

In this unit, you will study the intermolecular forces, the physica properties of liquids such as evaporation, vapour pressure, boiling point, viscosit and surface tension. You will be able to define molar heat of fusion and mo heat of vaporization. By the end of the unit, you will understand what i happening at the molecular level; relate energy changes with changes i intermolecular forces, and describe dynamic equilibrium between two physic states.

Liquid

The state of matter, which has definite volume but no definite shape, i called liquid.

5.1 Kinetic molecular interpretations of liquids

Important postulates of kinetic molecular theory are,

1. The liquid molecules have kinetic energy greater than solids and lesser than gas molecules at a given temperature.
2. The intermolecular forces of liquids are stronger than in gases and weaker than in solids.
3. The molecules are close to each other. Empty spaces are negligible. Thus, liquids have definite volume and are very difficult to compress.
4. The molecules are in constant motion by sliding over each other. Thus,liquids have no definite shape and so a liquid can flow, can be poured and assume the shape of the container.

5.1.1 Simple properties of liquids

Some simple properties of liquids can be explained on the basis of kinetic molecular theory.

i. Diffusion

According to kinetic molecular theory, the molecules of liquid are in constant random motion. So, they move from one place to another due to kinetic energy that is why the liquid molecules diffuse and form a homogenous mixture. However, this diffusion takes place very slowly, due to intermolecular attractive forces among liquid molecules and small empty space among the molecules.

ii. Compression (Effect of Pressure on Liquids)

As in Liquids, there is very little empty space among their molecules, so they cannot be compressed significantly by increasing pressure.

iii. Expansion (Effect of Temperature)

Liquids do not have a definite shape. They take the shape of the container. Thus, a liquid can be specified by its volume. Hence, we can speak of volume expansion for liquids, as expansion of liquids is greater than that of solids. Liquids have ability to expand at all temperatures.

When a liquid is heated in a container, heat flows through the container to the liquid, which means that the container expands first, due to which the level of the liquid falls. When the liquid gets heated, it expands more and beyond its original level. We cannot observe the intermediate state. We can only observe the initial and the final levels. This observed expansion of the liquid is known as the apparent expansion of the liquid. If we consider the expansion of the container also and measure the total expansion in volume of the liquid, then the expansion is termed as the absolute expansion of the liquid.

iv. Motion of molecules

The molecules of liquids have intermolecular attractive force. Because of these intermolecular attractive forces, they have less kinetic energy. However, th kinetic energy of these liquid molecules increases with increase in temperature.

v. Kinetic Energy Based on Kinetic Molecular Theory

According to kinetic molecular theory, the molecules of the liquids are i constant random motion. However, they have less free movement as compare to gas molecules, due to strong intermolecular forces. This less movement o molecules results minimum collisions.

Liquids have definite volume but no definite shape because intermolecula forces are not so strong to stop the molecules from sliding over each other. Thus, i takes the shape of its container. A liquid has the ability to flow also that is why it ca be poured from one container to another.

Molecular forces

There are two types of molecular forces.

a. Intra-molecular and
b. Intermolecular

a. Intra-molecular Forces

The attractive forces within a molecule of a liquid are called intra-molecular forces. The example of intra-molecular forces are (1). Covalent bond (2). Co-ordinate covalent bond etc.

b. Intermolecular Forces

The attractive forces among the molecules of a substance are calle intermolecular forces. The examples of intermolecular forces are hydroge bonding, dipole – dipole interactions and London dispersion forces. Collective these three weak forces are named as Van der Waals forces.

Generally, intermolecular forces are much weaker than intra-molecula forces. Very small amount of energy is required to evaporate a liquid than t break the bonds in the molecules of the liquid. For example in equation (5.1), i require 40.7kJ of energy to break the hydrogen bonding and to vaporize 1 mo of water at its boiling point; but in equation (5.2), about 930kJ of energy i required to break the two O – H covalent bonds in 1 mole of water molecule The intra-molecular forces hold the atoms in H_2O molecules together are 2 times stronger than intermolecular forces between water molecules.

$$H_2O_{(l)} \longrightarrow H_2O_{(g)} \qquad \Delta H = 40.7\text{kJ/mol} \qquad (5.1)$$

$$H_2O_{(g)} \longrightarrow 2H_{(g)} + O_{(g)} \qquad \Delta H = 930\text{kJ/mol} \qquad (5.2)$$

5.2 Intermolecular Forces (Van der Waals Forces)

Water (H_2O) and hydrogen sulphide (H_2S) have the same bent molecular shape. Both are polar molecules. However, water (H_2O), with a molar mass of 18g/mol, is a liquid at room temperature, while hydrogen sulphide (H_2S), with a molar mass of 34g/mol is a gas. Water's boiling point is 100°C, while hydrogen sulphide's (H_2S) boiling point is −61°C.

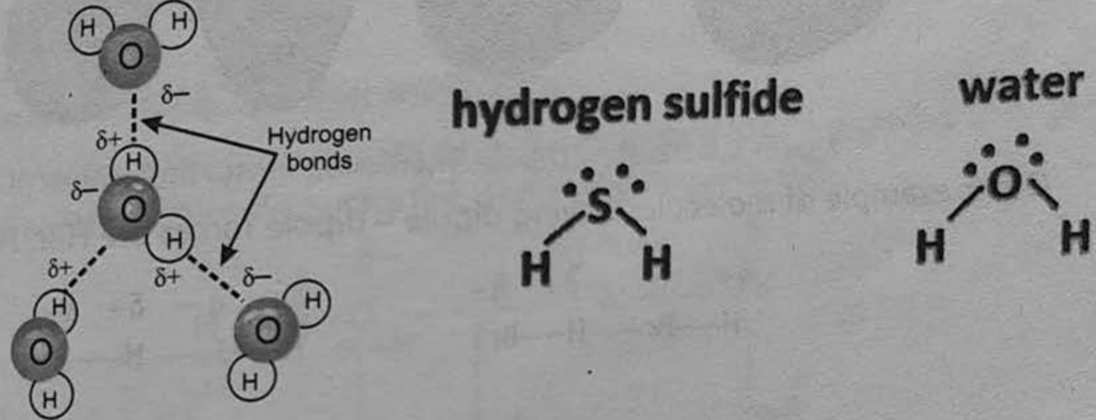


Figure 5.2 Intermolecular forces in H_2O and H_2S

The difference in such properties can be explained on the basis of intermolecular forces.

The intermolecular forces are (1) dipole – dipole interaction, (2) hydrogen bonding and (3) London dispersion forces. These intermolecular forces are called *Van der Waals forces,* after the Dutch physicist Johannes Van der Waals. These three forces follow the following order in strength.

Hydrogen Bonding > Dipole – Dipole Forces > London Dispersion Forces

5.2.1 Dipole – Dipole Interaction

Dipole-dipole forces are attractive forces between polar molecules, that is, between molecules that possess dipole moments.

The attractive forces between the positive pole of one polar molecule and negative pole of other polar molecule are called dipole – dipole forces.

Polar molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule and a separation of charge causes a *dipole.* Therefore, they are also called dipole molecules.

Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom has the partial negative charge, whereas the less electronegative H atom has the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attract force is called a dipole-dipole attraction – the electrostatic force between th partially positive end of one polar molecule and the partially negative end o another, as shown in figure 5.4.

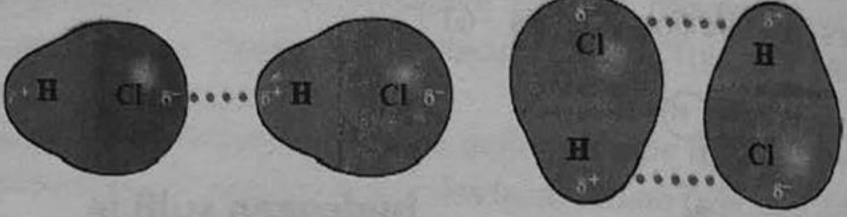


Figure 5.3 Dipole – Dipole Interaction in HCl Molecules

Other example of molecules having dipole – dipole forces are HBr, HI, etc

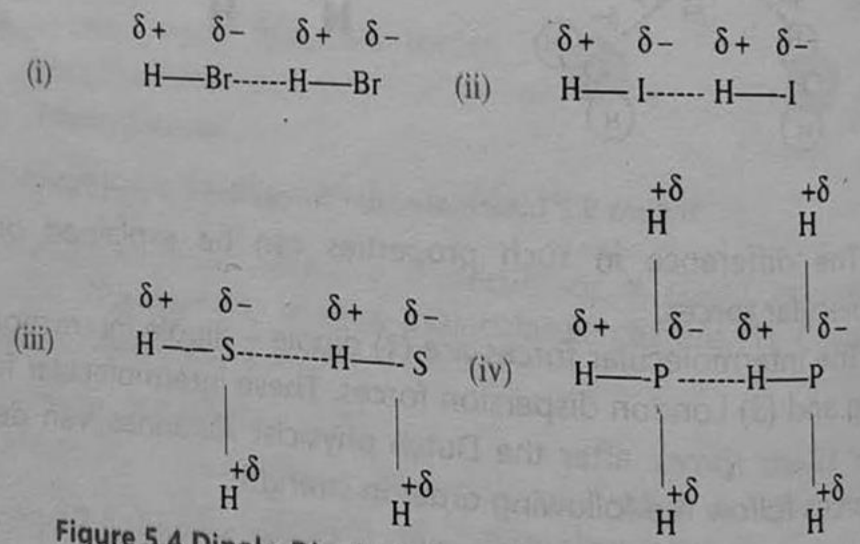


Figure 5.4 Dipole-Dipole Forces in HBr, HI, H_2S and PH_3

As a result of dipole-dipole forces of attraction, polar molecules will att one another more at room temperature than similar sized non-polar molecu The energy required to separate polar molecules from one another is greater th non-polar molecules of similar molar mass. Generally, stronger the dipole-dip forces , greater the values of thermodynamic properties like melting point, boi points, heat of vaporization and heat of sublimation etc.

5.2.2 Hydrogen Bonding

Hydrogen bonding is the strongest type of intermolecular force. It i particularly strong form of dipole-dipole attraction that exists in molecule which hydrogen is bonded to a highly electronegative atom, such as fluo oxygen or nitrogen. The strong force of attraction by these electronegative ato draws the electron from the hydrogen atom, leaving the hydrogen atom with a partial positive charge. This dipole is easily attracted to the partially negative and lone pair of electron on a nearby electronegative atom (such as, F, O or N). The intermolecular force acting between these polar molecules is called a *hydrogen bond*, which acts like a very weak bond between polar molecules.

Thus, *the force of attraction between partially positive charged hydrogen atom which is covalently bonded to a small size, high electronegative (F, O, N) and active lone pair of another electronegative atom (F, O, N) is called hydrogen bonding.*

Hydrogen bonding in water molecules

In water, a link is developed between hydrogen of one molecule with oxygen atom of another molecule. Such a link is called hydrogen bond.

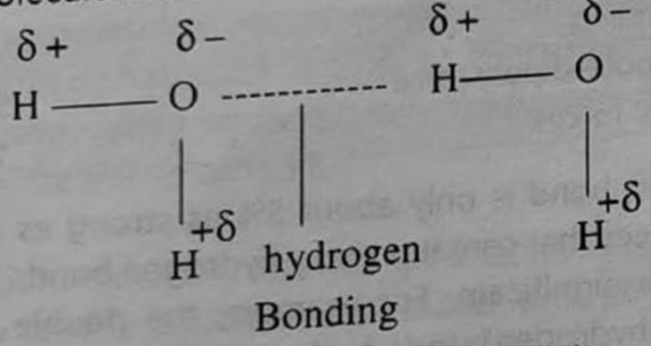


Figure 5.5 Hydrogen Bonding in water

Hydrogen bonding in HF molecules

In HF molecule, there is a hydrogen bond between the hydrogen atom of one molecule and the fluorine atom of another molecule. The hydrogen bond acts as a bridge between two F atoms.

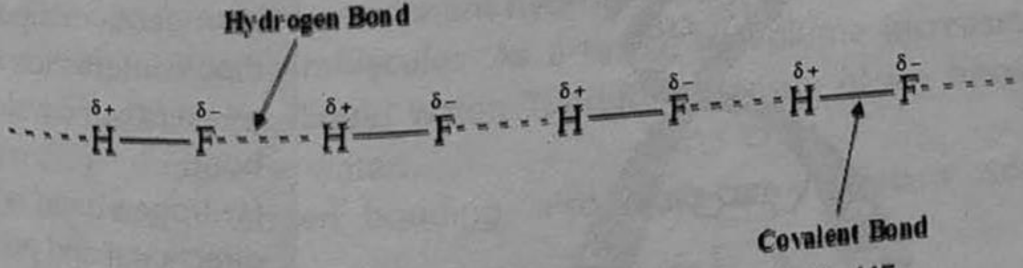


Figure 5.6 Hydrogen Bonding in HF

In the structure above, the dotted line (– – –) shows the hydrogen bond and the solid line shows the covalent bond.

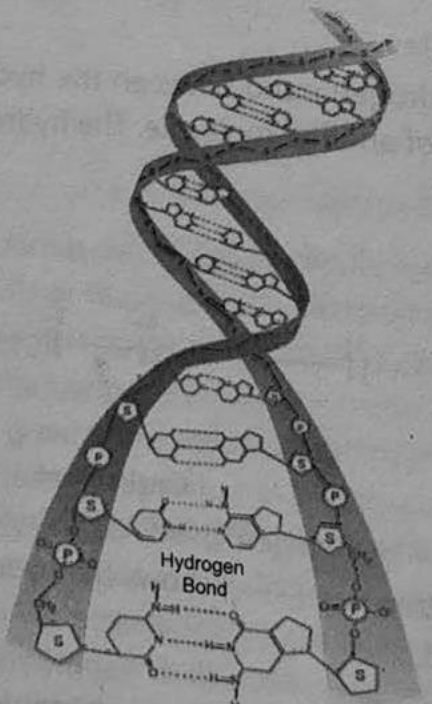
Proof of Hydrogen bonding

The evidence for existence of hydrogen bonding has been derived from the study of boiling points of hydrides. When the molecular mass of hydrides of group IV elements increases, their boiling points also increase. This is due to increas London dispersion forces (absence of polarity). The boiling point of V, VI and groups elements shows exactly the same trends as VI group elements except hydride of first elements of each group which are abnormally high. This shows there must be some additional intermolecular forces of attraction, which responsible for high boiling point. This additional intermolecular force is hydrogen bonding.

Table 5.1 Comparison of the relative strength of intermolecular forces and other bon

Type of bond	Bond strength / kJ mol^{-1}
Ionic bonding in sodium chloride	760
OH^- covalent bond in water	464
Hydrogen bonding	20 – 50
Permanent dipole–dipole force	5 – 20
Van der Waals' forces	1 – 20

A hydrogen bond is only about 5% as strong as a single covalent bon However, substances that contains many hydrogen bonds, the impact of hydrog bonding becomes significant. For example, the double-helix structure of DN occurs because of hydrogen bonds, as shown in Figure 5.8.



Tidbit

Properties of hydrogen bond

Hydrogen bond is stronger than dipole-dipole interaction but weaker than covalent bond.

Hydrogen bond is directional and results in the formation of long chains and networks of molecules.

Figure 5.7 Hydrogen Bonding in DNA (deoxyribonucleic acid) molecule

Application of Hydrogen Bonding

i. Strength of Acids

H – F is weaker acid than H–Cl, H–Br and H–I because hydrogen atom is entrapped between two highly electronegative atoms in H – F due to hydrogen bonding.

ii. Solubility

Organic substances which can form hydrogen bonds with water molecules, are soluble in water, for example, ethyl alcohol (C_2H_5OH) is miscible with water in all proportions because its molecules can form hydrogen bonds with molecules of water.

iii. In Biological Compounds

Large protein molecules in living organisms are stabilized due to hydrogen bondings. Fibers, hair, muscle proteins consist of long chains of amino acids. These chains are coiled around each other and form a spiral helix. Hydrogen bonds stabilize this spiral helix.

iv. DNA in Cells

DNA (Deoxyribonucleic acid) has two spiral strands which are coiled about a common axis. They form a double – helix ladder type structure. The steps of these ladders are formed by hydrogen bonds.

v. Structure of Ice

In liquid water, molecules form hydrogen bonding with each other. However, due to movement of molecules, bonds are broken and reformed. Hence, there is less regularity and less free space among them. However, when temperature of water is lowered below 4°C, its molecules start to become regularly arranged and form permanent hydrogen bonds. Thus, empty spaces are developed in between the molecules. As a result, its volume increases and ice occupies more space than liquid water. Therefore, density of ice becomes less than water and it floats over water.

Besides this, hydrogen bonding also plays an important role in the following:

- Cleaning action of soaps and detergents.
- Adhesive action of paints and dyes.
- Sticking action of glue and honey.
- Stabilization of large food material such as carbohydrates etc.

5.2.3 London Forces

In noble gases, like helium, neon, argon, etc atoms and molecules are non-polar and experience a weak intermolecular attraction. In any atom molecule, polar or non-polar, the electrons are in constant motion but motion of electrons of one atom affects the motion of electrons of the o atom. As a result, at any instant the electron distribution may be slightly une The momentary uneven distribution of charge creates a positive pole in one p of the atom or molecule and a negative pole in another. In other words, a no polar molecule becomes slightly polar for an instant. This is called instantane dipole.

The formation of this temporary dipole affects the electron distribution a neighbouring molecule. An *instantaneous dipole* that occurs in a molecule c then *induce* a similar dipole in a neighbouring molecule. This is called indu dipole.

This phenomenon leads to an inter molecule-attraction that is relati weak and short-lived but that can be very significant especially for lar molecules, as shown in figure 5.8. The momentary force of attraction crea between instantaneous dipole and the induced dipole is called dipole – indu dipole interaction or London force.

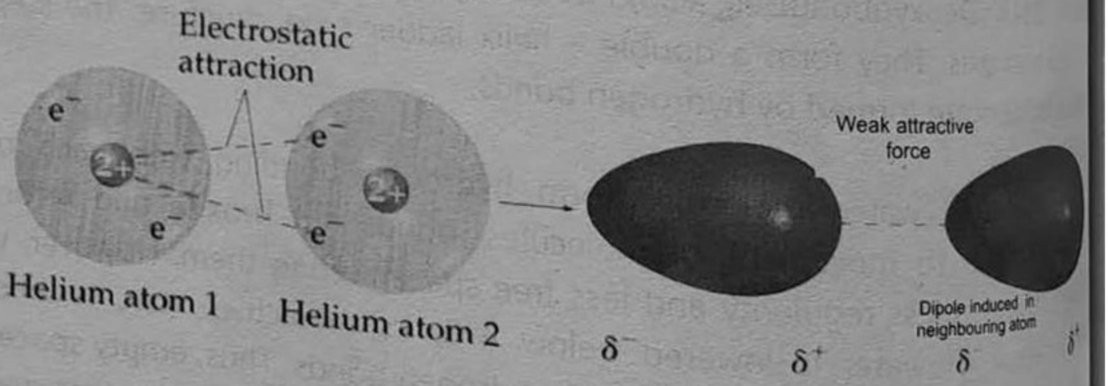


Figure 5.8 London Forces in Helium Atom

The weak intermolecular attractive forces resulting from the cons motion of electrons and the creation of instantaneous dipoles are called Lond dispersion forces.

London forces are also known as Dispersion forces. These forces named after German physicist, Fritz London, who studied this force in 19 London forces act between all atoms and molecules. However, they are the o intermolecular forces acting among noble-gas atoms and non-polar molec like H_2, Cl_2 etc.

London force is weaker than dipole – dipole interactions. The strength London forces are dependent on the,

- The number of electrons, and
- The shape of the molecule

(i) Effect of the number of electrons (size of molecules) on the strength of London dispersion forces

The sizes of atoms increase down a group in the periodic table due to increase in the electrons of valence shells. These create stronger temporary dipoles increasing the strength of London dispersion forces e.g. in group VIIIA, Neon has smaller size than xenon. Thus, neon molecules have weaker London dispersion forces than xenon molecules.

London forces usually increase with molar mass because molecules with larger molar mass tend to have more electrons and dispersion forces increase in strength with the number of electrons. As larger molecular mass often means larger atoms, which are more polarisable (more easily distorted to give instantaneous dipoles because the electrons are farther from the nuclei). The relationship of London forces to molecular mass is only approximate

(ii) Effect of shape of molecules on the strength of London dispersion forces

A molecule with a spherical shape has a smaller surface area than a straight chain molecule with the same number of electrons. The smaller surface area has less opportunity for the molecule to induce a charge on a nearby molecule. Therefore, for two substances that have a similar number of electrons, the substance with molecules that have a more spherical shape will have weaker dispersion forces and has a lower boiling point.

Shape of a molecule may be straight and long chain or branched and short chain. The straight – long chain molecules have greater London dispersion forces than the branched – short chain molecules, even if they have the same number of electrons.

Reading Check

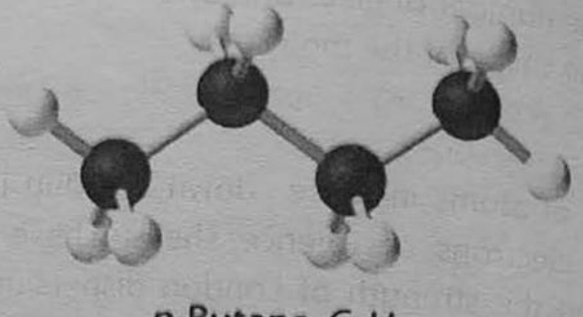
1. Define liquid and kinetically interpret the liquids.
2. What are the different properties of liquids?
3. What is dipole – dipole forces?
4. Explain the application of hydrogen bonding.

Example:

C_4H_{10} is the molecular formula for two compounds with same number of electrons.

(i) **n – Butane**

It is straight and long chain compound and having boiling point of 272.5 K.

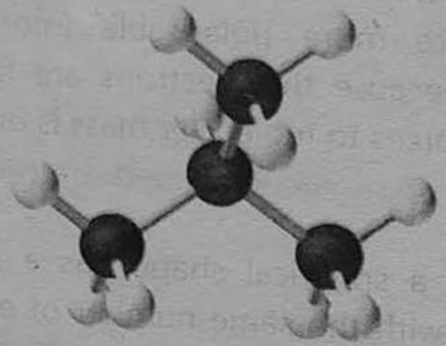


n-Butane, C_4H_{10}

Figure 5.9

ii) 2-Methylpropane

It is branched and short chain compound and having boiling point of 261 which is lower than the straight chain n-butane.



Isobutane (2-methylpropane), C_4H_{10}

Figure 5:10

5.3 Physical Properties of Liquids

Intermolecular forces give rise to a number of physical properties liquids.

1. Evaporation

The spontaneous change of a liquid into its vapours at any temperatu called evaporation.

According to kinetic molecular theory, the molecules of a liquid are al in motion. The energy is not equally distributed among the molecules. It chan after each collision of a molecule. The molecules with greater kinetic en move faster and reach to the surface. From the surface of liquid, these molec escape into vapours.

In an open container, at constant temperature evaporation continue the same rate until all the liquid is converted into vapours.

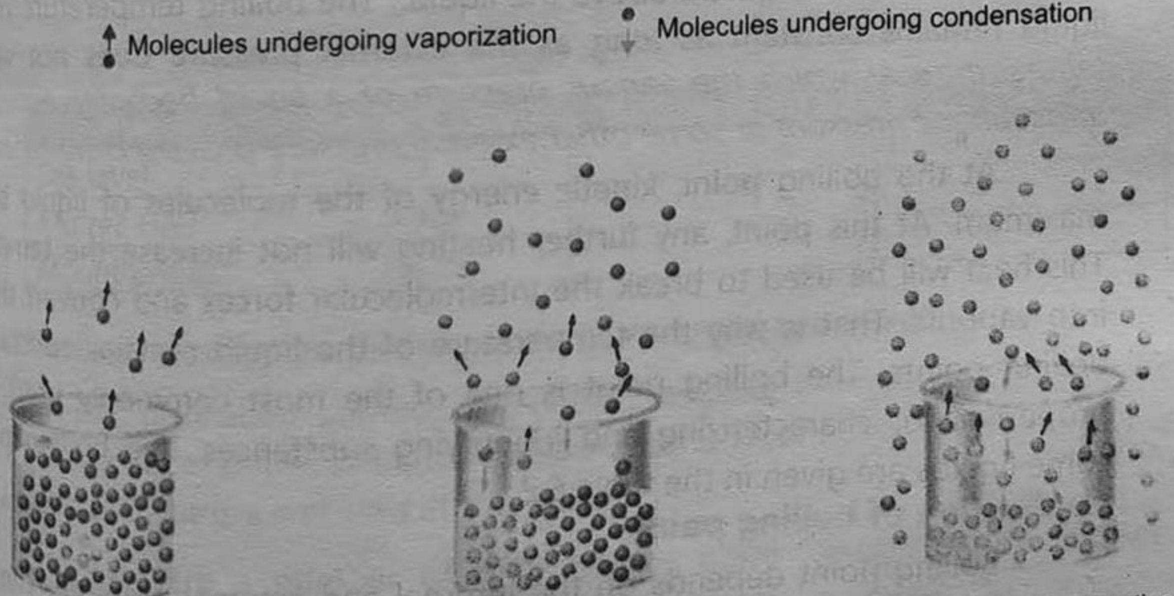
The process of evaporation rate depends on the surface area, temperature strength of intermolecular forces.

2. Vapours pressure

The pressure exerted by the vapours of the liquid when the rate of evaporation becomes equal to rate of condensation.

Consider a liquid in a closed container. The kinetic energy of all the molecules is not the same. The molecules of the liquid whose kinetic energy is greater than the average come to surface of the liquid and convert into the vapours. The vapours gather in the space above the surface of the liquid. Some vapours molecules strike back at the surface of the liquid and becomes liquid again by condensation. As the process of evaporation continues, the rate of condensation also increases. In the beginning, rate of evaporation is greater than rate of condensation, but after sometime both the rates become equal and a dynamic equilibrium is established as shown in the figure 5.11.

Therefore, the vapour pressure can be defined as *the pressure exerted by the vapours in state of equilibrium, at a given temperature.*



(a) Vaporization (b) Vaporization > condensation rate rate (c) Vaporization = condensation rate rate

Figure .11 Vapour pressure

Tidbit

Barometer is used to measure vapour pressure. Barometer consists of long glass tube. One end of the glass tube is closed, while the other is open. Hold a finger over the open end and invert the tube into a dish of mercury. When the finger is removed, the mercury level falls up to certain height "h". The force of gravity and the atmospheric pressure exerts pressure on the mercury in the container, air pressure pushing up. Therefore, it does not allow the mercury level fall down and keep it on certain height.

When these two forces balance each other, the mercury in the tube stops falling. The greater the air pressure, the higher the mercury stands in the tube above the level of mercury in the dish.

At sea level at 273.15 K temperature, the atmosphere can hold the mercury at a height of 760 mmHg or 76cm Hg. It is considered as *one atmospheric pressure.*

3. Boiling point

When the internal or vapour pressure of a liquid becomes equal t external pressure, the liquid boils. (By external pressure, we usually mea pressure of the atmosphere above the liquid.) The boiling temperature of a liquid remains constant as long as the external pressure does not vary *temperature at which the vapour pressure of a liquid becomes equal t atmospheric pressure or some other external pressure is called boiling point*

At the boiling point, kinetic energy of the molecules of liquid bec maximum. At this point, any further heating will not increase the tempera This heat will be used to break the intermolecular forces and convert the li into vapours. That is why the temperature of the liquid remains constant a boiling points. The boiling point is one of the most commonly used ph properties for characterizing and identifying substances. The boiling poi some liquids are given in the table 5.2.

Application of boiling point

Boiling point depends on the internal and external pressure. The ch of boiling point of a liquid with the external pressure has very impo application in chemistry as well as in our daily life.

Table 5.2 Boiling Points of Some compounds

S. No	Compound	Boiling point (°C)at 760mm Hg
1.	CS_2	46.30
2.	CCl_4	76.50
3.	C_2H_5OH	78.26
4.	C_6H_6	80.15
5.	H_2O	100
6.	CH_3COOH	118.50

a. Pressure Cooker (An Example of Increased Pressure)

Cooking in pressure cooker is based on the fact that increase in external pressure increases the boiling point of a liquid. At higher altitudes, atmospheric pressure is lower than normal (1atm) pressure. Thus, water boils at lower temperature at high altitudes where external pressure is lower. At these places, cooking takes more time. The boiling point of water can be raised in a pressure cooker.

Pressure cooker is a closed container, during heating the vapours formed are not allowed to escape from it. Therefore, they develop more pressure in the cooker and boiling point of water increases. As more heat is absorbed in water, therefore, food is cooked quickly under increased pressure.

Tidbit

Boling point of a liquid with stronger intermolecular forces will be higher than a liquid with weaker intermolecular forces at the same atmospheric pressure.

Table 5.3 Boiling of Point of Water at Different Places

Place	Pressure (atm)	Boiling point on Celsius Scale (°C)
Sea level	1	100
Murree Hills	0.921	98
Mount Everest	0.425	72

b. Vacuum distillation (an example of reduced pressure)

The distillation carried out under reduced pressure is called vacuum distillation. For example, at 1 atm Pressure,water boils at 100°C but if the pressure is reduced to 0.5 atm, water boils at only 82°C.

There are a number of high boiling point liquids, which cannot be purified by distillation at normal pressure i.e. 1 atm, because they decompose before their boiling points are reached. For example, the boiling point of glycerine is 290°C under normal atmospheric pressure. However, it decomposes at this temperature. Hence, glycerine cannot be distilled at 290°C. In order to get pure glycerine, the pressure is reduced; the boiling point of glycerine is reduced to 210°C at 50mm Hg. At reduced pressure, the glycerine is easily purified without breaking.

Thus, vacuum distillation has the following advantages. (a) It decreases the time for distillation, (b) It also avoids the thermal decomposition of many compounds.

4. Surface Tension

Molecules within a liquid are attracted in all directions by intermolecula forces. However, molecules at the surface are attracted downward and sideways by other molecules, but not from above, as shown in the figure 5.12.

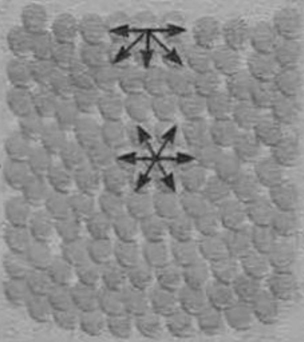
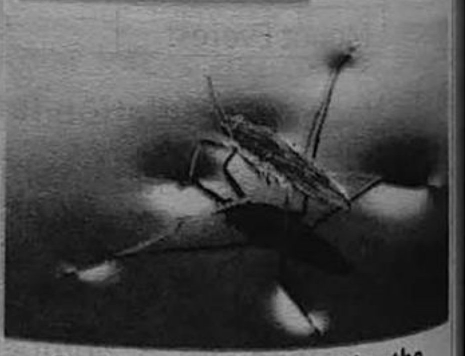


Figure5.12 Intermolecular forces acting on a molecule in the surface layer of a liquid and in the interior region of the liquid.

These intermolecular attractions, thus, tend to attract the molecules towards interior of liquid and cause the surface tightened like an elastic membrane due to net attraction inward, which creates surface tension.

Tidbit



Surface tension enables the water strider to "walk" on water.

The *surface tension* is *the amount of energy required to stretch or increase the surface of a liquid by a unit area.* It is measured in units of Nm^{-1} or Jm^{-2}. For a molecule to come to the surface, it must overcome the attractions directed towards interior of the liquid, it requires an input of energy and this energy is called liquid surface tension.

Surface tension of liquid depends on the intermolecular forces and temperature. Liquids that have strong intermolecular forces have high surface tension. Thus, because of hydrogen bonding, water has greater surface tension than most of other liquids. The surface tension of a liquid decreases with the increase in temperature. Because increase in kinetic energy of the molecules, decreases the effect of intermolecular forces of attraction.

Rain (water) drops have spherical shape due to surface tension. As the sphere has the least surface to volume ratio, which it acquires due to surface tension, other liquids also show the same tendency.

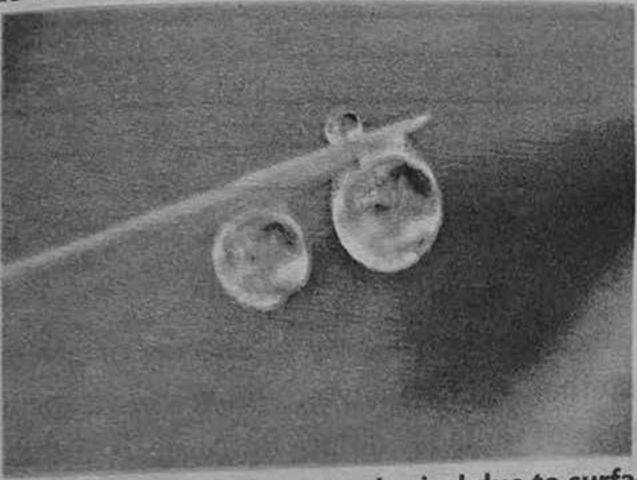


Figure 5.13 Rain (water) drops are spherical due to surface tension

Reduction in surface tension

When detergent is added into water (liquid), it reduces the surface tension of water by breaking up the hydrogen bonding. Detergents are the substances that reduce the intermolecular attractive forces between water molecules. These reductions of intermolecular forces increase the ability of water to wet a solid surface easily, thus, its cleaning action is increased. That is why detergents are used in laundry to wet fabrics easily and remove dirt particles.

5. Viscosity

Liquids have the ability to flow because molecules of the liquids can slide over each other. *The resistance of liquids to its flow is called viscosity.* In other words, viscosity of a liquid is a measure of its internal resistance to flow. Greater the viscosity, the more slowly the liquid will flow and vice versa. The viscosity of a liquid usually decreases as temperature increases; thus, hot honey flows much faster than cold honey.

Liquids that have strong intermolecular forces have higher viscosities than those that have weak intermolecular forces. The viscosity of water is higher than many other liquids because of hydrogen bonding in water molecules.

Consider the flow of the liquid in a tube as series of layers of liquid. The flow of liquid layers nearer to the sides of tube is less than the layers of liquid at the center of tube. The resistance to flow of a liquid is due to internal friction among the layers of molecules. Liquid layer, which flow near the walls of the tube, flow slowly or remains stationary. In the center of tube, the drag force decreases and flow increases as shown in the figure 5.14.

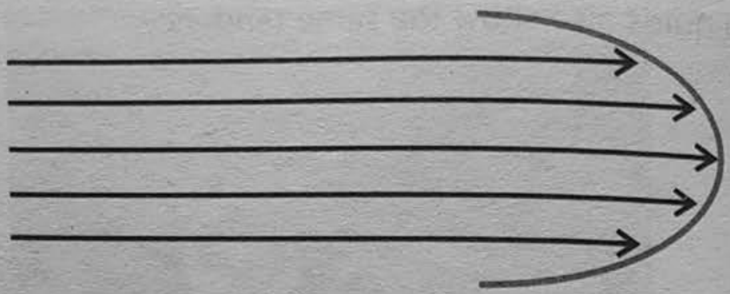


Figure 5.14 Viscosity of a Liquid

Liquids, which flow very slowly like honey or glycerine, have high viscositie as compared to ether and water, which have low viscosities.

Reading Check

Define and explain surface tension.

Viscosities of liquids differ from each other mainly due to molecular size, shape and intermolecular attractions. Furthermore, shapes of the molecules also contribute to the viscosity of the liquids, regular shape and small molecules flow easily and irregular, large molecules offer more resistance and contribute to its high viscosity.

Concept of Hydrogen Bonding to Explain Properties of Water

Many of the physical properties of water can be explained in terms o hydrogen bonding, e.g.

i. High Surface Tension

Surface tension of liquid depends on the intermolecular forces an temperature. In water, there occurs strong hydrogen bonding, so it has greate surface tension than most of other liquids. That is why surface of water acts lik stretched membrane. As a result of high surface tension, there is a tendency fo the surface area of water to be reduced as much as possible. This explains wh falling raindrops (water) are nearly spherical. (The sphere has the smallest surfac area for a given volume of any geometrical shape.)

ii. High Specific Heat

The amount of heat required to raise **the temperature of** *one gram o substance by 1°C (or 1 K) is the heat capacity* **of the substance**. Specific he capacity is usually expressed in units of J.g^{-1} °C^{-1}.

Water has a relatively high specific heat (about 4.2 J.g^{-1} °C^{-1}) due to stro hydrogen bonding. It is much higher than metals, as most metals have mu lower specific heats (usually less than 1 J.g^{-1} °C^{-1}). It takes almost ten times a much heat to raise the temperature of 1g of iron by 1°C. On the other hand, larg amount of heat is given off by water even a small drop in temperature occu

The water on the surface of earth acts like giant heat reservoir to moderate daily temperature variations.

iii. Low Vapour Pressure

The hydrogen bonding in water makes it difficult for the water molecules to escape into vapours. Therefore, the rate of conversion of water molecules into vapours is very low, so the vapour pressure of water is low.

iv. High Heat of Vaporization

Heat of vaporization is the heat required to change one gram of liquid to vapour at its boiling point.

High Heat of vaporization is the direct indication of the strong attraction between molecules in water. The strong attractive forces between the liquid molecules are due to hydrogen bonding. The hydrogen bonding in water molecules effectively gives the high heat of vaporization. As water is heated and energy is absorbed, hydrogen bonds are continually being broken until at 100°C, with the absorption of an additional 2.26 kJ/g, water separates into individual molecules, going into the gaseous state.

v. High Boiling Point

In water, there occurs stronger hydrogen bonding, so the vapour pressure of water is low. Water has high boiling point due to hydrogen bonding. Thus, the boiling point of water is 100°C at 1atm (760mm Hg).

It is clear from table 5.4, that boiling point is determined by the strength of hydrogen bonding. For example, methane (CH_4) and diethyl ether ($C_2H_5OC_2H_5$), has low boiling points due to weak intermolecular forces.

Both ethanol (C_2H_5OH) and water have strong hydrogen bonding, which accounts for their high boiling points.

Table 5.4 Boling Points of Some Compounds

Compounds	Boling point (°C) at 1 atm
Diethyl ether ($C_2H_5OC_2H_5$)	34.6
Ethyl Alcohol (C_2H_5OH)	78.3
Methane (CH_4)	-164
Water(H_2O)	100

vi. Anomalous Behaviour of Water

The maximum density of water is 1.000 g/cm^3 at 4°C. Water has the unusual property of contracting in volume as it is cooled to 4°C and then expanding when cooled from 4°C to 0°C. Therefore, 1 g of water occupies a volume greater than 1 cm^3 at all temperatures except 4°C. Although, most liquids contract in volume when temperature is decreased. However, a large increase (about 9%) in volume occurs when water changes from a liquid at 4°C to a solid (ice) at 0°C. The density of ice at 0°C is 0.917 g/ cm^3, which means that ice, being less dense than water, will float on the surface of water.

Self-Assessment

1. What are the different properties of liquids?
2. Explain the application of hydrogen bonding.
3. Use the concept of hydrogen bonding to explain the high surface tension,
4. high specific heat.
5. What is anomalous behaviour of water?

5.3 Energetics of Phase Changes

During physical and chemical changes, energy is evolved or absorbed; the change in energy at constant pressure, in a physical or chemical process is called enthalpy change. It is denoted as ΔH. It is expressed in kJ mol^{-1}. Three types of enthalpy changes are associated with physical changes at one atmospheric pressure.

The state of matter is often referred to as a *phase*. An ice cube floating in water makes up two phases of water, the solid phase (ice) and the liquid phase (water).

Any process of changing state (or phase) for a sample of matter is called a phase change. Phase changes, transformations from one phase to another, occur when energy (usually in the form of heat) is added or removed. When a solid changes to a liquid as a result of heating, the process is called melting or fusion. The process of changing a liquid to a gas is called evaporation or vaporization. A gas in contact with its liquid is often called a vapour state. Changing a solid directly into a gas is called sublimation. Changing a liquid to a solid is called freezing and changing a gas to a liquid is called condensation and to solid state directly is called deposition. These states and changes are summarized in figure 5.15.

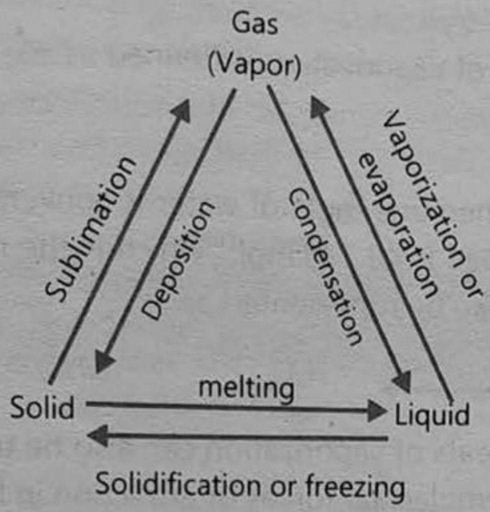


Figure 5.15 Phase Changes

As the temperature of the liquid increases, the particles move about more vigorously. The increased motion allows some particles to escape into the gas phase. As a result, the amount of vapours above the liquid surface increases with temperature. These gas-phase particles exert a pressure called vapour pressure. The vapour pressure increases with increasing temperature until it equals the external pressure or atmospheric pressure. At this point the liquid starts boiling and bubbles are formed within the liquid. The energy required to make the change of a given quantity of the liquid to the vapour state is called the heat of vaporization, ΔH_{vap}. For water, the heat of vaporization is 40.7 kJ.mol^{-1}.

$$H_2O_{(\ell)} \longrightarrow H_2O_{(g)} \qquad \Delta H_{vap} = 40.7 kJ.mol^{\ 1}$$

5.3.1 Molar Heat of Fusion, Molar Heat of Vaporization, Molar Heat of Sublimation

i. Molar Heat of Fusion (ΔH_{fus})

It is.defined as *the amount of heat absorbed when one mole of a solid substance is converted into the liquid state at its melting point.*

As an example, we can take the melting of 1 mole of ice at its melting point, 0°C or 273 K. The process can be represented as,

$$\underset{Ice}{H_2O_{(s)}} \longrightarrow \underset{Water}{H_2O_{(\ell)}} \qquad \Delta H_{fus} = +\ 6.02 kJ.mol^{-1}$$

It is accompanied by the absorption of 6.02 kJ.mol^{-1} of heat. From the values of heat of fusion of various substances, we can compare their magnitudes of intermolecular forces. Greater the heat of fusion of a substance, higher will be the magnitude of intermolecular forces.

ii. Molar Heat of Vaporization (ΔH_{vap})

The molar heat of vaporization is defined as *the amount of heat absorbed when one mole of a liquid is converted into vapour or gaseous state at its boiling point* (ΔH_{vap}).

For example, when one mole of water is converted into steam at 100°C or 373 K, the heat absorbed is 40.7 kJ.mol^{-1}, which is the molar heat of vaporization of water. The change can be represented as,

$$\underset{\text{water}}{H_2O_{(\ell)}} \longrightarrow \underset{\text{vapor}}{H_2O_{(g)}} \qquad \Delta H_{vap} = +\ 40.7\ \text{kJ.mol}^{-1}$$

The values of heats of vaporization can also be used for the comparison of the magnitude of intermolecular forces of attraction in liquids.

iii. Molar Heat of Sublimation (ΔH_{sub})

Heat of sublimation is defined as *the amount of heat absorbed when one mole of a solid is directly converted into the vapours or gaseous state at a constant value of pressure.*

For example, the heat of sublimation of iodine is 60.2 kJ.mol^{-1}. It can be represented as,

$$I_{2(s)} \longrightarrow I_{2(g)} \qquad \Delta H_{sub} = +\ 60.2\ \text{kJ.mol}^{-1}$$

The value of molar heats of sublimation can also be used for the comparison of magnitude of intermolecular forces.

5.3.2 Energy Changes and Intermolecular Attractions

When a liquid is heated, its temperature goes on increasing until its boiling point is reached. At boiling point, the temperature becomes constant. Now the heat supplied is used to convert the liquid into vapours by breaking intermolecular forces.

When a solid melts, small change occurs such as intermolecular distance changes and changes in potential energy of atoms, ions or molecules take place. However, when the liquid is converted into vapours (gaseous state), atoms, ions or molecules undergo large changes in their intermolecular distance and potential energy. Therefore, the heat of vaporization is much greater than heat of fusion.

It also depends on the nature of substance. Such as polar molecules have stronger intermolecular forces, thus large energy is required to change their physical state from solid to liquid or liquid to vapours or solid to vapours directly.

Hence, polar substances have higher values of ΔH_{vap}, ΔH_{sub} *e.g.* H_2O, and NH_3 etc, are polar substances and have considerably higher values of ΔH_{vap}. Thus, ΔH_{vap} is actually a measure of the strength of intermolecular forces.

Molar heat of fusion and molar heat of vaporization of some compounds are given below in the table 5.5.

Table 5.5 Molar Heat of Fusion and Molar Heat of Vaporization of Some Compounds

S. No	Substance	Molar heat of fusion $kJ.mol^{-1}$	molar heat of vaporization $kJ.mol^{-1}$
1.	H_2O	6.02	40.7
2.	NH_3	5.65	23.35

It clearly indicates that the values of molar heat of vaporization are higher than the molar heat of fusion. Beside this, the values of molar heat of vaporization of halogens are given below in the table 5.6.

Table 5.6 Molar Heat of Vaporization of Halogens

S. No	Compound	Molar heat of vaporization $kJ.mol^{-1}$
1.	I_2	20.27
2.	Br_2	15.43
3.	Cl_2	10.21
4.	F_2	3.26

It is evident from ΔH_{vap} of iodine, which is highest due to strong intermolecular forces, than the other halogens.

Non-polar molecules have weaker intermolecular forces, thus, their physical state can easily be changed. Hence, non polar substances have lower values of ΔH_{fus}, ΔH_{vap}, ΔH_{sub}.

5.3.3 Change of State and Dynamic Equilibrium

The physical or chemical processes in which both forward and reverse processes can occur are called reversible processes. The state of reversible process at which rate of forward change becomes equal to the rate of backward change is called equilibrium state. Since both changes are occurring simultaneously at equal rate, therefore, this equilibrium is called dynamic equilibrium.

When rates of two opposite changes are equal such as solid to liquid or liquid to solid, we say the system has reached a dynamic equilibrium. For example, at 0°C solid ice exists in dynamic equilibrium with liquid water.

$$\underset{ice}{H_2O_{(s)}} \xrightleftharpoons{0^{\circ}C} \underset{water}{H_2O_{(l)}}$$

5.4 Liquid Crystals

W. Heintz reported in 1850 that stearin melted from true solid to turbid liquid at 52°C. It changed to an opaque liquid at 58°C and became a clear and true liquid at 62.5°C. It means that stearin from 52.1°C to 62.6°C behaves like a liquid crystal. In 1888, an Austrian botanist Friedrich Reinitzer also reported an organic compound 'Cholesteryl Benzoate' as a liquid crystal substance. He observed that when cholesteryl benzoate was melted, it first became a cloudy liquid at 145°C and then cleared up as its temperature rose to 179 °C. Upon cooling, the liquid turned blue before finally crystallizing. This experiment showed the intermediate properties between those of liquid and solid that liquid crystal possessed.

The semisolid substances, which have properties in between the true solids (crystalline solids) and true liquids (clear liquids), are called liquid crystals.

5.4.1 Brief Description

Liquid crystals are organic materials, which have an additional state of matter between the liquid state and the solid state. When a solid is melted, it is converted to liquid. However, many organic solids do not melt to give the liquid substance directly. They, instead, pass through an intermediate turbid liquid state called the liquid crystal state, before finally converting into clear liquid. Thus, the liquid crystal state is intermediate between the liquid state and the solid state.

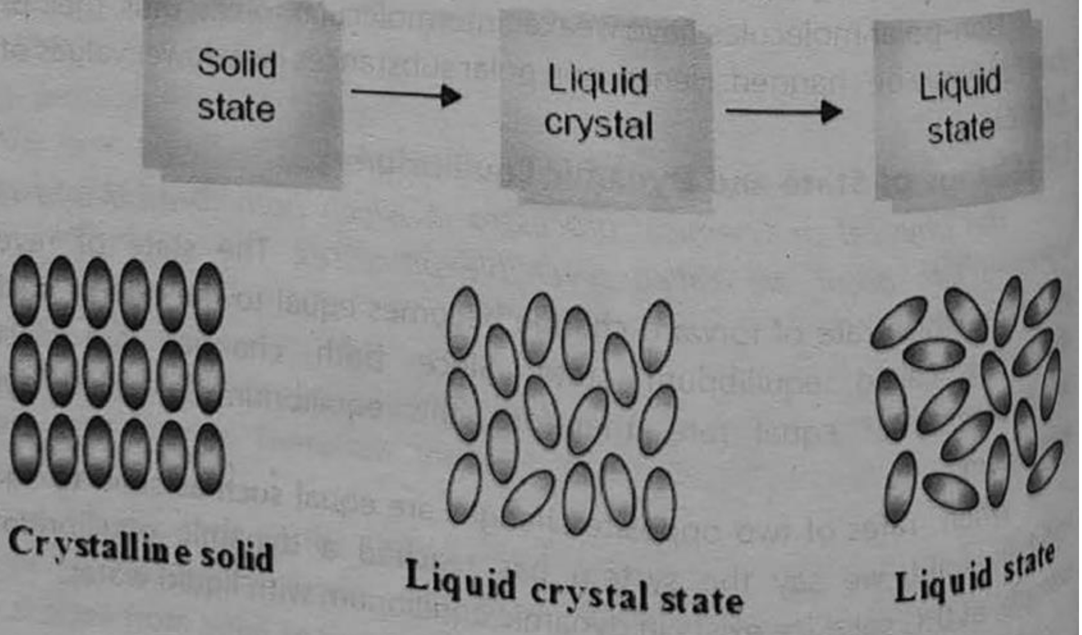


Figure 5.16 Liquid crystals

These are either semi-solids or turbid liquids. They show the optical properties like crystalline solids and surface tension or viscosity like liquids.

In a liquid, the molecules have a random arrangement and they are able to move. In a solid crystal, the molecules have an ordered arrangement and are in fixed positions. In liquid crystals, however, molecules are arranged parallel to each other and can flow like a liquid. Thus, the liquid crystals have the fluidity of liquid and optical properties of solid crystals.

Science, Technology and Society

Liquid crystals are used in a number of objects including liquid crystal display (LCD). A liquid crystal display is a flat panel display. Liquid crystal displays have replaced the old-fashioned heavy, bulky cathode ray tube (CRT) displays in nearly all appliances. Today LCD screens are available in a wider range of screen sizes than CRT. LCD screens are available in sizes ranging from small digital wrist watches to very large television displays.

Today liquid crystals objects are used in wide applications, including televisions, computer monitors, wrist watches, calculators, instrument panels, aircraft cockpit displays, thermometers. It is used in a number of medical instruments which are used for diagnoses of patients such as ultrasound, endoscopy etc. It is also used for indoor and outdoor signage.

Properties of Liquid Crystals

Some properties of liquid crystals are,

i. They have some degree of order like crystalline solids.
ii. They have fluidity like liquids.
iii. They have properties such as surface tension, viscosity etc like liquids.
iv. They have optical properties like crystalline solids.

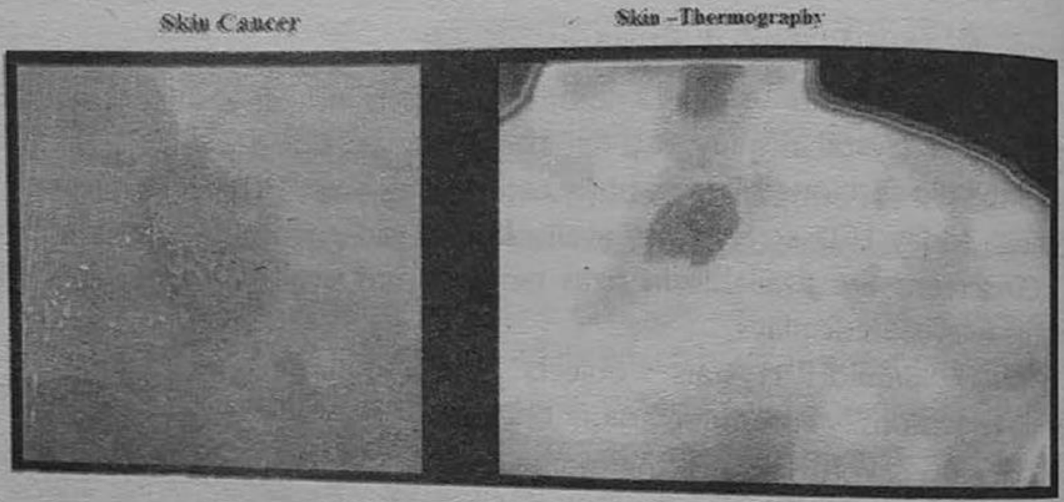
5.4.2 Uses from Daily Life

Earlier the liquid crystals were limited to laboratories but in modern days liquid crystals have many useful practical applications in daily life. Liquid crystals are temperature sensors and have many other useful applications, so they are used:

1. In medical instruments such as clinical thermometers.
2. To find the point of potential failure in electrical circuits.

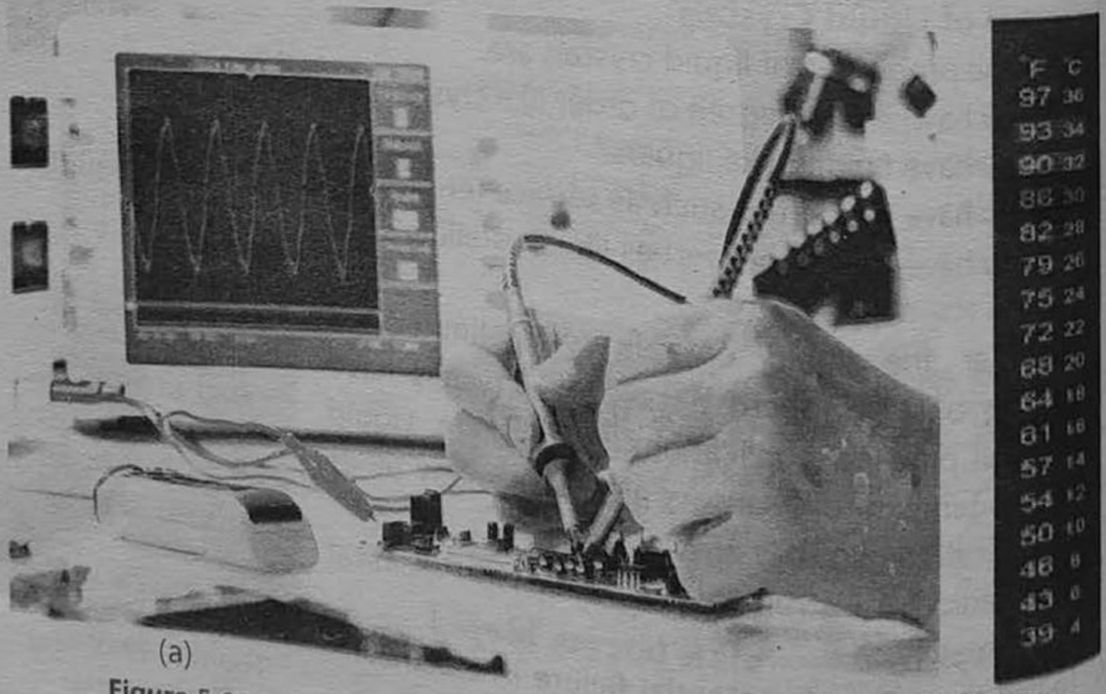
Figure 5.17Clinical Thermometer

3. To find the blockage in veins and arties by skin –thermography.
4. For display in calculators, digital watches, computers, cell phones, stop watches, room thermometers, etc.
5. For screen (LCD= liquid crystal display) in TV and Oscilloscope. (Oscilloscope: a instrument for indicating and recording time-varying electrical quantities, such as current and voltage).
6. As a solvent in liquid-solid chromatography.


Skin Cancer

Skin –Thermography

Figure 5.18 Skin –Thermography



(a)

(b)

Figure 5.19 (a) Oscilloscope (b) LCD Room thermometer without mercury

Self-Assessment

1. Define dynamic equilibrium between two physical states.
2. Define liquid crystals.
3. Differentiate liquid crystals from pure liquids and crystalline solids.
4. What is energetics of phase change?
5. Briefly explain the uses of liquid crystals in daily life.

KEY POINTS

- Liquid has definite volume but no definite shape.
- The attractive forces within a molecule are called intra-molecular forces. These are covalent bond, co-ordinate bond, etc.
- The attractive forces among the molecules are called intermolecular forces. These are hydrogen bond, dipole – dipole interactions and London dispersion forces. Collectively these three weak forces are named as Van der Waals forces.
- Dipole – dipole forces is the attractive forces between the positive pole of one polar molecule and negative pole of other polar molecule.
- Hydrogen bonding is a linkage formed between two molecules in such a way that partially positively charged hydrogen atom of one molecule is attracted to the lone pair of an electronegative atom of the other molecule.
- London forces (also called dispersion forces) are the weak attractive forces between molecules resulting from the small, instantaneous dipoles that occur because of the varying positions of the electrons during their motion about nuclei.
- Evaporation is the spontaneous change of a liquid into its vapours at any temperature.
- The pressure exerted by the vapours of the liquid when the rate of vaporization becomes equal to rate of condensation is vapour pressure.
- Barometer and manometer are used to measure vapour pressure of a liquid.
- Boiling point is the temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure or some other external pressure.
- Boiling point of a liquid is less at hilly areas like Murree.

- Cooking in pressure cooker is based on the fact that increase in extern pressure increases the boiling point of a liquid.
- Vacuum distillation is the distillation that is carried out under reduce pressure.
- The surface tension is the amount of energy required to stretch or increase the surface of a liquid by a unit area.
- Detergents reduce the surface tension of water by breaking the hydrogen bonding.
- Viscosity is the resistance of liquids to its flow. The S.I unit of viscosity is $kgm^{-1}s^{-1}$ (1poise = $10^{-1}kgm^{-1}s^{-1}$).
- The amount of energy required to raise the temperature of one gram of a substance by 1°C (or 1 K) is the specific heat capacity of the substance.
- Heat of vaporization is the heat required to change a liquid to vapour at its boiling point.
- The states of matter are often referred to as a phases.
- Phase change is any process of changing state (or phase) for a sample of matter.
- The amount of heat absorbed when one mole of a solid substance is converted into the liquid state at its melting point is molar heat of fusion.
- Sublimation is a process when a solid changes directly into gaseous state without changing into liquid state.
- Liquid crystals are the semisolid substances, which have properties in between the true solids (crystalline solids) and true liquids (clear liquids).

EXERCISE

Choose the Correct Option.

1. Forces of attraction which may be present between atoms of molecules are
   a. Intramolecular b. Intermolecular
   c. Van der Waal d. Dipole-induced dipole
2. When water freezes at 0°C its density decreases due to
   a. Change of bond angles
   b. Decrease in volume
   c. Empty space present in the structure of ice
   d. Change of bond length
3. London dispersion forces are only forces present among which of the following?
   a. Polar molecules of water at room temperature
   b. Molecules of HF at room temperature
   c. Molecules of solid iodine at room temperature
   d. Molecules of hydrogen chloride gas at room temperature
4. Molar heat of vaporization of water is
   a. 40.7 kJ/mole b. 40.7 J/mole c. 40.7 cal/mole d. 40.7 kcal/mole
5. The S. I unit of viscosity is
   a. $kgm^{-1}s$ b. $kgm.s^{-1}$ c. kgm.s d. $kg\,m^{-1}s^{-1}$
6. Liquid gets the shape of the container when it is poured into it. Which one of the following reasons justifies it?
   a. Liquid is incompressible
   b. Liquid does not has definite volume
   c. Liquid is highly compressible
   d. Liquid molecules can slide over each other
7. Hydrogen bonding is not involved in
   a. DNA structure b. The liquid properties of water
   c. Liquid HF d. Liquid CH_4
8. Which one is incorrect for evaporation
   a. Surface phenomenon b. Continuous process
   c. Exothermic process d. Causes cooling
9. Exceptionally low acidic strength of HF is due to
   a. strong polar bond b. small size of fluorine
   c. strong hydrogen bonding d. Van der Waals forces

10. Distillation under very reduced pressure is
    a. Vacuum distillation b. Steam distillation
    c. Destructive Distillation d. Fractional distillation
11. Which one of the following is more temperature sensitive
    a. Ionic crystals b. Solid crystals
    c. Liquid crystals d. Molecular crystals
12. Which of the following has weakest London dispersion forces
    a. F_2 b. Cl_2 c. Br_2 d. I_2
13. What is the boiling point of water at a mountain,
    a. It is 100°C
    b. It is $<$ 100°C, since the atmospheric pressure is greater
    c. It is $>$ 100°C, since the atmospheric pressure is greater
    d. It is $<$ 100°C, since the atmospheric pressure is less.

Short Questions

Give at least two of the effects on our lives if water had weak hydro bonding among its molecules.

2. Give the reason that why HF is a liquid at ordinary temperature while HCl i gas.
3. Why H_2O has high boiling point than HF, although fluorine is m electronegative than oxygen.
4. How would you justify that water and ethanol can mix easily in all proportio
5. How can you explain that neon and argon both are mono-atomic no gases of the same group, neon has boiling of -248°C, while argon has -189
6. How would you justify that different liquids have different rates evaporation even at the same temperature.
7. Justify the statement that earthenware vessels keep water cool even in summer days.
8. How vacuum distillation can be used to avoid decomposition of sensit liquids?
9. Why evaporation of a liquid causes cooling?
10. Explain that why a liquid boils at different temperature at sea level and mountains.
11. Why water droplet is spherical?
12. Temperature of a liquid remains constant during boiling although heat being supplied continuously, why?

Descriptive Questions

1. (a) Briefly explain the properties of liquids (i) Diffusion, (ii) Compression, (iii) Expansion, (iv) Motion of Molecules, (v) Intermolecular Forces on the basis of Kinetic Molecular Theory.

   (b) What is anomalous behaviour of water when its density shows maximum at 4°C?

   (c) Wet clothes dry more quickly on a hot, dry day than on a hot, humid day. Explain.

2. (a) Define and explain these terms along with their units: (i) Molar Heat of Vaporization, (ii) Molar heat of Fusion, (iii) Molar Heat of Sublimation.

   (b) Explain the origin of the London Force that exists between molecules.

3. (a) Define boiling point and how does the boiling point of a liquid dependent on the external atmospheric pressure?

   (b) Briefly explain physical properties of water with special reference to (i) Evaporation (ii) Vapour Pressure (iii) Boiling Point (iv) Viscosity (v) Surface Tension

   (c) Why does the vapour pressure of a liquid depend on the intermolecular forces?

4. (a)What is the relationship between the intermolecular forces that exist in a liquid and its surface tension?

   (b) What do you know about dipole – dipole interactions?

5. (a) Differentiate liquid crystals from pure liquids and crystalline solids? Also give some uses of liquid crystals in daily life.

   (b) Define phase change. Name all possible changes that can occur among the vapour, liquid and solid states of a substance.

Project

- Develop a set of criteria that will allow you to classify the following substances on the basis of intermolecular force i.e. Dipole – dipole forces, Hydrogen bonding and London dispersion forces: Water, Milk, Honey, Methylated Sprit, Glycerine ($C_3H_8O_3$), Carbon Tetrachloride (CCl_4), Acetone (CH_3COCH_3), Chloroform ($CHCl_3$), Benzene (C_6H_6), Kerosene oil, Ammonia (NH_3), Hydrochloric Acid (HCl) and Methane (CH_4). Present it in the classroom and give reason of your criteria of classification based on their molecular structures.
- Classify the above given substances on the basis of more volatile, less volatile and non-volatile at the same temperature based upon intermolecular forces, with suitable reason.

Unit - 06

States of Matter III: Solids

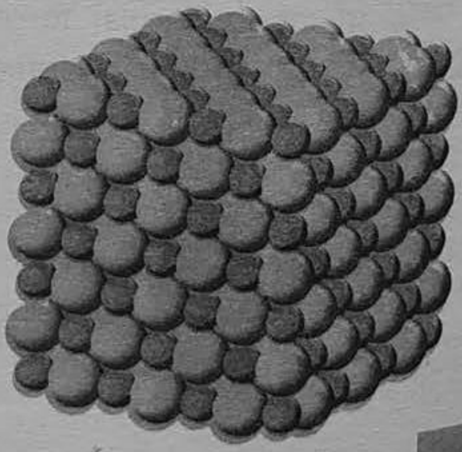
After reading this unit, the students will be able to:

- Describe simple properties of solids e.g., diffusion, compression, exp motion of molecules, spaces between them, intermolecular forces and energy based on kinetic molecular theory. (Understanding)
- Differentiate between amorphous and crystalline solids. (Understanding)
- Describe properties of crystalline solids like geometrical shape, melting cleavage planes, habit of a crystal, crystal growth, anisotropy, sym isomorphism, polymorphism, allotropy and transition temperature. (Understa
- Use oxygen and sulphur to define allotropes. (Understanding)
- Explain the significance of the unit cell to the shape of the crystal using NaC example. (Applying)
- Name three types of packing arrangements and draw or construct mo them.(Applying)
- Name three factors that affect the shape of an ionic crystal. (Understanding)
- Define lattice energy. (Remembering)
- Differentiate between ionic, covalent, molecular and metallic crystallin solids. (Applying)
- Explain the low density and high heat of fusion of ice. (Understanding)
- Define and explain molecular and metallic solids. (Understanding)

Teaching
10

Assessment
01

Weightage %
07



Introduction

Solid is one of the physical states of matter, other being the gas, the liquid and the plasma states. The solid state of matter is characterized by its rigidity, hardness, definite shape, definite volume and mechanical strength. The forces of attraction between its structural units (atoms, ions, molecules) are quite strong and, therefore, they cannot move at random (as in the case of gases and liquids). Consequently, these units remain fixed to mean position to about which they vibrate and make solids rigid and have definite shape.

After studying this unit, you will be able to differentiate between amorphous and crystalline solids, describe the classification and properties of crystalline solids, crystal lattice and lattice energy.

Tidbit

The particles in the solid are separated by a distance of only a few Pico meters (1pm = 1×10^{-12}m)

6.1 Kinetic molecular interpretation of solids

The Kinetic Molecular Interpretation of solids is as follows.

i. Solids are composed of closely packed particles.

ii. The particles of the solids are firmly held together by strong forces of attraction.

iii. Solids are rigid in nature as the particles of solids are held in fixed positions and cannot move freely. They can only vibrate about a mean position.

iv. In solids, particles are more ordered than liquids and gases.

v. The particles in solids are arranged in regular configurations in three dimensions. Therefore, they adopt the definite geometrical shape called a lattice.

vi. There is less empty space between particles in a solid than in a liquid.

vii. Solids are almost incompressible and possess definite shape and volume.

viii. As solids particles are closely packed, so they occupy minimum volume. The density is inversely proportional to volume; therefore, solids have high density.

ix. In solids, the particles vibrate about a mean position, so there is no collision among the solid particles.

x. The kinetic energy of the solids particles is due to vibration of particles, as there are no rotational and translational kinetic energy in solid particles.

6.1.1 Simple Properties of Solids Describing Vibration of Molecules, Intermolecular Forces, Kinetic Energy

i. Diffusion

Solid particles do not diffuse readily into other solids. However, analysis of two blocks of different solids, such as copper and lead, which have been pressed together for a period of years show that each block, contains some atoms of the other element. This demonstrates that solids do diffuse, but very slowly as shown in figure 6.1. The rate of diffusion is millions of times slower in solids than in liquids. The diffusion depends upon movement and velocity of particles. As in solids, the movement of the particles is very slow; therefore, the diffusion occurs to very small extent in very large time.

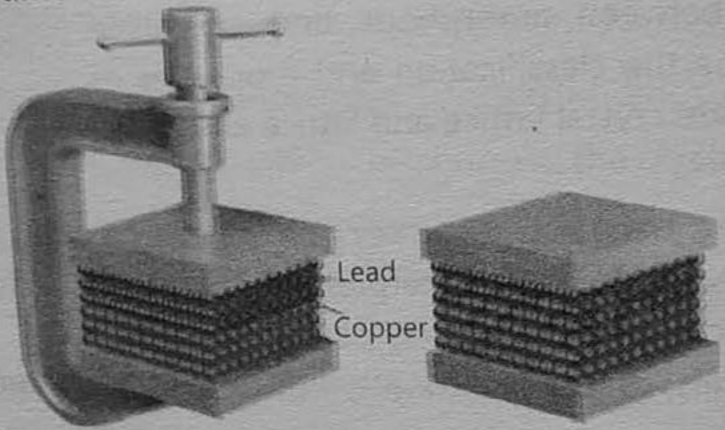


Figure 6.1: A Representation of Diffusion in Solids

ii. Compression (Effect of pressure)

Solids are generally less compressible than liquids. For practical purposes solids can be considered incompressible. Some solids, such as wood and cork may *seem* compressible, but they are not. They contain pores that are filled with air. When subjected to intense pressure, the pores are compressed, not the solid matter in the wood or cork itself.

iii. Expansion (Effect of Temperature)

The solids expand when temperature increases (heated) i.e. their volume increases. This is because the increase of temperature decreases the intermolecular attractive forces. As a result, the spaces between the molecules increase hence volume increases.

The expansions of solids are expressed in terms of co-efficient of expansion (α). It is defined as *the increase per unit volume when the temperatu is increase by 1°C*. When a solid is heated, its geometric shape changes until at certain temperature, it melts and changes into the liquid state. The temperature at which a solid changes into the liquid state is called melting point of the solids.

iv. Motion of Particles

In crystalline solids, the particles are strongly held with one another. The particles do not move freely as in liquid and in gases. There is no translational and rotational motion due to presence of strong intermolecular forces in the crystalline solid. The particles in the crystalline solids are closely packed together. However, the particles can vibrate about their mean positions and thus transfer the energy from one particle to another.

v. Spaces between Crystals

In crystalline solids, the particles are closely packed together, so there is less space between the particles. The intermolecular forces are maximum in between the particles. These maximum intermolecular forces and less space between the particles make them incompressible.

vi. Intermolecular Forces

In solids, there occur a number of intermolecular forces. These intermolecular forces are maximum in between the solid particles. These intermolecular forces held the solid particles together in fixed positions. They can vibrate only about their fixed positions and cannot move freely as in liquids and gases.

vii. Kinetic Energy Based on Kinetic Molecular Theory

According to kinetic molecular theory, the attractive forces between the solid particles are maximum. As the distance between the particles is minimum and attractive forces are maximum, therefore, particles of solids do not move from their fixed position. However, they can vibrate about their mean positions. Therefore, they possess only vibrational kinetic energy.

Reading Check

1. Define solid and kinetically interpret the solids.
2. What are the different properties of solids?

6.2 Types of Solids

Solids can be classified into two types on the basis of arrangement of constituent particles (atoms, ions or molecules).

- Amorphous solids
- Crystalline solids (True solids)

6.2.1 Amorphous Solids

Those solids in which particles are not arranged in three dimensional regular pattern are called amorphous solids. (Amorphous Greek word meaning 'without shape or geometry', 'no form or glassy'). An amorphous solid has atoms, molecules or ions arranged almost at random. It has disordered structure and lacks the well-defined regular arrangement of basic units (atoms, molecules, or ions) found in a crystal.

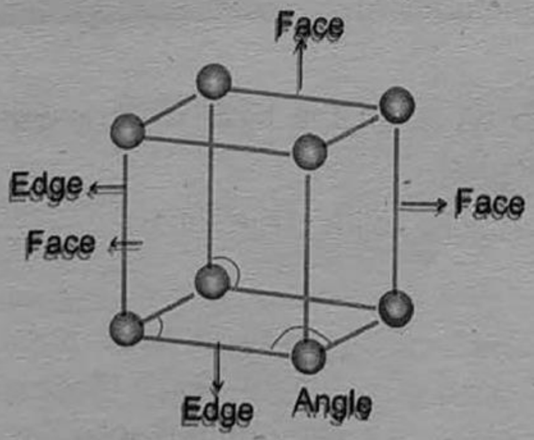
Large classes of materials with highly variable mechanical and optical properties that solidify from the molten state without crystallization are called amorphous solids. It is typically made by silicates fusing with boric oxide, aluminum oxide or phosphorus pentoxide. It is generally hard, brittle, transparent or translucent and is considered to be super cooled liquid rather than true solids.

Unlike crystalline solids, amorphous solids do not have sharp melting points. It means, they melt gradually over a long range of temperatures. Also they do not have any characteristic heat of fusion. Because of their disorderly arrangement of particles, they behave like liquids. They are, therefore, sometimes called super cooled liquids. Examples are rubber, plastics, gemstone, coal tar, glass etc. Thus, glasses are to be regarded as super-cooled or highly viscous liquids.

Amorphous solids have been used in electronic devices, including solar cells, photocopiers, laser printers and flat panel displays for computer monitors and television screens.

6.2.2 Crystalline Solids (True solids)

Solids in which particles are arranged in a regular three-dimensional order are called crystalline solids. In crystalline solids, the structural unit is arranged in an orderly manner, which repeats itself in three dimensions. Hence, they have rigid and definite geometrical shapes. A crystalline solid exists as small crystals, each crystal having a characteristic geometrical shape. They are also called true solids. Most of the solids are crystalline in nature. Examples of such solids are diamond, graphite, sodium chloride (NaCl), calcium carbonate ($CaCO_3.xH_2O$), copper sulpahte ($CuSO_4.5H_2O$) etc.



Tidbit

Crystal: Crystals are solid objects with a definite geometrical shape in which particles (atoms, molecules or ions) have a regular and repetitive three-dimensional arrangement.

Figure 6.2 Faces, interfaced angle and edges of a typical solid

6.3 Properties of Crystalline solids

Crystalline solids have a number of general properties, which distinguish them from amorphous solids. Some important properties of crystalline solids are,

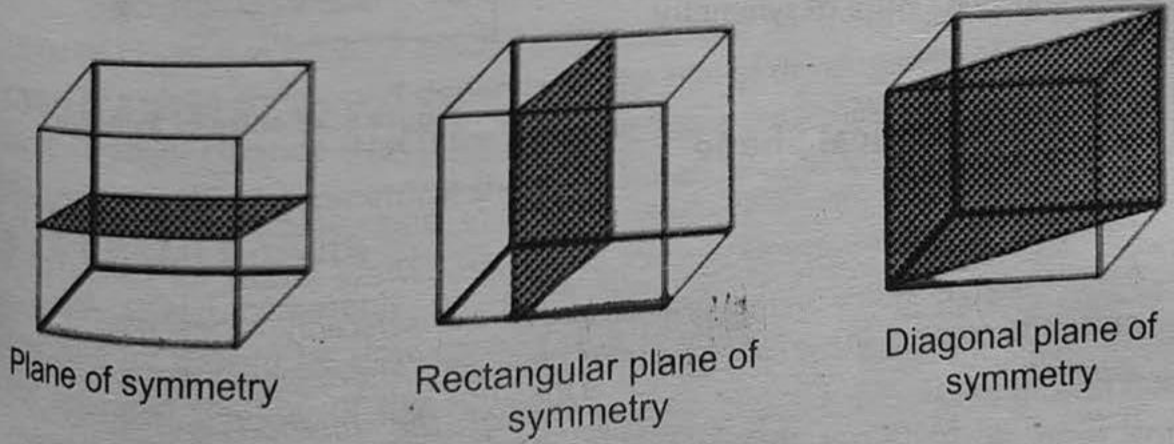
6.3.1 Symmetry

Symmetry is the consistency or the repetition of something. A crystal possesses a number of surfaces, known as faces, edges and interfacial angles. Symmetry in crystals may be due to a plane, a line or a point. This repetition is called symmetry.

There are three types of symmetry elements associated with a crystal.

a. Plane of Symmetry

When a crystal is divided by an imaginary plane into two equal parts, each of which is the exact mirror image of the other than this plane is called plane of symmetry.


Plane of symmetry

Rectangular plane of symmetry

Diagonal plane of symmetry

Figure 6.3 Plane of Symmetry

b. Axis of Symmetry

An axis of symmetry is an imaginary line drawn through the crystal such that rotating the crystal through 360°; the crystal presents exactly the same appearance more than once. If similar view appears twice, it is called an axis of two-fold symmetry or **diad axis.** If it appears thrice, it is an axis of three-fold symmetry or **triad axis,** and so on.

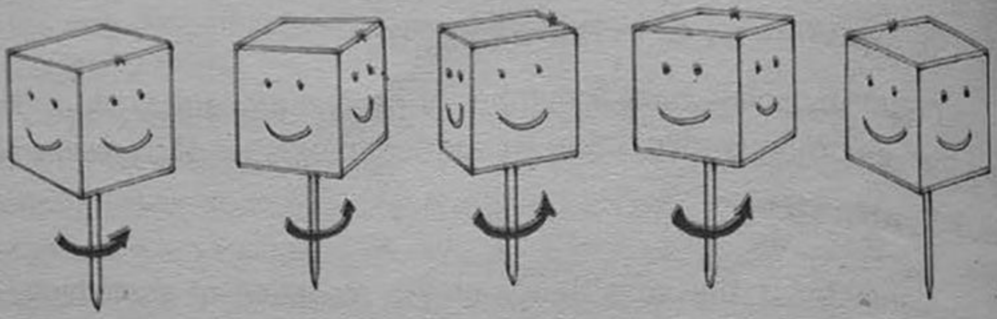


Figure 6.4 Axis of Symmetry

c. Centre of Symmetry

It is a point at the centre of the crystal so that any line drawn through i will meet the surface of the crystal at equal distances on either side.

Or It is a point at the centre of the crystal which is equidistant from opposite faces of a crystal.

It must be noted that a crystal may have a number of planes of symmetry or axis of symmetry but it can have only one centre of symmetry.

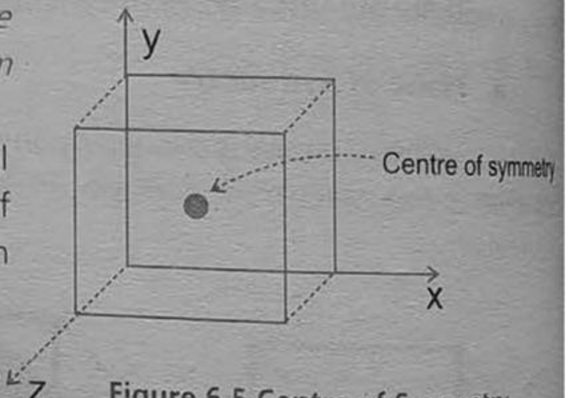


Figure 6.5 Centre of Symmetry

6.3.2 Geometrical Shape

Almost all the solids have a definite and orderly arrangement of the constituent particles (atoms, ions or molecules). These atoms, ions and molecules have fixed positions. They cannot move considerably. They give it definite geometry (shape).The arrangement of faces and interfacial angles are always the same for a given crystal, irrespective of the method and conditions o preparation. Moreover, the solids due to orderly arrangement of atoms, ions or molecules adopt the three-dimensional structure space e.g. NaCl is cubic in nature. Upon grinding to a very fine powder, the crystalline solids still retain their specific geometrical shapes.

6.3.3 Melting Point

Crystals being pure solids, have sharp melting points. As the crystal i solids are orderly arranged so when a solid is heated, the atoms, ions o molecules present in a solid start vibrating and transfer their kinetic ener throughout the solid. At the melting point, their vibrational energies become so much that they leave their fixed positions simultaneously and become a liquid

The temperature remain constant (even if heat is continuously being given), until all the particles become mobile

6.3.4 Cleavage Plane

When crystals break, they split along straight faces called cleavage planes, which are weak due to the atomic structure of the crystal.

Cleavage is the tendency of crystals to break along one or more sets of parallel plane. A crystal contains atoms, ions or molecules, which are closely packed to each other. When an external force (pressure) is applied to it, it breaks or splits into small crystals of the same shape as that of the original one.

Two adjacent cleavage planes intersect always at a definite angle. The magnitude of the interfacial angle, after cleavage has taken place, may differ from solid to solid and is a characteristic of a given solid.

6.3.5 Habit of Crystal

Habit refers to the way a *crystal* looks when it is found in its natural state. *The external shape is called the habit of the crystal.* In other words, *the shape of a crystal in which it usually grows is called habit of crystal.* The habit of a crystal of a given compound depends on the rate of development of the different faces. Sodium chloride (NaCl) for example, has a cubic habit. It means NaCl will always have cubical geometrical shape whenever its crystals are formed.

6.3.6 Crystal Growth

A crystal commonly grows in the typical shape. Crystal are usually prepared (or grown) by slow cooling of a substance in liquid state or cooling a hot saturated solution of the substance concerned. The apparent shape of the crystal depends on the method and conditions of preparation. Slow growth from a slightly super-saturated solution or a very slowly cooling solution gives large crystals. Different crystals of the same substance may not look alike. In the presence of certain impurities, different faces grow at different rates and give rise to many forms. For example, if sodium chloride is crystallized from its supersaturated solution, it forms cubic crystals. However, if 10% urea is present as impurity in its solution, it gives needle like crystals. As already stated, the external appearance or size of crystals of a substance may be different. It depends upon the conditions under which it is prepared. However, the interfacial angles are always the same. This is illustrated diagrammatically in figure 6.6.

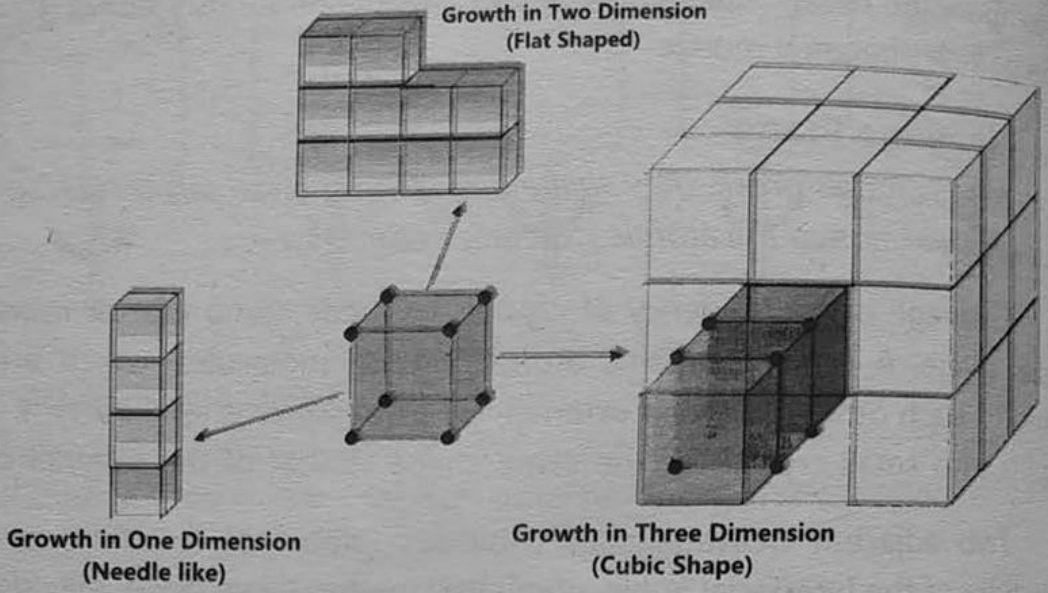


Figure 6.6 Crystal Growth in Different Shapes

For example, sodium chloride (NaCl) with cubic crystal habit may grow into a cubic (three-dimensional), a flat shaped (two dimensional) or a long needle like structure (one – dimensional) depending upon the conditions under which it is crystalized.

6.3.7 Anisotropy

The property of substance, which shows different intensities (magnitude) of physical properties in different directions, is called anisotropy. The substances, which show this property, are called *anisotropics* and such properties are called anisotropic properties.

Crystalline substances are anisotropic and the magnitude of a physical property varies with directions, because of regular and well-ordered arrangement of the constituent particles. For example, in a crystal of silver iodide, the coefficient of thermal expansion is positive in one direction and negative in the other. Similarly, electrical conductivity of graphite is greater in one direction than in another. Actually, electrons in graphite are mobile for electrical conduction parallel to the layers

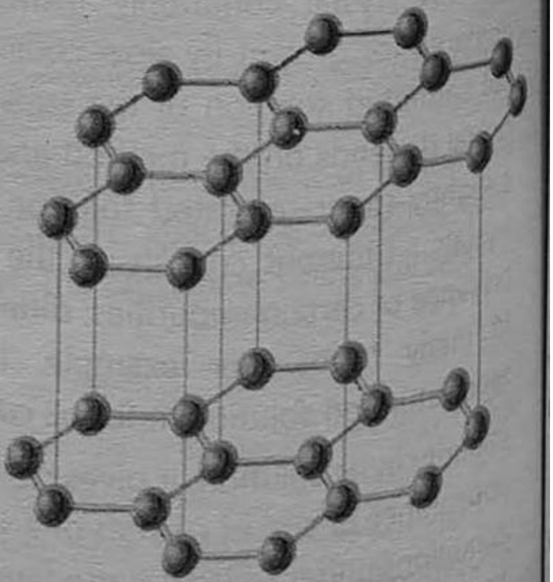


Figure 6.7 Structure of Graphite

only. Therefore, its conductivity in this direction is far better than perpendicular to the layers. Similarly, cleavage itself as an anisotropic behaviour.

6.3.8 Isomorphism

There are certain substances, which are similar in shape. Two or more different crystalline substances having the same crystalline shapes are called isomorphs of each other, and this phenomenon is called isomorphism.

The formula units of different isomorphs have usually the same atomic ratio. The example of some isomorphs is given in the table 6.1.

Table 6.1 Examples of Isomorphous Compounds

Isomorphs	Atomic ratio	Crystalline form
NaF and MgO	1:1	Cubic
KNO_3 and $NaNO_3$	1:1:3	Rhombohedral
ZnO and CdS	1:1	Hexagonal

It is to be noted that the physical and chemical properties of isomorphs are quite different from each other as they are totally different compounds of different nature.

6.3.9 Polymorphism

The occurrence of the same crystalline substance in more than one crystalline forms under different conditions is known as Polymorphism.

The substance showing polymorphism is said to be polymorphic and the different crystalline forms are called polymorphs of each other. Polymorphs have the same chemical properties but different physical properties due to different arrangement of particles in their structure. Examples of polymorphs are given in table 6.2.

Table 6.2 Examples of Polymorphic forms

Substance	Crystalline Forms
$AgNO_3$	Rhombohedral and Orthorhombic
$CaCO_3$	Trigonal and Orthorhombic
KNO_3	Rhombohedral and Orthorhombic

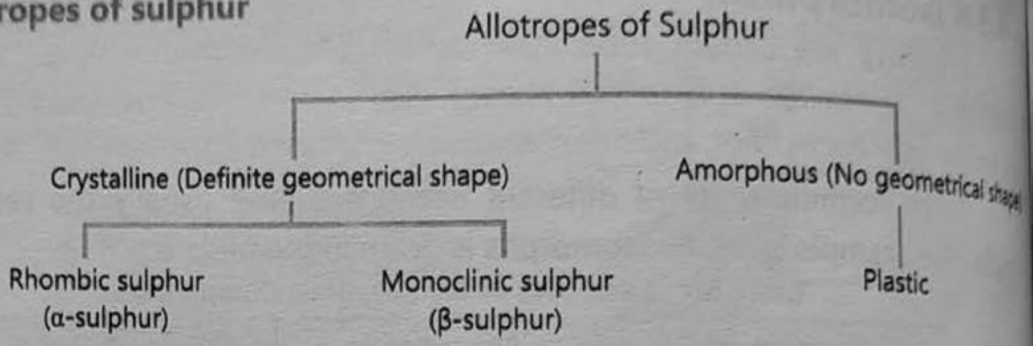
The different crystalline forms are inter-convertible into each other under different conditions of temperature.

6.3.10 Allotropy

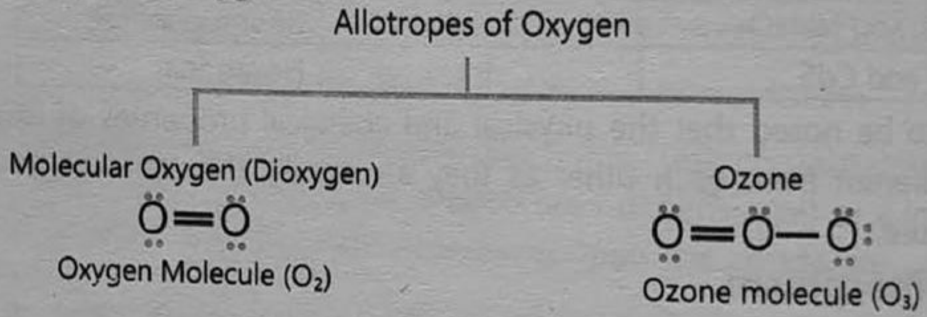
The occurrence of an element in different forms is called allotropy. These various physical forms are called allotropes or allotropic forms. For example, sulphur is found in orthorhombic and monoclinic form and plastic (amorphous) forms and

Oxygen occurs in the form of oxygen (dioxygen, O_2) and ozone (O_3). The allotrope sulphur and oxygen are discussed in detail.

Allotropes of sulphur



Allotropes of oxygen



$$3O_2 \xrightarrow{\text{UV light}} 2O_3$$

Figure 6.8 Allotropic of Sulphur and Oxygen

6.3.11 Transition Temperature

The temperature at which one crystalline form of a substance changes another crystalline form is called transition temperature. In other words, temperature at which more than one crystalline forms of a given substance can in equilibrium with each other is called transition temperature.

Above and below transition temperature only one polymorph or allotr can exist. The transition temperatures of some substances are shown below.

Sulphur (S_8) (Rhombic) $\xrightleftharpoons{95.6\,^{\circ}C}$ Sulphur (S_8) (Monoclinic)

Tin (gray) (Cubic) $\xrightleftharpoons{13.2\,^{\circ}C}$ Tin (white) (Tetragonal)

KNO_3 (Rhombohedral) $\xrightleftharpoons{128.5\,^{\circ}C}$ KNO_3 (Orthorhombic)

Table 6.3 Differences between Amorphous Solids and Crystalline Solids

Property	Amorphous Solids	Crystalline Solids
Shape	They do not have definite geometrical shape.	They have characteristic geometrical shape.
Melting point	Amorphous solids do not have particular melting point. They melt over a wide range of temperature.	They have sharp melting point.
Anisotropy	Physical properties of amorphous solids are same in different direction, i.e. amorphous solids are isotropic.	Physical properties of crystalline solids are different in different directions. This phenomenon is known as Anisotropy.
Symmetry	Amorphous solids are unsymmetrical	Crystalline solids are symmetrical
Cleavage plane	Amorphous solids do not break at fixed cleavage planes.	Crystalline solids break along particular direction at fixed cleavage planes.

Self-Assessment

1. Differentiate between amorphous solids and crystalline solids.
2. Define symmetry. What are elements of symmetry?
3. Explain the terms polymorphism and allotropy.
4. Differentiate between habit of crystal and crystal growth, isotropy and anisotropy.
5. Define allotropy. Use oxygen and sulphur as an example.

Science, Technology and Society

Crystalline and amorphous solids have specific uses in daily life. Examples of crystalline solids are table salt (sodium chloride), sugar, gemstones including quartz and diamond. Some of the uses of crystals are,

- Diamond is used in jewelry.
- Sodium chloride (NaCl) has been used to flavor and preserve foods for thousands of years. Doctors use an intravenous sodium chloride solution to supply water and salt to patients to decrease dehydration.
- Sodium fluoride (NaF) is used in toothpastes to prevent cavities. It makes teeth stronger.
- Sugar (sucrose) is used in daily life for sweet taste.

- Salts of iodine are used for treatment of goiter.

Examples of amorphous solids are plastic, glass, rubber, coal, c fiberglass, cellophane, teflon, polyurethane, polyvinylchloride (PVC). Some of uses of amorphous solids are,

- Plastics are used in the construction, industry, electrical and electr applications. It is also used in packaging goods, including containers, bo drums, trays, boxes, cups and baby products etc.
- Rubber is used in vehicles tyres, airbags, flooring, natural rubber ga erasers, adhesives and coatings, rubber gloves etc.
- Fiberglass is durable, safe and offers high thermal insulation. Fibergla widely used in industries such as beverage industry, chemical industry, co towers, fountains and aquariums, etc.
- Glass is used in making drinking vessels, barometer, windows pans, opt instruments etc.

6.4 Crystal Lattice

The regular three-dimensional array of atoms, ions, or molecule crystal is expressed in terms of points is called the **lattice** that identifi locations of the individual species.

The crystal lattice of a substance is represented by showing the posi particles (**structural units**) in space.

The location of particles in a crystalline solid can be represented as on a framework called crystal lattice.

The particles (atoms, ions or molecules) in crystals are highly order three dimensional pattern. It is the property of the crystal, which is respo for their specific geometrical shapes, smooth surfaces and specific inte angles. The particles in crystals are arranged in regular patterns that exten directions. The overall arrangement of particles in a crystal is called the C **lattice, Space lattice or simply lattice.** These positions of the cons particles in a crystal are represented by bold dots (or circles) and are refer as **lattice points** or **lattice sites** irrespective of the size and nature o particles. Each point in the lattice is occupied by a particle of the substance

To describe the structure of a crystal it is convenient to view it as made of a large number of basic units called the **Unit cell** as shown in fig

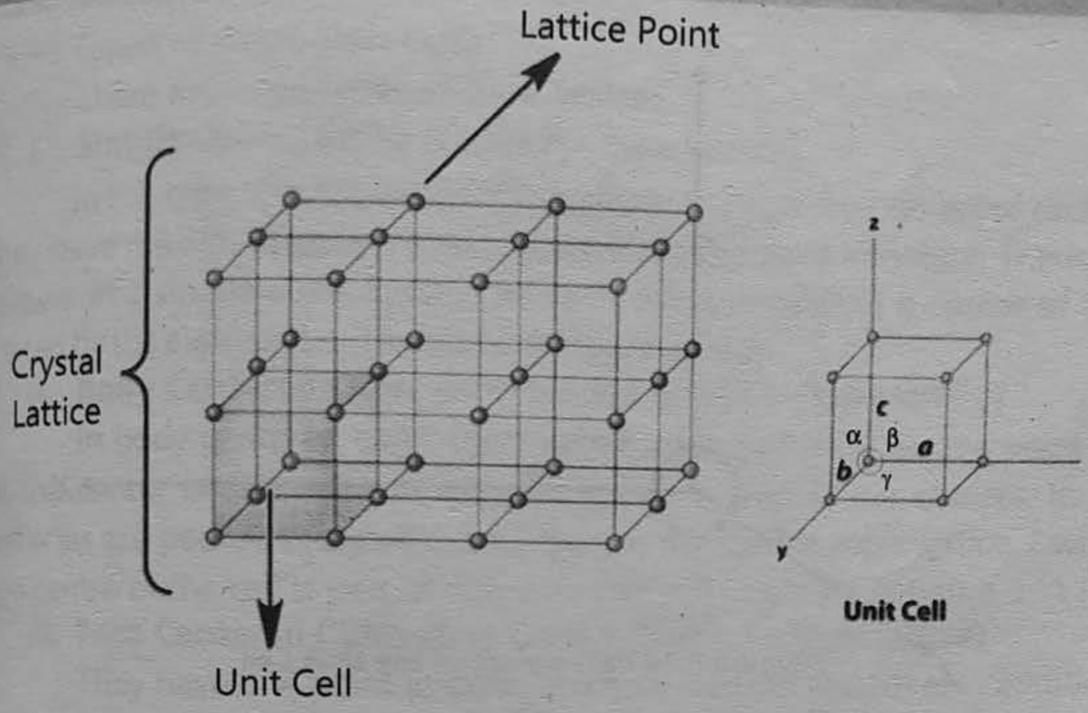


Figure 6.9 Crystal Lattice and Unit Cell

6.4.1 Unit cell

You can divide a crystal lattice into boxlike cells or unit cells. The **unit cell** of a crystal is the smallest boxlike unit (each box having faces that are parallelograms) from which you can imagine constructing a crystal by stacking the units in three dimensions.

The smallest portion of a crystal lattice that shows the three-dimensional pattern of the entire lattice is called a unit cell. On the other hand, you can say that the basic repeating structural unit of a crystalline solid is a unit cell. A unit cell being the structural unit carries complete information about the given crystal.

A unit cell has the smallest arrangement of atoms in a crystal lattice that has the same symmetry as the whole crystal. A unit cell is small, representative part of a larger whole. The unit cell can be thought of as a building block whose shape determines the shape of the crystal.

Parameters of the Unit Cell

The structures of all crystals can be classified according to the symmetry of the unit cells. There are in total seven groups, collectively called, crystal system. These are triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal and cubic. The unit cells are characterized by the following parameters:

(*a*) Relative lengths of the edges along the three axes (*a*, *b*, *c*),

(*b*) The three angles between the edges (α, β, γ).

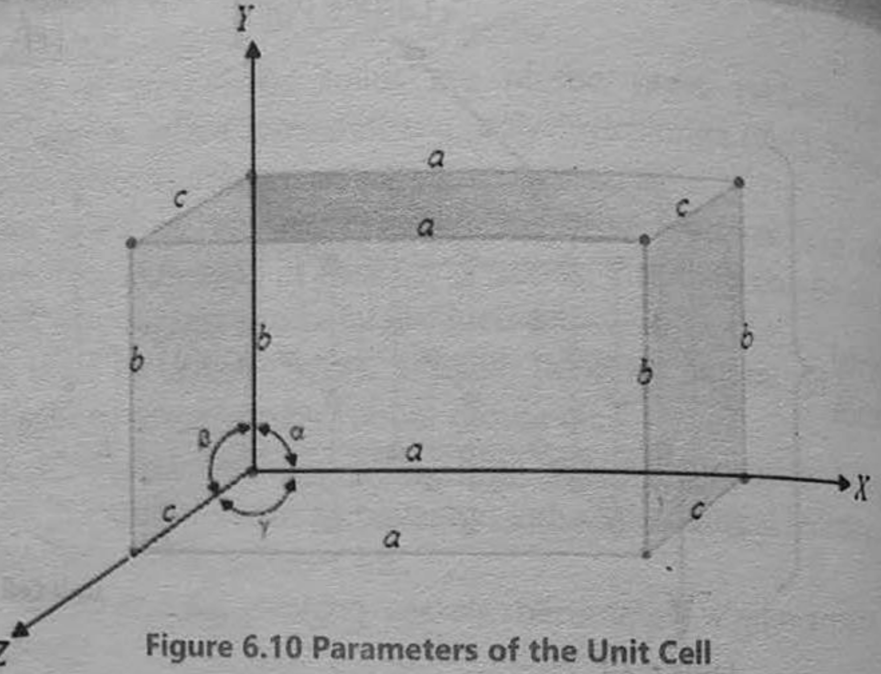


Figure 6.10 Parameters of the Unit Cell

The six parameters of a unit cell, 3 edges (a, b, and c) and 3 angles (α, β are called unit cell dimensions or crystallographic elements. These parame can be illustrated as in figure 6.10. Parameters of the seven Bravais unit cells listed in Table 6.4.

Table 6.4 The Seven Crystal Systems

Crystal system	Edge length	Angles	Example
Cubic	a = b = c	α= β = γ = 90°	NaCl, Cu
Tetragonal	a = b ≠ c	α= β = γ = 90°	TiO_2 (rutile), Sn (white tin)
Orthorhombic	a ≠ b ≠ c	α= β = γ = 90°	$CaCO_3$ (aragonite), $BaSO_4$
Monoclinic	a ≠ b ≠ c	α=β =90° , γ ≠ 90°	$PbCrO_4$
Hexagonal	a = b ≠ c	α=β = 90° ,γ = 120°	C (graphite), ZnO
Rhombohedral	a = b = c	α = β = γ ≠ 90°	$CaCO_3$ (calcite), HgS (cinnabar)
Triclinic	a ≠ b ≠ c	α≠ β ≠γ ≠ 90°	$K_2Cr_2O_7$, $CuSO_4.5H_2O$

Cubic Unit Cells

These are the simplest unit cells. These unit cells are particularly impo for two reasons.

First, a number of ionic solids and metals have crystal lattices comp cubic unit cells. Second, it is relatively easy to make calculations with these because in them all the sides are equal (i.e. a=b=c) and the cell angles are al (i.e. $a = \beta = r = 90^o$)

Three Types of Cubic Unit Cells

There are three types of cubic lattices.

i. **Simple Cubic Lattice (Cubic P – type lattice)**

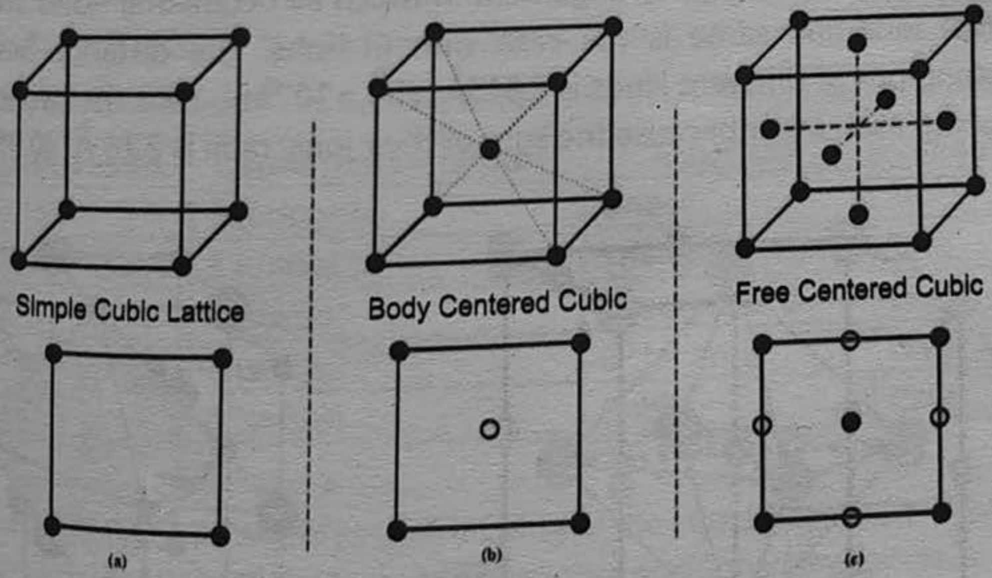
In this type of cubic lattice, the points are only at the corners of each unit cell. They have maximum vacant space and are rarely found in nature. There are eight corners in a simple cubic system ad each point occupying a corner of the cell is shared by the eight unit cell as shown in figure 6.11(a).

ii. **Body Centered Cubic (bcc) Lattice (Cubic I – type lattice)**

In body centered cubic (bcc) lattice, each unit cell has one point (particle) at the center of the cube in addition to the points at the corners. In this case particles are packed more efficiently than in the simple cubic lattice. Each point in the centre of the cell is part of only one unit cell as shown in figure 6.11 (b).

iii. **Face Centered Cubic (fcc) Lattice (Cubic F – type lattice)**

They have one point at each of the six faces of the cube, in addition to the points at the corners. Maximum space is occupied by the particles in this case. Here each point at the corner is shared by eight unit cells and the point at the centre of each face is shared by two unit cells figure 6.11 (c).



Simple Cubic Lattice (a)

Body Centered Cubic (b)

Free Centered Cubic (c)

Figure 6.11 (a), (b), (c) Three Cubic Units Cells

6.4.2 Sodium Chloride (NaCl) Crystal

Sodium chloride (NaCl) is a typical example of face centered cubic arrangement (system) and it consists of equal numbers of Na^+ and Cl^- ions arranged in a three-dimensional network as shown in figure 6.12. In such a compound, there is a 1:1 ratio of cations to anions so that the compound is electrically neutral.

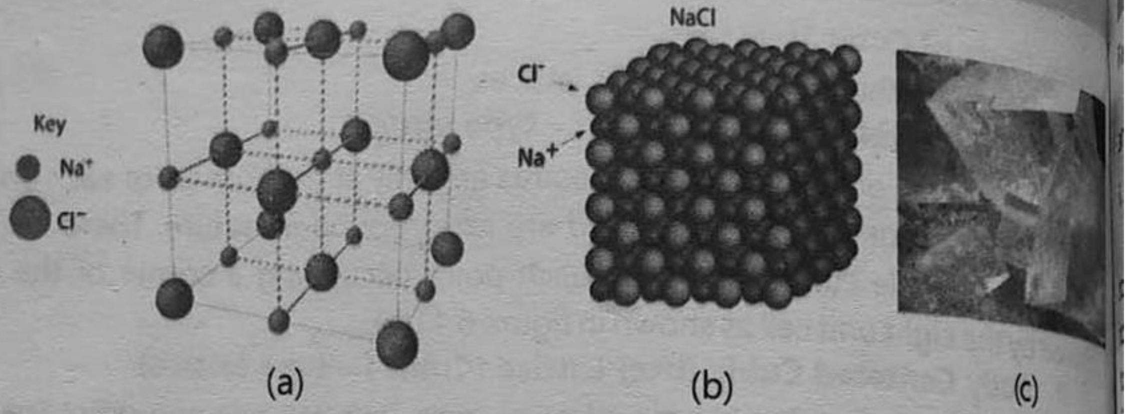
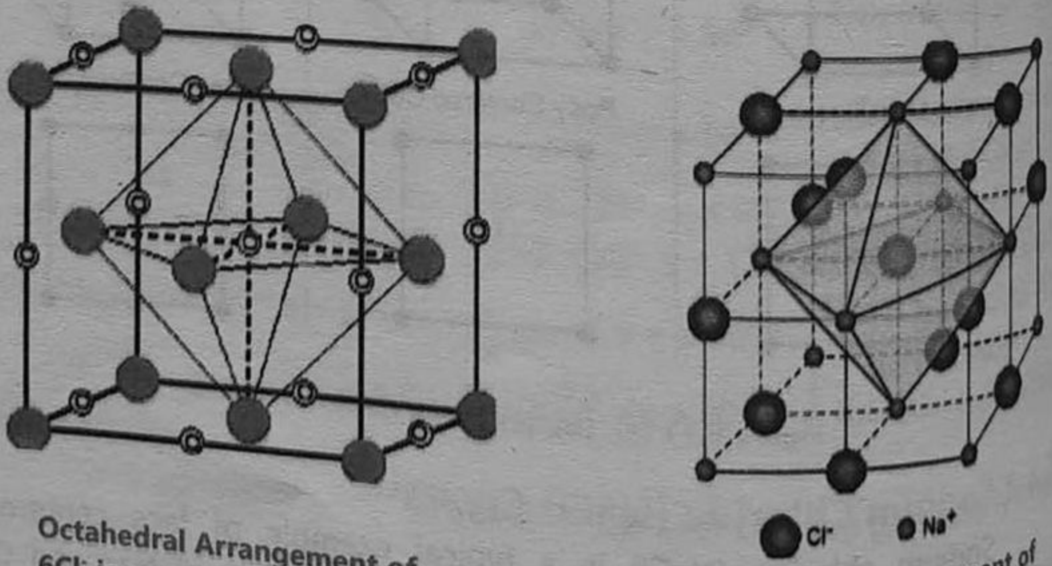


Figure 6.12(a) Structure of solid NaCl (b) In reality, the cations are in contact with the anions (c) Crystals of NaCl

As you can see in figure 6.12, one Na^+ ion in NaCl is associated with just one particular Cl^- ion. In fact, each Na^+ ion is equally held by six surrounding Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions. Thus co-ordination number of each ion is six.

NaCl has a face centered cubic arrangement and in the octahedral structure, shown in figure 6.13 (a) and (b), Cl^- ions may be regarded as having a cubic closed packed (ccp) arrangement in which all octahedral holes are occupied by Na^+ ions and same is the case with Cl^- ions. The distance between two adjacent ions of different kinds is $2.815\mathring{A}$ ($1\mathring{A} = 10^{-10}$m). Thus the two ions are not toughing each other because the sum of their ionic radii is $2.76\ \mathring{A}$ (0.95+1.81)



Octahedral Arrangement of $6Cl^-$ ions around Na^+ ion
(a)

Octahedral Arrangement of $6Na^+$ ions around Cl^- ion
(b)

Figure 6.13

Factors that Affect the Shape of an Ionic Solid

There are some factors which effect the shape of an ionic crystal. Few of them are given below.

i. Electrostatic Force of Attraction

Ionic crystals are formed between cations and anions which are strongly held together due to electrostatic forces. The strength with which these ions are held tougher is known as lattice energy. Due to high lattice energy ions are strongly held together and a crystal acquires a definite shape.

ii. Radius Ratio

In ionic crystals cations are surrounded by anions. Generally, cations are smaller in size than anions. The anions around the cations are located in such a way that they are at a suitable distance from each other to avoid repulsion between anions. Thus, around a given cations only a certain number of anions can be accommodated, this number is called Coordination number. The coordination number is related with relative size of cation and anion, called as radius ratio which is the ratio of size of cation to that of anion. For example, for NaCl the radius ratio of Na^+ to Cl^- is 0.54 which has coordination number of 6 and acquire an octahedral crystal structure.

Some examples of radius ratio and crystal structure are given in table 6.5.

Table 6.5 The structure and limiting radius ratio of certain crystalline substance

Radius ratio	**Coordination number**	**Structure**	**Example**
<0.155	2 (unstable)	Linear	----
0.155 – 0.225	3 (unstable)	Triangular planer	Non
0.225 – 0.414	4 (stable)	Tetrahedral	ZnS, $CuCl_2$
0.414 – 0.732	6 (stable)	Octahedral	NaCl, MgO
0.732 – 1	8 (stable)	Cubic	CsCl

iii. Effect of Temperature

A perfect crystal would require cooling of the liquid phase at a very slow rate so as to allow ions or particles to find their proper position in the lattice. In this way, proper temperature has significant impact upon the crystal formation.

iv. Effect of impurity

If there are impurities in solution from which the crystallization of a substance is to be carried out, the resulting crystal will have defects, called crystal defect. These impurity particles will fit into the holes of the crystal lattice causing a defect in the crystal structure.

6.4.3 Lattice Energy

When ions combine to form an ionic solid there is a huge release of energy. The reaction is highly exothermic. The energy given out when ions of opposite charges come together to form a crystalline lattice is called the lattice energy, $\Delta H_{L.E.}$

Lattice energy can be defined as *the amount of energy released when one mole of an ionic crystal is formed from gaseous ions of opposite charges*. It is expressed in $kJ.mol^{-1}$. For example,

Equations describing the lattice energy of sodium chloride and magnesium chloride are shown here.

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)} \qquad \Delta H_{L.E} = -787 kJmol^{-1}$$

$$Mg^{2+}_{(g)} + 2Cl^-(g) \longrightarrow MgCl_{2(s)} \qquad \Delta H_{L.E} = -2526\ kJ\ mol^{-1}$$

The large exothermic value of the lattice energy shows that the ionic lattice is very stable with respect to its gaseous ions. Higher the lattice energy the stronger the ionic bonding in the lattice.

It is impossible to determine the lattice energy of a compound by a single direct experiment. We can, however, calculate a value for $\Delta H_{L.E}$ using several experimental values and an energy cycle called a Born–Haber cycle.

Lattice energy increases with increase in charge and decrease in size of ions. Lattice energy of some ionic crystal is given in table 6.6.

Table 6.6 Lattice Energies of some Ionic Compounds

Compound	Lattice energy (kJ/mol)
NaF	895
LiCl	833
NaCl	787
NaBr	728
NaI	690
KBr	665
KI	630

6.4.4 Low Density and High Heat of Fusion of Ice

Liquid water is readily convertible under conditions to the solid and gaseous forms. Water has several unusual properties that make it to distinguish from other substances. For example, its solid phase, ice is less dense than liquid water.

i. Low density of Ice

The most striking property of water is that its solid form is less dense than its liquid form that is why ice floats on the surface of liquid water. The density of almost all other substances is greater in the solid state than in the liquid state as shown in figure 6.14.

The unusual properties of water are largely linked to its ability to form hydrogen bonds. For example, ice is less dense than liquid water because of hydrogen bonding. When the temperature is decreased, the molecules come close to each other. Each oxygen atom in ice is surrounded tetrahedrally by four hydrogen atoms, two by covalent bonds and two by hydrogen bonds. The tetrahedral angles give rise to a three-dimensional structure that contains open space. As a result, about 9% more space than liquid water is produced. As we have d = m/v, that is, density is inversely proportional to volume, the increase in volume decreases the density of ice. That is why ice floats over water.

ii. High Heat of Fusion of Ice

The energy (usually in kJ) required to melt 1 mole of a solid at its melting point is called the molar heat of fusion (ΔH_{fus}). For example,

$$\text{Ice} \xrightarrow{\qquad} \text{Liquid water} \quad \Delta H_{fus} = 6.02\ \text{kJmol}^{-1}$$

As Table 6.7 shows, ice has a high heat of fusion. This is consistent with the fact that molecules in a liquid are fairly closely packed together, so that high energy is needed to bring about the rearrangement from solid to liquid.

Tidbit

Ice structure extends in three dimensions due to tetrahedral arrangement. Because of empty spaces in its structure, ice has smaller density than liquid water and float on the surface of water.

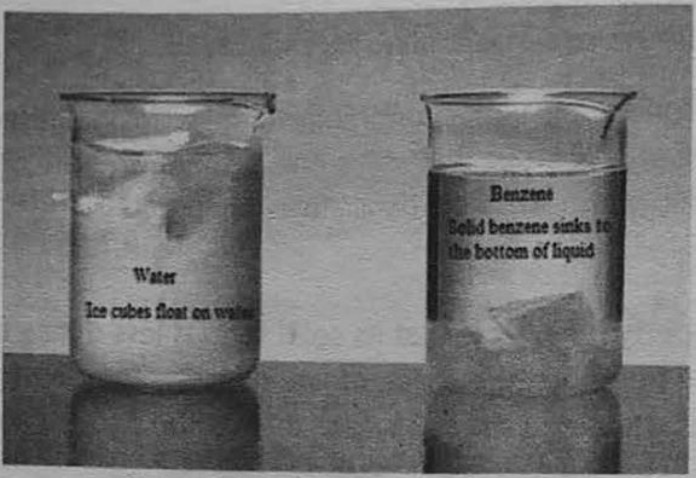


Figure 6.14 Water and Benzene

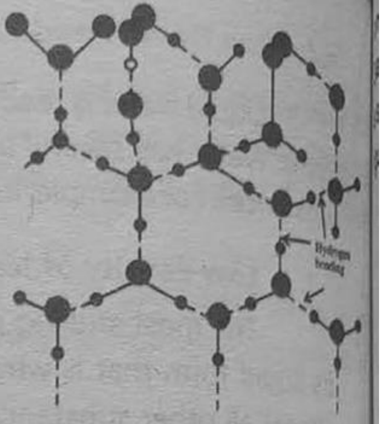


Fig. 6.15 Structure of Ice

Table 6.7 Molar Heats of Fusion for Selected Substances

Substance	Melting Point(°C)	H_{fus} (kJ/mol)
Argon (Ar)	−190	1.3
Benzene (C_6H_6)	5.5	10.9
Diethyl ether ($C_2H_5OC_2H_5$)	−116.2	6.90
Ethanol (C_2H_5OH)	−117.3	7.61
Mercury (Hg)	−39	23.4
Methane (CH_4)	−183	0.84
Water (H_2O)	0	6.02

6.5 Types of Crystalline solids

Crystalline solids are classified into categories according to the types of particles in the crystal and the bonding or interactions among them. The four categories are (1) ionic solids, (2) covalent solids (3) metallic solids, and (4) molecular solids.

Reading Check

i. What is Crystal Lattice?
ii. Define unit cell. What are the different parameters of the unit cell?

6.5.1 Ionic Solids

In an ionic crystal, the lattice is made of positive and negative ions. These are held together by ionic bonds. Ionic bonds are strong electrostatic attractions between oppositely charged ions. As a result, the cations and anions attract one another in such a manner so that the attractive forces maximize. The structure of an ionic crystal depends on the charges on the cation and anion and on their radii. Examples of ionic solids are NaCl, MgO, NaBr etc. In sodium chloride lattice, each ion is surrounded by opposite charge and there are no separate molecules as shown in figure 6.16.

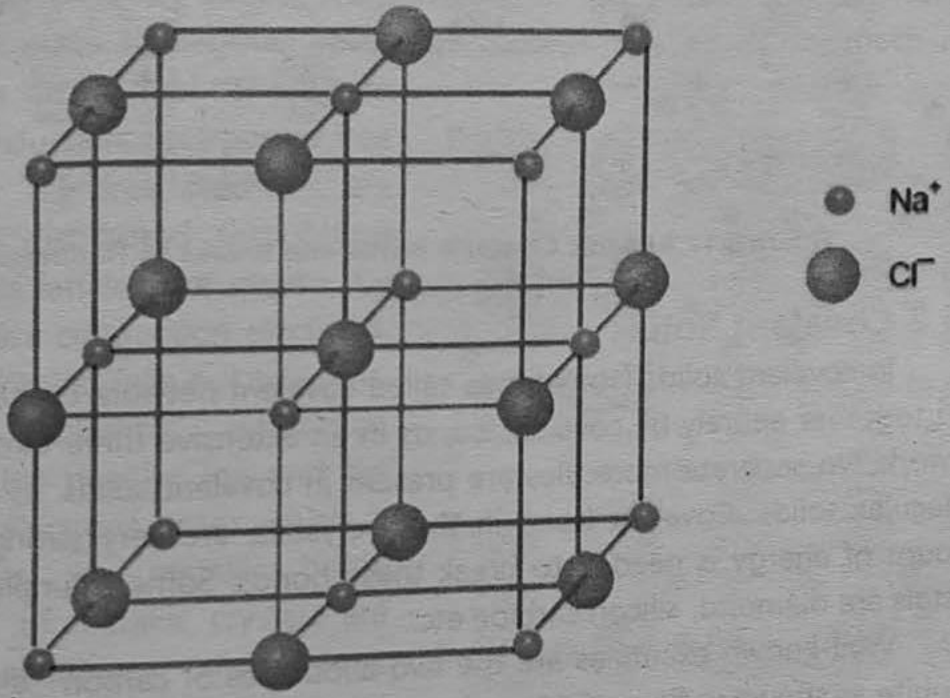


Figure 6.16 Sodium Chloride Crystal Lattice

Properties of Ionic Solids

Some of the properties of Ionic solids are,

1. In ionic solids, the cations and anions are closely packed into a compact specific geometrical shape and have strong ionic bond.
2. They are solid and usually very hard at room temperature. They never exist in liquid or gaseous form at ordinary temperature and pressure.
3. Ionic solids are brittle. They shatter easily by hammering as shown in figure 6.17.
4. Ionic solids have high melting points and heats of fusion (ΔH_{fus}).
5. These solids do not conduct heat and electricity because the ions can vibrate only about their fixed positions. However, in the molten state (that is, when melted) or dissolved in water, they conduct electricity.
6. They are soluble in polar solvent like water.

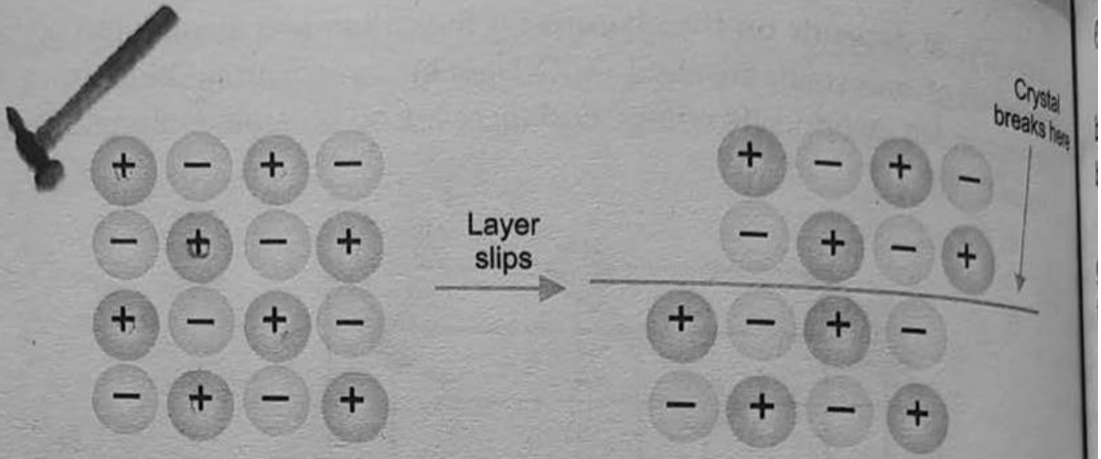


Figure 6.17 An Ionic Crystal is Brittle and Breaks by Hammering

6.5.2 Covalent Solids

In covalent solids (sometimes called covalent network crystals), atoms are held together entirely by covalent bonds in an extensive three-dimensional rigid network. No separate molecules are present in covalent solids, as in the case of molecular solids. Covalent bond in these crystals, are very strong and a huge amount of energy is needed to break these bonds. Some examples of covalent crystals are diamond, silicon carbide etc.

Well-known examples are the two allotropes of carbon: diamond and graphite as shown in figure 6.18.

Figure 6.18 Diamond and Graphite

Properties of Covalent Solids

Properties of covalent solids are,

1. Covalent solids are also very hard and cannot be broken easily.
2. They have high melting point and heat of fusion.
3. They are poor conductor of heat and electricity except graphite.
4. They are usually insoluble in polar solvents.

6.5.3 Metallic Solids

In metallic solids, the metal atoms are held together by a special type of bonding, called metallic bond, which is totally different from ionic or covalent bond.

In metals, the electrons in the outer most orbital of the atoms are generally very loosely bound. Thus, they have high mobility and can move freely from one place to another inside the metallic crystals lattice, much like the molecules in a gas. These are called conduction electrons, or free electrons. The free electrons are uniformly distributed throughout the metals lattice. The metals, by losing these conduction electrons, are transformed into positive ions. Thus a columbic interaction between the positive ion and the negative electrons arises which is termed as the metallic bond. Examples of metallic crystals are copper, aluminum, silver, iron, sodium etc.

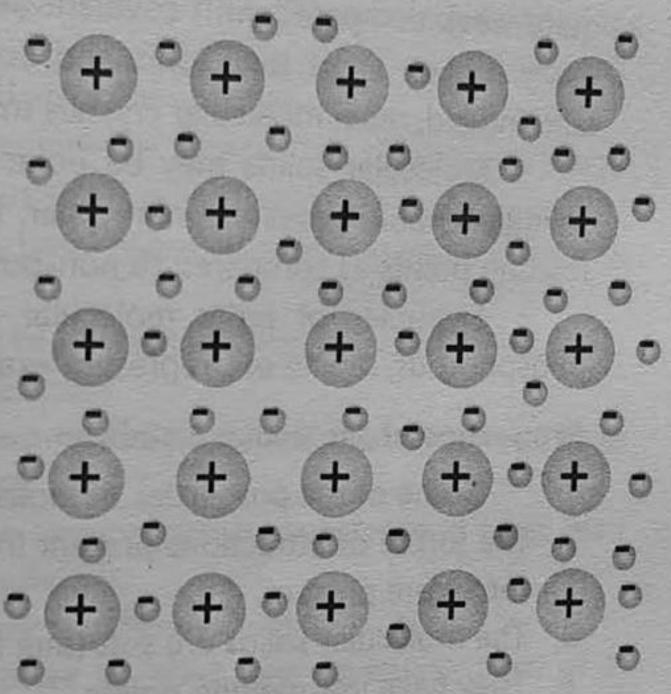


Figure 6.19 Internal Structure of Metallic Solids

Properties of Metallic Solids

Some of the properties of metallic solids are,

1. Metallic solids have usually compact structure and the atoms are closely packed together.
2. They are hard and have high melting point (A few of them are very soft and can be cut with a knife, e.g. sodium).
3. These crystals have metallic luster.
4. The free conduction electrons make the metallic solids good conductors of heat and electricity.
5. They are malleable (could be transformed into sheets) and ductile (could be drawn into wires).

6.5.4 Molecular Solids

Molecular solids consist of atoms or molecules held together by Van de Waal's forces.

Examples of molecular solids are I_2, P_4 and S_8. In general, except in ice molecules in molecular solids are packed together as closely as their size and shape allow. Because Van der Waals forces and hydrogen bonding are generally quite weak compared with covalent and ionic bonds, molecular solids are more easily broken apart than ionic and covalent crystals. These solids are relatively soft. Indeed, most molecular crystals melt below 200°C.

Molecular solids may be polar or non-polar. For example, the atoms in solidified noble gases are non-polar. Polar molecular crystals have usually high melting points as compared to non-polar molecular crystals.

Examples of polar molecular crystal are ice and sugar while sulphur phosphorous, iodine etc. represent example of non-polar molecular crystals.

Properties of Molecular Solids

Some of the properties of molecular solids are,

1. The forces of attractions present in these solids are very weak; Van der Waal's forces are present.
2. The molecular solids are soft (due to the presence of Van der Waal's forces).
3. They have low melting points.
4. Polar molecular solids are soluble in polar solvents and non-polar molecular solids are soluble in non-polar solvents.

Self-Assessment

1. Explain the significance of the unit cell to the shape of the crystal using NaCl as an example.
2. Name three types of packing arrangements and draw or construct models of them.
3. Name three factors that affect the shape of an ionic crystal.
4. Differentiate between ionic, covalent, molecular and metallic crystalline solids.
5. Explain the low density and high heat of fusion of ice.
6. Define and explain molecular and metallic solids.

Solid is the physical state of matter with definite shape and volume.

Particles in solids are closely packed and cannot move freely. They, however, vibrate about their mean position.

Kinetic energy in solid exists in the form of vibrational kinetic energy.

In solids, particles are closely packed so they have minimum empty spaces and rigid structure. This accounts for negligible diffusion and compressibility of the particles into each other.

Solids are classified into crystalline and amorphous solids.

Crystalline solids have definite geometrical shape with repetitive three-dimensional structure, while amorphous solids do not have.

Crystalline solids possess symmetry, have sharp melting points and specific cleavage planes.

The habit of crystal refers to the shape of a crystal in which it usually grows.

Anisotropy is the property of crystalline solids.

Isomorphism is the term used when two or more different crystalline substances having the same crystalline shapes exist.

Polymorphism is the occurrence of the same crystalline substance in more than one crystalline form under different conditions.

Allotropy is the occurrence of an element in different forms.

Transition temperature is the temperature at which one crystalline form of a substance changes to another form.

Crystal lattice is the location of particles in a crystalline solid which can be represented as points on a framework.

Unit cell is the smallest portion of a crystal lattice that shows the three-dimensional pattern of the entire lattice.

The unit cells have six parameters 3 edges (a, b, and c) and 3 angles (α, β, γ) and are called unit cell dimensions or crystallographic elements.

The coordination number is the number of atoms (or ions) surrounding an atom (or ion) in a crystal lattice.

Lattice energy is the amount of energy released when one mole of an ionic crystal is formed from gaseous ions of opposite charges.

Crystalline solids are classified into four categories. These are (i) Ionic solids, (ii) Covalent solids (iii) Metallic solids and (iv) Molecular solids, depending upon the forces present among the particles of the crystal.

Ionic, covalent and metallic solids are hard and have high melting point, while molecular solids are soft and have low melting points.

EXERCISE

Choose the Correct Option.

1. The crystal of ice in an example of

a. Metallic solid   b. Molecular solid

c. Covalent solid   d. Ionic solid

2. KNO_3 and $NaNO_3$, both have the atomic ratio of 1:1:3 in their crystals property is

a. Isotropy   b. Anisotropy

c. Isomorphism   d. Polymorphism

3. The number of center of symmetry of a cubic crystal is/are

a. One   b. Two

b. Three   d. Six

4. A pair of compounds, which are isomorphic in nature is,

a. NaCI and KNO_3 b.MgO and ZnO

c. $NaNO_3$ and CdS   d. NaF and $CaCO_3$

5. Crystals show variation in physical properties depending upon the dire The property is called

a. Isomorphism   b. Polymorphism

c. Anisotropy   d. Isotropy

6. The parameters of unit cell is

a. 4   b. 5   c. 6   d. 7

7. Sodium chloride (NaCl) on crystallization form the

a. Face centered cubic lattice   b. Orthorhombic lattice

c. Body centered cubic lattice   d. Simple cubic lattice

8. The molecules of CO_2 in dry ice form the

a Ionic crystals   b. Covalent crystals

c. Molecular crystals   d. Metallic crystal

9. The nature of bonds between atoms in graphite is

a. Ionic   b. Covalent

c. Molecular   d. Metallic

10. The example of metallic solid is

a. C   b. B   c. Si   d. Cu

11. In solid state, the crystals which are good conductor of heat and electri

a. Covalent   b. ionic

c. Molecular   d. Metallic

When a crystalline substance conducts current in one direction but not through other directions of the crystal, this property is

a. Anisotropy b. Isotropy
c. Allotropy d. Isomorphism

Crystals of the same substance can co-exist in equilibrium with each other at its

a. Boiling point b. Melting point
c. Transition temperature d. Heat of fusion

Crystal lattice is an arrangement of particles in

a. Four dimensions b. Three dimensions
c. Two dimensions d. One dimension

ort Questions

Briefly explains the term unit cell and crystal lattice.
Why crystalline solids are anisotropic?
Give the reason that metallic crystals are good conductors of electricity but ionic crystals are not.
Differentiate between crystalline and amorphous solids.
Justify that crystalline solids have sharp melting point.
What is transition temperature? Give examples.
Explain that isomorphic substances have usually the same atomic ratio.
Give the reason that covalent crystals are hard while molecular crystals are soft.
Define lattice energy and give examples.
Differentiate between polymorphism and isomorphism.

criptive Questions

(a) Explain the kinetic molecular interpretation of solids.
(b) Discuss in detail the following properties, keeping in view the Kinetic Molecular Theory.
(i) Diffusion (ii) Compression (iii) Expansion (iv) Motion of molecules

(a) Discuss in detail a sodium chloride lattice.
(b) Describe the following properties of crystalline solids:
(i) Habit of a crystal (ii) Cleavage planes (iii) Crystal growth
(iv) Anisotropy (v) Symmetry.

3. Differentiate between the following pairs:
   (i) Ionic solid and molecular solid
   (ii) Lattice energy and crystal lattice
   (iii) Plane of symmetry and axis of symmetry

4. (a) Define allotropy. Use oxygen and sulphur as an example to allotropes.
   (b) Explain the low density and high heat of fusion of ice.

5. (a) Define and explain molecular and metallic solids
   (b) What are the features of three types of packing arrangements system and construct models of them?

6. (a) Write down the three factors that affect the shape of an ionic
   (b) What is meant by unit cell of crystal? Sketch the unit cell of NaCl

Project

- Collect the different household items and classify them as amorpho crystalline substances,

Table salt	Sugar	Washing soda
Baking soda	Ice	Glass

Unit-07

Chemical Equilibrium

ter studying this unit, the students will be able to:

- Define chemical equilibrium in terms of a reversible reaction. (Remembering)
- Write both forward and reverse reactions and describe the macroscopic characteristics of each. (Understanding)
- State the necessary conditions for equilibrium and the ways that equilibrium can be recognized. (Understanding)
- Describe the microscopic events that occur when a chemical system is in equilibrium. (Understanding)
- Write the equilibrium expression for a given chemical reaction. (Understanding)
- Relate the equilibrium expression in terms of concentration, partial pressure, number of moles and mole fraction. (Applying)
- Write expression for reaction quotient. (Understanding)
- Determine if the equilibrium constant will increase or decrease when temperature is changed in given equation for the reaction. (Applying)
- Propose microscopic events that account for observed macroscopic changes that take place during a shift in equilibrium. (Applying)
- Determine if the reactants or products are favoured in a chemical reaction from the given equilibrium constant. (Analysing)
- State Le-Chatelier's Principle and be able to apply it to systems in equilibrium with changes in concentration, pressure, temperature, or the addition of catalyst. (Applying)

Teaching

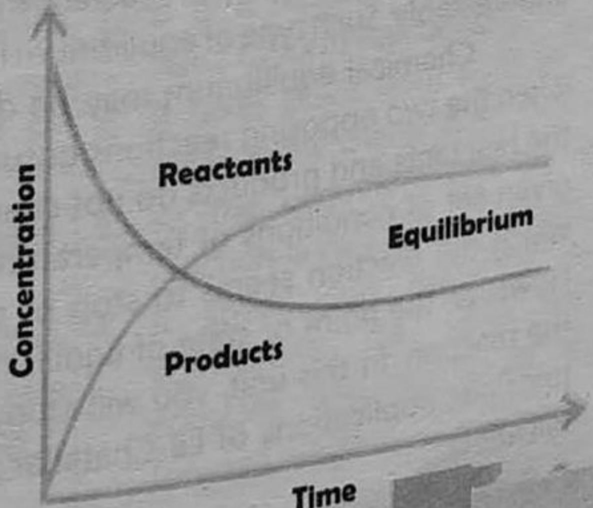
08

Assessment

01

Weightage %

07



- Explain industrial application of Le-Chatelier's Principle using Haber's process as example. (Analysing)
- Define and explain solubility product. (Understanding)
- Define and explain common ion effect giving suitable examples. (Applying)

Introduction

It is a well-established fact that many reactions do not go to completion ev if favourable conditions are maintained. Such reactions proceed to certain exten and then apparently stop. This is because the products react themselves to give bac the original reactants and a time reaches when there is no further change i composition of the reaction mixture occurs. The reaction when reaches the stag where no more products are formed is said to be at equilibrium state. Such reactio are called reversible reactions.

At the start of a reversible reaction, the reaction proceeds towards th formation of products. As soon as some product molecules are formed, the revers process begins to take place and reactant molecules are formed from the produc molecules. At the beginning rate of forward reaction is fast since the reactan concentration is high and rate of reverse reaction is low since the concentration o product is low. With the passage of time, rate of forward reaction graduall becomes slow and rate of reverse reaction becomes fast. Ultimately, a stage reache where both the rates become equal; this stage is called the equilibrium state.

At equilibrium state:

- Rate of forward reaction is equal to rate of reverse reaction.
- The concentrations of reactants and products become constant (no necessarily equal) and can be recognised by chemical and physical methods

Although at molecular level formation of product molecules from reactan molecules and formation of reactant molecules from product molecules continue undetectably. Such type of equilibrium is called dynamic equilibrium.

Chemical equilibrium may be defined as the state of a reversible reactio when the two opposing reactions occur at the same rate and the concentrations the reactants and products do not change with time. It is observed that under a given set of conditions of temperature, pressure, and concentration the poin which the reaction seems to stop or equilibrium is attained, is always the sa However, the point or state of equilibrium changes by changing the conditions the reaction. In this unit, you will study about dynamic equilibrium, Le-Chatelie principle, applications of Le-Chatelier's principle, solubility product and comm ion effect.

7.1 Reversible Reactions and Dynamic Equilibrium

7.1.1 Concept and Explanation

The reactions that do not go to completion and the products formed react to re-form the reactants are called reversible reactions.

A reversible reaction can be represented by two arrows (⇋) between the reactants and products. Let us consider a general reaction taking place in a close vessel.

$$A+B \rightleftharpoons C+D$$

Let the initial concentration of A and B be the same. As the forward reaction proceeds, the concentrations of the reactants (A, B) decrease and those of the products (C, D) increase continuously. Therefore, the rate of forward reaction goes on decreasing while that of backward reaction keeps on increasing. Ultimately, a stage reaches when the rate of forward reaction becomes equal to the rate of backward reaction. At this stage the concentrations of the reactants and products become constant. This is called the state of chemical equilibrium.

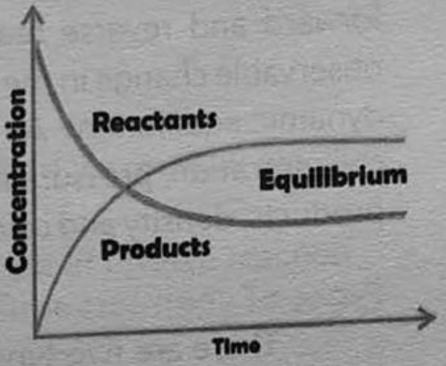


Fig: 7.1 Reversible Reaction and Equilibrium state

Some examples of reversible reactions in a closed vessel are given below.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

Table 7.1.Macroscopic Characteristics of Forward and Reverse Reactions

Forward Reaction	Reverse Reaction
a. It is a reaction in which reactants react to form products.	1. It is a reaction in which products react to form reactants.
b. It takes place from left to right as given in chemical equation.	2. It takes place from right to left as given in the chemical equation.
c. At initial stage the rate of forward reaction is fast.	3. At the beginning rate of reverse reaction is very slow.
d. The rate of reaction slows down gradually and at equilibrium its rate becomes constant and equals to that of reverse reaction.	4. It speeds up gradually and at equilibrium its rate becomes constant and equals to that of forward reaction.

The necessary conditions of equilibrium are as follows:

1) The equilibrium state can only be reached if the reaction is taking place in closed vessel wherein substances can neither leave nor enter.
2) Catalyst helps to attain equilibrium earlier but it does not change the positio of equilibrium.
3) The state of equilibrium is maintained only as long as the reaction conditions such as temperature and pressure etc. do not change.

Once the equilibrium composition has been attained no further change the quantities of the components will occur as long as the system remains u disturbed, although microscopically, (at molecular level) reactants are converted t products and product molecules are reacting to give the reactants back; both th forward and reverse reactions taking place at the same rate. Thus, there is n observable change in the concentration of both reactants and products, this is calle dynamic equilibrium. An equilibrium state can be recognized by the constancy c concentration, pressure in the case of gaseous reactants or products, density and colour, etc. of the reaction mixture.

Reading Che

Define chemical equilibrium.

Types of chemical equilibrium:

There are two types of chemical equilibrium:

i) **Homogeneous Equilibrium**: In homogeneous equilibrium all the components of reaction occur only in one phase. For example, a system containing only gases or totally miscible liquids e.g.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5\,(l)} + H_2O_{(l)}$$

ii) **Heterogeneous Equilibrium**: In heterogeneous equilibrium the reactio components occur in two or more phases. For example;

$$CaCO_{3\,(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

7.1.2. The law of Mass Action and expression for Equilibrium Constant

This law was first enunciated by C.M. Guldberg and P. Waage in 1864 tha helps us to find the relations between the concentrations of reactants an products at equilibrium in a chemical reaction. It states that *"the rate at whic substance reacts is proportional to its active mass and the rate of chemi reaction is proportional to the product of the active masses of the react substances"*. By the term active mass (or activity) we mean the mola concentration, or number of moles dm^{-3} in a dilute solution. Consider a genera reaction;

$$A+B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C+D$$

Where A and B are the reactants while C and D are the products. The equilibrium concentrations in mol dm^{-3} of A, B, C and D are represented in square brackets like [A], [B], [C], and [D], respectively. According to the law of mass action the rate of forward reaction is proportional to the product of molar concentrations of A and B.

Rate of forward reaction $\propto$ [A] [B]

Rate of forward reaction = k_f [A] [B]

k_f is the proportionality constant known as rate constant for the forward reaction. Since C and D are the reactants for the backward reaction so the rate of reverse reaction is given by

Rate of reverse reaction $\propto$ [C] [D]

Rate of reverse reaction = k_r [C] [D]

Where, k_r is the rate constant for the backward (or reverse) reaction.

At equilibrium,

The rate of forward reaction = The rate of reverse reaction

Therefore,

$$k_f [A] [B] = k_r [C] [D]$$

On rearranging the above relation we get,

$$\frac{[C][D]}{[A][B]} = \frac{k_f}{k_r} = K_c \qquad (7.1)$$

Where, K_c is the ratio of the rate constants (k_f/k_r). It is known as equilibrium constant of the reaction. K_c of the form as given in Eq.7.1 is defined as *the ratio of the product of the molar concentration of the products to that of the reactants.*

For a more general reaction of the following type

$$aA + bB \rightleftharpoons cC + dD$$

Where a, b, c, and d represents the number of moles of the species taking part in the chemical reaction. They are called the coefficient of the species (reactants or products) present in the balanced chemical equation. According to the law of mass action, the equilibrium constant expression is;

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad (7.2)$$

Eq. (7.2) is a general form of the mathematical representation of the equilibrium constant which can more appropriately be defined as *the ratio of the* *product of the molar concentrations of the products to that of the reactants eac raised to the power equal to the coefficients of the respective species that occu in the balanced chemical equation.* Thus, in the light of the above discussion the law of mass action can more appropriately be defined as *the rate of any chemica reaction is proportional to product of the active masses (or activity) of the reactants, with each reactant raised to a power equal to the coefficients of the reactants that occurs in the (balanced) chemical equation at a given temperature.* The value of K_c is independent of the initial concentrations of the reactants and products but changes only with change in temperature. Remember that the concentrations of reactants and the products appearing in equilibrium constant expression (Eq.7.2) are the equilibrium concentrations.

For a gaseous equilibrium, it is some times more convenient to express the concentration of gases in terms of their partial pressures at any given temperature. Let P_A, P_B, P_C, and P_D are the partial pressures of the gaseous species then the equilibrium constant K_p may be expressed as;

$$K_p = \frac{(P_C)^c}{(P_A)^a} \times \frac{(P_D)^d}{(P_B)^b} \qquad (7.3)$$

If the concentrations are expressed in terms of mole fractions, then the equilibrium constant K_X can be represented as;

$$K_X = \frac{(X_C)^c (X_D)^d}{(X_A)^a (X_B)^b}$$

Similarly, in terms of number of moles, the equilibrium constant K_n is written as

$$K_n = \frac{(n_C)^c (n_D)^d}{(n_A)^a (n_B)^b}$$

Here it should be mentioned that how to recognize that equilibrium has been reached. For this purpose the concentration of any of the reactant o product species is monitored, at different time intervals, by analysing them usin any suitable physical or chemical method of analysis. When the concentration o the chosen species becomes constant, after the elapsed interval, it is an indication o the fact that the equilibrium state has been reached.

Self-Assessment

- Define forward and backward reactions with examples.
- Expalin law of mass action with an example.
- Differentiate between homogeneous and heterogeneous equilibrium.

Example 7.1

An equilibrium mixture is found to contain 7g of N_2, 0.3g of H_2 and 1.53g of NH_3 per dm³ at 300°C. Find K_C for the reaction.

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

Solution

$$[N_2]=\text{mol dm}^{-3}\text{ of }N_2=\frac{7g}{28gmol^{-1}}=0.25mol$$

$$[H_2]=0.15mol=\frac{0.3g}{2gmol^{-1}}=0.15mol$$

$$[NH_3]=\frac{1.53g}{17gmol^{-1}}=0.09mol$$

$$K_c=\frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K_c=\frac{[0.09]^2}{[0.25][0.15]^3}=\frac{9.6\ (dm^3)^2}{mol^2}\text{ or }9.6M^{-2}$$

Practice Problem 7.1

Nitrogen and hydrogen are placed in an empty 5.00 dm³ container at 500°C. When equilibrium is established, 3.01 mol of N_2, 2.10 mol of H_2, and 0.565 mol of NH_3 are present. Find the K_c for the following reaction at 500°C.

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

7.1.3. Relationship between Equilibrium Constants (K_c, K_p, K_x, K_n)

i) Relation between K_p and K_c

Consider a general reaction

$$aA + bB \rightleftharpoons cC + dD$$

For an ideal gaseous system, the equilibrium constant expression is written as,

$$K_p=\frac{(P_C)^c}{(P_A)^a}\times\frac{(P_D)^d}{(P_B)^b}$$

Where P represents the partial pressure of the individual gas components present in the equilibrium state.

For 'n' number of moles the ideal gas equation is given as;

$$PV=nRT$$

$$P=(n/V)RT$$

Where P is the partial pressure of the gas and the volume 'V' is c
Since, n/V = C, the molar concentration

Hence, $P = C\,RT$

Substituting the values of partial pressures in Eq.7.3, we get

$$K_p = \frac{(C_C RT)^c}{(C_A RT)^a} \times \frac{(C_D RT)^d}{(C_B RT)^b}$$

$$K_p = \frac{[C_C]^c [C_D]^d}{[C_A]^a [C_B]^b} \times \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

$$K_p = K_c (RT)^{(c+d)-(a+b)}$$

$$K = K\,(RT)^{\Delta n} \qquad (7.4)$$

Where $\Delta n = (c+d) - (a+b)$ is the difference in co-efficients of the produc
reactants in balanced chemical equation. Furthermore, Δn may be positive, ne
or zero. When $\Delta n = 0$, the number of moles of the reactants are equal to the n
of moles of the products and Eq. (7.4) becomes $K_p = K_c$.

ii) Relation between K_P and K_X

According to the Raoult's law of partial pressure, P_A, of any gas compon
for example, is given by

Partial pressure of gas,

$$P_A = \frac{\text{No. of moles of gas A}}{\text{Total number of moles of gases in the mixture}} \times \text{Total pressu}$$

Or P_A = Mole fraction of gas A x total pressure i.e. $P_A = X_A P$

Where X_A is the mole fraction of the gas component A, and P is the
pressure of the system. Eq. (7.3) becomes;

$$K_p = \frac{X_C^c P^c}{X_A^a P^a} \times \frac{X_D^d P^d}{X_B^b P^b}$$

$$K_p = \frac{X_C^c X_D^d}{X_A^a X_B^b} \times \frac{P^{c+d}}{P^{a+b}}$$

$$K_p = \frac{X_C^c X_D^d}{X_A^a X_B^b} \times P^{(c+d)-(a+b)}$$

$$K_p = \frac{X_C^c X_D^d}{X_A^a X_B^b} \times P^{\Delta n}$$

As $$\frac{X_C^c X_D^d}{X_A^a X_B^b} = K_x$$

$$K_p = K_x P^{\Delta n}$$

Since $P=\frac{RT}{V}$ for one mole of an ideal gas

$$K_p = K_x (\frac{RT}{V})^{\Delta n} \qquad ....(7.5)$$

iii) **Relation between K_P and K_n**

K_P can be expressed in terms of K_n when the concentrations are expressed in terms of moles of the gases in the system. Dalton's law of partial pressure can be written as;

$$P_A = X_A P \left(\frac{n_A}{N}\right) = P = \left(n_A . \frac{P}{N}\right)$$

Where n_A is the number of moles of the component gas A and N is the total number of moles of all the gases in the system. Substituting the values of partial pressures of the gases into Eq.(7.3), we get;

$$K_p = \frac{n_C^c \left(\frac{P}{N}\right)^c \times n_D^d \left(\frac{P}{N}\right)^d}{n_A^a \left(\frac{P}{N}\right)^a \times n_B^b \left(\frac{P}{N}\right)^b}$$

$$K_p = \frac{n_C^c \times n_D^d}{n_A^a \times n_B^b} \times \left(\frac{P}{N}\right)^{(c+d)-(a+b)}$$

$$K_p = \frac{n_C^c \times n_D^d}{n_A^a \times n_B^b} \times \left(\frac{P}{N}\right)^{\Delta n} \qquad \text{Where } K_n = \frac{n_C^c \times n_D^d}{n_A^a \times n_B^b}$$

$$K_p = K_n \left(\frac{P}{N}\right)^{\Delta n} \qquad ....(7.6)$$

Thus, Eqs. (7.4), (7.5) and (7.6) show the relationship between K_P, K_C, K_X and K_n. These are related to each other as follows;

$$K_p = K_c (RT)^{\Delta n} = K_X \left(\frac{RT}{V}\right)^{\Delta n} = K_n \left(\frac{P}{N}\right)^{\Delta n}$$

If the number of moles of the reactants is equal to the number of moles of the products, then $\Delta n=0$ and $(RT)^{\circ}=1$, $\left(\frac{RT}{V}\right)^{\circ}=1$ and $(P/N)^{\circ}=1$, for such reaction;

$$K_p=K_c=K_X=K_n$$

Example 7.2

Equilibrium constant, K_P at 523 K is 0.82. Find K_c at the same temperature for the following reaction.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

Solution:

$T=523K$

$R=0.082dm^3\,atmK^{-1}mol^{-1}$

$K_p=0.82$

$\Delta n=(1+1)-1 = 1\ mol$

$K_p=K_c(RT)^{\Delta n}$

$0.82=K_c(0.082\times523)^1$

$K_c=0.82/0.082\times523$

$=1.91\times10^{-2}mol.dm^{-3}$

Practice Problem 7.2

We put 10.0 moles of N_2O into a 2.00 dm^3 container at some temperature, where it decomposes according to

$$2N_2O_{(g)} \rightleftharpoons 2N_{2(g)} + O_{2(g)}$$

At equilibrium, 2.20 moles of N_2O remain. Calculate the value of K_c for the reaction.

7.1.4 Importance of K_c and Reaction Quotient

The equilibrium constant can be used to predict the following:

1. The direction in which a chemical system would proceed to acquire an equilibrium state.
2. The extent to which a reaction will proceed before equilibrium is reached.
3. To calculate equilibrium concentrations of reactants and products if the initial concentrations are known.
4. The effect of change in conditions upon a chemical system in a state of equilibrium.

7.1.4.1 Prediction of Direction of Reactions and Reaction Quotient

According to law of mass action, equilibrium constant for any reaction is given by the relationship,

$$k_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

Where [Reactants] and [Products] are the equilibrium concentrations of the reactants and products, respectively. Hence, we come to know that at equilibrium only certain concentrations of the reactants and products are possible for a given reaction. The direction of a reaction at any time during the reaction can be predicted by means of the above relationship, before the reaction attains equilibrium. Initially, we can bring together the reactants or products in just about any concentrations (or partial pressures). An expression is built up which has the same form as Kc.

$$Q_c = \frac{[\text{Products}]_o}{[\text{Reactants}]_o}$$

Such an expression is called expression for the reaction quotient, Qc. The reaction quotient is not constant for the given reaction but it is quite useful in predicting the direction in which a net reaction must proceed to establish equilibrium. For example, the reaction quotient for the synthesis of $SO_{3(g)}$ is

$$2SO_{2(g)} + O_2 \rightleftharpoons 2SO_{3(g)}$$

$$Q_c = \frac{[SO_3]^2_o}{[SO_2]^2_o[O_2]_o}$$

Q_c has the same algebraic form of the concentration terms as does the K_c. We call them initial concentrations, represented as $[\,]_o$ and they are not necessarily the equilibrium concentrations. A certain value of is obtained when a set of initial concentrations are substituted into the equation of reaction quotient. In order to predict whether the system is at equilibrium or not, the magnitude of must be compared with that of Kc. Therefore, when

i. $Q_c = K_c$, the reaction is at equilibrium.
ii. $Q_c > K_c$, the system is not at equilibrium and the net reaction will occur in the reverse direction until equilibrium is reached.
iii. $Q_c < K_c$, the system is not at equilibrium and the net reaction will occur in the forward direction until equilibrium is established.

Example 7.3

For the dissociation of HI

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

K_c at 520°C is 1.6×10^{-2}. Predict the direction in which the system will move to attain the equilibrium if the initial concentration of HI is 1.02M and that of H_2 and I_2 are 0.01M each.

Solution:

$$Q_c = \frac{[H_2]_o [I_2]_o}{[HI]_o^2} = \frac{[0.01]_o [0.01]_o}{[1.02]_o^2} = 9.61 \times 10^{-5}\ M$$

Since the initial concentration ratio, 9.61×10^{-5}, is less than the given value of K_c, 1.6×10^{-2}, hence, the reaction will proceed in the forward direction and HI will dissociate further.

Practice Problem

At a very high temperature, $K_c = 65.0$ for the following reaction.

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

The following concentrations were detected in a mixture. Is the system at equilibrium? If not, in which direction must the reaction proceed for equilibrium to be established?

$[HI] = 0.500\ M$, $[H_2] = 2.80\ M$, and $[I_2] = 3.40\ M$

7.1.4.2 Prediction of the Extent of a Chemical Reaction

The extent of the reaction can be found from the value of the equilibrium constant.

i) If the equilibrium constant, K_c, is very large, then this indicates that the reaction is almost complete. The concentration of products is much greater than those of reactant at equilibrium.

ii) If the value of K_c is very small, then the reaction proceeds a little in the forward direction, and a small amount of product is formed at equilibrium.

iii) If the value of K_c is neither very small nor very large, this shows that both the reactants and products are in appreciable quantities at equilibrium.

Example 7.4

Predict the extent of the given reaction for which the equilibrium constant is 1×10^{-30} at 25°C.

Solution:

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

Since the value of $K_c = 1 \times 10^{-30}$, which is very small for this system, an equilibrium mixture of the three gases at 25°C will contain very little NO as compared to N_2 and O_2.

7.1.4.3. Calculation of the Equilibrium Concentrations

If the value of equilibrium constant and the initial concentrations of the reactants are known for a particular reaction, we can calculate the concentrations in the equilibrium mixture. This will be illustrated by following example.

Example 7.5

1.0 mole of hydrogen and 1.0 mole of iodine come to equilibrium at 457.7°C in a one dm^3 flask. What will be the concentration of each substance at equilibrium? Where K_c=48.9

Solution:

	$H_{2(g)}$	$+ I_{2(g)}$	$\rightleftharpoons$	$2HI_{(g)}$
Initial concentration in moles	1	1		0
Equilibrium concentrations	$1-x$	$1-x$		$2x$

$$K_c=48.9=\frac{[HI]^2}{[H_2][I_2]}=\frac{(2x)^2}{(1-x)(1-x)}=\frac{(2x)^2}{(1-x)^2}$$

$$\frac{2x}{(1-x)}=\sqrt{48.9}$$

$$x=\frac{6.99}{8.99}=0.778$$

Hence,

$$[H_2] = 1.0 - 0.778 = 0.222\ M$$

$$[I_2] = 1.0 - 0.778 = 0.222\ M$$

$$[HI] = 2 \times 0.778 = 1.556\ M$$

Practice Problem 7.4

The equation for the following reaction and the value of K_c at a given temperature are given. An equilibrium mixture in a 1.00 liter container contains 0.25 mol of PCl_5 and 0.16 mol of PCl_3. What equilibrium concentration of Cl_2 must be present? K_c = 1.9

$$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$$

7.2 Factors Affecting Equilibrium

Once a system has attained equilibrium, it is possible to change its position by changing the external conditions i.e., concentration, pressure, temperature etc. Chemists are interested in finding the best conditions to obtain maximum yield of the products in reversible reactions by favorably shifting the position of equilibrium of a reaction. For this purpose Le-Chatelier's principle is used.

Le-Chatelier's Principle

A French chemist Henry Le-Chatelier (1884) studied the effect o concentration, temperature, and pressure on a large number of systems i equilibrium. He summed up his conclusions in the form of a generalizatio known as Le-Chatelier's Principle. The principle states that "*if a system a equilibrium is subjected to a stress by a change in temperature, pressure o concentration, the system tends to adjust itself so as to minimize the effect o that change*".

This principle is a general one and is applicable to all physical and chemical equilibriums. We shall now explain the application of this principle to the following changes.

7.2.1 Effect of change in Concentration

If the concentration of one or more of the substances present in equilibrium is changed, the system is no longer in a state of equilibrium. According to Le-Chatelier's Principle the system will undergo changes in the concentration of various components so as to restore the equilibrium in the system. Consider for example the formation of NO.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

$$K_c = \frac{[NO]^2}{[N_2]\,[O_2]}$$

i) Adding N_2 or O_2 disturbs the position of equilibrium and as a result the reaction moves in the forward direction so a greater yield of NO is obtained till equilibrium is re-established.

ii) Removing nitric oxide (NO) causes the forward reaction to occur so that part of the NO removed from the system is reproduced.

7.2.2 Effect of change in Pressure or Volume

Liquids are relatively incompressible, changing the pressure above a liquid solution has negligible effect on the concentration of dissolved substance. Consequently, changes in external pressure have very little effect on equilibrium systems that contain only solids (incompressible) or liquids. In contrast, because gases are highly compressible, their concentrations vary considerably with pressure. From the ideal gas law, PV = nRT, the concentration (C) of a gas is related to its pressure as follows:

$$C = \frac{n}{V} = \frac{P}{RT}$$

Hence, the concentration in any gaseous reactant or product is directly proportional to the applied pressure and inversely proportional to the total volume (V). Consequently, the equilibrium compositions of system that contain gaseous substances are quite sensitive to changes in pressure, volume and temperature.

Consider the following examples:

(a) Effect of pressure on the formation of No$_2$

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

From the stoichiometry of the reaction, the ratio of N_2O_4 to $2NO_2$ is 1 to 2. Hence, by Avogadro's law this can be expressed as 1 to 2 volume ratio (1:2). By increasing pressure, a state of lower volume is favoured. Hence, the equilibrium moves towards the lower volume side i.e. reactant side and more will be produced (i.e. reverse reaction is favoured) and vice versa.

(b) Effect of pressure on the decomposition of HI.

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

The reaction shows that there is no change in volume during the decomposition of HI. Hence, there will be no effect of change in pressure on the equilibrium concentrations of reactants and products.

(c) Effect of pressure on thermal decomposition of PCl_5

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

In this reaction, one mole of reactant gives two moles of product after decomposition, all in gasous state. The effect of pressure on this system will result in decrease in volume which results when reaction goes from right to left in the reactant side. Thus this reaction is favourable under low pressure.

7.2.3 Effect of change in Temperature

If the temperature of a system at equilibrium is changed, the value of the equilibrium constant also changes. According to the Le-Chatelier's principle, *if the temperature of a reaction increases, the equilibrium shifts in the endothermic direction i.e. the direction in which heat is absorbed in an attempt to lower the temperature.*

Consider the following reactions, $\Delta H = -41.84 \text{kJ mol}^{-1}$

$$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$$

Since the reaction is exothermic in the forward direction and its reverse direction is endothermic so an increase in temperature would shift the equilibrium in the backward direction.

$\Delta H = 180.5 \text{ kJ mol}^{-1}$

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$$

The formation of NO_2 is an endothermic reaction. Thus according to Le Chatelier Principle, a high temperature will favour the formation of NO. Practically, the temperature used for its formation is about 3000°C.

7.2.4 Effect of Catalyst on Equilibrium

The presence of a catalyst does not affect the equilibrium constant value of reaction. A catalyst only increases the rate of a reaction by lowering the activatio energy of the reaction and thus equilibrium state is reached earlier. Since th increase in rate constant applies to both forward and reverse reactions so the ne effect is that there is no change in the value of the equilibrium constant or the position of equilibrium.

Self-Assessment

1. What are the effects of change in concentration and pressure on equilibrium.
2. Explain the relationship between K_p and K_x.
3. What are the uses of equilibrium constant.
4. Define Le-Chatelier's Principle.

7.3 Industrial Applications of Le-Chatelier's Principle

Haber's Process: Let us consider the synthesis of ammonia which is of great importance in industry used in the manufacture of nitrogen fertilizers.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons NH_{(g)} \qquad \Delta H = -92.384\ kJ\ mol^{-1}$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

i. Effect of Concentration

If nitrogen or hydrogen is added to the equilibrium mixture then more amount of ammonia will be formed according to Le-Chatelier's principle. This is due to the fact that an increase in the concentration of N_2 or H_2 will result in shifting the equilibrium towards right. If ammonia is removed from reaction chamber, the forward reaction must be favoured. Hence, efficient removal of ammonia results in a greater yield of ammonia.

ii. Effect of Pressure

According to the Le-Chatelier's principle, an increase in pressure on this system in equilibrium state, will change the system in a direction in which the volume is decreased. Since one volume of nitrogen and three volumes of hydrogen react to form two volumes of ammonia or a decrease in volume takes place in the forward direction, hence, the formation of ammonia will be favoured by high pressure.

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For industrial processes, it is important to maximize the concentration of the desired products and minimize the 'leftover' reactants. Le-Chatelier's Principle and the principles of reaction kinetics can both be used to design the best reaction conditions to give the highest possible yield of product in an economic way.

Formation of SO_3 for the Manufacture of H_2SO_4

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad \Delta H=-395.7kJmol^{-1}$$

Applying law of mass action

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

According to Le-Chatelier's principle, the addition of SO_2 or O_2 at equilibrium results in a greater yield of SO_3. The process is accompanied by a decrease in volume so it is favoured by slightly higher pressure (1.5 —1.7 atm.). Since the forward reaction is exothermic, the equilibrium will be shifted towards the product side by lowering the temperature. The optimum temperature for this reaction is 400—500°C.

iii. Effect of Temperature

The formation of ammonia from its elements is an exothermic reaction, and its reverse reaction is endothermic. Thus, the increase of temperature results in the increased dissociation of ammonia and decrease in temperature results in the increased production of ammonia. In practice, at lower temperature the reaction proceeds rather slowly and equilibrium is attained in a longer time.

Thus, a suitable temperature at which reaction occurs at reasonable rate and results in a reasonable production of products is selected, which is called optimum temperature. Hence, the synthesis of ammonia is carried out at 400 to 450℃(optimum temperature)in the presence of finely divided iron which acts as a catalyst and a high pressure of 200—500 atm.

7.4 Solubility Product and Precipitation Reactions

When a sparingly soluble salt such as AgCl is shaken with water it dissolves until a saturated solution is formed. The solution contains Ag^+, Cl^- ions and un-dissolved AgCl. It means that equilibrium between dissolved Ag^+ and Cl^-

ions, and un-dissolved AgCl is established.

$$AgCl_{(s)} \xrightleftharpoons{H_2O} Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$

Applying law of mass action, the equilibrium constant is

$$K_c = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

Since the concentration of a pure solid [AgCl] is constant, therefore, can write,

$$K_c [AgCl] = [Ag^+][Cl^-]$$

If $K_c [AgCl] = K_{sp}$

then $K_{sp} = [Ag^+][Cl^-]$

K_{sp} is called the solubility product. In general, *the solubility product substance is the product of molar concentrations of its ions in the satura solution each raised to an exponent equal to the coefficient of each ion in balanced equation*. K_{SP} is usually very small quantity at room temperature. value of Ksp is temperature dependent. In general, for a sparingly solu substance, A_xB_Y the equilibrium equation is

$$A_xB_{y(s)} \rightleftharpoons xA^{y+}_{(aq)} + yB^{x-}_{(aq)}$$

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

Example 7.6

Calculate the concentration of Pb^{+2} ions when solid $PbSO_4$ is added water. The solubility product of $PbSO_4$ is 1.6×10^{-8}.

$$PbSO_{4(s)} \rightleftharpoons Pb^{+2}_{(aq)} + SO^{-2}_{4(aq)}$$

$$K_{sp} = [Pb^{+2}][SO_4^{-2}] = 1.6x10^{-8}$$

From the above chemical equation $\left[Pb^{+2}\right] = \left[SO_4^{-2}\right]$

Let $\left[Pb^{+2}\right] = x \text{mol dm}^{-3}$ Then $\left[SO_4^{-2}\right] = x \text{mol dm}^{-3}$

$$K_{sp} = [x][x] = 1.6 \times 10^{-8}$$

$$\left[Pb^{+2}\right] = [x]^2 = 1.6 \times 10^{-8}$$

$$\left[Pb^{+2}\right] = x^2 = \sqrt{1.6 \times 10^{-8}}$$

$$\left[Pb^{+2}\right] = 1.265 \times 10^{-4} \ \text{M}$$

Applications

The solubility product principle can be used to predict whether precipitation will occur or not under given concentrations and conditions. Solubility product constant is the product of concentration of ions of electrolyte in a saturated solution each raised to the power of their coefficients in the balanced chemical equation. It is valid only for saturated solution and is constant for a solution at a given temperature. On the other hand, ionic product is the product of concentrations of ions of electrolyte at any concentration of solution each raised to the power of their coefficients in the balanced chemical equation.

The values of ionic product (IP) and solubility product constant (K_{sp}) of a solution help to know whether the solution is saturated, unsaturated or supersaturated. These three situations are discussed below.

(1) $IP = K_{sp}$

When actual amount of ions in solution is maximum, the resulting solution will be saturated but there is no precipitation.

(2) $IP < K_{sp}$

When actual amount of ions is less than equilibrium concentration, the solution will be unsaturated and there is no precipitation.

(3) $IP > K_{sp}$

When actual amount of ions is more than equilibrium concentration, the solution will be supersaturated and is accommodating more ions than it can keep in solution.

A supersaturated solution does not stay supersaturated and it has to precipitate out the excess ions that it cannot handle or hold in solution. The resultant outcome will be saturated solution and precipitate.

Practice Problem 7.5

Calculate the solubility of silver acetate, CH_3COOAg, in mol/dm^3, given the K_{sp} value for silver acetate, CH_3COOAg is $Ksp = 1.9 \times 10^{-3}$.

7.5 Common Ion effect

It is a phenomenon in which the extent of dissociation (or solubility) any weak electrolyte is suppressed by the presence of small amount of a stro electrolyte having a common ion with the weak electrolyte. In other words t shift of equilibrium towards left side, caused by the addition of an electroly having an ion in common with the dissolved electrolyte is called common i effect. Consider the following examples for explanation of common ion effect.

Example 7.7 Dissociation of Weak Acid

Ionization of weak electrolyte, acetic acid (CH_3COOH), is suppressed b adding strong electrolyte such as sodium acetate (CH_3COONa), containin common ion that is acetate ion (CH_3COO^-). Acetic acid in water dissociates an an equilibrium exists as follows.

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-{}_{(aq)} + H^+{}_{(aq)} \quad (i)$$

The acid dissociation constant, K_a, for this dissociation is written as;

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

When a small amount of strong electrolyte, like sodium acetate (CH_3COONa), is added to the aqueous solution of CH_3COOH, it gets dissociated as follows.

$$CH_3COONa_{(s)} \xrightarrow{H_2O} CH_3COO^-{}_{(aq)} + Na^+{}_{(aq)}$$

Here acetate ions (CH_3COO^-) are common in CH_3COOH and CH_3COONa. According to Le-Chatelier's principle equilibrium, (i), shifts towards left to keep the value of K_a constant, thus the concentration of CH_3COOH molecules is increased. In this way ionization of CH_3COOH is suppressed by adding CH_3COONa.

Example 7.8 Dissociation of Weak Base

Ionization of weak electrolyte such as ammonium hydroxide (NH_4OH), is suppressed by adding strong electrolyte, i.e. ammonium chloride (NH_4Cl) containing common ammonium ions (NH_4^+). NH_4OH dissociates in water as follows,

$$NH_4OH_{(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

The equilibrium constant i.e. base dissociation constant, K_b, is written as

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

If a small amount of strong electrolyte like ammonium chloride (NH_4Cl) is added to the aqueous solution of NH_4OH, it gets dissociated as follows

$$NH_4Cl_{(s)} \xrightarrow{H_2O} NH^+_{4(aq)} + Cl^-_{(aq)}$$

Here ammonium ions are common in NH_4OH and NH_4Cl and addition of NH_4Cl increases the concentration of NH_4^+ ions. Thus according to Le-Chatelier's principle, equilibrium of NH_4OH shifts towards left to keep the value of K_b constant, the concentration of NH_4OH molecules is increased. In this way ionization of NH_4OH is suppressed by adding NH_4Cl.

Example 7.9

Purification of NaCl is carried out by passing HCl gas through a saturated solution of NaCl.

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

$$HCl_{(g)} \xrightarrow{H_2O} H^+_{(aq)} + Cl^-_{(aq)}$$

Cl^{-1} is a common ion due to which equilibrium shifts to the backward direction whereby NaCl precipitates.

Reading Check

- Define common ion effect.
- Explain the solubility product of a substance with an example.

KEY POINTS

- In a chemical reaction when the rate of forward reaction becomes equal to the rate of backward reaction, the reaction is in the state of dynamic equilibrium.
- According to the Law of Mass Action, the rate at which a substance reacts, is directly proportional to its active mass and the rate of reaction is directly proportional to the product of active masses of the reacting substances.
- Equilibrium constant of the reaction, K_c,is defined as the ratio of the product of the molar concentrations of the products to that of the reactants.
- A large value of equilibrium constant, K_c,indicates that the reaction is almost complete. If the value of K_c is very small, then the reaction proceeds a little in the forward direction rather the reverse reaction is favoured.
- Le-Chatelier's Principle states that "if a stress is applied to a system at equilibrium, the equilibrium will shift in the forward or backward direction to reduce the effect of stress".
- The catalyst has no effect on the equilibrium composition of a reaction. However, it increases the rate of the reaction by lowering its energy of activation.
- If a soluble salt (say A^+C^-) is added to another less soluble salt (A^+B^-) containing a common ion A^+, the dissociation of A^+B^- is suppressed. It is called common ion effect.

EXERCISE

Choose the correct answer.

1. In which of the following values of K_c, the reaction goes to completion in the forward direction:
   a) 10^2 b) 10^{30} c) 10^{-30} d) 1
2. An appreciable amount of the product and reactants is present in a reaction if its equilibrium constant value is:
   a) Negative and large b) Negative and small
   c) Zero d) Neither large nor small.
3. Consider
   $$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = 92.46 kJ/mol$$
   The optimum temperature for the production of ammonia is:
   a) 5000 °C b) 450 °C c) 0°C d) Constant temperature
4. In the production of SO_3 from SO_2 and oxygen. The yield of SO_3 is increased by
   a) increasing temperature b) adding a catalyst
   c) adding more SO_2 d) removing O_2
5. Le-Chatelier's principle applies to
   a) mechanical system b) physical system
   c) chemical system d) both b and c
6. The unit of K_c for the system $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is
   a) mol^2/dm^6 b) dm^3/mol
   c) mol/dm^6 d) mol/dm^3
7. Forward reaction goes virtually to completion when K_c is
   a) positive and small b) positive and large
   c) negative and large d) unity
8. Endothermic reactions are favoured in the forward direction by
   a) cooling b) freezing
   c) heating d) adding a catalyst
9. Molecules of chlorine decompose to a very small extent into atomic chlorine i.e. $Cl_2 \rightleftharpoons 2Cl$; this is because K_c of this reaction is
   a) very large b) very small c) zero d) 1

10. How much reaction is complete when $K_c = 1$ for the system

$$A + B \rightleftharpoons C + D$$

a) 10% b) 25% c) 50% d) 100%

11. HCl when added to H_2S solution

a) suppresses the ionization of H_2S b) enhances the ionization
c) solution becomes coloured d) does not affect

12. The value of K_p is greater than K_c when the difference of the moles of th products and reactants is

a) zero b) positive c) negative d) one

Write answers for the given short questions.

1. The change in temperature changes the equilibrium position of th reaction $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ but change in pressure does not, why

2. Give the units of K_p for the following reversible reactions.
   a) $PCl_{5(g)} \rightleftharpoons PCl_{3\,(g)} + Cl_{2\,(g)}$
   b) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
   c) $H_{2(g)} + CO_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$
   d) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

3. Why does the value of K_c fall with the rise in temperature for the synthes of SO_3?

   $$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H = -94.58\,kJmol^{-1}$$

4. There is a dynamic rather than static equilibrium present between liqu and vapour at constant temperature; explain.

5. The change in concentration of reactants does not change the value equilibrium constant permanently, elaborate.

6. Discuss the equilibrium of a sparingly soluble salt.

7. Common ion effect operates best in the purification of certain substance explain.

8. The ionization of calcium oxalate is suppressed by adding $CaCl_2$ to it, why

9. The solubility of a sparingly soluble substance is calculated from th solubility product data, explain.

Numerical Questions

1. Calculate K_c for the synthesis of ammonia at 500°C. $K_p = 1.44 \times 10^{-5}$.

(Ans: 5.8 X 10

2. The solubility of CaF_2 in water at 25°C is found to be 2.05×10^{-4}M. What is the K_{sp} at this temperature? (Ans: 3.446×10^{-11})
3. The solubility product of AgCl is 1.8×10^{-10}. Calculate the molar solubility of the salt. (Ans: 1.34×10^{-5}M)
4. A mixture of 0.5 moles of H_2 and I_2 each was placed in a one litre flask at 400°C. Calculate the concentration of H_2, I_2 and HI at equilibrium. The K_C for the reaction is 54.3. (Ans: $[H_2] = [I_2] = 0.107$M, $[HI] = 0.786$M)
5. The equilibrium mixture contains 1 mole of PCl_5, 0.3 mole of PCl_3 and 0.08 mole of Cl_2 in a 10 L flask. Calculate K_c. (Ans: $K_c = 2.40 \times 10^{-3}$)
6. The equilibrium concentration of N_2 and O_2 is 0.25M each while its K_c is 0.1 at 2000°C. Calculate the equilibrium concentration of NO according to the following reaction.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

(Ans:[NO]=0.079M)

Descriptive Questions

1. Write down K_c for the following reversible reactions.
   i. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$
   ii. $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$
   iii. $H_{2(g)} + CO_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$
   iv. $2N_2O_{5(g)} \rightleftharpoons 4NO_{2(g)} + O_{2(g)}$
2. Predict the effect of increasing pressure on the following gaseous equilibria.
   i. $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$
   ii. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$
   iii. $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$
   iv. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
3. Derive the relationship between K_P and K_C.
4. What is the solubility product? Derive the solubility product expression for slightly soluble AgBr, $CaCO_3$, $Al(OH)_3$ and $PbCrO_4$.
5. Explain the following.
   i. (a) State the Law of Mass Action and derive the equilibrium constant expression for the given equation.

$$A+B \rightleftharpoons C+D$$

(b) Given the equilibrium concentrations of N_2, O_2 and NO as 0.05M, 0.05M, and 5.5×10^{-4}M respectively. Calculate K_C for the decomposition of NO at 1500°C for the reaction. (Ans: 8.26×10^3)

ii. Find the value of equilibrium constant K_C for following reaction.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

The equilibrium concentrations are $[SO_2] = 0.90M$, $[O_2] = 0.35M$ and $[SO_3] = 1.1M$. (Ans: 4.3)

ii. (a) State Le-Chatelier's principle and discuss its application to ammonia system.

(b) What is the effect of raising temperature on each of the following equilibria.

i. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H = -ve$

ii. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$ $\Delta H = -ve$

iii. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ $\Delta H = -ve$

iv. $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ $\Delta H = +ve$

iv. (a) With the help of chemical equilibrium constant expression, how will you predict the direction and the extent of a chemical reaction?

(b) The equilibrium constant for the reaction, $2O_3 \rightleftharpoons 3O_2$ is 1.0×10^{50} at 25°C. Predict the extent of the formation of O_2 at room temperature.

Project

Take two test tubes, add about 10 cm³ solution of potassium chromate (K_2CrO_4) in both of them. Note the colour of the solution. Place one test tube in test tube stand for colour comparison purpose and add dil.HCl solution to the second test tube till the colour changes from yellow to orange. Now add a few cm³ solution of dil. NaOH. You will observe that the yellow colour appears again. Compare the colour with that of the first test tube solution.

The reaction that is taking place due to the addition of acid is the following.

$$\underset{\text{Yellow}}{2CrO_{4(aq)}^{-2}} + 2H^+_{(aq)} \rightleftharpoons \underset{\text{Orange}}{Cr_2O_{7(aq)}^{-2}} + H_2O$$

Questions:

i. Which principle is governing this reaction to bring it from left to right and back?

ii. Why the reaction go back from right to left by the addition of base?

Unit-08

Acids, Bases and Salts

After reading this unit, the students will be able to:

- Define Bronsted and Lowery concepts for acids and bases. (Remembering)
- Define salts, conjugate acids and conjugate bases. (Remembering)
- Identify conjugate acid-base pairs of Bronsted–Lowery acid and base. (Analyzing)
- Explain ionization constant of water and calculate pH and pOH in aqueous medium using given K_w values. (Applying)
- Use the extent of ionization and the acid dissociation constant, K_a, to distinguish between strong and weak acids. (Applying)
- Use the extent of ionization and the base dissociation constant, K_b, to distinguish between strong and weak bases. (Applying)
- Define a buffer and show with equations how a buffer system works. (Applying)
- Make a buffered solution and explain how such a solution maintains a constant pH, even with the addition of small amounts of strong acid or strong base. (Understanding)
- Use the concept of hydrolysis to explain why aqueous solutions of some salts are acidic or basic. (Applying)
- Use concept of hydrolysis to explain why the solution of a salt is not necessarily neutral. (Understanding)
- Define and explain leveling effect. (Understanding)

Teaching

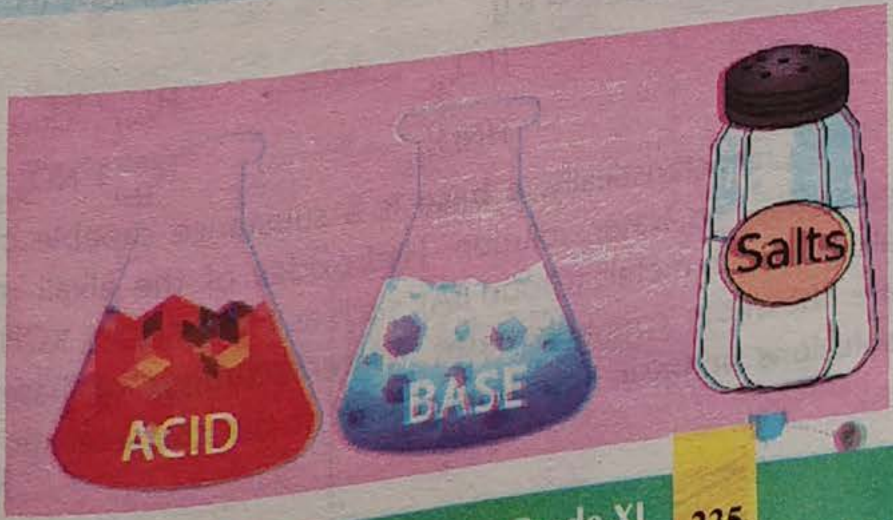
08

Assessment

01

Weightage %

06



Introduction

Acids and bases play key roles in your bodies, homes and in industrial society. Proteins, enzymes, blood and other components of living matter contain both acids and bases.

Acids were originally identified by their sour taste. Now they are recognized by the colour changes of dyes called indicators and by their reactions with metal oxide, hydroxide and carbonates and also with metals themselves. All of these reactions produce ionic compounds called salts.

Bases were originally identified by their slippery feel. Now they are recognized by their effect on indicators and by the fact that they react with or neutralize acids. If a base dissolves in water, it is called an alkali.

You have already learnt about acids and bases in grade X. In this unit, you will recall the Bronsted- Lowery concept and Lewis concept for acids and bases. You will also study in this unit about conjugate acid - base pairs, strength of acids and bases, pH and pOH, buffer solutions and their applications etc.

8.1 Acidic, Basic and Amphoteric Substances

The word "acid" is derived from the Latin word "acidus", meaning "sour". Some of the characteristic properties commonly associated with ***acids*** are the following:

1. Sour taste
2. The ability to change the colour of litmus, from blue to red
3. The ability to react with,
   - Metals such as zinc and magnesium to produce hydrogen gas
   - Hydroxide bases to produce water and an ionic compound (salt)
   - Carbonates to produce carbon dioxide gas.

These properties are due to the hydrogen ions (H^+) that are released by acids in a water solution e.g.

$$HCl_{(g)} \xrightarrow{H_2O} H^+_{(aq)} + Cl^-_{(aq)}$$

$$HNO_{3(\ell)} \xrightarrow{H_2O} H^+_{(aq)} + NO^-_{3(aq)}$$

Characteristically, a **base** is a substance capable of liberating hydroxide ions (OH^-), in water solution. Hydroxides of the alkali metals (Group IA) and alkaline earth metals (Group IIA), such as LiOH, NaOH, KOH, $Ca(OH)_2$ and $Ba(OH$ are the most common bases. Water solutions of bases are called ***alkaline*** **solutions or basic solutions.** Some of the characteristic properties common associated with bases are the following:

1. Bitter taste
2. A slippery, soapy feeling
3. The ability to change litmus from red to blue
4. The ability to interact with acids

Their properties are due to the hydroxide ions (OH^-), released by bases in a water solution.

$$NaOH_{(s)} \xrightarrow{H_2O} Na^+_{(aq)} + OH^-_{(aq)}$$

$$Ca(OH)_{2(s)} \xrightarrow{H_2O} Ca^{++}_{(aq)} + 2OH^-_{(aq)}$$

The process of neutralization of an acid by a base is represented by the reaction of H^+ with OH^- to form water.

$$H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(\ell)}$$

The substance, which behaves as an acid in basic solution and acts as a base in acidic solution is called amphoteric substance. For example, Water is the most common amphoteric substance. Water may either gain or lose a hydrogen ion (proton) under the appropriate conditions. A substance is said to be amphoteric if it can behave both as an acid and as a base.

For example, water is an amphoteric substance, which behaves as an acid and donates a hydrogen ion (proton) to a base.

$$NH_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

Water accepts a hydrogen ion (proton) and behaves as a base when reacts with hydrochloric acid.

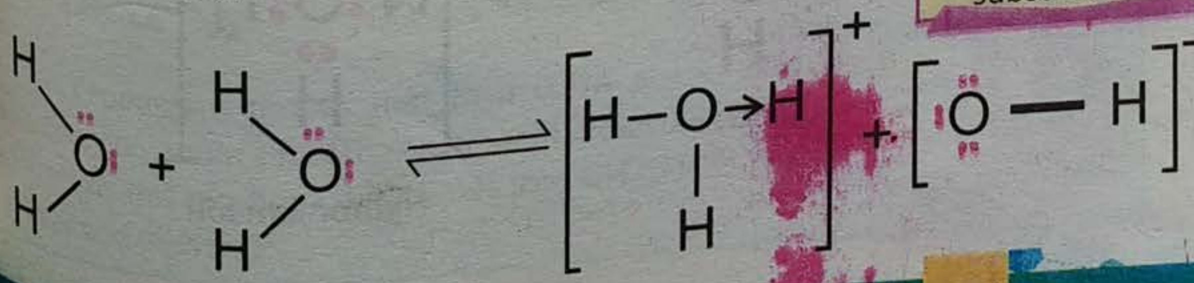
$$HCl_{(aq)} + H_2O_{(\ell)} \rightleftharpoons Cl^-_{(aq)} + H_3O^+_{(aq)}$$

This phenomenon can also be seen clearly in the autoionization (self) of water, which involves the transfer of a proton from one water molecule to another to produce a hydroxide ion and a hydronium ion.

Reading Check

Define acid, base and amphoteric substance.

$$\underset{\text{acid(1)}}{OH_2} + \underset{\text{base(1)}}{H_2O} \rightleftharpoons \underset{\text{acid(2)}}{H_3O^+} + \underset{\text{base(2)}}{OH^-}$$



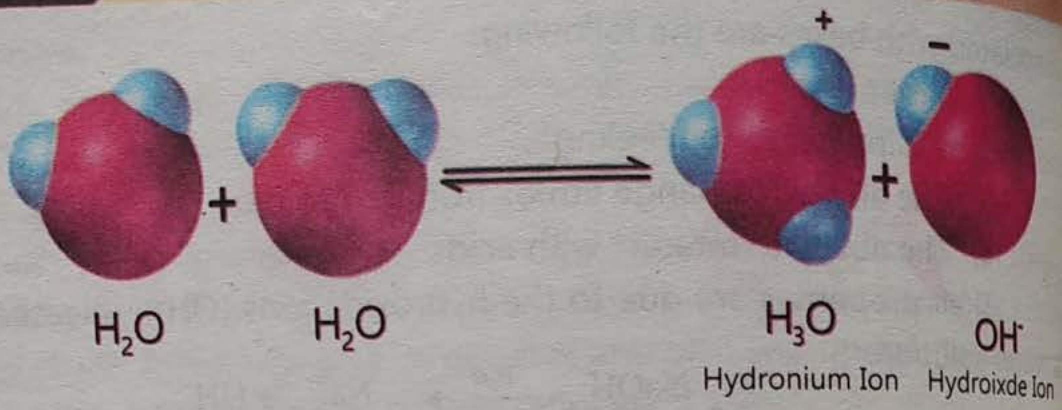


Figure 8.1 Autoionization (self) of Water

8.2 Bronsted – Lowery Definitions of Acids and Bases

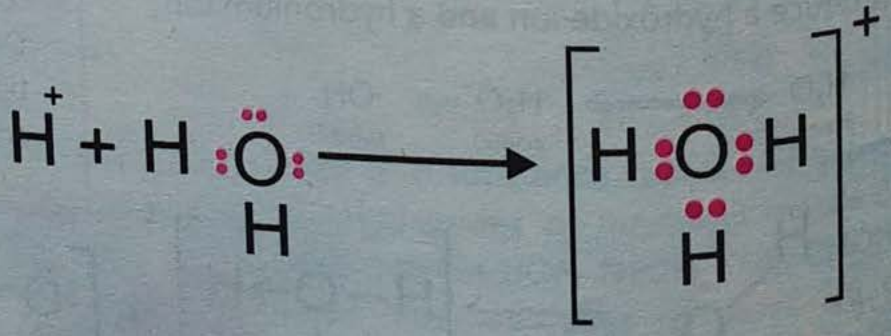
The limitations of the Arrhenius theory of acids and bases are overcom by a more general concept, called the Bronsted-Lowery concept. The Bronsted Lowery concept defines acids and bases as follows.

An acid is a species (molecule or ion) which donates or tends to donate proton, whereas, a base is a species (molecule or ion) which accepts or tends t accept a proton.

Tidbit

Hydronium ion

A hydrogen ion (H^+) is nothing more than a proton and does not exist b itself in an aqueous solution. In water H^+ combines with water molecule to form hydrated hydrogen ion (H_3O^+) commonly called a **hydronium ion**. For simplicit it is often used as H^+ instead of H_3O^+ in equations, with the clear understandin that H^+ is always hydrated in solution.



Hydronium Ion

8.2.1 Proton Donors and Acceptors

In acid-base reaction, the acid gives up proton (H^+) and a base accept it i.e. the transfer of a proton from an acid to a base occurs. In other words, a proton donor is an acid and a proton acceptor is a base. For example, hydrochloric acid (HCl) reacts with ammonia (NH_3) to form solid ammonium chloride (NH_4Cl). Hydrochloric acid (HCl) gives up a proton and ammonia accepts it.

$$HCl_{(aq)} + NH_{3(aq)} \rightleftharpoons NH^{+}_{4(aq)} + Cl^{-}_{(aq)}$$

Unlike the Arrhenius theory, however, the Bronsted-Lowery theory is not restricted to aqueous solutions.

8.2.2 Relative Strength of Acids and Bases

The Bronsted–Lowery concept considers an acid–base reaction as a proton-transfer reaction. *The stronger acids are those, which lose their protons more easily than other acids. Similarly, the stronger bases are those that hold on to protons more strongly than other bases.*

By comparing various acid–base reactions, you can observe relative strengths of acids and bases in table 8.1.

An acid is strong if it completely ionizes in water. For example, consider the reaction of hydro chloric acid with water.

$$\underset{\text{Acid}}{HCl_{(aq)}} + \underset{\text{base}}{H_2O_{(l)}} \longrightarrow \underset{\text{Base}}{Cl^{-}_{(aq)}} + \underset{\text{acid}}{H_3O^{+}_{(aq)}}$$

This reaction occurs in reverse only to an extremely small extent. Because the reaction goes almost completely to the right, so the HCl is a strong acid. The reason that HCl is a strong acid, as it loses its proton readily, more readily than H_3O^+ does. You would say that HCl is a stronger acid than H_3O^+.

As another example, look at the ionization of acetic acid (CH_3COOH), in water.

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^{-}_{(aq)} + H_3O^{+}_{(aq)}$$

Experiment proves that in a 0.1M acetic acid solution, only about 1% of the acetic acid molecules have ionized by this reaction. This shows that CH_3COOH is a weaker acid than H_3O^+.

Quick Check

What is mean by relative strength of acid and bases?

Table 8.1 Relative Strengths of Acids and Bases

	Acid	Conjugate Base	
Strongest Acids	$HClO_4$	ClO_4^-	**Weakest Bases**
	H_2SO_4	HSO_4^-	
	HI	I^-	
	HBr	Br^-	
	HCl	Cl^-	
	HNO_3	NO_3^-	
	HSO_4^-	SO_4^{2-}	
	H_2SO_3	HSO_3^-	
	H_3PO_4	$H_2PO_4^-$	
	HNO_2	NO_2^-	
	HF	F^-	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	HClO	ClO^-	
	HBrO	BrO^-	
	NH_4^+	NH_3	
	HCN	CN^-	
	HCO_3^-	CO_3^{2-}	
	H_2O_2	HO_2^-	
Weakest Acids	HS^-	S_2^-	**Strongest Bases**
	H_2O	OH^-	

8.3 Conjugate Acid – Base Pairs

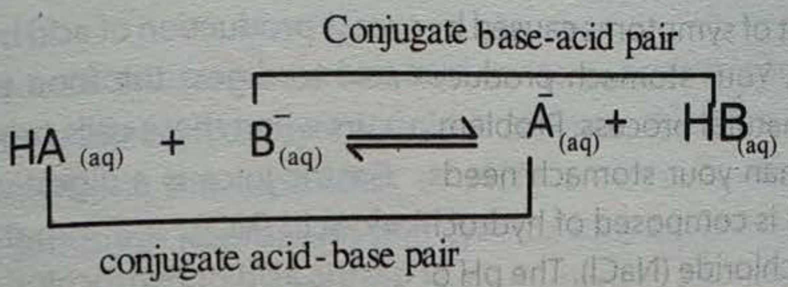
The expansion of the Bronsted – Lowery definition of acids and bases concept of the conjugate acid-base pair. The dissociation of an acid HA ca represented as follows:

$$HA \rightleftharpoons H^+ + A^-$$

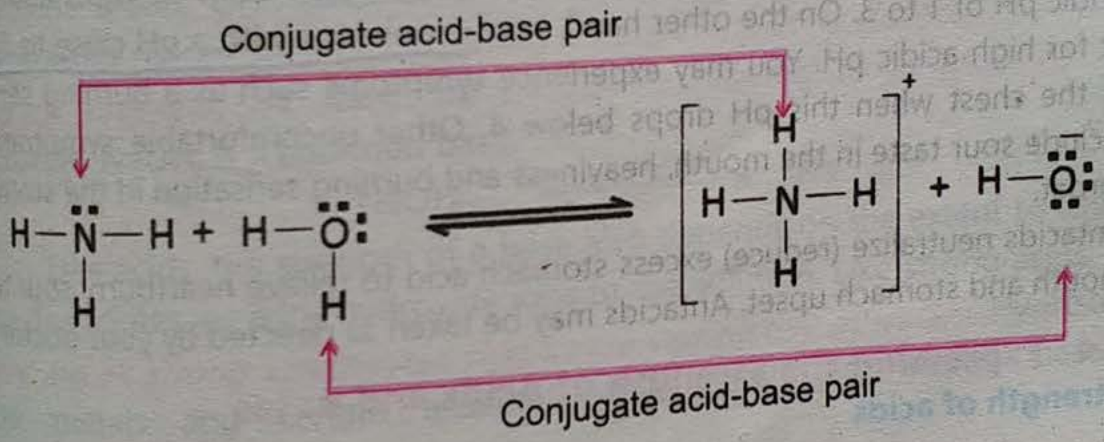
For example in case of H_2CO_3

$$H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{3(aq)}$$

The hydrogen carbonate ion (HCO_3^-) is a base by Bronsted definition is called a conjugate base of carbonic acid. According to Bronsted – Lo concept, *a reactant and product that differ by a proton (H^+) are called co acid – base pair.* Every acid has a conjugate base and every base has a co acid. Thus, in an acid base reaction, two conjugate pairs are formed.



A specie formed from an acid by the loss of a proton is called the conjugate base of that acid and a specie formed from a base by gaining a proton is called the conjugate acid of that base e.g. consider the following reaction.



$$\underset{\text{Base}}{NH_{3(aq)}} + \underset{\text{Acid}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{Conjugate Acid}}{NH_{4\,(aq)}^{+}} + \underset{\text{Conjugate Base}}{OH^{-}_{(aq)}}$$

In this case, NH_4^+ is the conjugate acid of the base NH_3, and OH^- is the conjugate base of the acid H_2O. The atom in the Bronsted – Lowery base that accepts an H^+ ion must have a lone pair.

Table 8.2: Some examples of Bronsted-Lowery acids and bases

Acid		Base		Conjugate acid		Conjugate base
HCO_3^-	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CO_3^{-2}
CH_3COOH	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CH_3COO^-
HCN	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CN^-
H_2S	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HS^-
H_2O	+	NH_3	$\rightleftharpoons$	NH_4^+	+	OH^-
H_2O	+	CO_3^{-2}	$\rightleftharpoons$	HCO_3^-	+	OH^-

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Acidity is a set of symptoms caused by excess production of acid by the gastric glands the stomach. Your stomach produces acid to digest the food that you eat. This is regular and natural process. Problem occurs when these cells produce large amount acid, more than your stomach needs. Gastric juice is a digestive fluid formed in th stomach and is composed of hydrochloric acid (HCl), potassium chloride (KC and sodium chloride (NaCl). The pH of gastric acid or hydrochloric acid (HCl) is 1 to 3 the human stomach. Gastric acid helps to digest and break down food.

Acidity issues arise when there is excess production of this acid. The excess production is due to acidic foods, dehydration, stress etc.

When acidity occurs, the excess acid may move up from your stomach to your esophagus. The lining of your stomach is designed as such to withstand a high acidic pH of 1 to 3. On the other hand, your esophagus with a pH close to 7, is not fit for high acidic pH. You may experience symptoms such as a burning sensation in the chest when this pH drops below 4. Other uncomfortable symptoms may include sour taste in the mouth, heaviness and burning sensation in the stomach or throat.

Antacids neutralize (reduce) excess stomach acid to relieve heartburn, sour taste in mouth and stomach upset. Antacids may be taken as directed by your doctor.

8.4 Expressing the Strength of Acids and Bases

Strength of acids

A strong acid is one that ionizes completely in aqueous solution. Stro acids are strong electrolytes, which for practical purposes, are assumed to ion completely in water.

Most of the strong acids are inorganic acids such as perchloric ac ($HClO_4$), hydrochloric acid (HCl), nitric acid (HNO_3) and sulphuric acid (H_2SO_4).

$$HClO_{4(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + ClO^-_{4(aq)}$$

$$HNO_{3(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + NO^-_{3(aq)}$$

$$HCl_{(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

$$H_2SO_{4(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + HSO^-_{4(aq)}$$

At equilibrium, solutions of strong acids will not contain any unioniz acid molecules.

Weak Acids:

A weak acid is one that ionizes only to a limited extent in water. Acids th are weak electrolytes are known as weak acids. At equilibrium, aqueous solutio of weak acids contain a mixture of unionized acid molecules, H_3O^+ ions, and the conjugate base. Examples of weak acids are hydrofluoric acid (HF), acetic acid (CH_3COOH).

The aqueous solution of a weak acid contains hydronium ions, anions, and dissolved acid molecules. Hydrocyanic acid is an example of a weak electrolyte. In aqueous solution, both the ionization of HCN and the reverse reaction occur simultaneously. Although hydronium and cyanide ions are present in solution, the reverse reaction is favoured. Most of the solution is composed of hydrogen cyanide and water.

$$HCN_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CN^-_{(aq)}$$

Strength of Bases

Most bases are ionic compounds containing metal cations and the hydroxide anion, OH^-. Because these bases are ionic, they dissociate to some extent when placed in solution. *When a base completely dissociates in water to produce aqueous OH^- ions, the solution is referred to as alkaline.* Sodium hydroxide, NaOH, is a common base.

$$NaOH_{(s)} \xrightarrow{H_2O} Na^+_{(aq)} + OH^-_{(aq)}$$

Like acids, the strength of a base also depends on the extent to which the base dissociates, or adds hydroxide ions to the solution. Like strong acids, *strong bases are all strong electrolytes that ionize completely in water.* Hydroxides of alkali metals and certain alkaline earth metals are strong bases e.g. KOH, $Ba(OH)_2$ etc.

Weak Bases: Like weak acids, *a weak base is one that ionizes only to a limited extent in water. Bases that are weak electrolytes are known as weak bases.* Ammonia ionizes in water as follows:

$$NH_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

In this reaction, NH_3 acts as a base by accepting a proton from water to form NH_4^+ and OH^- ions. It is a weak base because only a small amount of the molecules undergo this reaction.

Acids and bases when dissolved in water dissociate into electrically charged ions. The degree of ionization is characteristic of the acids and bases. Strong acids and bases are 100% ionized whereas, weak acids and bases ionize to a certain extent.

The strength of an acid is measured from the tendency to donate a proton and that of a base is the tendency to accept it, it is noted from the acid – base pair that:

A weak acid has a strong conjugate base and vice versa.

A weak base has a strong conjugate acid and vice versa.

For example,

Since acetic acid is a weak acid and its conjugate base (CH_3COO^-) is strong.

$$\underset{\text{weak acid}}{CH_3COOH_{(aq)}} + \underset{\text{Weak base}}{H_2O_{(aq)}} \rightleftharpoons \underset{\text{strong conjugate acid}}{H_3O^+_{(aq)}} + \underset{\text{strong conjugate base}}{CH_3COO^-_{(aq)}}$$

Similarly, ammonia is a weak base and its conjugate acid (NH_4^+) is strong acid.

$$\underset{\text{Weak base}}{NH_{3(aq)}} + \underset{\text{Weak acid}}{H_2O_{(aq)}} \rightleftharpoons \underset{\text{strong conjugate acid}}{NH_4^+{}_{(aq)}} + \underset{\text{strong conjugate base}}{OH^-_{(aq)}}$$

8.4.1 Ionization Equation of Water

Reading Check

Define strength of acids and bases.

Water, as you know, is a unique solvent. One of its special properties is its ability to act either as an acid or as a base.

Careful electrical-conductivity experiments have shown that pure water is an extremely weak electrolyte. Water undergoes self-ionization to a small extent, as shown in the model in figure 8.3.

∴ *In the self-ionization of water two water molecules produce a hydronium ion and a hydroxide ion by transfer of a proton.* This reaction is sometimes also called the *autoionization* of water.

- To describe the acid, base properties of water in the Bronsted – Lowery framework, you express its autoionization as follows.

$$\underset{\text{Acid1}}{H_2O} + \underset{\text{Base1}}{H_2O} \rightleftharpoons \underset{\text{Acid2}}{H_3O^+} + \underset{\text{Base2}}{OH^-}$$

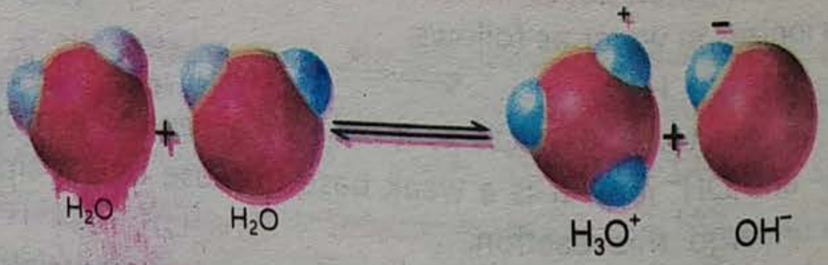


Figure 8.2 Self-Ionization of Water

You can observe the small amount to which the self-ionization of water occurs by noting the small value of its equilibrium constant K_c. Because you can use H^+ (*aq*) and H_3O^+(*aq*) interchangeably to represent the hydrated proton, the equilibrium constant can also be expressed more simply as,

$$H_2O \rightleftharpoons H^+ + OH^-$$

Tidbit

$$\underset{\text{Acid1}}{H_2O} + \underset{\text{Base1}}{H_2O} \rightleftharpoons \underset{\text{acid2}}{H_3O^+} + \underset{\text{Base2}}{OH^-}$$

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

$$[H_2O]^2 .\ K_c = [H_3O^+][OH^-]$$

$$K_w = [H_3O^+][OH^-]$$

The equilibrium constant expression is given by the equation.

$$K_c = \frac{[H^+][OH^-]}{[H_2O]} \qquad (8.1)$$

Water is in large excess and its concentration remains constant. So on rearranging the equation (8.1), placing $[H_2O]$ with K_C, the ion product $[H^+][OH^-]$ equals a constant.

$$[H_2O].\ K_c = [H^+][OH^-]$$

As

$$[H_2O].\ K_c = K_w$$

So

$$K_w = [H^+][OH^-] \qquad (8.2)$$

Where K_w is called the *ionic product constant* (or *the dissociation constant*) for water, always refers to the autoionization of water, which is *the product of the molar concentrations of H^+ and OH^- ions at a particular temperature*.

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25°C \qquad (8.3)$$

The concentrations of H^+ and OH^- ions are equal and found to be $[H^+] = 1.0 \times 10^{-7}$ M and $[OH^-] = 1.0 \times 10^{-7}$ M. Thus, from Equation (8.3), at 25°C,

or

$[H^+] = [OH^-] = 10^{-7}\ mol.dm^{-3}$ in neutral water.

Tidbit

In pure water at 25°C, the value of K_w is 1.0×10^{-14}. Like any equilibrium constant, K_w varies with temperature. At body temperature (37°C), K_w equals to 2.5×10^{-14}.

$$K_w = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

Whether you have pure water or an aqueous solution of dissolved species, the following relation always holds at 25°C,

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \qquad (8.4)$$

Whenever $[H^+] = [OH^-]$ the aqueous solution is said to be neutral. In a acidic solution, there is an excess of H^+ ions and $[H^+] > [OH^-]$. In a basic solutio there is an excess of hydroxide ions, so $[H^+] < [OH^-]$. In other words, a solutio which contains H^+ ions equal to 10^{-7} M, is said to be neutral. If the hydroge ions concentration is greater than 10^{-7} M, the solution is said to be acidi whereas, if the concentration is less than 10^{-7} M, the solution is basic.

Self-Assessment

1. Briefly explain amphoteric substance with examples.
2. Give examples of Bronsted-Lowery concept for acids and bases.
3. What is relative strength of acids and bases?
4. What are conjugate acid – base pairs? Give their examples.
5. Define ionization constant of water.

8.4.2 pH, pOH and pK$_w$

The concentrations of H^+ and OH^- ions in aqueous solutions are very smal and, therefore, difficult to work with these small numbers like 10^{-14}. The Danish chemist Soren Sorensen in 1909, proposed a more practical measure o expressing the concentration of H^+ and OH^- ions in terms of pH. The acidity of an aqueous solution depends on the concentration of hydrogen (hydronium) ions. This scale of acidity provides a simple, convenient, numerical way to state the acidity of a solution. Values on the pH scale are obtained by mathematical conversion of H^+ ion concentrations to pH by the expression

$$pH = -\log[H^+]$$

Where $[H^+]$ = H^+ or H_3O^+ ion concentration in *moles per dm^3. The pH is defined as the negative logarithm of the H^+ or H_3O^+ concentration in moles pe dm^3.*

$$pH = -\log[H_3O^+] \quad \text{or} \quad pH = -\log[H^+]$$

A neutral solution at 25°C has a $[H^+]$ of 1×10^{-7} M.

$$pH = -\log[H^+] \qquad (8.5)$$

$$pH = -\log(1 \times 10^{-7})$$

$$pH = -(-7) = 7$$

Therefore, the pH is 7.0.

$pH < 7.00$ for an acidic solution $[H^+] > 1.0 \times 10^{-7}$ M

$pH = 7.00$ for a neutral solution $[H^+] = 1.0 \times 10^{-7}$ M

$pH > 7.00$ for a basic solution $[H^+] < 1.0 \times 10^{-7}$ M

It must be noted that the pH increases as $[H^+]$ decreases.

If you know the pH value of a solution and want to calculate the H^+ ion concentration, then you need to take the antilog of equation (8.5) as follows,

$$[H^+] = 10^{-pH} \qquad (8.6)$$

You can also find simply the pOH, a measure of hydroxide-ion concentration similar to the pH. *The pOH is defined as the negative logarithm of the OH^- concentration in moles per dm^3.*

$$pOH = -\log [OH^-]$$

A solution at 25°C has a $[OH^-]$ of 1×10^{-7} M.

$$pOH = -\log[OH^-] \qquad (8.7)$$

$$pOH = -\log(1 \times 10^{-7})$$

$$pOH = -(-7) = 7$$

Therefore, the pOH is 7.0.

For example, the pH of pure water at 25°C is 7 and is said to be neutral; that is, it is neither acidic nor basic, because the concentrations of H^+ and OH^- are equal. Solutions that contain more H^+ ions than OH^- ions have pH values less than 7, and solutions that contain fewer H^+ ions than OH^- ions have pH values greater than 7.

As you know that $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 25°C

The pK_w is defined as the negative logarithm of K_w. It can be written as,

$$pK_w = -\log K_w$$

Then because, $pK_w = -\log K_w = [H^+][OH^-] = -\log(1.0 \times 10^{-14})$

Taking the logarithm of both sides of the equation,

$$[H^+][OH^-] = 1.0 \times 10^{-14}$$

ReadingCheck

Define pH, pOH and pKw.

You will get,

$$\log [H^+] + \log [OH^-] = \log (1.0 \times 10^{-14})$$

or $$(-\log [H^+]) + (-\log [OH^-]) = -\log (1.0 \times 10^{-14})$$

Hence, $pH + pOH = 14.00$

$$pK_w = 14 \text{ at } 25^\circ C$$

The value of pK_w decreases with increase in temperature.

$$pK_w = pH + pOH = 14.00 \qquad (8.8)$$

Table 8.3 pH Values of Some Common Items

Item	pH
Gastric juice	1 - 2
Lemon juice	2.3
Vinegar	2.8 - 3
Soft drinks	3
Orange juice	3.5 - 3.7
Tomatoes	4 – 4.1
Rainwater	6
Urine	6.0
Milk	6.6
Pure water	7
Human blood	7.3 - 7.4
Baking soda (aqueous)	8.5
Ammonia	11 - 12
Washing soda (aqueous)	12

Table 8.4 Relationship of H_3O^+, OH^-, pH and pOH

	H_3O^+	pH	OH^-	pOH
Basic	1×10^{-14}	14	1×10^{-0}	00
	1×10^{-13}	13	1×10^{-1}	01
	1×10^{-12}	12	1×10^{-2}	02
	1×10^{-11}	11	1×10^{-3}	03
	1×10^{-10}	10	1×10^{-4}	04
	1×10^{-9}	09	1×10^{-5}	05
	1×10^{-8}	08	1×10^{-6}	06
Neutral	1×10^{-7}	07	1×10^{-7}	07
Acidic	1×10^{-6}	06	1×10^{-8}	08
	1×10^{-5}	05	1×10^{-9}	09
	1×10^{-4}	04	1×10^{-10}	10
	1×10^{-3}	03	1×10^{-11}	11
	1×10^{-2}	02	1×10^{-12}	12
	1×10^{-1}	01	1×10^{-13}	13
	1×10^{-0}	00	1×10^{-14}	14

Example 8.1

What is the pH and pOH of 0.001 M HCl solution?

Solution

The concentration of HCl = 0.001 = 10^{-3}

You can write as, $[H^+] = 10^{-3}$

Taking negative log (– log) of both sides , you have,

$$-\log [H^+] = -\log 10^{-3} \qquad \text{as } (\log 10 = 1)$$

As you have,

$-\log [H^+] = pH$, so you can write,

$$pH = -(-3)$$
$$pH = 3$$

Since, you have equation (8.8),

$$pH + pOH = 14$$

or

$$pOH = 14 - pH$$
$$pOH = 14 - 3$$
$$pOH = 11$$

Example 8.2

Determine the pH of 0.15M NaOH solution.

Solution

The concentration of NaOH = 0.15 = 1.5×10^{-1}

You can write as, $[OH^-] = 1.5 \times 10^{-1}$

Taking negative log (–log) of both sides , you have,

$$-\log [OH^-] = -\log 1.5 \times 10^{-1}$$
$$-\log[OH^-] = -(0.2 - 1)$$
$$-\log[OH^-] = -(-0.8)$$
$$-\log[OH^-] = 0.8$$

Or you can write, $pOH = 0.8$

as you have,

$$pH + pOH = 14$$

or

$$pH = 14 - pOH$$
$$= 14 - 0.8$$

Example 8.3

Calculate the $[H^+]$ and $[OH^-]$ ions concentration of a solution, which has pH of 4.

Solution

pH of solution = 4

$[H^+] = ?$, $[OH^-] = ?$

Since you have the equation (8.6) ,

$$[H^+] = 10^{-pH}$$

Putting the values, you get,

$$[H^+] = 10^{-4}$$

As you have,

$$[H^+][OH^-] = 10^{-14} \quad \text{or} \quad [OH^-] = \frac{[10^{-14}]}{[H^+]}$$

Putting the values, you get,

$$[OH^-] = \frac{10^{-14}}{[10^{-4}]}$$

$$[OH^-] = 10^{-14+4} = 10^{-10}$$

Practice Problem 8.1

Calculate the pH of 0.002 M hydrochloric acid (HCl) solution.

Practice Problem 8.2

Find the pH of 0.082 M NaOH solution.

8.4.3 Acid Ionization Constant, K_a and pK_a

Consider a weak monoprotic acid, HA. Its ionization in water represented by

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

The equilibrium expression for this ionization is

$$K_c = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \qquad (8.9)$$

$$K_c[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

Where for acid is, $K_c \cdot [H_2O] = K_a$, so you can write the above equation as,

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad (8.10)$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Where K_a, the acid ionization or dissociation constant. It is the equilibrium constant for the ionization of an acid. At a given temperature, the strength of the acid HA is measured quantitatively by the magnitude of K_a. It is the ratio of product of concentrations of dissociated ions to the undissociated acid molecules in aqueous solution. It represents the extent to which an acid is dissociated. The larger the value of K_a, the stronger will be the acid, that is, the greater will be the concentration of H^+ ions at equilibrium due to its ionization. Keep in mind, however, that only weak acids have K_a values associated with them.

A negative logarithm of K_a is called pK_a. Since it is the negative logarithm, hence greater the value of pK_a, weaker would be the acid.

$$pK_a = -\log K_a \qquad (8.11)$$

Table 8.5 lists a number of weak acids and their K_a values at 25°C in order of decreasing acid strength. Although all these acids are weak, within the group there is great variation in their strengths.

Table 8.5 Ionization Constants of Some Weak Acids at 25°C

Substance	Formula	Ka
Acetic acid	CH_3COOH	1.7×10^{-5}
Benzoic acid	C_6H_5COOH	6.3×10^{-5}
Boric acid	H_3BO_3	5.9×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}
Cyanic acid	$HOCN$	3.5×10^{-4}
Formic acid	$HCOOH$	1.7×10^{-4}
Hydrocyanic acid	HCN	4.9×10^{-10}
Hydrofluoric acid	HF	6.8×10^{-4}
Hydrogen sulphide	H_2S	8.9×10^{-8}
Hypochlorus acid	$HOCl$	3.5×10^{-8}
Nitrous acid	HNO_2	4.5×10^{-4}
Oxalic acid	$(COOH)_2$	5.6×10^{-2}
Phosphoric acid	H_3PO_4	6.9×10^{-3}
Phosphorus acid	H_3PO_3	1.6×10^{-2}
Propionic acid	$C_3H_6O_2$	1.4×10^{-5}
Sulphurous acid	H_2SO_3	1.3×10^{-2}

8.4.4 Leveling Effect

Strong acids, such as HCl, HBr, and HI, all show nearly same strength i water. The water molecule is such a strong base compared to the conjugate bases Cl^-, Br^-, and I^- that ionization of these strong acids is essentially complete i aqueous solutions. *The phenomenon by which the strength of different stro acids having close values of pK_a is levelled (equalized) by a definite solvent i called leveling effect.* The acid strength depends upon the solvent chosen.

They appear to have nearly equal strengths because their strengths are due to that of hydronium ion (H_3O^+). All the acids, which are completely dissociated in aqueous solution, are expressed by H_3O^+ ion. It is not possible to find the order of increasing strengths of these acids because they are completely ionized.

In solvents less basic than water, you will be able to find that HCl, HBr, and HI differs clearly in their tendency to give up a proton to the solvent. For example, when dissolved in ethanol or acetic acid (a weaker base than water), the extent of ionization increases in the order HCl < HBr < HI, and so HI is demonstrated to be the strongest of these acids.

The same effect is noticed in the case of solutions of bases. Water also exerts a leveling effect on the strengths of strong bases. For example, the oxide ion, O^{-2}, and the amide ion, NH_2^{-1} are such strong bases that they react completely with water. When Na_2O and $NaNH_2$ are dissolved in water, they give following reactions.

$$O^{-2}_{(aq)} + H_2O_{(\ell)} \longrightarrow OH^-_{(aq)} + OH^-_{(aq)}$$

$$NH^{-1}_{2(aq)} + H_2O_{(\ell)} \longrightarrow NH_{3(aq)} + OH^-_{(aq)}$$

The reaction goes to competition and thus, O^{-2} and NH_2^- appear to have the same basic strength in water; they both give a 100% yield of hydroxide ion. The basic strength of O^{-2} and NH_2^{-1} is leveled to the strength of OH^- ions and they behave as equally strong bases in aqueous solution.

The approximate values of pK_a of some of the acids are given in table 8.6

Table 8.6 pK_a Values (Approximately) of Some Acids In Water

Acids	pK_a	Acids	pK_a
$HClO_4$	-10	$(COOH)_2$	1.3
HI	-10	H_2SO_3	1.8
HBr	-9	CH_3COOH	4.7
HCl	-7	H_2CO_3	6.4
H_2SO_4	-3 -2	H_2S	7.0
HNO_3	-3 -3	NH_4^+	9.3
$HClO_3$	-3	HCN	9.4

8.4.5 Base Ionization Constant, K_b and pK_b

The ionization of weak bases is treated in the same way as the ionization of weak acids.

Consider a weak Bronsted base, A^-. Its ionization in water is represented by

$$A^-_{(aq)} + H_2O_{(\ell)} \rightleftharpoons HA_{(aq)} + OH^-_{(aq)}$$

The equilibrium expression for this ionization is

$$K_c = \frac{[HA][OH^-]}{[H_2O][A^-]} \qquad (8.12)$$

$$K_c.[H_2O] = \frac{[HA][OH^-]}{[A^-]}$$

Where for base is, $K_c.[H_2O] = K_b$, so you can write the above equation as,

$$K_b = \frac{[HA][OH^-]}{[A^-]} \qquad (8.13)$$

Where K_b, the *base ionization or dissociation constant*. *It is the equilibrium constant for the ionization of base.* At a given temperature, the strength of the Bronsted base, A^- is measured quantitatively by the magnitude of K_b. The larger the value of K_b, the stronger will be the base, that is, the greater the concentration of OH^- ions at equilibrium due to its ionization. A negative logarithm of K_b is pK_b. Keep in mind, however, that only weak bases have K_b values associated with them.

$$pK_b = -\log K_b \qquad (8.14)$$

Table 8.7 Ionization Constants of Some Weak Bases at 25°C

Substance	Formula	K_b
Ammonia	NH_3	4 1.8×10^{-5}
Aniline	$C_6H_5NH_2$	8 4.2×10^{-10}
Dimethylamine	$(CH_3)_2NH$	1 5.1×10^{-4}
Ethylamine	$C_2H_5NH_2$	2 4.7×10^{-4}
Hydrazine	N_2H_4	5 1.7×10^{-6}
Hydroxylamine	NH_2OH	6 1.1×10^{-8}
Methylamine	CH_3NH_2	3 4.4×10^{-4}
Pyridine	C_5H_5N	7 1.4×10^{-9}
Urea	NH_2CONH_2	9 1.5×10^{-14}

8.4.6 Relationship of K_a and K_b

According to Bronsted – Lowery concept when a weak acid or a weak base is dissolved in water, a conjugate acid-base pair is produced. An important relationship between the acid ionization constant, K_a and the ionization constant of its conjugate base, K_b, can be derived as follows, using the general equation of an acid as an example is,

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

You have an equation for K_a, given in equation (8.10) previously,

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad (8.10)$$

The general equation of base as an example is,

$$A^-_{(aq)} + H_2O_{(\ell)} \rightleftharpoons HA_{(aq)} + OH^-_{(aq)}$$

You have an equation (8.13) for K_b,

$$K_b = \frac{[HA][OH^-]}{[A^-]} \qquad (8.13)$$

Multiplying the expression of K_a with that of K_b

$$K_a \times K_b = \frac{[H_3O][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]}$$

On simplification you get,

$$K_a \times K_b = [H_3O^+] \times [OH^-] = [H^+][OH^-]$$

$$K_a \times K_b = [H^+][OH^-]$$

As you know that, $[H^+][OH^-] = K_w$

$$K_a \times K_b = K_w \text{ ------------- } (8.14) \qquad (K_w = 1.0 \times 10^{-14})$$

You can write, the above equation (8.14), as

$$K_a = \frac{K_w}{K_b}$$

This enables you to draw an important conclusion: The stronger the acid (the larger K_a), the weaker its conjugate base (the smaller K_b), and vice versa. As K_w being constant, so, you can write as,

$$K_a \propto \frac{1}{K_b}$$

Using the equation $K_a \times K_b = K_w$ (8.14)

Taking negative logarithm (– log) of the equation (8.14),

$(-\log K_a) + (-\log K_b) = -\log K_w$

So you can write,

$$pK_a + pK_b = 14 \qquad (8.15)$$

$$pK_a = 14 - pK_b$$

Knowing the pK_a value of an acid, you can find the pK_b of its conjugate base and vice versa.

Example 8.4

Acetic acid (CH_3COOH) has a pK_a value of 4.7 at 25°C. What is the pK_b value of its cojuagte base, CH_3COO^-?

Solution

The value of $pK_a = 4.7$

Value of $pK_b = ?$

As

$pK_a + pK_b = 14$

or

$pK_b = 14 - pK_a$

or

$pK_b = 14 - 4.7$

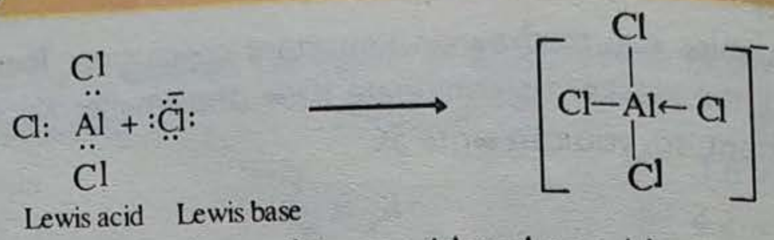
$pK_b = 9.3$

8.5 Lewis Definitions of Acids and Bases

A more general and broader concept of acids and bases was introduced by Gilbert N. Lewis. According to this concept, *a Lewis acid is any specie (molecule or ion) that can form a covalent bond by accepting an electron pair from another species; a Lewis base is a specie that can form a covalent bond by donating an electron pair to any other specie.*

The Lewis acid

Those compounds which are electron deficient or which have less than eight electrons (octet) in valence shell behave as Lewis acids, e.g.



Positive ions (cations) are often considered as acids.

$$\underset{\text{Acid}}{Ag^+} + \underset{\text{Base}}{2\ddot{N}H_3} \longrightarrow [Ag(NH_3)_2]^+$$

Lewis base

Molecules containing an atom with lone pair of electrons are bases. For example, $\ddot{N}H_3$ with a lone pair of electron is base.

Negative ions (anions) are Lewis bases e.g.

$$\underset{\text{Base}}{OH^-} + \underset{\text{Acid}}{H_3O^+} \rightleftharpoons H_2O + H_2O$$

$$\underset{\text{Base}}{Cl^-} + \underset{\text{Acid}}{H_3O^+} \rightleftharpoons HCl + H_2O$$

For example, in the protonation of ammonia, NH_3 acts as a ***Lewis base*** because it donates a pair of electrons to the proton H^+, which acts as a ***Lewis acid*** by accepting the pair of electrons.

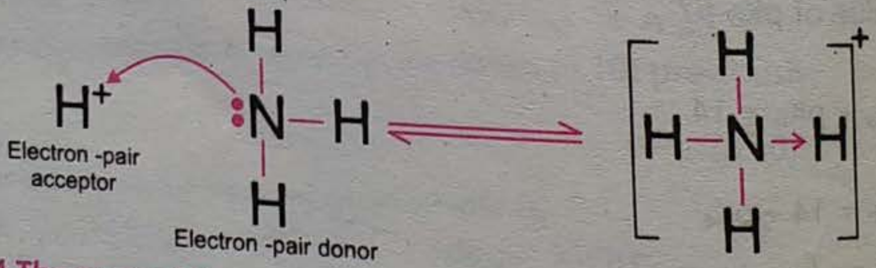
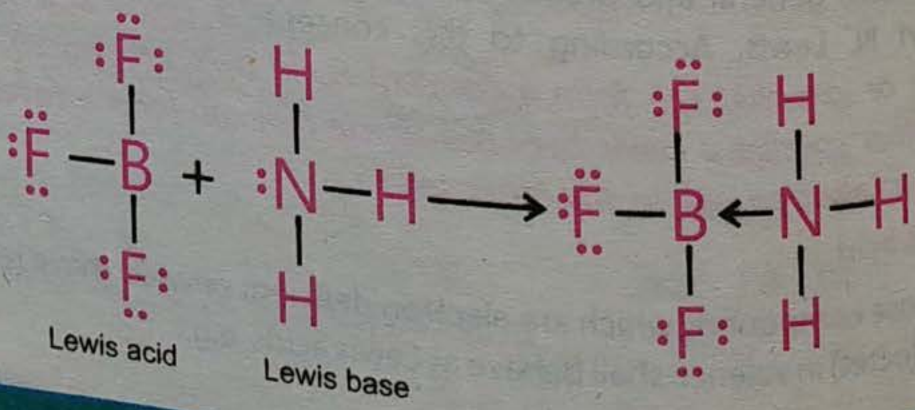


Figure 8.4 The proton H^+, acts as a Lewis Acid by accepting the pair of electrons

The significance of the Lewis concept is that it is much more general than other definitions; it includes many acid-base reactions that do not involve Bronsted acids and bases. Consider, for example, the reaction between boron trifluoride (BF_3) and ammonia.



A Lewis acid-base reaction, therefore, is one that involves the donation of a pair of electrons from one specie to another. Such a reaction does not produce a salt and water and is not restricted to any particular solvent.

Table 8.8 Summary of Three Concepts of Acids and Bases

Concept	Definition of acid	Definition of base
Arrhenius	H^+ producer	OH^- producer
Bronsted – Lowery	H^+ donor	H^+ acceptor
Lewis	Electron pair acceptor	Electron pair donor

Self-Assessment

1. What is pK_a and pK_b?
2. What is meant by leveling effect?
3. What is K_w?
4. What are Lewis acids, explain it with examples?
5. What is the significance of Lewis concept? Explain it with suitable examples.
6. How the sum of pK_a and pK_b is equal to 14.

SOCIETY, TECHNOLOGY AND SCIENCE

Milk is mixture of different components. The major components of milk are protein, fat and water. When you talk about the curdling of milk, you are mainly concerned with one specific milk protein called casein.

Casein groupings are spread evenly throughout the milk. Normally, casein groupings float around in the milk without bonding to anything. These groupings have a negative charge, which makes them repel other groupings of casein and keeps the casein evenly dispersed in the milk. Casein has a tendency to get precipitated and combined.

When lemon juice is added, it increases milk's acidity because lemon contains citric acid. When milk becomes acidic, the negative charge, which keeps the casein separate, is neutralized. Now instead of pushing each other apart, the casein starts to clump together. Eventually large enough clumps are formed that you can actually see the separation, and then you have curdled milk.

8.6 Buffer Solutions and their Applications

Pure water has a pH value equal to 7, but even the purest form of water cannot retain this value of pH for long time. The reason is that carbon dioxide in the air dissolve in water and gives it a slight acidic character or the silicates from the glass may change its pH.

A solution, which resists changes in pH when a small amount of a stro acid or a strong base is added to it, is called a buffer solution. In other words, y can say that a buffer is one which maintains its pH fairly constant even upon t addition of small amounts of acid or base.

Buffers are very important to chemical and biological systems. The pH the human body varies greatly from one fluid to another; for example, the pH blood is about 7.4, whereas the gastric juice in our stomachs has a pH of abo 1.5. Buffers in most cases maintain these pH values, which are crucial for t proper functioning of enzymes and the balance of osmotic pressure.

A ***buffer solution*** is usually prepared from

- A weak acid and its salt with a strong base. These are called **Acidi buffers,** such as CH_3COOH and CH_3COONa; such buffers are acidic with p less than 7.
- A weak base and its salt with a strong acid. These are called **Basi buffers,** such as NH_4OH and NH_4Cl; such solutions have a pH more than 7.

Buffer Action

The resistance offered by a buffer solution to change in pH on t addition of acid or base is called a buffer action. The buffer action for acidic a basic buffers is explained as under.

i. Weak Acid and its Salt Buffers

A simple buffer solution can be prepared by adding comparable amou of acetic acid (CH_3COOH) and sodium acetate (CH_3COONa) to water. A soluti containing these two substances has the ability to neutralize the added acid base.

The pH of the buffer is governed by the equilibrium

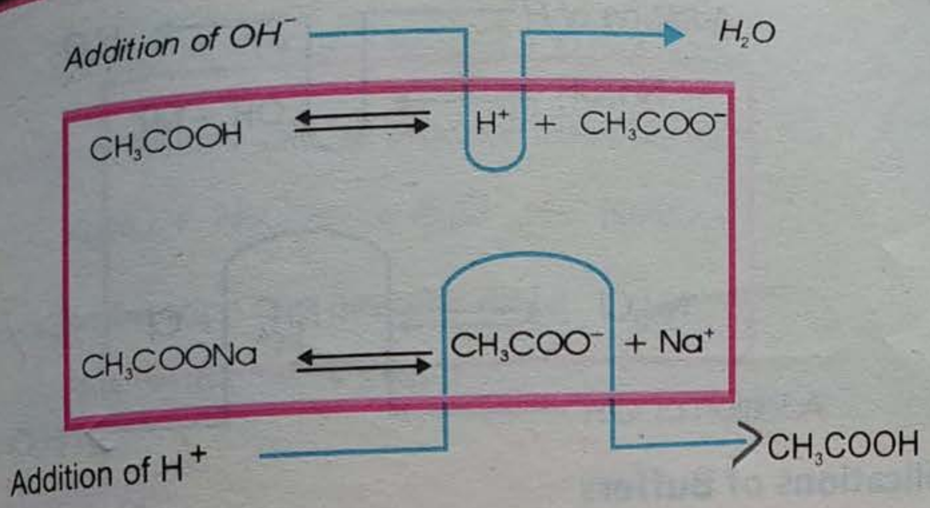
$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)} \qquad (8.16)$$

Sodium acetate, a strong electrolyte, dissociates greatly in water:

$$CH_3COONa_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

a. Addition of Strong Base

When a small amount of strong base like, NaOH is added, it will incre the concentration of OH^-. The excess of OH^- combine with the H^+ of acetic a to form water molecules. As a result, the equilibrium (8.16) shifts to the right produce more H^+ ions till all the excess OH^- ions are neutralized and the origi pH of the buffer is restored. More acetic acid is ionized to recover the deficie of H^+ ions. Therefore, the pH of the buffer solution will not change.



Addition of Strong Acid

When a strong acid is added, H^+ ion of the acid reacts with the acetate ion f the buffer.

$$H^+_{(aq)} + CH_3COO^-_{(aq)} \rightleftharpoons CH_3COOH_{(aq)}$$

Both of these reactions go to completion. Hence, the added OH^- and H^+ ns are removed and the pH of the buffer solution remains constant.

Weak Base and its Salt Buffers

The example of this buffer is, *NH_4Cl and NH_4OH*. Its resistance to change pH can also be explained on the same lines as that of an acid buffer.

Addition of Strong Acid

When a small amount of strong acid like HCl is added to the buffer; the H^+ ons combine with OH^- ions of the NH_4OH to form water molecules.

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

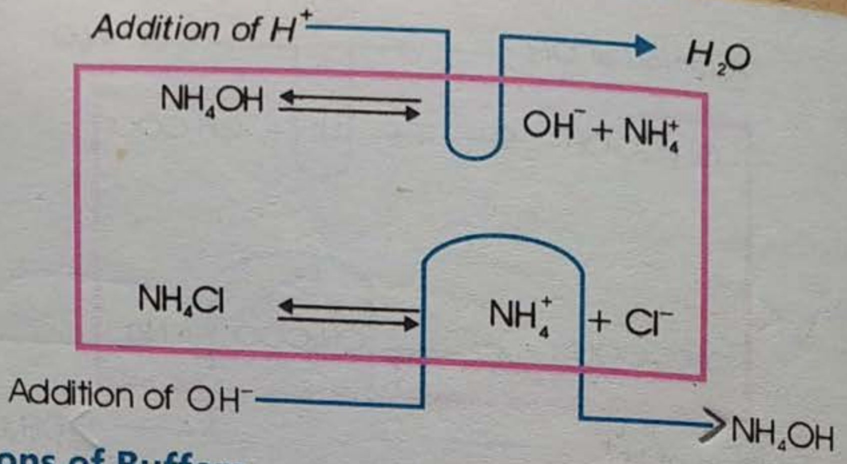
The equilibrium is shifted to the right till all the additional H^+ ions are eutralized and the original buffer pH is restored.

$$H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)}$$

Addition of Strong Base

When small amount of strong base such as, NaOH is added to the buffer olution, concentration of the OH^- increases. The OH^- combines with excess of NH_4^+ ions to form the NH_4OH. Thus, the pH of the buffer remains constant.

$$NH_4^+{}_{(aq)} + OH^-_{(aq)} \rightleftharpoons NH_4OH_{(aq)}$$



Applications of Buffers

i. The use of buffers is important in some industrial processes, which wo be interrupted by large change in pH. Examples are manufacture leather, photographic materials and dyes.

ii. In bacteriological research, culture media are generally buffered maintain a constant pH required for the growth of the bacteria bei studied.

iii. Buffer is important in biological systems because biological reactions both plants and animals are often very sensitive to pH changes. Huma blood is buffered to a pH of 7.4 by means of bicarbonates, phosphat and complex protein systems.

iv. Protein studies must be performed in buffered media because th magnitude and kind of electrical charge carried by protein molecul depend on the pH.

Reading Check

What is buffer solution?

Tidbit

Salt

A salt is formed when a base is neutralized by an acid. A salt consists of metallic and acidic radical. Examples are NaCl, $NaNO_3$, Na_2SO_4, KCl etc

Salt are prepared by the following methods.

Neutralization of a base by an acid.

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(aq)}$$

Reaction of an acid with a reactive metal

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

Reaction of an acid with carbonate (CO_3^{-2}) or bicarbonate (HCO_3^{-})

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

Reaction of soluble salts to produce insoluble salts

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

Direct combination of a gas with metal

$$2Na + Cl_2 \longrightarrow 2NaCl$$

8.7 Salt Hydrolysis

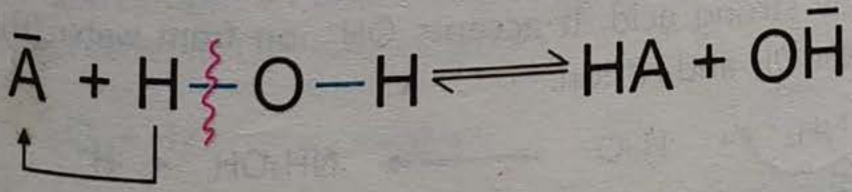
A salt is an ionic compound formed by the reaction between an acid and a base. Some salts are strong electrolytes that completely dissociate in water and in some cases partially dissociate in water.

The term salt hydrolysis describes the reaction of an anion or a cation or both the ions of a salt with water to produce acidic, basic or neutral solutions.

Hydrolysis is defined as, the reaction of an anion or cation with water accompanied by cleavage of H–O–H bond.

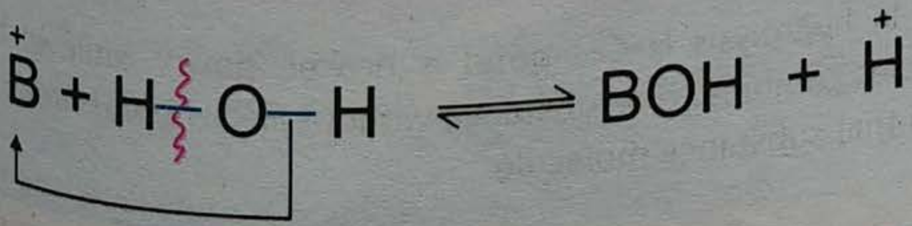
When a salt is dissolved in water, it is dissociated into positive and negative ions. These ions separately react with water by breaking the H–OH bond. As a result, an acidic or basic solution is formed depending upon the nature of the dissolved salt.

It may be noted that in **anionic hydrolysis** the solution becomes slightly basic due to the generation of excess OH^- ions.



$$\bar{A} + H-O-H \rightleftharpoons HA + O\bar{H}$$

In **cationic hydrolysis**, there is excess of H^+ ions, which makes the solution slightly acidic.



$$\overset{+}{B} + H-O-H \rightleftharpoons BOH + \overset{+}{H}$$

The different salts may be classified into the following types accordin their hydrolytic behaviour:

(1) Salts of weak acids and strong bases
(2) Salts of weak bases and strong acids
(3) Salts of weak acids and weak bases
(4) Salts of strong acids and strong bases.

1. Salts of Weak Acids and Strong Bases

pH = >7

When a salt of weak acid (CH_3COOH) and Strong base (NaOH), f example, sodium acetate (CH_3COONa) is dissolved in water. It ionizes in aqueo solution, into CH_3COO^- and Na^+.

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

Being the conjugate base of a weak acid, CH_3COOH, CH_3COO^- is relatively strong base. Thus, CH_3COO^- accepts H^+ ion from water and undergoe hydrolysis.

strong C.B

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

The resulting solution is slightly basic due to excess OH^- ions present.

2. Salts of Weak Bases and Strong Acids

pH = <7

When a salt of weak base (NH_4OH) and strong acid (HCl), for examp ammonium chloride (NH_4Cl) is dissolved in water. In aqueous solution, it ioniz into NH_4^+ and Cl^-.

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

NH_4^+ is a Bronsted conjugate acid of the weak base NH_4OH. Therefor is a relatively strong acid. It accepts OH^- ion from water (H_2O) and forms unionized NH_4OH and H^+ ion.

Strong C.A

$$NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$$

The accumulation of H^+ ions in solution makes it acidic.

Tidbit

Hydration and Hydrolysis

In hydrolysis H–OH bond is broken down; while in hydration wate molecules combine to a substance without H–OH bond breaking and becom part of that substance molecule.

3. Salts of Weak Acids and Weak Bases

When a salt of weak acid (CH_3COOH) and weak base (NH_4OH), for example, ammonium acetate (CH_3COONH_4) is dissolved in water. It ionizes into CH_3COO^- and NH_4^+. Since the acid and the base are both weak, their conjugate base (CH_3COO^-) and conjugate acid (NH_4^+) are relatively strong. They accept H^+ and OH^- ions, respectively, from water and undergo considerable hydrolysis.

$$CH_3COO^- + H_2O \longrightarrow CH_3COOH + OH^-$$

$$NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$$

The overall hydrolysis may be represented as,

$$CH_3COO^- + NH_4^+ + H_2O \longrightarrow CH_3COOH + NH_4OH$$

The pH of the resulting solution will depend on the relative extent of anionic hydrolysis and cationic hydrolysis. The solution of such salt may be acidic, basic or neutral depending upon the K_a and K_b values of acid and base, respectively. If both the ions react to the same extent (as shown for CH_3COONH_4), $[OH^-] = [H^+]$. Then solution is neutral.

4. Salts of Strong Acids and Strong Bases

The salts of strong acid (HCl) and strong base (NaOH) such as, NaCl, does not show hydrolysis. When NaCl is added into water, NaCl dissociates in water to give Na^+ and Cl^- ions.

Since HCl is a strong acid, Cl^- is very weak conjugate base of HCl, Cl^- is unable to accept a proton (H^+) from an acid, particularly water. That is why Cl^- does not hydrolyse. It cannot generate OH^- ions as follows.

$$Cl^- + H_2O \not\longrightarrow HCl + OH^-$$

Similarly, in NaOH case, Na^+ is not hydrolyzed because it is conjugate acid of strong base NaOH. Thus, the pH of sodium chloride solution remains unaffected and neutral.

Self-Assessment

1. What is buffer action also write its application.
2. What is hydrolysis? Explain why aqueous solutions of some salts are acidic or basic.
3. Explain why the solution of a salt is not necessarily neutral.

KEY POINTS

- Brontsed acid is a species (molecule or ion) which donates or tends to don a proton.
- Brontsed base is a species (molecule or ion) which accepts or tends to acc a proton.
- Stronger Brontsed acids are those that lose their protons more easily th other acids.
- Stronger Brontsed bases are those that hold on to protons more stron than other bases.
- A species formed from an acid by the loss of a proton is called the conjug base of that acid and a specie formed from a base by gaining a proton called the conjugate acid of that base.
- A strong acid is one that ionizes completely in aqueous solution.
- A weak acid is one that ionizes only to a limited extent in water.
- Acid-base reaction involves the transfer of a proton from an acid to a base weak acid has a strong conjugate base while a weak base has always a stro conjugate acid.
- Ionic product of water, K_w is a constant quantity equal to 1×10^{-14} at 25°C.

$$K_w = [H^+][OH^-] = 1 \times 10^{-14}$$

- When a base completely dissociates in water to yield aqueous OH^- ions, t solution is referred as alkaline.
- Strong bases are all strong electrolytes that ionize completely in water.
- A weak base is one that ionizes only to a limited extent in water.
- In the self-ionization of water, two water molecules produce a hydronium i and a hydroxide ion by transfer of a proton. This is called the autoionizati of water.
- Water is an amphoteric substance: it behaves both as an acid and a base.
- pH is the negative logarithm of the H^+ or H_3O^+ concentration in moles p dm^3, smaller the value of pH, greater is the acidity.
- The pOH is defined as the negative logarithm of the OH^- concentration moles per dm^3.
- K_a, the acid ionization constant, is the equilibrium constant for the ionizati of an acid.

$$HX_{(aq)} \rightleftharpoons H^+_{(aq)} + X^-_{(aq)}$$

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

A strong acid has a very large K_a value.

pK_a is the negative logarithm of K_a. So greater the value of pK_a, lower is the strength of an acid.

Base – ionization constant, K_b, is the dissociation constant of a base and pK_b is the negative logarithm of K_b. If a substance has greater value of dissociation constant K_b, and smaller pK_b value then it will be strong base.

K_b, the base ionization constant, is the equilibrium constant for the ionization of base.

- A Lewis acid is a species that can accept an electron pair from another species.
- A Lewis base is a species that can donate an electron pair to another species.
- Lewis acid – base reaction involves the exchange of a proton from an acid to a base. A weak acid has a strong conjugate base while a weak base has always a strong conjugate acid.
- A solution, which resists a change in pH when a small amount of a strong acid or a strong base is added to it, is called a buffer solution.
- Acid buffer contains a weak acid and its salt with a strong base.
- Basic buffer contains a weak base and its salt with a strong acid.
- Buffer action is the resistance offered by a buffer solution to change in pH on the addition of small amount of an acid or base.
- Hydrolysis is the reaction of an anion or cation of a salt with water accompanied by cleavage of H–O –H bond.

EXERCISE

Choose the correct option.

1. Which one is the example of buffer
   a. HCl/ NaCl
   b. NaOH/ H_2CO_3
   c. NH_4OH/NH_4Cl
   d. NaOH/ NaCl
2. Conjugate acid – base pair differs by
   a. A proton
   b. A proton pair
   c. An electron
   d. An electron pair
3. 1 M solution of $Ca(OH)_2$ is mixed with 1M solution of HCl. The produc solution is
   a. Acidic
   b. Basic
   c. Neutral
   d. Amphoteric
4. Cl^- is the conjugate base of
   c. $AlCl_3$
   b. NaCl
   c. HCl
   d. KCl
5. pH of an aqueous solution is 9. Its pOH is
   a. 11
   b. 9
   c. 7
   d. 5
6. Salt of a weak base and strong acid has a pH, approximately
   a. 8
   b. 6
   c. 7
   d. 9
7. The unit of K_w is,
   a. $Mole\ .dm^{-3}$
   b. $Mole^{-2}\ .dm^{-6}$
   c. $Mole^{2}\ .dm^{-6}$
   d. $Mole^{2}\ .dm^{-3}$
8. Very large Ka value means that the substance is a
   a. Strong acid
   b. Weak acid
   c. Weak base
   d. Strong base
9. In following halogen acids which one is the strongest acid
   a. HF
   b. HCl
   c. HBr
   d. HI
10. Which one of following solution have zero pH
    a. 1M HCl
    b. 0.5M H_2SO_4
    c. 0.1M HNO_3
    d. 1M CH_3COOH
11. Which one is not true for acids
    a. Liberate H^+
    b. Accepts electrons
    c. Have high pH
    d. Turn blue litmus red
12. 10^{-3} moles of HNO_3 is dissolved /dm^3. Its pH is
    a. –3
    b. 5
    c. 3
    d. 1

13. A solution with a pK_a value of 9, suggest that it is a
    a. Strong acid b. Weak acid
    c. Weak base d. Strong base

14. Cl^- is a / an
    a. Acid b. base c. Amphoteric d. None

15. An acidic buffer solution can be prepared by mixing
    a. Weak acid and its salt with strong base
    b. Strong acid and its salt with weak base
    c. Weak base and its salt with strong acid
    d. Strong base and its salt with weak acid

Short Questions

1. What information would you use to support the view that water can act either as a weak acid or as a weak base?
2. Explain that why the sum of pK_a and pK_b is always equal to 14.
3. Explain why the conjugate base of a strong acid is a weak base and the conjugate acid of a strong base is a weak acid.
4. Justify your answer with equations that CH_3COONa gives a basic solution while NH_4Cl an acidic solution in water.
5. Why do you call $AlCl_3$ and BF_3 as Lewis acids, Cl^- and NH_3 as Lewis bases?

Numerical Questions

1. What is the pH of 0.0001M $Ca(OH)_2$ solution. (Ans. pH = 10.3)
2. What is $[H^+]$ and $[OH^-]$ ions concentration of solution, which has a pH of 4.87? (Ans. $[H^+] = 1.35 \times 10^{-5}$, $[OH^-] = 7.41 \times 10^{-8}$)
3. What is the pH of a 1.0×10^{-4} M KOH solution? (Ans. pH = 10)
4. What is the pH of a solution if the $[H_3O^+]$ is 6.7×10^{-4}M. (Ans. pH = 3.17)
5. What is the pH of a solution for which $[OH^-]$ is 0.15M. (Ans. pH = 13.2)

Descriptive Questions

1. (a) What is Bronsted–Lowery acids and bases? Explain it with suitable examples.
   (b) Write equations and indicate the conjugate acid – base pairs for the following; (i) Acetic acid and water, (ii). Ammonia and hydrochloric acid
   (c) Justify that NH_3 is a base according to Lewis concept.
2. (a) Define buffer solution. What is buffer action and show with equations how a buffer system works?
   (b) What are the applications of buffers solutions?
   (c). Justify that buffer solution resists changes in pH, when a small amount of

an acid or a base is added.

3. (a) Briefly describe the leveling effect.

   (b) What is the relationship between K_a and K_b?

   (c) Write the equation relating K_a for a weak acid and K_b for its conjugate base. Use NH_3 and its conjugate acid NH_4^+ to derive the relationship between K_a and K_b.

4. (a) What is meant by the term amphoteric? Give an example of a substance or ion with amphoteric characteristics.

   (b) Define pH, pOH, pK_a and pK_b.

   (c) Explain ionization constant of water and calculate pH and pOH in aqueous medium using given K_w values.

5. (a) Define salt hydrolysis. Categorize salts according to how they affect the pH of a solution.

   (b) (i) What are conjugate acids and bases? Give the conjugate bases of the following acids; $HClO_4$, HCN, H_2CO_3, NH_4^+

   (ii) Classify as acids and bases giving reasons; BF_3, NH_3, NH_4^+, Ag^+, CaO, KCN, H_2S, SO_4^{2-}, Na^+, Cl^-

   (iii) Classify the following as Lewis acid or Lewis base; CO_2, H_2O, SO_2, I^-, NH_3, OH^-, BCl_3

PROJECT:

i. Arrange the following common substances in order of increasing pH:

Eggs	Apple	Tomato	Milk	Banana
Potatoes	Lemon	Shampoo	Water	Carbonated drink

ii. Group Work and Discussion

- Make a buffer solution in the laboratory.
- Record the pH of the buffer solution.
- Add small amount of strong acid to the buffer solution and record the pH of the solution.
- Add small amount of the strong base to the buffer solution and record the pH of the solution.
- Explain how such solution maintains a constant pH, even with the addition of small amounts of strong acid or strong base.
- Present your group work in the class and answer the questions of your classmates.

Unit -09

Chemical Kinetics

After studying this unit, the students will be able to:

- Define chemical kinetics. (Remembering)
- Explain and use the terms rate of reaction, rate equation, order of reaction, rate constant and rate determining step. (Understanding)
- Explain qualitatively factors affecting rate of reaction. (Applying)
- Give the order with respect to each reactant; write the rate law for the reaction. (Applying)
- Explain what is meant by the terms activation energy and activated complex. (Understanding)
- Relate the ideas of activation energy and the activated complex to the rate of a reaction. (Applying)
- Use the collision theory to explain how the rate of a chemical reaction is influenced by the temperature, concentration and size of molecules. (Applying)
- Give a potential energy diagram for a reaction, discuss the reaction mechanism for the reaction. (Applying)
- Explain effects of concentration, temperature, and surface area on reaction rates. (Applying)

Teaching

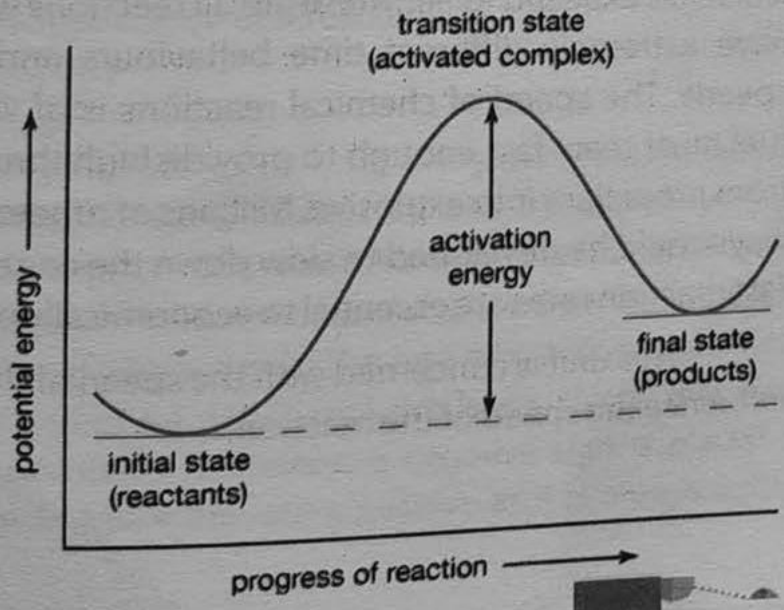
10

Assessment

01

Weightage %

07



- Explain the significance of the rate determining step on the overall rate multi-step reaction.(Analysing)
- Describe the role of the rate constant in the theoretical determinatio reaction rate. (Applying)
- Describe that increase in collision energy by increasing the temperature improve the collision frequency. (Applying)
- Define terms catalyst, catalysis, homogeneous catalysis and heterogene catalysis. (Understanding)
- Explain that a catalyst provides a reaction pathway that has low activat energy. (Applying)
- Describe enzymes as biological catalysts. (Understanding)
- Explain why powdered zinc reacts faster. (Analysing)

Introduction

A candle remains in contact with air indefinitely without observa reaction but it reacts (burns) when given a start with a lighted match. A mixture natural gas and air in a closed room remains indefinitely without reacting bu may explode violently if a spark is brought into the room. A piece of iron rea quite slowly with air (rusting) but a piece of white phosphorous burst into fla when it is exposed to air. These are all reactions with oxygen from the air but t have extremely different time behaviours and proceed at different rates speeds. The speed of chemical reactions is of vital interest to chemists. Roc fuel must react fast enough to provide high thrust but not so fast that they t from propellant into explosive. Millions of rupees could be saved each year if n ways could be developed to slow down the corrosion of metals. Also, sufficien fast reaction rates are essential to economically produce industrial chemicals.

This unit is concerned with the speed of the reaction and the factors wh influence the speed of the reaction.

9.1 Chemical Kinetics

The branch of chemistry which deals with the speed or rate, at which a chemical reaction occurs, factors affecting the rate and the mechanism of the reaction is called Chemical Kinetics. The knowledge of chemical kinetics is important for the industry, engineering, biological reactions, and other fields. For example, industrial chemists are interested in speeding up of reaction and obtaining products in shorter period of time.

In this connection it is important to know some basic terminologies used in the study of chemical kinetics, for example, rate of the reaction, rate equation and order of reaction etc.

9.2 Rate of Reaction

Rate of reaction is the change in the concentration of reactant or product per unit time. Consider, for example, the reaction between carbon monoxide and nitrogen dioxide. The products are carbon dioxide, CO_2, and nitric oxide, NO. The chemical equation for the reaction is;

$$CO_{(g)} + NO_{2(g)} \longrightarrow CO_{2(g)} + NO_{(g)} \qquad (9.1)$$

The rate of this reaction can be taken to be the change in concentration of reactants or products per unit time, i.e.

$$\text{Rate} = \frac{\text{change in concentration of } CO_2}{\text{Time interval}} = \frac{\Delta[CO_2]}{\Delta t}$$

$$\text{Rate} = \frac{\text{Quantity of } CO_2 \text{ produced}}{\text{Time interval}} \qquad (9.2)$$

i.e. quantity of CO_2 produced per unit time. Alternatively, the rate could be expressed in term of the disappearance of a reactant, i.e.

$$\text{Rate} = \frac{-\Delta[CO]}{\Delta t} \qquad (9.3)$$

Notice that, according to equation 9.1, for every mole of CO_2 formed one mole of CO is consumed. Thus rate expressions 9.2 and 9.3 are equivalent. If, in one second, the concentration of CO_2 were to increase by 0.02 mol dm^{-3} ($\Delta[CO_2]=+0.02 mol.dm^{-3}$), then the concentration of CO would have to decrease by the same amount ($\Delta[CO]=-0.02 mol.dm^{-3}$). The rate of reaction calculated from either equation 9.2 or 9.3 would be +0.02 $mol.dm^{-3}sec^{-1}$. (Note that since the concentration of reactant decreases, therefore, a negative sign is placed before the rate expression in order to make the rate a positive as it is always considered to be a positive quantity).

It can be demonstrated that the rate of the reaction is not a con quantity but changes with the concentration of reactant molecules pre Initially, when the concentration of reactant is high, the rate is correspond high. With the passage of time the concentration of the reactants decre therefore, the rate also gradually decreases and eventually becomes zero whe of the reactants have been consumed completely. Fig. 9.1 shows the profi reactant concentration with time. As can be seen from it, initially concentration decreases rapidly and at later stage the decrease is slow. The s of the curve gives the rate of the reaction

i.e. $$\frac{\Delta y}{\Delta x} = \frac{-\Delta[\text{Reactant}]}{\Delta \text{time}}$$

Fig. 9.1 shows that the rate of reaction decreases as the concentratio the reactants decreases. At initial stage it takes 15 minutes to decrease concentration from 1.2 to 1.1 mol. dm^{-3}, while at later stage of the reactio takes 150 minutes to decrease the concentration by the same amount i.e f 0.2 to 0.1mol.dm^{-3}.

A graph, similar to that shown in Fig. 9.1 can be plotted for concentration of product against time which would demonstrate that the ra formation of product is higher initially and low at the later stage.

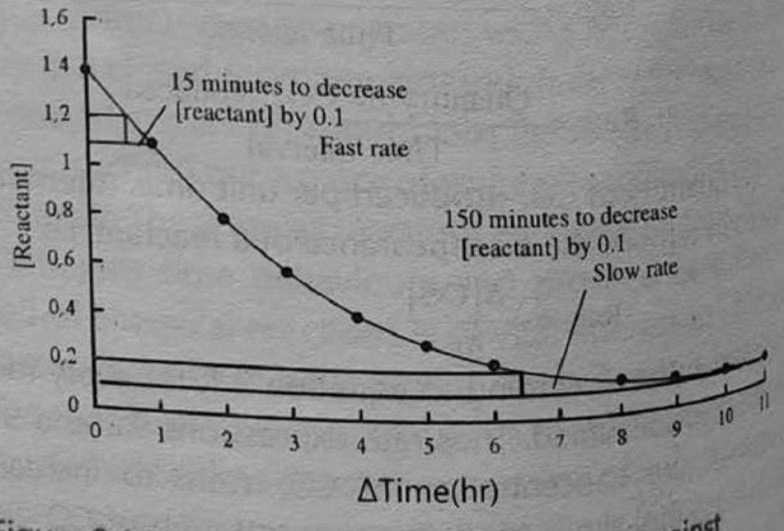


Figure 9.1 Plot of concentration of reactant against

Rate of reaction or formation of product is given by $\frac{\Delta[\text{Product}]}{\Delta t}$, or if we u for the product concentration, it can be expressed as $\frac{\Delta x}{\Delta t}$. This rate is calle average rate which is measured between larger interval of time, Δt, however, if we use very small interval of time then we express the rate as $\frac{dx}{dt}$ and this rate is called the *instantaneous rate* i.e. rate at a particular instant.

Elementary Reaction and Rate Determining Step

A chemical reaction is usually written in a single stoichiometric equation showing reactants, products, and other conditions of the reaction.

Most of the chemical reactions take place in a series of steps, called as elementary steps. A complete sequence of these elementary reactions is called a reaction mechanism. The overall reaction is the sum of these elementary steps. In each step some chemical species, called as reaction intermediates are produced, these reaction intermediates are consumed in subsequent steps. The overall reaction equation is obtained by adding these elementary reactions; while adding these reactions, the intermediate species are cancelled out and in the final equation only reactants and products are left. Each of these elementary reactions will have their own rate. The overall rate of the complete reaction will be determined by the step which has the slowest rate, the slowest step will be the rate determining step.

Let us consider a reaction $A \longrightarrow B$, which is occurring in the following elementary steps.

i) $A \longrightarrow X$ fast

ii) $X \longrightarrow Y$ slow (Rate determining step)

iii) $Y \longrightarrow B$ fast

Overall reaction

$$A + X + Y \longrightarrow X + Y + B$$

The reaction intermediates X and Y are present on both sides, therefore, they will be cancelled out and net reaction will be $A \longrightarrow B$.

The above sequence of reactions of elementary steps is referred to as mechanism of reaction. The slowest step is called the rate determining step. The rate of overall reaction depends on this step. It is also the step with the highest activation energy.

9.2.1 Rate Expression or Rate Law (Rate Equation)

In the example discussed in Section 9.2 it can be noted that the rate of reaction decreases with time. This is because the concentration of reactants, CO or NO_2 decreases. This observation is generally valid for a number of chemical reactions. We generally find that reactions proceed more slowly as the concentrations of reactants decrease. Increasing the concentration of reactants increases the reaction rate.

Justification

In order to study the effect of concentration on reaction rate we may conduct a series of experiments in which we measure the initial rate of CO-NO_2 reaction at different concentration of CO, holding the concentration of NO_2 constant. Data for three such series are presented in Table 9.1

$$CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g) \text{ at } 400\ ^\circ C$$

Table 9.1 Initial Rates of Reaction (mole dm^{-3}sec^{-1}) (k = 0.50 litre mole^{-1}sec^{-1})

SERIES 1			SERIES 2			SERIES 3		
[CO]	[NO_2]	Rate	[CO]	[NO_2]	Rate	[CO]	[NO_2]	Rate
0.10	0.10	0.005	0.10	0.20	0.010	0.10	0.30	0.015
0.20	0.10	0.010	0.20	0.20	0.020	0.20	0.30	0.030
0.30	0.10	0.015	0.30	0.20	0.030	0.30	0.30	0.045
0.40	0.10	0.020	0.40	0.20	0.040	0.40	0.30	0.060

Looking at the vertical columns in Table 9.1 we observe that the rate is directly proportional to the concentration of CO. If, for example, the concentration of CO is doubled (e.g. from 0.1 to 0.2 mol.dm^{-3}), the rate also doubles (from 0.005 to 0.01 mol.dm^{-3} sec^{-1} in series 1, from 0.01 to 0.02 mol. dm^{-3} sec^{-1} in series 2, and so forth). Thus we conclude that the rate of the reaction is directly proportional to the concentration of CO.

Thus we can write as,

$$\text{Rate} \propto [CO] \qquad (9.4)$$

In a similar way we can deduce the effect of NO_2 concentration on rate by examining the horizontal rows of data in Table 9.1. Notice, for example, that when the concentration of CO is held constant at 0.1 mol dm^{-3} (first horizontal row) the rate increases in direct proportion to the concentration of NO_2, thus,

$$\text{Rate} \propto [NO_2] \qquad (9.5)$$

Thus, we conclude that the rate of this reaction is directly proportional to the concentration of both CO and NO_2. Combining Eq. 9.4 and 9.5 we can write that

$$\text{Rate} \propto [CO][NO_2]$$

$$\text{Rate} = k[CO][NO_2] \qquad (9.6)$$

Such expression as given in Eq. 9.6 is called the rate expression, rate equation, or rate law. The rate equation gives the dependence of the rate of *reaction on the concentrations of the reactants. It states that the rate of chemical reaction is proportional to the product of molar concentrations of the reacting substances raised to appropriate powers. Here, the proportionality constant 'k' is called specific rate constant or simply rate constant.*

9.2.2 Specific Rate Constant

Consider a general reaction, $A + B \longrightarrow$ Products.

Rate of this reaction can be expressed as

$$\text{Rate} = \frac{-\Delta[A]}{dt} = \frac{-\Delta[B]}{dt} = k\,[A]^m[B]^n$$

The proportionality constant "k" is called rate constant or velocity constant. m and n may be either whole numbers, zero, or fraction. If the concentrations of A and B are taken as unity, the rate constant k is equal to the rate of the reaction. "k" has a fixed value for a reaction under given conditions of temperature.

$$\frac{dx}{dt} = k[1]^m\,[1]^n$$

$$\frac{dx}{dt} = k$$

In this case the rate is independent of the concentrations of reactants

9.2.3 Order of Reaction and its Determination

Consider a general reaction, $A \longrightarrow$ Products

Rate of the reaction,

$$\frac{dx}{dt} \propto [A] \qquad \text{or} \qquad \frac{dx}{dt} = k[A]$$

This expression is called as *rate expression which shows a relationship between the rate of reaction and the concentration of the reacting species. It is also called as rate equation or rate law*. The power of reactant terms in the rate equation is called the order of reaction. The order of reaction indicates the way the rate depends on the concentration of the reactants or it shows the proportional relation between rate and concentration of reactants. Thus, *the order of reaction is defined as the sum of the exponents (powers) of the concentration terms of the reactants in the rate expression of the reaction* For example, in the above rate equation power of reactant term is one, it is first order reaction. Here the rate of the reaction is proportional to the first power of the concentration of single reactant. The reactions may be zero order, 1st order, 2nd order, 3rd order and also may have a fractional order. For a hypothetical reaction

$$A + B \longrightarrow \text{Product.}$$

At constant temperature, the rate of reaction depends on the concentrations of the reactants A and B. This dependence can be written in the form of the rate equation

$$\text{Rate} = \frac{dx}{dt} = k\,[A]^m[B]^n$$

Where 'k' is the rate constant of the reaction, the power, m is the order with respect to reactant A and n is the order with respect to reactant B and the overall order of the reaction is (m+n). Remember that the order is strictly an experimental parameter, it cannot be predicted from coefficients of the reactants in the balanced chemical equation or calculated theoretically. Some examples of the reactions of different orders are given in the subsequent sections.

Tidbit

1. Molecularity is the number of reacting species taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction.
2. It cannot be zero, and must be a positive integer, 1, 2, or 3.
3. It can be calculated by simply adding the number of molecules of the reactants in the slowest step.
4. Generally, molecularity of the slowest step is same as the order of the overall reaction.

9.2.3.1 First Order Reactions

The reactions in which the rate of reaction is proportional to the first power of the concentration of a single reactant. e.g.

(i) $Br_2 \longrightarrow 2Br$

$$\frac{dx}{dt} = k[Br_2]$$

(ii) ${}_{88}Ra^{226} \rightarrow {}_{86}Rn^{222} + {}_{2}He^{4}$

$$\frac{dx}{dt} = k[Ra]$$

(iii) The thermal decomposition of nitrogen pentaoxide in gaseous state.

$$N_2O_{5(g)} \longrightarrow 2NO_{2(g)} + \frac{1}{2}O_{2(g)}$$

$$\frac{dx}{dt} = k[N_2O_5]$$

9.2.3.2 Second Order Reactions

The reactions for which the rate of the reaction is proportional to the second power of concentrations of reactants are second order reactions.

$$2A \rightarrow \text{Products}$$

$$\frac{dx}{dt} = k[A]^2$$

It is a second order reaction because the rate of reaction is proportional to the second power of concentration of the reactant.

Example: 9.1

(i) Thermal decomposition of nitrogen dioxide,

$$2NO_2 \rightarrow N_2 + 2O_2$$

$$\frac{dx}{dt} = k[NO_2]^2$$

(ii) Thermal decomposition of hydrogen iodide

$$2HI \rightarrow H_2 + I_2$$

$$\frac{dx}{dt} = k[HI]^2$$

The second order reaction can also be represented in general form as

$$A+B \rightarrow \text{Products}$$

$$\frac{dx}{dt} = k[A][B]$$

It is a second order reaction because the rate of reaction is proportional to the concentrations of two reactants A and B each raised to the first power.

Example: 9.2

(i) Formation of hydrogen iodide from hydrogen and iodine.

$$H_2 + I_2 \longrightarrow 2HI$$

$$\frac{dx}{dt} = k[H_2][I_2]$$

9.2.3.3 Third Order Reactions

(i) Those reactions for which the rate of reaction is proportional to the third power of concentrations of reactants. It can be represented as

$$A+B+C \longrightarrow \text{products}$$

And rate of the reaction is given as follows

$$\frac{dx}{dt} = k[A][B][C]$$

It is third order reaction, provided that it is first order with respect to concentration of each of the reactants A, B and C,

(ii) Similarly for reaction of the type

$$A + 2B \longrightarrow \text{products}$$

The respective rate equation is as follows

$$\frac{dx}{dt} = k[A][B]^2$$

It is first order with respect to A and second order with respect to B.

(iii) For the reaction

$$3A \longrightarrow \text{products}$$

The rate equation is,

$$\frac{dx}{dt} = k[A]^3$$

It is also a third order reaction.

Example: 9.3

Gas phase oxidation of nitric oxide

$$2NO + O_2 \longrightarrow 2NO_2$$

$$\frac{dx}{dt} = k[NO]^2[O_2]$$

Tidbit

Units of Rate Constant

For a general reaction $A + B \longrightarrow \text{Product}$

The rate equation is

$$\frac{dx}{dt} = k[A]^{\alpha}[B]^{\beta}$$

The overall order 'n' of this reaction is $n = (\alpha + \beta)$

The expression for the units of rate constant can be given as;

$k = (\text{concentration})^{1-n}\ \text{time}^{-1}$, concentration is given in mol dm^{-3} and time may be in any unit of sec., min., hr. etc. Thus, the unit of zero order is mol dm^{-3} s^{-1}, for first order is s^{-1}, for second order dm^3 mol^{-1} s^{-1} and for third order reaction the unit is $(dm^3)^2$ mol^{-2} s^{-1}.

Role of Rate Constant in Theoretical determination of Reaction Rate

The rate equations, discussed in the preceding sections, *give relationship between rate of reaction, the concentration of reactants, and the rate constant 'k' which is the rate of the reaction when the concentration of reactants is unity.* Rate constant is temperature dependent and is constant for a given reaction at a particular temperature. It is important to realize that the rate equation can only be obtained by experiment, since the values of order therein are experimental quantities, and cannot be deduced either theoretically, or from the stoichiometric equations. Once the rate equation has been established with the knowledge of the order; the rate equation can be used to calculate rate of reaction theoretically for any desired concentrations of the reactants, provided that the value of rate constant is known. The following example illustrates this further.

Self-Assessment

- Define order of reaction.
- Differentiate between first order and second order reactions.

Example 9.4

For a first order reaction A → B, the rate constant is $0.0458\ s^{-1}$, calculate rate of the reaction if the concentration of reactant is $0.35\ mol\ dm^{-3}$.

Solution:

Rate constant $k = 0.0458 s^{-1}$

Concentration of reactant $[A] = 0.35 mol\ dm^{-3}$

Equation: Rate = $k \times [A]$

Rate= $0.0458\ s^{-1} \times 0.35 mol\ dm^{-3} = 0.016\ mol\ dm^{-3} s^{-1}$

Example 9.5

For the decomposition of nitrogen pentaoxide N_2O_5, dissolved in carbon tetrachloride $2N_2O_5 \xrightarrow{CCl_4} 4NO_2 + O_2$

The following data was obtained at 30°C

Rate of decomposition of N_2O_5 (mole dm^{-3} $hour^{-1}$)

Mole dm^{-3}	Rate of reaction
0.170	0.050
0.340	0.10
0.680	0.20

(a) Write the rate equation for the reaction. What is the order of the reaction?
(b) Calculate the rate constant for the reaction at 30C°.

Solution

(a) The data show that doubling the concentration of N_2O_5 from 0.170 to 0.340 mol dm^{-3}, or from 0.340 to 0.680 mol dm^{-3}, doubles the rate from 0.05 to 0.10 mol dm^{-3} $hour^{-1}$, or from 0.10 to 0.20 mol dm^{-3} $hour^{-1}$. Therefore, the rate of this reaction is directly proportional to the first power of N_2O_5 concentration, or.

$$\text{Rate} = k\,[N_2O_5]$$

Since the rate is proportional to the first power of one reactant, the reaction is first order.

(b) To calculate the rate constant, we first solve the rate equation for k:

$$k = \text{rate}/\,[N_2O_5]$$

Then substitute any of the three sets of data

$$k = \frac{0.05\ \text{mol dm}^{-3}\ \text{hour}^{-1}}{0.170\ \text{mol dm}^{-3}} = 0.29/\text{hour}$$

$$\text{or} \qquad k = \frac{0.10\ \text{mol dm}^{-3}\ \text{hour}^{-1}}{0.340\ \text{mol dm}^{-3}} = 0.29/\text{hour}$$

$$\text{or} \qquad k = \frac{0.20\ \text{mol dm}^{-3}\ \text{hour}^{-1}}{0.680\ \text{mol dm}^{-3}} = 0.29/\text{hour}$$

Notice that, in a first order reaction the rate constant has only the unit of $time^{-1}$.

9.2.4 Factors affecting Rate of Reaction

Experimentally, we find that the rate of a chemical reaction depends upon a number of factors. These are:

i. The nature of the reactants.
ii. The concentration of the reactants.
iii. The particle size of a solid reacting with gases.
iv. The temperature of the reaction mixture.
v. The presence or absence of a catalyst.
vi. Light (in photosensitive reactions).

i. The nature of the reactants

During a chemical reaction chemical bonds are broken and new bonds are formed. The nature (or type) and number of these bonds and their strength play a critical role in the rate of reaction. Ionic compounds react faster than covalent compounds as in the aqueous medium ions are only exchanged which were already separated (dissociated) in aqueous solution, e.g.

$$AgNO_{3(aq)} + NaCl_{(aq)} \longrightarrow AgCl_{(s)} \downarrow + NaNO_{3(aq)}$$

On the other hand, reactions between covalent compounds take place slowly because they require energy for breaking of existing bonds and for the formation of new bonds, the molecules must come in contact at particular orientations, e.g. esterification of acetic acid occurs slowly due to the given reasons.

$$CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$$

The reaction of magnesium with oxygen in the presence of a flame proceeds very rapidly to form magnesium oxide. However, under identical conditions, copper reacts slowly to form copper oxide. The rate of oxidation is different for the two metals.

ii. Effect of Concentration on Rate of the Reaction

Reactions occurring in gaseous mixtures or in solutions are said to be homogeneous if they occur only in one phase. If the gaseous mixture or solution is concentrated it contains more active particles per unit volume and reaction is faster than in a dilute mixture, since in the former case more particles come in contact with each other per unit time.

The effect of concentration on reaction rate is observed from the fact that a piece of wood burns much more rapidly in pure oxygen (high concentration, 100% oxygen) than it does in ordinary air, in which the oxygen makes up only about 21% of the mixture (low concentration).

iii) The Particle Size of a Solid Reacting in Heterogenous Reactions

In the case of heterogeneous system, in which the reactants are in different states, the area of contact between the reacting substances will influence the reaction rate considerably.

Thus magnesium powder will react much rapidly than magnesium ribbon with dilute sulfuric acid. Similarly, zinc powder reacts more rapidly with acid to liberate hydrogen gas than lumps of zinc metal. In general, smaller the size of the reacting particles, the greater is the total surface area exposed for reaction and, consequently, the faster the reaction.

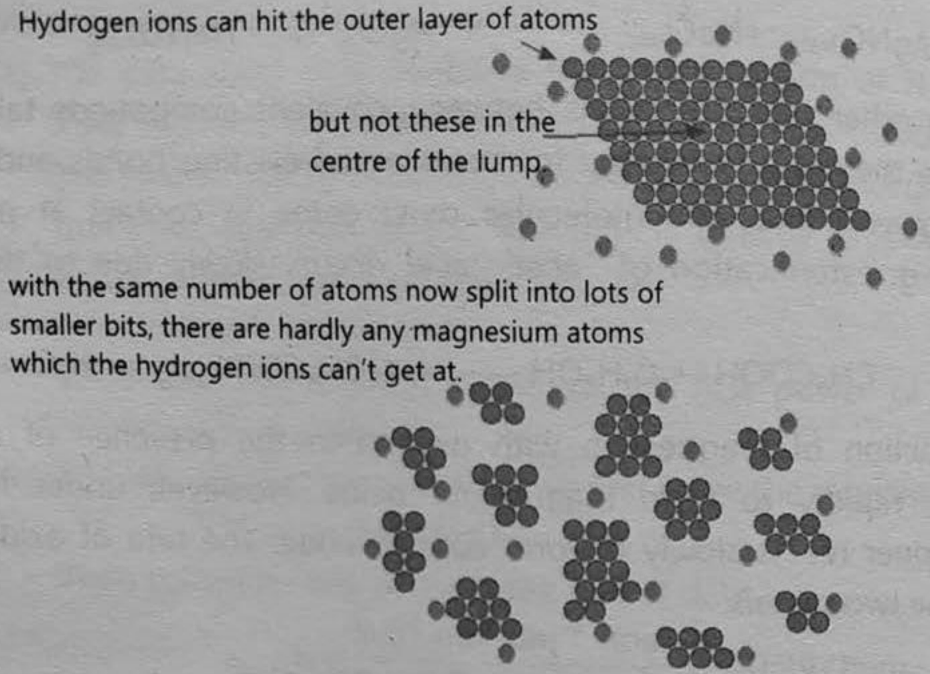


Fig. 9.2

iv. Effect of Temperature on Rate of Reaction

In general, an increase in temperature increases the rate of the reaction. Temperature affects the rate of reaction in two ways:

1. Raising the temperature increases the kinetic energy of the molecules and hence speeds up the molecular motion. This results in more collisions between molecules in a given time and chances of the reaction increase.
2. Secondly, the molecules (or atoms) to react, they must have a minimum energy available to them; known as activation energy. The higher the temperature, the greater is the chance of the reactants having energy greater than the activation energy of the reaction and higher will be the rate of the reaction.

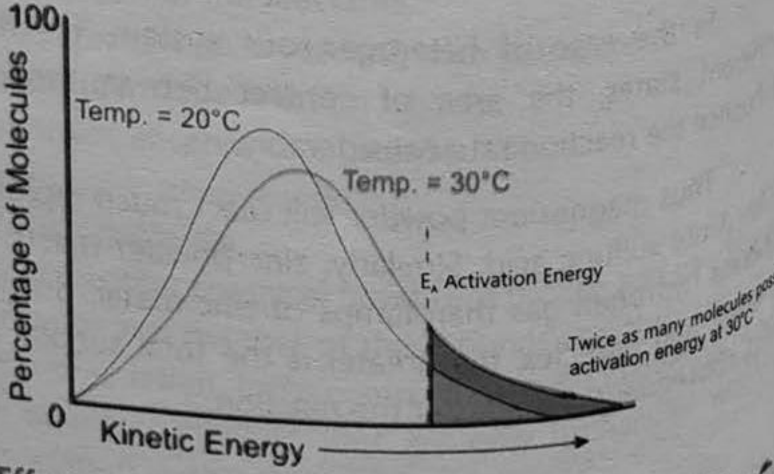


Fig: 9.3 Effect of Temperature on Rate of Reaction

Only those particles represented by the area to the right (shaded with colours) will have enough energy to react when they collide. With the increase in temperature, the number of particles with energy equal to or greater than activation energy increases (total shaded area under the curve), thus the rate of reaction increases.

v. The Presence or absence of Catalyst

A reaction rate generally increases by the presence of a substance called a catalyst. A catalyst is a substance that increases the rate of a chemical reaction but is left chemically unchanged at the end of the reaction. This substance is certainly involved in the reaction but is not permanently changed by it. Often only a very small quantity is needed to influence the reaction. In the laboratory preparation of oxygen, a sample of potassium chlorate is heated as shown:

$$2\,KC\ell O_3 \xrightarrow{\Delta} 2\,KC\ell + 3O_2$$

However, this thermal decomposition is very slow in the absence of a catalyst. By adding a small amount of manganese dioxide (MnO_2) the reaction rate can be increased. The detailed discussion on catalyst will appear in Section 9.4.

vi) Light

Reactions which are influenced by light are called photochemical reactions. Photosynthesis and photography both involve light sensitive reactions. The leaves of the plant contain a green pigment called chlorophyll. This can absorb sunlight and use this energy to transform carbon dioxide and water into oxygen and sugar such as glucose. Thus, photosynthesis is very useful both for the plants and other living organisms. Without light, such an important reaction could not take place and it would have made life impossible. Other examples of photochemical reactions include; decomposition of hydrogen peroxide, and reaction between methane and chlorine etc. In such reactions molecules of reactants get activated by absorption of light and react rapidly.

Reading Check

- Name the factors affecting the rate of reaction.
- Explain the effect of temperature on rate of reaction with graph.

9.3 Collision Theory, Transition State and Activation Energy

Kinetic studies give us information about the effects of concentration, temperature, and catalyst on reaction rates. One of the goals of the chemical kinetics is to explain these effects on a theoretical basis so that we can better understand the mechanism of the reaction. In this section, we shall discuss important theory, but first let us familiarize ourselves with the concept activation energy.

9.3.1 Activation Energy and Transition State

For a reaction to occur between molecules, a certain amount of ener must be absorbed to weaken the bonds holding the atoms of the reacta molecules together. The quantity 'E$_a$' represents the minimum energy required bring the reactants to a state where they can rearrange to form products.

For two molecules to react, they must collide with each other but energy o collision may not be enough for the reaction to take place. Any molecule in motio possesses kinetic energy; the faster it moves, the greater is the kinetic energy. A fas moving molecule, when collides with another molecule a part of their kinetic energ is converted to potential energy (e.g.; as vibrational energy). If the initial kineti energies are large, then the colliding molecules will vibrate so strongly as to brea some of the chemical bonds. If the initial kinetic energies are small, the molecule will just touch each other with certain force without bringing any change. Thus, ther is some minimum collision energy below which no reaction occurs. This energy i called 'activation energy', Ea. *It is the minimum amount of energy required to initiate a chemical reaction.*

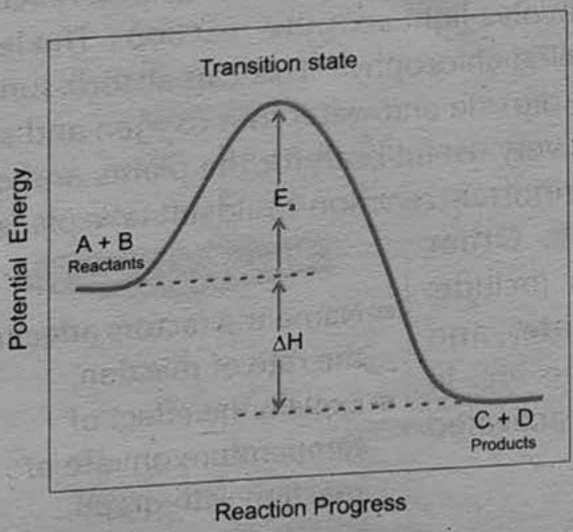


Fig. 9.4.A. A potential energy diagram for an exothermic reaction

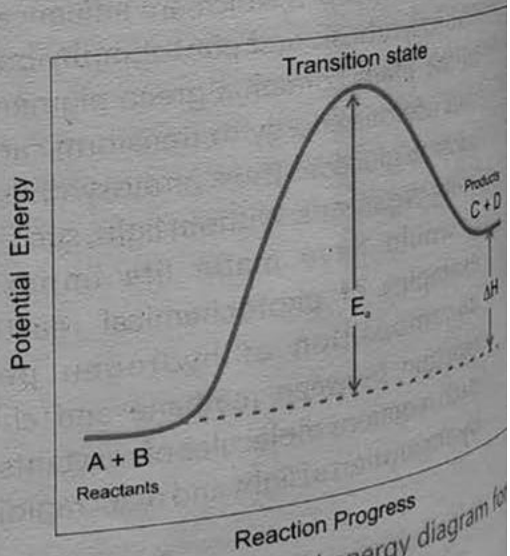


Fig. 9.4.B. A potential energy diagram fo an endothermic reaction

Note: Where E$_a$ is activation energy and ΔH is heat of reaction.

We can represent the potential energy of the reacting system during a chemical reaction using a potential energy diagram in which potential energy of a reaction is plotted against the progress of the reaction through time (Fig. 9.4 A and B). The 'hill' or energy barrier in diagram shows the activation energy of the reaction. If the activation energy is high, the reaction may be slow because a few molecules would be able to cross this high energy barrier, and on the other hand, if the activation energy is less, the reaction will be fast as more number of molecules can cross this barrier.

A potential energy diagram for an exothermic reaction is shown in Fig 9.4 A. The reactants at the beginning of the reaction are at a higher energy level than the products. The overall difference in the potential energy between the energy of the reactants and the products is the enthalpy change 'ΔH' of the reaction. A potential energy diagram of an endothermic reaction is shown in Fig 9.5B. The reactants at the beginning of the reaction are at a lower energy level than the product. The overall difference in potential energy is the enthalpy change of the reaction.

The top of the activation energy barrier of a potential energy diagram represents the transition state of the reaction. The chemical species that exists at the transition state is referred to as the activated complex. The activated complex is the transition species that is neither product nor reactant. It has partial bonds and is highly unstable. It can either break down to form products or it can decompose to reform the reactants. It cannot be isolated as a chemical species and it has short life span. Its formation can be shown in Fig. 9.4.

There is a difference between the transition state and the activated complex. The transition state refers to the top of the energy barrier on the potential energy diagram, while the chemical species that exists at this transition point is called the activated complex.

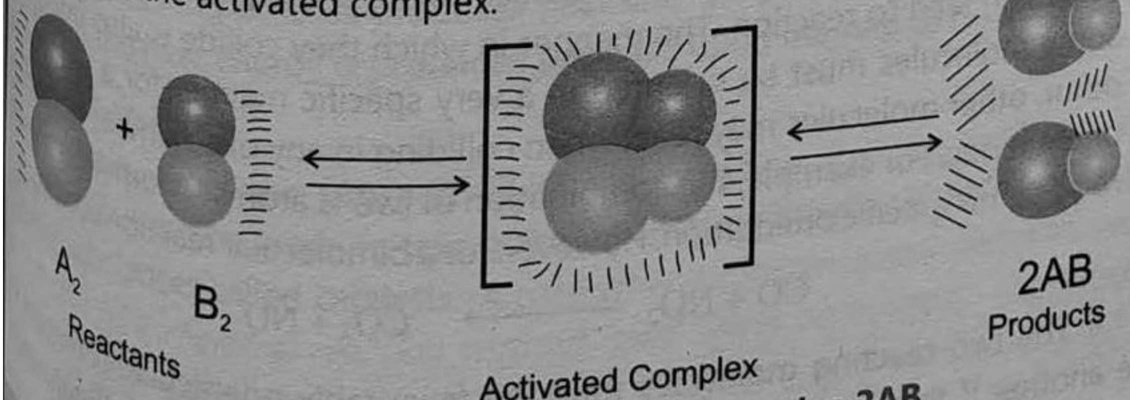


Fig. 9.5 Collision of A_2 and B_2 to give 2AB

9.3.2 Collision Theory of Reaction Rate

It is obvious that for a chemical reaction between two molecules to occur they must come into contact with each other i.e.; the chemical reactions occur as a result of collision between reacting molecules. This fact is the basis of the collision theory of reaction rate. This theory is based upon the following assumptions:

1) For a chemical reaction to occur, particles (atoms, molecules etc.) of the reactants must collide with each other. In the resulting collisions, atoms are re-arranged, bonds are broken and formed, leading to the production of new substances as products.
2) Reaction between the colliding particles can only take place if upon collision they possess a certain minimum amount of energy, the activation energy.
3) Not every collision between the molecules having the required energy of activation leads to reaction. Only those collisions are effective which take place with proper orientation or arrangement of the colliding molecules.

Explanation

1. The first postulate tells us that if we increase the number of molecules present in a given volume, the number of collisions increases, an consequently, the rate of reaction increases.
2. The second assumption of the theory that molecules react only if upo collision they possess a certain minimum amount of energy, the energy o activation, necessary to break the bonds of reactant molecules. The activatio energy depends upon the nature of the reactants (associated with bon energies) and is therefore, a characteristic value for each reactant. If energy colliding molecule is equal to or greater than the energy of activation th reaction would occur, if it is less than that, no reaction would occur.
3. However, not all collisions between molecules possessing the required energy activation lead to reaction. The manner in which they collide is also importa Some molecules must be oriented in a very specific manner for a reaction occur, other molecules may react when colliding in any of a number of rando orientations. For example, the combination of two H atoms to form H_2 molecu requires no specific orientation. However, for a bimolecular reaction such as,

$$CO + NO_2 \longrightarrow CO_2 + NO$$

The two reacting molecules must be favourably oriented with respect one another if they are to react upon collision. On CO and NO_2 collision, wh carbon and nitrogen atoms come in contact with one another it is unlikely that the necessary transfer of an oxygen atom will take place from NO_2 to CO molecule. The probability of such transfer increases when carbon atom of CO happens to collide with one of the oxygen atoms of NO_2. (Fig.9.6)

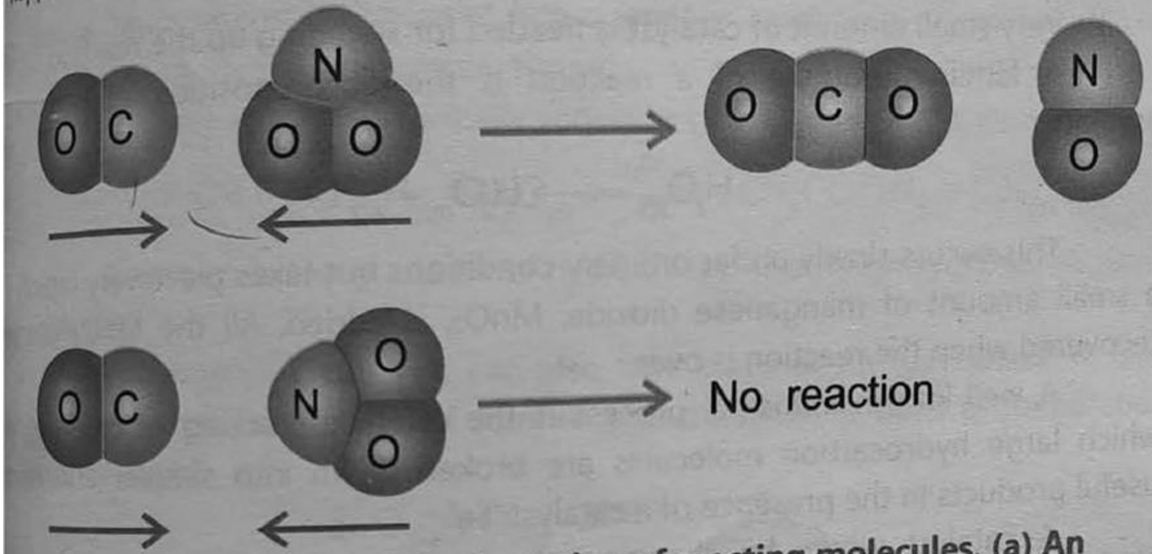


Figure 9.6. Relative orientation of reacting molecules. (a) An effective collision and (b) An ineffective collision

Science, Technology and Society

Walkers and climbers use warm packs in hilly area covered with snow to keep their body warm. These packs, when in use become hot and maintain the temperature at about 40°C for several hours.

A warm pack contains chemicals like, finely powdered iron, water, sodium chloride absorbed on an inert powdered carbon catalyst, evenly mixed together in a porous bag. The whole pack is contained in a polythene bag. When the polythene bag is opened, air enters the pack. The iron in the pack rusts, forming iron oxide, Fe_2O_3.

The rusting process produces heat and the pack becomes warm. The rate at which the heat energy is produced depends upon the rate of rusting.

9.4 Catalysis

Many reactions proceed quite slowly when the reactants are mixed together but can be made to take place much more rapidly by the introduction of other substances called catalysts. *A catalyst is a substance that generally increase the rate of a chemical reaction without itself being consumed. The process of increasing the rate of a reaction through the use of a catalyst is referred to as catalysis.*

9.4.1 Characteristics of Catalysts

Catalysts have the following characteristics:

1) Catalyst generally increases the rate of reaction
2) They are not consumed in the reaction and are recovered chemically unchanged at the end of the reaction.
3) Very small amount of catalyst is needed for speeding up the reaction.

A familiar example of a reaction is the decomposition of hydrogen peroxide;

$$H_2O_{2(l)} \longrightarrow H_2O_{(l)} + \frac{1}{2}O_{2(g)}$$

This occurs slowly under ordinary conditions but takes place very rapidly if a small amount of manganese dioxide, MnO_2, is added. All the MnO_2 can be recovered when the reaction is over.

A well-known industrial process is the catalytic cracking of crude oil, in which large hydrocarbon molecules are broken down into simpler and more useful products in the presence of a catalyst 'Fe'.

A catalyst works by changing the reaction path via a lower energy activated complex requiring lower activation energy than the un-catalyzed reaction

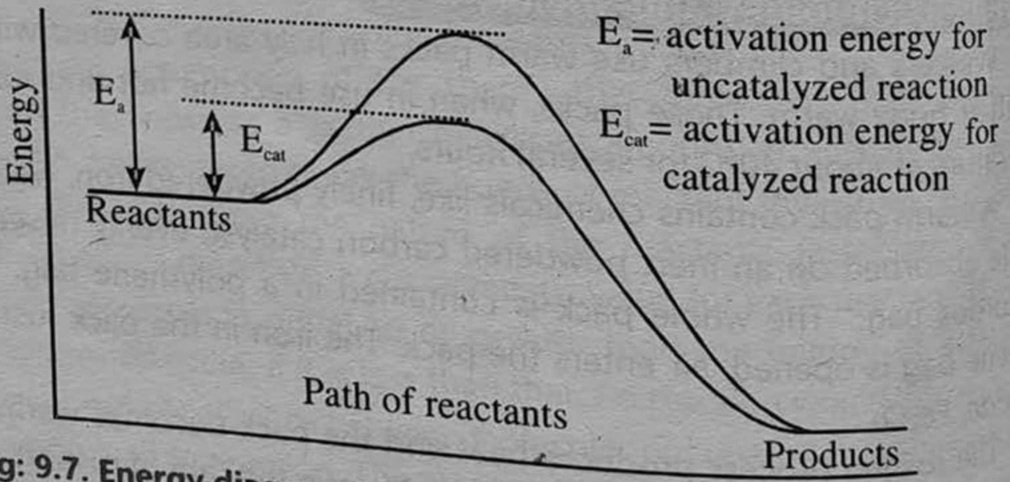


Fig: 9.7. Energy diagram for catalyzed and uncatalyzed reaction.

Fig. 9.7 compares the reaction paths for catalyzed and un-catalyzed reactions. E_a is the activation energy in the presence of a catalyst. Many molecules that do not have kinetic energy to overcome the E_a (potential energy barrier), are able to cross the lower energy E_{cat} (energy barrier) thus making the reaction faster.

Catalysts exist in several different forms, accordingly, there are corresponding catalysis processes. We shall discuss three main types of catalysis i.e. homogeneous catalysis, heterogeneous catalysis and enzyme catalysis.

9.4.2 Homogenous Catalysis

In homogeneous catalysis, the reactants and catalyst are in a single phase. Most important types of homogeneous catalysis in liquid solution is the acid-base catalysis. For example, the reaction of ethyl acetate with water to form acetic acid and ethanol is normally very slow in the absence of catalyst.

$$CH_3COOC_2H_{5(\ell)}+H_2O_{(\ell)} \xrightarrow{H_3O^+_{(aq)}} CH_3COOH_{(\ell)}+C_2H_5OH_{(\ell)}$$

However, in the presence of hydrochloric acid as catalyst the reaction rate increases.

Homogenous catalysis can also take place in the gas phase. A familiar example is the production of sulphur trioxide which is used in preparation of sulphuric acid.

$$2SO_{2(g)}+O_{2(g)} \xrightarrow{catalyst} 2SO_{3(g)}$$

In this reaction, sulphur dioxide is not converted directly to sulphur trioxide; this reaction is more efficiently carried out in the presence of $NO_{2(g)}$ as a catalyst.

9.4.3 Heterogeneous Catalysis

The catalysis in which reactants and the catalyst are not in the same phase is called heterogeneous catalysis. Mostly catalyst is solid and reactants are gases or liquid in such catalysis. On catalyst's surface a reactant molecule can be held (adsorbed) in a position favourable for reaction until a molecule of another reactant reaches the same point on the solid. Metals such as iron, nickel, platinum and palladium seem to act in this way in reactions involving gases or liquids. There is evidence that in some cases of surface adsorption, bonds of reactant molecules are weakened or broken, thus addition of other reactants takes place easily.

Heterogeneous catalysis is the most important type of catalysis in industrial processes for the production of many important and useful chemicals such as ghee and ammonia. A good example is the reaction between ethene and hydrogen.

$$C_2H_{4(g)}+H_{2(g)} \xrightarrow{Ni_{(g)}} C_2H_{6(g)}$$

This reaction is catalysed by nickel. Hydrogenation of vegetable oil to form ghee is increased if nickel (Ni) is present in powdered form as it has a much larger surface area than a large lump.

9.4.4 Enzyme Catalysis

A large number of catalysts called enzymes are found in living tissu Enzymes are proteins with high molecular weight and act as catalyst biochemical reactions occurring in all living matter. For example ptyalin, a enzyme found in saliva, accelerates the conversion of starch into sugar. Althoug starch will react with water to form sugar, several weeks will require for th conversion to occur in the absence of the enzyme. A trace of ptyalin makes th reaction proceed in minutes at body temperature. Likewise, pepsin in gastric jui breaks down protein into simpler molecules which can be utilized by body cel Nearly every step of breakdown of a complex molecule to a series of smal ones, in biological systems, is catalysed by specific enzymes.

Self-Assessment

1. Define activation energy and transition state.
2. Differentiate between homogenous and heterogenous catalysis.

KEY POINTS

- A study of rates and mechanisms of chemical reactions is chemical kinetics.
- The change in concentration of a given substance per unit time is called rate of reaction.
- An equation which relates the rate of a reaction to the molar concentration of the reactants raised to appropriate,experimentally determined powers, is known as rate equation.
- A proportionality constant relating the reaction rate to the molar concentrations of reactants that appear in the rate equation is called rate constant 'k'

$$\text{rate} = k[A][B]$$

- The sum of powers of the concentration terms appearing in the rate equation is known as order of a reaction; for example,

  if $\text{rate} = k[A]^2[B]^1$, the reaction is (2+1=3) of third order.

- Order is experimentally determined parameter.
- Rate of reaction depends on the nature of reactants, concentration, particle size (in case of solid reactants), temperature, and catalyst.
- A catalyst is a substance which changes the rate of reaction without apparently being consumed.
- The minimum energy needed for a reaction to take place is called activation energy.
- According to collision theory a reaction occurs when molecules collide with sufficient energy called activation energy, to break the bonds and initiate the reaction.
- Catalysis may be homogeneous or heterogeneous while enzymes are also catalysts which play their role in living organisms.

EXERCISE

Choose the suitable option.

i. Activated complex is a substance which is

a. stable
b. unstable
b. can be isolated
d. can exist as product

ii. A reaction is first order with respect to A and second order with respect to B, the rate equation is

a. rate = k $[A][B]^2$
b. rate = k $[A]^2[B]$
c. rate = k $[A][B]$
d. rate = k $[A]$.

iii. For a reaction A → Product, doubling the concentration of A, quadruples the rate. The reaction is;

a. first order
b. second order
c. zero order
d. third order

iv. With the increase in temperature the rate of reaction increases due to

a. decrease in collisions
b. decrease in activation energy
c. increase in kinetic energy of the molecules
d. more number of molecules attains activation energy.

v. You can speed up a reaction by:

a. using less concentrated solution.
b. by lowering the temperature.
c. using more concentrated solution.
d. stopping stirring.

vi. When the catalyst and reactants are in different physical phases, we call the catalysis:

a. Heterogeneous
b. Homogeneous
c. Concentrated
d. positive catalysis

vii Increasing the temperature increases the rate of reaction by

a. lowering the activation energy.
b. increasing the activation energy.
c. lowering the frequency of effective collisions between reacting molecules.
d. increasing the frequency of effective collisions between reacting molecules.

viii. The energy needed to start the reaction is called

a. potential energy b. activation energy

c. kinetic energy d. ionization energy

ix. As the number of effective collisions between the reacting particles increases, the rate of reaction

a. Decreases b. Increases

c. remains the same d. both b and c

x. Which condition will increase the rate of reaction?

a. Decrease in temperature and concentration of reactants.

b. Decrease in temperature and increase in concentration of reactants.

c. Increase in temperature and decrease in concentration of reactants.

d. Increase in temperature and increase in concentration of reactants.

xi. A catalyst

a. decrease the activation energy and decrease the rate of reaction.

b. decrease the activation energy and increase the rate of reaction.

c. increase the activation energy and decrease the rate of reaction.

d. increase the activation energy and increase the rate of reaction.

xii. Which aluminum sample would react most rapidly with 1 M $CuSO_4$ solution under the same conditions?

a. 1 g Al rod b. 1 g Al pellets

c. 1 g Al ribbon d. 1 g Al powder

xiii. One mole of a reactant reacts with a rate of 0.6 mol $dm^{-3}\ s^{-1}$. What is the rate constant of this reaction?

a. 1 s^{-1} b. 0.3 s^{-1}

c. 0.6 s^{-1} d. 0.9 s^{-1}

Short Questions

i. Determine the overall orders from the following rate equations

a. $\text{rate} = k[NO]^2[O_2]$

b. $\text{rate} = k[NO]^2$

ii. Explain why a molecular collision should be sufficiently energetic to cause a reaction.

iii. Name the four factors that increase the rate of reaction.

iv. In the light of collision theory of reaction rate, give reasons of increase in the rate by the increase of temperature.

v. Consider two gases, A and B, in a container at room temperature. What effe would the following changes have on the rate of the reaction between the gases?

a. The pressure is doubled.

b. The number of molecules of gas A is doubled.

c. The temperature is decreased by 10 °C

vi. The rate constant for the reaction

$$CO + NO_2 \longrightarrow CO_2 + NO$$

at 400 °C is 0.50 $dm^3\ mol^{-1}\ sec^{-1}$, and the reaction is first order with respect t both CO and NO_2.

a. What is the overall order of the reaction?

b. What is the rate of the reaction at 400°C when the concentration of CO is 0.025 mol dm^{-3} and that of NO_2 is 0.040 mol dm^{-3}?

(Ans: 5×10^{-4} mol $dm^{-3} sec^{-1}$

vii. Explain briefly why all collisions between reactant molecules do not lead t reaction?

Descriptive Questions

Q1: Define the following terms.

a. Rate of the reaction

b. Rate constant.

c. Order of the reaction.

d. Rate law or rate equation.

e. Catalyst

Q2: (a) Define the activation energy. What role does it play in chemical reaction

(b) Household gas (methane) burns in the presence of oxygen and gives ener for our daily use. If a mixture of methane and oxygen is kept in a contai for indefinite period, no reaction takes place, explain?

Q3. Explain how does a catalyst increase the rate of a reaction? Compare catalyzed and un-catalyzed reaction on a potential energy diagram.

Q4. Explain the relationship between reactant concentration and rate of reaction.

Q5. Discuss why, (according to collision theory of chemical reactions) so molecular collisions result in a chemical reaction while others do not. D and explain a reaction energy diagram (reaction profile) for

a. an exothermic reaction.

b. an endothermic reaction.

Also show in the diagram

a. position of the energy of reactants

b. position of the energy of products

c. activation energy.

d. ΔH of the reaction.

Numerical

1. The conversion of X to Y follows second order kinetics. If concentration X is increased 3 times to what factor the rate of formation of Y will be increased. (Ans. 9 times)

2. A first order reaction (A→ Product) has a rate of 0.008 Ms^{-1} with [A]=0.002 M, what is the rate constant for this reaction? (Ans. 4 s^{-1})

3. (a) The decomposition of N_2O_5 proceeds according to the following equation.

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

(b) If the rate of decomposition of N_2O_5 at a particular instant is 4.2×10^{-7} Ms^{-1}, what is the rate of appearance of (a) NO_2 (b) O_2?

(Ans.(a)$8.4\times10^{-7}Ms^{-1}$ (b)$2.1\times10^{-7}Ms^{-1}$)

Project

Hydrogen peroxide decomposes to produce oxygen and water according to reaction shown below.

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

The reaction is quite slow unless catalysed by substances such as iodide ions, manganese dioxide, ferric ions etc. Take a test tube and add about 10 to 15cm^3 of hydrogen peroxide in it. Add a few crystals of potassium iodide to it and watch the bubbles of oxygen coming out from the test tube. Bring a glowing match stick at the mouth of the test tube and observe. What do you expect to happen with the stick? Explain.

Unit-10

Solutions and Colloids

After studying this unit, the students will be able to:

- List the characteristics of colloids and suspensions that distinguish them fr solutions. (Applying)
- Define hydrophilic and hydrophobic molecules. (Remembering)
- Explain the nature of solutions in liquid phase giving examples of complet miscible, partially miscible and immiscible liquid-liquid solutions. (Applying
- Explain the effect of temperature on solubility and interpret the solubil graph. (Analysing)
- Express solution concentration in terms of mass percent, molarity, molali parts per million, billion and trillion and mole fraction. (Remembering)
- Define the term colligative properties. (Remembering)
- Describe on a particle basis why a solution has a lower vapour pressure th the pure solvent. (Applying)
- Explain on a particle basis how the addition of a solute to a pure solve causes an elevation of the boiling point and depression of the freezing poi

Teaching

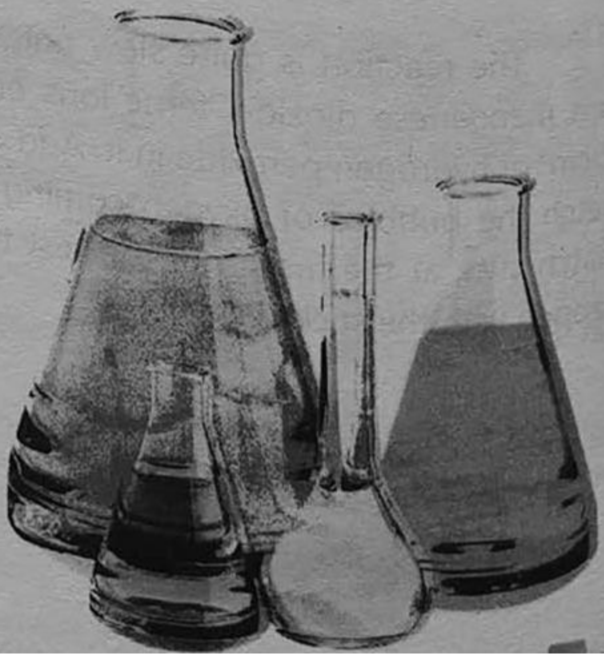
12

Assessment

01

Weightage %

09



of the resultant solution. (Applying)

- Describe the role of solvation in the dissolving process. (Understanding)
- Define the term water of hydration. (Remembering)
- Explain concept of solubility and how it applies to solution saturation. (Applying)
- Distinguish between the solvation of ionic species and molecular substances. (Understanding)
- List three factors that accelerate the dissolution process. (Understanding)
- Define heat of solution and apply this concept to the hydration of ammonium nitrate crystals. (Applying)
- Explain how solute particles may alter the colligative properties. (Applying)
- Explain osmotic pressure, reverse osmosis and give their daily life applications. (Applying)
- Describe types of colloids and their properties. (Applying)
- List some colligative properties of liquids. (Understanding)

Introduction

In the grade IX, you have learnt the basic information about solution, like omogenous and heterogeneous mixture, types of solution, saturated and saturated solutions, concentration and its units, solubility and factors affecting lubility, dissolution process, and some introduction to colloids and suspension. n the basis of these concepts you will develop more knowledge about the lution in this unit.

10.1 General Properties of Solutions

A **solution** is a homogeneous mixture of two or more substances in which the ratio of the constituent substances remains the same throughout the solution. Generally a solution consists of two components, the solute and solvent. The substance that is present in lesser amount is the solute while the one with the greater amount is called solvent. Solute may be solid, liquid or gas or combination of these. The particles of solute may be at ionic or molecular level. The particle size ranges from 0.01 to 1 nm, which cannot be seen by naked eye. A solution is stable if it is not separated on standing. Solute and solvent cannot be separated by filtration or by centrifugation. It is composed of one phase. At a given temperature and pressure, the composition of solution can be varied to a maximum value up to the saturation value. A solution does not allow a beam of light to scatter when passed through it. The mixture of salt or sugar in water is an example of solution.

Colloids, on the other hand, are heterogeneous mixture of larger particles or aggregate of particles of size ranging from 1 to 1000nm dispersed in solvent or dispersion medium. They do not settle down on standing and cannot be separated by filtration. They scatter light when passed through them, a phenomena, called the Tyndal effect. Gum in water is an example of colloidal dispersion. Suspensions are also heterogeneous mixtures with size of the particles greater than 1000nm. Particles are settled down on standing and can be separated by filtration. They can scatter light or may be opaque, e.g., finely ground clay mixed with water is an example of suspension.

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When a bottle containing a carbonated beverage (soda water) is opened, bubbles of carbon dioxide rise to the liquid's surface. Sometimes violent release of carbon dioxide gas can be stopped if the bottle's cap is retightened. If the beverage is at room temperature, an energetic evolution of gas may occur. This observation can be explained as follows.

The solubility of gas depends on the pressure acting upon the system. If the pressure of the system is reduced, the dissolved gas rapidly leaves the solution phase as small bubbles. As these bubbles rise within the solvent, their size is increased because they are encountering less pressure. On reaching the liquid's surface, the bubbles burst.

When the container is closed, there is equilibrium between the gas above the liquid and the gas dissolved in the solvent. If the container is opened, the pressurized gas escapes. The reduced pressure on the liquid's surface allows additional gas molecules to leave the solution. Beverages are packaged in sealed bottles and cans to prevent the escape of carbon dioxide. The beverages can be kept indefinitely without losing their carbonation (CO_2) until they are opened by the consumer.

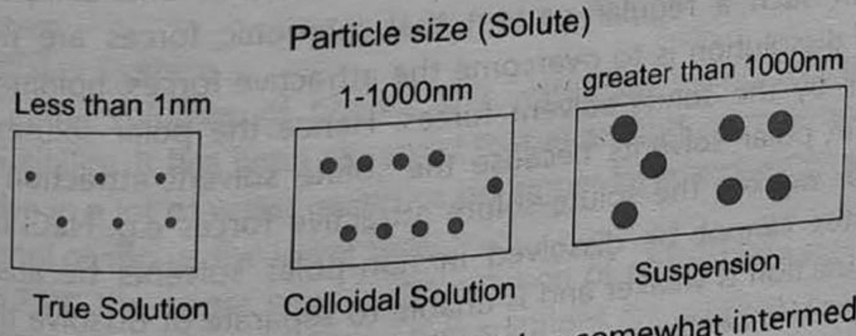
10.1.1 Solution, Suspension and Colloids

Colloids are mixtures of two substances which are intermediate between true solution and suspension. The particles in such a mixture are smaller than those in a suspension but larger than those in a true solution. A detailed discussion on colloids is given in section 10.5.

The name colloid was coined by Graham (Greek: kolla: glue, eidos, like) Colloids are substances consisting of a continuous, homogenous medium known as dispersion medium (or outer phase) and particles of a discontinuous medium termed as dispersed medium (or inner phase). The milky dispersion of sulphur, starch, gum in water and blood serum are all examples of colloids.

Tidbit

The general pattern of dissolution can be stated as "like dissolves like" that means inorganic solute such as sodium chloride, ammonia etc. are soluble in inorganic solvent e.g. water. Organic substances e.g. fats, oils etc are soluble in organic solvents such as benzene, alcohol etc.



Since colloidal dispersion of a substance is a somewhat intermediate stage between a true solution and a course suspension, it is impossible to draw a line of difference between true solution and colloidal dispersion at one end and between colloidal dispersion and suspension at the other end. There is a gradual change from one type of system to the other, however, colloidal system have certain properties which place them in a separate group. The properties and the behaviour of colloids depend chiefly on the size, shape and charge of the dispersed particles. Some distinctive properties of colloids are compiled and compared with true solutions and coarse dispersion in Table (10.3)

10.1.2 Hydrophilic and Hydrophobic Particles

The stability of colloids depends upon the charge of dispersed particles and particles of dispersion medium. When water is used as dispersion medium and there exist an attractive force between water molecules and dispersed particles, then colloidal particles are called hydrophilic particles which means "liking water". The hydrophilic particles containing colloids are much stable. When such colloids are once precipitated they can be directly return into the colloidal form and are, therefore, called reversible colloids.

Hydrophobic means "Fearing water". When water is used as dispersion medium and no attractive force exists between water molecules and dispersed particles, the particles to be dispersed, are called hydrophobic.

The colloids formed by hydrophobic particles are less stable. If, once precipitated they cannot be directly converted into the colloidal form and are thus termed as irreversible colloids.

10.1.3 The Nature of Solutions in Liquid Phase

When a solid comes in contact with a suitable liquid, it dissolves forming a solution. This process of dissolution can be explained in terms of attraction between particles of a solute and that of a solvent. In ionic compounds ions are arranged in such a regular pattern that interionic forces are maximum. The process of dissolution is to overcome the attractive forces, holding together the solute ions by the solute-solvent forces. Hence, the polar solutes can only be dissolved in polar solvents because the solute solvent attraction is enough to separate or weaken the solute-solute attractive forces e.g. NaCl in water. Polar solid solutes cannot be dissolved in non-polar solvents because the solute-solvent attraction is weaker and is unable to separate or dissolve the solid solute ions e.g. $CaCl_2$ in benzene.

Similarly, non-polar solid solutes cannot be dissolved in polar solvents because no attractive forces are established between solute and solvent molecules e.g. naphthalene in water. However, non-polar solutes can only be dissolved in non-polar solvents because the attractive forces found in molecules of solute are less than the attractive forces between solute-solvent molecules. e.g. naphthalene is soluble in benzene,both being non-polar.

Solutions of Liquids in Liquids

There are three types of liquids in liquids systems:

1. Completely miscible liquids.
2. Partially miscible liquids.
3. Completely immiscible liquids.

Completely Miscible Liquids

Miscible liquids mix in any proportion. Immiscible liquids do not mix completely; rather make two separate layers. Miscible liquids usually are similar in their chemical structures, e.g., alcohol and water when mixed they form homogeneous solutions. Their molecules are both polar and contain OH- groups that give rise to hydrogen bonding among them.

Partially Miscible Liquids

There are a number of liquids which are not completely miscible but they are partially miscible and mix with each other up to a limited extent.

Ether dissolves water upto the extent of about 1.2% and water dissolves ether upto the extent of about 6.5%. If you mix them in proportion greater than this you would find that they will separate into two layers. Each layer is a saturated solution of the other liquid. Such solutions are called conjugate solutions. The mutual solubility of these conjugate solutions is affected by temperature changes. Typical examples of such systems are phenol-water system, trimethylamine-water system, nicotine-water system.

Phenol-Water System

If equal volumes of phenol and water are mixed together, they show partial miscibility. It has been observed that at around room temperature, phenol will dissolve in a lot of water giving us the upper layer and water will dissolve in a lot of phenol giving us the lower layer.

At 25°C the upper layer is 5% solution of phenol in water and the lower layer is 30% water in phenol. These two solutions are *conjugate solutions* to each other. The lower layer has a greater density due to greater percentage of phenol. Water acts as a solute in the lower layer while phenol is a solute in the upper layer. When the temperature of water-phenol system is increased, the compositions of both layers change. Water starts travelling from upper to the lower layer and phenol travels from lower to the upper layer. When the temperature of this system approaches 65.9°C, a homogeneous mixture of two components is obtained. This homogeneous mixture contains 34% phenol and 66% water. *The temperature above which two conjugate solutions merge into* *one another, is called critical solution temperature.* Thus phenol-water system has critical solution temperature of 65.9°C. Other partially miscible pairs of liquids have their own critical solution temperature with definite compositions of solutions.

Completely Immiscible Liquids

Such liquids are incapable of being mixed or blended together. The reason is as mentioned earlier, that polar dissolve polar and non-polar dissolve non-polar (like dissolves like). Such liquids when shacked together will form two distinct layers. Examples of immiscible liquid pairs are as follow:

a. Water and benzene.

b. Carbon disulphide and water

10.1.4 The effect of Temperature and Pressure on Solubility

It is our common observation that some substances dissolve readily, while others do not. e.g glucose dissolve easily in water to form solution as compared to cane sugar. *The weight in grams of a solute necessary to satu [illegible] 100 grams of a solvent at constant temperature and pressure is called solubility.* Solubility of a solute depends on the following three factors.

1. Nature of solute and solvent.
2. Pressure.
3. Temperature.

1. **Nature of solute and solvent**

An ionic or polar solute dissolves in polar solvent while a non-polar solute dissolves in non-polar solvent. In all the cases the limit of solubility is the saturated solution. The concentrations of various solutes in a solvent necessary for saturation range over wide limits. Thus at 20 °C, 100 g of water dissolve 192 grams of NH_4NO_3, 6.5 grams of mercuric chloride ($HgCl_2$) and only 8.4×10^{-4} grams of Ag Br. In ethyl alcohol, on the other hand, the order of solubility is reversed that is 47.6 grams of $HgCl_2$ and only 3.8 grams of ammonium nitrate. Generally, most of the inorganic substances dissolve in water than in an organic solvent, while the reverse is true for organic substances because they dissolve in organic solvent like benzene.

2. **Pressure**

The effect of pressure on the solubility of solids in liquids is generally quite small. The solubility of gases is affected much by varying the pressure. At constant temperature the solubility of a gas in a liquid is directly proportional to the pressure of the gas above the liquid. CO_2 is filled in soft drinks at pressure of 3-5 atm. So when pressure is released on the bottle by opening it, CO_2 comes out with effervescence.

3. Temperature (Solubility curve)

The solubility of most of the solid and liquid solutes increase with a rise in temperature. There is, however, no general rule to correlate temperature and solubility. For example: the solubility of KNO_3 and $Al_2(SO_4)_3$ increases with the increase in temperature but the solubility of certain solids like $Ce_2(SO_4)_3$ and Li_2CO_3 decreases with the increase in temperature. The solubility of NaCl and KBr is almost not affected by increase or decrease in temperature but remains constant. The solubility of sodium sulphate increases upto 305.4 K and on raising the temperature further, it decreases. Sodium sulphate forms decahydrate ($Na_2SO_4.10H_2O$) in water. Below 305.4 K the decahydrate is present but above 305.4K it adopts the anhydrous form (Na_2SO_4). The maximum solubility is at 305.4K.

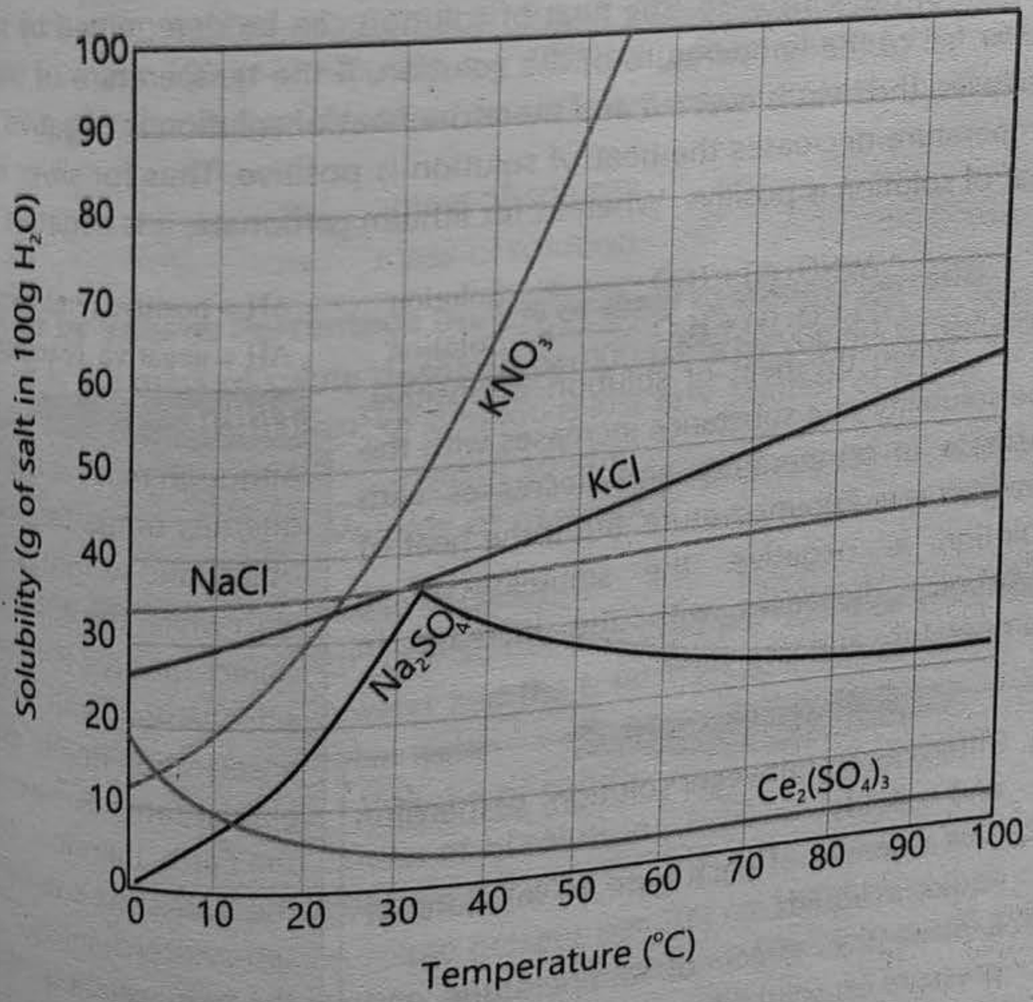


Figure 10.1 Solubility curves

Table : 10.1 Solubility of different Substances at different Temperatures

Substance	Solubility in grams per 100 grams of water					
	273K	283K	293K	303K	313K	323K
KNO_3	13.3	20.9	31.6	45.8	63.9	85.5
$Al_2(SO_4)_3$	31.2	33.5	36.4	40.4	46.1	52.2
$AgNO_3$	122	170	222	300	376	455
NaCl	35.7	35.8	36.00	36.3	36.6	37.0
$Ce_2(SO_4)_3$	20.75		10.08	6.79	-	4.67
Li_2CO_3	1.54	1.43	1.33	1.25	1.117	1.68
Na_2SO_4	5.0	9.0	19.4	40.8	48.8	44.7

10.1.5. Solubility and Heat of Solution

The change in solubility with temperature is closely related to the heat of solution of the substance. The heat of solution can be determined by noting the rise or fall of the temperature of the solution. If the temperature of the solution increases, the heat is evolved and therefore, heat of solution is negative and if the temperature decreases the heat of solution is positive. Thus, for silver nitrate the heat of solution is positive. Whereas for lithium carbonate, it is negative.

$$AgNO_3\,(s) + H_2O \longrightarrow \text{Solution} \qquad \Delta H = \text{positive (endothermic)}$$

$$Li_2CO_3\,(s) + H_2O \longrightarrow \text{Solution} \qquad \Delta H = \text{negative (exothermic)}$$

When the heat of solution is positive, the solubility of a substance increases with the increase in temperature and decreases with the decrease in temperature. But if the heat of solution is negative, the solubility of a substance decreases with the increase in temperature and vice versa.

Tidbit

Although mass is the quantity of matter in an object and weight is force with which the earth pull the object towards it, however, since W=mg, and acceleration due to gravity is almost same everywhere on the Earth, therefore, most of the books use these two terms interchangeably i.e. the term weight is mostly used for mass.

Self-Assessment

1. Differentiate between solution, suspension and colloids.
2. Give example of each type of solutions of liquids in liquids.
3. Explain the effect of temperature and pressure on solubility.

10.2 Concentration Units

The physical properties of solutions depend, to a large extent, upon the relative amounts of solute and solvent e.g. colour of a dye, the sweetness of a sugar solution or the saltish taste of common salt solution depends on the quantity of solute present. The amount of solute present in a given amount of solvent or solution is called concentration of a solution. Greater the amount of solute present in a solution the higher would be its concentration. The amount of solute, solvent and solution may be measured by volume, weight or number of moles. Accordingly, the concentration of a solution can be expressed in many ways.

10.2.1 Percentage Composition

The percentage of solution is expressed in four ways.

i) Percentage by Mass (m/m% or mass to mass percentage)

It is the number of grams of solute dissolved in sufficient amount of solvent to make 100 g of solution e.g 10% solution of glucose by mass means that 10 g of glucose are dissolved in sufficient water so that solution mass is 100g.

$$\frac{m}{m}\% = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$$

ii) Mass by Volume Percentage (m/V% or mass to volume percent)

It is the mass of solute dissolved per 100 parts by volume of solution. 10g of NaOH dissolved per 100 cm^3 of solution is 10% m/V solution of NaOH.

$$\frac{m}{V}\% = \frac{\text{mass of solute}}{\text{Volume of of solution}} \times 100$$

iii. Volume by mass Percentage (V/m%)

It is the number of cm^3 of a solute dissolved per 100 g of solution. If we dissolve 10 cm^3 of alcohol in water and the total mass of solution is 100g then it is 10% V/m solution of alcohol in water.

$$\frac{V}{m}\% = \frac{\text{Volume of solute}}{\text{mass of of solution}} \times 100$$

iv. Volume by volume Percentage (V/V%)

It is the volume of the solute present per 100 cm^3 of the solution e.g. 10 cm^3 of alcohol is dissolved in water so that the volume of solution is 100 cm^3. It is 10% V/V solution of alcohol in water.

$$\frac{V}{V}\% = \frac{\text{Volume of solute}}{\text{Volume of of solution}} \times 100$$

10.2.2. Molarity (M)

The molarity (M) of a solution is the number of moles of solute per dm^3 o solution.

$$\text{Molarity (M)} = \frac{\text{Number of moles of solute}}{\text{Volume of solution } (dm^3)}$$

$$1dm^3 = 1000cm^3 = 1 \text{ litre}$$

$$\text{Number of moles of solute} = \frac{\text{mass of solute in g}}{\text{Mol. mass of solute}}$$

Therefore,

$$\text{Molarity (M)} = \frac{\text{mass of solute in g}}{\text{Mol. mass of solute}} \times \frac{1}{\text{volume of solution } (dm^3)}$$

For example, one molar solution (1M) of sugar, $C_{12}H_{22}O_{11}$, contains 1 mole or 342 g of sugar per dm^3 of solution. It is prepared by adding 342 g of sugar i one dm^3 volumetric flask and then by adding water first to dissolve and then dilute the solution until the level of the liquid reaches the etched mark i.e when the volume of the solution becomes exactly one dm^3.

10.2.3 Molality (m)

Molality is another concentration unit of solution. Molality is defined as the number of moles of solute present in 1kg of solvent. In other words the molality of a solution is equal to the number of moles of solute dissolved i 1000g of solvent.

$$\text{Molality (m)} = \frac{\text{Number of moles of solute}}{\text{Number of kilogram of solvent}}$$

Or

$$= \frac{\text{mass of solute}}{\text{mol. mass of solute}} \times \frac{1}{\text{Kilogram of solvent}}$$

When 58.5grams (1 mole) of NaCl is dissolved in 1000 grams of water, the solution will be 1.0molal or 1.0m. Similarly, 1.0molal solution of glucose will contain 180g of glucose in 1000g of solvent. If 18g of glucose is dissolved in 1kg of water the molality (m) of glucose solution will be 0.1. Molality is independent of temperature.

Example 10.1

4.5g of glucose are dissolved in 100g of water. Calculate the molality of lution. Molecular mass of glucose is 180g mol^{-1}.

Solution

Mass of glucose = 4.5g.

Mass of water = 100g.

Molecular mass of glucose = 180g mol^{-1}

Calculations

$$\text{Moles of glucose} = \frac{4.5\ g}{180\ g.\ mol^{-1}} = 0.025\ mol$$

$$\text{mass of water in kilograms} = \frac{100 g}{1000} = 0.1kg$$

$$\text{molality (m)} = \frac{0.025}{0.1kg} = 0.25\ mol\ kg^{-1}$$

Practice Problem 10.1

A sample has 3.50 dm^3 of solution that contains 90g of sodium chloride, NaCl. What is the molarity of that solution?

Practice Problem 10.2

What is the molality of a solution containing 18.2g HCl and 250 g of water?

10.2.4 Mole Fraction (X)

Mole fraction of any component of a solution is defined as the number of moles of that particular component divided by the total number of moles of all the components in the solution. For example, if n_1 is the number of moles of solvent and n_2 is the number moles of solute. X_1 and X_2 are mole fractions of solvent and solute respectively, then mathematically X_1 and X_2 are expressed as

$$\text{Mole fraction of solvent, } X_1 = \frac{n_1}{n_1 + n_2}$$

$$\text{Mole fraction of solute, } X_2 = \frac{n_2}{n_1 + n_2}$$

$$X_1 + X_2 = \frac{n_1}{n_1 + n_2} + \frac{n_2}{n_1 + n_2} = 1$$

Note that the sum of the mole fractions is equal to one. The importance of mole fraction is, like molality, this method of expressing concentration is also independent of temperature. Moreover, concentrations of more than one solutes can easily be expressed by this method.

Example 10.2

A solution contains 2.0 moles of alcohol and 3.0 moles of water. Calculate mole fractions of alcohol and water.

Solution

Number of moles of water: $(n_1) = 3.0$ moles

Number of moles of alcohol: $(n_2) = 2.0$ moles

Mole fraction of water and alcohol are represented by X_1 and X_2 respectively.

Formula

$$\text{Mole fraction (water)}\ X_1 = \frac{n_1}{n_1+n_2} = \frac{3.0}{3.0+2.0} = \frac{3}{5}$$

$$\text{Mole fraction (alcohol)}\ X_2 = \frac{n_2}{n_1+n_2} = \frac{2.0}{3.0+2.0} = \frac{2}{5}$$

Practice problem 10.3

Calculate the mole fraction of methyl alcohol in a solution composed of 1.46 mol of methyl alcohol and 2.19 mol of ethyl alcohol.

10.2.5 Parts per million, billion, and trillion

i) Parts per million (ppm)

It is defined as the number of parts (by mass or volume) of a solute per million parts (by mass or volume) of the solution. Parts per million is used for very low concentration of solution. The concentration of impurities of substances in water is expressed by this unit.

$$\text{ppm} = \frac{\text{mass or vol. of solute}}{\text{mass or vol. of solution}} \times 10^6$$

Example 10.3

Sea water contain $5.65\text{x}10^{-3}$g of dissolved oxygen per kilogram of solution. Calculate the concentration of oxygen in parts per million in sea water.

Solution

Mass of solute (dissolved oxygen) = $5.65\text{x}10^{-3}$g

Mass of solution =1kg

Concentration of solute in ppm=?

As

$$\text{Concentration (ppm)} = \frac{\text{mass of dissolved oxygen}}{\text{mass of solution}} \times 10^6$$

$$\text{ppm of oxygen} = \frac{5.65\times10^{-3}\ \text{g}}{1000\ \text{g}} \times 10^6$$

$$= \frac{5.65\times10^{-3}\ \text{g}}{10^3\ \text{g}} \times 10^6 = 5.65\ \text{ppm}$$

Parts per billion (ppb)

It is defined as the number of parts (by mass or volume) of a solute per lion parts (by mass or volume) of the solution. Parts per billion is used for very w concentration of solution.

$$\text{Concentration (ppb)} = \frac{\text{mass or vol. of solute}}{\text{mass or vol. of solution}} \times 10^9$$

ample 10.4

A 2.0dm^3 gas cylinder contains a mixture of various gases. If 5.0cm^3 of H_2 s is present in this mixture. Calculate the concentration of H_2 gas in parts per lion (ppb).

lution

Volume of H_2 gas =5.0cm^3.

Volume of cylinder= 2.0 dm^3 = (2000 cm^3).

Concentration of H_2 gas in ppb = ?

$$\text{Concentration of } H_2 \text{ gas (ppb)} = \frac{\text{Vol. of } H_2 \text{ in}(\text{cm}^3)}{\text{Vol. of solution in}(\text{cm}^3)} \times 10^9$$

$$\text{Concentration of } H_2 \text{ gas in ppb} = \frac{5.0\ \text{cm}^3}{2000\ \text{cm}^3} \times 10^9$$

$$= 2.5\times10^{-3}\times10^9$$

$$= 2.5\times10^6\ \text{ppb}$$

Parts per trillion (ppt)

It is defined as the number of parts (by mass or volume) of a solute per llion parts (by mass or volume) of the solution. Parts per trillion is used for wer concentrations.

$$\text{Parts per trillion (ppt)} = \frac{\text{mass or volume of solute}}{\text{mass or volume of solution}} \times 10^{12}$$

Self-Assessment

1. In how many ways, percentage of solution can be expressed.
2. Differentiate between molarity (M) and Molality (m).

10.3 Raoult's Law

When a solid solute dissolves in a solvent, it changes the vapour press of the solvent. Similar effect is observed for a liquid solute in a liquid solve However, there is a major difference; a solid solute is usually non-volatile, whi liquid solute is volatile. For example, if we analyse the vapour above a sug solution in water, we would find only water vapours, whereas, the vapours abo a solution of ethanol and water always contain both water and ethanol.

This fact allows us to classify the solutions on the basis of solutes i.e. (i) t solution of volatile solute and solvent and (ii) the solution of non-volatile and no electrolyte solute in volatile solvent.

The quantitative relationship between the vapour pressure of solution a composition of components of solution was given by F. M. Raoult. *The Raou law states that the partial vapour pressure of any volatile component of solution is equal to the vapour pressure of the pure component multiplied by t mole fraction of that component in solution*. Those solutions which obey Raou law are called ideal solutions.

Mathematically, Raoult's law can be written as $P = P^{\circ}X$ where P and P° a the partial vapour pressure of the component and that of the pure compone respectively, and X is the mole fraction of the component in the solution.

10.3.1 The solution of Volatile Solute and Solvent (bo components are volatile)

Consider an ideal solution of two liquids A and B. According to Raou law partial vapour pressure of both components A and B is given by:

$$P_A = P^{\circ}_A X_A$$

$$P_B = P^{\circ}_B X_B$$

P°_A is the vapour pressure of pure component A and P°_B is vapour pres of pure component B. X_A and X_B are the mole fractions of components A an respectively. By applying Dalton's law of partial pressures, vapour pressu solution is

$$P_{Total} = P_A + P_B$$

$$P_t = P^{\circ}_A X_A + P^{\circ}_B X_B \qquad (10.1)$$

Since $X_A + X_B = 1$

Therefore $X_A = (1 - X_B)$

The eq.(10.1) becomes

$$P_t = P^\circ_A(1 - X_B) + P^\circ_B X_B$$

$$P_t = P^\circ_A - P^\circ_A X_B + P^\circ_B X_B$$

On rearranging the above equation.

$$P_t = (P^\circ_B - P^\circ_A)X_B + P^\circ_A$$

This equation shows that when $X_B = 0$, $X_A = 1$ it means pure component A is present and P_{Total} becomes equal to P°_A and if $X_A = 0$, then $X_B = 1$ then pure component B is present, then P_{Total} becomes equal to P°_B.

The graph in Fig. 10.3 shows variation of total pressure (solid line) and partial vapour pressures of components (dotted lines) of solution with changes in concentration of both A and B components. At any concentration, the total pressure is the sum of the partial pressures of the two components.

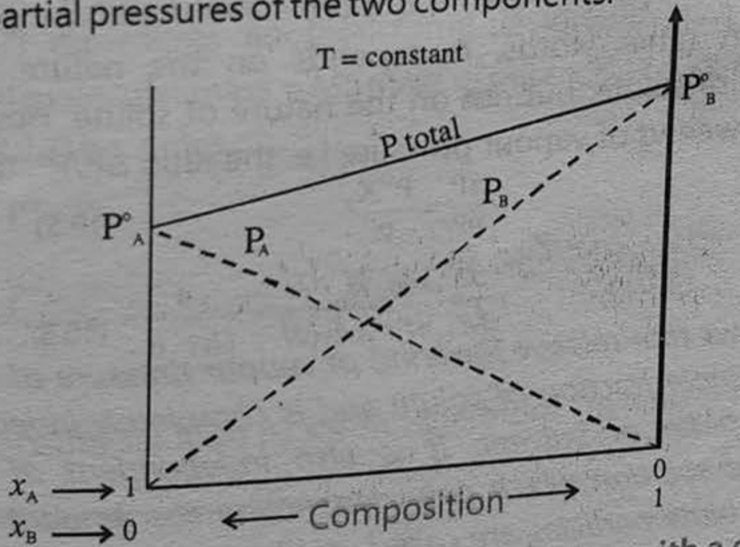


Figure 10.2: Variation of vapour pressure of solution with a change in concentration of A and B

10.3.2 Non-Volatile and Non-Electrolyte Solute in Volatile Solvent

In the case of solution of non-electrolyte and non-volatile solute the solute particles remain in the (un-dissociated) molecular form. Such solute lowers the vapour pressure of the solvent. The vapour pressure lowering, suffered by the solvent, can be readily understood in terms of Raoult's law.

Let us consider a solution of component A and B where A is solvent of mole fraction X_1 and B is solute of mole fraction X_2. P° is the vapour pressure of pure solvent and P is the vapour pressure of solution. According to Raoult's law, vapour pressure P is given by

$$P = P^{\circ}X_1 \qquad (10.2)$$

Since X_1 in any solution is less than unity, P must always be less than P°. Consequently, a solute in a solvent tends to lower the vapour pressure of the pure solvent. Furthermore, if the solute is non-volatile it does not contribute to the total vapour pressure, and hence Eq. (10.2) gives the total vapour pressure above the solution, which in this case is due to solvent only and is always less than P°. The extent of the vapour pressure lowering ΔP is

$$\Delta P = P^{\circ} - P \qquad (10.3)$$

$$\Delta P = P^{\circ} - P^{\circ}X_1$$

$$\Delta P = P^{\circ}(1 - X_1)$$

$$\Delta P = P^{\circ}X_2 \qquad (10.4)$$

According to Eq.(10.4), *the lowering of vapour pressure of solution depends both on vapour pressure of pure solvent and the mole fraction of solute in solution.* In other words, it depends on the nature of solvent and the concentration of solute, but not on the nature of solute. However, if we consider the relative lowering of vapour pressure i.e. the ratio $\Delta P/P^{\circ}$, then from Eq. (10.4).

$$\frac{\Delta P}{P^{O}} = \frac{P^{O}X_2}{P^{O}} \qquad (10.5)$$

$$\frac{\Delta P}{P^{O}} = X_2$$

(10.6)

It shows that relative lowering of vapour pressure of the solution depends only on the mole fraction of solute and is completely independent of either the nature of solute or solvent. It is also independent of temperature. Those properties of solution which only depend on the amount of the solute or the number of solute particles are called colligative properties. Thus the lowering in vapour pressure is a colligative property.

10.4 Colligative Properties of Dilute Solutions

Colligative (or collective) properties are those properties which depend only on the number of solute particles but not on the nature of the solute particles. The study of colligative properties is important especially because they provide methods for determining the molecular weight of dissolved substances. The colligative properties of a dilute solution containing a non-volatile non-electrolyte solute are:

a. Lowering of vapour pressure.
b. Elevation of boiling point.
c. Depression in freezing point.
d. Osmotic pressure.

10.4.1 Vapour Pressure lowering

The lowering of vapour pressure can be used to calculate the molecular mass 'M' of solute as follows.

Since $X_2 = \frac{n_2}{n_1 + n_2}$

So Equation (10.6) becomes. $X_2 = \frac{\Delta P}{P^\circ}$

$$\frac{P^\circ - P_s}{P^\circ} = \frac{\Delta P}{P^\circ} = \frac{n_2}{n_1 + n_2} \qquad (10.7)$$

Eq. (10.7) represents another form of Raoult's law. If mass of pure solvent = W_1 and molecular mass = M_1, mass of pure solute = W_2 and molecular mass = M_2 then Eq. (10.7) becomes

$P^\circ - P_s$

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n_2}{n_1 + n_2} = \frac{W_2/M_2}{W_1/M_1 + W_2/M_2} \qquad (10.8)$$

For a very dilute solution $n_2 << n_1$: therefore, $(n_1 + n_2) = n_1$, Thus $\frac{W_2}{M_2}$ can be neglected from the denominator.

The Eq. (10.8) then can be written as

$$\frac{P^\circ - P_s}{P^\circ} = \frac{W_2 M_1}{W_1 M_2} \qquad (10.9)$$

Eq. (10.9) can be used to calculate molecular mass of the dissolved substance if relative lowering of vapour pressure and the definite mass of solute in a given amount of solvent are known.

10.4.2 Boiling Point Elevation and Freezing Point Depression

(i) Boiling Point Elevation

Boiling point of a solution is the temperature at which its vapour pressure becomes equal to external pressure or atmospheric pressure. Since the presence of a non-volatile solute lowers the vapour pressure of the solution, therefore boiling point must increase. This fact has been qualitatively expressed by Raoult's law.

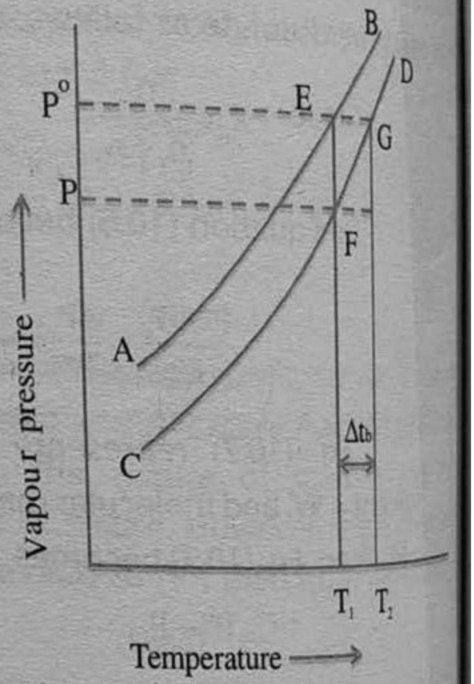


Figure 10.3 Boiling Point Elevatio

According to Raoult's law the vapour pressure of solution containing non-volatile solutes is always less than that of pure solvent. As a result of lowering of vapour pressure the solution will boil at a temperature higher than the boiling point of the pure solvent at the atmospheric pressure. *This difference in the boiling points of solution and its pure solvent is known as boiling point elevation of the solution.* It depends on the nature of solvent and the concentration of solute. The boiling point elevation in dilute solution is independent of the nature of solute if it does not ionize, associate, or react with the solvent. *For 1.0 mole of any solute if dissolved in 1 kg of pure solvent, the elevation of boiling point is called molal boiling elevation constant or ebullioscopic constant.* If 1 mole of a solute is dissolved in 1 kg of pure water the solution now boils at 100.52°C instead of 100°C. The difference 0.52°C is the ebullioscopic constant, k_b, of water. Elevation of boiling point can be explained by plotting a graph, of vapour pressure verses temperature for pure water and an aqueous solution.

Consider Fig. 10.3 the curve AB and CD represent vapour pressure of the pure solvent and solution, respectively, as a function of temperature. Temperature T_1 on curve AB is boiling point of pure solvent. The solvent bo when its vapour pressure become equal to the external pressure represented by P^o. T_2 on curve CD is the boiling point of solution. CD curve is lower than the curve AB because vapour pressure of solution is less than that of pure solvent. Thus the solution will boil at higher temperature T_2 to equalize its vapo ressure to P°. Hence elevation of boiling point ΔT_b is given as,

$$\Delta T_b = T_2 - T_1$$

Increase in concentration of solute particles will increase the boiling point f the solution. So $\Delta T_b \propto m$ where m is the molality of solution.

$$\Delta T_b = K_b m \qquad (10.10)$$

K_b is called molal boiling point elevation constant or ebullioscopic constant, when solution is 1 molal or m=1 then $\Delta T_b = K_b$.

It means that *If a solution is of unit molality its elevation of boiling point is lled ebullioscopic constant.*

The molality (m) of the solution containing W_2 gram of solute of molecular ss M_2 dissolved in W_1 gram of solvent of molecular mass M_2 is.

$$m = \frac{W_2}{M_2} \times \frac{1000}{W_1}$$

Substituting the value of "m" in Equation (10.10) we get.

$$\Delta T_b = K_b \left(\frac{1000 W_2}{M_2 W_1} \right) \qquad (10.11)$$

Or $$M_2 = \frac{K_b}{\Delta T_b} \times \frac{W_2}{W_1} \times 1000 \qquad (10.12)$$

Thus if masses of solute and solvent are known along with ebullioscopic nstant and elevation of boiling point then molecular mass of solute can be lculated.

mple 10.5

The boiling point of 50g of carbon tetrachloride was raised by 0.402 K en 0.5126g of naphthalene (mol.mass =128g/mol) was dissolved in it. Calculate e ebullioscopic constant of carbon tetrachloride.

lution

Mass of carbon tetrachloride = W_1 = 50g

Mass of naphthalene = W_2 = 0.5126g

Molecular mass of naphthalene = M_2 = 128 g mol^{-1}

Boiling point elevation ΔT_b = 0.402K

Ebullioscopic constant" = K_b =?

As we have

$$K_b = \frac{\Delta T_b \times W_1 \times M_2}{1000 W_2}$$

Putting values in the above equation.

$$= \frac{0.402\text{K}}{1000\text{gkg}^{-1}} \times \frac{50\text{g} \times 128\text{gmol}^{-1}}{0.5126\text{g}}$$

$$= 5.02\text{K kgmol}^{-1}$$

(ii) Freezing Point Depression

The freezing point of a liquid is the temperature at which the solid pha begins to separate out from the liquid phase. At this temperature solid and liqu phases are in equilibrium and have equal vapour pressure. A solution freezes lower temperature as compared to its pure solvent. This lowering of freezing point of solution as compared to its pure solvent is called depression of freezing point. This lowering is due to lowering in vapour pressure of solution as a result of addition of small amount of non-volatile solute. The depression of freezing point of a substance depends on:

i. The nature of solvent.

ii. Concentration of solute particles.

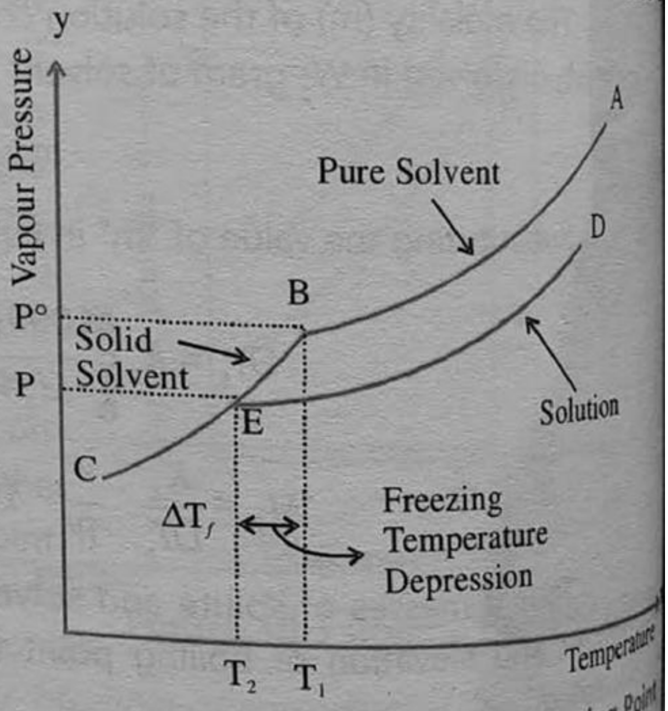


Figure 10.4 Depression in Freezing Poin

In order to understand the relationship between lowering in freezin point, ΔT_f, and concentration in terms of molality 'm', consider Fig. 10.4 whic shows the vapour pressure of solution and pure solvent as a function o temperature.

The curve AB is for the vapour pressure of the pure solvent and curve for that of the solution. The curve CB is the sublimation curve of the solid solve The solvent freezes at temperature T_1 corresponding to the point B where vapo pressure of freezing solvent is P°. The portion of the curve BC is for the s solvent. The curve DE for solution intersects curve BC at point E. This is freezing point of solution T_2. Hence

$$\Delta T_f = T_1 - T_2$$

ΔT_f, the depression in freezing point is related to the molality (m) of th

solution as

$$\Delta T_f \propto m$$

$$\Delta T_f = k_f m \qquad (10.13)$$

K_f is the molal freezing point elevation constant also called as the cryoscopi constant. We know that

$$\text{molality}\ (m) = \frac{1000W_2}{M_2.W_1}$$

Then from Equation 10.13

$$\Delta T_f = k_f \frac{1000W_2}{M_2.W_1} \qquad (10.14)$$

W_2 and M_2 are the mass and molar mass of solute, respectively, W_1 is the mass of solvent in gram and the factor of 1000 is for converting g into kg. In order to calculate M_2 molecular mass of solute, Eq. (10.14) is rearranged as

$$\boxed{M_2 = k_f \frac{1000\,W_2}{DT_f W_1} \qquad (10.15)}$$

Thus, if we know the mass of solute and solvent, molal freezing point constant (k_f) and depression in freezing point ΔT_f. We can calculate molar mass of solute. Moreover, this equation can also be used to ascertain the purity of solvent from the k_f value. From Eq. 10.13 ΔT_f is equal to k_f when molality is unity. Thus for solution of unit molality, if the calculated value of ΔT_f does not match with the literature value of k_f then this is an indication of impure liquid. Here it is instructive to define *the molal freezing point constant or cryoscopic constant 'k_f' as the depression in freezing point of a solution of unit molality.* Different solvents have their own specific k_f values.

10.4.3 Molar Mass determination by Vapour Pressure lowering, Boiling Point Elevation, and Freezing Point depression

Molar mass of substances can be determined by vapour pressure lowering, boiling point elevation, and freezing point depression methods using equations 10.9, 10.12, and 10.15, respectively.

Example 10.6

If 3.60g of glucose is dissolved in 100g of water and the freezing point depression is found to be 0.372K. Calculate the molecular mass of glucose. k_f for water is 1.86 K kg mol^{-1}.

Solution

Weight of glucose = W_2 =3.60g

Weight of water = W_1 =100g

Freezing point depression = ΔT_f = 0.372K

Molal freezing point of water = k_f = 1.86K kg mol^{-1}

Molecular mass of glucose M_2 = ?

As we know $M_2 = \frac{K_f}{\Delta T_f}\frac{1000W_2}{W_1}$

$$M_2 = \frac{1.86 \times 1000 \times 360}{0.372 \times 100}$$

$$M_2 = 180g/mol$$

Practice problem 10.4

A solution containing 1.66 g of nonionic solute in 171 g of water freezes a 0.602°C. Calculate the molar mass of the solute. K_f of water is 1.86 K kg mol^{-1}.

Osmosis

When a solution is separated from its pure solvent, by a semi-permeab membrane, it is observed that solvent tends to pass through the membran spontaneously into the solution and thereby dilute it. The phenomenon is calle osmosis. A membrane which allows the passage of solvent molecules only, no the solute, through it is called a semi-permeable membrane. Osmosis also take place when a dilute solution is separated from a concentrated solution th solvent molecules from dilute solution pass through the membrane towards th concentrated solution region. For low molecular mass solutes in water the be semi-permeable membrane is a film of copper ferrocyanide $Cu_2[Fe(CN)_6]$. Fo high molecular weight solutes in organic solvents the membranes used, mo frequently, are thin films of either cellulose or cellulose nitrate.

Osmosis can easily be understood with the help of an apparatus shown Fig. 10.5. A semi-permeable membrane e.g. egg membrane, is tied over the e of a thistle funnel. It is, then, filled with a solution of sugar and dipped in beaker containing water (solvent). Due to osmosis, water will pass through membrane and the level of sugar solution will rise until the hydrostatic pres of the liquid column equalizes the osmotic pressure of the solution.

Thus, the flow of solvent molecules from lower concentration regio higher concentration region is called osmosis or endosmosis.

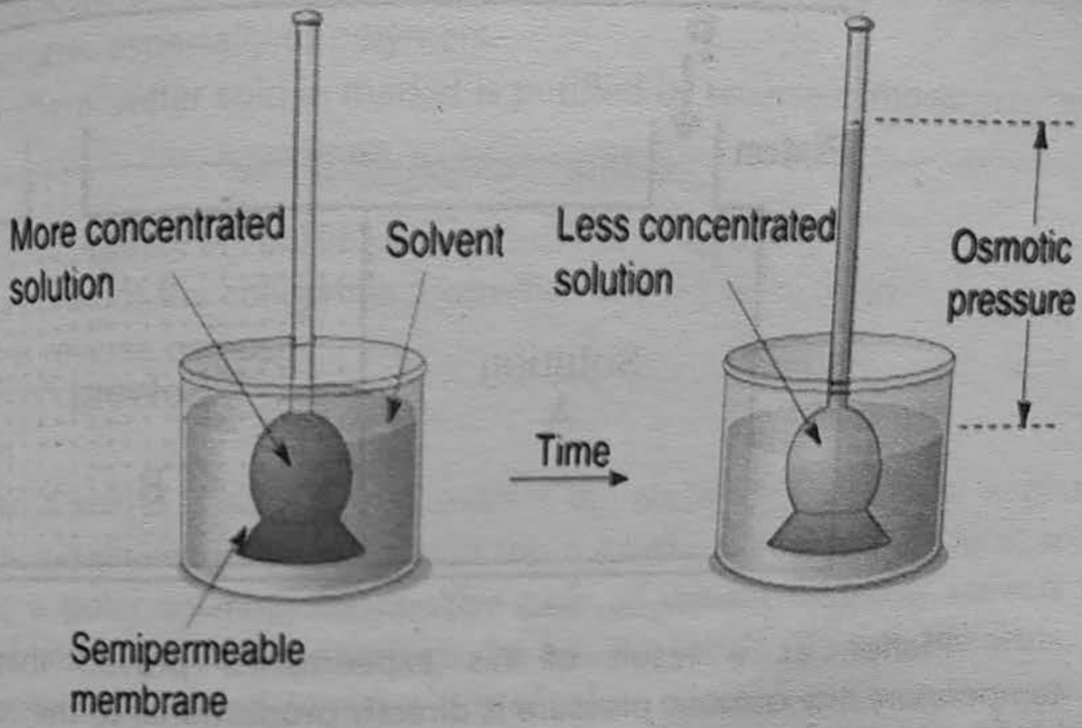


Figure 10.5 Osmosis

10.4.4 Osmotic Pressure and Reverse Osmosis

Another example may be given to illustrate the phenomenon of osmosis and osmotic pressure. Consider Fig.10.6, the chamber is divided by a semipermeable membrane into two compartments. The left compartment 'A' is filled with the solution and the opening of the compartment is provided with a moveable piston while the right compartment 'B' contains the pure solvent and its mouth is open to atmosphere. The solvent will pass through the semipermeable membrane into the solution compartment due to the osmosis and will push the piston upward. The upward movement of the piston can be prevented by applying pressure on the piston to keep it in the original position. *The pressure that must be applied on the solution in order to prevent the osmosis is called the osmotic pressure of the solution. It is denoted by 'π'*. If the solvent in the above experiment is replaced by a solution of different concentration, osmosis will still occur from dilute solution towards concentrated solution. If the solutions have same concentration on both sides, no osmosis will occur and the solutions are said to be isotonic (having same osmotic pressure). *If we apply external pressure on the concentrated solution side, more than the osmotic pressure, the solvent will move from concentrated region towards the dilute region. This process is called reverse osmosis or exosmosis.*

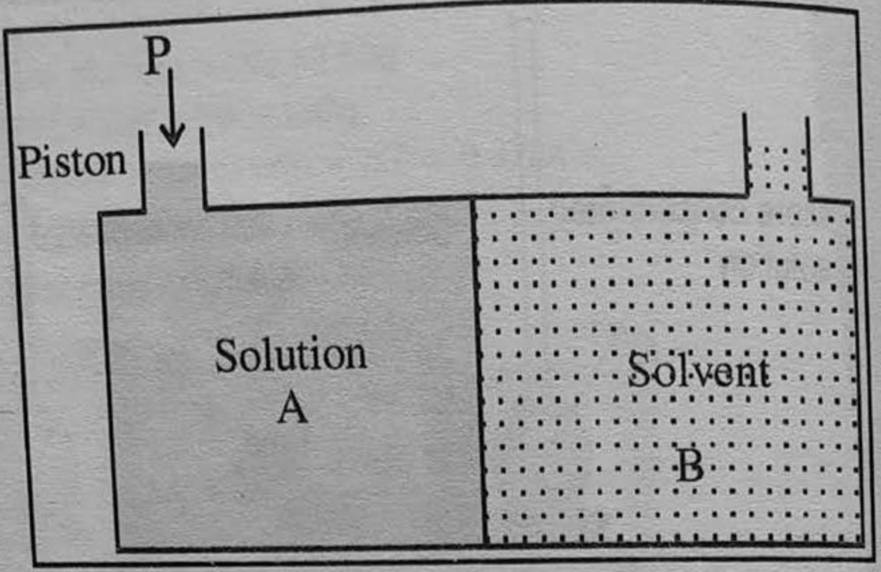


Figure 10.6 Osmotic Pressure

Pfeffer, as a result of his experiments, proved that at consta temperature, the osmotic pressure is directly proportional to the concentration solution as is shown in Table 10.2. This indicates that osmotic pressure is colligative property.

Table: 10.2: Variation of Osmotic Pressure with Concentration of Sucros

% Concentration (C)	Osmotic pressure (mm of Hg)
1	535
2	1016
2.47	1518
4	2082
6	3075

10.4.5 Application of Osmosis in Daily Life

1. The process is used in many industries.
2. The victims of ship wreckage purify seawater, which has very h concentration of salts, by reverse osmosis, to make it drinkable.
3. By osmotic pressure the plant cell become turgid and these turgid provide support to weak parts of plant.
4. Ascent of sap in plants from roots to upper parts takes place by osm and osmotic pressure
5. Isotonic (same osmotic pressure) solution have been prepared to pre plasmolysis (shrinkage of cytoplasm) and hemolysis (deficiency of blood cells).

6. The concept of osmotic pressure can be used to calculate molar mass of substances, especially of polymers.
7. The mineral water sold in market is purified by reverse osmosis process.

Self-Assessment

1. Define colligative properties.
2. Name some of the colligative properties of a dilute solution.
3. What is reverse osmosis.

Solvation

When a solute is added to a solvent the dissolution of solute begins by he interaction between its particles and the solvent molecules. If an ionic solute s added to a polar solvent, the positive pole of solvent molecule attracts the egative ion and negative pole attracts the positive ion. In this way, the attractive orces between positive and negative ions of solute diminish and now they are far part from one another. Both the positive and negative ions are surrounded by a phere of solvent molecules and keep them in the dissolved form. This process is alled solvation, on the other hand if water is used as solvent the solvation is called ydration.

The hydration of KCl, for example, is shown in Fig.10.7. It can be seen that ations, K^+, and anions, Cl^-, get separated from one another and are surrounded y oppositely charged poles of water molecules

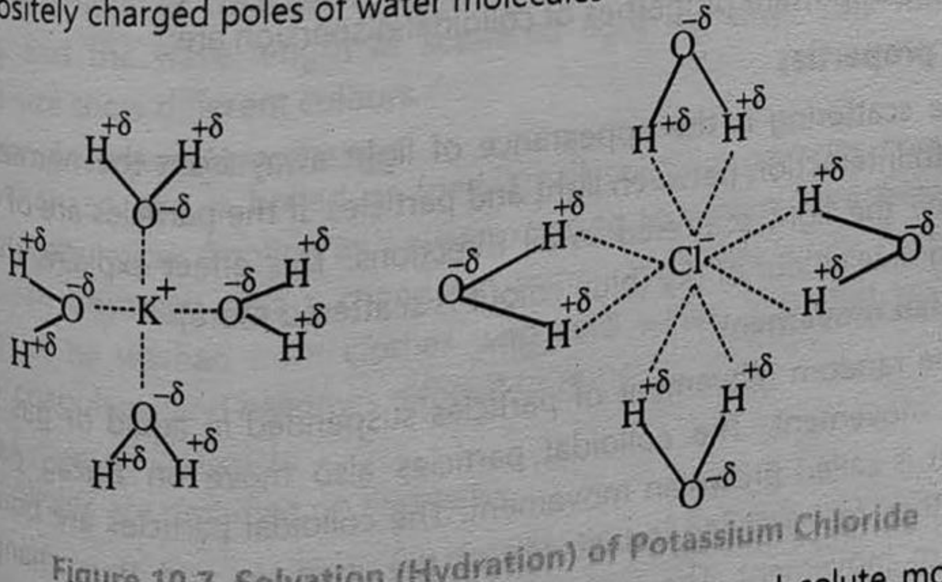


Figure 10.7 Solvation (Hydration) of Potassium Chloride

Solvation is a process of reorganizing solvent and solute molecule into solvent complex. Solvation involves bond formation, hydrogen bonding, and Van der Waals forces or dispersion forces. Ionic substances are solvated by polar solvents, like water. However, non-polar solutes are solvated by non-polar solvent. The forces involved in such case are predominantly Van der Waals forces.

Water of Crystallization

Whenever an acid-base neutralization reaction takes place, salt and water are formed i.e. we get a salt solution. In order to get salt, water is dried from it by evaporation. In some types of salts some of the water molecules remain inside the salt crystals, that is just a physical presence of water molecules and is called *water of hydration or water of crystallization*. Some salts absorb water molecules from the atmosphere if kept open and get hydrated. Examples of such salts are: Pentahydrate copper sulphate ($CuSO_4.5H_2O$), heptahydrate magnesium sulphate ($MgSO_4.7H_2O$) or decahydrate sodium carbonate ($Na_2CO_3.10H_2O$).

10.5 Colloids

A colloidal solution or colloidal dispersion is a heterogeneous mixture in which one substance is dispersed (called dispersed phase), as very fine particles, in another substance (called dispersion medium). The size of the dispersed particle is larger than that of true solution and smaller than that of suspension. The size ranges between 1 to 1000 nm. It is intermediate between suspension and true solution. The particles of collides remain suspended and do not settle down at the bottom of the mixture. They are visible under high resolving microscope.

10.5.1 Properties of colloids

Some important properties of colloidal dispersion are:

I. Optical properties

The scattering is the appearance of light away from the normal optical path due to interaction between light and particles. If the particles are of colloidal size we see the light scattered in all directions. This effect explains the tail of comet and blue colour of sky (blue colour is scattered more).

ii. Brownian movement

The random movement of particles suspended in liquid or gas is called Brownian movement. The colloidal particles also move on zigzag path. This movement is called Brownian movement. The colloidal particles are bombarded by the other fast moving molecules of the medium and thus change their direction of movement. The higher the temperature, the more vigorous is the movement and hitting by the molecules. A zigzag motion of colloidal particles can be observed by an ultramicroscope.

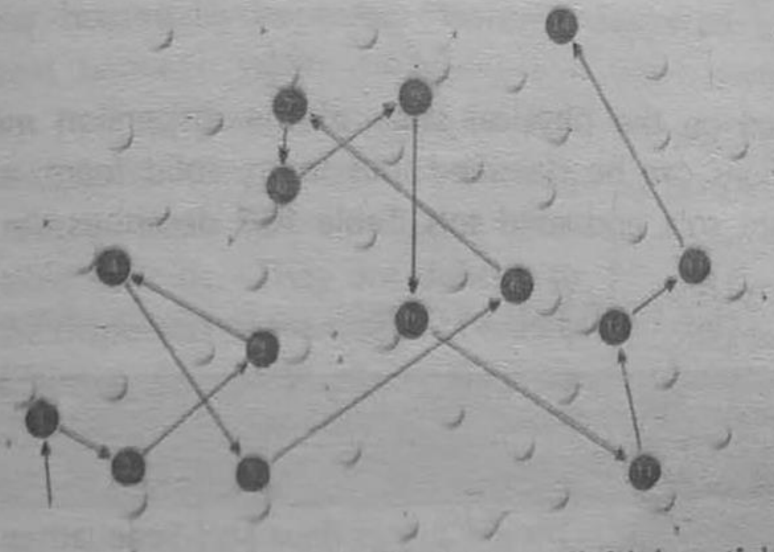


Figure 10.8 Brownian movement of a single colloidal particle

ii. Filterability

Colloidal particles cannot be separated by ordinary filtration but these particles can be removed generally by specially designed filters of extremely fine porosity called ultrafilters. This process of separation of colloidal particles by ultrafilters is called ultrafiltration.

v. Diffusibility

The colloidal particles have very large size as compared to ordinary solute particles hence they have little power of diffusion.

v. Colour

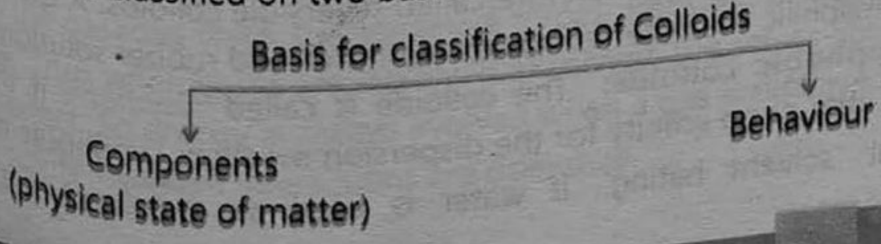
The colour of colloidal solution depends on size and shape of colloidal particles and the wave length of scattered light e.g. silver sols with different particles size show different colours.

vi. Effect of temperature change

When an egg is boiled or fried, small colloidal particles convert into a lump by coagulation. Cooling and even exposing to sunlight may help jellies set. It has been observed that a change in temperature coagulate colloids. Blood stains must be washed from clothes with cold water. With hot water protein material coagulates and becomes difficult to remove.

10.5.2 Types of colloids

Colloids are classified on two basis.



a. On the basis of physical states of dispersed phase and dispersion medium

Based on the physical state of the dispersion medium and dispersed phase, collides can be classified into foam, solid foam, aerosol, emulsion, gel, solid aerosol, sols, and solid sols. Table 10.3 describes the types along with the examples.

Table.10.3 Types of Colloids on the basis of Physical State

S#	Dispersed Phase	Dispersion Medium	Name of the colloidal system	Examples of collides
1	Gas	Liquid	Foam	Soap lather, Soda water, Froth, etc.
2	Gas	Solid	Solid foam	Cake, bread, lava.
3	Liquid	Gas	Aerosol	Mist, fog, clouds.
4	Liquid	Liquid	Emulsion	Milk, cream, butter, oil in water
5	Liquid	Solid	Gel	Curd, chees, jellies, butter, shoe polish
6	Solid	Gas	Solid aerosol	Smoke, dust
7	Solid	Liquid	Sol	Paint, ink
8	Solid	Solid	Solid sol	Alloys, coloured glass, gem stone

b. Classification of colloids on the basis of Interaction between Dispersed Phase and Dispersion medium

Classification of colloids on the basis of interaction between dispersed phase and dispersion medium can be made as *lyophilic and lyophobic colloids.*

Lyophilic colloids. Lyophilic means liquid loving or solvent attracting. If the dispersion medium is water then the term *hydrophilic colloids* is used. In these colloids dispersed particles generally have same chemical nature as that of solvent or dispersion medium, such as –OH group able to form hydrogen bond. When such colloids are once precipitated they can be directly returned into the colloidal form and are, therefore, called reversible colloids. A gel is a semisolid mass of a lyophilic sol, other examples are starch and rubber solutions.

Lyophobic colloids: The colloide is called *lyophobic* if the dispersed phase has little or no affinity for the dispersion medium. Lyophobic means 'liqui fearing' or 'solvent hating'. If water is used as a solvent then the ter *hydrophobic colloids* is used. Hydrophobic means "Fearing water". In this case no attractive force exist between water molecules and dispersed particles. The colloids formed by hydrophobic particles are less stable. If, once, precipitated they cannot be directly reconverted into the colloidal form and are, thus, termed as irreversible colloids. They are difficult to prepare because the dispersed phase does not readily form colloide with the dispersion medium. They are unstable and require stabilizing agent for their preservation. Examples are sols of metals like silver and gold, sols of metal hydroxide such as $Al(OH)_3$ etc. Moreover, homogenized milk and lassi (casein suspended in water) are the examples of hydrophilic and hydrophobic sols, respectively.

ReadingCheck

- Differentiate between Lyophilic and Lyophobic colloids.
- What are the basis for the classification of colloids?

10.6 Heat of Solution and its application

The formation of a solution is accompanied with the change in temperature. If solid sodium hydroxide (NaOH) is dissolved in water, the temperature of water will rise. This is an exothermic process. On the other hand, when NH_4NO_3 is dissolved in water the temperature of the water decreases due to endothermic process. That is heat is either absorbed or evolved during the process of dissolution.

The dissolution process is comprised of three processes.

i) Breaking of solute-solute attraction (endothermic process, ΔH positive)
ii) Breaking of solvent-solvent attraction (endothermic process, ΔH positive)
iii) Resulting solute-solvent attraction (exothermic process, ΔH negative)

The value of heat of solution is the net effect of these three heats i.e. the algebraic sum of these three heats. If heat evolved is higher than the heat absorbed the dissolution process will be exothermic and vice versa

The heat of solution is defined as amount of heat evolved or absorbed when one mole of a substance is completely dissolved in large amount of solvent at constant temperature and pressure.

In the gaseous state, the attractive forces between the gas molecules are very weak. Thus when gases are dissolved in solvent, the solute-solute interaction has little effect. So energy is always evolved when a gas is dissolved in solvent, as only the solute - solvent interactions are operative.

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Heat changes occur when a solute is dissolved in solvent. 'Hot and Cold Packs' use this property. These packs are used by patients to treat their muscle strain and sore joints and to reduce swellings in body muscles.

These packs contain solute and the solvent in separate bags inside the pack. At the time of use, the pack is squeezed and the solvent bag is broken. Solvent reacts with solute and the temperature effect is utilized by the patient.

Mostly, the hot packs use calcium chloride, which produce heat when dissolved in water as below

$$CaCl_{2(s)} \longrightarrow Ca^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \qquad \Delta H = -\ 82.8\ kJ\ mol^{-1}$$

The molar heat of solution of $CaCl_2$ is 82.8kJ mol^{-1} and it is an exothermic reaction.

The cold packs utilize ammonium nitrate (NH_4NO_3) which absorbs heat from surrounding when it is dissolved in water

$$NH_4NO_{3(s)} \longrightarrow NH_4^{+}{}_{(aq)} + NO_3^{-}{}_{(aq)} \qquad \Delta H = +25.7\ kJ\ mol^{-1}$$

It is an endothermic reaction and reduce the pain by cooling effect.

KEY POINTS

- A homogenous mixture of two or more substance is called solution.
- When solute particles are greater in size and do not dissolve completely, then the mixture is called suspension.
- When a solution is in between true solution and suspension, it is called colloidal dispersion or colloidal system.
- Solution of liquids-in-liquids are of three types, completely miscible liquids, partially miscible liquids, completely immiscible liquids.
- Ideal solution is one which obeys Raoult's Law over all ranges of temperature and pressure.
- Molarity, molality, ppm, ppb, ppt, and mole fraction are also concentration units of solution.
- The properties which depends on number and not on nature of solute particles are called colligative properties.
- Lowering of vapour pressure, elevation of boiling point, depression of freezing point, and osmotic pressure are colligative properties.
- Colloids are mixtures whose particle size is between that of true solution and suspension.
- Colloids are classified on the basis of physical states and interaction between the particles of dispersed phase and those of dispersion medium i.e. lyophilic and lyophobic.

EXERCISE

Choose the correct answer

1. In atmospheric gaseous solution, nitrogen is a
   - a) solvent
   - b) solute
   - c) mixture
   - d) dispersed phase
2. In ice cream, sugar is
   - a) solute
   - b) mixture
   - c) solvent
   - d) none
3. Elevation of boiling point is a property
   - a) additive
   - b) constitutive
   - c) colligative
   - d) none
4. Change in enthalpy, ΔH_{sol}, is heat of solution which is
   - a) positive
   - b) negative
   - c) zero
   - d) may be positive or negative.
5. Freezing point of solution as compared to the solvent is
   - a) higher b) lower c) variable d) remains the same
6. Phenol - water system is the example of
   - a) completely miscible liquids
   - b) completely immiscible liquids
   - c) partially miscible liquids
   - d) none
7. Fog is an example of
   - a) solution b) colloid c) suspension d) coarse mixture
8. Which of the following solute would not form a solution if added to water?
   - a) KCl b) CH_4 c) HCl d) NH_3
9. Vapour pressure of a given liquid will decrease if
   - a) surface area of liquid is increased.
   - b) total volume of liquid in the container is decreased.
   - c) volume of the vapour phase is increased.
   - d) the temperature is decreased.
10. For a dilute solution Raoult's law states that
    - a) The lowering of vapour pressure is equal to the mole fraction of solute.
    - b) The relative lowering of vapour pressure is equal to the mole fraction of solute.
    - c) The relative lowering of vapour pressure is proportional to the amount of solute.

d) The vapour pressure of the solution is equal to the mole fraction solvent.

11. The boiling points of C_6H_6, CH_3OH, $C_6H_5NH_2$, and $C_6H_5NO_2$ are 80° 65°C, 184°C and 112°C respectively. Which one will show the highes vapour pressure at room temperature?

a) C_6H_6. b) CH_3OH

c) $C_6H_5NH_2$ d) $C_6H_5NO_2$

12. The process in which the water molecules surround and interact with the solute ions or molecules is called

a) neutralization b) hydration

c) hydrolysis d) hydrogenation

13. The molarity of pure water in itself is

a) 18 b)50 c) 59.5 d)55.6

Short Questions

1. Define the following concentration units:
   i) ppm ii) ppb iii) ppt iv) mole fraction
2. Which concentration unit, from molarity and molality, depends on temperature.
3. Prove mathematically that sum of the mole fractions of all the components of a solution is equal to one.
4. Define and name four colligative properties.
5. Define osmosis and give it applications in daily life.

Numerical

1. Calculate Molarity (M) of the following solutions:
   - i) 2.0 g of H_2SO_4 /2dm³ of aqueous solution Ans. (0.01M)
   - ii) 0.4 g of NaOH/100 cm³ of aqueous solution Ans. (0.1M)
   - iii) 0.5 g of Na_2CO_3/250 cm³ of aqueous solution Ans. (0.02M)
2. Calculate mole fraction of each component in the following solutions.
   - i) 2.5 moles of water (H_2O)+1.5 moles of NaCl. Ans.(0.625, 0.375)
   - ii) 500 g of water (H_2O)+600 g of glucose ($C_6H_{12}O_6$). Ans. (0.89,0.11)
   - iii) 800 g of water (H_2O)+120 g of acetone $(CH_3)_2CO$. Ans. (0.955, 0.044)
3. A 3.0 cm³ cylinder contains a mixture of oxygen, nitrogen, and chlorine gases. If their amounts are 4.64×10^{-5}g, 3.5×10^{-4} g and 2.3×10^{-5}g respectively. Calculate the concentration of each in
   - i) Parts per million (ppm)

ii) Parts per billion (PPb)

Answers

i) ppm O_2 15.46 N_2 116.6 Cl_2 7.7

ii) ppb O_2 1.546×10^4 N_2 1.16×10^5 Cl_2 7.7×10^3

4. In an experiment 6.4g of an organic compound was dissolved in 25.6g benzene and 1.0 °C depression of freezing point was observed. Calculate the molecular weight of the substance. (k_f of benzene=5.12)

Ans. 1280 gmol

5. Calculate molecular weight of Iodine (I_2) when a solution containing 1.19 g of I_2 in 35.0 grams of ether shows a raise in boiling point by 0.296 °C (k_b for ether: 2.22)

(Ans. M.Wt of I_2 = 254g mol^{-1})

Long Questions

1. How a given mixture can be differentiated into a true solution or coarse suspension.
2. Define solubility, what are the factors that affect the solubility o substances?
3. Classify colloids on the basis of their behaviour towards medium and the physical states of matter.
4. Give the statement of Raoult's law. Explain the lowering of vapour pressure of a solution based on this law.
5. Explain the phenomenon of osmosis.
6. Explain the phenomenon of depression of freezing point. How molecular mass of solute can be calculated on the basis of depression in freezing point?
7. Explain the elevation of boiling point, how molecular mass of solute can be calculated on the basis of elevation of boiling point?

Project

Take a potato of four to five centimetres length. Peel off it and cut rod shaped finger chips of equal length. Measure the length of these chips. Plac three chips in distilled water and three in concentrated sodium chloride solution After one hour take out the chips and measure the length of the chips. Recor the difference in length of the chips before and after dipping. You will observ that the chips in distilled water will be longer than before and those in th solution of NaCl will be shorter than before. Guess what might be the reason fo this observation?

Unit -11

Thermochemistry

After reading this unit, the students will be able to:

- Define thermodynamics. (Remembering)
- Classify reactions as exothermic or endothermic. (Understanding)
- Define the terms system, surrounding, boundary, state function, heat, heat capacity, internal energy, work done and enthalpy of a substance. (Remembering)
- Name and define the units of thermal energy. (Remembering)
- Relate a change in enthalpy to the heat of reaction or heat of combustion of a reaction. (Applying)
- Relate change in internal energy of a system with thermal energy at constant temperature and constant pressure. (Applying)
- Define bond dissociation energy. (Remembering)
- Use the experimental data to calculate the heat of reaction using a calorimeter.
- Specify conditions for the standard heat of reaction. (Applying)
- Apply Hess's Law to construct simple energy cycles. (Understanding)
- Describe how heat of combustion can be used to estimate the energy available from foods. (Analysing)
- Explain reaction pathway diagram in terms of enthalpy changes of the reaction. (Born Haber's Cycle) (Applying)

Teaching

11

Assessment

01

Weightage %

08

Introduction

Thermochemistry, is the part of thermodynamics which, deals with the stuc measurement, and calculations of thermal energy changes occurring durir chemical reactions. The SI unit of thermal energy is Joule (J). Since, the therm energy changes associated with chemical reactions are usually large, it is appreciab to express it in kilojoules (kJ). Thermodynamics is branch of science which deals wit the study of transformation of thermal energy that takes place in physical c chemical processes.

11.1 Energy in Chemical Reactions

Thermodynamics has importance in chemistry because energy change take place during chemical and physical processes. For example, burning c natural gas (CH_4), dissolution of sodium hydroxide in water and neutralization o acid and base produce heat while, heat is absorbed during evaporation o liquids, melting of ice, dissolving of ammonium chloride in water and cracking o alkanes etc. The first type of processes are called exothermic and second type a endothermic processes.

Exothermic processes

Exothermic processes are those in which energy is released in some form. In these reactions energy is released because the bonds of reactant molecules are broken and new bonds between the atoms are formed to make product molecules. For example, in burning of methane gas, CH_4, in the presence of oxygen produces water, carbon dioxide, and energy. In this reaction, bonds in CH_4 and O_2 molecules, are broken which needs energy (endothermic reaction) and new bonds are formed between hydrogen and oxygen to make H_2O and between carbon and oxygen to make carbon dioxide (CO_2). This is exothermic reaction. In exothermic reactions the total energy of the products is less than the total energy of the reactants. *An exothermic reaction gives out energy or heat to the surrounding and the system loses energy.* In this case change in enthalpy (ΔH) has negative value. For example, consider the combustion of methane gas as follows.

$$CH_{4(g)} + O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)} \quad \Delta H = -890.3\ kJ$$

Endothermic processes

An endothermic process takes in energy from surrounding and the system gains energy, here the change in enthalpy, ΔH, is given positive sign. For example, consider the following endothermic reaction ,

$$H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)} \quad \Delta H = +53.0\ kJ$$

In this reaction, one mole of H_2 gas reacts with one mole of gaseous I_2 to form two moles of HI and 53.0 kJ of energy is ~~evolved~~. absorbed

A few examples of exothermic and endothermic processes measured at 25°C and one atmospheric pressure are given as follows:

(i) $CH_{4\,(g)} + 2O_{2\,(g)} \longrightarrow CO_{2\,(g)} + 2H_2O_{(g)}$ $\Delta H = -890.3$ kJ

(ii) $2H_{2\,(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$ $\Delta H = -571.7$ kJ

(iii) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2\,(g)}$ $\Delta H = -393.5$ kJ

(iv) $S_{(s)} + O_{2(g)} \longrightarrow SO_{2\,(g)}$ $\Delta H = -296.8$ kJ

(v) $N_{2\,(g)} + 3H_{2(g)} \longrightarrow 2NH_{3\,(g)}$ $\Delta H = -92.3$ kJ

(vi) $H_{2\,(g)} + I_{2(g)} \longrightarrow 2HI_{(g)}$ $\Delta H = +53.0$ kJ

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The most common forms of energy are: heat, electromagnetic radiations, electric, kinetic, potential, and mechanical energies. Albert Einstein in 1905 proposed his classic theory that matter and energy are equivalent. A simple relationship that expresses this equivalence is $E=mc^2$. According to this expression, the conversion of one gram of matter to energy yields 2.2x10^{13} calories of heat. This amount of heat could raise the temperature of 250,000 tons of water from 0°C to 100 °C.

It should be recognized that the amount of this energy available in a given sample of matter is dependent only on the mass of the matter and not on the characteristics of the matter itself.

The amount of energy evolved during an ordinary chemical reaction is extremely small in contrast to the total mass of matter involved in the chemical change. For instance, during the combustion of 3000 tons of coal the amount of energy evolved is equal to the energy evolved by 1 gram of matter in a nuclear reaction. Since this minute difference in mass cannot be detected by routine procedures, the loss in mass during the burning process is usually ignored.

11.2 Thermodynamics

Thermodynamics deals with the flow of heat or any other form of energy into or out of a system. In the study of thermodynamics, it is essential to understand the meanings of some terms employed in it.

a) System and Surrounding

To analyse energy changes involved in chemical reactions it is important to define first the system and surrounding. *A system is the specific part of the* *universe that is of interest to us for the purpose of scientific observations, whil the surrounding is rest of the universe outside the system where we make ou measurements. Both system and surroundings are separated by a real o imaginary surface called boundary.* For instance, if boiling water in a beaker is under observation then, boiling water is the system, the beaker and the heat source is surroundings. Consider the reaction between sodium chloride and silver nitrate solutions, which can be called a system under observation. The flask and the air are the surroundings.

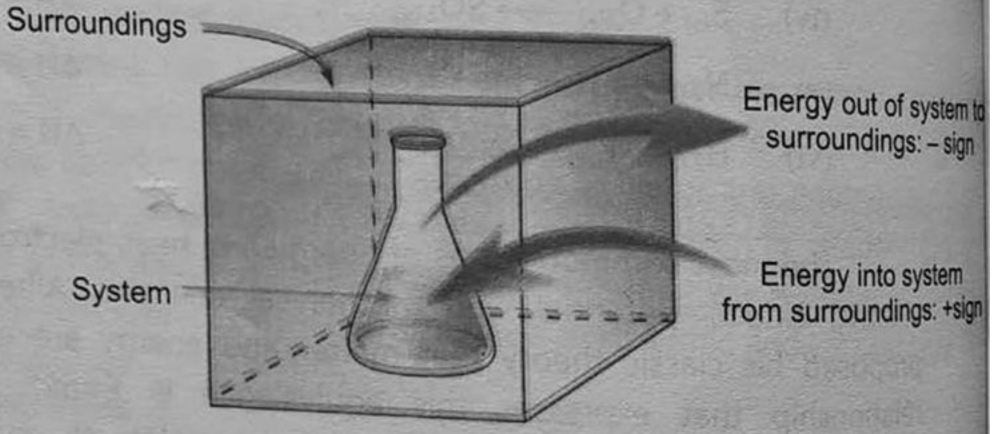


Fig. 11.1 The system and surrounding

b) State and State Function

In thermodynamics, we study changes in the state of the system. The state of the system is defined by the values of macroscopic properties, such as temperature, pressure, volume, energy, and composition. In other words, the state of a system is the condition of the system in terms of temperature, pressure, volume and composition. State functions or state variables are the properties that are determined by the state of the system and dependent only on the current state of the system and independent of the path by which that state is reached. It means that when the state of a system changes, the magnitude of change in any state function depends only on the initial and final state of the system and not on how the change was carried out. If one mole of a gas in a state of V_1 at temperature T_1 is heated to the temperature T_2, the volume of the gas becomes V_2. Hence V_1, T_1 specifies the initial state while V_2, T_2 is the final stat of the gas. The change in temperature changes the volume of the system. Henc such properties, like volume, temperature and pressure, in which the change one property changes the state of the system, are called state variables or sta functions. There are two characteristics of state function.

1. A state function is that property of the system which depends on the initial and final states and is independent of the path adopted to bring about the change. For example, if we heat a sample of water from 0°C to 25°C, the change in temperature is equal to the difference of the final and initial temperatures. The way the temperature change is brought about has no effect on the result.

$$DT = T_{final} - T_{initial}$$
$$25^\circ C - 0^\circ C = 25^\circ C$$

2. When a state of the system is specified by giving values to some of the state functions, the values of all other state functions are fixed. For example, if one mole of a gas occupies a volume of 5 dm^3 at 25°C, the pressure must have some fixed value (governed by $P=RT/V$).

There are some properties which are path dependent and are not state functions, e.g. heat and work. They are not the property of a system but simply represent mode of transfer of energy from the system to the surrounding and vice versa.

Reading Check

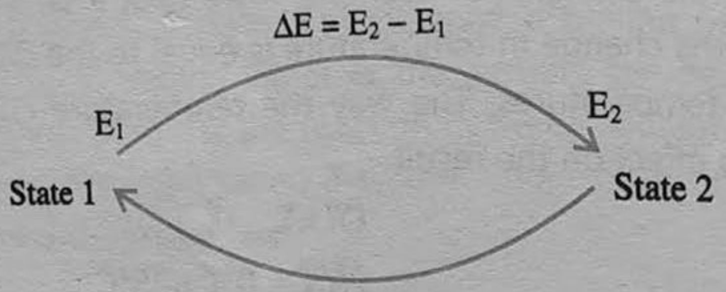
- Define exothermic and endothermic processes.
- Explain the terms:
  (i) system and surrounding
  (ii) state and state function.

11.3 Internal Energy 'E'

The internal energy is the sum of the kinetic and potential energies of all the atoms, ions, and molecules in the system. Internal energy is a definite energy possessed by a system. It is the sum of all possible types of energies that are possessed by all the atoms, molecules or ions within a system. Internal energy is a state function. It is the property of the state of the system. This implies that the change in the internal energy between two states of a system is independent of the path followed to achieve it.

The energy of the system changes because energy is transferred into or out of the system. The two ways of transferring energy from the system to surroundings and vice versa are heat and work. Moreover, as you will know later that, internal energy change of a reaction, ΔE, is the heat change when the reaction is carried out at constant volume. i.e. $\Delta E = q_v$ where q_v is heat supplied at constant volume.

Internal energy of a system cannot be determined, however, change internal energy, denoted by ΔE, can be measured and calculated.



An increase in internal energy of a chemical system has three possib consequences.

i. Increase in internal energy of a system can increase the temperature the system by increasing the kinetic energy of the molecules.

ii. Increase in internal energy of a system can result in phase change of system, e. g., melting or evaporation may occur.

iii. Increase in internal energy can result in a chemical reaction if energ supplied is sufficient to break the bonds.

11.4 First Law of Thermodynamics

It was Josiah Willard Gibbs who in 1873, on the basis of experimental wo stated the First Law of Thermodynamics. The first law of thermodynamics is, i fact, the law of conservation of energy. According to Gibbs the *first law sta that energy can neither be created nor destroyed although it may be transfer or changed from one form to another. It can also be stated that "the total ene of the system and its surroundings is conserved"*. For example, an electric bu converts electric energy into light energy. The potential energy of a falling ball converted into kinetic energy.

Energy is exchanged between the system and surroundings in the form heat and work. A system may lose energy to the surroundings in the form of he but, at the same time, the same amount of energy is absorbed by th surroundings. Hence, the amount of energy lost by the system is equal to t amount of energy gained by the surroundings.

A way of expressing the first law of thermodynamics is that, any change internal energy (ΔE) of a system is given by the sum of the heat (q) that flo across its boundaries and the work (w) done on the system by the surrounding

$$\Delta E = q + w \qquad (11.1)$$

Eq.11.1 says that the change in the internal energy of a system is the sum of the heat exchanged 'q' between the system and the surrounding and the work done 'w' on (or by) the system. The sign convention for 'q' and 'w' are as follows.

Table 11.1: Sign Convention for Work and Heat

Process	Sign
Work done by the system on the surrounding	w (negative)
Work done on the system by the surrounding	w (positive)
Heat absorbed by the system from the surroundings	q (positive)
Heat absorbed by the surroundings from the system	q (negative)

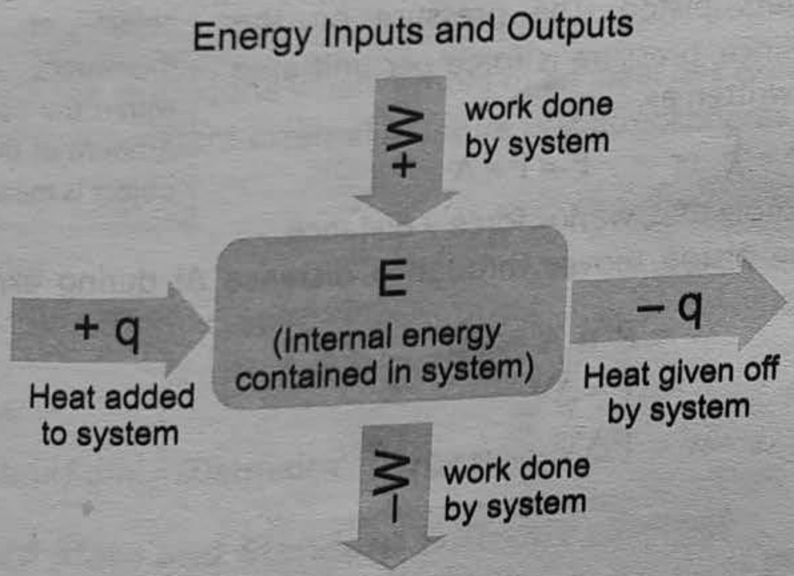


Fig. 11.2 Sign convention for work and heat

The first law of thermodynamics states hat the change in internal energy for the ystem (Δ E) is equal to the amount of heat rovided to the system (q) minus the amount f work done by the system (w).

$\Delta E = q - w \qquad$ (i)

n some books you can find this equation as

$\Delta E = q + w \qquad$ (ii)

Tidbit

Work has opposite signs in physics and chemistry. Work done by system is represented as negative (-w) in chemistry and as positive (+w) in physics.

The difference between the two equations is that in the first one 'w' is work done by the system, whereas, in the second one, it is the work done on the system.

Tidbit

Units of Work

In physics work is product of force and displacement. SI unit of work is Joule (J), which is defined as the work done by a force of one Newton through a displacement of one meter i.e. Newton meter (Nm). One Nm is equal to one Joule which is SI recommended unit of work.

Thermal energy is the energy possessed within an object or system due to movement of the particles within the object or the system. Amount of thermal energy in an object is measured in Joules (J)

Pressure-Volume Work

The only type of work in thermodynamics is the work of expansion or pressure-volume (PV) work. This is the work done when a system expands against an opposing pressure.

Consider a gas contained in a cylinder of cross sectional area, A, fitted with a weightless and frictionless piston. The pressure on the piston is P. Since, pressure is force per unit area so P can be written as.

$$P = \frac{F}{A} \quad \text{or} \quad F = P \times A$$

We know that, work= force × distance

If the piston moves through a distance Δl during expansion, the work done will be,

$$w = P \times A \times \Delta l,$$

Since, $A \times \Delta l = \Delta V$

Thus, $w = P\Delta V$ (11.2)

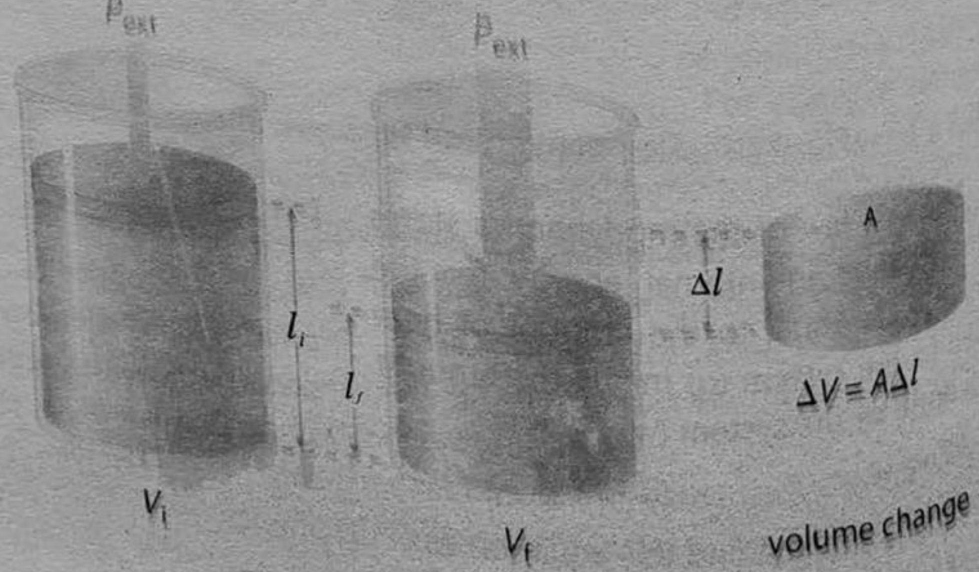


Fig.11 :3 Pressure-volume work

This is called pressure-volume work and is positive when it is done on the system. Here, ΔV is change in volume in the case of expansion or contraction. In the light of Equation 11.2 Equation 11.1 becomes

$$\Delta E = q + P\Delta V \qquad (11.3)$$

Whereas, work is negative ($-P\Delta V$), when it is done by the system.

$$q = \Delta E - P\ \Delta V \qquad (11.4)$$

If the volume of the system is kept constant then $\Delta V=0$ and hence, $P\Delta V=0$, so Eq.11.3, at constant volume becomes

$$\Delta E = q_v \qquad (11.5)$$

Hence, heat absorbed at constant volume is utilized to increase the internal energy only and no work is done.

Units of work and heat in SI system are,

$$Nm^{-2} \times m^3 = Nm \text{ or Joules (J).}$$

Example 11.1

Calculate the work done when 1 mole of an ideal gas expands from 15 dm^3 to 20 dm^3 against a constant external pressure of 2 atmospheres.

Solution:

$P = 2atm$

$\Delta V = V_2 - V_1 = 20dm^3 - 15dm^3 = 5dm^3$

Since

$w = P\Delta V$

$w = 2atm \times 5dm^3 = 10atm\ dm^3$

Self-Assessment

- What are the consequences of an increase in internal energy of a chemical system.
- Define first law of thermodynamics.

11.5 Standard State and Standard Enthalpy changes

First law of thermodynamics can be applied to processes carried out under different conditions. There are two main conditions under which the processes can occur, i.e., at constant volume and at constant pressure which is the most common way of carrying out chemical reactions. Eq.(11.3) shows the first law of thermodynamics. It has also been shown that processes at constant volume follow the equation $\Delta E = q_v$.

Now let us establish equation for most commonly occurring processes which take place at constant pressure. Starting from first law equation

$$\Delta E = q + P\Delta V \qquad (11.3)$$

When we supply heat 'q' to a gas it expands to keep its pressure constant which results in performing work on the surrounding against external pressure, thus, the equation takes the form, considering the sign convention, as $\Delta E = q - P\Delta V$. On rearranging this equation we get

$$q_p = \Delta E + P\Delta V \qquad (11.4a)$$

Here q_p stands for heat supplied at constant pressure condition. Now we introduce a new thermodynamic function of a system called *enthalpy (H)*, or heat content of the system which is defined by the equation

$$H = E + PV \qquad (11.6)$$

Thus, the total heat content of a system, 'H', at constant pressure is equal to the internal energy plus PV work

Change in enthalpy, 'ΔH' at constant pressure is given by

$$\Delta H = \Delta E + P\Delta V \qquad (11.7)$$

Comparing Eq.(11.4a) and (11.7) we can easily demonstrate that

$$q_p = \Delta H \qquad (11.8)$$

Thus, from Eq.(11.8), heat supplied at constant pressure is equal to change in enthalpy.

Thus, we have proved that heat supplied at constant volume, $q_v = \Delta E$ and heat supplied at constant pressure, $q_p = \Delta H$

Hence, heat evolved or absorbed at constant pressure during a process or a reaction is equal to change in the enthalpy of the system. Since, ΔH is the heat of the reaction, it can be calculated theoretically and measured experimentally. Its units are expressed in energy units, i.e. kJ or Joules.

From the above discussion it is concluded that.

1. Since E, P, and V are state functions so according to Eq. (11.6), enthalpy is also a state function.
2. ΔH is positive when the heat is absorbed and it is negative when the heat is released by the system.
3. Processes involving solids and liquids have their $\Delta H = \Delta E$, since the change in volume (ΔV) is very small and closed to zero hence the term $P\Delta V$ in Eq. (11.7) can be neglected.

Example 11.2:

When 1 mole of ice melts at 0°C and constant pressure of 1 atmosphere, 6025 J of heat is absorbed by the system. The molar volumes of ice and water are 0.020 and 0.018 dm^3, respectively. Calculate ΔH and ΔE.

Solution:

a. $\Delta H = q_p = 6025\,J$

$P = 1atm$

$P\Delta V = P \times (V_2 - V_1)$

$= 1atm \times (0.018\,dm^3 - 0.020\,dm^3)$

$P\Delta V = -0.002\,dm^3\,atm$

Since $1dm^3 = atm = 101.25\,J$

So $P\Delta V = -0.002dm^3\,atm \times 101.25Jdm^{-3}\,atm^{-1} = -0.2025J$

b. $\Delta H = \Delta E + P\Delta V$

$\Delta E = \Delta H - P\Delta V$

$= 6025J - (-0.2025J)$

$\Delta E = 6025.20J$

(i) Standard Enthalpy Change, ΔH°

The change in enthalpy measured at room temperature (298K) and one atmospheric pressure when the reactant and products are in their standard (natural) states is called the standard enthalpy change.

It should be mentioned that there is no way to measure absolute value of enthalpy of a substance; only values relative to an arbitrary reference can be determined. Furthermore, it is important to state the conditions under which a reaction is performed. Thus, arbitrary reference point is the set of conditions of temperature and pressure. These conditions of temperature and pressure, for thermochemical measurements, are 298 K (25°C) and one atmosphere respectively. Any enthalpy change measured under these conditions is described as a standard enthalpy change and given the symbol ΔH° or ΔH°_{298}. This implies that all the substances involved in the reaction are in their normal and natural state at 298K and 1 atmosphere. This state is called the standard state. Thus, ΔH°_{298} for reaction corresponds to gaseous hydrogen, oxygen and liquid water (not steam) which are their most stable and normal state or standard states.

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(\ell)}$$

(ii) The standard enthalpy of formation (ΔH°_f)

It is defined as the heat change that results when 1 mole of a compound is formed from its elements where all the reactants and products are at their standard state i.e. 298K and 1 atm. pressure. The standard enthalpy of formation of all the elements in their most stable form is arbitrarily taken as zero. For example molecular oxygen (O_2) is more stable than its allotropic form ozone (O_3) at 1 atm and 25°C. A list of standard enthalpies of formation for some elements and compounds is given in Table 11.2. These values are helpful to calculate standard enthalpies of reactions ($\Delta H^\circ_{reaction}$).

The standard heat of formation of CO_2 is - 393.5l kJ mol^{-1} and that of SO_2 is -296.83 kJ mol^{-1} as shown below.

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \rightarrow \quad \Delta H^\circ_f = -393.51 \text{ kJ mol}^{-1}$$

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \quad \rightarrow \quad \Delta H^\circ_f = -296.83 \text{ kJ mol}^{-1}$$

Table 11.2: Standard Enthalpies of Formation at 298K

Substance	ΔH°_f	*Substance*	ΔH°_f
All elements in their standard states	0.00	$CaC_{2(s)}$	−62.5
$C_{(s)}$ (graphite)	0.00	$CS_{2(l)}$	+89.7
$C_{(s)}$ (diamond)	+1.90	$HCl_{(g)}$	−92.31
$P_{(s)}$ (white)	0.00	$NaCl_{(s)}$	−411.00
$P_{(s)}$(red)	−17.60	$HBr_{(g)}$	−36.40
$H_2O_{(l)}$	−285.84	$HI_{(g)}$	+26.48
$SO_{2(g)}$	−296.83	$NH_{3(g)}$	−46.11
$CO_{(g)}$	−110.53	$H_2S_{(g)}$	−20.63
$CO_{2(g)}$	−393.51	$CH_{4(g)}$	−74.81
$Fe_2O_{3(s)}$	−824.2	$C_2H_{2(g)}$	+226.73
$Fe_3O_{4(s)}$	−1118.4	$H_2SO_{4(l)}$	−813.99
$CaO_{(s)}$	−635.5	$HNO_{3(l)}$	−174.10

(iii) Standard Enthalpy of Reaction ($\Delta H^\circ_{Reaction}$)

The standard enthalpy of reaction, (ΔH°_r), is the change in enthalpy for a given reaction calculated from the standard enthalpies of formation for all reactants and products. It can be calculated from the difference between the total enthalpies of formation of products and reactants as follows

$$\Delta H^{\circ}_{r} = \sum \Delta H^{\circ}_{(products)} - \sum \Delta H^{\circ}_{(Reactants)}$$

For example, $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(\ell)}$ $\Delta H^{\circ}_{(Reaction)} = -572\ kJ\ mol^{-1}$

(iv) Standard Enthalpy of Combustion (ΔH_c°)

It is the amount of heat produced when one mole of a compound in its standard state, is completely burnt in excess of air or oxygen at 298K and 1atm. pressure. All the substances involved are in their standard states and the reaction is carried out under standard conditions, i.e. 298 K (25°C) and one atmospheric pressure. For example, the enthalpy of combustion of CH_4 is -890 kJ mol^{-1}.

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)} \qquad \Delta H_c = -890 kJ/mol$$

Example 11.3

The heats of formation of $CH_{4(g)}$, $CO_{2(g)}$, and $H_2O_{(g)}$ are: -74.85kJ mol^{-1}, -393.50kJ mol^{-1} and -285.81kJ mol^{-1}, respectively. Calculate the heat of combustion of the following reaction.

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)} \qquad \Delta H^{\circ}_{c} = ?$$

Solution:

$$\text{Heat of the reaction} = \Delta H_r^{\circ} = \sum [\Delta H^{\circ}_{f\ products}] - \sum [\Delta H^{\circ}_{f\ reactants}]$$

$$\Delta H_c^{\circ} = [\Delta H^{\circ}_{fCO_2} + 2\Delta H^{\circ}_{fH_2O}] - [\Delta H^{\circ}_{fCH_4} + 2\Delta H^{\circ}_{fO_2}]$$

$$\Delta H_c^{\circ} = [-393.50 + 2(-285.81)] - [-74.85 + 2 \times 0]\ kJ\ mol^{-1}$$

$$\Delta H_c = [-965.12 + 74.85]\ kJ\ mol^{-1} = -890.27\ kJ\ mol^{-1}$$

Tidbit

The potential energy stored in food stuff is experimentally determined by combustion analysis. Calculate your daily intake of food calories, the method of calculation is given in an example given below.

To calculate energy available from food, multiply the number of grams of carbohydrate, protein, and fat by 4, 4, and 9, respectively. Then add the result together.

Example: One slice of bread with a tablespoon of peanut butter on it contains 16 g carbohydrate, 7 g protein, and 9 g fat. Calculate total energy consumed in this intake.

Solution: 16 g carbohydrate x 4 kcal/g =64 kcal
=28 kcal
7 g protein x 4 kcl/g = 81 kcal
9 g fat x 9kcal/g = 173 kcal
Total

(v) Standard Enthalpy of Neutralization (ΔH°_{n})

It is the amount of heat evolved when one mole of hydrogen ions, (H^+) from an acid, react with one mole of hydroxide ions, (OH^-) from a base, to form one mole of water. A strong acid and a strong base are completely ionized in solution. The reaction between such acid and a base is given below. The following net reaction takes place in neutralization reaction.

$$OH^- + H^+ \longrightarrow H_2O \quad \Delta H^{\circ}_{n} = -57.4\,kJmol^{-1}$$

Since, the same reaction occurs for neutralization of any strong acid with any strong base, hence their heat of neutralization is approximately the same i.e. -57.4 kJ mol^{-1}.

(vi) Bond Dissociation Energy

Bond dissociation energy (BDE) is a measure of the bond strength. It is defined as the enthalpy change taking place when a particular bond is broken at 298K, e.g. BDE of H_2 is 436 kJ/mol, O_2 is 499kJ/mol.

Reading Check

Define the following:
- Standard enthalpy change ΔH^{o}
- Standard enthalpy of formation ΔH^{o}_{f}
- Standard enthalpy of reaction ΔH^{o}_{r}
- Standard enthalpy of combustion ΔH^{o}_{c}

11.6 Heat Capacity

There are three different heat capacity terms namely, heat capacity, specific heat capacity, and molar heat capacity. These are defined as follows.

(i) Heat Capacity

The heat capacity (C) of a substance is the amount of heat required to raise the temperature of a given amount of the substance by 1 degree Celsius (°C) or Kelvin (K). It is an *extensive property* and depends on the amount of the substance. The SI units of heat capacity is JK^{-1}.

(ii) Specific Heat Capacity

The specific heat (s) of a substance is the amount of heat required to raise the temperature of one gram of the substance by one degree Celsius or Kelvin. It is also called as specific heat capacity. It is an *intensive property* which does not depend on the quantity of substance. The SI units of specific heat capacity is $Jg^{-1}K^{-1}$.

The relationship between specific heat capacity and heat capacity is

$$C = m\,s \qquad (11.9)$$

Where, m is the mass of the substance in gram. The specific heat of water, for example, is 4.184 J $g^{-1}K^{-1}$ and heat capacity of 50 g of water can be calculated using Eq.(11.9), as

$$209.2\ J\,K^{-1} = (50g)\,(4.184\ J\,g^{-1}\,K^{-1})$$

If we know the specific heat and amount of substance, then the change i the temperature of the sample (Δt) will tell us the amount of heat (q) that ha been absorbed or released in a particular process. The equation for calculatin the heat change is given by

$$q = m\,s\,\Delta t \qquad (11.10)$$

or in the light of Eq.(11.9) and 11.10 may be written as,

$$q = C\,\Delta t \qquad (11.11)$$

(iii) Molar Heat Capacity

In chemistry we come across another unit of heat capacity that is the *Molar Heat Capacity. It is defined as the amount of heat required to raise the temperature of one mole of a substance through 1°C or 1K.* The units of molar heat capacity is J mol^{-1} K^{-1}.

11.7 Calorimetry

The enthalpy changes, brought about by chemical or physical processes, are measured using an apparatus called the calorimeter. *The process or method of measurement of enthalpy changes during chemical reactions or physical changes is called calorimetry.* Here we will discuss the use of simple constant pressure calorimeter for the measurement of enthalpy changes.

Measurement of Enthalpy Change

The enthalpy changes occurring in chemical processes may be measured by two main methods. One is direct calorimetry and other is indirect calorimetry.

1. Direct Calorimetry

In a calorimeter, heat changes (ΔH) of those reactions are measured which go to completion without side reactions. For example, the heat of neutralization, of an aqueous solutions of a strong acid by a strong base, can be measured by a calorimeter.

A schematic diagram of a simple calorimeter is shown in Figure 11.3. It consists of an insulated container in which a reaction vessel is placed, wherein the reaction under investigation is carried out. In case of an exothermic reaction, the heat generated cause an increase in temperature of water, which is measured with a thermometer.

The heat given out by the reactants = heat gained by the water

From the specific heat of the system, and the temperature change, the amount of heat (Q) evolved or absorbed in the reaction can be calculated by using equation.

$Q = n\,C\,\Delta T$ where, n may be taken as number of moles and C is the molar heat capacity and ΔT is the change in temperature.

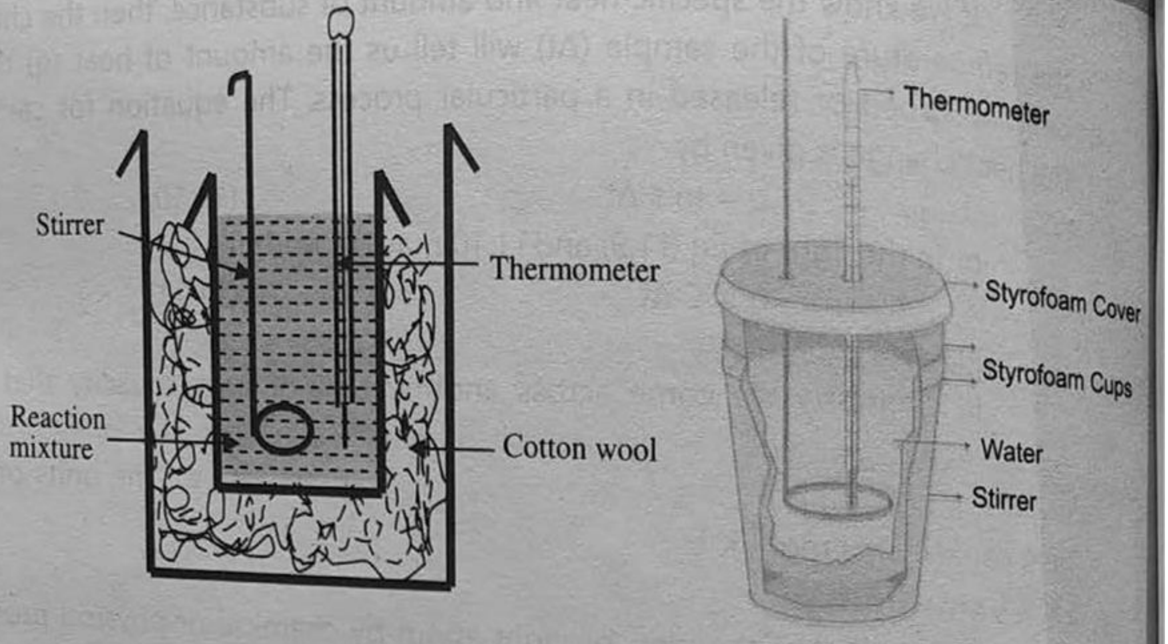


Fig. 11.4: A simple calorimeter

Example 11.4

When 50 cm^3 of 2 mol dm^{-3} HCl is added to 50 cm^3 of 2 mol dm^{-3} NaOH solution. The temperature rise is 13.6 °C. Calculate the heat of neutralization per mole where the specific heat of water is 4.2 J g^{-1}K^{-1}.

Solution:

$$NaOH_{(aq)} + HC\ell_{(aq)} \longrightarrow NaC\ell_{(aq)} + H_2O_{(\ell)}$$

$$\text{No. of mole of } HC\ell = \frac{50}{1000} \times 2 = 0.1 \text{ mol}$$

$$\text{No. of mole of NaOH} = \frac{50}{1000} \times 2 = 0.1 \text{ mol}$$

$$\text{Total volume of solution} = 50 + 50 = 100 \text{ cm}^3$$

Since the solutions are dilute so we can use the density of water instead the density of solution. Where density of water = 1gm/cm^3

$$\text{Mass of solution} = dv = 1 \times 100 = 100 \text{ g.}$$

$$\text{Heat of neutralization} = m \times t_c^{\circ} \times c_w$$

$$\text{Heat neutralization} = 100 \times 13.6 \times 4.2$$

$$= -5712 \text{ J} / 0.1 \text{ mol}$$

0.1 mole of acid and 0.1 mole of NaOH give heat of neutralization $= -5712$ J

1 mole of acid and 1 mole of NaOH give heat of neutralization $= \frac{-5712}{0.1}$

$= -57120$ J

Or heat of neutralization $= -57.12$ kJ mol^{-1}.

2. Indirect Calorimetry

In this method, enthalpy change is calculated indirectly using Hess's law.

11.8 Hess's Law (Enthalpy change calculations)

In certain chemical reactions enthalpy of formation (ΔH^o_f) cannot be determined directly due to the following reasons:

(i) Some compounds cannot be directly synthesized from their elements.

(ii) The rate of some reactions are very slow to be subjected for enthalpy measurement.

(iii) In some cases side reactions take place and produce products other than the desired one.

In such cases ΔH^o_f can be determined by an indirect method, which is based on the Hess's law of constant heat summation, or simply *Hess's law which states that the amount of heat, evolved or absorbed in a chemical reaction is the same whether the reaction takes place in a single or several steps.* This means that the net heat of reaction depends only on the initial and final states and not on intermediate steps.

Let a substance 'A' changes to 'B' in two ways:

i) 'A' changes directly to 'B' and 'Q' is the amount of heat absorbed in this process.

$DH^o = +Q$

A ¾® B

ii) 'A' changes to 'B' indirectly in three steps, as represented diagrammatically, in Fig. 11.5. According to Hess's law, the total absorption of heat is the sum of heats involved in different steps.

Hence $Q = q_1 + q_2 + q_3$

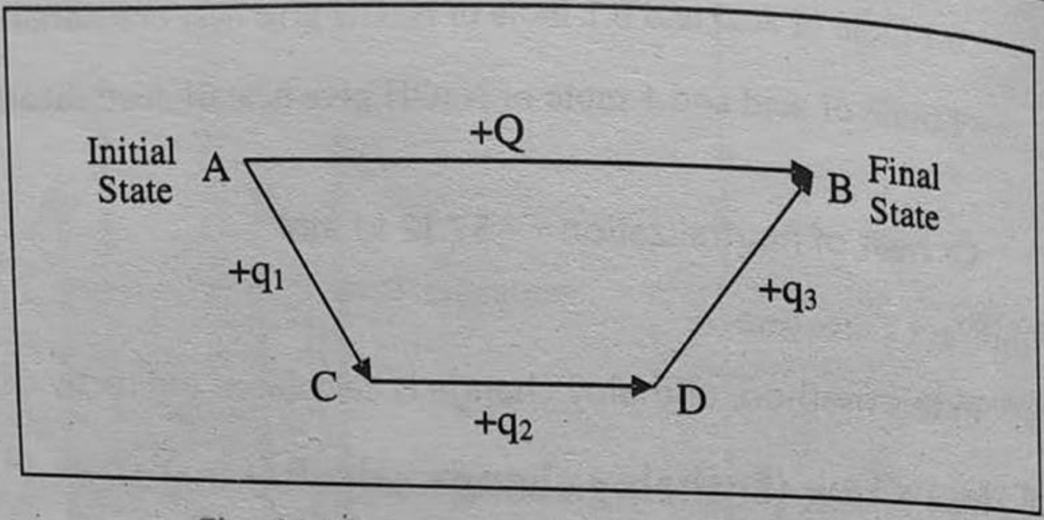


Fig. 11.5Two ways of changing A to B.

Following example of formation of Na_2CO_3 with the reaction of NaOH and CO_2 illustrates the Hess's law

Single step process

$$2NaOH_{(aq)} + CO_{2(g)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(\ell)} \quad \Delta H = -89.08\ kJ$$

Two step process

$$NaOH_{aq)} + CO_{2(g)}\ \text{¾ ¾®}\ NaHCO_{3(aq)} \qquad DH_1 = -48.06kJ$$

$$NaHCO_3 + NaOH_{(aq)}\ \text{¾ ¾®}\ Na_2CO_{3(aq)} + H_2O_{(l)} \quad DH_2 = -41.02kJ$$

According to Hess's Law $DH = DH_1 + DH_2$

Putting the values

$$DH = -48.06 - 41.02$$

$$DH = -89.08kJ$$

By applying the Hess's law the heat of all those reactions can b calculated, which cannot be measured directly. Some of its applications are a follows.

Heat of Formation

Carbon monoxide, for example, is prepared by reacting carbon w oxygen, but along with carbon monoxide, carbon dioxide is also formed. So determine the heat of reaction for CO formation, an indirect method is used follows.

$C_{(s)} + \frac{1}{2}O_{2(g)}$ ¾¾® $CO_{(g)}$ DH° = ?

i) $C_{(s)} + O_{2(g)}$ ¾¾® $CO_{2(g)}$ DH°₁ = - 393.5kJ mol⁻¹

ii) $CO_{(g)} + \frac{1}{2}O_{2(g)}$ ¾¾® $CO_{2(g)}$ DH°₂ = - 285.7 kJ mol⁻¹

Substracting equation (ii) from (i) and similarly subtracting DH_2 from DH_1 We get

$C_{(s)} + \frac{1}{2}O_{2(g)}$ ¾¾® $CO_{(g)}$ DH° = - 108.88 kJ mol⁻¹

The **lattice energy** can be calculated from the available thermodynamic data by a cyclic process known as Born-Haber Cycle, which is based on Hess's law.

11.9 Born Haber Cycle

The Born-Haber Cycle is based on the principle, that the sum of energy changes which occur in a closed cycle, from the same initial and final states, is zero. This principle involves the law of conservation of energy in accordance with the first law of thermodynamics.

The Born Haber cycle may be considered for NaCl as an example. *The standard heat of formation $\Delta H°_f$ of NaCl is the amount of heat given out when one mole of NaCl is formed from its elements, solid Na and gaseous chlorine.* Lattice energy cannot be measured directly, but it can be determined indirectly. We measure ΔH^o_f for NaCl as follows:

Direct

$$Na_{(s)} + \frac{1}{2}C\ell_{2(g)} \rightarrow NaC\ell_{(s)} \qquad \Delta H^o_f = -411 kJmol$$

Stepwise

i) $Na_{(s)} \rightarrow Na_{(g)}$ $\Delta H^o_{Sub} = 109 kJmol^{-1}$

ii) $Na_{(g)} \rightarrow Na^+_{(g)} + \bar{e}$ $\Delta H^o_{I.E} = 496 kJ\ mol^{-1}$

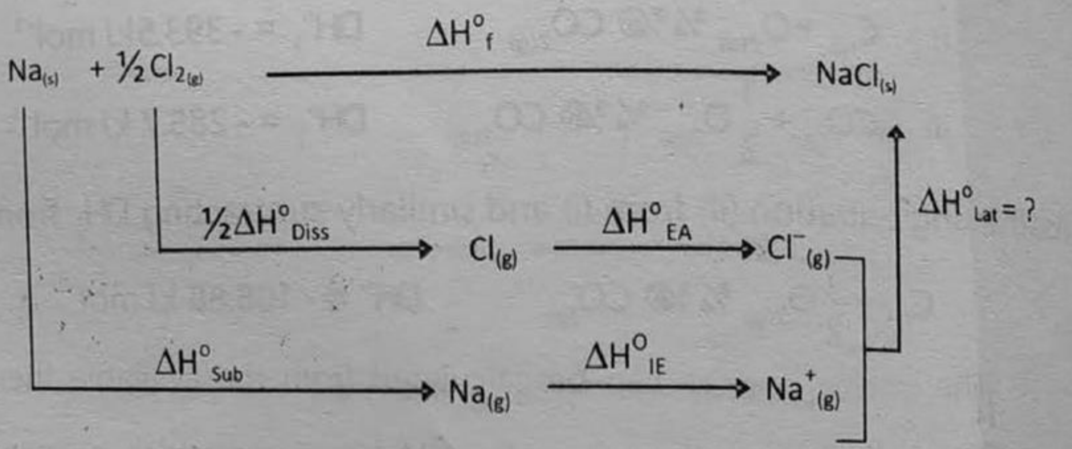
Similarly Cl is formed in the following two steps:

iii) $Cl_{2(g)} \rightarrow 2Cl^-_{(g)}$ $\Delta H^o_{Diss} = 242 kJmol^{-1}$

iv) $Cl_{(g)} + \bar{e} \rightarrow Cl^-_{(g)}$ $\Delta H^o_{EA} = -348 kJmol^{-1}$

v) $Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)}$ $\Delta H^o_{Lat} = U = ?$

The various energies involved in Born Haber Cycle for NaCl can be summarized as follows



According to Hess's law the sum of all the five steps lead to the heat of formation of $NaCl_{(s)}$.

$$\Delta H^\circ_f = \Delta H^\circ_{Sub} + \Delta H^\circ_{I.E} + \frac{1}{2}\Delta H^\circ_{Diss} + \Delta H^\circ_{EA} + \Delta H^\circ_{Lat}$$

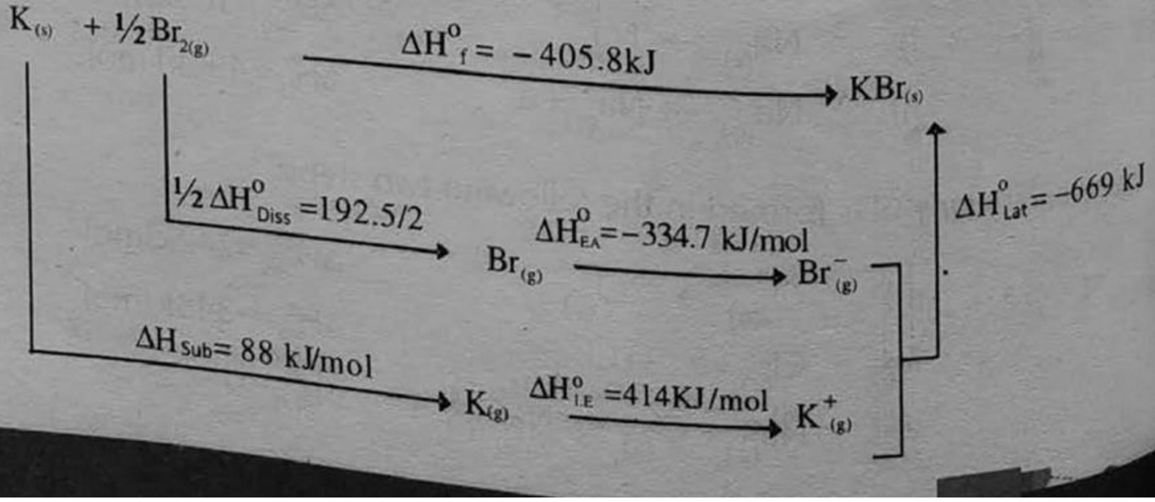
$$\Delta H^\circ_{Lat} = \Delta H^\circ_f - \Delta H^\circ_{Sub} - \Delta H^\circ_{I.E} - \frac{1}{2}\Delta H^\circ_{Diss} - \Delta H^\circ_{EA}$$

$$= -411 kJ/mol - 109 kJ/mol - 496 kJ/mol - 121 kJ/mol - (-348 kJ/mol)$$

$$\Delta H^\circ_{Lat} \text{ of } NaCl_{(s)} = -789 kJ/mol$$

Example 11.5

Calculate the lattice energy of KBr. The heat of sublimation of potassium is 88 kJ/mole, the heat of dissociation of bromine gas is 192.5 kJ/mole. The ionization energy of K is 414 is kJ/mole, the electron affinity of Br is -334.7 kJ/mole and the heat of formation of KBr is −405.8 kJ/mole.



$$DH^{\circ}_{f} = DH^{\circ}_{Sub} + DH^{\circ}_{I.E} + \frac{1}{2}DH^{\circ}_{Diss} + DH^{\circ}_{EA} + DH^{\circ}_{Lat}$$

$$DH^{\circ}_{Lat} = DH^{\circ}_{f} - DH^{\circ}_{Sub} - DH^{\circ}_{I.E} - \frac{1}{2}DH^{\circ}_{Diss} - DH^{\circ}_{EA}$$

$$= -405.8 - 88 - 414 - \frac{1}{2}192.5 - (-334.7)$$

$$DH^{\circ}_{Lat} = -669.3 kJ/mol$$

Self-Assessment

1. Define calorimetry and how to measure enthalpy change with the help of calorimeter.
2. State the Hess's law.
3. On which principle Born Harber cycle is based?

KEY POINTS

- Thermochemistry is the branch of chemistry which deals with the heat changes involved in chemical reactions and physical processes.
- The reactions are exothermic if internal energy of the reactants is greater than that of the products.
- The difference of internal energy is released as heat energy.
- The reactions in which the internal energy of the products is greater than that of the reactants, heat is absorbed from the surroundings such reactions are called endothermic reactions.
- According to first law of thermodynamics, the energy of the system and surrounding is conserved, mathematically, it can be written as $q = \Delta E + w$. In SI system, the unit of work and heat is Nm or Joules (J).
- Enthalpy is a state function. It is the heat content of a system.
- The change in enthalpy (ΔH) is the amount of heat absorbed or released at constant pressure.
- Standard enthalpy change, $\Delta H°$ is enthalpy change at 298K and 1 atmospheric pressure when all the reactants and products are in their standard states.
- Standard enthalpy change can be expressed in different ways depending on the nature of a reaction. Heat of formation ($\Delta H°_f$) is the change of enthalpy when one mole of a substance is formed from its elements. Similarly heat of combustion ($\Delta H°_c$) is the enthalpy change when one mole of a substance is completely burnt in excess of air.
- The heat capacity of a system is the heat absorbed by a system, in raising the temperature by one degree (K or °C). SI units of heat capacity is Joules per Kelvin i.e., JK^{-1}
- The lattice energy can be calculated from the available thermodynamic data by cyclic process known as Born-Haber Cycle, which is based on Hess's law. Th Born-Haber Cycle is based on the principle, "that the total enthalpy change of th reaction is the net sum of enthalpy changes of all the individual steps of t reaction.

EXERCISE

Choose the correct option.

1. ΔH per mole is expressed in the units of
   a) k J b) °F c) °C d) K
2. Which one of the following is NOT a state function?
   a) enthalpy b) heat c) temperature d) pressure
3. For solids and liquids
   a) $\Delta H = \Delta E$ b) $\Delta H > \Delta E$ c) $\Delta H < \Delta E$ d) $\Delta E = 0$
4. 1 k cal is equal to
   a) 41.8×10^3 J b) 418×10^3 J c) 4.18×10^3J d) 0.418×10^3J
5. Standard enthalpy (ΔH^o) for 1 mole of a substance, which exists in its natural state, at 1 atm. pressure is measured at
   a) 0 K b) 298 K c) 273 K d) 0 °C
6. ΔH can be measured indirectly by applying
   a) Avogadro's law b) Gas laws
   c) Hess's law d) Faraday's law
7. Enthalpy means
   a) Disorder b) Transition state
   c) Rate constant d) Heat content
8. No work is done at constant
   a) Pressure b) Volume c) Temperature d) Mass
9. Heat capacity depends on
   a) Pressure b) Volume c) Composition d) Mass
10. Which one of the following reactions is spontaneous?
    a) Endothermic b) Exothermic c) Reversible d) Irreversible
11. The energy possessed by water in a dam is
    a) Potential Energy b) Kinetic Energy
    c) Electric Energy d) Heat Energy
12. When heat is absorbed from the surrounding, the process is
    a) Reversible b) Mechanical
    c) Exothermic d) Endothermic
13. The sum of all the energies of all the molecules or atoms of a substance is called its:
    a) Specific heat b) Heat capacity
    c) Latent heat d) Internal energy

14. Which one of the following processes has ΔH positive

a) Ionization energy
b) Electron affinity
c) Combustion
d) Exothermic reaction

Short Questions

1. Explain the following short questions with reasons.
   (i) Total energy of the system and its surroundings remains constant.
   (ii) Ionic reactions are very fast.
   (iii) The work done has positive and negative values.
   (iv) Heat of combustion is always negative.
   (v) Enthalpy change is a state function but heat is not.
   (vi) ΔH for solids and liquids becomes equal to ΔE.
   (vii) Enthalpy of neutralization of strong acids and strong bases has always the same value.
2. What do you mean by state of a system? What are state functions?

Long Questions

1. State and explain Hess's law of constant heat summation. Show that it is a direct consequence of the first law of thermodynamics.
2. How does Born Haber cycle help in calculating lattice energy?
3. What is meant by heat of a reaction? Explain how the heat of a reaction at constant volume differs from the heat of a reaction at constant pressure?
4. What is meant by pressure volume work? How it is related to the first law of thermodynamics?

Numerical

1. Apply Hess's law to calculate ΔH° for the sublimation of one mole of iodine from the following equations.
   (i) $H_{2(g)} + I_{2(s)} \rightarrow 2HI_{(g)}$ $\Delta H^\circ = 51.8\,kJ\,mol^{-1}$
   (ii) $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$ $\Delta H^\circ = -10.5\,kJ\,mol^{-1}$ (Ans. $62.3\,kJ\,mol^{-1}$)
2. Calculate heat of formation of an aqueous solution of NH_4Cl from the following data.
   (i) $NH_{3(g)} + aq \rightarrow NH_{3(aq)}$ $\Delta H^\circ = -35.16\,kJ\,mol^{-1}$
   (ii) $HCl_{(g)} + aq \rightarrow HC1_{(aq)}$ $\Delta H^\circ = -72.41\,kJ\,mol^{-1}$
   (iii) $NH_{3(aq)} + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)}$ $\Delta H^\circ = -51.48\,kJ\,mol^{-1}$

(Ans. $-159.08\,kJ\,mol^{-1}$)

3. Liquid ethanol when burnt in oxygen at 25°C liberates heat i.e. $\Delta H^\circ =$ 1402.14 kJ mol^{-1}. The heats of formation of CO_2 and H_2O are -393.50 and 285.81 kJ mol^{-1}, respectively, at the same temperature. Calculate the hea of formation of ethanol at 25°C. (Ans. -242.37 kJ mol^{-1})

4. A chemical reaction takes place in a container of cross sectional area o 0.01 m^2, fitted with a weightless and frictionless piston. The piston i moved up through 0.01m against an external pressure of 101325 Pa as result of the reaction. Calculate the work done by the system. (Ans. 101.3 J)

5. Determine ΔH° for the following reaction with the help of given data.

$$2C_{(s)} + 2H_{2(g)} \rightarrow C_2H_{4(g)} \qquad \Delta H^\circ = ?$$

i) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\qquad \Delta H^\circ_1 = -393.5$ kJ mol^{-1}

ii) $H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(g)}$ $\qquad \Delta H^\circ_2 = -285.7$ kJ mol^{-1}

iii) $C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(g)}$ $\qquad \Delta H^\circ_3 = -1430.9$ kJ mol^{-1}

(Ans 72.8 kJ mol^{-1})

Project

Determination of specific heat capacity of iron.

Take two beakers and an iron bolt. Determine the weight of the bolt and record it. Place the bolt in a beaker containing water in it and leave for a while so as the temperature of the water and the bolt comes to an equilibrium and record the temperature of the water by a thermometer, this corresponds to the temperature of the bolt. Now, take another dry beaker and record its weight. Add 100 mL water in this beaker and weigh again. Find the weight of the water by difference. Heat the water up to 70 to 80°C and transfer the water into a calorimeter. Record the temperature of the water T_1 in calorimeter and transfer the bolt from cold water to the calorimeter and record the temperature of water in calorimeter carefully. The temperature will fall to a minimum value. Record it as T_2. Calculate $\Delta T = T_1 - T_2$ heat delivered to the bolt by water $q_w = m_w \times s_w \times \Delta T$ where m_w and s_w are the mass and specific heat of the water, respectively. Note that the same amount of heat, $(q_b = q_w)$, has been absorbed by the bolt. Thus, specific heat of the bolt, s_b, can be calculated as $s_b = q_b/m_b$.

Unit -12

Electrochemistry

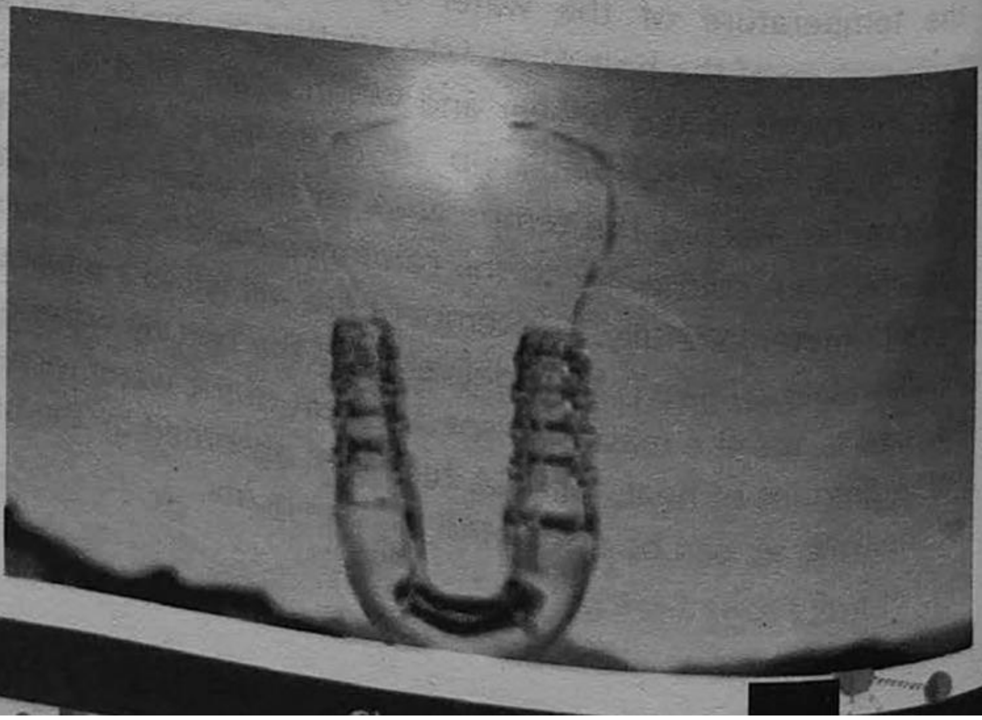
After reading this unit, the students will be able to:

- Give the characteristics of a Redox reaction. (Understanding)
- Determine the oxidation number of an atom of any element in a pure substance. (Applying)
- Define oxidation and reduction in terms of a change in oxidation number. (Applying)
- Use the oxidation-number change method to identify atoms being oxidized or reduced in redox reactions. (Applying)
- Use the oxidation-number change method to balance redox equations. (Applying)
- Balance redox reactions that take place in acid solutions. Break a redox reaction into oxidation and reduction half reactions. (Applying)
- Use the half reaction method to balance an unbalanced a redox equation. (Applying)
- Define cathode, anode, electrode potential and S.H.E. (Standard Hydrogen Electrode). (Remembering)
- Identify the substance oxidized and the substance reduced in a dry cell. (Applying)

Teaching
10

Assessment
01

Weightage %
08



- Use the activity series of metals to predict the products of single replacement reactions. (Applying)
- Define cell potential and describe how it is determined. (Understanding)
- Describe the reaction that occurs when a lead storage battery is recharged. (Applying)
- Explain how a fuel cell produces electrical energy. (Applying)
- Define the standard electrode potential of an electrode. (Remembering)
- Distinguish between electrical terms such as coulomb, ampere and volt. (Understanding)
- State and explain Faraday's laws. (Understanding)
- Describe how dry cell supplies electricity. (Understanding)
- Explain how a lead storage battery produces electricity. (Understanding)
- Define corrosion and describe simple methods like electroplating and galvanizing for its prevention. (Applying)

Introduction

Electrochemistry is the branch of chemistry which deals with the chemical changes that take place in the matter by passage of electric current and conversion of chemical energy into electrical energy and vice versa. The passage of electricity through the solutions of acids, bases and salts is accompanied by a chemical change. Such substances which allow electric current to pass through them in solution form or in molten form are called electrolytes.

In this unit, you will refresh your knowledge about certain basic terminologies used in the field of electrochemistry.

Conductors

Substances which allow the flow of electric current through them are known as conductors. The flow of current in metallic conductors, e.g. Cu, Ag etc. is due to the movement of electrons in the metal without any chemical change, while passage of electricity through the solutions of acids, bases and salts is accompanied by a chemical change.

Electrolytes

The substance which in solution or in molten state conducts electricity is called an electrolyte. Electrolytes may be strong or weak depending upon the extent of ionization.

Strong Electrolytes

The substance which is completely converted into its ions in the solution or in the molten state is called a strong electrolyte e.g. NaCl, NaOH and H_2SO_4.

Weak Electrolytes

The substance which is partially dissociated into its ions is called a weak electrolyte e. g. NH_4OH and H_2CO_3.

Electrolytic Conduction or Electrolysis

Electrolysis is a phenomenon in which chemical change takes place at the surface of electrodes due to the passage of the electric current. On passing the current through an electrolytic solution, ions migrate to the opposite electrodes where the gain and loss of electrons take place which bring about the chemical change.

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Application of Redox Reactions and Electrolysis

Some important applications of electrolysis on industrial scale are as follows:

1) Batteries use oxidation and reduction reactions to produce direct current (DC).
2) Inside the rocket propellant, a redox reaction takes place.
3) Many metals are separated from their ores with the help of redox reactions.
4) Production of hydrogen gas by electrolysis of water.
5) Manufacture of heavy water, D_2O.
6) The metals, like Na, K, Mg, Al etc. are obtained by electrolysis of fused electrolytes containing these metals.
7) Compounds, like NaOH, KOH, Na_2CO_3, $KClO_3$, $KMnO_4$ etc. are synthesized by electrolysis.
8) Electroplating is the process of coating an object made of inferior metal with a superior metal by electrolysis is known as electroplating.
9) Purification of metal by electrolysis. In this method pure metal is deposited at cathode from a solution containing metal ions, e.g. Ag, C etc., where anode is a piece of impure metal.

12.1 Oxidation-Reduction Concepts

12.1.1 Oxidation and Reduction

Oxidation and reduction can be defined in different ways.

A. The Classical Concept

According to this concept, oxidation and reduction are defined as

i. The addition of oxygen is oxidation while the removal of oxygen is reduction. e.g. SO_2 is oxidized to SO_3 by gaining O while CO_2 is reduced to C by removal of O.

$$2SO_2 + O_2 \longrightarrow 2SO_3 \quad \text{(oxidation)}$$
$$CO_2 \longrightarrow C + O_2 \quad \text{(reduction)}$$

ii. The removal of H_2 is oxidation while its addition leads to reduction reaction. e.g. NH_3 is oxidized to N_2 while Cl_2 is reduced to HCl.

$$2NH_3 \longrightarrow N_2 + 3H_2 \text{ (oxidation)}$$
$$H_2 + Cl_2 \longrightarrow 2HCl \quad \text{(reduction)}$$

B. Electron Transfer Concept

This concept is about the transfer of electrons from one element to another. The concept is explained below.

The atom which loses electrons is said to be oxidized and this process is called oxidation. The atom which gains electrons is reduced and the phenomenon is called the reduction. In terms of oxidation number an increase in oxidation number is oxidation and decrease in oxidation number is reduction. For example

$Al_{(s)} \longrightarrow Al^{3+}_{(aq)} + 3\bar{e}$ (Electron loss and increase in oxidation number; oxidation)

$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ (Addition of electron and decrease in oxidation number; reduction)

$2Al_{(s)} + 3Cu^{2+}_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3Cu_{(s)}$ (Net reaction)

12.1.2 Oxidation State or Oxidation Number

The oxidation state is the apparent charge, positive or negative, which an atom would have in a molecule or ion. It is different from the valency because valency is only a number while oxidation state indicates the positive or negative charge of the atom. The oxidation state of an atom is described by its oxidation number which is assigned according to the following rules.

Rules for assigning the Oxidation number

i. The oxidation number of a free element is zero, e.g. oxidation number of H_2, O_2 and Mn is zero.

ii. The oxidation number of hydrogen in its compounds is +1 but in metal hydrides it is −1, e.g. NaH and MgH_2.

iii. The oxidation number of oxygen in the compounds is -2 but in peroxides it is −1 and in OF_2 is +2.

iv. The oxidation numbers of the elements of groups I, II and III in the compounds are +1, +2 and +3 respectively.

v. The oxidation number of the halogens of group VII in the binary compounds is −1.

vi. The algebraic sum of the oxidation numbers of all the atoms in a molecule is zero.

vii. The algebraic sum of the oxidation numbers of all the atoms in an ion is equal to the charge on the ion.

Example 12.1:

Calculate the oxidation number of Cr in $K_2Cr_2O_7$.

Oxidation Number of K = +1 Oxidation Number of O =-2

Oxidation Number of Cr = X

Putting these values in the formula $K_2Cr_2O_7$

$2(+1) + 2X + 7(-2) = 0$

$2 + 2X - 14 = 0$ $2X = 12$ $X = 6$

Practice Problem: 12.1

Calculate the oxidation number of S in H_2SO_4.

12.1.3 Recognizing oxidation and reduction reactions

Oxidation reduction reactions are reactions in which electrons are lost by an atom or ion in one reactant and gained by an atom or ion in another reactant. In order to tell whether a redox reaction has occurred or not, we need a way to keep track of electrons and assign oxidation numbers to the atoms or ions involved in a chemical reaction.

In any redox reaction, you can recognize the species oxidized or reduced by noting the change in their oxidation number. A species with an increase in oxidation number is said to be oxidized and the one with decrease in oxidation number is said to be reduced as clear from the following example. In organic reactions, the concept of addition or removal of oxygen or hydrogen can also be helpful in such case.

Example 12.2:

Determine which element is oxidized and which one is reduced in the following reactions.

a) $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$

b) $2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu$

Solution:

a. Zn is oxidized (oxidation number: $0 \rightarrow +2$); H^+ is reduced (Oxidation number $+1 \rightarrow 0$).

b. Al is oxidized (oxidation number: $0 \rightarrow +3$); Cu^{2+} is reduced ($+2 \rightarrow 0$). Thus when oxidation occurs, an element loses electrons and its oxidation number increases (become more positive). When reduction occurs, an element gains electrons and it oxidation number decreases or is reduced (becomes more negative).

(i) Oxidizing Agent

The substance which oxidizes other substances and itself gets reduced during this process is called oxidizing agent. The oxidation number of the oxidizing agent is decreased in the reaction e.g. the oxidation number of Cl_2 in above reaction is decreased from 0 to -1, therefore, Cl_2 is an oxidizing agent.

(ii) Reducing Agent

The substance which reduces other substances and itself gets oxidized during this process is called reducing agent. The oxidation number of the reducing agent is increased e.g. the oxidation number of Na in above reaction is increased from 0 to +1 so it is a reducing agent.

Balancing Oxidation Reduction Equations

A large variety of chemical reactions involve oxidation and reduction processes which are expressed in the form of chemical equations. There are two systematic ways for balancing these equations.

12.1.4 Balancing Redox Equations by Oxidation Number Method

Oxidation and reduction are simultaneous processes; collectively called redox process. If one substance in a reaction is oxidized, it loses electrons and acts as reducing agent, then the other substance, simultaneously, is reduced, gains electrons and acts as oxidizing agent. The number of electron gained and lost must be equal. This principle builds the basis of balancing the redox equation. The following steps are involved in balancing equations by oxidation number method.

i. Write down the skeleton of the unbalanced redox equation.
ii. Write the oxidation numbers over the symbol of the elements whose oxidation numbers change during the reaction.

iii. Identify the oxidizing and reducing agents, which undergo change in their oxidation number.

iv. Indicate the change in oxidation number by means of arrows which show the number of electrons gained or lost.

v. Multiply the formula of the oxidizing and the reducing agents by a number such that the number of electrons lost during oxidation becomes equal to the gain of electrons during reduction.

vi. Balance the rest of the equation by simple inspection.

Example 12.3

Let us balance the following equation by oxidation number method, by using the above mentioned steps.

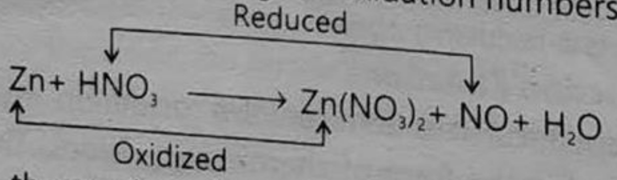
(i) $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO + H_2O$

(ii) Oxidation number of Zn is 0, oxidation number of Zn in $Zn(NO_3)_2$ is +2. Oxidation numbers of Zn increases from 0 to +2, so it is oxidized and is a reducing agent. Oxidation number of N decreases from +5 in HNO_3 to +2 in NO so it is reduced and acts as an oxidizing agent.

(iii) Write the oxidation numbers over the symbols of the elements oxidized and reduced.

$$\overset{0}{Zn} + HN^{+5}O_3 \longrightarrow Zn^{+2}(NO_3)_2 + N^{+2}O + H_2O$$

(iv) Indicate the change in oxidation numbers by means of arrows.



$$Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO + H_2O$$

Hence, the species reduced and oxidized can be written as follows:

a) $Zn^0 \longrightarrow Zn^{2+} + 2e^-$ (Zn oxidized)

b) $HN^{+5}O_3 + 3e^- \longrightarrow N^{2+}O$ (N reduced)

(v) Multiply equation (a) by 3 and (b) by 2, so that the number of electrons gained becomes equal to the number of electrons lost. By this way we get coefficients of different species appeared in equation given in part (i) above which takes the following form

$$3Zn + 2HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + O_2$$

(vi) Add six more NO_3 in the form of HNO_3 to the reactant's side, to balance $6NO_3$ of $Zn(NO_3)_2$ in the products side. Also balance H and O atom by inspection.

$$3Zn + 2HNO_3 + 6HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$$

Now the final balanced equation is:

$3Zn + 8HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$

12.1.5. Balancing the Redox Equations by the Half Reaction Method

This method of balancing is also called the *ion electron method.* No oxidation numbers are assigned in this method. It applies to redox reactions taking place in aqueous medium. The following steps are used for balancing redox equation by this method.

i. Split the equation into two half reactions, one for oxidation and the other for reduction showing only the oxidizing and reducing agents.
ii. Balance number of atoms on both sides of the two half reactions independently. In neutral medium H_2O and H^+ can be added on either side.
iii. In acidic medium the H^+ ion may be used for greater number of oxygen and H_2O can be added to the other side.
iv. Balance the charge by adding electrons (e) to the side deficient in negative charge.
v. Multiply each half reaction by a number chosen so that the total number of electrons lost by the reducing agent equals the number of the electrons gained by the oxidizing agent.
vi. Add the two half reactions resulting from the multiplications. Cancel anything appearing to both sides in the net equation.
vii. Check the final equation by counting the number of atoms and the net charge on either side.

Example 12.4

Balance the following equation of the reaction taking place in acidic medium by ion electron method.

$I^- + NO_2 \longrightarrow I_2 + NO$

i) Split the reaction into two half reactions, one for oxidation and the other for reduction.

a) $I^- \longrightarrow I_2$ (increase in oxidation number shows oxidation)

b) $NO_2 \longrightarrow NO$ (decrease in oxidation number of N shows reduction)

ii) Balance the number of O-atoms on each half reaction by adding H^+ (oxygen excess side) and H_2O to other side. Also multiply I^- by 2 in Equation (a)

a) $2I^- \longrightarrow I_2$

b) $NO_2 + 2H^+ \longrightarrow NO + H_2O$

iii) Balance the charges on both sides of each half reaction by adding electrons to either side.

a) $2I^- \longrightarrow I_2 + 2e^-$

b) $NO_2 + 2H^+ + 2e^- \longrightarrow NO + H_2O$

iv) The total number of electrons lost and gained in the two half reactions are the same. So adding the two half reactions after canceling the electrons gained with the lost, we get a balanced net equation.

a) $2I^- \longrightarrow I_2 + 2e^-$

b) $NO_2 + 2H^+ + 2e^- \longrightarrow NO + H_2O$

Balanced equation $2H^+ + NO_2 + 2I^- \longrightarrow NO + I_2 + H_2O$

12.1.6 Chemistry of Some Important Oxidizing and Reducing Agents

a) Reaction of Oxidizing Agents

Potassium dichromate ($K_2Cr_2O_7$) and $KMnO_4$ (potassium permanganate) are strong oxidizing agents.

1. **Potassium dichromate** ($K_2Cr_2O_7$) is a strong oxidizing agent. In presence of dilute sulphuric acid it acts as a strong oxidizing agent and oxidizes a number of compounds. In all these reactions chromium ion is reduced from +6 to +3 oxidation state.

i) It oxidizes iodide to iodine

$$K_2\overset{+6}{Cr}_2O_7 + 6K\overset{-1}{I} + 7H_2SO_4 \longrightarrow \overset{+3}{Cr}_2(SO_4)_3 + 4K_2SO_4 + 3\overset{0}{I_2} + 7H_2O$$

ii) It oxidizes ferrous salts to ferric salts.

$$K_2\overset{+6}{Cr}_2O_7 + 6\overset{+2}{Fe}SO_4 + 7H_2SO_4 \longrightarrow \overset{+3}{Cr}_2(SO_4)_3 + 3\overset{+3}{Fe}_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

2. **Potassium permanganate ($KMnO_4$)** is a strong oxidizing agent. In presence of dilute sulphuric acid it acts as a strong oxidizing agent and oxidizes a number of compounds.

i) $KMnO_4$ oxidizes KI in the presence of (dil) H_2SO_4 to I_2.

$$2K\overset{+7}{Mn}O_4 + 10K\overset{-1}{I} + 8H_2SO_4 \longrightarrow 2\,\overset{+2}{Mn}SO_4 + 6K_2SO_4 + 5\,\overset{0}{I_2} + 8H_2O$$

ii) $KMnO_4$ oxidizes oxalic acid in the presence of sulphuric acid to CO_2

$$2K\overset{+7}{Mn}O_4 + 5\,(COO)_2H_2 + 3H_2SO_4 \longrightarrow 2\,\overset{+2}{Mn}SO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

b) Reactions of Reducing Agents

H_2S and SO_2 are reducing agents.

1. **Hydrogen sulphide (H_2S)** is reducing agent in acidic medium.

i) It reduces halogens to halogen acids.

$$H_2\overset{-2}{S} + Cl_2 \longrightarrow 2HCl + \overset{0}{S}$$

$$H_2\overset{-2}{S} + Br_2 \longrightarrow 2HBr + \overset{0}{S}$$

ii. It reduces ferric salt to ferrous salt

$$H_2S + 2FeCl_3 \longrightarrow 2FeCl_2 + 2HCl + S$$

2. **Sulphur dioxide (SO_2)** is reducing agent in the acidic medium

i. SO_2 reacts with KIO_3 and reduces it to I_2.

$$2\overset{+1}{K}\overset{+5}{I}O_3 + 5\overset{+4}{S}O_2 + 4H_2O \longrightarrow 2\overset{+1}{K}H\overset{+6}{S}O_4 + 3H_2\overset{+6}{S}O_4 + \overset{0}{I_2}$$

ii. SO_2 reduces $KMnO_4$ in acidic medium.

$$2K\overset{+7}{Mn}O_4 + 5\overset{+4}{S}O_2 + 2H_2O \longrightarrow K_2\overset{+6}{S}O_4 + 2\overset{+2}{Mn}\overset{+6}{S}O_4 + 2H_2\overset{+6}{S}O_4$$

12.2 Electrodes, Electrode Potential and Electrochemical Series

An electrolytic cell is composed of two electrodes suspended in an electrolytic solution. They are connected to a battery. The electrode, by which electrons enter the solution, are connected to the negative terminal of the battery and serves as a cathode, while anode is connected to the positive terminal of the battery where the electrons leave the cell. The electrodes are metallic plates, wires, or rods through which the current enters or leaves the electrolyte in a cell. The positive electrode is called anode and the negative electrode is called cathode in electrolytic cell. The electrolytic solution contains ions produced by the spontaneous dissociation of the dissolved electrolyte. The positive ions, called cations move towards the negative electrode (cathode), whereas, the negative ions which are called anions move towards the positive electrode (anode).

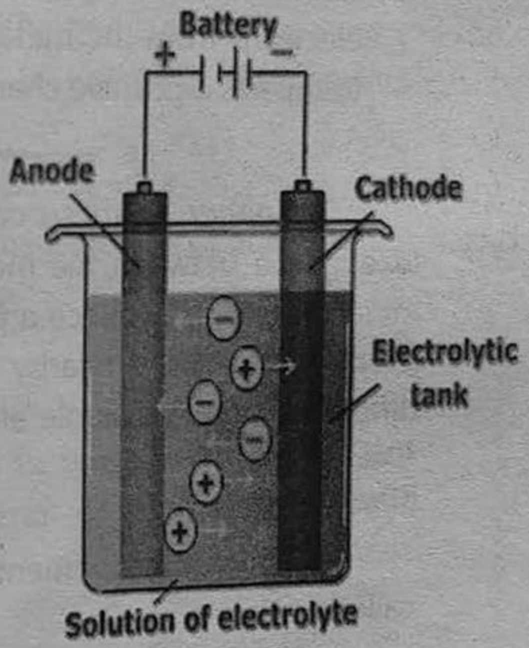


Figure 12.1 Electrolytic Cell

When the current passes through the solution, the anions move towards the anode. They get discharged by giving their electrons to the electrode. The loss of electrons at anode is called oxidation. On the other hand, the cations tend to move towards the cathode. They gain the electrons from the electrode and neutralize their charge. Hence, reduction occurs at cathode. The two half-cell reactions taking place at the two electrodes are as follows:

At anode $2X^{-1} \longrightarrow X_2 + 2e^-$ (oxidation)

At cathode $M^{+2} + 2e^- \longrightarrow M$ (reduction)

Net Reaction $2X^{-1} + M^{+2} \longrightarrow X_2 + M$

In the above reaction two electrons are gained by the metal ion and it is deposited on cathode whereas the same number of electrons are lost in oxidation. The net result is that the number of electrons gained in reduction is equal to the number of electrons lost in oxidation.

Electrode Potential

When a metal strip is placed in a solution of its own ions, there are tw possible tendencies.

(1) The metal atoms may dissolve as positive ions.

$$M \longrightarrow M^+ + e^- \qquad (12.1)$$

In this way, the electrons are deposited on the metal strip and it acquire negative charge, let us call it as an electrode.

(2) Another possibility is that the metal ions present in solution may take u electrons from the metal and get discharged as atoms on the metal surface It imparts a positive charge to the metal plate.

$$M^+ + e^- \longrightarrow M \qquad (12.2)$$

In either of these cases a separation of negative and positive charges takes place between the metal plate and the solution immediately close to the metal surface, and hence a potential difference is set up between the metal plate (electrode) and the nearby solution surrounding the metal plate. This potentia difference is called single electrode potential or simply electrode potential. Thus *the electrode potential of an element is the potential difference between a aqueous solution of its ions and the element when it is in equilibrium with that solution.* Such arrangement of an electrode dipping into a solution of ions is called a *half-cell*.

It is impossible to measure the potential difference between an electrode and the solution making up a half cell. If a high resistant volt meter is used fo this purpose, one probe of the volt meter is connected to the metal electrode and the other probe must be dipped into the solution. The dipped metal probe will act as another half-cell creating its own electrode potential. Thus the voltmeter will read the difference in potential between the two electrodes rathe than the potential of the electrode under investigation. In such case, when it is difficult to measure the absolute value of electrode potential, one electrode mus be arbitrarily assigned a zero value of potential and the value of other electro is measured with reference to this electrode, considered as a standard electrod For this purpose, hydrogen electrode is used as a standard electrode and potential has arbitrarily been assigned a zero value. This is called as *stand hydrogen electrode (SHE)*. The potential of all other electrodes is measured w reference to SHE.

The potential created when an electrode is in contact with one mola solution of its own ions at 298 K at one atmosphere pressure is known a standard electrode potential of the element with reference to the standard hydrogen electrode. It is represented as E°. Now, whenever the electrode potential of an element is to be measured its half-cell is connected with SHE and a voltmeter, connected between them, reads directly the potential of the electrode under investigation since the potential of the SHE is chosen to be zero.

A rod of zinc, for example, will bear an accumulation of negative charges. This is due to the ionization of some of its atoms. The negative charge on the Zn-rod will attract an atmosphere of positively charged zinc ions around the rod to form an electrical double layer as shown in Fig. 12.2. The equilibrium can, therefore, be represented as:

$$Zn_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2e^-$$

The potential of Zn electrode can be measured by connecting this half-cell with the SHE.

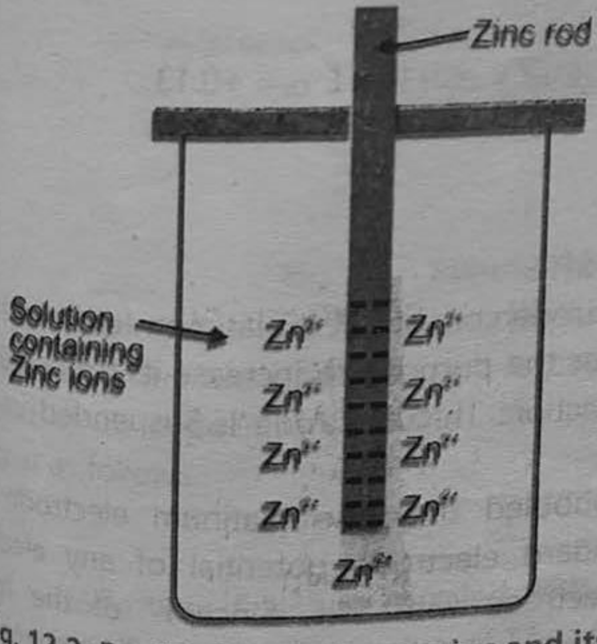


Fig. 12.2: Equilibrium between zinc and its ions in solution

Reading Check

- Differentiate between oxidising agent and reducing agent with examples.
- Define electrodes, electrode potential and oxidation number.
- Name the two types of electrodes and the ions discharged on them.

Cell Reaction and Cell Voltage

Table 12.1 can be used to predict the reaction and voltage of any cell consisting of any two standard electrodes. The net reaction undergoing in a cell is the algebraic sum of the two half reactions taking place at the two electrodes. For instance, the H_2/Cu^{2+} cell reaction can be summed up as follows

$$H_2 + Cu^{2+} \longrightarrow 2H^+ + Cu$$

The cell voltage recorded by a voltmeter is the sum of the two half-cel potentials, one for oxidation and the other for reduction. Hence, the cell potentia can be written as;

$$E^{o}_{cell} = E^{o}_{Red} + E^{o}_{Ox}$$

or $$E^{o}_{Cell} = E^{o}_{cathode} - E^{o}_{anode}$$

Example 12.5

Calculate $E°_{Cell}$ from the following half-cell reactions.

$Zn \rightarrow Zn^{2+} + 2e^{-}$ $E°_{Red} = -0.76V$ or $E°_{Ox} = +0.76V$

$Cu^{2+} + 2e^{-} \rightarrow Cu$ $E°_{Red} = +0.34V$

$E^{o}_{cell} = E^{o}_{Red} + E^{o}_{OX}$

$E^{o}_{Cell} = 0.34 + 0.76 = 1.10\ V$

Example 12.6

Calculate cell potential of a galvanic cell composed of the following two half cells. Write their half-cell reactions.

Pb^{2+}/Pb $E^{o}_{Red} = -0.13V$

Cl_2/Cl^{-} $E^{o}_{Red} = +1.36V$

$Pb \rightarrow Pb^{2+} + 2e^{-}$ $E^{o}_{Red} = -0.13$ or $E^{o}_{Ox} = +0.13$

$Cl_2 + 2e^{-} \rightarrow 2Cl^{-}$ $E^{o}_{Red} = +1.36V$

$E^{o}_{cell} = E^{o}_{red} + E^{o}_{OX}$

$E^{o}_{Cell} = 1.36V + 0.13V = 1.49V$

Standard Hydrogen Electrode, SHE

A standard hydrogen electrode consists of a platinum foil, coated with a layer of finely divided platinum for the purpose to increase its surface area and, hence, to increase the rate of reaction. This electrode is suspended in 1M HC solution at 25°C.

Pure hydrogen gas is bubbled over the platinum electrode at one atmospheric pressure. The standard electrode potential of any electrode is obtained by combining the electrode with SHE. Since E° of the hydrogen electrode is zero in either case i.e. reduction as well as oxidation (as shown below), so the measured potential is the standard electrode potential of the other electrode. When SHE acts as anode, oxidation of hydrogen gas takes place at the surface of the electrode as follows.

$$H_{2(g)} \rightleftharpoons 2H^{+}_{(aq)} + 2e^{-} \qquad E^{o}_{Ox} = 0\ volt$$

Here, E^{o} stands for standard oxidation potential, symbolically written $E^{o}_{(H_2/2H^{+})}$ and when SHE acts as cathode, reduction of hydrogen ions takes pl at the surface of the SHE as follows,

$2H^{+}_{(aq)(1M)} + 2e^{-} \rightleftharpoons H_{2(g)\ (1\ atm)}$ $E^{o}_{Red} = 0$ volt

In this case E^{o}_{Red} shows the standard reduction potential represented as $E^{o}(2H^{+}/H_2)$. In both of these cases the electrode potential of SHE is arbitrarily given the value as z

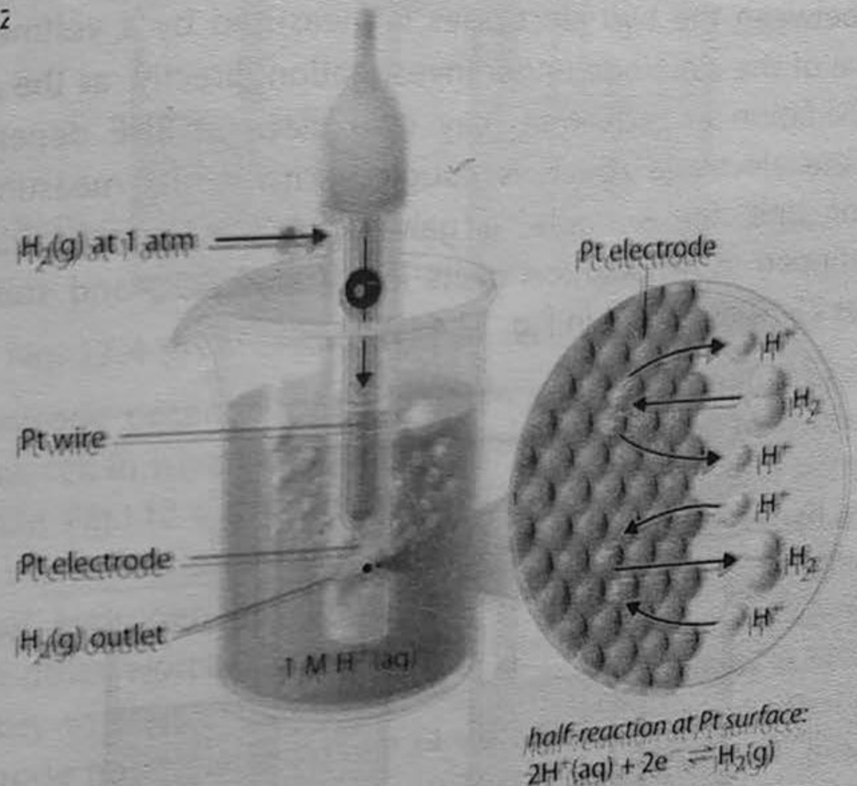


Fig. 12.3 Standard hydrogen electrode

Hydrogen electrode when coupled with the electrode which has positive E^{o}_{Red} value, the electrode will act as cathode and SHE as the anode. e.g. E^{o}_{Red} value of Cu is positive (+ 0.34V), the reaction of H_2/Cu cell will spontaneously occur as follows.

$$H_2 \longrightarrow 2H^{+} + 2e^{-} \quad \text{(oxidation)}$$
$$Cu^{2+} + 2e^{-} \longrightarrow Cu \quad \text{(reduction)}$$

Whereas, if SHE is coupled with Zn electrode then reduction will take place at SHE, because the value of E^{o}_{Red} for Zn is negative as compared to SHE. The two half reactions are as under.

$$Zn \longrightarrow Zn^{2+} + 2e^{-} \quad \text{(oxidation)}$$
$$2H^{+} + 2e^{-} \longrightarrow H_2 \quad \text{(reduction)}$$

Measurement of Electrode Potential

We can use the SHE to measure the potentials of other electrodes. For the measurement of electrode potential the concerned electrode is joined electrically with the standard hydrogen electrode (SHE) and a galvanic cell is established. The two solutions are separated by a porous partition or a salt bridge containing a concentrated solution of potassium chloride. The salt bridge is used to provide a highly conducting path between the two electrolytic solutions. The potential difference between the two electrodes is measured by a voltmeter which gives the potential of the electrode under investigation directly as the potential of SHE is zero. Oxidation or reduction may take place at SHE depending upon the nature of the electrode which is coupled with it. To measure the electrode potential of zinc, for example, a galvanic cell is established between zinc electrode dipped in 1M solution of its ions (as $ZnSO_4$) and standard hydrogen electrode at 25 °C as shown in Fig. 12.4 (a).

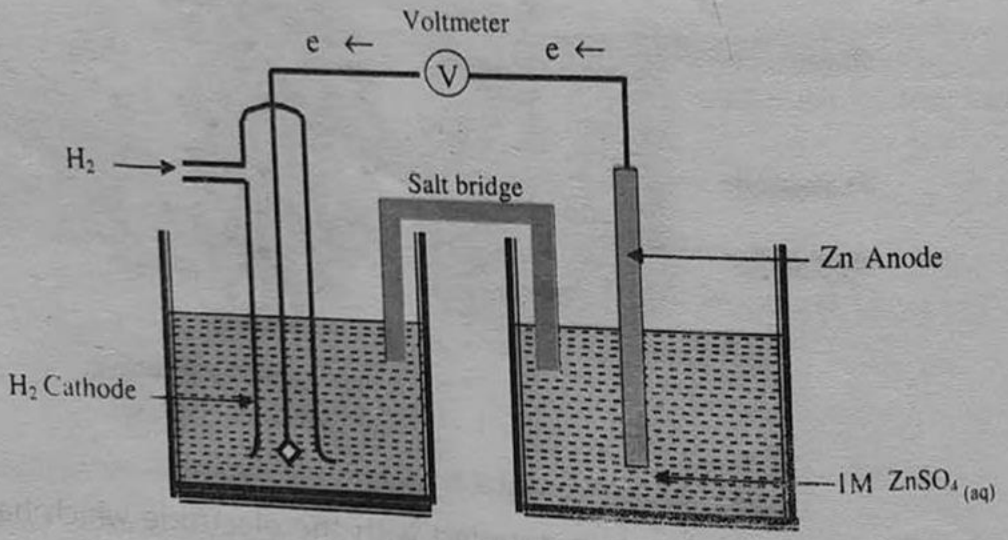


Fig.12.4(a) Measurement of electrode potential of Zn

Under the standard conditions, the voltmeter reads 0.76 volts and the deflection of the voltmeter needle is in such a direction as to indicate that zinc has a greater tendency to give off electrons than hydrogen. In other words, the half reaction

$Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$ has greater tendency to occur than $H_{2(g)} \rightarrow 2H^+{}_{(aq)} + 2e^-$ by 0.76 volts. The standard electrode potential of zinc is, therefore, 0.76 volts. It is called oxidation potential of Zn and is given positive sign. The reduction potential of Zn-electrode is -0.76 volt. The electrode reactions are shown as follows.

At anode $Zn_{(s)} \longrightarrow Zn^{2+}{}_{(aq)} + 2e^-$ (oxidation)

At cathode $2H^+{}_{(aq)} + 2e^- \longrightarrow H_{2(g)}$ (reduction)

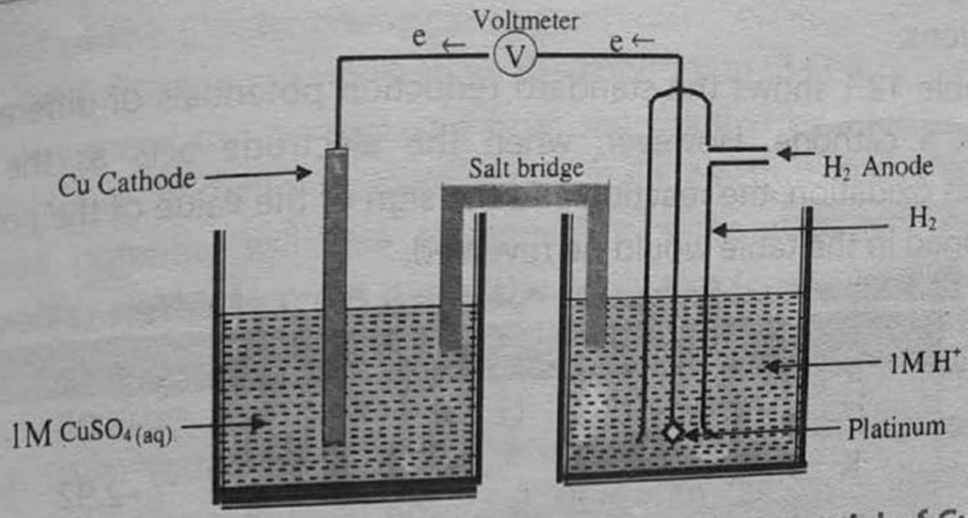


Fig. 12.4 (b) Measurement of electrode potential of Cu

The electrode potential of copper can also be measured using the same type of galvanic cell in which copper is an electrode dipped in 1M solution of its ions (say $CuSO_4$) Fig. 12.4 (b). Under standard conditions, the voltmeter reads 0.34 volts and the deflection f the needle of the voltmeter is in such a direction as to indicate that hydrogen has a greater tendency to give off electrons than copper has. In other words, the half reaction $H_{2(g)} \longrightarrow 2H^{+}_{(aq)} + 2e^{-}$ has a greater tendency to occur than $Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^{-}$ by 0.34 volt. So the standard electrode potential of Cu is 0.34 volts. It is called reduction potential of Cu. When the sign is reversed, then the -0.34 V is called oxidation potential of Cu electrode. The reactions taking place at the two electrodes are shown as follows.

At anode $H_{2(g)} \longrightarrow 2H^{+}_{(aq)} + 2e^{-}$ (oxidation)

At cathode $Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)}$ (reduction)

Electrochemical Series

Every element has its own tendency to give or take electrons. This tendency has been represented in terms of their oxidation or reduction potentials, respectively. The standard electrode potentials of a large number of elements have been measured using standard hydrogen electrode (SHE) as the reference electrode. These elements can be arranged in increasing order of the reduction potential. The arrangement of elements in order of increasing reduction potential values is called electrochemical series (E.C.S) or activity series. According to the recommendations of IUPAC these potentials are listed as *standard reduction potentials* (E^{o}_{Red})in Table 12.1.The standard oxidation potential, on the other hand, can be determined just by reversing the sign of the standard reduction potential without changing the numerical value. The voltage created by a cell is actually the difference between the reduction potentials of the two half reactions.

Table 12.1 shows the standard reduction potentials of different elements, acting as a cathode. However, when the electrode acts as the anode and undergoes oxidation, the reaction and the sign of the value of the potential which is mentioned in the table would be reversed.

Table 12.1:Standarad Reduction Potentials (E°_{Red}) of different Elements

Element	Half Cell Reduction Reaction	E° (Volts)
Li	$Li^+ + e^- \rightleftharpoons Li$	-3.05
K	$K^+ + e^- \rightleftharpoons$	-2.92
Ba	$Ba^{2+} + 2e^- \rightleftharpoons Ba$	-2.90
Ca	$Ca^{2+} + 2e^- \rightleftharpoons Ca$	-2.76
Na	$Na^+ + e^- \rightleftharpoons Na$	-2.71
Mg	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.38
Al	$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.67
Mn	$Mn^{+2} + 2e^- \rightleftharpoons Mn$	-1.03
Zn	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76
Cr	$Cr^{3+} + 3e^- \rightleftharpoons Cr$	-0.74
Fe	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44
Ni	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	-0.25
Pb	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	-0.13
H_2	$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
Cu	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
I_2	$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
Fe	$Fe^{3+} + 3e^- \rightleftharpoons Fe$	+0.77
Ag	$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
Hg	$Hg^{2+} + 2e^- \rightleftharpoons Hg$	+0.09
Br_2	$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.08
Cl_2	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
Au	$Au^{3+} + 3e^- \rightleftharpoons Au$	+1.50
F_2	$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87

Features of the Electrochemical series (ECS)

The following examples show the application of ECS.

Any metal can be replaced from salt solution by another metal. Element having higher reduction potential will gain electron and that having lower reduction potential will lose electron. The same statement can be given in another way as the element placed higher in the series can give electron to the element below it in the ECS and replace it from its salt solution. For example, Zn displaces Cu from $CuSO_4$ because Zn (E°=-0.76V) is placed higher in the series and has lower reduction potential, while Cu (E°=+0.34V) is placed lower in the series with higher reduction potential. Hence, Zn can easily displace Cu from its solution.

$$Zn_{(s)} + CuSO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + Cu_{(s)}$$

Or $$Zn_{(s)} + Cu^{2+}{}_{(aq)} \longrightarrow Zn^{2+}{}_{(aq)} + Cu_{(s)}$$

Similarly, Cu metal is oxidized by silver as Cu is higher in ECS (lower reduction potential) and silver (E°=+0.80V) is lower in the series (higher reduction potential)

$$Cu_{(s)} + 2Ag_{(aq)} \longrightarrow Cu^{2+}{}_{(aq)} + 2Ag_{(s)}$$

Moreover, if two metals are made the electrodes a Galvanic cell, the metal with lower reduction potential will act as anode and the one with the higher reduction potential as cathode

12.3 Types of Electrochemical Cells

A device in which interconversion of electrical and chemical energies takes place, is called an electrochemical cell. Electrochemical cells are of two types.

1. Electrolytic Cell

In electrolytic cells, the electrical energy from an external source is used to bring about a chemical change within the cell. Electrolytic purification of metals, electroplating and charging of batteries are application of electrolytic cells.

2. Voltaic or Galvanic Cell

It is a device in which chemical energy is converted into electrical energy. For example, dry cells and lead storage batteries are galvanic cells.

12.3.1 Electrolytic Cell

It is a device in which a non-spontaneous chemical reaction is carried out by passing electric current from outside. The electrolytic cell consists of a vessel containing electrolyte in which two metallic plates acting as electrodes, are suspended. The electric current enters and leaves the cell through these electrodes. The electrode connected to the negative terminal of the battery is called cathode while the other one connected to the positive terminal is anode.

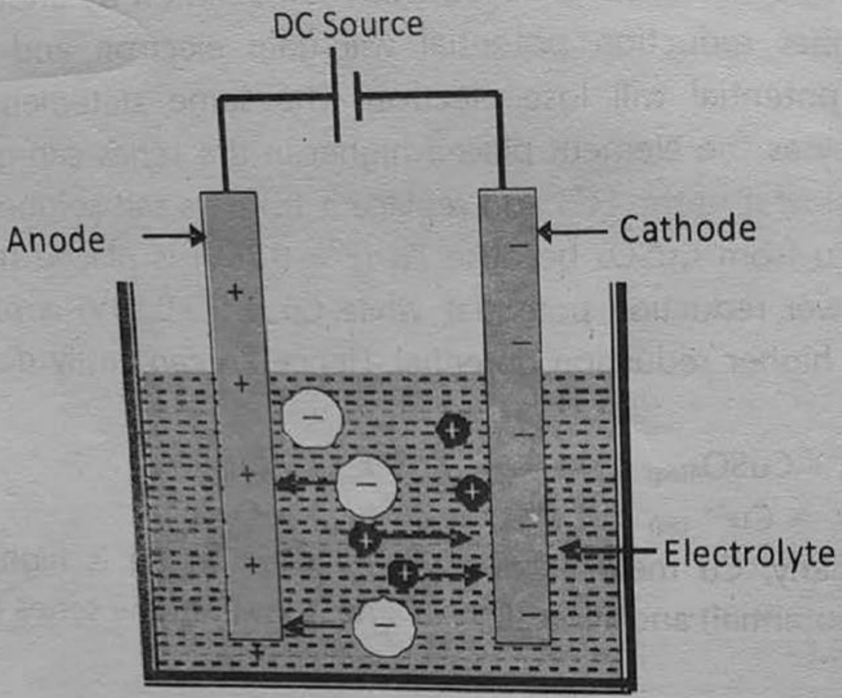


Figure 12.5: Electrolytic cell

When electric current is passed through the electrolytic solution, its ions move towards the respective electrodes. The anions liberate electrons at the anode and are oxidized. These electrons pass through the outer circuit to the cathode. The cations which surround the cathode, consume those electrons, get reduced and deposited or liberated at the cathode. Remember that the number of electrons lost at the anode is always equal to the number of electrons gained at the cathode.

Self-Assessment

1. Differentiate between oxidation and reduction potential with an example.
2. How reduction potential value effect the position of elements in the electrochemical series.

12.3.2 Electrolysis of Aqueous NaCl

Caustic soda, NaOH is very important industrial chemical, manufactured on a large scale by the electrolysis of aqueous solution of NaCl. The electrolysis is carried out in a cell called Nelson's cell (Fig. 12.6). It is an oblong steel tank containing a concentrated aqueous solution of NaCl. The graphite anode is suspended in the solution. Cathode is made of a sheet of perforated steel. When connected to the battery, the half reactions taking place at the electrodes are as follows.

$$2NaCl_{(s)} \longrightarrow 2Na^{+}_{(aq)} + 2Cl^{-}_{(aq)}$$

At anode $2Cl^{-} \longrightarrow Cl_2 + 2e^{-}$ (oxidation)

At cathode $2H_2O + 2e^{-} \longrightarrow H_2 + 2OH^{-}$ (reduction)

Overall reaction $2NaCl_{(s)} + 2H_2O \longrightarrow 2Na^{+} + H_2 + Cl_2 + 2OH^{-}$

$$2Na^{+} + 2OH^{-} \longrightarrow 2NaOH$$

Cl_2 is released at anode and H_2 at cathode. NaOH is collected at the bottom of the cell.

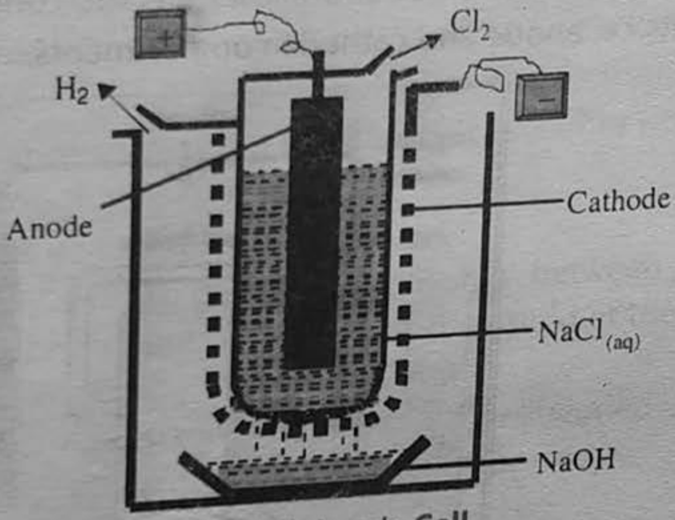


Figure 12.6 Nelson's Cell

Advantages of the Electrolytic Cell

1. Charging of the lead storage batteries is done electrolytically by passing the current through the discharged battery so that the reactions are reversed and the battery is recharged.
2. Various types of electrolytic cells are employed on industrial scale for the manufacture/extraction of industrially important metals and gases e.g. manufacture of NaOH, Na, Mg, Al, Cl_2 etc.
3. Electrolytic cells can be used for the purification of some important metal like Cu etc.
4. Copper, silver, chrome, nickel and tin plating is done by various types of electrolytic cells, for the purpose of protection, beauty and repair of the metal.

12.3.3 Voltaic Cell

In the voltaic cell a spontaneous oxidation-reduction reaction occurs and electrical current is produced. It consists of two half cells externally connected with a metallic wire acting as a conductor. At each half-cell one half of the total cell reaction takes place. At one electrode electrons enter resulting in reduction reaction while at the other they leave the solution and oxidation takes place. A typical example of the voltaic cell is that of a Daniell cell.

Daniell Cell:

As you have studied in your ninth grade, this cell has a Zn electrode dipped into 1M $ZnSO_4$ solution and a Cu electrode immersed in a 1M solution of Cu^{2+} ions. These two half cells are externally connected through a metallic wire while internally they are connected by a salt bridge. The salt bridge contains an aqueous KCl solution in a gel and allows electric connectivity between the two compartments i.e. anode and cathode compartments.

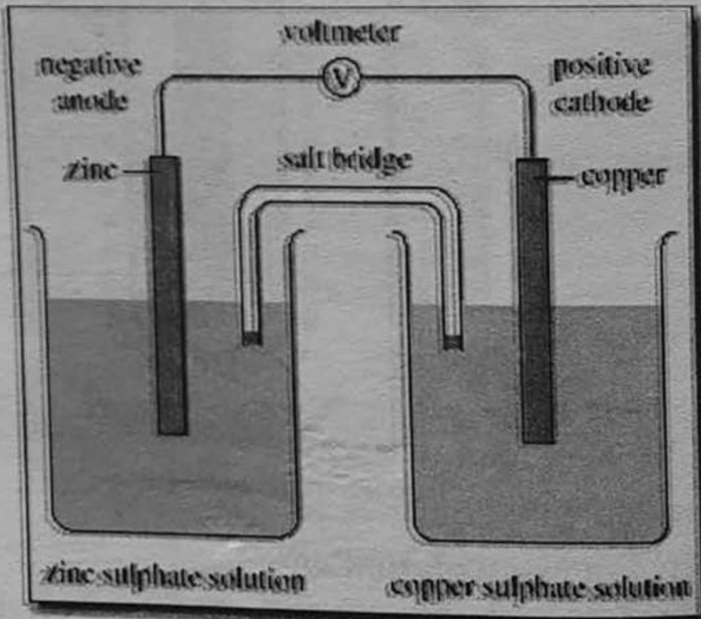


Fig: 12.7 Daniell Cell

Zn tends to lose electrons more readily than Cu giving its electrons to the electrode at the anode and get oxidized. Electrons flow from the Zn electrode to the Cu electrode through external circuit. The Cu^{2+} ions, surrounding the cathode, pick up the electrons and get deposited as neutral metal at the copper cathode where reduction of Cu^{+2} takes place. The following half reactions occur at the electrodes.

At anode $Zn \longrightarrow Zn^{2+} + 2e^-$ $E^\circ_{Ox} = +0.76V$

At cathode $Cu^{2+} + 2e^- \longrightarrow Cu$ $E^\circ_{Red} = +0.34V$

Net reaction $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$ $E^\circ_{Cell} = 1.10V$

The cell is represented as follows,

$Zn_{(s)}/Zn^{2+}_{(aq)}(1M)//\ Cu^{2+}_{(aq)}(1M)/Cu_{(s)}$

Tidbit

Some Electrical Terms

A *Coulomb* is the SI unit for quantity of electricity, it is defined as the quantity of electric charge carried by a current of on ampere flowing through a wire for one second. 1 Coulomb =1 ampere x1 sec or 1C=1Ax1s.

Ampere: It is basic SI unit used for measuring the rate of electron flow or electric current in an electric conductor. One ampere of current represents one coulomb of electric charge (carried by 6.24×10^{18} electrons) moving through a specific point in one second. 1 Ampere= 1Coulomb/second.

Volt: It is the measure of how strongly an electric current is sent around an electric circuit. It is unit of electric potential or electromotive force. A potential of one volt appears across a resistance of one ohm when a current of one ampere flows through that resistance. $V = IR$

★ Faraday's Laws of Electrolysis

Michael Faraday (1813) gave a relationship between the quantity of electricity passed and the amount of substances deposited at the electrode.

Faraday's First Law:

The amount of any substance (W) deposited or liberated at an electrode is directly proportional to the quantity of electricity (Q) passed.

$$W \propto Q$$

Or

$$W=ZQ \qquad (12.3)$$

Where, W is the mass in gram, Q is amount of charge in Coulombs and Z is the proportionality constant. Z is called the *electrochemical equivalent*. When Q=1C then Eq.(12.3) becomes

$$W=Z \qquad (12.4)$$

Here with the help of Eq. (12.4) we can now define the electrochemical equivalent as the mass of substance liberated when one Coulomb electricity is passed through the electrolyte solution.

Moreover, amount of charge, Q = I t where, I is current in amperes and t is time in seconds. Thus, we can also write Eq.(12.3) as

$$W=ZIt \qquad (12.5)$$

Faraday's Second Law

It states that, 'if the same amount of electricity is passed through the solutions of different electrolytes, the amounts of different substances deposited are in the ratio of their chemical equivalents. Or the masses of different substances liberated for the same quantity of electric charge during the electrolysis are proportional to their equivalent masses. Suppose a certa amount of current passing through the dil. $CuSO_4$ and dil. $AgNO_3$ solutions f the same interval of time, then, we will find that the ratio of the masses liberated silver and copper is 107.88/31.54 because equivalent mass of silver 107.88 and that of copper is 31.548.

Thus $W \propto$ Equivalent mass (e)

Also from the Faradays first law

$W \propto Q$ or $W \propto It$

Combining above two equations we get $W \propto Ite$

Introducing the proportionality constant I/F, we get.

$$W = \frac{1}{F} Ite \qquad (12.6)$$

Where "F" is called Faraday's constant which is equal to 965 Coulomb/mol.

Faraday's second law can also be derived mathematically from equati (12.6). It can be concluded from this equation that for a fixed amount of electric passed for a fixed time the term It/F assumes a fixed value and under t condition $W \propto e$ which, as the law states that the amount of substance, liberated, is directly proportional to the equivalent mass 'e'.

Example 12.7

A certain amount of current is passed through $AgNO_3$ solution for th hours. The net amount of Ag deposited was found to be 60.8 g. Calculate current when gram equivalents (e) of Ag is 107.8.

Solution

Time (t)=3 hours = 3 x 60 x 60 s

W (amount of Ag)= 60.8g

Gram equivalent mass of Ag (e)=107.8g, $F=96500\ C\ mol^{-1}$

$$W = \frac{1}{F} Ite$$

$$I = \frac{WF}{te}$$

$$I = \frac{60.8g \times 96500 c/mol}{3 \times 60 \times 60s \times 107.8g/mol} = 5.04A$$

12.3.4 Batteries

There are four major types of batteries.

1 **Primary batteries:**

These batteries are not reversible and once discharged cannot be recharged, e.g. dry cell.

2 **Secondary batteries:**

They are reversible and can be recharged, e.g. Lead storage battery.

3 **Solar batteries:**

They are photoelectrical cells and generate energy.

4 **Fuel batteries:**

They are the super batteries and have high charge density.

(i) Primary Batteries

Dry Cell

As you have studied in your previous class, the container of the cell is made of Zn, which acts as an anode. The container is lined with a porous paper, which separates anode from inside material. A graphite rod in the centre of the cell acts as cathode. Electrolyte is a moist mixture of NH_4Cl, MnO_2, $ZnCl_2$ and powdered carbon. The dry cell is sealed to prevent the evaporation of moisture. When the dry cell delivers current, Zn oxidizes to Zn^{2+} ions and leaves electrons on the Zn container. The electrons move through outer circuit to the graphite cathode, where NH_4^+ ions pick up the electrons and release NH_3 at the cathode. NH_3 produced at the cathode reacts with Zn^{2+} ions to form a complex ion. The redox reactions taking place at the two electrodes are as follows.

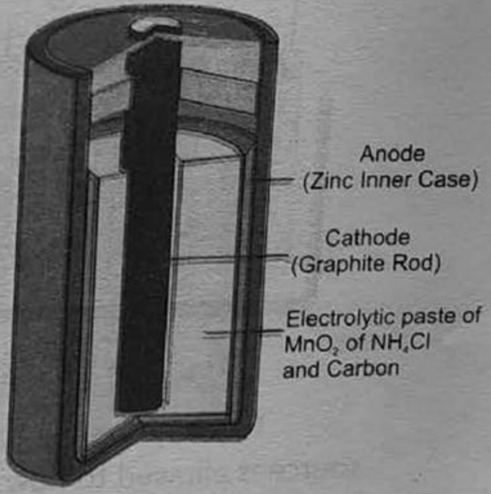


Fig. 12.8: The Dry Cell

At anode (Oxidation) $Zn \longrightarrow Zn^{2+} + 2e^-$

At cathode (Reduction) $2MnO_2 + 2NH^{+}_{4} + 2e^- \longrightarrow Mn_2O_3 + 2NH_3 + H_2O$

Net reaction $Zn + 2MnO_2 + 2NH^{+}_{4} \longrightarrow Zn^{2+} + Mn_2O_3 + 2NH_3 + H_2O$

This is irreversible because Zn and NH^{+}_{4} are consumed during the process of working and cannot be reversed back to their initial states by the application of the external electrical potential.

(ii) Secondary Batteries

The Lead Storage Battery

The lead storage battery commonly used in automobiles and generators. It is a combination of six voltaic cells of the same kind, arranged in series with the anode of one cell connected to the cathode of the other. The anodes are Pb plates while the cathodes are made of lead dioxide (PbO_2). Both the anode and cathode are immersed in an aqueous solution of sulfuric acid, which acts as the electrolyte (Fig.12.9). When the anodes and cathodes are connected, the current flows and the following reactions take place.

At Anode $Pb(s) + H_2SO_4(aq) \longrightarrow PbSO_4(s) + 2H^+ + 2e^-$

At Cathode $PbO_2(s) + H_2SO_4(aq) + 2H^+ + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$

Net Reaction $Pb(s) + PbO_2(s) + 2H_2SO_4 \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

When the cell works insoluble $PbSO_4$ goes on depositing on both the electrodes, H_2SO_4 is consumed and water is formed.

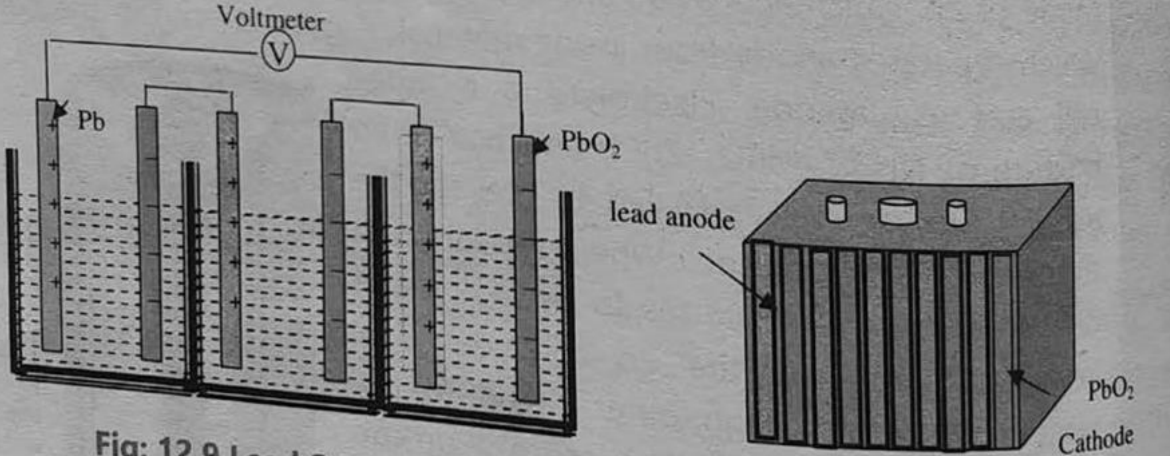


Fig: 12.9 Lead Storage Battery (internal and external)

It is a reversible battery. If, during recharging, the current from an external source is allowed to flow in the opposite direction all the above chemical changes are reversed and converts lead sulphate back to lead and lead dioxide on the respective electrodes. During recharging the negative electrode is connected to the negative terminal of the direct current (DC) source and positive electrode to the positive terminal of DC source. The reactions are;

At negative electrode: $PbSO_{4(s)} + 2e^- \rightarrow Pb_{(s)} + SO_4^{2-}$ (Reduction)

At positive electrode: $PbSO_{4(s)} + 2H_2O \rightarrow PbO_{2(s)} + 4H^+ + SO_4^{2-} + 2e^-$ (Oxidation)

Net reaction: $2PbSO_{4(s)} + 2H_2O \rightarrow Pb_{(s)} + PbO_{2(s)} + 2SO_4^{2-} + 4H^+$

Thus, Pb, PbO_2 and H_2SO_4 are reformed and the battery is again ready for generating useful electricity.

(iii) Fuel Cells

A fuel cell is a primary cell of special type which converts chemical energy of fuel directly to electrical energy. The chemicals that produce electricity are constantly replaced as soon as they are consumed. Fuel cells differ from common batteries such that in these, electricity is produced from chemical fuels fed to them as needed, so that their operating life is unlimited. One of the most important fuel cell is the hydrogen/oxygen fuel cell. In this cell the negative terminal (anode) is porous graphite coated with nickel and the positive terminal (cathode) is porous graphite coated with nickel and nickel oxide. The nickel and nickel oxide act as catalyst on the surface of the terminal. Nickel can be replaced by platinum.

Hydrogen is passed into the negative compartment of the cell and oxygen into the positive compartment. Under pressure the gases diffuse through the porous graphite terminals into the warm potassium hydroxide solution located between the terminals. At the anode, hydrogen reacts with hydroxide ions from the warm $KOH_{(aq)}$ and electrons are released. Thus, the reaction

At anode $2H_{2(g)} + 4OH^-_{(aq)} \longrightarrow 4H_2O_{(l)} + 4e^-$ (Oxidation)

Or $2H_2 \longrightarrow 4H^+ + 4e^-$

At cathode oxygen and water take electron to form hydroxide ions.

At cathode $O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)}$ (Reduction)

Adding above two equations we get the overall reaction as follows:

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

Fuel cells based on hydrogen and oxygen has a significant future as a power source for electric automobiles and in space vehicles. The cell is shown in Fig. 12.10. Electrodes are hollow tubes made of porous compressed carbon impregnated with platinum or nickel (increased surface area acts as a catalyst). The electrolyte is KOH. Hydrogen is oxidized at the anode giving electrons to the outer circuit while the electrons are accepted at the cathode where reduction occurs and in this way current flows. The cell products can be regenerated externally into fuel for returning to the cell.

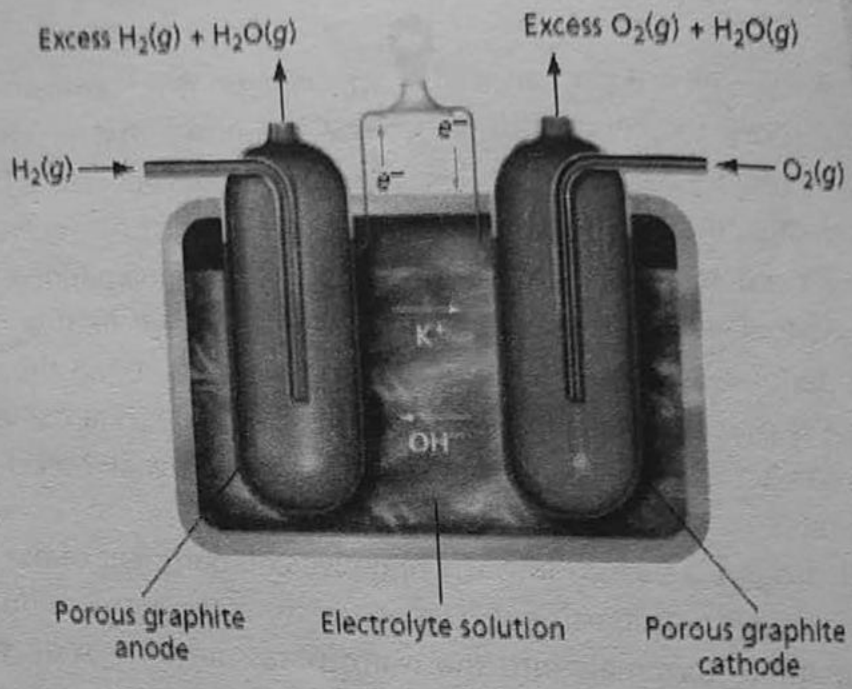


Figure 12.10: Hydrogen-Oxygen Fuel Cell

Fuel cells are very efficient and convert about 75% of the fuel into electricity. The major drawback of the fuels cells is that they are very costly. The gases must be of very high purity, otherwise even a trace of impurity may poison the platinum which severely degrades its efficiency.

12.3.5 Corrosion and its Prevention

The slow and continuous eating away of any metal by the action of environment is called corrosion e.g. pure iron is silvery white but when exposed to moist air its surface is corroded and converted to a reddish brown mass known as rust. The corrosion is not limited to iron only. Similarly, aluminium is most commonly used metal in house-hold things and to make airplanes. It has the tendency to react with atmospheric oxygen and form a layer of aluminium oxide (Al_2O_3). This layer protects it from further corrosion. Copper also corrode slowly and forms copper carbonate ($CuCO_3$) as a green layer on the copper surface which protects the metal from further corrosion. Similarly, silver utensils whe come into contact with the foodstuffs develop a layer of silver sulphide (Ag The rust that forms on the surface of iron is too porous to protect the underlyi metal.

Chemically, rust of iron is hydrated iron (III) oxide. For rust formation the must be a thin film of water on the surface of the metal and air surrounding

The impurities or the strained portions are responsible for the formation of sma electrolytic cells, with anode of pure iron and cathode of impure or straine portions as shown in the diagram. Iron is oxidized at the anode producing Fe (I ions and electrons. It moves along the surface of the metal to cathode where i reacts with water and oxygen to form hydroxyl ions.

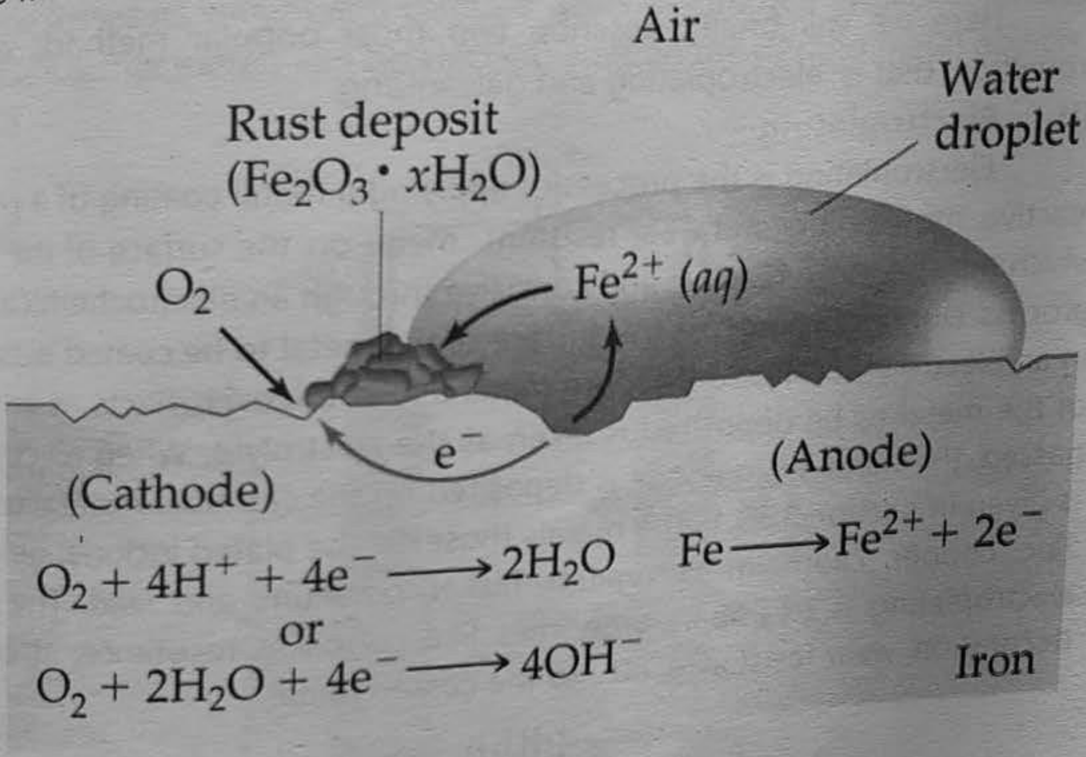


Fig. 12.11 Corrosion of iron piece

Anode 2Fe ¾¾® 2Fe^{+2}+4e$^-$

Cathode $2H_2O+O_2+4e^-$ ¾¾® 4OH$^-$

Fe (II) hydroxide, is further oxidized by atmospheric oxygen to form hydrated Fe(III) oxide, (rust).

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$
$$Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3$$

The rust of iron is soft and porous in nature and therefore, rusting cannot be prevented from further deeper atmospheric action. The result is that once corrosion starts it continues until the whole iron piece is rusted.

Few methods for preventing rust formation are as under.

1. Coating the metal surface with paint, grease etc.
2. Coating the metal with sacrificial metal such as zinc (galvanizing) or tin (tinning)

3. Dipping the iron into a phosphate bath (orthophososphoric acid with zinc & manganese phosphates)
4. Alloying the metal – steel formation
5. Electroplating with nickel or chromium
6. Cathodic protection

Here we will briefly describe two most popular methods of corrosion protection, that is, electroplating and galvanizing.

(i) Electroplating

Electroplating is the process of applying a metal coating of a precious, less reactive, more stable and wear resistant metal on the surface of the other metal which may be more reactive and corrosive through an electrochemical deposition process. During this process, the surface of the metal to be coated acts as cathode in an electrolytic cell and the pure metal that is to cover it acts as an anode. Salt of the metal to be deposited is taken as the electrolyte. When electric current is passed, the metal from anode is deposited on the cathode. A detailed discussion is given in section 12.9.1. The metals those can be plated include, gold, silver, tin, zinc, copper, cadmium, chromium, nickel, platinum, and lead. The purpose of electroplating is to impart properties like corrosion resistance, strength, shine, decoration, wear resistance, etc., to the coated metal.

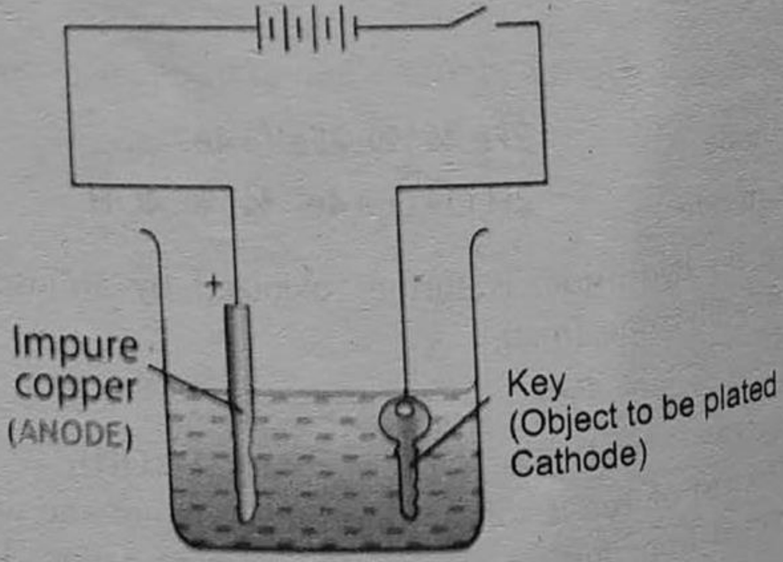


Fig: 12.12 Electroplating

(ii) Galvanizing

A typical electroplating cell in which an iron object is being electroplate with zinc. This process is also called as galvanizing. The anode is zinc metal pie and cathode is the object that is to be coated by zinc layer. The electrolyte is th zinc salt, like zinc sulphate. When the battery is turned on, zinc metal from the anode surface oxidizes and is dissolved as Zn^{2+} ions and at the same time zinc ions from the electrolyte solution are reduced at the cathode surface as zinc metal. Thus, the concentration of zinc in the solution remains the same and zinc electrode losses its weight and cathode gains weight due to deposition of zinc on it. Similarly, other metals can be electroplated on the desired metal objects.

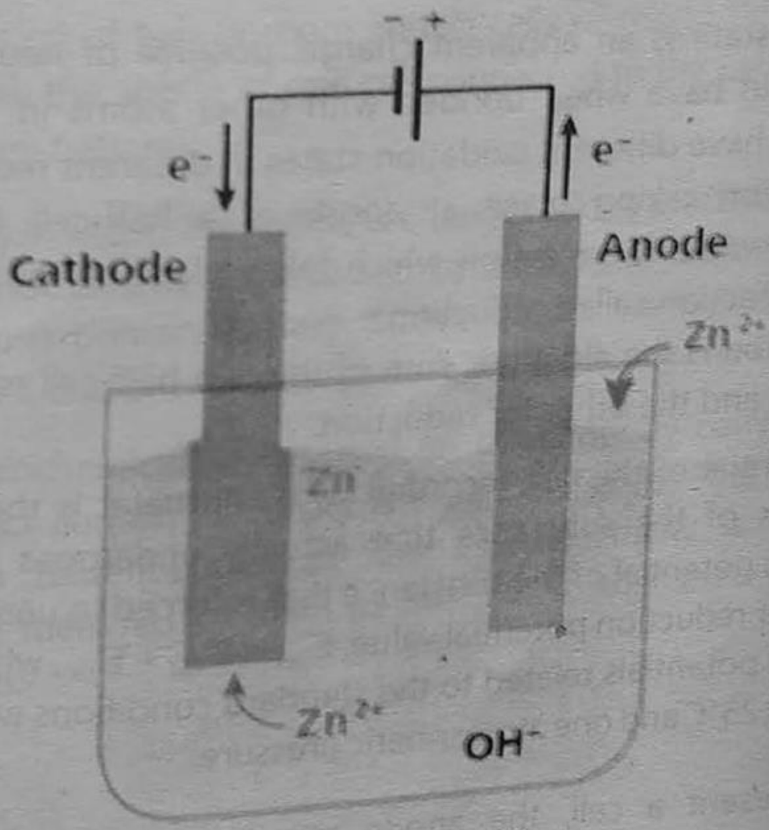


Fig. 12.13 Galvanizing

Self-Assessment

1. Define electroplating.
2. Explain three ways for prevention of corrosion.
3. Name the major types of batteries.
4. Give few advantages of the electrolytic cell.

KEY POINTS

- Loss of electrons is oxidation. There is an increase in oxidation number of the element oxidized.
- Gain of electrons is reduction. There is a decrease in oxidation number of the element reduced.
- Oxidation state is an apparent charge, positive or negative, which an atom would have when bonded with other atoms in a molecule. An atom may have different oxidation states in different molecules.
- The reaction taking place at anode is a half-cell reaction called, oxidation, while the reaction which takes place at cathode is another half-cell reaction called reduction.
- Cell reaction is the algebraic sum of the two half-cell reactions one for oxidation and the other for reduction.
- The potential of the cell recorded by a voltmeter is the sum of reduction potentials of the substance that actually undergoes reduction and the oxidation potential of the substance that is forced to undergo oxidation due to smaller reduction potential value. $E^\circ_{cell} = E^\circ_{Red} + E^\circ_{OX}$, where, E° denotes the standard potentials related to the standard conditions which is 1 M solution of ions at 25°C and one atmospheric pressure.
- To represent a cell, the anode at which oxidation takes place is represented at the left hand. Cathode is represented on the right hand. The ions of the two half cells are written in between separated by a double line which represents a salt-bridge. For example, the Daniel cell is represented as follows

$$Zn/Zn^{2+}\ (1M)\ //\ Cu^{2+}\ (IM)/Cu$$

- Electroplating is a process by which one metal is deposited over the other by electrolysis. The metallic article to be electroplated is made cathode and a sheet of pure metal to be deposited is made anode in a tank. Salt of the metal to be deposited acts as the electrolyte. When electric current is passed, the metal from anode is deposited on the cathode.

- The electrode potential of an electrode in contact with a solution of its ions of unit activity at 25°C and one atmospheric pressure, when measured relative to the standard hydrogen electrode is termed as standard electrode potential.
- An electrochemical device that generates electric current by carrying out spontaneous chemical reactions is called a battery. It is a combination of two or more voltaic cells of the same kind, arranged in series with the anode of one cell connected to the cathode of the other (secondary battery).
- A battery in which, the chemical changes taking place during working of a cell cannot exactly be reversed by passing a current in the opposite direction is primary battery. Such cells are irreversible and cannot be recharged, and once discharged are discarded e. g. dry cells.
- An electrochemical device used for continuously converting chemicals into direct current electricity is called fuel cells. Fuel cells differ from common batteries that in fuel cells electricity is produced from chemical fuels fed to them as needed, so that their operating life is unlimited.

EXERCISE

Choose the correct option.

1. Weak electrolyte in solution is
   a) completely ionized b) slightly ionized
   c) never ionized d) destroyed
2. Which one of the following is a strong electrolyte in solution?
   a) Ammonium hydroxide b) Carbonic acid
   c) Potassium iodide d) Acetic acid
3. In electrolytic cell the cathode has a charge
   a) Positive b) Negative
   c) Neutral d) Zero
4. The oxidation number of Cl in $HClO_3$ is
   a) -I b) + 1
   c) + 3 d) + 5
5. The oxidation number of magnesium in $MgCO_3$ is
   a) +3 b) +2
   c) +1 d) -I
6. Which one of the following is a reduction reaction
   a) $Br_2 \rightarrow 2Br^-$ b) $Fe^{2+} \rightarrow Fe^{3+}$
   c) $Zn \rightarrow Zn^{2+}$ d) $Sn^{2+} \rightarrow Sn^{4+}$
7. A cell in which a non-spontaneous redox reaction is carried out by passing an electric current is a/an
   a) Galvanic cell b) Voltaic cell
   c) Daniell cell d) Electrolytic cell
8. Zinc rod acts as anode in the Daniell cell but acts as cathode when coupled with aluminum electrode, this is because the standard reduction potential of
   a) Zn>Al b) Zn < Al
   c) Zn=Al d) Zn=0
9. Electrolysis is a process in which the cations and anions liberated from electrolyte are
   a) hydrated b) hydrolyzed
   c) charged d) discharged
10. A cell which produces electric current by a redox reaction is called a/an
   a) Voltaic cell b) Electrolytic cell
   c) Half-cell d) Standard cell

11. The lead storage battery is a/an
    - a) Daniell cell
    - b) Voltaic cell
    - c) Dry cell
    - d) Electrolytic cell
12. The electrode potential of the standard hydrogen electrode is chosen as
    - a) 0 V
    - b) 1V
    - c) -1 V
    - d) 2V
13. A cathode has the reduction potential
    - a) Less than the anode
    - b) More than the anode
    - c) same as that of anode.
    - d) zero

Short Questions

1. What is the oxidation number of N in N_2O, NO_2, N_2O_3, HNO_3, and NH_4^+.
2. Na^+ is an oxidizing but Na is a reducing agent, why?
3. The lead storage battery is rechargeable. Why?
4. Why a solution of sugar is non-conductor but that of table salt is a good conductor of electricity?
5. NaCl is non-conductor in the solid state but is a good conductor in molten form. Why?
6. During electrolysis of fused NaCl, sodium metal is collected at cathode and not at anode, why?
7. SHE acts as anode with Cu electrode but acts as cathode when connected to Zn electrode.
8. In electroplating, the article to be plated is made cathode, why?

Numerical

1. Balance the following equation by Oxidation Number method

i. $KMnO_4 + H_2S + H_2SO_4 \longrightarrow KHSO_4 + MnSO_4 + S + H_2O$

ii. $Fe + V_2O_3 \longrightarrow Fe_2O_3 + VO$

iii. $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + H_2O$

iv. $Mg + HCl \longrightarrow MgCl_2 + H_2$

v. $Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$

vi. $KMnO_4 + KNO_2 + H_2SO_4 \longrightarrow MnSO_4 + KNO_3 + K_2SO_4 + H_2O$

2. Balance the following redox equations by the half reaction method

i. $Sn^{2+} + Fe^{3+} \longrightarrow Sn^{4+} + Fe^{2+}$ (Acidic medium)

ii. $Zn + Cr_2O_7^{2-} + H^+ \longrightarrow Zn^{2+} + Cr^{3+} + H_2O$ (Acidic medium)

iii. $H_2O_2 + MnO_4^- + H^+ \longrightarrow Mn^{2+} + O_2 + H_2O$ (Acidic medium)

iv. $Sn^{2+} + I_2 \longrightarrow Sn^{4+} + I^-$ (Neutral)

3. Given the following cells at 25°C.

(a) Write the cell reactions

(b) Calculate the cell voltage

i. 1) Mg^{2+}/Mg $E^\circ_{Red} = -2.38$ V
2) Cu^{2+}/Cu $E^\circ_{Red} = +0.34$ V

ii. 1) $2H^+/H_2$ $E^\circ_{Red} = 0.00$ V
2) Ag^+/Ag $E^\circ_{Red} = +0.80$ V

Descriptive Questions

1. (a) Define the term electrolysis. State and explain Faraday's laws of electrolysis.
(b) A certain amount of current is passed through $CuSO_4$ solution for fifty minutes. The net amount of Cu deposited was found to be 25g. Calculate the current when Z =1 and At. Mass of Cu is 63.5g.

2. What is an electrode potential? How it can be measured?

3. What is the difference between the following? Give examples.
i) Reversible and irreversible cells ii) Electrolytic and voltaic cell

4. i) Explain the term oxidation and reduction with example.
ii) What is oxidation state? Give the oxidation number of Mn in $KMnO_4$, MnO_2, and Mn_2O_7.

5. What is an electrolytic cell? Explain Daniell cell in detail.
a) Calculate the electrical energy obtained from a Daniell cell.
b) What are the half-cell reaction? Give the half-cell reactions of the Nelson's cell for the production of NaOH.

6. What are electrochemical cells? Explain it in detail.
7. Write down the types of batteries. Explain fuel cells?

Project

Take two lead pencils and sharp them from both the ends in order to expose the inner carbon cores. Take a beaker filled with 100 mL water acidified with sulphuric acid. Fix the two pencils in the beaker in vertical position about 2cm from each other. Connect the pencil cores with electrical wires with the terminals of a 9 volt battery, one pencil with the positive pole and other with the negative pole of the battery. When the battery is switched on you will see bubbles coming from the lower ends of the pencil cores. What do you think about the nature of the bubbles? Which reactions are carried out at the pencil ends? Identify the anode and the cathode?