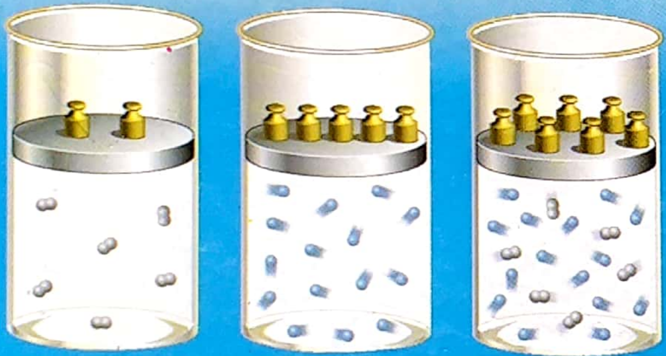
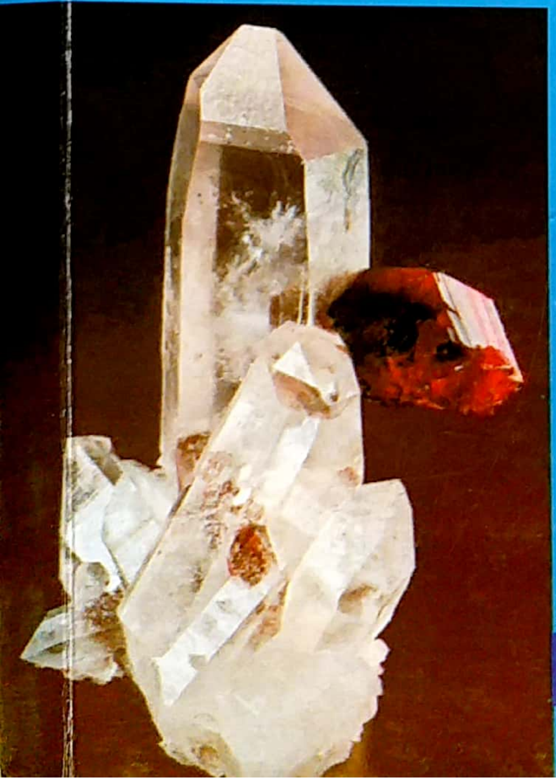
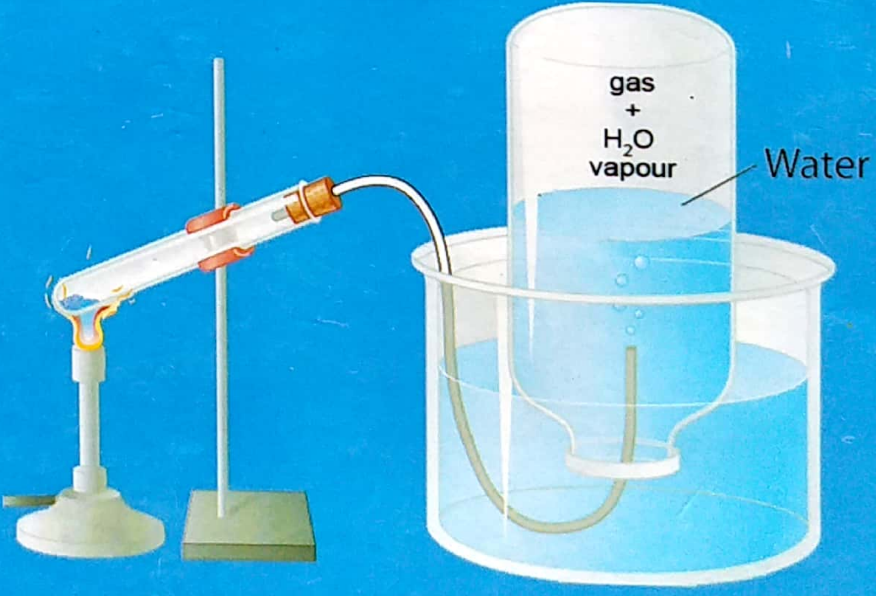
Chemistry

FOR CLASS-XI







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CHEMISTRY

FOR
Class XI

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PREFACE

The developments in the science of chemistry which have taken place during the past decade or two, have involved change in the content of the syllabuses. Ministry of Education (curriculum wing), Islamabad, prepared the new syllabus of chemistry and got it approved by the government.

This text book has been prepared by the Sindh Textbook Board in accordance with the new syllabus of chemistry for class XI of the Higher Secondary Education. The board has been able to secure the services of the competent teachers of various institutions of Sindh.

In producing this text, every effort is made to provide the students and tutors with a book that will assist the reader in bringing the science of chemistry as smoothly and effectively as possible.

In preparing this text book, the authors have had in their mind a student of higher secondary level, but in our opinion, it should continue to serve him well beyond that.

At secondary level, the study of chemistry is begun before the student has acquired enough needed background in elementary mathematics for true understanding. However, mathematics is part of the language of chemistry and a lack of familiarity with that language can become a barrier to success in understanding chemistry. Chapter 1 has been introduced for this purpose in the new syllabus. This chapter covers the mathematical operations (exponents, logarithm, significant figures). The comparative and integrated study of the three states of matter is covered in chapter 2. Chapter 3 deals with the structure of atom, atomic radii, ionization energies, electron affinity, shapes of orbitals. Chapter 4 covers chemical bonds, hybridization and shapes of molecules. The topic of energy changes accompanying the physical and chemical changes has been introduced in Chapter 5.

Keeping the need of laboratory programmes in mind, molar concentration, solubilities and properties of solutions are covered in Chapter 7. Chapters 6 and 8 develop major themes of chemical equilibria and the rates which are widely applied throughout chemistry. S.I Units are employed from the start.

We are deeply indebted to Mr. Muhammad Umar Mangrio, Principal and Professor of Chemistry at Govt. College, Umarkot for his patience, understanding, encouragement and helpful advice.

We apologize for any errors or omissions and welcome criticisms which might improve the book.

Editors :
Professor Dr. M. Sharif Memon
Professor Muhammad Ashraf Qureshi.

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بِسْمِ اللّٰهِ الرَّحْمٰنِ الرَّحِيْمِ

CHAPTER 1

INTRODUCTION TO FUNDAMENTAL CONCEPTS OF CHEMISTRY

1.1 INTRODUCTION

Chemistry is the branch of science which deals with the properties, composition and the structure of matter. It also deals with the changes in matter and the principles which govern these changes.

Chemistry has the task of investigating the materials of which the universe is made. It is not concerned with the forms into which they may be fashioned. For example the composition and structure of rubber is of really significance as compared to the shapes into which this has been fashioned like pipes, tyres and sheets etc. The materials are constantly undergoing change in nature. For example, iron rusts, spirit evaporates quickly, coal burns, animals digest their food, plants synthesize their own food material (photosynthesis) and so on. Chemistry investigates such changes - the conditions under which they occur, the new substances that are formed as their result, and the energy that is absorbed or liberated by them. Chemistry also studies the way in which similar changes can be brought about in the laboratory and on a large scale in industries. As a result of investigation along these lines, chemistry has found how metals can be extracted from their ores, how infertile fields can be made fertile, and how the materials that are found in nature can be converted into thousands of new substances to help feed the race, to cure the sick and to provide such comfort to the common man.

1.2. SIGNIFICANT FIGURES

The students in carrying out additions, subtractions, multiplications and divisions are confronted with the problems of the number of digits to retain in the answer, specially the last figure in a number when measured on a scale is usually an estimated one. Actually all measuring instruments such as metre sticks, clocks and balances have scales which are sub divided into various units and subunits. Suppose, for example a glass rod 'A' whose length is to be measured by two different scales which can be seen in the given figure (1.1) Scale (1) is divided only in centimetres while scale (2) is divided in millimetres also.

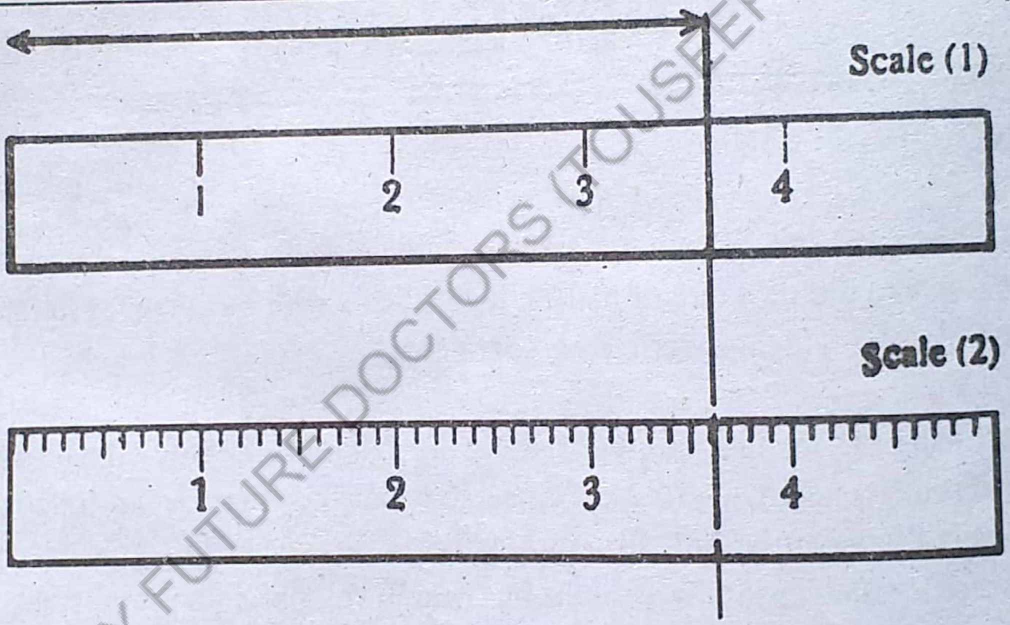


fig. 1.1

In scale (1) the length of the glass rod 'A' is about 3.6 cm. The length of 'A' on scale (2) however is 3.62 cm. Thus the value 3.6 cm contains two significant digits while the value 3.62 cm contains three significant digits. This show that one factor which is very important in determining the number of significant digits is the accuracy of the measuring instrument and the second factor which also counts is the size of the object to be measured.

For example, an Iron ball has mass 68.35 g and a smaller one has mass

7.55 g. The first represents four significant digits while the second has only three significant digits. Zero has its own importance in expressing a number, sometimes it is significant and sometimes it is not significant.

RULES FOR DETERMINING SIGNIFICANT FIGURES

Below are given the rules that will help students to determine the number of significant figures:

(i) Non zero digits are all significant; for example 363 has three significant figures and 0.68 has only two significnt figures.

(ii) Zeros between non zero digits are significant, for example, 5004 has four significant figures and likewise 20.4 has three significant figures.

(iii) Zeros locating the decimal point in numbers less than one are not significant; for example, 0.062 has two siginificant figures and 0.001 has only one significant figure.

(iv) Final zeros to the right of the decimal point are significant; for example, 2.000 has four significant figures and 506.40 has five significant figures.

(v) Zeros that locate the decimal point in numbers larger than one are not necessarily significant; for example, 40 has one significant and 2360 has three significant figures.

Thus significant figures by definition are the reliable digits in a number that are known with certainty. The last digit of a number is generally considered uncertain by ± 1 in the absence of qualifying information. For example the mass of an object can be expressed as 0.0112g or as 11.2 mg without changing the uncertainty of the mass or the number of significant figures. The mass is still uncertain by ± 1 in the last digit, this can be expressed as 0.0112 ± 0.0001g or as 11.2 ± 0.1 mg.

ROUNDING OFF DATA: We know that significant figures are those digits in a measured number that include all certain digits plus a final one having some uncertainty.

To round off means to reduce a number to the desired significant figures. It is the procedure of dropping nonsignificant digits in a calculation and adjusting the last digit reported. In order to get desired significant figures, one or more digits from extreme right can be dropped according to certain rules.

RULES FOR ROUNDING OFF DATA:

1. If the digit to be dropped is greater than 5, then add 1 to the last digit to be retained and drop all digits farther to the right. Thus 5.768 is rounded off to 5.77 to three significant digits (the last digit "8" dropped is greater than 5) and to 5.8 to two significant figures (the last digit "6" dropped is greater than 5).

2. If the digit to be dropped is less than 5, then simply drop it and also all digits farther to the right. Thus 5.734 is rounded off to 5.73 to three significant digits (the last digit "4" dropped is less than 5) and 5.7 to two significant digits (the last digit "3" dropped is also less than 5).

3. If the digit to be dropped is exactly 5, then two possible situations arise due to even and odd nature of the last digit to be retained:

   (i) If the digit to be retained is even, then just drop the "5". Thus 7.865 is rounded off to 7.86 to three significant digits (the digit to be retained "6" is even).

   (ii) If the digit to be retained is odd, then add 1 to it. Thus 6.75 is rounded off to 6.8 to two significant digits (the digit to be retained "7" is odd).

NOTE: If you use a calculator, you can simply enter numbers in the calculator one after the other, performing each arithmetic operation and rounding just each final answer to the desired significant figures.

USE OF SIGNIFICANT DIGITS IN ADDITION AND SUBTRACTION

The proper use of significant figures in addition and subtraction involves a comparison of only the absolute uncertainties of the numbers. This means that only as many digits are to be retained to the right of the decimal point in the answer as the number with the fewest digits to the right of the decimal. It will be necessary to round the last retained digit up if the next discarded digit is 5 or greater. For example.

$$1.31 + 2.1 = 3.41 = 3.4$$
$$8.741 - 5.31 = 3.431 = 3.43$$

If numbers with positive or negative exponents are involved, adjust exponents so that they are all the same before adding or subtracting.

Example 1.1

Consider the addition of following numbers 5.00×10^{-3}, 0.775×10^{-3} and 0.0001×10^{-3}

Solution : 5.00×10^{-3}
0.775×10^{-3}
0.0001×10^{-3}
Total 5.7751×10^{-3}
(Round up) 6.0×10^{-3}

Example 1.2

Add 15.5m, 651.8 cm. and 4291 mm.

Solution :

For the addition of significant figures, all measurements should be in the same unit, so values are to be changed in metres and then are added.

15.5 m = 15.5 m
651.8 cm = 6.518 m
4291 m.m = 4.291 m

Total = 26.309 m
(Round up) = 26.3 m

USE OF SIGNIFICANT DIGITS IN MULTIPLICATION AND DIVISION

The proper use of significant figures in multiplication and division involves a comparison of only the relative uncertainties. The number obtained as a result of multiplication or division of two or more numbers obtained by measurement must have no more significant figures than that number used in the multiplication or division which has the least number of significant figures, for example;

$$(1.32) \times (4.421) = 5.84$$

$$15.88 \div 7.95 = 1.997 = 2.00$$

$$\frac{31.23 \times 4.5}{9.41395} = 15$$

The numbers which determine the number of significant figures in the answers are 1.32 (Three significant figures), 7.95 (Three significant figures) and 4.5 (Two significant figures) respectively.

THE GENERAL APPLICATION OF SIGNIFICANT FIGURES :

The rules of addition, subtraction, multiplication and division of significant figures will save time and give results of accuracy when calculations are made, specially when a series of multiplications and divisions are involved.

Example:
Simplify $\frac{56 \times 725 \times 273}{760 \times 298}$

Solution :

(i) $56 \times 725 = 40600 = 41000$ (2 significant figures retained)
(ii) $41000 \times 273 = 11193000 = 11000000$ (2 significant figures retained)
(iii) $760 \times 298 = 226480 = 230000$ (2 significant figures retained)

Finally

(iv) $\frac{11000000}{230000} = 47.8 = 48$ (2 significant figures retained)

(Note : Zeros after a number are not significant digits which means 300 has only one significant figure).

1.3 USE OF EXPONENTS (LOGARITHMS)

We know that in scientific work, there are many occasions when we are confronted with the measurements of very small numbers or very large numbers, for example the mass of an electron is found to be 0.000000000000000000000000000911 g and the number of atoms in 1 mole of an element is found to be 602,300,000, 000,000,000,000,000 such numbers are much more conveniently expressed as multiples of 10. For example the first number may be written as 9.11×10^{-28} g and the second number as 6.023×10^{23}. By the same approach 0.0005 becomes 5×10^{-4} and 5000 becomes 5×10^{3}. Thus all numbers may be expressed as a power of 10 and 10^2, 10^3, 10^5, 10^{-1}, 10^{-2} etc. are generally called as exponential terms in which the base is 10. The powers to the base 10 are known as exponents. Any other number may also be used as a base but it is always convenient to have 10 as the base.

The exponential notation is of immense help in simplifying many types of arithmetical computaters and aids in minimization of errors. For example suppose you wish to divide 0.00016 by 80,000. This may be written as :

$$\frac{0.00016}{80,000} = \frac{16\times10^{-5}}{8 \times 10^{4}} = 2\times10^{-5} \times 10^{-4} = 2 \times 10^{-9}$$

The following, more involved calculation shows more clearly, the usefulness of exponential notation.

$$\frac{(0.00042)\ (560)}{(84,000)(0.007)} = \frac{(4.2\times10^{-4})(5.6 \times 10^{2})}{(8.4\times10^{4})\ \ (7\times10^{-3})} = \frac{4.2\times5.6}{8.4 \times 7} \times \frac{10^{-4} \times 10^{2}}{10^{4} \times 10^{-3}}$$

$$= 0.4 \times \frac{10^{-2}}{10^{1}} = 0.4 \times 10^{-3} = 4.0 \times 10^{-4}$$

Setting up calculations in this manner is very convenient and easy.

In the expression $a^x = y$, x is called the logarithm of y to the base a, where a must be positive number other than one. A logarithm is, therefore, an exponent and as such, follows the rules applying to exponents.

In logarithm the base is usually 10.

Suppose $N = 10^x$, now if N = 1,000, then $x = 3$ i.e. $1000 = 10^3$. The power (or exponent) x is called logarithm of the number N. This may be written in algebraic form

$$\log N = x$$

This is read : "the logarithm of N is x"

The logarithm is divided into two parts, the integer part called the characteristic and the decimal fraction called the mantissa. It must be remembered that the mantissa of a logarithm is always positive, the characteristic may be either positve or negative. Characteristic may be determined by just looking at the numbers. Mantissa may be found out with the help of logarithm tables.

For example, the numbers 0.0025, 0.25, 2.5, 25,000 etc. have the same mantissa but different characteristics.

To illustrate how to find the characteristic of a number it is simpler to just consider only numbers of the power of 10.

N	Characteristic
1000 (10^3)	3
100 (10^2)	2
10 (10^1)	1
1 (10^0)	0
0.1 (10^{-1})	–1
0.001 (10^{-3})	–3

Note that characteristic is simply the exponent of the number written as a power of 10. Each of the above numbers has the mantissa 0.000 ... as given in the logarithm table, Thus.

$\log 1000 = 3.000$
$\log 100 = 2.000$
$\log 10 = 1.000$
$\log 1 = 0.000$
$\log 0.1 = -1.000$
$\log 0.001 = -3.000$

Now consider a number 273. The value of 273 will lie between 100 and 1000 i.e. between 10^2 to 10^3 which means $273 = 10^x$ where x is between 2 and 3. According to Logarithm table the value of x is equal to 2.4362. It means that $10^{2.4362} = 273$ so $\log 273 = 2.4362$

(Characteristic 273 = 2
Mantissa 273 = 0.4362)

THE USE OF LOGARITHMS IN COMPUTATIONS

There are three fundamental rules in logarithms which help us in many calculations in multiplication, division and obtaining roots and powers.

$\log ab = \log a + \log b$
$\log a/b = \log a - \log b$
$\log (a)^n = n \log a$

Where a and b are any two positive numbers and n is any positive or negative number.

Examples :

(i) $\log (450 \times 566) = \log 450 + \log 566$
$= 2.6532 + 2.7528$
$= 5.4060$

Antilog of 5.4060 = 25470

since the characteristics is 5

Antilog 0.4060 = 254200

$$\text{(ii)}\quad \log(878 \div 122) = \log 878 - \log 122$$
$$= 2.9435 - 2.0864$$
$$= 0.8571$$

$$\text{Antilog } 0.8571 = 7194 + 2 = 7196 = 7.196$$

$$\text{(iii)}\quad \log(68)^{1/8} = \frac{1}{8}\log 68 = \frac{1}{8}(1.8325)$$
$$= 0.2290$$

$$\text{Antilog } 0.2290 = 1.694$$

1.4 ERROR AND DEVIATION

We know that in experimental observations we come across with errors and deviations in repeated measurements due to the factors like "defect in the instrument", or "Lack in handling the apparatus", or "improper functioning of the instrument". etc. Errors in analysis may be classified a systematic (determinate) and as random (indeterminate).

Systematic errors are caused by the defect in the analytical method or by the improper functioning of instrument. For example, in titrations if the indicator is not properly prepared, then the colour change will occur before the equivalence point, this systematic error or if burette is not properly cleaned or rinsed, then it will cause a systematic error. To avoid this type of error, the cause of error should be rectified. There is no strict definition of systematic errors, since what is a systematic error for one experiment may not be for another.

Nevertheless, when all the systematic errors have either been eliminated or corrected for, we still do not obtain "exact" or "true" measurements because there is some uncertainty in every physical measurement. The errors that the remaining variations indicate are called random errors. Random errors are unavoidable for example in a 50cm^3 burette, we can read the burette reading accurately only to the nearest 0.1 cm. A random error may be positive or negative. That is why we take the average of the several replicate measurements which is more reliable than any individual measurement.

ATOMIC MASS

Atomic mass is defined as the mass of one atom of the element compared with the mass of one atom of C^{12} (the stable light isotope of carbon). Thus one atom of hydrogen which weighs approximately $\frac{1}{12}$ the mass of one atom of carbon (12) has an atomic mass of $1\left(\frac{1}{12}\times 12=1\right)$. It may be noted that atomic mass is a ratio and hence has no unit. Thus an atomic mass may be given in any unit of measure i.e. grams, pounds, ounces and so on. Generally atomic masses are expressed in atomic mass units (a.m.u). One atomic mass unit, therefore equals exactly one twelfth the mass of a carbon–12 atom.

MOLECULAR MASS AND FORMULA MASS

Every molecule must have a mass since it is composed of atoms. For instance the molecule of water is composed of the elements hydrogen and oxygen. The atoms of these elements form molecules, each consisting of two hydrogen atoms bonded to one oxygen atom and the molecule of water is represented by the molecular formula, H_2O. The mass of a molecule is referred as its molecular mass and is defined as the sum of the atomic masses of the atoms of all the elements present in a molecule shown by its molecular formula. For example, the molecular mass of water (H_2O) is (1+1+16)=18 a.m.u.

In many substances atoms do not aggregate into molecules. For instance in sodium chloride (NaCl), the atoms are not organised into discrete molecules, but are bonded to one another in a network structure. The same is true for silicon carbide (SiC). Such compounds are represented by their simplest (empirical) formulas. We can not assign molecular mass to such compounds because there are no discrete molecules; we, therefore, assign a quantity called formula mass for such compounds. Hence formula mass is the sum of the atomic masses as given in the simplest (empirical) formula of the substance. Sodium chloride is represented by the simplest formula NaCl which means that in its crystalline form, the sodium ions $\left(Na^+\right)$ and chloride ions $\left(Cl^-\right)$ occur in the ratio 1:1. Thus the formula mass of NaCl is 23+35.5=58.5 a.m.u.

1.5 EMPIRICAL FORMULA

The empirical formula is that formula which is found by experiment. It represents the simplest ratio of the combining atoms in a compound for example, the empirical formula of benzene (C_6H_6) is CH; it indicates that the benzene molecule is composed of the elements carbon and hydrogen in the ratio of 1:1. Generally, empirical formula does not represent the actual number of atoms in a molecule. There are some compounds (specially ionic compounds) which have same empirical and molecular formulas. For example, MgO, NaCl, $CaCO_3$ etc. (Ionic) and CH_4, H_2O etc. (Covalent).

To work out empirical formula: As mentioned above, the empirical formula is determined from the results of different experiments. The determination of empirical formula involves the following steps:

(i) To detect the elements present in the compound (element detection by experiments)
(ii) To determine experimentally the masses of the elements.
(iii) To calculate the percentage of elements from their masses (Estimation)
(iv) To calculate the mole ratio of the elements; (Divide the percentages of elements by their Atomic masses).
(v) To obtain the simplest ratio of atmos (Empirical formula):[Divide the quotients obtained from (iv) by the smallest quotient].

It is interesting to note that the first three steps concern to the determination of composition of a compound.

Illustrated Example

Suppose that you are given an unknown compound whose Empirical formula is to be determined. The theoretical set of experimental results are quoted below which will be used to show you how to work out the empirical formula.

(i) By performing tests, it is found that the compound contains magnesium and oxygen elements.

(ii) The masses of the elements are experimentally determined to be magnesium = 2.4g and oxygen = 1.6g.

(iii) The next step is to estimate the percentage of each element as shown below:

Mass of the sample of magnesium oxide = 2.4 g Mg + 1.6 g O = 4.0 g

Now, 4.0 g of the compound contain 2.4 g Mg

$\therefore$ 100 g of the compound contain $\frac{2.4 \text{ g} \times 100 \text{ g}}{4.0 \text{ g}} = 60 \text{ g}$

$\therefore$ Mg = 60.0%

Mass of Oxygen = 100 g – 60 g = 40g per 100 g compound.

O = 40.0%

upto this stage, the composition of the compound is fully established.

(iv) Mole ratio of the elements is obtained by dividing percentage of each element with its atomic mass.

$$\text{Mg} = \frac{60}{24} = 2.5 \quad ; \quad \text{O} = \frac{40}{16} = 2.5$$

(v) To obtain the simplest ratio of atoms, the quotients obtained from (iv) are divided by the smallest quotient (Here both quotients are same).

$$\text{Mg} = \frac{2.5}{2.5} = 1 \quad ; \quad \text{O} = \frac{2.5}{2.5} = 1$$

Thus the empirical formula of the compound = MgO

Remember, if the percentage composition of the compound is given in the numerical, then only steps (iv) and (v) are followed in calculating the empirical formula.

Worked Example I : 1.367 g of an organic compound containing C, H, and O, was combusted in a stream of air to yield 3.002 g CO_2 and 1.640 g H_2O. What is its empirical formula?

Solution : The masses of CO_2 and H_2O are used to find out the masses of carbon and hydrogen:

$$\text{Mass of C} = \frac{1 \text{ mole C}}{1 \text{ mole } CO_2} \times 3.002 \text{ g } CO_2 = \frac{12 \text{ g C}}{44 \text{ g } CO_2} \times 3.002 \text{ g } CO_2$$

$$= 0.819 \text{g C}$$

$$\text{Mass of H} = \frac{2 \text{ moles H atoms}}{1 \text{ mole } H_2O} \times 1.640 \text{ g } H_2O = \frac{2 \text{g H}}{18 \text{ g } H_2O} \times 1.640$$

$$= 0.18 \text{ g H}$$

(ii) Now, the percentage of C and H is calculated:

1.367 g compound contain 0.819 g C

100 g compound contain $\dfrac{0.819 \text{ g} \times 100 \text{ g}}{1.367 \text{ g}} = 59.9 \text{ g}$

C = 59.9%

1.367 g compound contain 0.18 g H

∴ 100 g compound contain $\dfrac{0.18 \text{ g} \times 100 \text{ g}}{1.367 \text{ g}} = 13.16 \text{ g H}$

∴ H = 13.16%

Percentage of oxygen is calculated by subtracting the % of C and H from 100:

$$\% \text{ O} = 100 - 59.9 - 13.16 = 26.94 \%$$

$$\text{O} = 26.94\%$$

(iii) To obtain mole ratio of C, H, and O, their percentages are divided by their atomic masses:

$$\text{C} = \frac{59.9}{12} = 5$$

$$\text{H} = \frac{13.16}{1} = 13.6$$

$$O = \frac{26.94}{16} = 1.68$$

(iv) The quotients are divided by the smallest quotient (1.68) to obtain the simplest ratio of atoms:

$$C = \frac{5}{1.68} = 3$$

$$H = \frac{13.6}{1.68} = 8$$

$$O = \frac{1.68}{1.68} = 1$$

Thus the empirical formula of the compound = C_3H_8O

1.6 MOLECULAR FORMULA

A formula that expresses not only the relative number of atoms of each element but also the actual number of atoms of each element in one molecule of the compound is called a molecular formula. For example, the molecular formula of benzene is C_6H_6. This indicates that the benzene molecule is composed of 6 atoms of carbon and 6 atoms of hydrogen. The molecular formula is an integral multiple (1, 2, 3 etc.) of the empirical formula.

Molecular formula = (Empirical formula)$_n$ Where n = 1, 2, 3, etc.

Glucose, for instance has the empirical formula $(CH_2O)_n$. Thus molecular formula of Glucose = $(CH_2O)_6 = C_6H_{12}O_6$. As pointed out earlier, the ionic compounds are mostly represented by their empirical formulas as they consist of ions in their crystals. However in certain cases, ionic compounds are not expressed by empirical formulas e.g. $Na_2S_4O_6$ is not represented as NaS_2O_3 because it has been proved experimentally that there are four sulphur atoms and six oxygen atoms which are held together by covalent bonds in tetrathionate ion $S_4O_6^{2-}$. The covalent compounds on the other hand exist as discrete molecules which are represented by their molecular formulas. For example, sodium chloride and magnesium chloride are ionic compounds, hence they are represented by their empirical formulas NaCl and $MgCl_2$; water, methane on the other hand are represented by their molecular formulas H_2O and CH_4.

To work out Molecular formula: As mentioned above, the molecular formula of a compound is an integral multiple of its empirical formula, hence the first step in the determination of molecular formula is to calculate empirical formula by usual procedure as explained earlier. After that, the next step is to calculate the value of integer 'n'.

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

e.g. in case of glucose where molecular mass is 180 and the mass of empirical formula (CH_2O) is 30,

$$\therefore \quad n = \frac{180}{30} = 6$$

Now the molecular formula of glucose is $(CH_2O)_6$ or $C_6H_{12}O_6$.

Worked Example 1: 1.0 g of the sample of butane, a hydrocarbon fuel was burned in an excess of oxygen to yield 3.03 g CO_2 and 1.55 g H_2O. If molecular mass of the compound is 58, find out its molecular formula.

Solution : To determine empirical formula

(i) To calculate masses of carbon and hydrogen for the masses of CO_2 and H_2O:.

$$\text{Mass of carbon} = \frac{1 \text{ mole C}}{1 \text{ mole } CO_2} \times 3.03 \text{ g } CO_2 = \frac{12\text{g}}{44\text{g}} \times 3.03 = 0.83 \text{ gC}$$

$$\text{Mass of Hydrogen} = \frac{2 \text{ mole H}}{1 \text{ mole } H_2O} \times 1.55 \text{ g}H_2O = \frac{2 \text{ g}}{18 \text{ g}} 1.55 \text{ g} = 0.17 \text{ g H}$$

(ii) To calculate percentage of carbon and hydrogen:

1.0 g of the compound contain 0.83 g C

∴ 100 g of the compound contain

$$0.83 \text{ g} \times \frac{100 \text{ g}}{1.0 \text{ g}} = 83 \% \text{ C}$$

Since butane contains only carbon and hydrogen, hence :

Percentage of Hydrogen = 100 — 83 = 17% H

(iii) To calculate mole ratio of the elements by dividing the percentages by their atomic mass.

$$C = \frac{83}{12} = 6.91 \quad ; \quad H = \frac{17}{1} = 17$$

(iv) To obtain the simplest ratio, the quotients are divided by the least ratio:

$$C = \frac{6.91}{6.91} = 1 \quad ; \quad H = \frac{17}{6.91} = 2.5$$

In order to obtain nearest whole number ratios, both the members are multiplied by 2:

$C = 1 \times 2 = 2 \quad ; \quad H = 2.5 \times 2 = 5$

Thus the empirical formula of the compound $= C_2H_5$.

The empirical formula mass of $C_2H_5 = (12)2+(1)5$

$= 24 + 5 = 29$

(v) The value of the integer 'n' is calculated as follows :

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{58}{29} = 2$$

Molecular formula $= (\text{Empirical formula})_n$

$= (C_2H_5)_2$

$= C_4H_{10}$

Hence molecular formula of Butane = C_4H_{10}

1.7 MOLE AND AVOGADRO'S NUMBER

In routine chemical problems, it is necessary to consider quantities of substances in terms of the number of atoms or ions or molecules present. The unit devised by chemists to express number of atoms or ions or molecules is called the mole (mol).

A mole is defined as gram atomic mass or gram molecular mass or gram formula mass of any substance (atoms, molecules, ions) which contains 6.02×10^{23} particles.

The purpose of relating unit number of particles to the standard atomic masses is to provide a ready method of calculating the mass of a mole of any substance (*molar mass*).

Consider a mole of carbon-12, atoms and a mole of magnesium atoms. By definition, a mole of C-12 is 12 g of this substance. The atomic mass of magnesium is 24 which means each atom of magnesium is twice as heavy as carbon atom, it follows that mole of magnesium is 24g. Similarly a mole of oxygen atoms is 16 g and a mole of oxygen molecules is 32g.

Modern experimental methods for the determining atoms, molecules and ions show that in one g mole of a substance, there are 6.02×10^{23} particles. This huge number is called the Avogadro's Number. It is given in the honour of Amadeo Avogadro (1776-1856). It is denoted by N_A.

In the light of Avogadro's number, ***mole*** is comprehensively defined *as the mass in grams of atoms or molecules or ions (gram atomic mass or gram molecular mass or gram formula mass) which contains Avogadro's number of particles* (6.02×10^{23}).

Example:

A mole of hydrogen atom = 1 g = 6.02×10^{23} atoms
A mole of hydrogen molecule = 2 g = 6.02×10^{23} molecules
A mole of NaCl = 58.5g = 1 mole Na^+ + 1 mole Cl^-
= 6.02×10^{23} Na^+ + 6.02×10^{23} Cl^-
A mole of H_2O = 18 g = 6.02×10^{23} molecules
2 moles of H_2O = 36g = $2 \times 6.02 \times 10^{23}$ = 1.204×10^{24} molecules

1.8 CALCULATIONS BASED ON CHEMICAL EQUATIONS

We already know that a balanced chemical equation tells us the exact mass ratio of the reactants and products in the chemical reaction. For example, from the equation,

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2\,(g)$$

We can say that 1 mole of Zn reacts with two moles of HCl to give one mole of $ZnCl_2$ and one mole of H_2 gas or 65.4 parts by mass of Zn react with 73 parts by mass of HCl to give 136.4 parts by mass of $ZnCl_2$ and 2 parts by mass of H_2. From this relationship, we can calculate the mass of any given species from the mass of any one of the species. Thus from the chemical equation for certain reaction, the ratio of the moles of the reactants and the products can be determined. Hence the study of the relationships between the amounts of the reactants and the products in chemical reactions as given by chemical equations is called stoichiometry.

IMPORTANT ASSUMPTIONS FOR STOICHIOMETRIC CALCULATIONS

There are two important assumptions, while considering calculations based on the stoichiometry of chemical reactions:

(i) Reactants are completely converted to products.

(ii) No side–reactions occur.

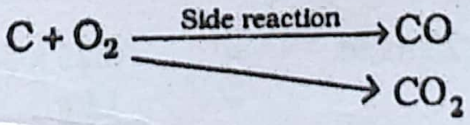
Suppose we want to calculate the mass of carbon dioxide formed when a given mass of carbon burns in air, we know the equation for the reaction i.e.

$$C + O_2 \longrightarrow CO_2$$

In actual practice, it is possible that we get less carbon dioxide than the calculated mass. This is because that the given mass of carbon can also form carbon monoxide in addition to carbon dioxide.

$$2C + O_2 \longrightarrow 2CO$$

This means that we have to avoid the formation of carbon monoxide which is a side–reaction.



There are three relationships involved for the stoichiometric calculations from the balanced chemical equations which are :

(a) Mass — Mass Relationships
(b) Mass — Volume Relationships and
(c) Volume — Volume Relationships

(a) Mass – Mass Relationships :

In such relationships, we can determine the unknown mass of a reactant or product from a given mass of the substance in a chemical reaction with the help of balanced chemical equation. Actually from a balanced chemical equation we get the exact relationships between the masses of the reactants and products. The calculation of mass from chemical equation is illustrated in the following examples:

Example - 1

Calculate the weight (mass) of carbon dioxide (CO_2) that can be obtained by heating 25 g of limestone ($CaCO_3$). And also calculate the weight (mass) of calcium Oxide (CaO).

Solution:

Equation of the reaction is as follows :

$$\begin{array}{lclcl} CaCO_{3(S)} & \xrightarrow{\text{Heat}} & CaO_{(S)} & + & CO_{2(g)} \\ 1\text{ mole} & & 1\text{ mole} & & 1\text{ mole} \\ 100\text{ g} & & 56\text{ g} & & 44\text{ g} \end{array}$$

Method - I

No. of moles in 25 g of $CaCO_3$ $= \frac{25}{100} = 0.25$ mole

1 mole of $CaCO_3$ yields 1 mole of CO_2

∴ 0.25 mole of $CaCO_3$ yields 0.25 mole of CO_2

= 0.25 mole of CO_2

∴ Mass of CO_2 in 0.25 mole = 0.25 x 44

= 11 g

1 mole of $CaCO_3$ yields 1 mole of CaO

∴ 0.25 mole of $CaCO_3$ yields 0.25 mole of CaO

= 0.25 mole of CaO

∴ mass of CaO in 0.25 mole = 0.25 x 56

= 14 g.

Method - II

100 g of $CaCO_3$ yield 44 g of CO_2

1 g of $CaCO_3$ yields $\frac{44}{100}$ g of CO_2

$\therefore$ 25g of $CaCO_3$ yield $\frac{44\text{ g}}{100\text{ g}} \times 25\text{ g} = 11\text{ g of } CO_2$

100 g of $CaCO_3$ yield 56 g of CaO

1 g of $CaCO_3$ yields $\frac{56}{100}$ g of CaO

$\therefore$ 25 g of $CaCO_3$ yield $\frac{56\text{g} \times 25\text{g}}{100\text{g}} = 14\text{g of CaO}$

Example - 2

Chlorine is produced on large scale by the electrolysis of NaCl aqueous solution. Calculate the weight (mass) of NaCl required to produce 142 g of chlorine.

Solution :

The equation of the reaction is:

$$2NaCl_{(S)} + 2H_2O_{(l)} \xrightarrow{\text{Electrolysis}} Cl_{2(g)} + H_{2(g)} + 2NaOH(s)$$

$2(58.5) = 117\text{ g}$ $\qquad\qquad$ 71 g

Method - I

71 g of Cl_2 are produced by 117 g of NaCl

1 g of Cl_2 is produced by $\frac{117}{71}$ g of NaCl

$\therefore$ 142 g of Cl_2 are produced by $\frac{117\text{ g}}{71\text{ g}} \times 142\text{ g}$

$= 234$ g of NaCl.

Method -II

No. of g moles of Cl_2 in 142 g $= \frac{142\text{ g of } Cl_2}{71\text{ g } Cl_2}$

$= 2$ g moles of Cl_2

According to above equation

One mole of Cl_2 requires 2 moles of NaCl

2 g moles of Cl_2 require $2 \times 2 = 4$ moles of NaCl.

Weight (mass) of NaCl in 4 moles $= 4 \times 58.5$

$= 234$ g of NaCl.

(b) Mass - Volume Relationships

The molar quantities of gases can be expressed in terms of volumes as well as weights (Mass). According to Avogadro, one gram mole of any gas at standard temperature (0°C) and standard pressure (1 Atm. or 760 mm Hg) occupies a volume 22.4dm³. It is a mathematical coincidence that one ounce mole of any gas at standard temperature and pressure occupies a volume 22.4 cubic feet. This relationship allows us to interchange mass and volume units of a gas through mass- volume relationship in a chemical equation. The following examples will illustrate by mass – volume relationship.

Example-1

Calculate the volume of CO_2 gas produced at standard temperature and pressure by the combustion of 20grams of CH_4

Solution

The equation for the reaction is

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

Method - 1

$$\text{No. of moles of } CH_4 \text{ in 20grams} = \frac{\text{Given mass of } CH_4}{\text{Molar mass of } CH_4}$$

$$= \frac{20\,g}{16\,g} = \frac{5}{4} = 1.25 \text{ moles}$$

One mole of CH_4 gives one mole of CO_2

1.25 mole of CH_4 gives 1.25 mole of CO_2

No. of mole of CO_2 gas S.T.P. = 1.25
One mole of CO_2 gas at S.T.P. occupies a volume 22.4 dm^3
1.25 mole of CO_2 gas at S.T.P. occupies a volume 22.4 x 1.25 = 28 dm^3

Method-II

Molecular weight (mass) of CH_4 = 16
Molecular weight (mass) of CO_2 = 44
16 grams of CH_4 give 44 gram of CO_2
1 gram of CH_4 gives 44/16 gram of CO_2

20 gram of CH_4 give $\frac{44\text{ g}}{16\text{ g}}$ x 20 g = 55 grams of CO_2

44 grams of CO_2 at S.T.P. occupy a volume 22.4 dm^3

1 gram of CO_2 at S.T.P. occupies a volume $\frac{22.4}{44}$ dm^3

55 grams of CO_2 at S.T.P. occupy a volume $\frac{22.4\text{ dm}^3}{44\text{ g}}$ x 55 g

= 28 dm^3

Example - 2

Calculate the volume of O_2 at S.T.P. for the complete combustion of two moles of carbon disulphide (CS_2). Calculate the volume of CO_2 and SO_2 produced also.

Solution:

$$CS_{2(l)} + 3O_{2(g)} \longrightarrow CO_{2(g)} + 2SO_{2(g)}$$

This equation shows that 1 mole of CS_2 reacts with 3 moles of O_2 to give 1 mole of CO_2 and 2 moles of SO_2.

Thus

1 mole of CS_2 reacts with 3 moles of O_2
∴ 2 moles of CS_2 react with 3 x 2 = 6 moles of O_2
∴ Volume of 6 moles of O_2 at S.T.P. = 6 x 22.4
= 134.4 dm^3

1 mole of CS_2 gives 1 mole of CO_2

$\therefore$ 2 moles of CS_2 give 2 mole of CO_2

$\therefore$ Volume of 2 moles of CO_2 = $2 \times 22.4\ dm^3$

= $44.8\ dm^3$

1 mole of CS_2 gives 2 moles of SO_2

$\therefore$ 2 moles of CS_2 give $2 \times 2 = 4$ moles of SO_2

$\therefore$ volume of 4 moles of SO_2 = $4 \times 22.4\ dm^3$

= $89.6\ dm^3$

(C) Volume – Volume Relationships

Gases react in volumes and the relationship between volumes of gases in a chemical equation is governed by Gay-Lussac's Law of combining volumes which states that gases react in the ratio of small whole numbers by volume under similar condition of temperature and pressure. For example in the reaction:

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

One volume of CH_4 gas reacts with two volumes of O_2 gas to give one volume of CO_2 gas and two volumes of water vapours. The co-efficients of the formulae give the volume relationships. We already know that one mole of any gas at S.T.P. occupies a volume of $22.4\ dm^3$. Thus in the above equation we can say $22.4\ dm^3$ of CH_4 gas react with $44.8\ dm^3$ of O_2 gas to give $22.4\ dm^3$ of CO_2 gas and $44.8\ dm^3$ of H_2O vapours. This relationship permits us to calculate the volume of one gas from the known volume of another gas involved in a chemical change.

The following examples will illustrate the application of volume - Volume relationship from a chemical equation.

Example - 1

What volume of O_2 at S.T.P. is required to burn $500\ dm^3$ of Ethene (C_2H_4) gas? What volume of CO_2 will be formed?

Solution:

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

According to the equation one dm^3 of C_2H_4 will require three dm^3 of oxyge gas. So, 1 dm^3 of Ethene (C_2H_4) requires 3 dm^3 of O_2

∴ 500 dm^3 of Ethene require 3 x 500

= 1500 dm^3 of O_2

1 dm^3 of Ethene (C_2H_4) produces 2 dm^3 of CO_2

∴ 500 dm^3 of Ethene produce 2 x 500 = 1000 dm^3 of CO_2

Example -2

Hydrogen sulphide burns in oxygen according to the equation.

$$2H_2S_{(g)} + 3O_{2(g)} \longrightarrow 2H_2O_{(g)} + 2SO_{2(g)}$$

Calculate the volume of O_2 at S.T.P. required to burn 900 dm^3 of H_2S and also find the volume of SO_2 gas produced.

According to equation :

Solution:

2 dm^3 of H_2S gas require 3 dm^3 of O_2 for combustion

1 dm^3 of H_2S gas requires $^3/_2$ dm^3 of O_2 for combustion

∴ 900 dm^3 of H_2S gas require $^3/_2$ x 900 = 1350 dm^3 of O_2

2 dm^3 of H_2S gas give 2 dm^3 of SO_2

∴ 900 dm^3 of H_2S gas give 900 dm^3 of SO_2 = 900 dm^3 of SO_2

1.9 LIMITING REACTANT:

In the stoichiometry of chemical reactions, some complexities arise which make the system comparatively difficult and it is not so simple to get direct relationships in chemical equations. In such cases, one aspect is the determination of the "Limiting reactant" which helps in calculating the amount of any one of the products. In irreversible reactions, the reactions go to completion in the direction of the arrow, untill one of the reactant which will be limiting reactant, is consumed entirely and the reaction stops. Calculations are made on the basis of the amount of limiting reactants. This can be illustrated by the following example.

Example: Sodium thiosulphate $(Na_2S_2O_3)$ can be prepared by the reaction given below:

$$2Na_2S_{(aq)} + Na_2CO_{3(aq)} + 4SO_{2(g)} \rightarrow 3Na_2S_2O_{3(aq)} + CO_{2(g)}$$

How many grams of sodium thiosulphate will be produced when 200g each of the three reagents $Na_2S, Na_2CO_3 and SO_2$ are reacted together?

Solution: According to balanced chemical equation, the exact mole ratios of the reactants $(Na_2S, Na_2CO_3 and SO_2)$ are 2:1:4.

Amount of each of the reactants is 200 g .

Number of moles of Na_2S in 200 g is $\frac{200}{78} = 2.56$ moles.

Number of moles of Na_2CO_3 in 200 g is $\frac{200}{106} = 1.886$ moles.

Number of moles of SO_2 in 200 g is $\frac{200}{64} = 3.12$ moles.

Because the quantity of Na_2CO_3 is the smallest amount of all the reagents used in the reaction, this can be the limiting factor, so the amount of the other reagents used will be as:

(i) 1 mole of Na_2CO_3 reacts with 2 moles of Na_2S

$\therefore$ 1.886 moles of Na_2CO_3 react with $2 \times 1.886 = 3.772$ moles.

(ii) 1 mole of Na_2CO_3 reacts with 4 moles of SO_2.

$\therefore$ 1. 886 moles of Na_2CO_3 react with $4 \times 1.886 = 7.544$ moles.

From the calculations, we got that neither Na_2S nor SO_2 are available in the quantities to consume 1.886 moles of Na_2CO_3, so Na_2CO_3 is present in excess.

Let us see Na_2S.

2 moles of Na_2S react with 4 moles of SO_2.

$\therefore$ 2.56 moles of Na_2S react with $\frac{4 \times 2.56}{2} = 5.12$ moles.

But the actual amount of SO_2 available is only 3.12 moles which means the Na_2S is in excess and SO_2 is the limiting reactant. So the amount of SO_2 is used to calculate the amount of $Na_2S_2O_3$.

According to balanced chemical equation:

4 moles of SO_2 produce 3 moles of $Na_2S_2O_3$

1 mole of SO_2 produces $\frac{3}{4}$ moles of $Na_2S_2O_3$

$\therefore$ 3.12 moles of SO_2 produce $\frac{3 \times 3.12}{4} = 2.34$ moles.

Amount in grams $= 2.34 \times 158 = 369.72g$

(Molecular mass of $Na_2S_2O_3 = 158$ g)

PROGRESS TEST 1

1. (a) Explain (i) Empirical formula (ii) Molecular formula (iii) Mole.
   (b) Calculate the number of moles in 2400 g of (i) CO_2 (ii) Oxygen molecule (iii) $CaCO_3$ (iv) $MgBr_2$

   [Ans: (i) 54. 54 moles (ii) 75 moles (iii) 24.0 moles (iv) 13.04 moles]

2. (a) What is Avogadro's number? Calculate the number of atoms in 9.2g of Na (Atomic mass of Na = 23 a.m.u)

   [Ans: 2.408×10^{23} atoms]

   (b) Calculate the mass in grams of 3.01×10^{20} molecules of glucose ($C_6H_{12}O_6$). [Ans: 0.09 grams]

3. A compound of C, H and N contains 66.70% carbon, 7.41% hydrogen and 25.90% Nitrogen. The Molecular mass of the compound was found to be 108.
   (i) Find the empirical formula of the compound. [Ans: C_3H_4N]
   (ii) Find the Molecular formula of the compound. [Ans: $C_6H_8N_2$]

4. Determine the significant figures in the followings:
   (a) 15.01 (b) 7000 (c) 3.200 (d) 0.004

   [Ans: (a) Four (b) One (c) Four (d) One]

   Simplify the followings according to the rules of significant figures.

   (a) 1.41×3.546 (b) $\dfrac{31.23 \times 4.56}{9.41395}$ [Ans: (a) 5.00 (b) 15.1]

5. Express the followings as the power of 10:
   (a) 6782 (b) 565.2 (c) 0.00019 (d) 70,000 (c) 0.00000067

   [Ans: (a) $6.78\ 2 \times 10^3$ (b) 5.652×10^2 (c) 1.9×10^{-4} (d) 7×10^4 (c) 6.7×10^{-7})]

6. With the help of logarithm table, find the values of:
   (a) $(25.4)^3 \times (416.2)^{3/4}$ (b) 294×0.0006

   (c) $0.18 \div 108$ (d) $\dfrac{57 \times 365 \times (566)^{1/2}}{78 \times 221 \times (356)^{2/3}}$

   [Ans: (a) 150938.4 (b) 0.1764 (c) 0.00167 (d) 0.5718]

7. Round off the following numbers into (a) four (b) three and (c) two significant digits:

(i) 8.7483 (ii) 5.36748 (iii) 15.145 (iv) 188.55

8. Acetic acid contains carbon, hydrogen and oxygen. 4.24g of sample of acetic acid on complete combustion gave 6.21g of CO_2 and 2.54 of H_2O. The molecular mass of acetic acid is 60. Find (i) Empirical formula of acetic acid and (ii) Molecular formula of acetic acid.

[Ans: (i) CH_2O (ii) $C_2H_4O_2$]

9. Ethylene glycol is used as an antifreeze. Combustion of 6.38 g of ethylene glycol gives 9.06 g of CO_2 and 5.58 g of H_2O. Ethylene glycol contains carbon, hydrogen and oxygen and its molecular mass is 62. Find empirical formula and molecular formula.

[Ans: (i) CH_3O (ii) $C_2H_6O_2$]

10. When dinitrogen pentoxide (N_2O_5), a white solid is heated, it decomposes to nitrogen dioxide and oxygen.

$$2N_2O_{5(s)} \xrightarrow{\text{heat}} 4NO_{2(g)} + O_{2(g)}$$

Find the volume of NO_2 and O_2 gases produced at S.T.P when a sample of 54 g of N_2O_5 is heated.

[Ans: (i) Volume of NO_2 = 22.4 dm^3 (ii) Volume of O_2 = 5.6 dm^3]

11. Hydrogen cyanide is prepared from ammonia, air and natural gas (CH_4) by the following process:

$$2NH_{3(g)} + 3O_{2(g)} + 2CH_{4(g)} \longrightarrow 2HCN_{(g)} + 6H_2O_{(g)}$$

If a reaction vessel contains 51g of NH_3. What is the maximum mass of HCN that could be made, assuming the reaction goes to completion? Find also the volumes of O_2 and CH_4 gases required for the reaction at S.T.P.

[Ans: (i) Mass of HCN=81g (ii) Volume of O_2 = 100.8 dm^3 (iii) Volume of CH_4 = 67.8 dm^3]

12. Ammonia gas can be produced by heating together the solid NH_4Cl and $Ca(OH)_2$. If a mixture containing 100g of each of these solids is heated, how many grams of NH_3 are produced? Also find the volume of NH_3 gas at S.T.P.

$$2NH_4Cl_{(s)} + Ca(OH)_{2(s)} \rightarrow 2NH_{3(g)} + CaCl_2 + 2H_2O$$

CHAPTER 2

THE THREE STATES OF MATTER
GASES, LIQUIDS AND SOLIDS

INTRODUCTION

Matter is defined as any thing which occupies space and has mass. The three states of matter-gas, liquid and solid are easily recognized through their properties.

A gas has no shape of its own; rather it takes the shape of its container. It has no definite volume but can be compressed or squeezed into smaller volume. A gas diffuses, that is, it distributes itself through out a vessel.

A liquid has no definite shape; it takes the shape of its container. It however occupies a definite volume of its own. Although it is not absolutely in-compressible, it is compressed to a negligible extent even by high pressures.

A solid possesses both definite shape and definite volume. Like a liquid, it is not compressed or squeezed appreciably by high pressures.

The same substance, say water, can exist in all the three states, for example, as solid ice, liquid water and the gaseous steam. Despite the same chemical composition, water shows different behaviour in three different states. The only conclusion which can be drawn,is that the particles which make up the three states of matter for any given substance differ only in the manner in which they are arranged and they are not different in kind. The theory which deals with the way in which the arrangement of particles of a substance determines the properties that substance will possess, and particularly the state in which it is likely to be found under a given set of conditions is known as the kinetic theory.

2.1 KINETIC THEORY

The Kinetic theory is so named because it deals with that property of the particles which is so crucial in understanding the three states of matter, namely the motion of the particles. Because the particles are in constant motion, they possess kinetic energy which tends to keep the particles well spaced out in any substance. Thus in terms of kinetic theory.

1. The gaseous state is the one in which the molecules are widely separated from one another but having negligible volume. The gases are easy to compress due to large empty spaces.

2. The gas molecules are in continuous motion, travelling in straight paths between collisions, but in random directions (Fig. 2.1). The average distance between collisions is the mean free path.

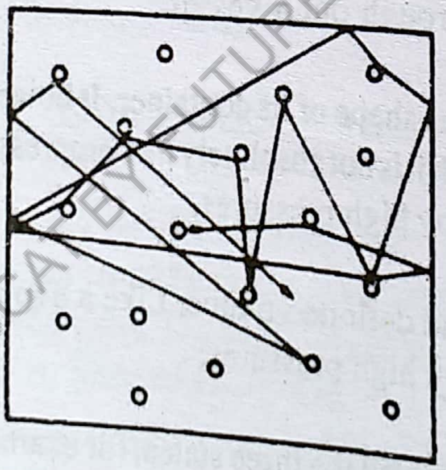


FIGURE 2.1
The random motion of a gas molecule. The average distance between collisions is the mean free path.

3. The molecules collide with one another and with the walls of container, but these collisions are perfectly elastic (result in no loss of energy).

4. Gas pressure is the result of the collision of gas molecules with the walls of the container (fig. 2.2).

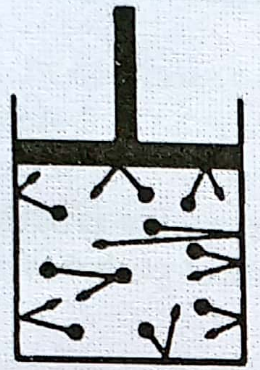


FIGURE 2.2
Gas pressure is the result of the collision of the gas molecules with the walts of the container.

5. In an ideal gas, there are no attractive or repulsive forces between molecules. Thus each molecule acts quite independently of the others.

6. The average kinetic energy of gas molecules depends upon the absolute temperature. At any given temperature, the molecules of all gases have the same average kinetic erergy ($^1/_2$ mv^2).

The kinetic theory was extended to account for the behaviour of liquids and solids.

For a liquid, the kinetic theory suggests that the particles of a liquid are fairly randomly arranged (as in gas), but consists of clusters' in which they are very close together. This makes liquid have a definite volume, but since the particles are still fairly free to move, it does not have any definite shape of its own.

For a solid, the kinetic theory postulates that the molecules are closely packed, so that the forces of attraction between the molecules are very strong and free movement of particles can not take place. Thus in a solid, the particles are arranged in a fixed pattern and they form a lattice of vibrating masses. This makes a solid have a definite shape.

2.2 GASEOUS STATE

We select to begin our study of matter with the gaseous state because (i) it is the simplest to study and (ii) it can be readily converted into the condensed states – liquid and solid; hence many of our conclusions concerning gases apply directly to these states.

BEHAVIOUR OF GASES

The assumptions of kinetic theory account for most of the properties associated with gases and we can obtain better understanding of gas behaviour.

1. Diffusibility

The distribution or spreading of gas molecules through out the vessel is known as **diffusion**. Unlike liquids or solids, the gases diffuse very rapidly. A drop of perfume for instance, slowly evaporates out the fragrant gas announces the presence of wearer. It is due to the diffusions of perfume through the air.

In terms of kinetic theory, diffusion is explained as follows. The molecules of a gas are widely separated and there are large empty spaces due to which they are free to move. Due to this free movement the molecules of gases intermingle and spread out easily throughout the vessel. The opposite of diffusions is effusion in which a gas passes through the pores or tiny holes in the vessel (fig. 2.3), for example, the air effuses from the tire as a result of which the tire loses pressure gradually.

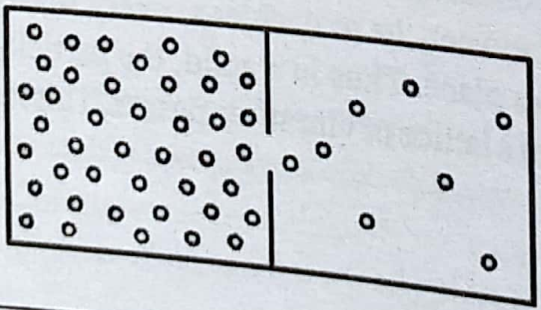


FIGURE 2.3
Effusion of gas through a small hole.

2. Compressibility:

In contrast to liquids or solids, all the gases are easily compressed or squeezed. In terms of 'kinetic theory', gases are easily compressed due to large empty spaces. By applying pressure, the molecules come closer. Air, for instance is squeezed into automobile tires. When the tire is punctured, the air rushes out. It is the reverse of compressibility – the expansibility, thus volumes of gases are highly affected by the changes in pressure. [Volume is measured in cubic decimetres, dm^3 or cubic centimetres, cm^3. [$1\ dm^3 = 1000\ cm^3$]

3. Pressure:

All the gases exert pressure. It may appear surprising but it is a fact that we are being pressed upon by an enormously heavy blanket of atmosphere. The mass of atmosphere on our body at seal level and at 0°C is 14.7 psi (pounds per square inch, lb/in^2) or there is about 20 tons total pressure on our bodies.

When a gas is confined in a closed container, it exerts pressure on the walls of the container which is due to the collisions of gas molecules with the walls The tires of automobiles are filled with air until the guage shows the pressure of about 28 psi. This means that the pressure inside the tire is 28 psi greater than the outside pressure; since the external atmospheric pressure is 14.7 psi, hence the total pressure on the tire is $28 + 14.7 = 42.7$ psi.

Since pressure is defined as a force pushing on a unit of area, therefore pressure may be measured in psi (pounds per square inch, lb/in^2), Kilograms per square metre (Kg/m^2). The S.I. unit of pressure is pascal ($1\ pa = 1N/m^2$). Since the units of a newton of force are $Kg/m.s^2$, the S.I. units of pressure are:

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{\text{newton}}{m^2} = \frac{Kg\ m/s^2}{m^2} = Kg/\ m\ s^2$$

Normal atmospheric pressure at sea level at 273 K (0°C) is expressed in several ways.

14.7 psi; 760 mm of mercury = 760 torr (∴ 1 mm = 1 torr);
76 cm = 1 atmosphere (atm). Since they are more useful for our purpose than the S.I. units, therefore we will use these units).

Problem 1 : What is the pressure in torr of 3.5 atm?

Solution: ∴ 1 atm = 760 torr

$$\therefore\ 3.5\text{ atm} = \frac{760\text{ torr}}{1\text{ atm}} \times 3.5\text{ atm} = 2660\text{ torr}$$

Problem 2 : How many atmospheres correspond to 950 torr?

Solution : ∴ 760 torr = 1 atm

$$\therefore\ 950\text{ torr} = \frac{1\text{ atm} \times 950\text{ torr}}{760\text{ torr}} = 1.25\text{ atm}$$

Temperature may be defined as that property which determines the flow of heat. The common scale of temperature is Celsius (Centigrade). The S.I. unit is however, Kelvin (K).

$$K = {}^{\circ}C + 273$$

e.g. 7°C = 7 + 273 = 280 K.

2.3 GAS LAWS

The mass, volume, temperature and pressure of gases bear a simple mathematical relationship to each other. Further, other variables, such as rates of diffusion of different gases are related mathematically. The precise statements of these relationships are known as the gas laws.

BOYLE'S LAW

Robert Boyle studied the effect of pressure changes on the volume of the gases. For this purpose, he designed a J - shaped glass tube and its shorter arm was closed. (Fig. 2.4). He then poured mercury in the longer arm so as to enclose some amount of air in the shorter arm. The equal level of mercury in the two arms indicated that the confined air was subjected to the atmospheric presure Fig:

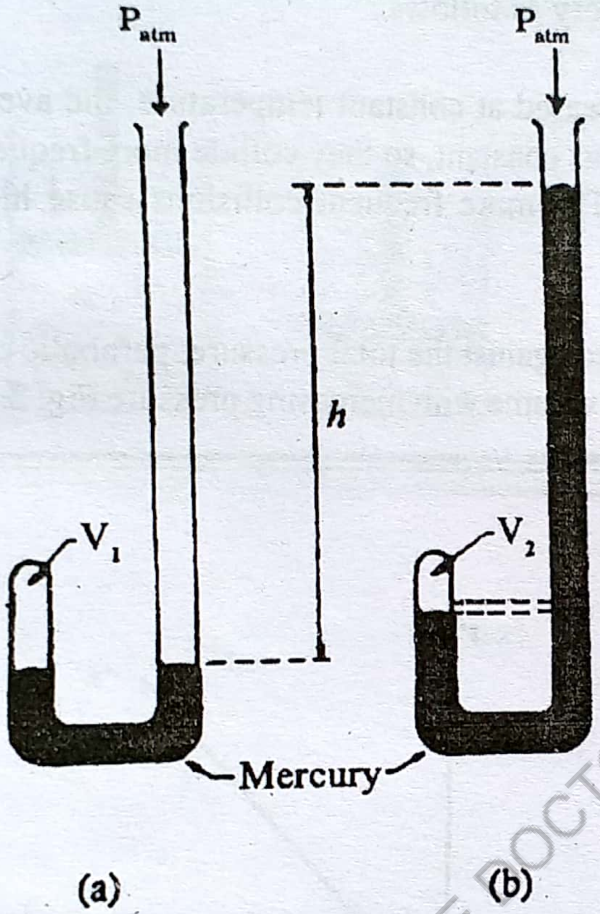


FIGURE 2.4
Boyle's J-tube experiment. Adding mercury to the open arm of the tube compresses the trapped sample of air to a smaller volume.

2.4(a). Boyle added more mercury as a result of which the mercury level raised above the original level (h) and the increased pressure reduced the volume of the air Fig:. 2.4(b). The total pressure was calculated as:

$$P_{total} = P_{atm} + P_h, \text{ where } P_h = \text{excess pressure.}$$

Boyle compared the volume of the air with the total pressure and observed the inverse or non-linerar relationship:

"The volume of a given mass of a gas is inversely proportional to the pressure exerted on it at a given temperature".

This relationship reported in 1660 is known as Boyle's law. According to this law, at constant temperature, if pressure is doubled, volume will be reduced to half, if pressure is reduced to half, the volume will be doubled. Boyle's law can be explained in terms of kinetic theory as follows :

If the volume of a gas is decreased at constant temperature, the average velocity of the gas molecules remains constant, so they collide more frequently with the walls of smaller vessel. The more frequent collisions cause higher pressure.

If the volume of a gas is plotted against the total pressure, parabolic curve is obtained showing the decrease in volume with increasing pressure Fig: 2.5(a).

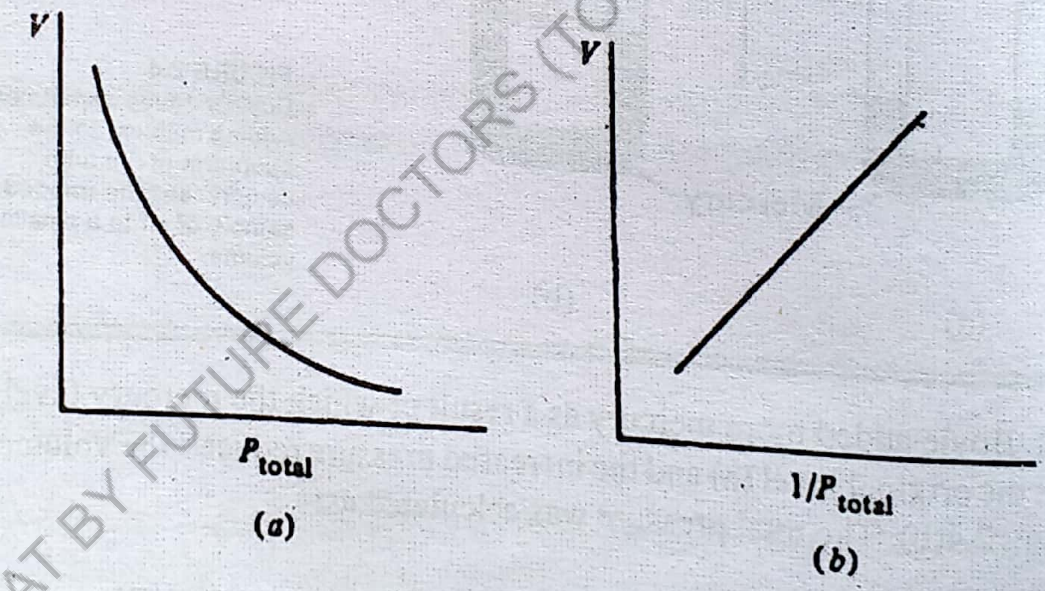


FIGURE 2.5
Graphical representation of Boyle's law. (a) A plot of volume versus total pressure is nonlinear showing that the relationship is inverse. (b) A plot of volume versus the reciprocal of the pressure is a straight line.

A graph of volume with I/P gives a straight line Fig. 2.5(b) The Boyle's law i interpreted in terms of molecules in the Fig. 2.6. Applying the pressure brings th molecules closer together causing the reduction in volume. Mathematically Boyle's law can be represented as :

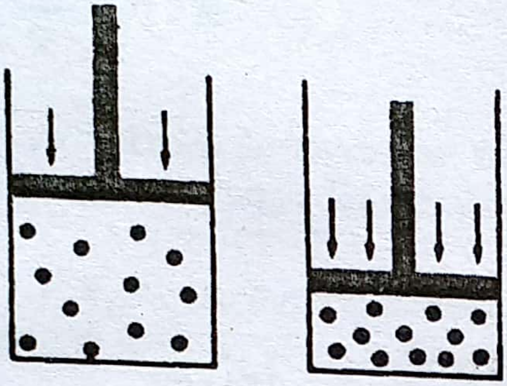


FIGURE 2.6
Increasing the pressure on a mass of gas forces the molecules closer together.

$$V \propto \frac{1}{P} \quad \text{(Temperature constant)}$$

$$V = K \times \frac{1}{P}$$

PV = K i.e. the product of pressure and volume of a given gas at constant temperature is always constant. If P_1 and V_1 are the initial pressure and volume, P_2 and V_2 are the changed pressure and volume, then according to Boyle's law:

$$P_1 V_1 = K; \; P_2 V_2 = K \text{ i.e.}$$

$$P_1 V_1 = P_2 V_2$$

This is the mathematical expression of Boyle's law which is used while solving the problems on Boyle's law.

Problem : What volume does 400 cm^3 sample of a gas at 700 torr occupy when the pressure is changed to 2 atm?

Solution: Tabulate the data. (700 torr = 700/760 = 0.92 atm)

	P	V	T
Original	0.92 atm	400 cm^3	K
Changed to	2.0 atm	V	K

According to the Boyle's law,

$$P_1 V_1 = P_2 V_2$$

$$V_2 = \frac{P_1 V_1}{P_2}$$

$$= \frac{0.92 \text{ atm} \times 400 \text{ cm}^3}{2 \text{ atm}} = 184 \text{ cm}^3$$

CHARLES S LAW:

It is a matter of common observation that substances expand on heating and contract on cooling. Change in volume due to expansion and contraction is very small in case of solids and liquids because of their compact structure and lack of inter molecular spaces. Gases exhibit enormous changes due to the presence of large intermolecular spaces. Changes of volumes of gases due to changes of temperature at constant pressure were studied by charles (1746-1823).

The volume of a given mass of a gas increases or decreases by $\frac{1}{273}$ times of its original volume at 0^oC for every degree rise and fall of temperature at a given pressure. It is also stated as the volume of a given mass of a gas is directly proportional to the absolute temperature at given pressure.

In terms of kinetic theory, Charles's law can be explained as follows: A decrease in temperature, decreases the average kinetic energy of the ga molecules, that is, average molecular velocity decreases. At constant pressure the decreased velocity causes the sample of gas to shrink and occupy a smalle volume.

Mathematically this law can be represented as :

$$V \propto T \text{ (absolute)} \quad \text{(P is constant)}$$
$$V = KT$$
$$\frac{V}{T} = K$$

In other words the ratio of volume of a given mass of a gas to its absolute temperature is always constant provided the pressure is kept constant.

If V_1, V_2 are the original and changed volumes; T_1, T_2 are the original and changed temperatures, then according to the Charles's law.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\therefore \quad \frac{V_1}{T_1} = \frac{V_2}{T_2} = K$$

This is the mathematical representation of Charles 's law which is used while solving the problems on Charles's law.

The graphical representation of the observation of Charles is shown in Fig. 2.7. When the volume of the gas is plotted against the temperature, a straight line is obtained. If this straight line is extra plotted, it will be seen that it intercepts the temperature axis at –273.16°C (Fig. 2.7)

It suggests that the volume of a gas would theoretically be zero at –273.16°C. In fact this temperature has never been achieved for any gas. In fact all the gases condense to liquid at a temperature above this point, so that gas behaviour can no longer be observed. The temperature of –273.16°C is referred to as the *Absolute zero* or zero degree of the *absolute scale* (Kelvin Scale). At absolute zero, the volume of gases is considered to be zero and all the motion ceases to exist. As already pointed out that centigrade scale is changed into Kelvin scale by adding 273.

$$^\circ C + 273 = K$$
$$K - 273 = {}^\circ C$$

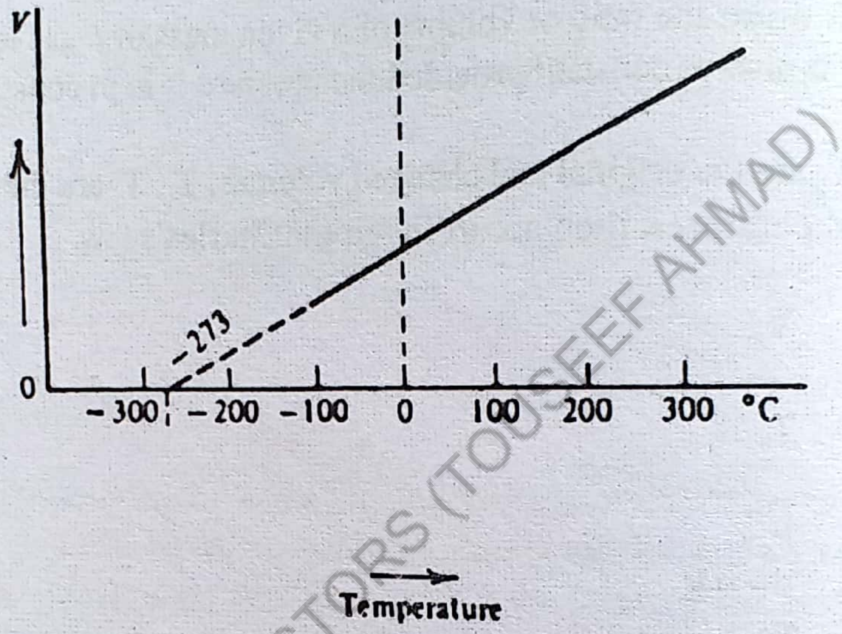


FIGURE 2.7
Graphical representation of the volume temperature relationship of a sample of gas. The gas volume decreases with decreasing temperature.

Problem.1 A child's balloon has a volume of 3.80 dm^3 when the temperature is 35°C. What is the volume, if the balloon is put into a refrigerator and cooled to 5°C? Assume that pressure inside the balloon is equal to atmospheric pressure at all times.

Solution : Tabulate the data.

Original

$V_1 = 3.80\ dm^3$, $T_1 = 35+273 = 308\ K$, $P = K$

Changed to $V_2 = ?$, $T_2 = 5+273 = 278\ K$, $P = K$

According to Charles's law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{V_1 T_2}{T_1}$$

$$= \frac{3.8 \text{ dm}^3 \times 278 \text{ K}}{308 \text{ K}} = 3.42 \text{ dm}^3$$

AVOGADRO'S LAW :

In 1811, Amadeo Avogadro advanced a brilliant hypothesis regarding the relationship between the volume and the number of molecules of a gas. This hypothesis, now called Avogadro's law which states:

"Equal volumes of all gases at the same temperature and pressure contain the same number of molecules". Thus the volume of a gas is directly proportional to the number of molecules of the gas at constant temperature and pressure.

i.e $V \propto n$ (at constant temperature and pressure) where 'n' is the number of molecules of a gas. Thus 1 dm^3 (or cm^3, m^3 or other unit of volume) of oxygen contains the same number of molecules as 1dm^3 (or cm^3 etc.) of hydrogen or of any other gas, provided the volumes are measured under the same conditions.

Based on Avogadro's law, 22.4 dm^3 of any gas at S.T.P. (standard temperature is 273 K and standard pressure is 1 atmosphere) constitutes 1 mole of that gas; 22.4 dm^3 at S.T.P. is called the molar gas volume or the volume of one mole of a gas at S.T.P.

The mass in grams of 22.4 dm^3 of a gas at S.T.P. is the mass of one mole of that gas, e.g. 22.4 dm^3 of SO_3 at S.T.P. is equal to 80 g (one mole). It is shown in the fig. 2.8.

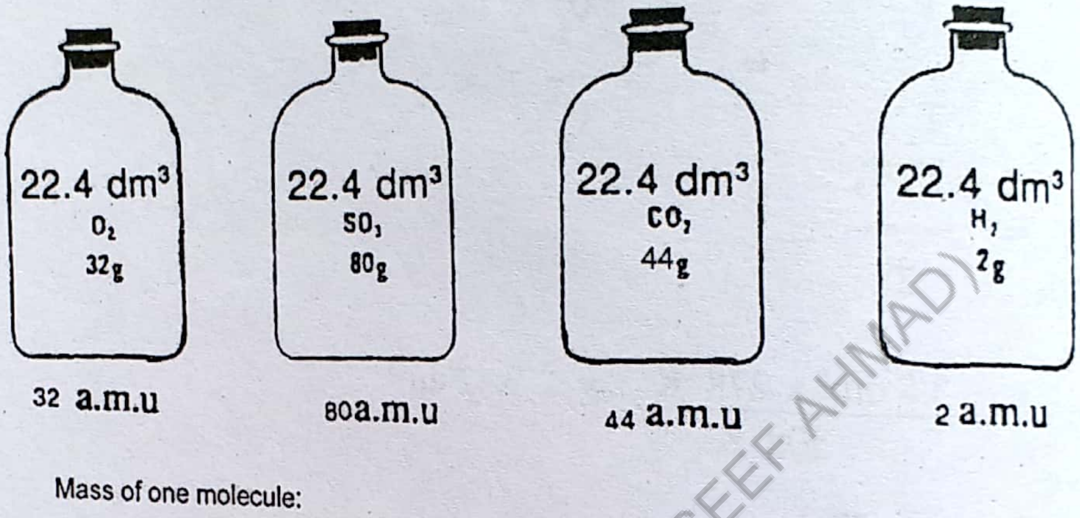


FIGURE 2.8
Measured at STP, 22.4 dm³ of a gas equals a mole.

Avogadro's law enables us to determine the relative molecular mass of gases as illustrated in the following example:

Example :

At standard conditions, 1 dm³ of Oxygen weighs 1.43 g and 1 dm³ of Carbon monoxide weighs 1.25 g. According to the Avogadro's law, 1dm³ of CO at S.T.P. contains the same number of molecules as 1dm³ of O_2 under similar conditions. Hence a molecule of CO has mass 1.25/1.43 times as much as a molecule of O_2. Accordingly, if we take the molecular mass of O_2 as 32, then the molecular mass of CO would be :

$$\frac{1.25}{1.43} \times 32 \quad = \quad 28 \text{ g/mol}$$

The General Gas equation (Ideal gas equation).

Equation of state: Boyle's law, Charles's law and Avogadro's law may be combined together to give a general relation between the volume, temperature, pressure and number of moles of a gas.

According to Boyle's law: $V \propto 1/P$

According to Charles's law $V \propto T$ (absolute) (P is constant)
According to Avogadro's law $V \propto n$ (P and T constant)

Combining these laws we get :

$$V \propto \frac{1}{P} \times T \times n$$

$$V = R \times \frac{1}{P} \times T \times n$$

$\therefore$ $PV = nRT$. This is known as the equation of state because when we specify the four variables – pressure, temperature, volume and number of moles, we define the state for a gas.

Where R is a constant and is called gas constant. The above equation is known as the equation of state or ideal gas equation.

For 1 mole of a gas , $n = 1$ therefore $PV = RT$.

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

If pressure changes to P_1 and temperature to T_1 then volume also changes to V_1

Then $$\frac{P_1V_1}{T_1} = R$$

Similarly $$\frac{P_2V_2}{T_2} = R$$

$$\therefore \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \cdots\cdots\cdots \frac{P_nV_n}{T_n} = R$$

This relationship is used to solve problems regarding changes of volumes of gases, due to the changes in the pressure and temperature.

The value of R (The gas constant):-

(i) When P is expressed in atmospheres, V in litres or dm^3.

$$R = \frac{PV}{nT} \qquad P = 1 \text{ atmosphere}, \quad V = 22.4\ dm^3 \text{ (Molar volume)}$$

$$= \frac{1 \text{ mole} \times 22.4 dm^3}{1 \text{ mole} \times 273\ K} \qquad \text{Since } n = 1, \quad T = 273 K$$

$$= 0.0821\ dm^3 \text{ atmosphere } K^{-1} \text{ mole}^{-1}$$

(ii) When P is expressed in newtons per square metre

$N\ m^{-2}$, V in cubic metres;

$P = 101300\ Nm^{-2}$

$V = 0.0224\ m^3$ (since $1\ dm^3 = 10^{-3}\ m^3$)

$n = 1$

$T = 273\ K$

$$R = \frac{P V}{nT} = \frac{101300\ (Nm^{-2}) \times 0.0224\ (m^3)}{1\ (\text{mole}) \times 273\ (K)}$$

$$= 8.3143\ N\ m\ K^{-1}\ mol^{-1} = 8.3143\ J\ K^{-1}\ mol^{-1}$$

$$= 8.3143\ J/(mol\ K)$$

Problem – 1

What will be the volume occupied by 14 g of nitrogen at 20°C and 740 torr pressure?

Data:

$$P = 740 \text{ torr} = \frac{740}{760} = 0.974 \text{ atm.}$$

$$V = ?$$

$$n = \frac{14g}{28} = 0.5 \text{ mole}$$

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

$$T = 20 + 273 = 293 \text{ K.}$$

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$= \frac{.5 \times .0821 \times 293}{0.974} = 12.345 \text{ dm}^3$$

Problem - 2

A certain mass of nitrogen gas at 20°C and at 740 torr pressure occupies 12.345 dm^3. Calculate the volume that it will occupy at S.T.P.

Data:
$V_1 = 12.345 \text{ dm}^3$
$V_2 = ?$
$P_1 = 740 \text{ torr}$
$P_2 = 760 \text{ torr}$
$T_1 = 20 + 273 = 293 \text{ K}$
$T_2 = 273 \text{ K}$

We know that:

$$\frac{P_2 V_2}{T_2} = \frac{P_1 V_1}{T_1}$$

$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2}$$

$$= \frac{740 \text{ torr} \times 12.345 \text{dm}^3}{293 \text{ K}} \times \frac{273 \text{ K}}{760 \text{ torr}} = 11.12 \text{ dm}^3$$

Problem - 3

Calculate the volume that will be occupied by 0.8 moles of oxygen gas taken at 30°C and at 800 torr of pressure?

Data:

$V = ?$

$n = 0.8$ mole

$R = 0.0821\ dm^3\ atm/K\ mole$

$T = 30 + 273 = 303\ K$

$P = \frac{800\ torr}{760} = 1.053$ Atmosphere

Solution:

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$V = \frac{0.8 \times 0.0821 \times 303}{1.053}$$

$$= 18.899\ dm^3$$

GRAHAM'S LAW OF DIFFUSION:

Diffusion means mixing up of molecules of different gases moving in opposite directions. We know that gas molecules are constantly moving in haphazard direction. Therefore when two gases are placed separated by a porous membrane, they diffuse through the membrane and intermingle with each other. Light gases diffuse more rapidly than the heavier one. Graham (1881) established a quantitative relationship between the rates of diffusion of gases and their densities and is termed as Graham's law of diffusion.

This law states "Rate of diffusion of a gas is inversely proportional to the square root of the density of that gas provided the pressure and temperature are the same for the two gases". This law is stated mathematically.

$$r \propto \frac{1}{\sqrt{d}}$$

where 'r' is the rate of diffusion and 'd' the density of the gas.

If we consider two gases, having densities d_1 and d_2 respectively ; then;

$$r_1 \propto \frac{1}{\sqrt{d_1}}$$

$$\therefore \quad r_1 = \frac{K}{\sqrt{d_1}}$$

Similarly :

$$r_2 \propto \frac{1}{\sqrt{d_2}}$$

$$r_2 = \frac{K}{\sqrt{d_2}}$$

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

Since the density of a gas is proportional to its molecular mass, we can write the above equation as : $\left(d_1 = \frac{M_1}{V} \text{ and } d_2 = \frac{M_2}{V}\right)$

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

Problem - 1

The ratio of the rates of diffusion of two gases A and B is 1.5 : 1. If the relative molecular mass of gas A is 16, find out the relative molecular mass of gas B?

Solution:

According to Graham's law :

$$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}$$

$$\frac{1.5}{1} = \sqrt{\frac{M_B}{16}}$$

By taking square of both sides

$$\left(\frac{1.5}{1}\right)^2 = \left(\sqrt{\frac{M_B}{16}}\right)^2$$

$$\therefore M_B = (1.5)^2 \times 16$$
$$= 2.25 \times 16$$
$$= 36$$

Problem -2

Compare the rates of Helium and sulphur dioxide.

Solution :

The molecular masses of Helium and sulphur dioxide are 4 and 64 respectively. Hence,

$$\frac{r_{He}}{r_{SO_2}} = \sqrt{\frac{M_{SO_2}}{M_{He}}} = \sqrt{\frac{64}{4}} = \frac{8}{2} = 4$$

Helium diffuses four times as fast as SO_2.

DALTON'S LAW OF PARTIAL PRESSURES:

When two or more gases which do not react chemically, are mixed in the same container, each gas will exert the same pressure as it would exert if it alone occupied the volume containing the mixed gases. This portion of the total pressure of a mixture is known as the *partial pressure*. Based on this behaviour of gases, John Dalton formulated a law in 1801 which is known as the *Dalton's law of partial pressures*. It is stated as :

"The total pressure of a mixture of gases is the sum of the partial pressures of the gases in the mixture". This law is stated mathematically.

$$P = p_1 + p_2 + p_3 \ldots\ldots$$

P is the total pressure; the small p's refer to the part of the pressure (partial pressure) exerted by each gas in the mixture. If the gas 'A' exerts a pressure of 0.3 atm., and gas 'B' 0.2 atm., the total pressure of the mixture would be 0.5 atm (fig 2.9). Partial pressure of a gas is calculated by using the equation:

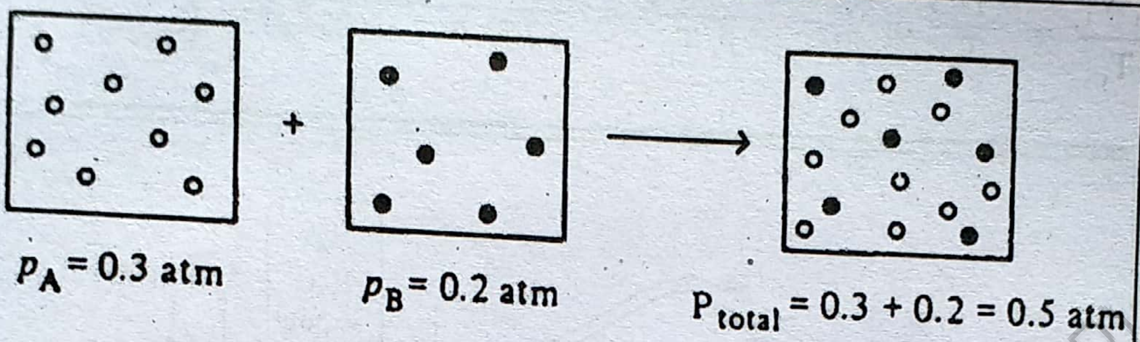


FIGURE 2.9

$$\frac{\text{Partial pressure of gas}}{\text{Total pressure}} = \frac{\text{moles of the gas}}{\text{Total moles}}$$

$$p_{gas} = \frac{P \times n_{gas}}{n_{(total)}}$$

In terms of *kinetic theory*, Dalton's law can be explained as follows: In a non-reactive mixture, each gas exerts a separate pressure on the container because of collisions of its molecules with the walls of container. Thus the total pressure in the container is caused by the sum of all the collisions.

Application: This law applies most commonly to the case of a gas collected over water (See fig. 2.10). For example, suppose 100 cm^3 of an insoluble gas are collected over water at a pressure of 745 torr and at 15°C. If it is saturated with water vapour, the pressure of the dry gas is (745-13) torr, since the vapour pressure of water at 15°C is 13 torr. Thus

The pressure of moist gas = Pressure of dry gas + pressure of water vapour
The pressure of dry gas = Pressure of moist gas - pressure of water vapour
745 torr – 13 torr
∴ P dry gas = 732 torr

Now using gas equation, we can calculate the volume of the dry gas at S.T.P.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \text{ or } V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{732 \text{ torr} \times 100\text{cm}^3 \times 273 \text{ K}}{760 \text{ torr} \times (15+273) \text{ K}} = 91.3\text{cm}^3$$

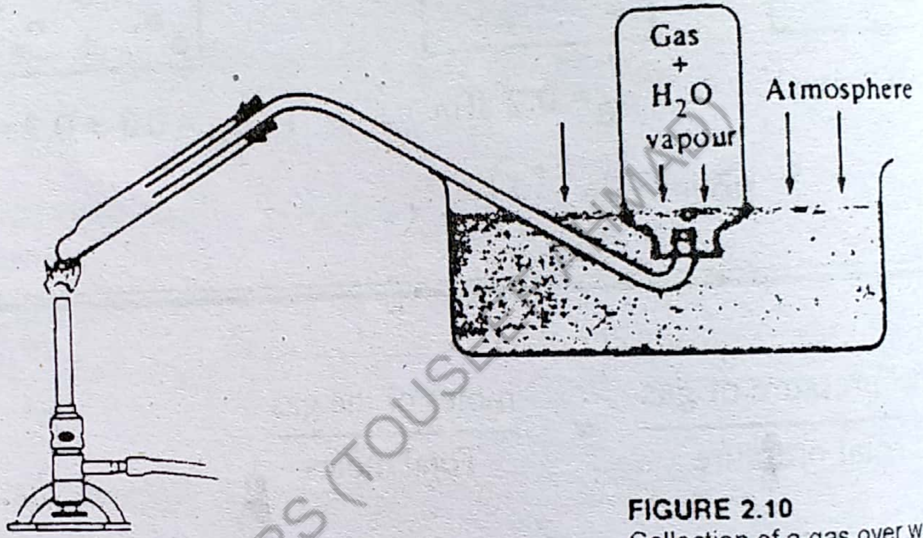


FIGURE 2.10
Collection of a gas over water.

Problem - 1

In the preparation of oxygen in the laboratory, 500 cm^3 of the moist was collected over water at 25°C and 724 torr. What volume of dry oxygen S.T.P. was produced? (Pressure of water vapours at 25°C = 24 torr).

Solution:

Pressure of dry O_2 is calculated by using Dalton's law:

$$p_{\text{dry } O_2} = p_{\text{moist gas}} - p_{H_2O}$$

$$= 724 \text{ torr} - 24 \text{ torr}$$

$$= 700 \text{ torr}$$

Now calculate the volume of dry gas at S.T.P.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{(Gas equation)}$$

$$V_{\text{dry gas}} = \frac{P_1 V_1 T_2}{P_2 T_1}$$

$$= \frac{700 \text{ torr} \times 500 \text{ cm}^3 \times 273 \text{ K}}{760 \text{ torr} \times 298 \text{ K}} = 421.9 \text{ cm}^3$$

Problem - 2

A mixture of gases at 760 torr contains 2 moles nitrogen and 4 moles carbon dioxide. What is the partial pressure of each gas in torr?

Solution:

Total moles (n) = 6 moles; total pressure = 760 torr

$$P_{\text{gas}} = \frac{P_{(\text{total})} \times n_{(\text{gas})}}{n_{(\text{total})}}$$

$$P_{N_2} = \frac{760 \text{ torr} \times 2 \text{ mol}}{6 \text{ mol}} = 253.33 \text{ torr}$$

$$P_{CO_2} = \frac{760 \text{ torr} \times 4 \text{ mol}}{6 \text{ mol}} = 506.67 \text{ torr}$$

Check: Total pressure = Sum of partial pressures = 760 torr

2.4 IDEAL GASES

An ideal gas is one whose behaviour can be predicted precisely on the basis of kinetic molecular theory and gas laws. Two significant properties of an ideal gas are that the molecules do not attract each other and they occupy negligible space. Actually, no such gas exists, although gases such as hydrogen and oxygen do not deviate greatly from the ideal behaviour at moderate temperatures and pressures. The main cause of deviation of the real gases from the ideality, is the presence of intermolecular forces like vander Waal's forces between their molecules.

2.5 - CHANGE OF STATE (LIQUEFACTION)

Gases are liquefied at low temperatures. According to the kinetic theory, at lower temperatures, the kinetic energy of the molecules is less, and the slower moving molecules become subject to inter molecular attractions. At a sufficiently low temperature, the attractive forces are capable of holding the molecules to one another and the gas changes to liquid.

2.6 - LIQUID STATE

The liquid state is the intermediate between gaseous and solid state. In liquids, the kinetic energy of the molecules is sufficiently high enough to keep the molecules close together. Like gases, liquid molecules are able to move and thus flow and diffuse. However, due to more compact nature, liquids are not compressed to any noticeable extent. The intermolecular distance in liquids is much less than that of the gases. 1 mole of a gas, for instance, occupies a volume of 22,400 cm^3 under standard conditions (Avogadro's law), but 1 mole of a liquid occupies the volume of 10 cm^3 to 100 cm^3.

BEHAVIOUR OF LIQUIDS: The extended kinetic molecular model accounts for most of the properties of liquids.

1. **DIFFUSIBILITY:** Like gases, liquids also diffuse. One liquid may diffuse into another, e.g., a drop of a dye or any coloured solution diffuses through water. Diffusions in liquids is much slower than that of gases.

In terms of molecular model, the diffusion of liquids can be explained as follows: The freedom of liquid molecules permits diffusion to take place but the closeness of molecules and resulting large number of collisions cause diffusion to be slow.

2. **COMPRESSIBILITY:** Though the liquids are not absolutely incompressible, but they may be compressed to a little extent by the high pressures. This fact leads to their use in hydraulic brake systems.

At nominal pressure, however the brake liquids can transmit the applied force to perform certain machenical function such as braking the motions in a motor car.

In terms of molecular model, the compressibility of liquids can be explained as follows: The liquid molecules due to their closeness roll over one another. Owing to very little space the liquid molecules cannot be pushed close by pressure. Very high pressures are required for squeezing a liquid.

3. EXPANSION AND CONTRACTION: A liquid normally expands on heating and contracts on cooling (as does mercury or alcohol in thermometers). The molecular model explains this behaviour as follows: On heating, the kinetic energy and so the velocity of molecules increases. As a result, the volume taken by each molecule increases on heating. It results in the expansion. Contraction may similarly be explained.

The distance between liquid molecules are so small that properties of liquids are largely determined by the intermolecular attractions. Viscosity, surface tension and vapour pressure, for intrance, are not only dependent on the intermolecular forces but they are also modified with the temperature changes.

2.7 - VISCOSITY

Like gases, liquids have the ability to flow (fluids) but unlike gases they have definite surface. Different liquids have different rates of flow. Some liquids like honey, mobil oil etc. flow slowly and are called viscous liquids, while gasoline, ether etc. which flow quickly are called less viscous. The intermolecular attractions account for this behaivour of liquids.

Inter molecular attractions between the molecules within the bulk of liquid occur in all directions (Fig. 2.11) i.e. the molecules are attracted mutually in all

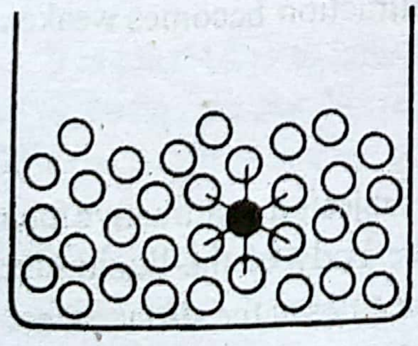


FIGURE 2.11
Intermolecular attractions between molecules in the bulk of a liquid occur in all directions.

directions. These intermolecular attractions which draw the liquid molecules together are responsible for the *viscosity*, that is, *'its resistance to flow'*. The liquids that have stronger intermolecular attraction have greater viscosities, their molecules are less easily moved about with respect to each other. Ethyl alcohol (C_2H_5OH), for instance, is more viscous than ether ($C_2H_5.O.C_2H_5$) because there are hydrogen bonds among alcohol molecules. The grading of motor oils is done on the basis of viscosity for example, sea grade 30 oil is less viscous than the grade 40 oil.

The viscosity is expressed in poises (1 poise = 1 gm/cm.S) or its multiples - centipoises and millipoises. The S.I. unit is newtonx seconds per square metre $N.s.m^{-2}$

1 centipoise = 10^{-3} $N.s.m^{-2}$

Viscosity of certain liquids at different temperatures is given in the table 2.1.

Table 2.1 – Viscosity (centipoise) at different temperatures.

LIQUID	VISCOSITY		
	0°C	20°C	50°C
Water	1.789	1.005	0.55
Ethyl alcohol	1.78	1.19	0.701
Glycerine	12100	1499	—
Acetone	0.395	0.322	0.246

From the above table, you must have noticed that the viscosity of a liquid decreases with the rise in temperature. In fact, with the rise of temperature, the volume of liquid increases and the intermolecular attraction becomes weaker.

2.8 - SURFACE TENSION (γ)

As pointed out earlier, all molecules in a liquid are subjected to attractive forces from neighbouring molecules. For molecules in the body of the liquid, these forces balance each other (See fig. 2.11), but for molecules at the surface there is

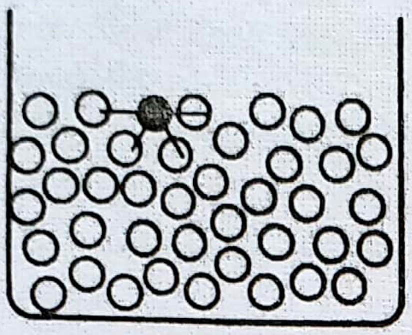


FIGURE 2.12
Intermolecular attractions at a liquid surface occur only within the surface and below

resultant attractive force acting downwards. (Fig. 2.12). These forces which tend to pull the surface molecules downwards are responsible for the surface tension. It is designated by γ. The dimensions of surface tension are dynes/cm or ergs/cm^2 (numerically the values in both the units are equal). *Hence the surface tension may be regarded as the force per unit length or energy per unit area of the surface of liquid.* Table 2.2 gives the surface tension of some liquids at 20°C.

Table 2.2 — Surface tension (dynes/cm or erg/cm^2) at 20°C.

Liquid	γ	Liquid	γ
Water	72.583	Acetone	23.7
Ethyl alcohol	22.03	Benzene	28.88
Chloroform	27.1	Mercury	471.6

This table shows that the surface tension of water is higher than most of the organic liquids because there are stronger intermolecular attraction in water (Hydrogen bonds).

It is interesting to note that the surface tension tends to reduce the surface area of the liquids. For this reason, a freely falling drop of liquid is spherical (Fig. 2.13), since sphere has the smallest ratio of surface area to volume.

It is our common observation that a liquid always rises in a capillary tube (fig. 2.14), the effect is referred to as the *'capillary action'*. Capillary

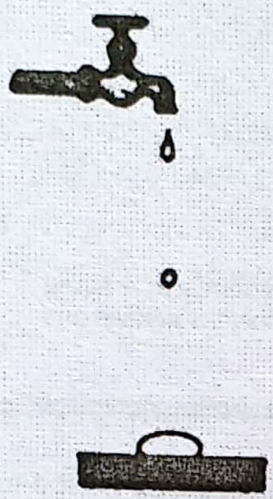


FIGURE 2.13
A free-falling drop of water is nearly spherical. A droplet of water on a waxed surface forms a "bead" as it attempts to become spherical.

action of liquids is also due to their surface tension. The surface area to volume ratio of a capillary of small bore is much smaller than the container in which liquid is placed.

FIGURE 2.14
Capillary action

Like viscosity, the surface tension of a liquid also decreases with the rise of temperature owing to the weakening of the inter molecular attractions.

2.9 - VAPOUR PRESSURE

Water slowly evaporates at room temperature. Gasoline evaporates quite readily without boiling. A liquid that evaporates readily is said to be *volatile*.

If a quantity of a liquid is contained in a tightly covered container at a certain temperature, molecules will evaporate from the liquid surface into the enclosed space. Since these molecules move about above the liquid and can not escape, some of them will collide with the liquid surface and re-join it (condensation) Fig. 2.15). As a result of the two opposite processes-evaporation and condensation, a state of equilibrium is finally established. This equilibrium is marked by the attainment of a *vapour pressure* which is defined as *the pressure exerted by the vapours when they are in equilibrium with the liquid phase*. It is constant at constant temperature. The vapour pressure is independent of the amount of liquid present. For example the vapour pressure of water at 20°C is 17.5 torr.

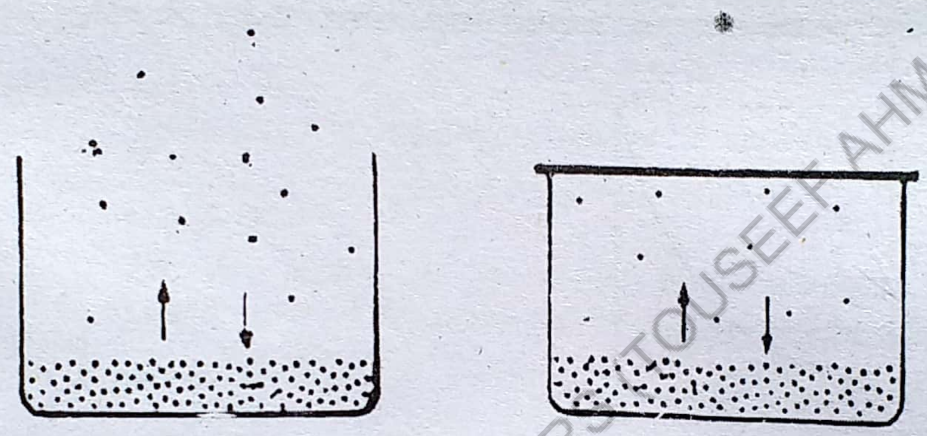


Figure 2.15. In an open container a liquid will evaporate away but in a closed container the rate of condensation becomes equal to the rate of evaporation, and the liquid-vapour system is in equilibrium.

The evaporation and the vapour pressure can be explained in terms of kinetic theory. Evaporation occurs when high energy of molecules at the surface of liquid break away from their neighbours and escape into the gas phase. During evaporation, the escape of high energy molecules lowers the average kinetic energy of the remaining molecules, consequently the temperature of the remaining liquid falls down. Thus it is said that evaporation is a cooling process.

2.10 - CHANGE OF STATE – BOILING

When a liquid is heated, the more molecules acquire increased kinetic energy and escape into the air and the evaporation becomes more rapid. As a consequence, the vapour pressure of the liquid increases. For example at 40°C the vapour pressure of water is 55.3 torr and at 95°C it is 634 torr. It is illustrated by the vapour pressure-temperature curve in fig. 2.16. When the vapour pressure of liquid equals the atmosphere pressure, the bubbles of vapour form easily and rise to the surface. The liquid is said to *boil*. Thus the ***boiling point*** of a liquid is the temperature at which the vapour pressure of the liquid equals the outside pressure. When the outside pressure is the atmospheric pressure (760 torr), the boiling point is referred to as the ***normal boiling point***.

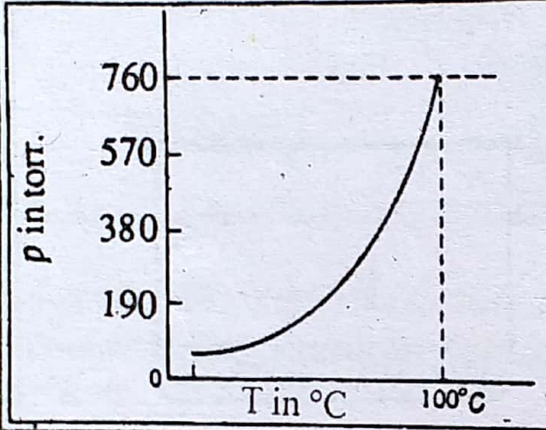


FIGURE 2.16
The vapour pressure-temperature curve for water.

The boiling point of liquids varies with the outside pressure. In mountainous regions, the boiling point of water will be below 100°C because the atmospheric pressure is below 760 torr. Thus in such regions of high altitude, foods take longer time to cook because of the low boiling temperatures. In the pressure cookers, on the contrary, food cook more rapidly because of the higher boiling temperatures.

It may be pointed out that certain liquids tend to decompose at their boiling point temperatures. Such liquids are distilled at low temperatures under reduced *pressure*. By lowering the pressure, boiling point of the liquid is reduced and their decomposition is prevented. For example, glycerine boils at 290°C at 760 torr but it decomposes at this temperature. If it is heated under reduced pressure (50 torr), it boils at 210°C and can easily be distilled without decomposition.

2.11 SOLID STATE

A solid state is that state of matter in which atoms, molecules or ions are held together by strong attractive forces. Due to strong attractive interatomic, molecular or ionic forces, the particles constituting the solid can not move, however, they possess some vibrational energy at even near absolute zero.

Progress in science and technology leads to advancement in knowledge about solid state also. Hence we must endeavour to understand the nature and behaviour of solids.

1– Behaviour of Solids

Compared with the other two states of matter i.e. gases and liquids, the solids have highest degree of order. This orderlines accounts for many behaviour of solids. Some of these are:

(i) Compressibility:– The compressibility of solids is nearly zero. In terms of kinetic theory, the particles of solids are so tightly bound together that only slight unfilled space is left, hence density of solids is much higher than gases and liquids, so they can withstand considerable external stress.

(ii) Deformity:– Solids are deformed or shattered by high pressure. This is because when some particles are dislocated the force of attraction is so strong that the rearranged atoms are held equally well to their new neighbours as shown in Fig.2.17.

(iii) Diffusibility:– In terms of kinetic theory, there is no translational movement of molecules in solid, but nevertheless particles are vibrating at their mean positions. This vibrational motion is responsible for diffusion in solids.

(iv) Melting:– Solids on heating melt at a particular temperature.

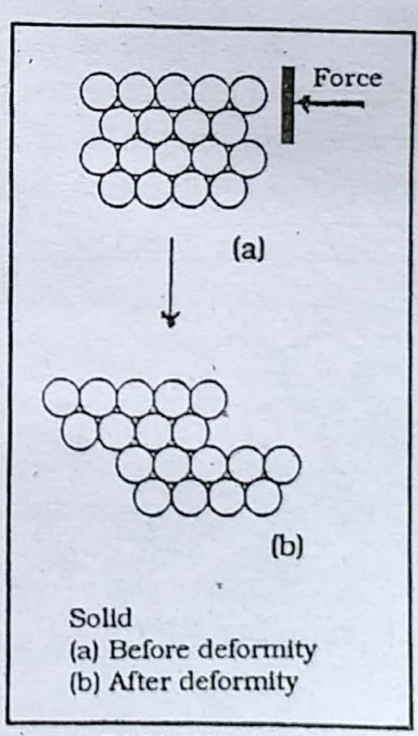


FIGURE:2.17

In terms of kinetic theory when solids are heated vibrational energy of their particles increases; until at melting point some particles are vibrating with sufficient energy to overcome the forces holding them, hence they become mobile i.e. solids fuse.

(v) Sublimation:– There are some solids substances, as camphor, iodine, solid CO_2, naphthalene etc. which change directly to vapour on heating without passing through liquid phase. This phenomenon is called sublimation. In terms of kinetic theory, the inter–molecular force in such solids is less than ordinary solids, hence high–energy molecules at solid surface overcome the attractive forces and directly pass into vapours.

2– Classification of solids:– Solids have been classified mainly as:

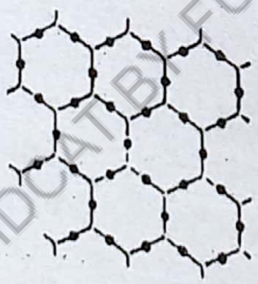
(i) Crystalline (ii) Amorphous

(i) Crystalline solids:– Crystalline solids have characteristic geometrical shape due to highly ordered three dimensional arrangement of particles. They are bounded by plane surfaces called faces; which intersect each other at particular angles.

The reason for the formation of regular pattern or crystal is that atoms or ions or molecules tend to arrange themselves in positions of maximum attraction or in positions of minimum energy. Examples are: sugar, alum, metals, diamonds etc.

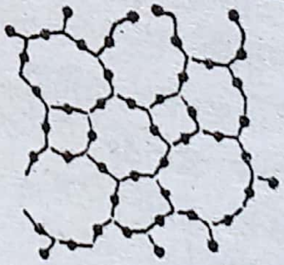
(ii) Amorphous solids:– These are the solids which do not have a definite shape. The word amorphous means "without form".

The particles of such solids have a random i.e. non–repetitive three dimensional arrangements. If a substance in liquid state is cooled rapidly, the particles are unable to arrange themselves in an orderly fashion, hence an amorphous solid results. Examples are: glass, plastic, rubber etc.



Crystalline quartz

FIGURE. 2.18



Amorphous quartz
It is formed when crystalline quartz is melted and cooled rapidly.

FIGURE. 2.19

The difference between crystalline and amorphous solids is summarized below:

Crystalline Solids	Amorphous Solids
(i) Geometry	
Particles of crystalline solids are arranged in an orderly three dimensional network called crystal lattice, hence they have definite shape.	Particles of amorphous solids are not arranged in a definite pattern, hence they do not have a definite shape.
(ii) Melting point	
Crystalline solids have sharp melting point, this is because attractive forces between particles are long range and uniform. These forces breakdown at the same instant, at melting point.	Amorphous solids melt over a wide range of temperature i.e. they do not have sharp melting point, because the inter-molecular forces vary from place to place.
(iii) Cleavage and cleavage plane	
The breakage of a big crystal into smaller crystals of identical shape is called cleavage. Crystals cleavage along particular direction, the plane which contains the direction of cleavage is called cleavage plane.	Amorphous solids do not break down at fixed cleavage planes.

Crystal before cleavage

FIGURE.2.20

Crystal after cleavage

Note: Smaller parts are of same shape as big crystal.

FIGURE.2.21

Crystalline Solids	Amorphous Solids
(iv) Anisotropy and isotropy	
Physical properties of crystals such as electrical conductivity, refrac-	Amorphous solids are isotropic i.e. their physical properties are

tive index, etc. are different in different direction. This property is called anisotropy. For example graphite can conduct electricity parallel to its plane of layers but not perpendicular to plane.

same in all directions.

(v) Symmetry

When crystalline solids are rotated about an axis, their appearance does not change i.e. they possess symmetry.

Amorphous solids are not symmetrical.

2.12 TYPES OF CRYSTALS

Crystals are classified in the following four types:
(i) Atomic crystals (ii) Ionic crystals (iii) Covalent crystals
(iv) Molecular crystals

This classification is based on the nature of forces or bonding between the atoms, ions or molecules constituting the crystal.

(i) Atomic crystals:– Examples of such crystals are metals, hence they are also called metallic crystals. They consist of atoms packed and held together by metallic bond.

In metals, the valence electrons move freely in crystal lattice and are said to form an electron gas, in which positive ions are immersed. Such crystals are characterised by:
(a) Lustre (b) High melting point (c) Electrical and thermal conductivity (d) Malleability (drawing into sheets) (e) Ductility (drawn into wires).

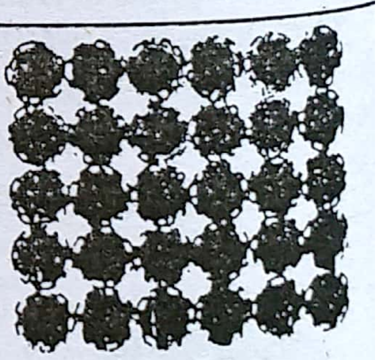
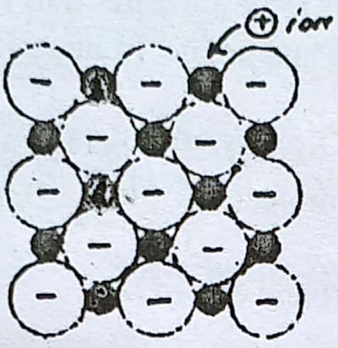


FIGURE:2.22

Two dimensional view of atomic crystals. Atoms vibrate at their mean position.

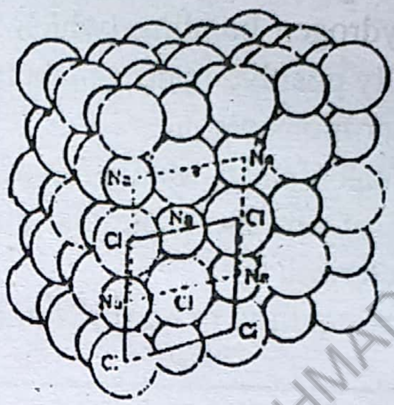
(ii) Ionic crystals:– Such crystals consist of positively and negatively charg ions, held together by electrostatic forces of attraction. Individual ions have identity. They are characterised by:
(a) High melting point (b) Conduction of electricity in fused state; as well as solution form. (c) Brittleness and hardness (d) Indefinite growth of crystal, u

it is broken or is stopped from growing.



Two dimensional view of ions in ionic crystal.

FIGURE.2.23



Three dimensional view of ions packing in Na Cl

FIGURE.2.24

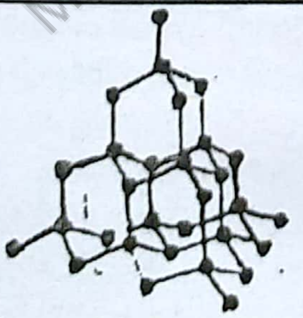
(iii) Covalent crystals:– Such crystals consist of atoms held together by covalent bonds. Covalent bonds are very strong. They require large amount of energy to break them. Examples of covalent crystals are: graphite, diamond, silica and carborundum.

In diamond each carbon atom is joined to four other carbon atoms at an angle of 109°, called tetrahedral angle. Due to close packing of atoms and large number of covalent bonds, diamond is very hard and has high melting point.

In graphite each carbon atom is joined to three other carbon atoms at an angle of 120°, forming layers of hexagons. Adjacent layers are held together by weak Vander waal's forces. Due to space between layers graphite is soft and as layers easily slide over one another so graphite has greasy texture. Graphite conducts electricity in the plane of layers, as each carbon has one free electron.

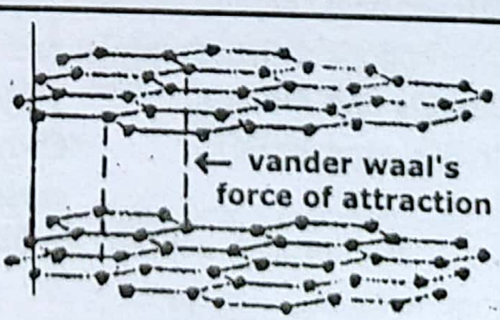
Covalent crystals are characterised by:

(a) High melting point (b) Low density (c) High refractive index



Space lattice of diamond

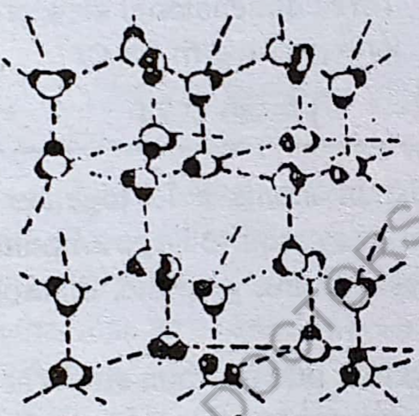
FIGURE.2.25



Space lattice of graphite

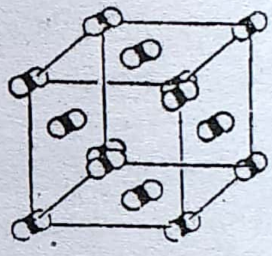
FIGURE.2.26

(iv) Molecular crystals:– Such crystals are composed of molecules, such as ice, I_2, CO_2. The molecules are held together either by the following forces:
(a) Hydrogen bonding (which is an electrostatic force of attraction between partially positive hydrogen atom of one molecule and an electronegative atom of other molecules).
(b) Weak Vander waal's forces (which arise due to attraction between atomic nuclei of one molecule and electrons of other molecule). Such crystals are characterised by:
(a) Low melting point (b) Non-conduction of heat and electricity.



Structure of ice
Each water molecule is attached to four others through hydrogen bonding.

FIGURE:2.27



Unit cell of solid CO_2

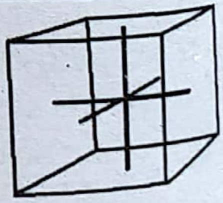
FIGURE:2.28

2.13 ISOMORPHISM

When two substances have same crystal structure, they are said to be isomorphous and phenomenon is called isomorphism. For example NaF and MgO both form cubic crystals hence are isomorphous. Other examples are:

$CaCO_3$ and $NaNO_3$	Trigonal crystals
$ZnSO_4$ and $NiSO_4$	Orthorhombic crystals

Isomorphic substances have following properties:
(i) They have different physical and chemical properties.



A cube

A cube crystal

FIGURE:2.29

(ii) They have same empirical formula.

Pairs	Ratio in atoms
NaF and MgO	1:1
$NaNO_3$ and $CaCO_3$	1:1:3
$ZnSO_4$ and $NiSO_4$	1:1:4

(iii) When their solutions are mixed, they form mixed crystals.

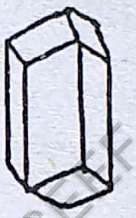
(iv) They show property of over growth; i.e. if crystal of one substance is suspended in saturated solution of other substance, the crystals of latter begin to grow over the former in similar pattern.

2.14 POLYMORPHISM

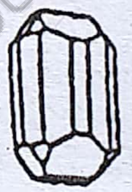
A substance under different conditions can form more than one type of crystal.

The substance which can exist in more than one crystalline form is called Polymorphous and the phenomenon is known as Polymorphism. For example $CaCO_3$ exists in nature in two crystalline form (i) Calcite, which is trigonal (ii) Aragonite, which is orthorhombic

FIGURE:2.30



Trigonal crystal



Orthorhombic crystal

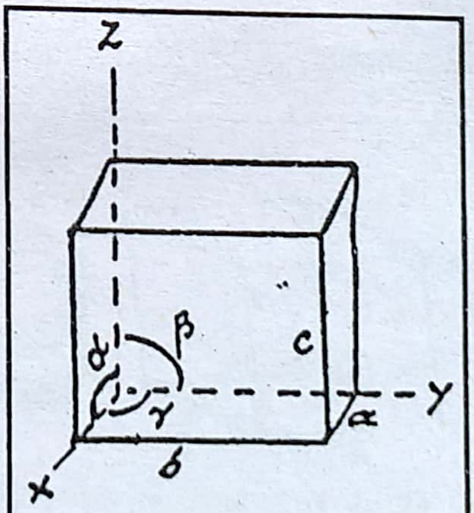
FIGURE:2.30

UNIT CELL: A crystal is formed by a large number of repetition of basic pattern of atoms, ions or molecules in space.

The basic structural unit which when repeated in three dimensions generates the crystal structure is called a unit cell.

A unit cell has a definite geometric shape and hence is identified on the basis of (i) Length of its edges, denoted by letters, a , b and c. (ii) Angle between the edges, represented by letters, α, β and γ.

The length and angles of a unit cell are collectively known as Cell Dimensions or Cell Parameters.

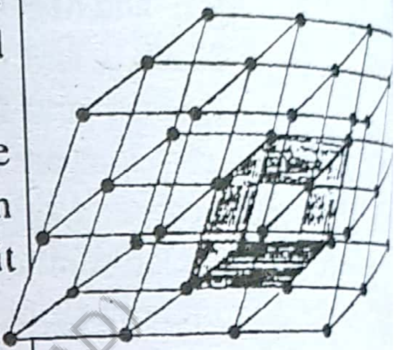


Parameters of a unit cell.

FIGURE:2.31

Space or crystal lattice:– If atoms, ions or molecules constituting a crystal are replaced by points and placed at the same places as in a unit cell, then the three dimensional array of points is called crystal lattice or space lattice.

All points in a crystal lattice have same environment and can not be distinguished from each other. Three dimensional lattice with a unit cell is shown in the diagram.



Crystal lattice
with a unit cell
FIGURE:2.32

The crystal systems:–Based on the difference in shapes and dimensions of unit cells, all the known crystals have been classified into seven groups called crystal systems. The seven crystal systems are as follows:

(i) Cubic system:– In cubic system, all axes are of equal length and all angles are of 90° i.e.

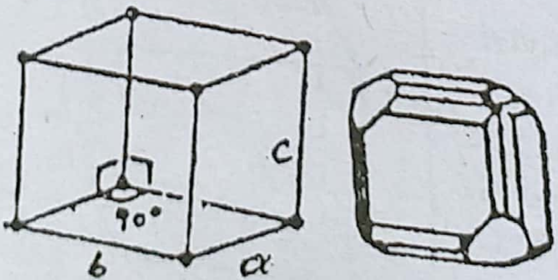
$$a = b = c$$
$$\alpha = \beta = \gamma = 90^\circ$$

Examples: NaCl, ZnS and diamond.

(ii) Tetragonal system:– It has two axes of equal length, the third is differe All angles are of 90° i.e.

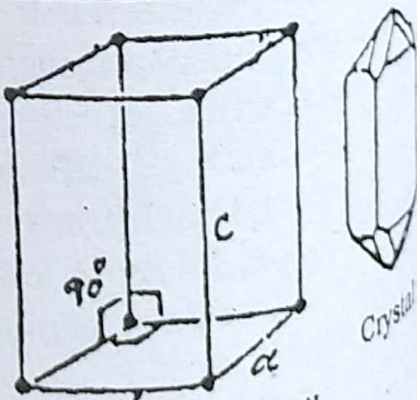
$$a = b \neq c$$
$$\alpha = \beta = \gamma = 90^\circ$$

Examples: SnO_2(white), $BaSO_4 \cdot 4H_2O$



Cubic unit cell Crystal

FIGURE:2.33



Tetragonal unit cell Crysta

FIGURE:2.34

(iii) Orthorhombic system:– In this system, all three axes are of di length; but all angles are of 90° i.e.

$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

Examples are: $FeSO_4 \cdot 7H_2O$, $ZnSO_4 \cdot 7H_2O$, KNO_3

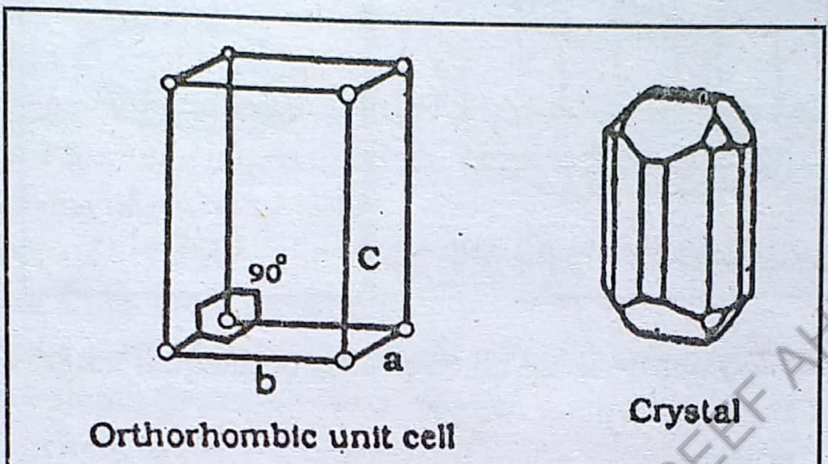


FIGURE:2.35

(iv) Trigonal or rhombohedral system:– It has three axes of equal length. All angles are equal but more than 90° and less than 120° i.e.

$a = b = c$
$\alpha = \beta = \gamma \neq 90°$
(Angles >90°<120°)

Examples: Calcite, KNO_3, $AgNO_3$, and ice.

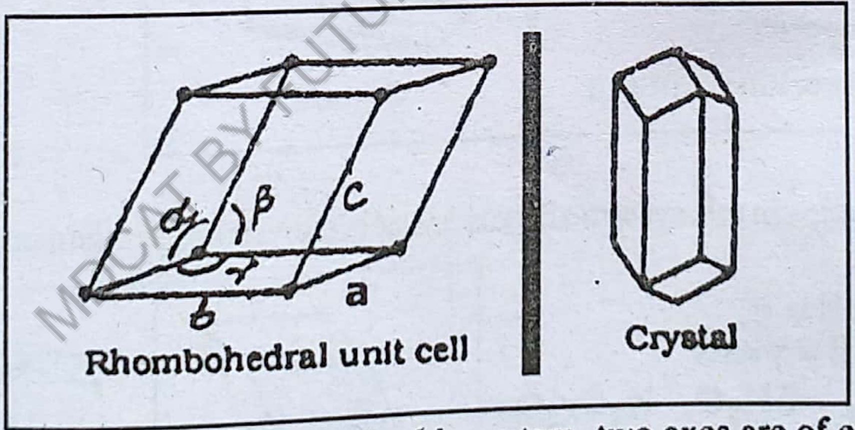


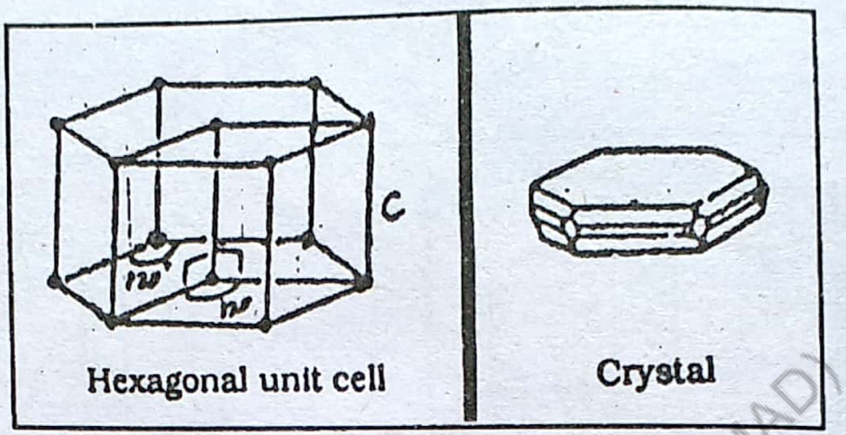
FIGURE:2.36

(v) Hexagonal system:– In this system, two axes are of equal length, but the third is different. Two angles are of 90° and third is of 120° i.e.

$a = b \neq c$
$\alpha = \beta = 90°$
$\gamma = 120°$

Examples: Graphite, snowflakes and quartz (SiO_2)

FIGURE:2.37

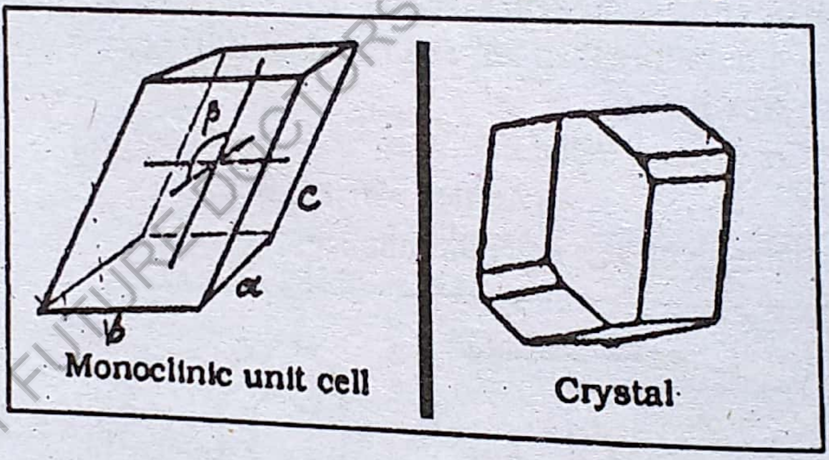


(vi) Mono clinic system:– It has all three axes of unequal lengths. One of the axis is at right angle to the other two i.e.

$$a \neq b \neq c$$
$$\alpha = \gamma = 90^\circ$$
$$\beta \neq 90^\circ$$

Examples: $CuSO_4$ $5H_2O$, Na_2CO_3 $10H_2O$, cane sugar.

FIGURE:2.38

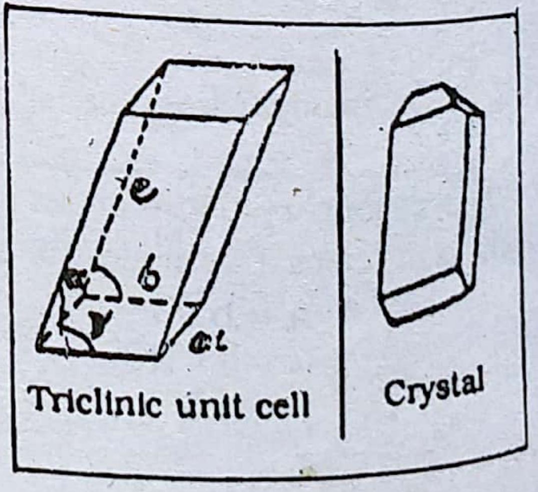


(vii) Triclinic system:– In this system all axes are of different lengths and angles are also different.

$$a \neq b \neq c$$
$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$

Examples: $CuSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$

FIGURE:2.39



2.15 CHANGE OF STATE (MELTING OR FUSION)

(i) The melting point:– When a pure crystalline solid is heated, a temperature is reached where it changes sharply into liquid. This is melting point of solid. Melting point is defined as that temperature at which there is equilibrium between solid and liquid phases.

Melting point is affected by: **(a) Impurity:–** Pure substances have sharp melting point. Moreover impurities lower the melting point. Hence melting point is used as criteria of purity of solids.

(b) Pressure:– Those substances which expand on melting, have a rise in melting point when pressure is increased.

Melting point of ice decreases on applying pressure because ice is the solid whose volume decreases on melting.

(ii) The latent heat of fusion:– It is defined as the heat energy required to change 1 g of a solid into liquid at its melting point.

Even though heat is being supplied during melting but temperature remains constant because all of the energy is used up by the molecules to over come the intermolecular forces.

PROGRESS TEST 2

1. In terms of the atoms, ions, and molecules that comprise substances, why are some materials solids, some liquids and still others gases at 25°C.?

2. The process of diffusion occurs most rapidly in gases, less rapidly in liquids, and very slowly in solids. Why?

3. Why does water spilled on a floor evaporate more rapidly than the same amount of water in a glass?

4. Would a pressure cooker be of any value on the Mount Everest?

5. No liquid ionic compounds are known, but many of the known covalent compounds are liquids and some are gases. Account for these differences.

6. What is kinetic theory and how does it account for the following properties of gases, liquids and solids?
   (i) Diffusibility (ii) Compression (iii) Expansion

7. 1.40 dm^3 volume of a gas measured at a temperature of 27°C and a pressure of 900 torr was found to have mass 2.273 g. Calculate the molecular mass of the gas [Hint: Calculate "n" by the formula $PV=nRT$ and then molecular mass] (33.72 amu) Ans.

8. A 12.5 dm^3 vessel contains 4.0 g CH_4, 1.8 g N_2 and 10.0g Xe. What is the pressure in the vessel at 0°C?(0.698 atm) Ans.
   (Hint: Find out the total moles of the gases and then apply $PV = nRT$).

9. (a) State and explain the Graham's law of Diffusion.
   (b) Compare the rates of diffusion of the following pairs of gases:
   (i) H_2 and D_2 (ii) CH_4 and He (iii) SF_6 and SO_2 [(i) 1.41/1, (ii) 2/1, (iii) 1.5/1. Ans.

10. State the following gas laws and explain in terms of Kinetic theory.
(a) Boyle's law (b) Charles's law (c) Dalton's law of partial pressure.

11. Define the following :(i) Melting point (ii) Boiling point (iii) Diffusion (iv) Latent heat of fusion.

12. Four containers of equal volume are filled as follows:
(i) 2.0g H_2 at 0°C (ii) 1.0g H_2 at 273°C (iii) 24 g O_2 at 0°C
(iv) 16 g CH_4 at 273°C.
Which container (a) is at the greatest pressure (b) is at the lowest pressure.
[a = (iv) b = (iii)] Ans.

13. Explain the relationship between intermolecular attractions and the kinetic energy of molecules in determining the physical state of a substance.

14. Describe gases, liquids and solids on a molecular basis and explain their behaviour and change of state.

15. Co-relate the energy changes accompanying changes of state.

16. Explain in terms of kinetic molecular model:
(a) Why liquids and solids cannot be compressed as gases can?
(b) Why solids do not flow as liquids and gases do?
(c) Why food is cooked more quickly in a pressure cooker than in a covered pot?

17. Explain (i) Viscosity (ii) Surface tension (iii) Vapour pressure.

18. What are crystalline and amorphous solids ? Explain different crystal systems.

19. State and explain Avogadro's law. How it helps in determining relative molecular mass?

20. What are solids? Describe Atomic, Ionic and Molecular solids.

21. Explain the following:
    - (i) A falling drop of a liquid is spherical.
    - (ii) A drop of ink spreads on a blotting paper.
    - (iii) Evaporation is a cooling process.
    - (iv) Boiling point of a liquid remains constant although heat is continuously supplied to the liquid.
    - (v) Honey is more viscous than water.
    - (vi) Mercury has its meniscus upward.

22. 40 dm^3 of hydrogen gas was collected over water at 831 torr Hg pressure at 23°C. What would be the volume of dry hydrogen gas at standard conditions ? The vapour pressure of water at 23°C is 21 torr of Hg.

    (Ans :– 39.23 dm^3).

23. What is the density of methane gas (CH_4) at 127°C and 3.50 atmosphere.

    (Ans:– density = 1.70 g/dm^3).

CHAPTER - 3

THE ATOMIC STRUCTURE

INTRODUCTION

The theory that matter was made from small indivisible particles called atoms dates back to some five centuries B.C. to Democritos and a century B.C to a Roman Poet Leukiphos. This theory was put on a sound scientific basis by John Dalton in 1808.

Today it is well established that atoms are complex organizations of matter and energy. Many particles have been discovered within the atom. These sub-atomic particles include electron, proton, neutron, positron, neutrino and several types of mesons and hyprons etc. Since electrons, protons and neutrons in atom play a major role in determining the chemical and physical properties of matter, we will, therefore, restrict ourselves to the study of these particles.

Evidence for the presence of electrons, protons and neutrons in the atom is derived through many experiments such as:

(i) Faraday's experiment indicates the existence of electrons.
(ii) Crooke's tube experiments show the presence of electron and protons in the atoms.
(iii) Radioactivity further confirms the presence of electrons and protons.

(iv) Chadwick experiment shows the presence of neutrons.

(v) Spectroscopic experiments reveal the electronic structure of atoms. These are discussed one by one.

3.1 FARADAY'S EXPERIMENT – Passage of Electricity through solutions

Clue about Electrons: We first consider the passage of electricity through chemical solutions called *electrolytes*. Earlier Davy had noticed that electric charges appear when solutions decompose by the passage of an electric current. Later this phenomenon was studied in greater details by Faraday.

Faraday observed that, when two metal plates called electrodes, are placed in an electrolytic solution and an electric current is passed, the solution breaks up into charged particles called ions. There are positive ions and negative ions, depending upon the type of charge they carry. These ions travel to the oppositely charged electrodes, give up their charge and are liberated as neutral particles. He also determined the charges carried by different ions and also the amount of different elements liberated from the electrolytic solution when a given amount of charge passes through different electrolytic solutions. What is of interest here, is that there is some elementary unit of electric charge associated with these ions which can be calculated. The ions were observed to carry some integral multiple of this charge. The basic unit of electric charge was later named by Stoney (1891), as "ELECTRON".

3.2 CROOKES'S TUBE OR DISCHARGE TUBE EXPERIMENTS—Passage of electricity through gases at low pressure

Discovery of Electrons and Protons : We know that air or gases normally do not conduct electricity, unless a very high voltage is applied. The work on the passage of electricity through gases was initiated by a German instrument maker Heinrich Geissler. This work was later extended by W. CROOKES.

To appreciate what happens when an electric current passes through some gas, imagine two metal plates, known as electrodes sealed in a glass tube containing some gas. The tube is provided with an outlet through which gas inside the tube can be evacuated at will. At ordinary pressure, unless very high potential difference is applied, there would be no discharge, and the electric spark cannot be made to pass from one electrode to the other. If the gas inside is gradually pumped out of the tube, the number of molecules of gas present inside is reduced.

and fewer molecules inside make it convenient for the spark to pass.

When the pressure inside the tube is reduced to a centimetre of Hg, a potential difference of a few thousand volts would be enough for the spark to pass like a flash of lightening (Fig: 3.1) At further reducing pressure to about a few

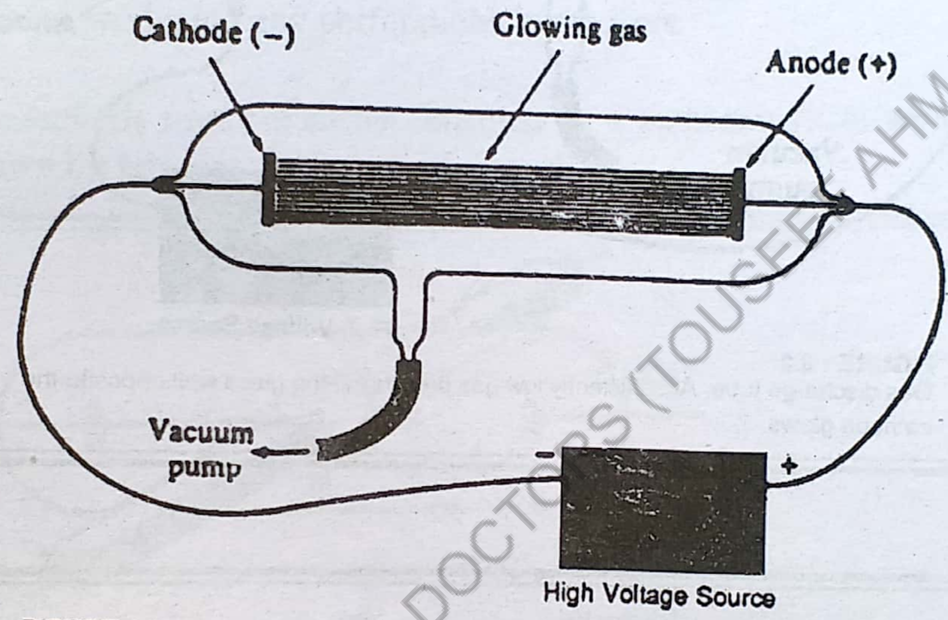


FIGURE 3.1
Gas discharge tube. The gas is seen to glow in the region between the electrodes

m.m of Hg, the spark disappears, the two electrodes are seen to glow and the rest of the discharge stream is dark. At about one m.m. of Hg, the tube is mostly filled with a glow extending from the positive electrode and is called positive column. The colour of this glow depends upon the gas filled in the tube. As the pressure is continuously lowered, beautiful phenomena are seen. When the pressure inside the tube is lowered to about 0.001 m.m of Hg, the glow disappears and the walls of the glass tube begin to glow with a brilliant green light (Fig. 3.2)

It is obvious that some sort of radiation is passing between the two electrodes. This radiation consisted of a vast swarm of particles emitted by the cathode and were called Cathode Rays. Various experiments were thus performed by various researchers like Hertz, Lenard, Gold stein, Perrin and J.J. Thomson to determine the properties of these cathode rays.

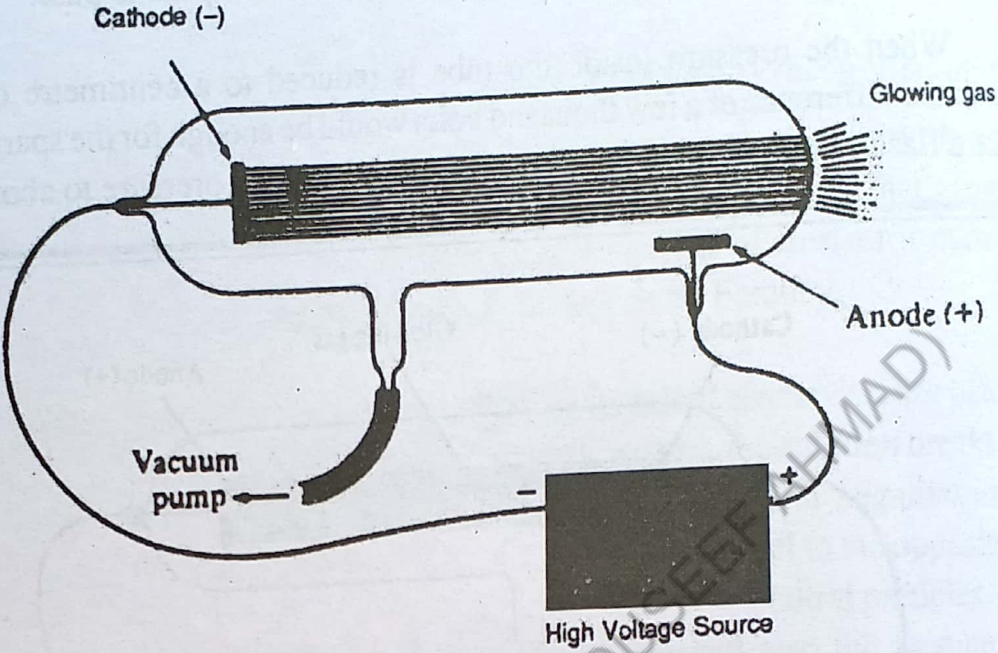


FIGURE : 3.2
Gas discharge tube. At sufficiently low gas pressures, the glass wall opposite the cathode glows.

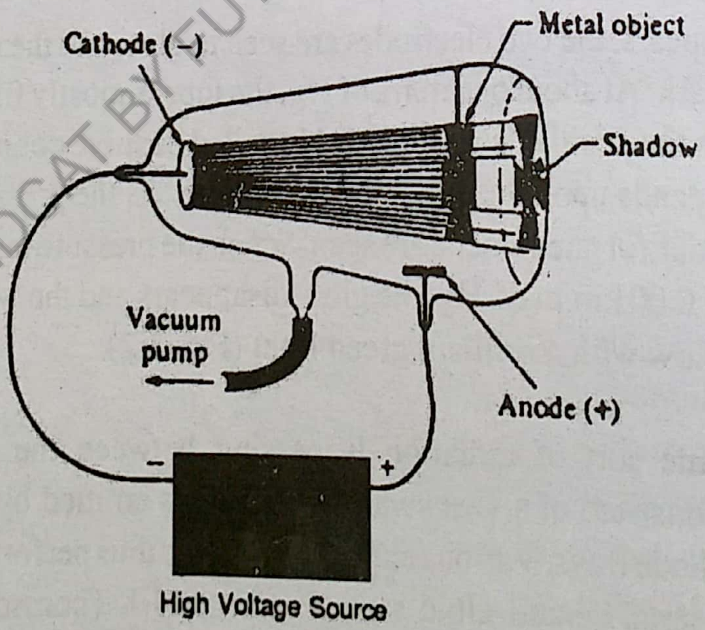


FIGURE : 3.3
Cathode ray tube. An object in the beam of the cathode rays casts its shadow.

The cathode rays were seen to possess the following properties:

1. The rays travel in straight lines, as they produce sharp shadows of objects placed in their path.

2. The rays emerge normally from the cathode and can be focused by using a concave cathode.

3. The rays penetrate small thicknesses of matter, like aluminium or gold foil without producing any perforations in the foils.

4. The cathode rays are easily deflected by a magnetic field, which can be shown by bringing a magnet close to them.

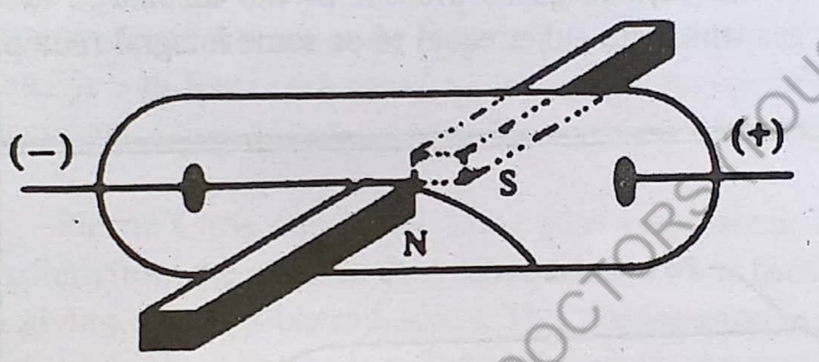


FIGURE 3.4
The behaviour of the negatively charged electron in a magnetic field.

5. The rays carry a negative charge.

6. The rays can also be easily deflected by an electrostatic field.

7. The rays can exert mechanical pressure, showing they possess kinetic energy.

8. The rays were seen neither to depend upon the material of which the electrodes were made nor upon the gas which is filled in the tube.

9. These rays consist of particles now called *Electrons* carrying a fixed unit of charge and a fixed mass.

Different discharge tubes with different electrodes and residual gases were tried by a number of workers besides Thomson. All the experiments gave the same value for charge to mass ratio (e/m). This shows that electrons could be produced from any kind of matter and hence perhaps were constituent of all matter.

3.3 POSITIVE RAYS – Protons

During the study of the passage of electricity through gases at low pressure, it was observed by Goldstein that if thin holes are made in the cathode, then some radiations appear behind the cathode (Fig. 3.5). These rays were found to be positively charged and hence called positive rays. It was found that these rays consist of atoms and ions of the various gases present in the discharge tube. They carry positive charges which are either equal to or some integral multiple of the electronic charge 'e'.

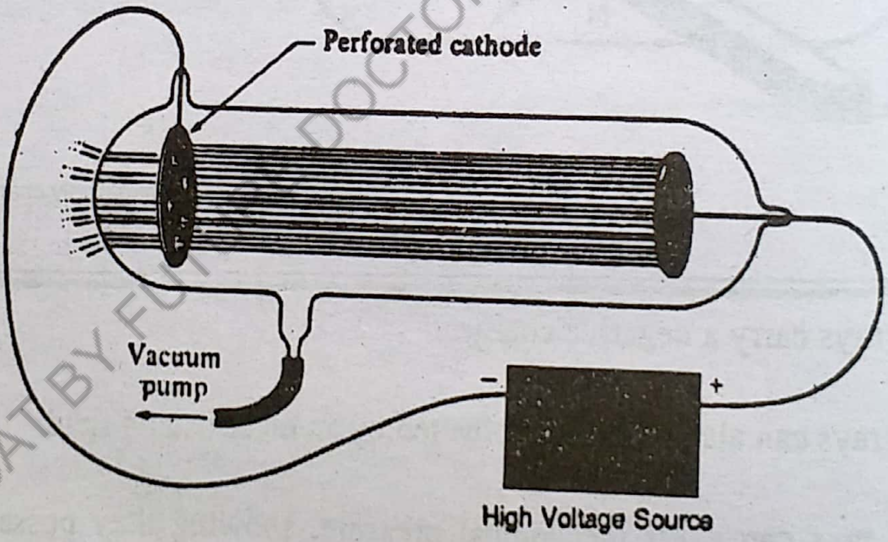


FIGURE 3.5
Cathode ray tube with a perforated cathode. Positive canal rays pass through the cathode and cause the glass wall to glow.

J.J. Thomson discovered that positive rays, unlike cathode rays, have values of e/m dependent on the gas present in the Crookes's tube. The lightest particle found, was that from hydrogen. This particle, which has a mass

1836 times that of the electron is now known as proton (Greek, "first").

3.4 RADIOACTIVITY – Confirmation of Electrons and Protons

It was thought that the electrons are emitted by atoms of various substances. When they are subjected to an external field or heated to high temperatures then a new phenomenon was observed. A new mineral pitchblende was found to produce a clear image of itself even when the photographic plate was wrapped in a thick black paper and there was no light. Henry Becqueral repeated his experiments under different conditions and found that only when the mineral pitchblende was wrapped in lead sheet, the radiation coming out of it could be stopped. The pitchblende could be heated or cooled, it might be compressed or made into thin sheet. All these changes had no effect on the radiations that were coming out of this mineral. This emission of charge went on at a uniform rate. Later it was found that most of the radiation given out by pitchblende were electrons.

Pierrie Curie and Marie Curie after great labour isolated a new element Radium from the mineral. This element radium was found to be extremely active in giving out invisible radiations. This phenomenon in which certain elements emit invisible radiation is called *radioactivity* and the elements which give out these radiations are called *radioactive elements*. Most of the elements after lead in the periodic table are naturally radioactive.

The radiation emitted by radium was subjected to a magnetic field prependicular to the direction of emission. If the magnetic field was strong enough, the radiations emitted were found to split up into three different streams of rays, which were labelled α, β and γ - rays.

The α-rays were found to carry positive charge and the β-rays a negative charge. The third, the γ-rays, remained undeflected no matter how strong was the magnetic field and hence were considered to be uncharged. The γ-rays were found to be extremely penetrating and hence identified with x-rays.

An element after giving out radiations breaks down to a more stable element. For example $^{238}_{92}U$ on emission of α - particles would be converted to $^{234}_{90}Th$

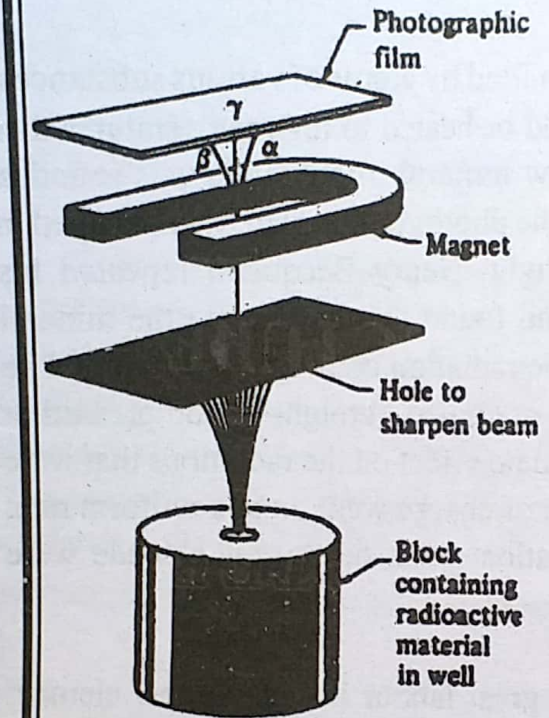


FIGURE 3.6
Rays given off by a radioactive material are separated in a magnetic field. The negatively charged β rays are deflected in one direction, the positively charged α rays are deflected in the opposite direction, and the uncharged γ- rays are not deflected.

$$^{238}_{92}U \longrightarrow ^{234}_{90}Th + ^{4}_{2}He$$

α - Particle

The emission of radiation would continue until the formation of lead as stable end product.

Properties of these radiations are summarized below :

1. α-rays are fast moving helium nuclei. They ionize air i.e. they knock out electrons from other atoms. They produce bright flashes on fluorescent screen and have a very small range (1-2 cm) in air, before they are completely stopped.

2. β-rays are fast moving electrons with a range of (1-2 m) in air and can pass through small thickness of matter.

3. γ-rays are very penetrating. These are short wave electro-magnetic radiations like x-rays, only that these are much more penetrating. These rays will pass through (15-20 cm) of lead. On passing through matter, γ-rays would eject high speed electrons from the matter.

The evidence of radioactivity shows that the atom is not an indivisible particle. If it can emit electrons and helium nuclei, it must have a sub structure of its own.

3.5 CHADWICK EXPERIMENT — Discovery of Neutron

Chadwick investigated the effect of the radiation on other elements both in the solid and in the gaseous form. During his studies with beryllium, Chadwick found that very penetrating radiations were given out when beryllium was bombarded with α - particles. Chadwick put forward the suggestion that these penetrating radiations were due to material particles with mass comparable with that of an atom of hydrogen but carrying no charge. These particles were called neutrons. The neutrons must have come out from atoms on disintegration of the bombarded element. This is indicated by the equation.

$$ {}_4Be^9 + {}_2He^4 \longrightarrow {}_6C^{12} + {}_0n^1 $$

We have so far seen three particles which come out of atoms on their disintegration and these are:

(a) Electrons, which carry a negative charge of 4.803×10^{-10} esu $= 1.602 \times 10^{-19}$ coulombs with $e/m = 1.758 \times 10^8$ C/g and $m_e = 9.115 \times 10^{-31}$ Kg $= 0.000550$ amu.

(b) *Proton* carries a positive charge equal to that of an electron

$m_p = 1.008$ amu

(c) *Neutron* carries no charge but has a mass $m_n = 1.009$ amu

3.6 SPECTROSCOPIC EXPERIMENTS — Spectroscopy

Electronic Structure of Atom:

Once the presence of fundamental particles was established, the next question concerned the electronic structure of atom. This objective was mainly achieved through *spectroscopic experiments* which investigate the electromegnetic radiation emitted or absorbed by the substances. At this point, it is appropriate to describe briefly the *Planck's Quantum Theory* which had tremendous impact on the development of the theory of structure of atom.

3.7 PLANCK'S QUANTUM THEORY - Quantization of Energy

This theory was proposed in 1900 by the German physicist *Max Planck* to account for the observed radiations from heated bodies.

Max Planck suggested that the energy could not be absorbed or emitted by the atoms in any arbitrary quantity, but only in specified amounts called *quanta*. That is to say, an atom cannot change its energy continuously but only by a series of steps. The amount of energy depends upon the frequency (υ) of radiation absorbed or emitted. It is given by relation:

$E = h\upsilon$ where h = Planck's constant (6.625×10^{-34} J.S.
$= 6.625 \times 10^{-27}$ erg. S)

The main consequence of Planck's quantum theory is that the amount of energy gained or lost is quantized i.e., energy change occurs in small packets or multiple of those packets, $h\upsilon$, $2h\upsilon$, $3h\upsilon$ and so on.

3.8 SPECTRA

Our knowledge of the way in which electrons are distributed in atoms comes largely from the evidence of spectra.

When an element absorbs sufficient energy, for example, from a flame or an electric arc, it emits radiant energy. When this radiation is passed through a prism in a spectroscope, it is separated into component wave lengths to form an image called an Emission spectrum. Emission spectra are of two types, continuous and line spectrum.

Continuous Spectrum: When white light from sun or any incandescent lamp is allowed to pass through a prism, the light is not only deviated, but also breaks up into its constituent colours, a phenomenon called dispersion. The band of colours into which the incident light breaks up is called spectrum.

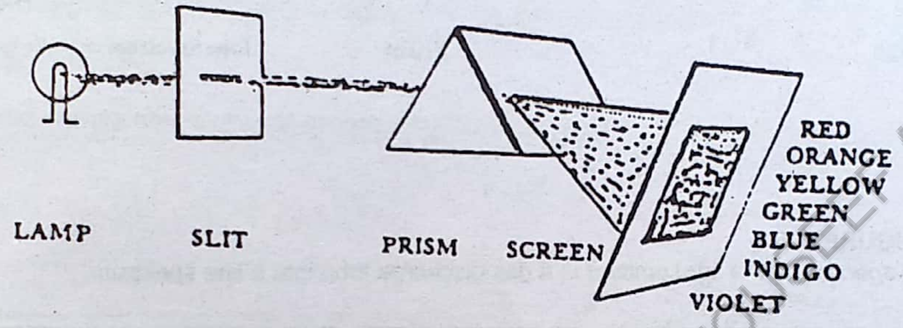


FIGURE 3.7
Continuous spectrum.

The white light gives a continuous band of colours. On one end the least deviated is red and at the other end is violet which suffers the maximum deviation. The colours of the spectrum are so mixed up that there is no line of demarcation between different colours. Such spectrum is called continuous spectrum. It is given not only by sunlight but also by the light from any hot solid or liquid body. The colour of light depends on its wave length. Violet has the shortest wave length (about 4000Å), and red light the longest (about 7000 Å). Light of a single wave length is called monochromatic.

Line Spectrum : A different kind of spectrum may be obtained when light emitted from a gas source passes through a prism. In order to emit light, the gas must be excited in some way. A common way of doing this is to pass an electric current through the gas at low pressure (Crookes's tube experiment). The neon lights used in advertisement make use of this method for producing light and so do sodium vapour street lights. If the light from the discharge tube is allowed to pass through a prism, some discrete sharp lines on an otherwise completely dark back ground are obtained. Such spectrum is called *line spectrum*. Each line corresponds to a definite wave length.

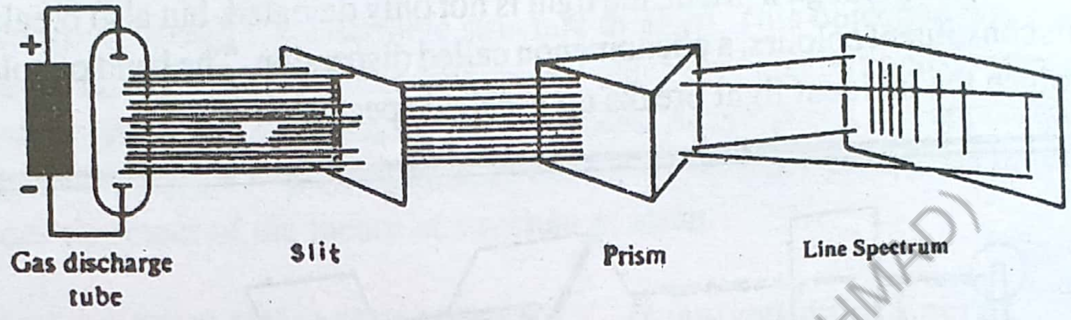


FIGURE 3.8
Dispersion of the light emitted in a gas discharge tube into a line spectrum.

On analysis of the sodium vapour light through a prism, it is found that the spectrum consists of a series of lines. The dominant lines in this area are the two yellow lines which give sodium vapour lamps their characteristic colour. Each element produces a characteristic set of lines, so *line spectra came to serve* as *"finger prints"* for the identification of elements.

The facts are that (1) samples of the same element always emit the same wave lengths of radiation and (2) under the right conditions only certain wave lengths are emitted by any one element. This leads to the belief that electrons are arranged around the nucleus in definite energy levels, E_1 and when they are excited they go to definite excited levels E_2. This means that the difference in the energy of electrons, $E_2 - E_1$ is same for a given transition and this explains the fact that the energies emitted by a given excited element always have the same wave lengths.

3.9 RUTHERFORD'S MODEL OF AN ATOM – Evidence for Nucleus and Arrangement of Particles.

Though the nature of the proton was well established by 1900, the role of this positive particle in the structure of atom was uncertain. A clue to the arrangement of positive and negative particles within atoms was finally provided by the experiments of Rutherford.

Rutherford and his co-workers performed several experiments on the scattering of α-particles by thin films. In one of such experiments α-particles emitted from polonium bombarded on thin gold foil, it was found that most of the α-particles penetrated the foil and emerged undeflected on the other side. However, one particle in 8000 suffered a deflection greater than 90° and remerged on the same side. A number of particles suffered deflections of varying degrees.

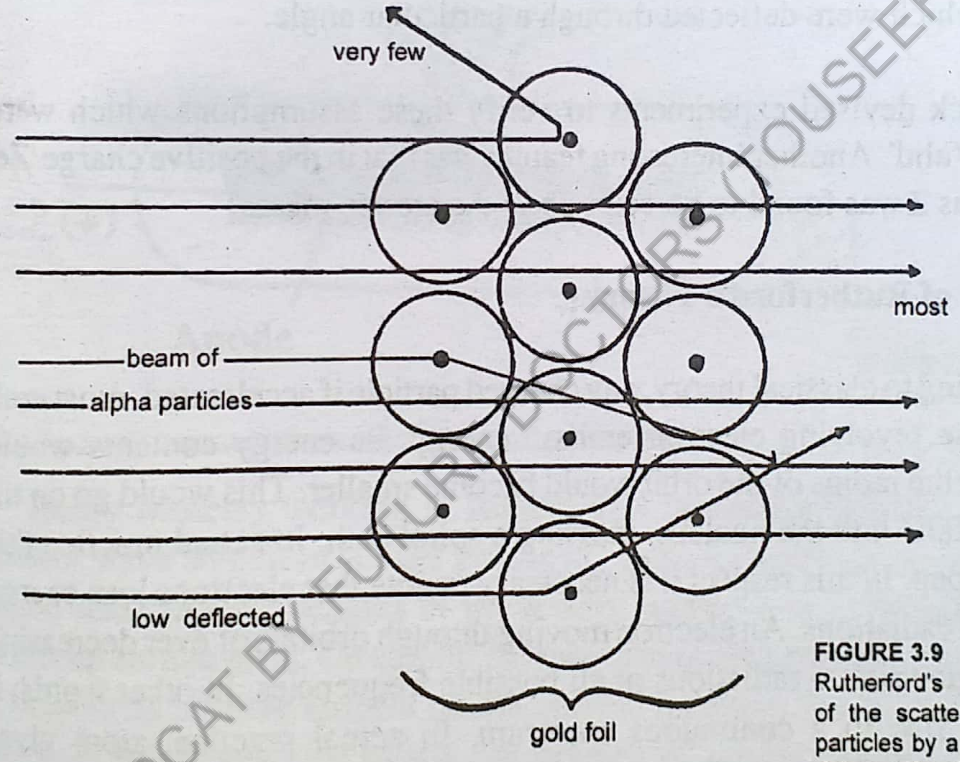


FIGURE 3.9 Rutherford's interpretation of the scattering of alpha particles by a gold foil. The dots on the right represent the nuclei of the gold atoms greatly magnified relative to the sizes of the atoms.

To explain this scattering of α-rays, Rutherford made some basic assumptions:

(a) The mass of the atom is concentrated in its nucleus, the dimensions of which are negligible in comparison with the radius of the atom.

(b) The nucleus carries a positive charge,'+ Ze'

(c) There must be 'z' number of negatively charged electrons outside the nucleus and at fairly large distances, arranged in some manner.

(d) The greater part of the atomic volume comprises of empty space in which the electrons revolve and spin.

On these assumptions, Rutherford derived an expression, giving the number of particles which were deflected through a particular angle.

Chadwick devised experiments to verify these assumptions which were found to be 'Valid'. Another interesting feature was that in the positive charge 'Ze' on the nucleus Z was found to be nearly half the atomic mass.

Weaknesses of Rutherford's Theory :

According to classical theory, any charged particle if accelerated, must emit energy. If the revolving electron emits energy, its energy contents would decrease and the radius of the orbit would become smaller. This would go on till the electron falls into the nucleus, charting a spiral path. In actual practice this does not happen. In this respect it is necessary to note that electrons lose energy in the form of radiations. An electron moving through orbitals of ever decreasing radii would give rise to radiations of all possible frequencies. In other words, it would given rise to a continuous spectrum. In actual practice, atom gives discontinuous spectrum. Thus according to classical principles of physics, the Rutherford model of the atom could not exist.

3.10 X-RAYS AND ATOMIC NUMBER

W. Roentgen in 1895 found that a photographic plate he developed had been struck by invisible radiation coming from a cathode ray tube (Crookes's tube expt.). These previously unknown rays were labelled X-rays. These rays are some times known as Roentgen rays (after the discoverer). These rays had the ability to penetrate paper, rubber, glass, metal and human flesh. X-rays were soon identified as short wave, high energy electromagnetic radiation. They were put to medical uses immediately.

The X-rays arise from the anode of the Crookes's tube experiment as it is struck by the fast moving electrons from the cathode. X-rays have played a vital part in the determination of structure at subatomic levels.

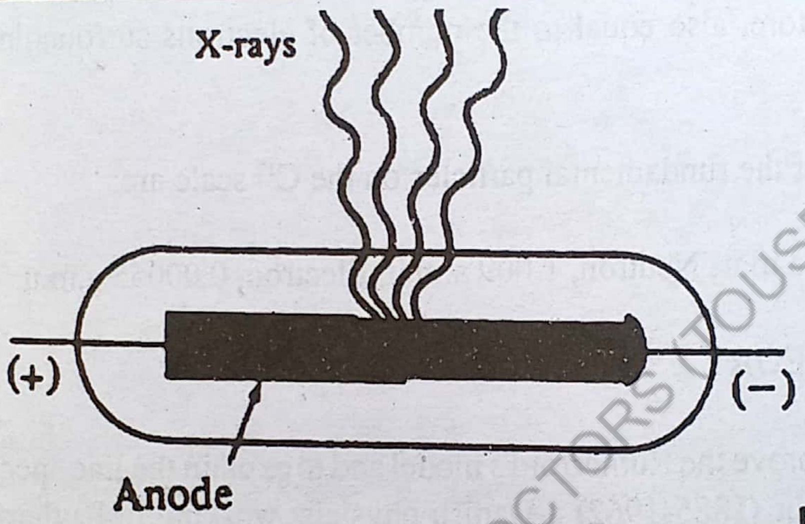


FIGURE 3.10
An X-ray tube.

Henry Moseley working in Rutherford's laboratory in 1911 studied the different wave lengths of X-rays produced from anodes of different metals. He noticed that the wave lengths of the X-rays emitted decreased regularly with increasing atomic mass. On careful examination of his data, Moseley found that the number of positive charges on the nucleus increases from atom to atom by single electronic unit. He called the number of positive charges the atomic *number*. Thus atomic number of an element is the number of protons present in its nucleus. For the first time, it became apparent that what distinguishes one element from another is not the atomic mass, but the nuclear charge, that is, the atomic number. It is denoted by 'Z'.

It is worth mentioning here that Rutherford's theory of the nuclear atom was supported by the Moseley's experiment.

We now have a picture of the atom which can be summarized:

(a) The atom consists of a small, dense, positively charged nucleus, containing protons.

(b) The nucleus is surrounded by a number of electrons equal to the number of protons in the nucleus.

(c) The atomic number 'Z' of an atom is equal to the number of protons in the nucleus and therefore, also equal to the number of electrons surrounding the nucleus.

(d) The masses of the fundamental particles on the C^{12} scale are:

Proton, 1.008 a.m.u, Neutron, 1.009 a.m.u, Electron, 0.00055 a.m.u.

3.11 BOHR'S THEORY

In order to improve the Rutherford's model and to explain the line spectra of elements, Niels Bohr (1885-1962) a Danish physicist working in Rutherford's laboratory proposed a theory for the electronic structure of an atom in 1913.

Bohr assumed that on the basis of the quantum theory, there exists the possibility that electron in certain orbits may not give out radiation and an electron revolving in any one of such orbits would be completely stable. Such orbits were called '*Stationary states.*' Bohr envisioned the stationary states as circular orbits around the nucleus. He considered that an electron in a certain orbit has a certain energy and as long as it keeps revolving in that orbit, it neither absorbs nor radiates energy. If the electron absorbs energy equal to the energy difference between the two orbits, the electron is excited, i.e. it jumps to higher energy state. If it falls back to lower level, it must emit energy equal to the energy difference between the two orbits. (Fig: 3.11). If this energy is absorbed or emitted as light, a single photon (quantum) of absorbed or emitted light must account for the required energy differences, so that

$$h\upsilon = \Delta E$$

Where ΔE is the difference between the energies of the final and initial orbits, h = Planck's constant (6.625×10^{-34} J.S.) which has the dimensions of energy X time.

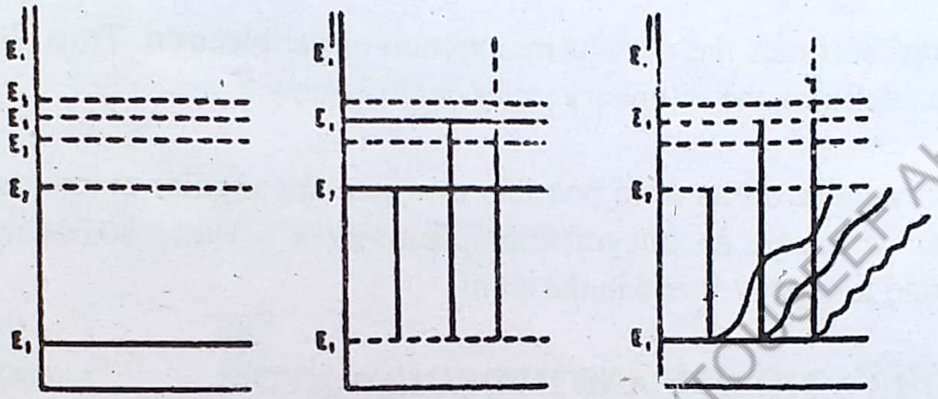


FIGURE 3.11
Excitation of electrons from low energy levels to higher energy levels is a process that requires energy. When electrons fall from the excited levels, e.g., E_2, E_4, or E_1, radiant energy is given off, possibly as visible light.

Bohr assumed that all the transitions that electrons make between two orbits, yield a single unique spectral line.

Bohr further assumed that the stationary states were only those orbits in which the product momentum (mv) x circumference ($2\pi r$), sometimes called the action', was equal to the Planck's constant 'h' or some integral multiple of 'h' therefore for the first possible orbit.

momentum x circumference = h

$$mv \times 2\pi r = h$$

or for any other orbit,

$$mv \times 2\pi r = nh$$

Where 'n' was a simple integer, n = 1 for first orbit, n = 2 for the second and so on.

This equation could be re-written as,

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

Here 'mvr' becomes the angular momentum of the electron. Thus Bohr's first condition defining the stationary states could be stated as,

"Only those orbits were possible in which the angular momentum of the electrons would be an integral multiple of h/2π". These stationary states correspond to energy levels in the atom.

3.12 BOHR'S THEORY AND HYDROGEN ATOM

The truth of the basic assumptions of Bohr was established when applied to hydrogen atom. The hydrogen atom consists of a single electron revolving around a single positively charged nucleus, each of which would behave as a point charge, and hence exact calculations of the stationary orbits can be made. Let 'e' be the charge, m mass of electron, 'Ze' the positive charge on the nucleus, 'r' the radius of the orbit in which electron is moving with a velocity 'V'

If we equate the centrifugal force, mv^2/r to the centripetal force which is due to the attraction between the electrons and the nucleus.

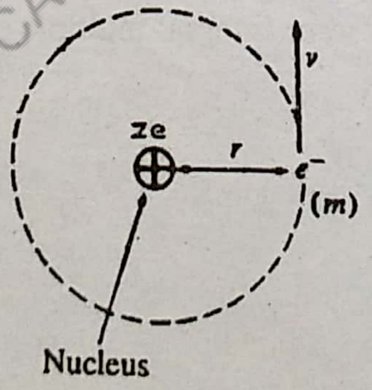


FIGURE 3.12
The Bohr model for the hydrogen atom
An electron of mass m moves with velocity v in an orbit with radius r from the nucleus.

$$\frac{mv^2}{r} = \frac{Ze.e}{r^2} \quad ...(1)$$

The Bohr's postulate states that only those orbits are possible in which:

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

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

Substituting the value of 'v' in the above equation, we get

$$\frac{m}{r}\left(\frac{nh}{2\pi mr}\right)^2 = \frac{Ze^2}{r^2}$$

$$\frac{m}{r}\left(\frac{n^2 h^2}{4\pi^2 m^2 r^2}\right) = \frac{Ze^2}{r^2}$$

$$\therefore \quad r = \frac{n^2 h^2}{4\pi^2 m Ze^2} \quad ...(2)$$

This equation gives the radii of all the possible stationary states. All the quantities on the right hand side of the equation are known and if we substitute $Z = 1$ for hydrogen atom, $n = 1$ for the first orbit.

If we put the values of the constants,

$h = 6.625 \times 10^{-27}$ erg. sec. (or 6.625×10^{-34} J.S. which is the S.I. unit).
$m_e = 9.11 \times 10^{-28}$ g (or 9.11×10^{-31} Kg which is the S.I. unit).
$e = 4.802 \times 10^{-10}$ esu (or 1.602×10^{-19}C which is the S.I. unit).

We get, $r = 0.529 \times 10^{-8}$ cm $(10^{-8}\text{ cm} = 1\mathring{A})$

$\therefore \; r = 0.529\mathring{A}$

$r_1 = 0.529\ \mathring{A}$ as the radius of the first stationary state for the hydrogen atom.

We can also write the equation 2 for the radius as

$$r = n^2 \left(\frac{h^2}{4\pi^2 mZe^2}\right) = n^2 a_o \;.....(3)$$

For the first orbit n = 1 and r = 0.529Å. This is the value of the terms in the bracket sometimes written as a_o, called Bohr's radius. For the second, third and so on orbitals, we would take n = 2, 3....

Thus we see that the radii of the orbits are proportional to the squares of the first natural numbers. To test the validity of these values, the spectrum of the hydrogen atom offers the best example.

3.13 DETERMINATION OF ENERGY

The single electron of hydrogen atom with mass 'm' revolves around the nucleus, its kinetic energy is given by the expression $\frac{1}{2}mv^2$, 'v' being the velocity of electron in circular motion. The potential energy possessed due to the position of isolated electron from the nucleus at a distance 'r' is given by the expression $-\frac{Ze^2}{r}$ (the energy of electron at infinity being zero) Fig: 3.12.

E, the total energy is given by:

$$E = \frac{1}{2}mv^2 - \frac{Ze^2}{r} \quad \text{———————}(4)$$

From equation (1) we have

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \qquad \therefore\; mv^2 = \frac{Ze^2}{r}$$

Substituting the value of mv^2 in equation (4) we get,

$$E = \frac{1}{2}\frac{Ze^2}{r} - \frac{Ze^2}{r}$$

$$\therefore \; E = -\frac{Ze^2}{2r} \quad \text{———— (5)}$$

Substituting the value of $r = \left(\frac{n^2h^2}{4\pi^2 mZe^2}\right)$ from equation (2) in equation (5).

we get,

$$E = -\frac{Ze^2}{2\left(\frac{n^2h^2}{4\pi^2 mZe^2}\right)} = \frac{-2\pi^2 mZ^2e^4}{n^2h^2} \quad \text{———— (6)}$$

This is the expression of energy of an electron in any orbit.

Expression for frequency and wave number:

Energy of an electron in a lower orbit (n_1) and higher orbit (n_2) can be expressed as follows:

$$E_1 = -\frac{2\pi^2 mZ^2e^4}{n_1^2h^2}$$

and $$E_2 = -\frac{2\pi^2 mZ^2e^4}{n_2^2h^2}$$

When an atom or gas is electrically heated, its electrons jump to higher orbit. In this state, it is said to be excited.

The excited state is unstable. Electron has to come back to original ground level by radiating energy equal to the difference of energies of the excited and ground state. Then

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

$$E_2 - E_1 = -\frac{2\pi^2 mZ^2e^4}{n_2^2h^2} - \left(-\frac{2\pi^2 mZ^2e^4}{n_1^2h^2}\right)$$

Rearranging

$$E_2 - E_1 = \frac{2\pi^2 mZ^2e^4}{n_1^2h^2} - \frac{2\pi^2 mZ^2e^4}{n_2^2h^2}$$

or $$E_2 - E_1 = \frac{2\pi^2 mZ^2e^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{———} (7)$$

According to Bohr's postulate

$$E_2 - E_1 = h\upsilon$$

$$h\upsilon = \frac{2\pi^2 mZ^2e^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\boxed{\upsilon = \frac{2\pi^2 mZ^2e^4}{h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{---------} (8)}$$

This is the expression for frequency of emitted wave or photons therein.

Now $\upsilon = c\overline{\upsilon}$ where $\overline{\upsilon}$ is called wave number and is defined as number of waves per unit distance.

$$c\overline{\upsilon} = \frac{2\pi^2 mZ^2e^4}{h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

or $$\overline{\upsilon} = \frac{2\pi^2 mZ^2e^4}{ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{———} (9)$$

Putting $$\frac{2\pi^2 me^4}{ch^3} = R_H$$

Where R_H is called Rydberg constant. Its value is 109678 cm^{-1}

$$\therefore \bar{\upsilon} = R_H Z^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \quad ----------(10)$$

This is the expression for wave number. Where for hydrogen Z=1.

3.14 HYDROGEN SPECTRUM

Historical background:– It is well known that when a gas is heated in a discharge tube at low pressure, it emits radiation. Balmer in 1885, studied the spectrum of hydrogen gas. He found a series of lines in visible region (i.e, having λ between 4000 to 7000 A°). They were called Balmer series. He proposed an empirical formula to find wave number $\bar{\upsilon}$ of each line.

$$\bar{\upsilon} = R_H\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

R_H is called Rydberg constant where n_2=3,4,5,6,----etc.

Lyman later on discovered another series in ultraviolet region. Wave number of each line was found by a formula similar to that given by Balmer.

$$\bar{\upsilon} = R_H\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

Where $n_2 = 2,3,4,5,---$etc.

Paschen discovered an other such series in infrared region. $\bar{\upsilon}$ of each line was given by:

$$\bar{\upsilon} = R_H\left(\frac{1}{3^2}-\frac{1}{n_1^2}\right)$$

Where $n_2 = 4,5,6,7,---$etc.

Brackett found another series infar–infrared region.
Pfund also found another series infar–infrared region.
General expression:– A general expression can give wave number of each line of each series. It is:

$$\vec{\upsilon} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Where n_1 is fixed for each series. n_2 keeps increasing (value of $R_H = 109678\ \text{cm}^{-1}$)

BOHR'S THEORY AND HYDROGEN SPECTRUM

Bohr's theory success lies in the fact that it provided logical proof and reason for the formation of hydrogen spectrum. According to Bohr's theory, "At ordinary temperature, the electron in hydrogen atom resides in lowest energy level i.e. first orbit or ground state. When electrically it is heated at low pressure in a discharge tube, the electrons of different hydrogen atoms absorb different amount of energy and jump to an appropriate high energy level. They are now said to be in excited state.

All the atoms in excited state, due to their high energy, are unstable. So now the electrons jump back to the original first orbit directly or to some other level of lower energy. In doing so they emit energy equal to the difference of energies of two levels. These energetic waves are separated by a prism according to their wavelength and thus hydrogen spectrum is obtained.

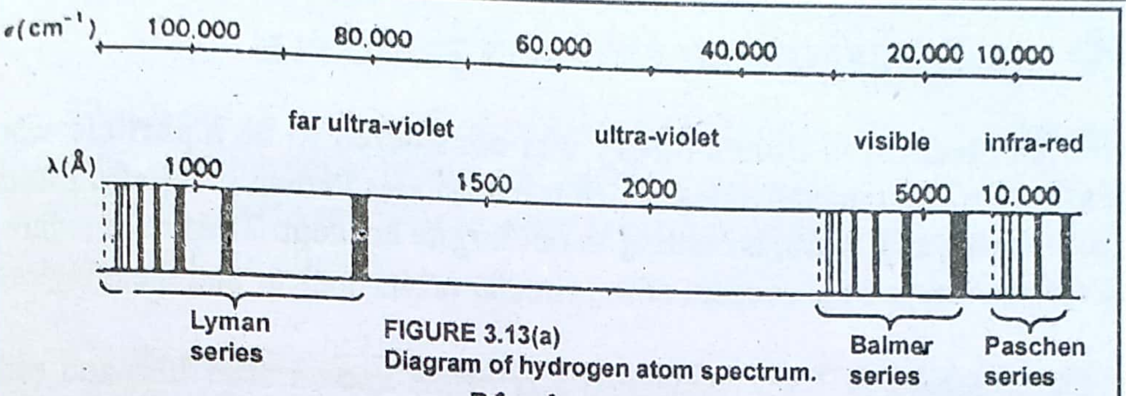


FIGURE 3.13(a)
Diagram of hydrogen atom spectrum.

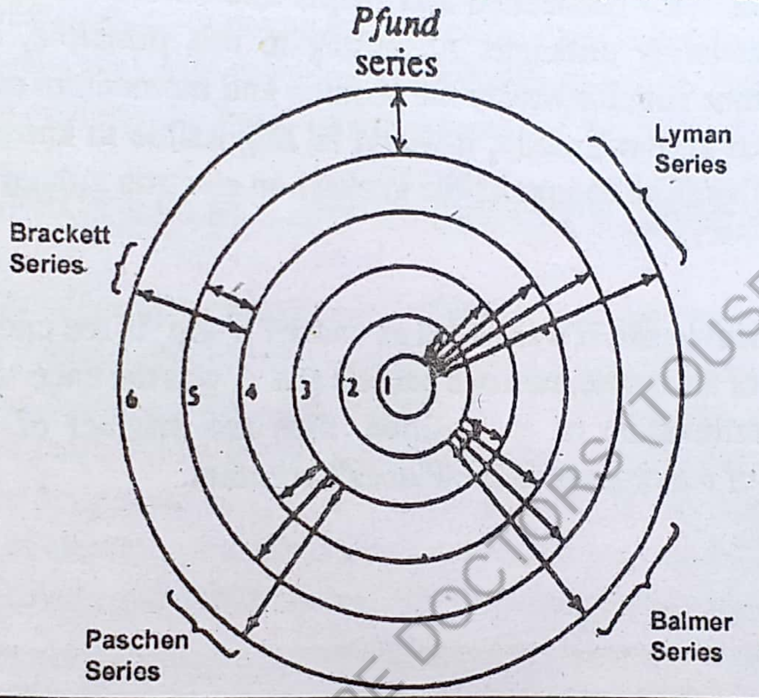


FIGURE 3.13(b)

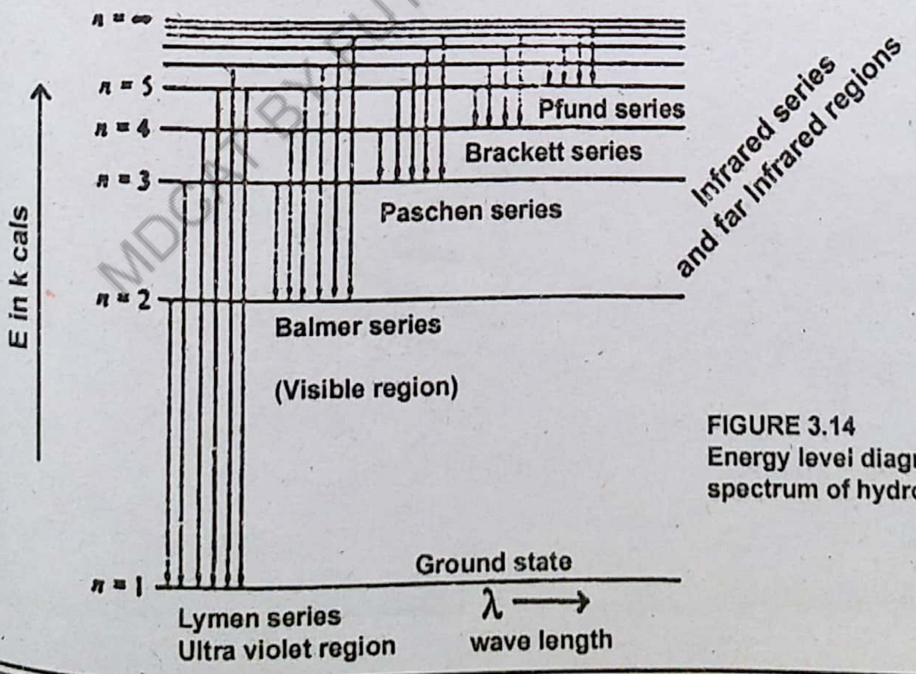


FIGURE 3.14
Energy level diagram for the spectrum of hydrogen

3.15 HEISENBERG'S UNCERTAINTY PRINCIPLE

An electron in Bohr's theory was considered to be a particle whose momentum and the path along which it moved was known precisely. Electron also behaves as a wave, according to *de Borglie* concept. Thus dual nature of an electron makes the concept of the circular orbits unclear and meaningless.

Heisenberg in 1925 enunciated a principle known after him and called Heisenberg's Uncertainty principle. According to this principle, it was not possible to determine simultaneously the position and momentum of a moving particle. If one was known exactly, it would be impossible to know the other exactly. It would therefore be impossible to chase an electron around its path or to locate it.

In mathematical terms, it was stated as under : If Δp_x is the uncertainty in the determination of the momentum of a particle and Δ_x was the uncertainty in the simultaneous determination of its position, then the product of these two uncertainties was of the order of h, the Planck's constant.

$$\Delta p_x \cdot \Delta_x \simeq h$$

Thus if one of the two i.e. p_x or x was known exactly, then the uncertainty in its determination could be zero and that of the other would become infinite. As a matter of fact, it is applicable to a very small particle when the ordinary laws of mechanics are not obeyed.

On this principle, it is impossible to think of an electron or any other particle to be at rest or to say it possesses zero energy and is at a particular location. The Bohr's orbits thus lose meaning as a circular path. The Heisenberg's principle, therefore explains the basic incompleteness of the Bohr model of atom.

3.16 ENERGY LEVELS AND ENERGY SUB-LEVELS

Bohr suggested the existence of certain circular orbits at definite distance from the nucleus. These orbits are associated with definite energy of the electron increasing outwards from the nucleus. Its evidence is given by the line spectra. The Bohr's circular orbits are usually referred to as "Energy levels" or "Shells". These are designated as 1, 2, 3, 4. etc. or K. L, M, N. etc. The maximum possible number of electrons a shell 'n' can accomodate is given by $2n^2$, i.e. 2, 8, 18, and 32 respectively in the first, second, third and fourth energy level. It may be pointed

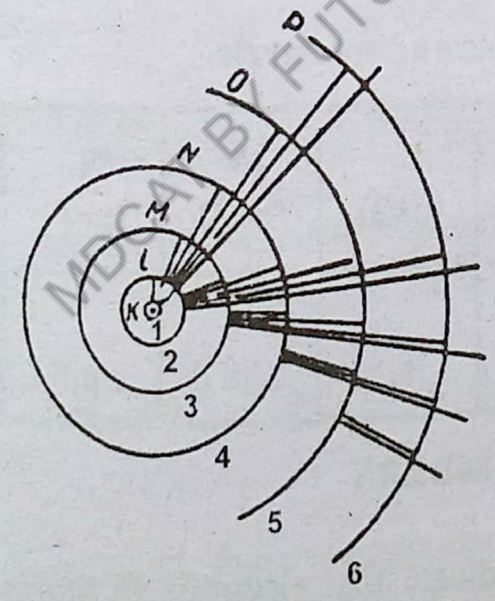


FIGURE 3.15

Electron orbits or Energy levels.

out that in the outer most shell of any atom, the maximum number of electrons possible is 8 (Except hydrogen whose outer most orbit being first orbit, is to be filled by "2" electrons).

Table 3.1 Energy Levels and Maximum Electrons.

n	1	2	3	4
Designation	K	L	M	N
Maximum electrons	2	8	18	32

The spectral lines, which correspond to the transition of an electron from one energy level to another, have for the most part, a fine structure, i.e. each line actually consists of several separate, close lying lines as doublets, triplets and so on indicating that some of the electrons of the given energy level have different energies. That is to say, that the electrons belonging to same energy level may differ in their energy. The energy levels are accordingly divided into sub energy levels denoted by the letters s, p, d, f.... for the first four series of lines in the spectra of the alkali metals, based on the terms Sharp, Principal, Diffuse and Fundamental. The number of sub level in a given energy level or shell is equal to its value of 'n' for example, with in a principal energy level (n=2) i.e. second energy level, two sub levels are possible which are s and p.

Table 3.2 Energy levels and sub levels

ENERGY LEVEL	K (n=1)	L (n=2)	M (n=3)	N (n=4)
SUB-LEVEL	s	s, p	s, p, d	s,p,d,f.

3.17 ORBITALS AND QUANTUM NUMBERS

Although the spectroscopic data indicate that electrons in atoms have various energies and that these energies may be described as main energy levels and sub-levels, these data do not give information about the movement of electrons in atoms. Bohr's concept of circular path was disproved by the Heisenberg's Uncertainty principle.

Through the use of mathematical methods known as wave mechanics, Schrodinger in 1926 was able to calculate the probability of locating the electron in a region of space about the nucleus. Thus on the basis of wave mechanics, it would not be proper to have a picture of an orbit or to think of an electron following a specific path. At best what can be said is that around the nucleus there are certain regions of space, where the likelihood of finding an electron is maximum. Such regions around the nucleus are called *orbitals*.

Each orbital in an atom is completely described by four quantum numbers. The *principal quantum number* specifies the size of orbital. This is given the symbol 'n'. As the value of 'n' increases, the size and also the energy of orbital increases. The *azimuthal* or *subsidiary* quantum number, symbol 'ℓ governs the shape of the orbital. This can have values $\ell = 0$ to $(n - 1)$. When value of $\ell = 0$, the orbital is called s orbital, when $\ell = 1$, it is 'p' orbital, when $\ell = 2$, d orbital and $\ell = 3$, it is 'f' orbital. The third quantum number is the *magnetic quantum number*, symbol 'm'. The value of $m = -\ell$, to $+\ell$ through zero e.g. when $\ell = 1$ (p orbital), $m = -1, 0, +1$ and if $l = 2$, $m = -2, -1, 0, +1, +2$ and so on. In fact the magnetic quantum number gives different orientations of an orbital in space in applied magnetic field. Finally, the spin quantum number, Symbols can have value of either $+1/2$ or $-1/2$ it specifies the spin of electron in an orbital.

3.18 PAULI'S EXCLUSION PRINCIPLE.

It is an empirical rule but agrees fully with experimental observations. It was enunciated by Wolfgang Pauli in 1925 and states that:

"In an atom no two electrons can have the same set of four quantum numbers"

In an atom, therefore, two electrons may have a maximum of three same quantum numbers of same values but the fourth would be different. Thus in any orbital, when the values of n, ℓ and m are same, two electrons can occupy the same orbital only if their spins are opposed or paired, ↑↓.

Table : 3.3 SUB-DIVISION OF ENERGY LEVELS

Energy Level 'n	Sub-Level 'ℓ' (0 to n-1)	Orientations of orbitals 'm' (+ℓ to −ℓ)	Number of orbitals (n^2)	Number of electrons (Paulis principle)	Maximum number of electrons ($2n^2$)
n= 1(K)	ℓ = 0 (s)	m = 0	1	s^2	2
n=2 (L)	ℓ = 0 (s) ℓ = 1 (p)	m = 0 m = 1, 0, −1	1 (s) 3p 4 (Total orbitals)	s^2 p^6	8
n=3 (M)	ℓ = 0 (s) ℓ = 1 (p) ℓ = 2 (d)	m = 0 m = 1, 0, − 1 m = 2, 1, 0, − 1, −2	1 (s) 3 (p) 5 (d) 9 (Total orbitals)	s^2 p^6 d^{10}	18
n = 4 (N)	ℓ = 0 (s) ℓ = 1 (p) ℓ = 2 (d) ℓ = 3 (f)	m = 0 m = 1, 0, −1 m = 2, 1, 0, −1, −2 m = 3, 2, 1, 0, −1, −2, −3	1 (s) 3 (p) 5 (d) 7 (f) 16 (Total orbitals)	s^2 p^6 d^{10} f^{14}	32

The first energy level (K) contains only one orbital; therefore it does not contain more than two electrons,it is not strictly speaking divided into sub levels.

The second energy level (L) consists of four orbitals and maximum of eight electrons. One of the four orbitals is an s orbital and the other three are p orbitals. Thus the second energy level consists of two sub levels, the 2s sub level and 2 p sub level, the 2 s sub level consists of a single s orbital and the 2 p sub level consists of three orbitals.

The third energy level (M), with a maximum of 18 electrons, contains three sub levels consisting of nine orbitals,one s orbital, three p orbitals, five d orbitals.

The fourth energy level (N) consisting of four sub levels, contains 16 orbitals: one s, three p, five d and seven f orbitals. The maximum number of electrons in the fourth level is 32.

3.19 SHAPES OF ORBITALS

All 's' orbitals are spherical in shape with the nucleus at the centre. Therefore in an 's' orbital, the probability of finding the electron is uniformly distributed around the nucleus. It has only one possible orientation in space in the magnetic field because it spreads over all the three axes uniformly. It has no nodal plane.

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

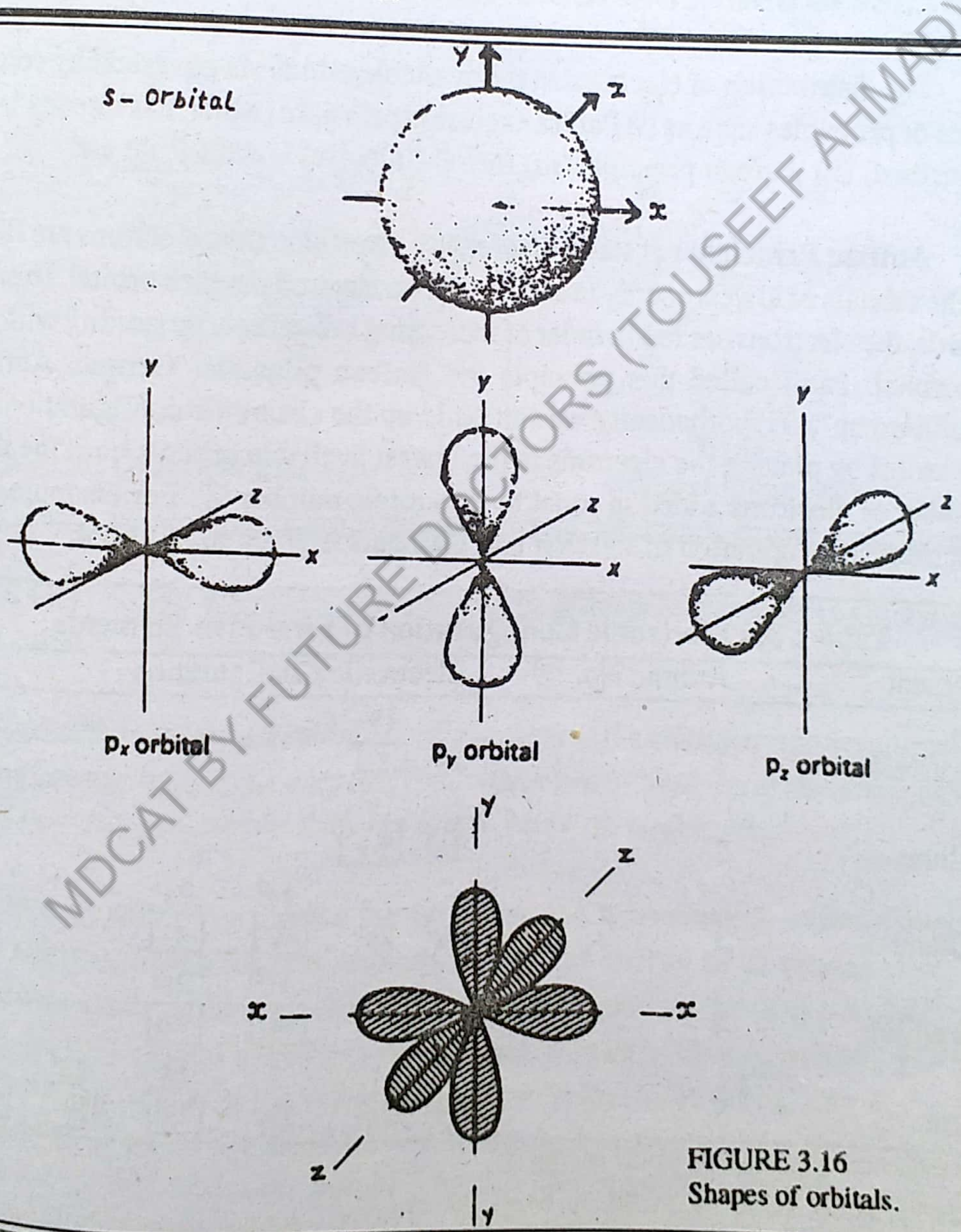


FIGURE 3.16
Shapes of orbitals.

Each p orbital has two lobes. One of which is labelled (+) and the other (–). Each lobe is like a pear. It is worthwhile to note that it would be wrong to imagine an electron moving along from one lobe to another. The point when the two lobes meet each other is usually referred to as the nodal plane along which the probability of finding the electorn is zero. Here we are not concerned with the shapes of d and f orbitals which are rather more complicated.

3.20 ELECTRONIC CONFIGURATION

The distribution of electrons in the available orbitals is governed by certain rules or principles such as (i) Pauli's exclusion principle (which has already been described) (ii) Aufbau principle (iii) ($n+\ell$) Rule, (iv) Hund's Rule etc.

(i) **Aufbau Principle :** It states that for any given atom, the electrons are filled to the orbitals of lowest energy in sequence, two electrons to each orbital. In other words, the electrons are fed in order of increasing orbital energy starting with the 1s orbital. Pauli called this principle the Aufbau principle(German Aufbau "building up"). Hypothetically we can build up the electronic configurations of the atoms by placing the electrons in the lowest available orbitals until the total number of electrons added is equal to the atomic number 'Z'. For example, the electronic configuration of the first five elements is given in table 3.4.

Table : 3.4 Electronic Configuration of First Five Elements

Element	Atomic No. 'Z'	Electronic Configuration
Hydrogen	1	$1s^1$ $\overset{1s^1}{\boxed{\uparrow}}$
Helium	2	$1s^2$ $\overset{1s^2}{\boxed{\uparrow\downarrow}}$
Lithium	3	$1s^2\ 2s^1$ $\overset{1s^2}{\boxed{\uparrow\downarrow}}$ $\overset{2s^1}{\boxed{\uparrow}}$
Beryllium	4	$1s^2\ 2s^2$ $\overset{1s^2}{\boxed{\uparrow\downarrow}}$ $\overset{2s^2}{\boxed{\uparrow\downarrow}}$
Boron	5	$1s^2\ 2s^2\ 2p^1$ $\overset{1s^2}{\boxed{\uparrow\downarrow}}$ $\overset{2s^2}{\boxed{\uparrow\downarrow}}$ $\overset{2p^1}{\boxed{\uparrow}\boxed{}\boxed{}}$

The sequence of increasing orbital energy is:

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

The scheme for the order of the filling of orbitals is shown in the table 3.5 :

The same order of the building up of orbitals may be simplified as shown in the table 3.6

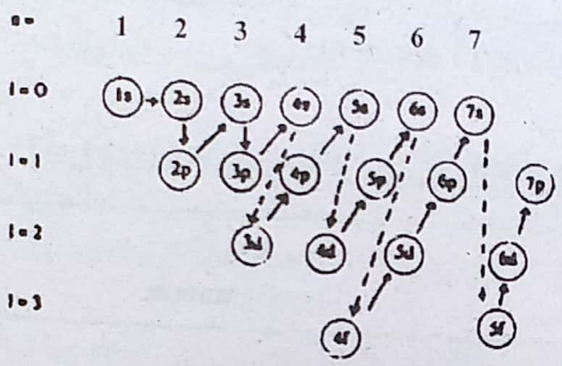


Table 3.5 Order of filling of orbitals

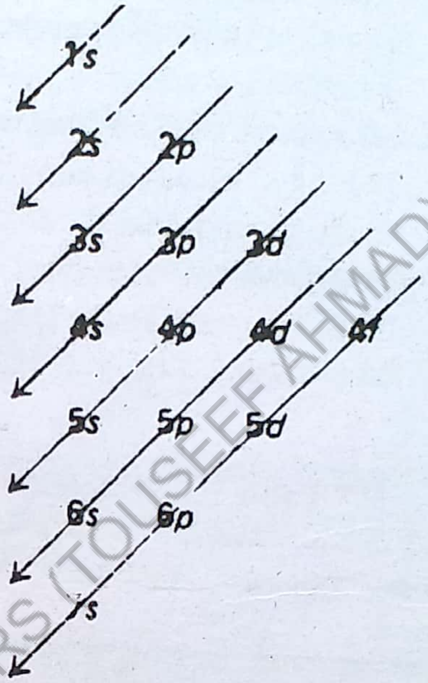


Table 3.6
Order of filling orbitals

(ii) **(n + ℓ) Rule** : The order of the filling of orbitals in elements is guided by (n + ℓ) rule.

> *"In building up the electronic configuration of the elements, the orbital with the lowest value of (n + ℓ) fills first; when two orbitals have the same value of (n + ℓ), the orbital with the lower value of 'n' fills first"*

Here 'n' and 'ℓ' stand for the principal and azimuthal quantum numbers respectively. This useful rule reminds us that the energy of an orbital of multi electron atoms depends upon the value of both the quantum numbers, n and ℓ, but mainly on the value of n. For example, which fills first 3d or 4s orbital? For the 3d orbital ($n = 3$; $\ell = 2$); the value of $(n + \ell) = 5$; for the 4s orbital ($n = 4$; $\ell = 0$), the value of $(n + \ell) = 4$. Hence 4 s which has the lower value of (n + ℓ) and thus lower energy fills first. Likewise, 4 p orbital fills before 5s although the (n + ℓ) value for both is same, but 4p orbital has the lower value of the principal quantum number 'n'

(iii) **Hund's Rule of Maximum Multiplicity:** The orbitals which are degenerated (having equal energy) like p, d, f, where these begin to fill up, they do so according to a Rule called the Hund's Rule of Maximum Multiplicity. It states:

(a) The electrons tend to avoid being in the same orbital. Thus as electrons are successively added, a maximum number of electrons will try to occupy orbitals singly. Only when all the orbitals are singly occupied only then the pairing of electrons commences.

(b) In the ground state, the electrons occupying the orbitals singly will have their spin parallel.

Making use of the above mentioned principles, we could consider in the table 3.7 the electronic configuration of the first 11 elements.

Table : 3.7 Electronic Configurations of Elements 1 to 11.

Atomic No. Z	Element	1s	2s	$2p_x$	$2p_y$	$2p_z$	3s	Electronic configuration
1	H	↑						$1s^1$
2	He	↑↓						$1s^2$
3	Li	↑↓	↑					$1s^2\ 2s^1$
4	Be	↑↓	↑↓					$1s^2\ 2s^2$
5	B	↑↓	↑↓	↑				$1s^2\ 2s^2\ 2p_x^{\ 1}$
6	C	↑↓	↑↓	↑	↑			$1s^2\ 2s^2\ 2p_x^{\ 1}\ \ 2p_y^{\ 1}$
7	N	↑↓	↑↓	↑	↑	↑		$1s^2\ 2s^2\ 2p_x^{\ 1}\ \ 2p_y^{\ 1}\ \ 2p_z^{\ 1}$
8	O	↑↓	↑↓	↑↓	↑	↑		$1s^2\ 2s^2\ 2p_x^{\ 2}\ 2p_y^{\ 1}\ \ 2p_z^{\ 1}$
9	F	↑↓	↑↓	↑↓	↑↓	↑		$1s^2\ 2s^2\ 2p_x^{\ 2}\ 2p_y^{\ 2}\ 2p_z^{\ 1}$
10	Ne	↑↓	↑↓	↑↓	↑↓	↑↓		$1s^2, 2s^2, 2p_x^{\ 2}, 2p_y^{\ 2}, 2p_z^{\ 2}$
11	Na	↑↓	↑↓	↑↓	↑↓	↑↓	↑	$1s^2\ 2s^2\ 2p^6\ 3s^1$

From the above studies, it is gathered that :

(a) The maximum number of orbitals in a particular energy level is equal to n^2. For example K, L, M and N contain 1, 4, 9, 16 orbitals.

(b) An orbital cannot contain more than two electrons (Pauli's principle).

(c) The maximum number of electrons that a particular energy level specified by 'n' can hold, is given by $2n^2$. For example, K, L, M and N energy levels can hold 2, 8, 18 and 32 electrons respectively.

(d) The number of sub levels in an energy level specified by 'n' is equal to n.e.g. energy level with n = 2 has two sub levels.

(e) The number of orbitals in each sub energy level specified by 'l' is given by $(2l + 1)$. For example s, p, d and f energy sub levels contain 1, 3,5 and 7 orbitals respectively.

(f) The maximum number of electrons which can be accomodated in an energy sub level is given by $2(2l + 1)$. Thus s, p, d and f sublevels contain 2, 6, 10 and 14 electrons respectively: s^2 p^6 d^{10} f^{14}

(g) The orbitals given by a particular value of 'l' if 'n' is same, have the same energy and such orbitals are called *degenerate*. Like $l = 1$ gives three p orbitals specified as p_x, p_y, p_z and the p orbitals are said to be three fold degenerate. These orbitals are filled according to Hund's Rule.

(h) The notation used to indicate the number of electrons present in a given energy level is nl^x, where 'n' may be 1,2,3....; 'l' may be s, p, d... and 'x' represents the number of electrons actually present for example, Na has Z = 11; these electrons are distributed as $1s^2 2s^2 2p^6 3s^1$. This indicates that the inner three orbitals 1s, 2s and 2p are full while the outer most orbital is 3s and contain only one electron.

3.21 ATOMIC RADIUS

According to wave mechanics, an electron could be any where around the nucleus, hence it would be improper to talk of a fixed radius of an atom. The presence of other atoms also affects the outer charge distribution. Still it is useful to talk about the radius of an atom. The radius of an atom is taken as half the bond length between two homonuclear diatomic molecules like H – H; O = O; Cl – Cl etc. The values of the distances between the two nuclei are determined from the spectroscopic data and X-ray diffraction measurements. For example the distance between two atoms of carbon in diamond is 1.54Å, giving the radius of carbon atoms as 0.77Å (1Å = 10^{-8} cms). Similarly the internuclear distance between two sulphur atoms is 2.06Å, there by giving the radius of sulphur atom as 1.03Å. Some atomic and ionic sizes are shown in the table 3.8

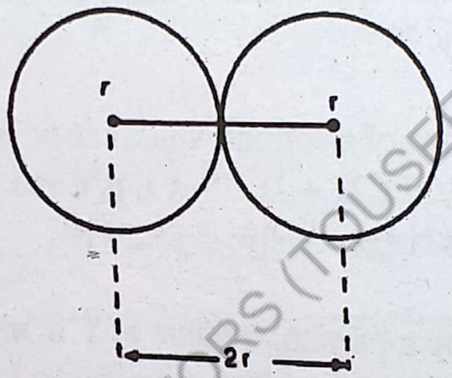


FIGURE 3.17

In case of heterogeneous diatomic molecules i.e. where two different kinds of atoms A, B are joined together, the bond length is ($r_A + r_B$) and if any one of the radii is known, the other can be found. The knowledge of the atomic radii is useful in predicting chemical behaviour, e.g. phosphorus combines with chlorine to give PCl_5, but does not combine with iodine to give PI_5. The reason is that the iodine atom is much bigger than the Cl atom and 5 of the iodine atoms cannot be accomodated around a single phosphorus atom.

TABLE 3.8

Sizes of the atoms and their ions

atoms	C	N	O	F	Na	Mg	Al	Si
size	0.77	0.70	0.66	0.64	1.51	1.36	1.25	1.17
ions	C^{4-}	N^{3-}	O^{2-}	F^-	Na^+	Mg^{+2}	Al^{3+}	Si^{4+}
size	2.60	1.71	1.40	1.36	0.95	0.65	0.50	0.41

IONIC RADII

	H^-	Li^+	Be^{2+}	B^{3+}	C^{4+}			
	1.54	0.60	0.31	0.20	0.15			
O^-	F^-	Na^+	Mg^{2+}	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}	Cl^{7+}
1.40	1.36	0.95	0.65	0.50	0.41	0.31	0.29	0.26
S^-	Cl^-	K^+	Ca^{2+}	Sc^{3+}	Ti^{4+}	V^{5+}	Cr^{6+}	Mn^{7+}
1.84	1.81	1.33	0.99	0.81	0.68	0.59	0.52	0.46
Se^-	Br^-	Rb^+	Sr^{2+}	Y^{3+}	Zr^{4+}	Nb^{5+}	Mo^{6+}	Tc^{7+}
1.98	1.95	1.48	1.13	0.93	0.80	0.70	0.62	—
Te^-	I^-	Cs^+	Ba^{2+}	La^{3+}	Hf^{4+}	Ta^{5+}	W^{6+}	Re^{7+}
2.21	2.16	1.69	1.35	1.15	0.79	0.71	0.65	0.50

3.22 IONIC RADIUS.

When an electron is removed from a neutral atom, the atom is left with an excess of positive charge called a positive ion or cation. Instead of a neutral atom takes up an electron it becomes a negative ion or anion.

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

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

The magnitude of the charge on the. ion depends upon the number of electrons removed or added to the neutral atom.

$$M^+ \longrightarrow M^{++} + e^-$$

$$M^- + e \longrightarrow M^{--}$$

As in case of atomic radius, the ionic radii are known from X-ray analysis. The ionic radii are also deduced from the way the ions are packed together. The monoatomic ions are considered as spheres and their radii are determined from the packing in crystals. The value of the ionic radius also depends on the ions that surround it.

(i) Ionic radii show that the cations have smaller radii than neutral atoms. On removal of an electron the effective charge on the nucleus increases and pulls the remaining electrons more firmly e.g.

radius of Na atom = 1.57Å
radius of Na^+ ion = 0.95 Å

(ii) Anions have a larger radii than the neutral atoms as an excess of negative charge results in greater electron repulsion e.g.

radius of Cl atom = 0.99 Å
radius of Cl^- ion = 1.81 Å

(iii) In case of ions which have the same electronic configuration like Na^+, Mg^{++}, Al^{+++}, ($1s^2$, $2s^2$, $2p^6$) the radii decrease with increasing nuclear charge.

Element	Na^+	Mg^{++}	Al^{+++}
Atomic No.	11	12	13
Ionic radius in Å	0.95	0.65	0.50

The ions which have the same electronic configuration, as given above, are called isoelectronic. The ionic sizes are shown in table 3.8.

3.23 IONIZATION POTENTIAL

It is defined as the minimum amount of energy require to remove the least strongly bound electron from a neutral gaseous atom, ion or molecule. It is called Ionization potential or ionization Energy.

$$M_{(gas)} \longrightarrow M^+_{(gas)} + e^-$$

It is possible to remove more than one electron from an atom or ion, giving doubly or triply charged ions and the energies needed are called:

$M_{(gas)} \rightarrow M^+_{(gas)} + e^-$ ΔE is the first Ionization potential.
$M^+_{(gas)} \rightarrow M^{++}_{(gas)} + e^-$ ΔE is the Second Ionization potential
$M^{++}_{(gas)} \rightarrow M^{+++}_{(gas)} + e^-$ ΔE is the third Ionization potential.

The ionization potential is measured in Kilo-Joules per mole and is determined from spectroscopic methods or by measurement of current passing through a discharge tube. The ionization potential depends upon the distance of the electron from the nucleus. Farther the electron is from the nucleus,more easily it is removed. When one electron is removed, the positive charge on the nucleus becomes unbalanced and binds the remaining electrons more firmly. It is therefore, becomes more and more difficult to remove the second and then the third electron. Due to their larger distance, it is easier to remove an electron from 'f' shell than *a* 'd' shell and removal from *a* 'd' shell is easier than *a* 'p' shell., The first, second and third ionization potentials of first 20 elements are given in Table 3.9.

Table 3.9 Ionization Potentials (KJ mol^{-1})

Element	Symbol	At. No:	Ist	2nd	3rd
Hydrogen	H	1	1312		
Helium	He	2	2372	5250	
Lithium	Li	3	520	7297	11,810
Beryllium	Be	4	900	1757	14,850
Boron	B	5	800	2427	3658
Carbon	C	6	1086	2352	4619
Nitrogen	N	7	1403	2858	4578
Oxygen	O	8	1314	3391	5300
Fluorine	F	9	1681	3381	6046
Neon	Ne	10	2081	3964	6150
Sodium	Na	11	495	4563	6912
Magnesium	Mg	12	738	1450	7730
Aluminium	Al	13	577	1816	2745
Silicon	Si	14	787	1577	3230
Phosphorus	P	15	1060	1896	2908
Sulphur	S	16	1000	2258	3381
Chlorine	Cl	17	1255	2297	3849
Argon	Ar	18	1520	2665	3947
Potassium	K	19	418	3069	4439
Calcium	Ca	20	590	1146	4941

3.24 ELECTRON AFFINITY

It is easy to remove an electron from a metal to form a positive ion according to the equation $M - e \rightarrow M^+$

e.g.

$$Na_{(g)} - e \rightarrow Na^+_{(g)} \quad \Delta H = +495 \text{ KJ mole}^{-1}$$

The non metals on the other hand try to gain an electron to complete their shells. *The energy change accompanying the gain of an electron by a neutral gaseous atom to form a negative ion is called its electron affinity.* The addition of electron to an atom, is mostly an exothermic change. For example;

$$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)} \quad \Delta H = -348 \text{ KJ mole}^{-1} \text{ (Electron affinity).}$$

Some non-metallic elements particularly halogens of VIIA group evolve large amounts of energy, that is, their electron affinities are large and negative. (Refer Table 3.10). The large values of the electron affinity show thast these elements are very strong oxidizing agents. The large electron affinities of halogens are attributed to their small atomic radii and greater attraction for the electrons. Moreover, the addition of an electron produces the stable inert gas configuration (i.e. Octet). The value for fluorine is anomalous, probably because the fluorine atom is very small and the incoming electrons are repelled by the electrons already present.

Table 3.10 **Electron Affinities (KJ mole^{-1})***

IA	IIA	IIIA	IVA	VA	VIA	VIIA	ZERO
H							
-73							He
							+54
Li	Be	B	C	N	O	F	Ne
-57	+66	-15	-123	+31	-141	-333	+99
Na	Mg	Al	Si	P	S	Cl	
-21	+67	-26	-135	-60	-196	-348	
						Br	
						-340	
						I	
						-297	

*Positive values signify that the reaction $A + e \rightarrow A^{-1}$ is endothermic.

Looking at the table 3.10 you might note that the electron affinities of group IA elements are somewhat negative, even though these elements have very little attraction for the electron. The elements of group IIA, Beryllium and Magnesium have positive electron affinities (change is endothermic) because the electron is being added to higher energy p-level. In VA group elements such as Nitrogen, the value is positive because the electron must enter the half filled p-orbital and becomes paired, a process which is not energetically favourable.

The addition of second electron to oxygen or sulphur must overcome the repulsion of the negative charge already present on O^- and S^-. The process is, therefore,endothermic e.g. for O^{2-} it is + 844 and for S^{2-} it is + 532 KJ $mole^{-1}$

3.25 ELECTRONEGATIVITY (E.N)

In a molecule the tendency or power of an atom to attract a shared pair of electrons to itself, is called the electronegativity of that atom. The polarity of covalent bond depends upon the electronegativities of held atoms. The electronegativity values of elements are listed in table 3.11.

The numerical values of the electronegativity of fluorine is fixed as 4 which is the highest value from the values listed in table 311 It is clear that the E.N. values in general, increase as we go from left to right in any horizontal period, while they decrease as we go down from top to bottom a group in the periodic table.

TABLE 3.11

Electronegativities of representative Elements

H 2.1							He —
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne —
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	F 2.1	S 2.5	Cl 3.0	Ar —
K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr —
Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe —
Cs 0.7	Ba 0.9	Ti 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn —
Fr 0.7	Ra 0.9						

On the basis of electronegativity values. It is *predictable* that what type of bond will be formed. If the difference between E.N. values of any two bonded atoms is less than 1.7 the bond will be covalent. The polarity of covalent bond also depends upon the E.N. values, that is, the covalent bond between two similar atoms (H—H, O=O, N=N etc), the E.N. are equal, the covalent bond is non-polar in character. The covalent bond between dissimilar atoms is always polar in nature, the polarity increase with difference in their E.N. values. For example, bond between N and H is more polar than bond between C and H, because E.N. difference in case of N and H is more than E.N. difference between C and H.

PROGRESS TEST 3

1. What is the experimental evidence for the presence of small nucleus containing most of the mass and all of the positive charge in the atom?

2. What information about the structure of atom is obtained from the experiments on the passage of electricity through gases under low pressure?

3. Criticize the following statement, "An electron moves about the nucleus of an atom in a manner analogous to the movement of a planet about the sun"?

4. What information about the electron in the atom is obtained from the fact that the emission spectra of the elements are frequently discontinuous?

5. Explain quantized energy states in terms of Bohr's orbits and electron transition between the orbits.

6. What principles and rules are followed in the electronic configuration of atoms?

7. Explain the origin of X-rays and relationship between their wave length and nuclear charge in the atoms from which they originate.

8. (a) State the restrictions placed on our ability to know the position and momentum of an electron.

(b) Explain the significance of Pauli's Exclusion principle in relation to the electronic structure of atoms.

(c) Write down the electronic configuration for the ground states of each of the following (i) Na (Z = 11) (ii) Ca (Z = 20) (iii) Sc (Z = 21) (iv) Mg^{2+} (Z = 12) (v) Cl^{-}(Z = 17).

9. Explain the distinction between the following:

(a) α and β - Particles (b) Orbit and orbital (c) Ground state and excited state (d) Continuous and discontinuous spectrum.

10. Describe the contribution made by the following individuals toward the structure of atom (a) Rutherford (b) Bohr (c) Moseley.

11. Give the number of protons, neutrons and electrons in each of the following:

(a) ${}^{19}_{39}K$ (b) ${}^{8}_{16}O$ (c) ${}^{3}_{7}Li^{+}$ (d) ${}^{9}_{19}F^{-}$ (e) ${}^{11}_{23}Na$

Also write down their electronic configuration.

12. What do you understand by the terms:

(a) Atomic Radius (b) Ionization potential (c) Electron affinity (d) Electronegativity.

13. List the four quantum numbers that define the energy state of the electrons in a hydrogen atom along with their possible values and explain their significance in terms of orbitals.

14. (a) The ionization potential of Lithium and potassium are 5.4 and 4.3 ev. what do you predict for the I.P. of Na.

(b) What is the shape of orbital for which $\ell = 0$.? Those for which $\ell = 1$?

15. (a) How is emission of radiation from an atom explained by Bohr's model?

(b) Why was the nucleus of hydrogen atom was assumed to be a fundamental particle?

CHAPTER – 4

CHEMICAL BONDING

4.1 ENERGETICS OF BOND FORMATION

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

The force of attraction or chemical bond between two atoms is formed due to the interaction of valence electrons of combining atoms.

In 1916 two kinds of chemical bonds were described: *The ionic bond by* W. Kossel (Germany) and *Covalent* bond by G. N. Lewis (U.S.A.). Both these chemists based their ideas on the fact that atoms attain greatest stability when they acquire an inert gas electronic configuration (Octet Rule). As a matter of fact atoms of the inert gases have eight electrons in their outermost orbit, excepting helium which has only two electrons. These gases are very stable and do not enter into chemical combination under ordinary conditions and therefore they are assumed to have stable orbits. Atoms of all the other elements have incomplete outermost orbits and tend to complete them by chemical combination with the other atoms. This inert gas configuration can be achieved either by the transference or sharing of electrons among themselves. It is the tendency of atoms to acquire inert gas configuration which causes the atoms to form chemical bonds.

4.2 ELECTROVALENT OR IONIC BOND

This type of chemical bond proposed by Kossel is formed as a result of complete transference of one or more electrons from one atom to the other so that both the atoms acquire inert gas configuration (the octet rule). The atom that loses electrons becomes positively charged and the atom that gains electrons becomes negatively charged. The charged atoms (called ions) so produced are held together by electrostatic force of attraction. The ionic bond is, therefore, defined as *the electrostatic attraction between positive and negative ions.*

Ionic compounds such as NaCl and MgO are formed by the elements of low electronegativity (metals) and the elements of high electronegativity (non-metals). If difference in electronegativity, ΔE.N, is greater than 1.7 between two elements usually leads to an ionic bond.

The metal of groups IA, IIA and Aluminium in IIIA due to their low ionization potential and low electronegativity, lose one, two or three electrons to form M^+, M^{2+} and M^{3+} ions respectively. The non-metals of groups VIA and VIIA due to their high electron affinity and high electronegativity tend to gain two electrons and one electron to form A^{2-} and A^{1-} ions respectively. Nitrogen and phosphorus in VA group will under some circumstances gain three electrons to form N^{3-} (Nitride) and P^{-3} (Phosphides) ions

In order to understand why ionic bonds are formed readily between the metals and non-metals of the above mentioned groups, let us consider the energy changes involved in the formation of say, sodium chloride from sodium and chlorine atoms.

(i) Sodium in the ground state has the electronic configuration of $1s^2, 2s^2, 2p^6$ $3s^1$, i.e. it has one valence electron. The loss of the valence electron requires 495 KJ mole^{-1}, the resulting Na^+ has complete octet.

$$\underset{\substack{1s^2,\, 2s^2,\, 2p^6,\, 3s^1 \\ (11\bar{e})}}{Na_{(g)}} \longrightarrow \underset{\substack{1s^2,\, 2s^2,\, 2p^6 \\ (10\bar{e})}}{Na^+_{(g)}} + e^- \qquad \Delta H = +495\ \text{KJ/mole}$$

(ii) Chlorine atom in its ground state has the electronic configuration of $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$, that is, it needs one more electron to complete its octet. The gain of one electron by chlorine releases energy which is equal to 348 KJ $mole^{-1}$.

$$\underset{\substack{1s^2, 2s^2, 2p^6, 3s^2, 3p^5 \\ (17\ e^-)}}{Cl_{(\omega)} + e^-} \longrightarrow \underset{\substack{1s^2, 2s^2, 2p^6, 3s^2, 3p^6 \\ (18\ e^-)}}{Cl^-_{(\omega)}} \qquad \Delta H = -348\ KJ/mole$$

The energy difference (495-348=147KJ/mole) is more than compensated when the oppositely charged ions form a crystal lattice consisting of a closely packed array, in which each ion is surrounded by six opposite ions (Fig. 4.1) The great attractive forces in the crystal lattice greatly reduce the energy of the system there by making it stable. Thus the more important step is the third step which involves the formation of crystal lattice.

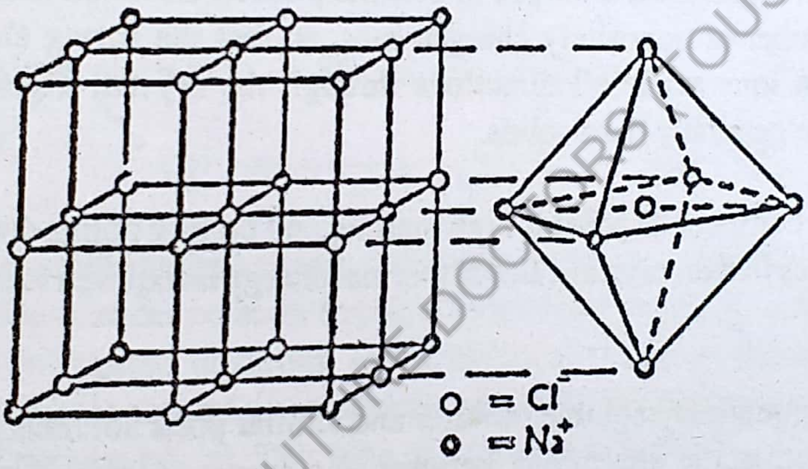


FIGURE 4.1
Crystal structure of sodium chloride, showing (right) the octahedral arrangement of six sodium ions around one chloride ion.

(iii) $Na^+_{(\omega)} + Cl^-_{(\omega)} \rightarrow Na^+Cl^-_{(s)}$ $\qquad \Delta H = -788.0$ KJ/mol

The energy released when one mole of gaseous ions arrange themselves in definite pattern to form crystal lattice is referred to as the lattice energy. It is this energy which over comes the loss of energy encountered in the formation of the ions.

From the above discussion, we conclude that it is essential for the formation of ions and the ionic bond that the sum of the energies released in the second and third steps must be larger than what is required in the first step.

Characteristics of Ionic Compounds

(i) A single ion of a metal is never associated with a single ion of non-metal i.e. separate units of ionic compounds do not exist and therefore it is wrong to talk about a molecule of an ionic compound. The formula only indicates the relative number of atoms of each element. The solid crystal is made up of large number of oppositely charged ions, arranged in definite pattern. Each ion is surrounded by a fixed number of oppositely charged ions, so that the strong electrostatic forces between ions act in all directions through the crystal. Thus the ionic compounds are generally hard solids.

(ii) The ionic compounds possess high melting and boiling points due to strong inter ionic forces in their crystals. Lot of thermal energy is required to break those forces.

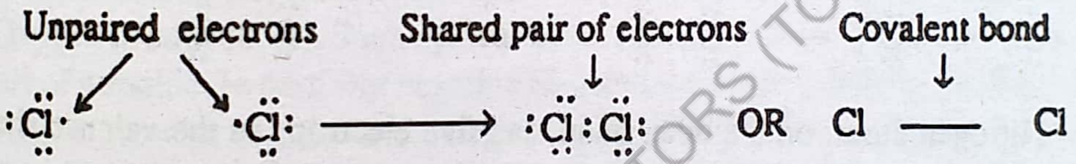
(iii) Ionic compounds are soluble in water and similar polar solvents because of the strong electrostatic attractions between the ions and polar molecules of solvent. The surrounding of the ions by the solvent molecules solvation releases the energy which is known as the energy of solvation. This energy usually overcomes the high lattice energy of the ionic compound.

Insoluble ionic compounds (e.g. the sulphates, phosphates and fluorides of Ca, Sr and Ba) have very high lattice energies and insufficient solvation energy is available from the ions to overcome the high lattice energies for these compounds to be soluble. The ionic compounds are insoluble in the organic solvents like Benzene, carbon tetrachloride etc. because there is no attraction between the ions of ionic compounds and the molecules of non polar solvents.

(iv) Ionic componds are invariably electrolytes, because in the presence of a polar solvent such as water, the interionic forces are so weakened that the ions are separated and the free ions are able to move under the influence of electric current. In fact the ionic compounds conduct electricity even in the fused or melted state.

4.3 COVALENT BOND

The atoms in an ionic compound are held together by the transfer of valence electron or electrons from one atom to the other atom. In covalent bonding, no such transfer is involved, instead two atoms both of which tend to gain electrons may combine with each other by sharing one or more pairs of electrons. This concept of electron pair bond was proposed by G.N. Lewis in 1916. Two atoms of chlorine for instance, each having seven electrons in its valence shell unite by sharing two of these fourteen electrons between them. This is shown diagramatically as follows, using dots to indicate only the valence electrons:



Electrons that are shared between two atoms are the bonding electrons and are to be counted toward the octet (or duplet in case of hydrogen) of each of the bonding atom. As the shared electrons spend much of the time between the nuclei, resulting in the attractive forces between negative charge of electrons and positive charges of the two nuclei. This type of chemical bonding is known as covalent bond.

In chlorine molecule, for instance, the one shared pair of electrons forms a single covalent bond between two chlorine atoms (Cl — Cl). The sharing of electrons in a covalent bond brings the bonded atoms closer together which is reflected from the bond energy data of the bonds. For example, when two chlorine atoms form a single covalent bond, 242 KJ/mole of energy are released.

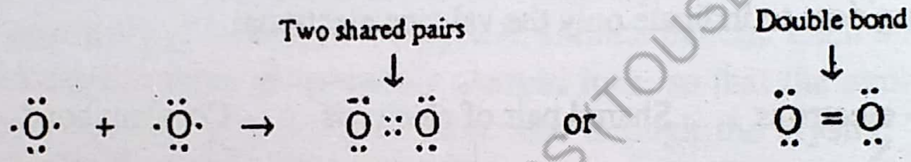
$$:\ddot{\underset{..}{\mathrm{Cl}}}\cdot_{(g)} + \cdot\ddot{\underset{..}{\mathrm{Cl}}}:_{(g)} \longrightarrow :\ddot{\underset{..}{\mathrm{Cl}}} - \ddot{\underset{..}{\mathrm{Cl}}}:_{(g)}, \qquad \Delta H = -242\ \mathrm{KJ\ mol^{-1}}$$

The release of energy lowers the energy of the molecule and thus makes it more stable.

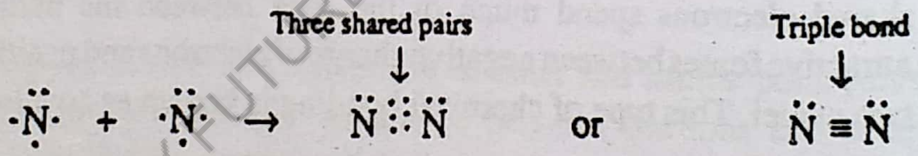
Another normal feature of a single covalent bond is that the spins of the bond forming electrons, unpaired with separate atoms, becomes paired in the bond formation.

In addition to single covalent bond as mentioned in Cl_2 molecule, atoms also form multiple bonds, that is, double and triple bonds as in case of Oxygen and Nitrogen molecules.

An oxygen atom has six valence electrons, therefore the formation of O_2 molecule would involve sharing of two electrons from each oxygen atom. As sharing involving one electron pair is indicated by a single short straight line, the sharing of two electron pairs would be indicated by two short straight lines:



Nitrogen atom, on the other hand, has five electrons in the valence shell, therefore, the formation of N_2 molecule would involve sharing of three electrons from each of the two atoms as shown below. A triple bond as in N_2 is represented by three short lines.



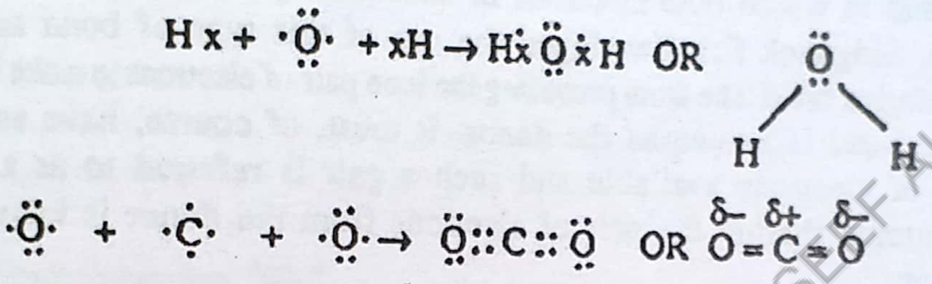
The bond distances of multiple bonds are shorter and the bond energies are higher as shown in the table 4.1 (Also refer 4.7).

Table 4.1 Bond distances and Bond Energies of Single, Double, Triple bonds.

Covalent Bond	Bond Distance	Bond Energy
C – C	1.54A	347 KJ mol^{-1}
C = C	1.34A	598 KJ mol^{-1}
C ≡ C	1.20A	820 KJ mol^{-1}
Cl – Cl	1.99A	242 KJ mol^{-1}
O = O	1.21A	498 KJ mol^{-1}
N ≡ N	1.10A	946 KJ mol^{-1}

Generally there is shortening of 0.20Å for any double bond and 0.34 Å shortening for any triple bond.

Notice that the examples given so far involve the equal sharing of electrons between similar atoms which form pure covalent bonds. Examples of bonding in water and CO_2 present an interesting situation, where sharing of electrons takes place between dissimilar atoms.



The shared electrons are attracted more towards more electro negative atom (Oxygen in both cases). Such a pair of electrons constitute *polar bond* making one part of a molecule partially negative (δ–) and the other partially positive (δ +). A molecule with a positive and negative pole is referred to as *dipole*. A covalent bond is directed in space so that the atoms in a covalent compound are linked in a definite position in relation to each other and the molecules formed may exist as distinct particles.

Characteristics of Covalent Compounds

(i) Unlike ionic compounds, the covalent compounds exist as separate covalent molecules, because the particles are electrically neutral and have little attractive forces for each other.

(ii) Covalent compounds, since they exist as separate molecules are expected to be volatile liquids or gases or low melting solids (held together by weak Vander waals forces).

(iii) These are non-electrolytes i.e. they do not conduct electricity.

(iv) Covalent compounds are generally insoluble in water and similar polar solvent but soluble in the organic solvents.

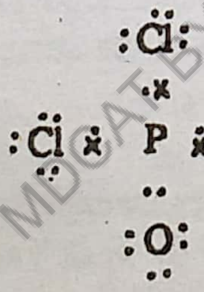
4.4 CO-ORDINATE OR DATIVE COVALENT BOND

An atom in groups VA, VIA or VIIA, having filled its valence shell by sharing its unpaired electrons to form covalent bonds, may use its remaining paired electrons (lone pairs) to form further bonds. It does this by sharing a pair with another atom having an empty orbital. The result is a dative or co-ordinate bond in which both electrons in the shared pair originate from the same atom. Sidgwick first developed the use of this type of bond and he called it as dative bond. The atom providing the lone pair of electrons to make up the co-ordinate bond is known as the donor. It must, of course, have an 'un-used' pair of electrons available and such a pair is referred to as a lone pair. The atoms sharing the pair of electrons from the donor is known as the acceptor.

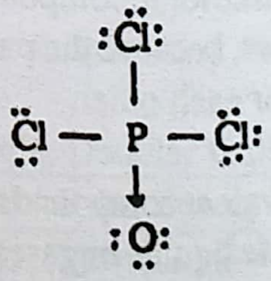
The dative bond is represented either by the use of an arrow, from the donor to the acceptor atom or by means of line, conveniently used to represent a covalent bond, but with inclusion of charges (+) for the donor and (-) for the acceptor atom. On this basis, the dative bond can be regarded as a covanlent bond with a certain amount of ionic character, and the term co-ionic instead of dative, is intended to describe this state of affairs.

EXAMPLES

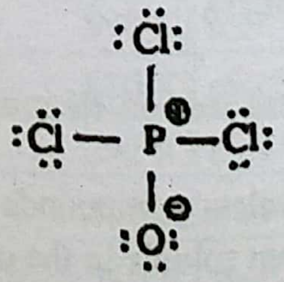
(i). Phosphorus Oxychloride, $POCl_3$.



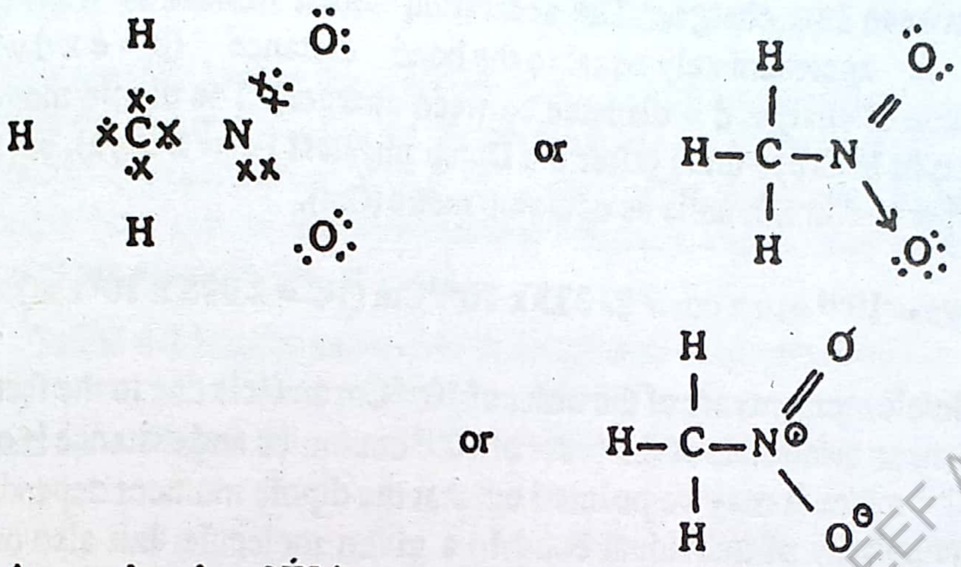
which may be represented as



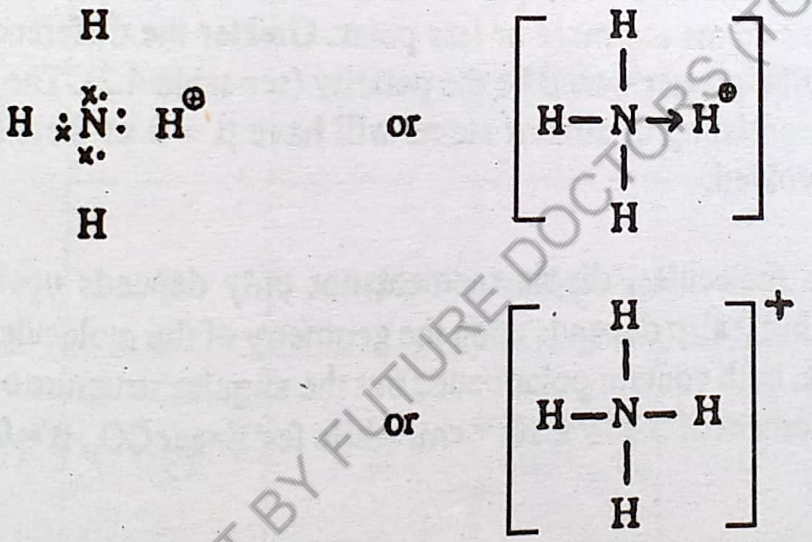
or as



(ii) Nitro methane, CH_3NO_2



(iii) Ammonium ion, NH_4^+



It may be pointed out that the co-ordinate bond and a covalent bond once formed are indistinguishable i.e. both are alike.

4.5 DIPOLE MOMENT

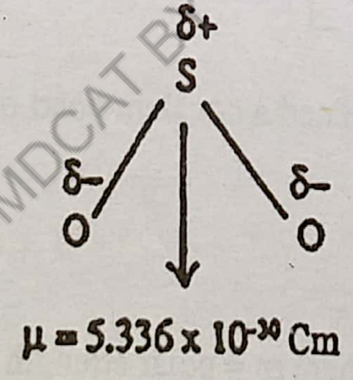
A magnet has the magnetic moment ml, where m = polar strength and l = distance between the two poles. A magnet tends to become oriented in a magnetic field. Likewise a dipole (polar molecule)-tends to become oriented in an electrical field. The extent of this tendency is referred to as the *dipole moment*,

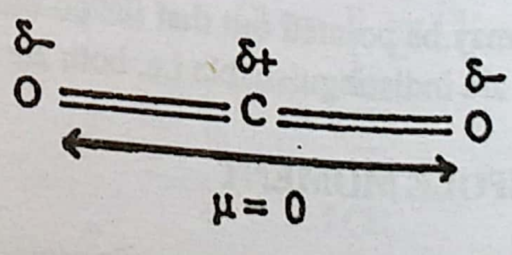
μ. It is measured by the magnitude of charge at each pole multiplied by the distance between two charges. The separation which in case of a diatomic molecule is approximately equal to the bond distance ($\mu = e \times d$ where e = magnitude of charge, d = distance between charges). The dipole moments were expressed in debye units (after the Dutch physicst Peter Debye), but now they are expressed in S.I. units as coulomb metre (Cm).

$$1 \text{ debye} = 10^{-18} \text{ esu} \times \text{cm} = 3.335 \times 10^{-30} \text{ Cm } (1C = 2.998 \times 10^9 \text{ esu})$$

The dipole moments are of the order of 10^{-30} Cm and it is due to the fact that the charge on an electron is of the order of 10^{-19} coulombs and distance is of the order of 10^{-10} metre. It may be pointed out that the dipole moment depends not only on the polarity of individual bond in a given molecule, but also on the geometry of a molecule as a whole. For diatomic molecule, polar bond means polar molecule, that is the two concepts coincide. The diatomic molecules consisting of different atoms are more or less polar. Greater the difference of electronegativity, Δ EN, greater would be the polarity (see table 4.2). The pure covalent molecules consisting of similar atoms will have $\mu = 0$ as there is no charge separation involved.

For polyatomic molecules, dipole moment not only depends upon the polarity of its bonds but it also depends upon the geometry of the molecule. SO_2 and CO_2, for instance, both contain polar bonds but the angular structure of SO_2 results in a dipole moment of 5.336×10^{-30} cm, while for linear CO_2, $\mu = 0$.





The net molecular moment is indicated by (→) and it is the vector sum of the individual bond moments. In CO_2, the double bonds lie on one straight line, that is, molecule is perfectly symmetrical. Hence although both bonds in CO_2 are polar, the two dipole moments of the molecule are equal oppositely directed, thus the molecule as a whole is nonpolar. Likewise CS_2 is also non polar ($\mu = O$)

Now consider carbon tetra chloride ($C\,Cl_4$) which contains four C – Cl bonds which are definitely polar but the symmetry gives $C\,Cl_4$ a zero dipole moment. Chloroform molecule ($CHCl_3$) on the other has a dipole moment of 3.40×10^{-30} cm due to its asymmetrical structure. Dipole moments of some molecules are given in the table 4.2.

Table 4.2 Dipole moments in debye and coulomb metre.

Molecule	μ = debye	μ = Cm	Molecule	μ = Debye	μ = Cm
(i) H_2	O	O	(vi) HCl	1.03	3.436×10^{-30}
(ii) Cl_2	O	O	(vii) H_2O	1.84	6.137×10^{-30}
(iii) CCl_4	O	O	(viii) NH_3	1.46	5.002×10^{-30}
(iv) CO_2	O	O	(ix) C_6H_6	O	O
(v) HF	1.90	6.369×10^{-30}	(x) $CHCl_3$	1.02	3.40×10^{-30}

4.6 IONIC CHARACTER OF COVALENT BOND

It was made clear in the previous section that in case of Cl_2, O_2 and N_2 molecules where the atoms are identical, the shared electrons are equally attracted due to identical electronegativities; neither atom attracts electrons more strongly than the other and the electron density is distributed equally over the two atoms in a molecule. Cl_2, O_2 and N_2 molecules are therefore *non-polar.*

The molecules consisting of different atoms such as H_2O, HF etc. present a different situation. In these cases, the shared electrons are not equally attracted. In H_2O, for instance, oxygen attracts the bonding electrons to a greater extent. The electron cloud of the molecule is shifted towards oxygen so that this end of molecule has a greater concentration of negative than positive charge. Similarly in HF molecule, fluorine is more electronegative, so this end has greater portion of the negative charge (Fig. 4.2). Consequently in both the molecules, H_2O and HF, the hydrogen end is correspondingly more positive. This situation is indicated by using the symbols δ and δ^+ when δ (delta) represents the partial electrostatic charge separated between the two atoms ($\delta^- + \delta^+ = O$)

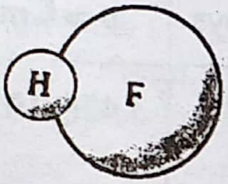
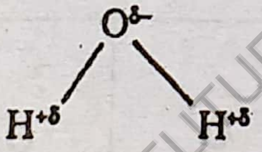


FIGURE 4.2
The electron density distribution in the HF molecule. The more electronegative fluorine atom attracts a large portion of the electron density cloud.



$H^{\delta+} - F^{\delta-}$

The covalent bonds in H_2O and HF are therefore *polarbonds.* These covalent bonds are not pure covalent but they have *partial ionic character.* The difference in the electronegativity of the two bonded atoms determines the extent of the ionic character of a covalent bond. For instance the H–F bond is 64% ionic and H–Cl is only 17% ionic. The partial ionic character greatly affects the properties of a molecule. For example, melting and boiling points of polar molecules are high and they are soluble in the polar solvent such as H_2O. Further more, the presence of partial character shortens the covalent bond, that is, pulls the atoms closer together. For example, the expected H–F bond distance is 1.01A where as the actual value is 0.92Å. Due to shortened bond distance it is quite obvious that the bond energy must increase accordingly. For example the bond energy of H–F molecule is 268 KJ/mol more than the calculated value.

4.7 BOND ENERGY

The energy change in chemical reactions is due to the bonds being formed and broken. A chemical bond is the link between two atoms and represents the lowering of energy. Work must be done if the atoms are to be separated. *The energy required to break a bond between two atoms in a diatomic molecule is known as the bond energy.* It is expressed in kilo joules per mole (i.e. the energy change per 6.02 x 10^{23} bonds):

$$\underset{\text{Hydrogen molecule}}{H-H_{(g)}} \rightarrow \underset{\text{Free atoms of Hydrogen}}{2H_{(g)}} \qquad \Delta H = 435\ KJ\ mol^{-1}$$

$$\underset{\text{Oxygen molecule}}{O=O_{(g)}} \rightarrow \underset{\text{Free atoms of oxygen}}{2\,O_{(g)}} \qquad \Delta H = 498\ KJ\ mol^{-1}{}_{(g)}$$

Alternatively, the bond energy might be taken as the energy released in forming a bond from the free atoms (not from the elements in their standard states):

$$H_{(g)} + H_{(g)} \rightarrow H-H_{(g)} \qquad \Delta H = -435\ KJ\ mol^{-1}$$

$$O_{(g)} + O_{(g)} \rightarrow O=O_{(g)} \qquad \Delta H = -498\ KJ\ mol^{-1}$$

Notice that the breaking of bonds is endothermic and making of bonds is exothermic process.

Bond energy is the measure of the strength of bonds. Generally, bond energies of polar bonds are greater than the pure covalent bonds (non polar):

$$\underset{\text{Non-polar molecule}}{Cl-Cl_{(g)}} \rightarrow 2\,Cl_{(g)} \qquad \Delta H = 244\ KJ\ mol^{-1}$$

$$\underset{\text{Polar molecule.}}{H^{\delta+} — Cl^{\delta-}_{(g)}} \rightarrow H^{+}_{(g)} + Cl^{-}_{(g)} \qquad \Delta H = 431\ KJ\ mol^{-1}$$

It is worth while to remember that the bond energy depends upon the partial ionic character of a covalent bond. Larger the ionic character greater the value of bond energy.

Polar molecules	$\overset{\delta^+}{H}-\overset{\delta^-}{F}$	$\overset{\delta^+}{H}-\overset{\delta^-}{Cl}$	$\overset{\delta^+}{H}-\overset{\delta^-}{Br}$	$\overset{\delta^+}{H}-\overset{\delta^-}{I}$
Bond energy (KJmol^{-1})	565	431	364	299

The value of bond energy also depends upon the *bond distance*. Shorter the bond distance, stronger the bond and greater would be the bond energy. For example triple bonds are usually shorter than the double bonds which in turn are shorter than the single bonds. Hence the bond energies for multiple bonds would generally be greater than those of single bonds (See table 4.3)

Table 4.3 Bond distances and Bond energies for single, double and triple bonds.

BOND	BOND DISTANCE (A)	BOND ENERGY (KJ mol^{-1})
C — C	1.54 A	347
C = C	1.34	598
C ≡ C	1.20	820
N ≡ N	1.10	946

Information of bond energy can help in understanding of chemical reactivity. For instance, bond energies of H_2 and O_2 are higher than for most diatomic molecules and are sufficiently high so that when their molecules collide with each other at room temperature, they simply rebound and no chemical reaction occurs.

4.8 SIGMA AND PI BONDS

In 1916, Lewis introduced the electron pair concept of a covalent bond.

However, it failed to account for the geometry and magnetic properties of molecules. In 1927, Heitler and London extended the Lewis theory and proposed *valence Bond Theory* (VBT) and in the early 1930's Hund, Huckle, Mulliken and others developed an alternative theory which is known as the Molecular Orbital Theory (MOT). According to both these theories, a covalent bond is formed by the overlap (fusion) of the atomic orbitals. Nevertheless, valence bond theory suggests that the bonding electrons occupy the *atomic orbitals* of the bonded atoms and molecular orbital theory assumes that the electrons occupy the *molecular orbitals* which belong to the molecule as a whole.

An essential difference between atomic orbital and molecular orbital is that an electron in the atomic orbital is influenced by one nucleus (mono centric) and in the molecular orbital, it is influenced by more than one nucleus (polycentric). According to the molecular orbital theory, linear combination of atomic orbitals (LCAO) gives two kinds of molecular orbitals. A molecular orbital with high electron density in the region between two nuclei having lower energy (greater stability) than either of the parent atomic orbitals from which molecular orbital is derived known as molecular bonding orbital. The other molecular orbital having higher energy with a nodel plane or of low electron density between the two nuclei, is less stable than either of the parent atomic orbitals from which it is derived, is known as antibonding molecular orbital. The energy difference of bonding and antibonding orbitals is shown by the energy diagram in Fig.4.4.

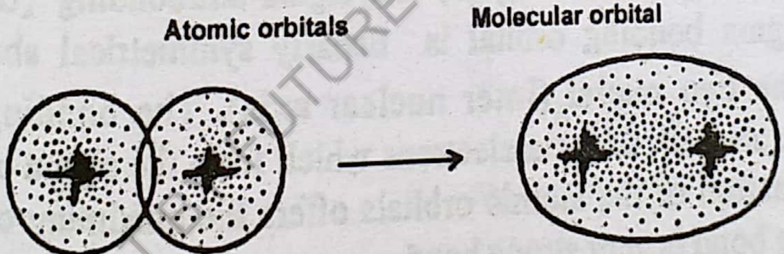


FIGURE 4.3
The two Is atomic orbitals and the resulting molecular orbital represented in terms of charge clouds.

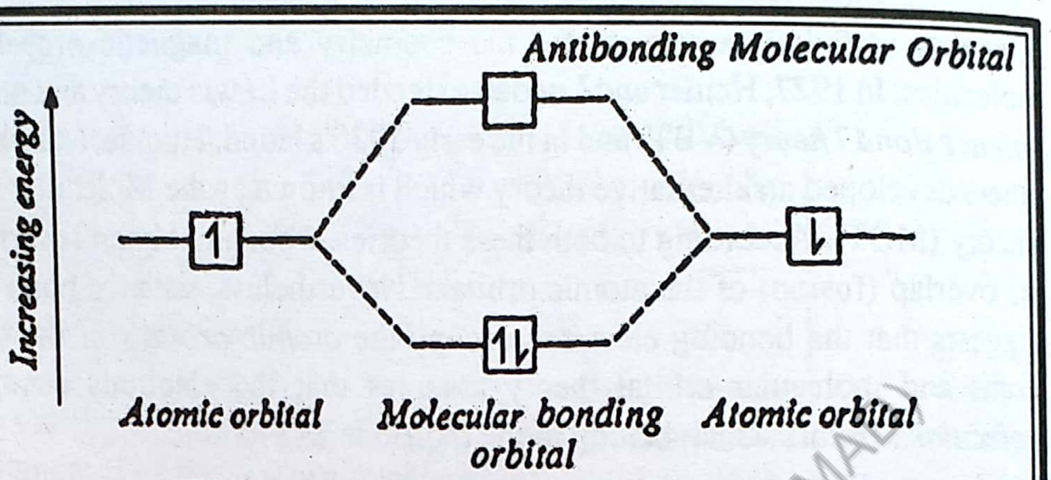


FIGURE 4.4
Energy diagram of bonding and anti bonding orbitals.

The bonding molecular orbitals which are formed by the linear combination or over lap of the two atomic orbitals, are designated by the Greek letter σ (sigma) and the bonding molecular orbitals which are formed by the parallel over lap of the two atomic orbitals, are designated by the Greek letter π (pi).

σ Bond: The 'linear' or 'head to head' overlap of the atomic orbitals like s - s, s - p, p - p give sigma bonding (σ) and sigma antibonding (σ^*) molecular orbitals. A sigma bonding orbital is linearly symmetrical about the axis connecting the two nuclei (inter nuclear axis). The bonding electrons contained in it are called sigma electrons which form the sigma bond. As the end on combination of the atomic orbitals offers the maximum overlape, the resulting sigma bond is very strong bond.

s-s type overlap is found in H_2 molecule when $1s^1$ orbital of one hydrogen overlaps $1s^1$orbital of the other to form sigma bonding orbital which constitutes the single covalent bond in H_2 molecule. The antibonding orbital remains unoccupied (Fig: 4.5).

s-p type overlap occurs in HF molecule when $1s^1$ orbital of hydrogen overlaps 2 p orbital of fluorine to form sigma bonding orbital which constitutes the single covalent bond in HF molecule (Fig. 4.6)

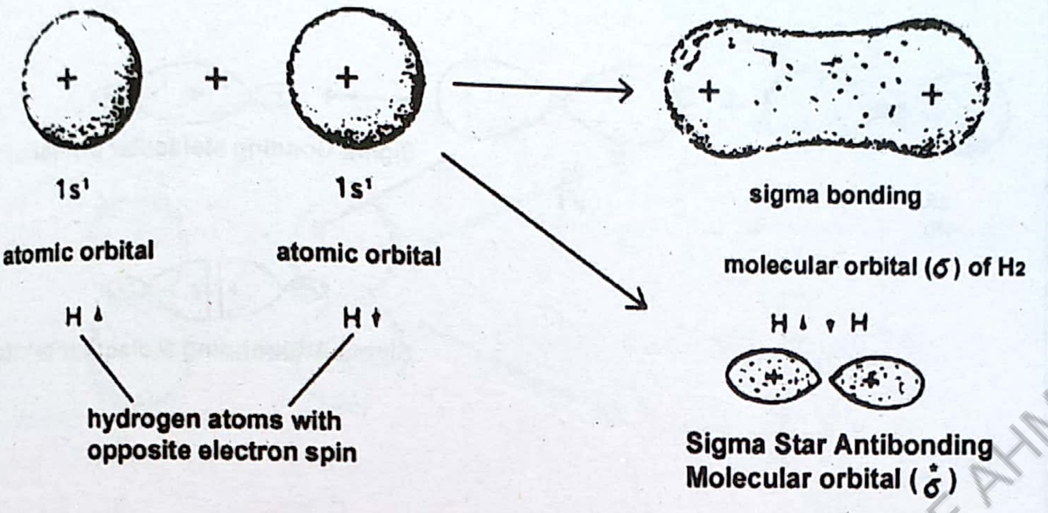


FIGURE 4.5
The hydrogen molecule.

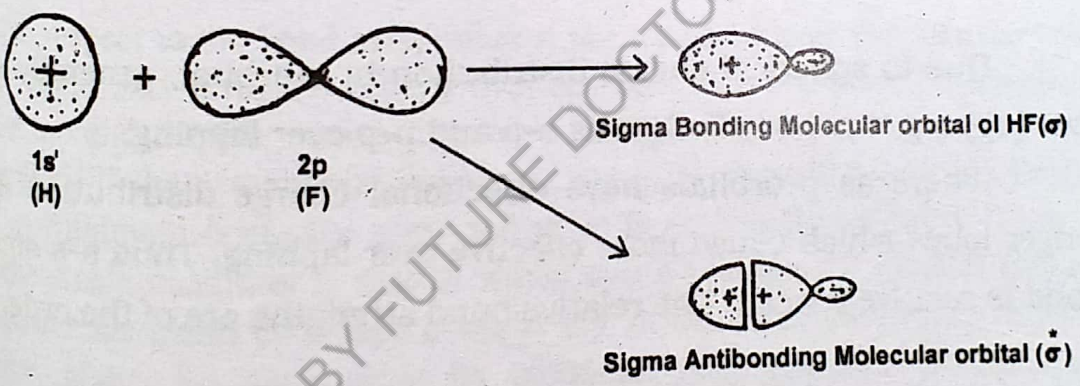


FIGURE 4.6
Hydrogen Fluoride molecule (HF)

p-p type overlap is seen in F_2 molecule where $2p_z$ orbital of one fluorine overlaps $2p_z$ orbital of the other fluorine to form F-F sigmabond. (fig. 4.7).

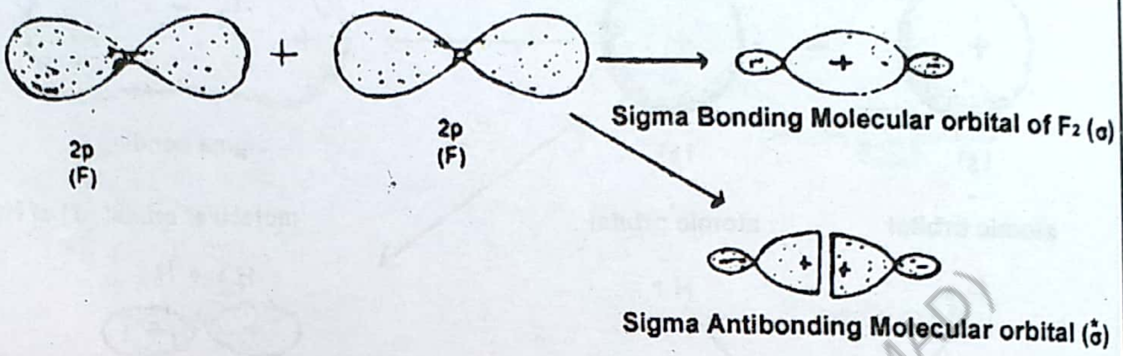


FIGURE 4.7
Flourine molecule (F_2)

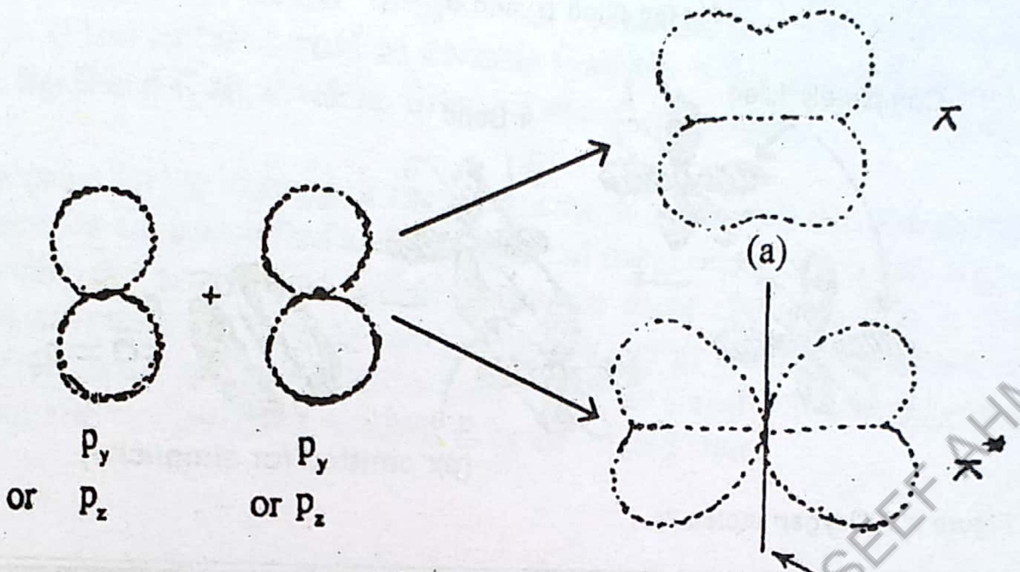
The relative strength of a sigma bond is related to the extent of overlap of the atomic orbitals. This is known as the *principle of maximum overlap*.

Due to spherical charge distribution in s–orbital, generally s–s over lapping is not so effective as s–p and p–p over lapping.

Where as p–orbitals have directional charge distribution and longer lobes which cause more effective over lapping. Thus s–s sigma bond is relatively weak. The relative bond strengths are of the order:

s − s,	s − p,	p − p
1.0	1.732	3.0

p_i Bond: The 'lateral or side ways' overlap of the p-orbitals provided they are on the two atoms which are already bonded through a sigma bond and their axes are co-planar, gives two molecular orbitals – pi bonding (π) and pi antibonding (π^*). The pi bonding orbital has two regions of electron density below and above the nodal plane (Fig. 4.8). The electrons contained in it are called pi bonding electrons which form the pi bond. It is not linearly symmetrical



(a) π bonding

(*b*) π^* Antibonding

FIGURE 4.8

with respect to the bond axis, rather it has a nodal plane; the rotation about the bond axis seriously affects overlap between the p-orbitals. Maximum overlap and therefore maximum bond strength requires two p orbital to be parallel. If the two atomic orbitals are mutually perpendicular, this overlap is at minimum (virtually zero) and there is essentially no bond. Thus the most stable condition is that in which two p-orbitals are parallel and this requires the atoms or groups at either end of the molecule should lie in the same plane, i.e. they must be coplanar. Any rotation of the atoms or groups at either end, with relative to one another requires sufficient energy to break the pi-bond. At room temperature, the molecules containing pi bond such as alkenes do not have sufficient energy to allow the rotation to take place, and the result is the restriction of rotation.

O_2 molecule is formed by the combination of two oxygen atoms. Each oxygen atom consists of two partially filled $2p_y$ and $2p_z$ orbitals. $2p_y$ orbitals of the two atoms overlap end on to form a sigma bond leaving $2p_z$ orbitals parallel on the two atoms. The side to side overlap of $2p_z$ orbitals form a pi bond between the two oxygen atoms.

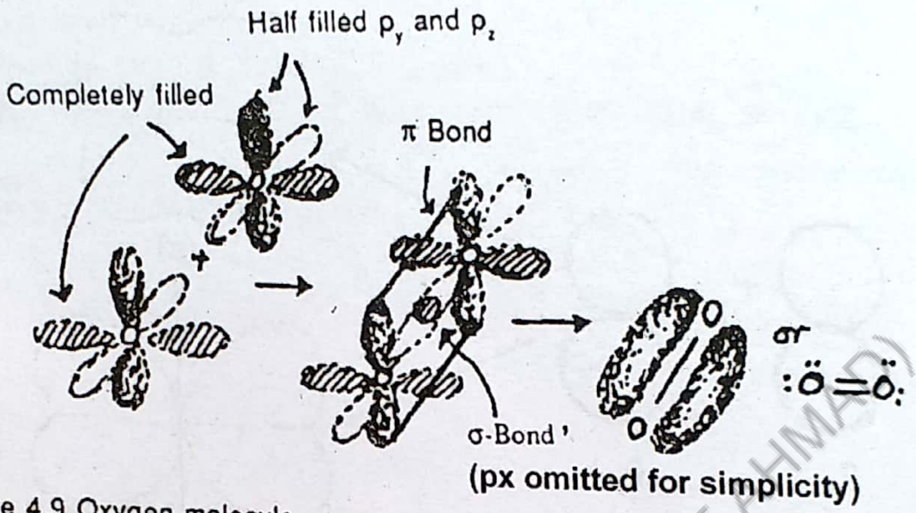


Figure 4.9 Oxygen molecule.

Fig: 4.9 Formation of sigma bond and pi bond between two oxygen atoms. Thus oxygen molecule consists of one sigma plus one pi bond (i.e. double bond). Similarly in nitrogen molecule, there is one sigma plus two pi bonds (i.e. triple bond).

From the above discussion we conclude that all the single bonds are sigma bonds, double bonds are one sigma plus one pi bond and the triple bonds are one sigma plus two pi bonds. Further more, a pi bond is weaker than sigma bond as the side ways overlap is less effective than the end on overlap.

4.9 HYBRIDIZATION

Valency is generally regarded as the number of unpaired electrons in the valence shell of an atom. However, this rule is disregarded in some cases such as Beryllium, Boron, Carbon etc. The electron arrangements of these elements in their ground states (low energy states) are given below:

		Is	2s	$2p_x$	$2p_y$	$2p_z$
$_4Be$	=	↑↓	↑↓			
$_5B$	=	↑↓	↑↓	↑		
$_6C$	=	↑↓	↑↓	↑	↑	

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

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

		Is	2s	$2p_x$	$2p_y$	$2p_z$
Be*	=	⇅	↑	↑		
B*	=	⇅	↑	↑	↑	
C*	=	⇅	↑	↑	↑	↑

The asterisk denotes the excited state of the atoms. The excited structure for carbon would give three bonds involving p–orbitals which would be at right angles to each other together with a single bond involving an s-orbital. CH_4, for instance would be expected to contain three s–p bonds mutually at right angles, and one, weaker s-s bond. It is well established however, that the four bonds in CH_4 are all alike. Similarly in BCl_3, all the three B–Cl bonds are identical or equivalent.

To account for the equivalence of bonds, the concept of *hybrid orbitals* was introduced by *Linus Pauling*. He assumed that the atomic orbitals having nearly equal energies can be combined in various ways within an atom to form equivalent hybrid orbitals. The mixing of different atomic orbitals to produce the same number of equivalent orbitals, having same shape and energy is known as hybridization. The orbitals so formed are called hybrid orbitals and are designated according to the number of mixing orbitals.

Mixing Orbitals	No. and type of Hybrid orbitals produced.	Type of Hybridization
One s–and three p	Four sp^3 orbitals	sp^3
One s–and two p	Three sp^2 orbitals	sp^2
One s–and one p	Two sp^1 orbitals	sp^2

The case of carbon and its compounds is of great importance, for carbon forms such a wide variety of well known organic compounds. The various types of hybridization are therefore, discussed below with special reference to carbon compounds.

sp^3 (Tetra hedral) hybridization: Combination of one s– and three p–orbitals to produce four sp^3 hybrid orbitals is known as sp^3 or tetrahedral

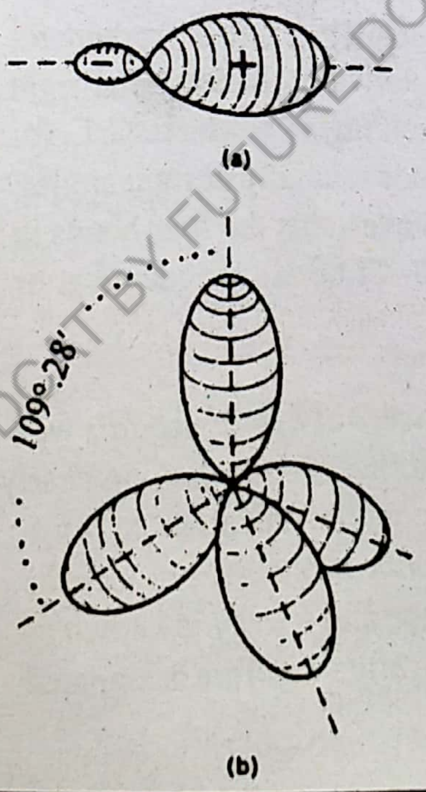


FIGURE 4.10
(a) A Sing sp^3 hybrid orbital.
(b) Four tetrahedrally disposed sp^3 hybrid orbitals.
(The smaller lobes are not shown).

hybridization. (Fig. 4.9). The hybrid orbitals are different than the pure s – or p– orbitals; they possess the character of both s– and p– orbitals in the ratio of 1:3. Sp^3 orbitals are directed towards the four corners of regular tetrahedron in which each angle is 109°. 28'. (Fig. 4.10). These orbitals can form stronger bonds than either s– or p– orbitals because of their size they can overlap more effectively. Sp^3 hybridization occurs in the saturated compounds in which the carbon is attached to four atoms. In methane, CH_4, for example Is– orbital of each hydrogen atom overalp with sp^3 hybrid orbital of the carbon atom to form four sigma bonds; the bond angle in CH_4 is 109°.28 (fig. 4.11). Other similar, symmetrical molecules involving sp^3 hybridization are CCl_4, $SiCl_4$, $SnCl_4$ etc. All such molecules have tetrahedral geometry like methane.

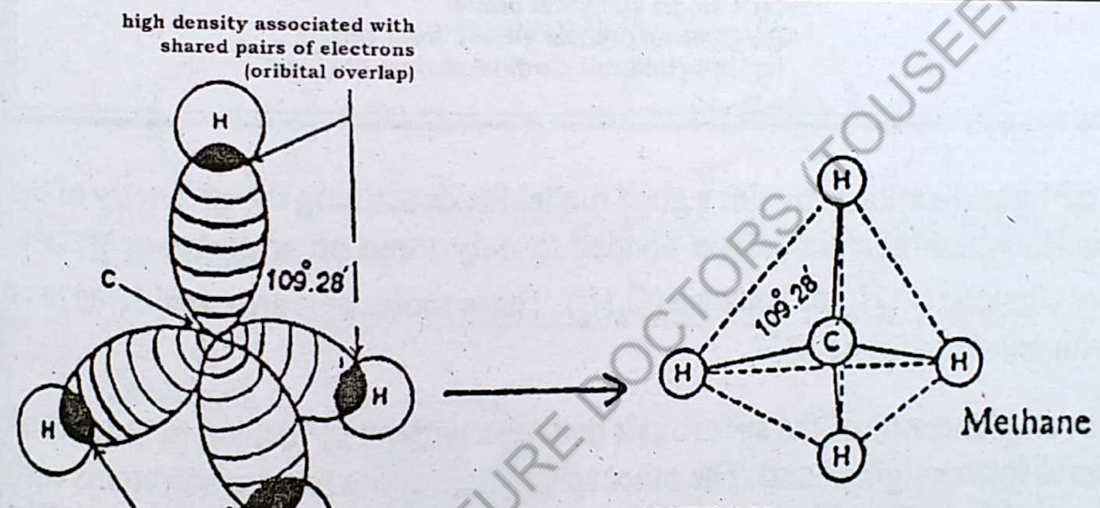


FIGURE 4.11
Orbital overlaps in methane between hydrogen 1s-orbitals (spherical) and carbon sp^3 orbitals.

sp^3 (Trigonal) hybridization: The mixing of one s- and two p- orbitals to produce three sp^2 hybrid orbitals is referred to as sp^2 or trigonal hybridization. These orbitals are co-planar and directed towards the corners of an equilateral triangle (trigonal) at angles of 120° to each other (fig. 4.12). sp^2 orbitals are different than either s – or p – orbitals and they are considered to have a character that is one third s and two thirds p. The fourth pure p – orbital which is not involved in hybridization remains unhybridized at right angles to the plane of the sp^2 orbitals (Fig. 4.12). Like sp^3 orbitals, the sp^2 orbitals can also form stronger bonds because on account of their size, they can overlap more effectively with the orbitals of the other atoms.

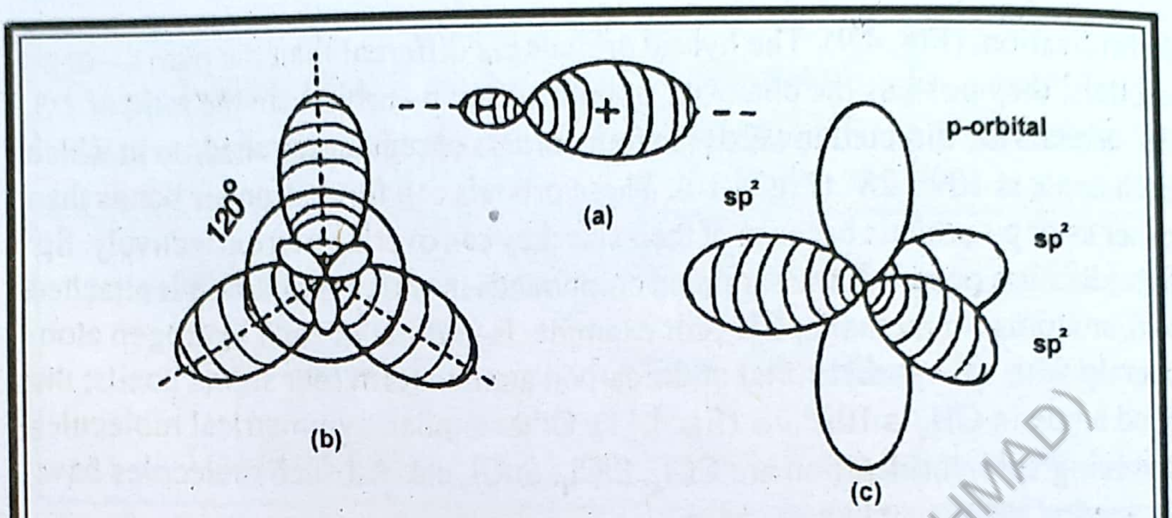


FIGURE 4.12
(a) A single sp^2 hybrid orbital
(b) Three sp^2 orbitals viewed from above
(c) Un-hybridized p-orbital at right angles

sp² hybridization provides a good model for describing the geometry of the molecules which contain carbon bonded to only three other atoms or groups, such as ethylene (C_2H_4) or benzene (C_6H_6). These molecules are considered to be flat with bond angles of 120°.

In ethylene, one of the sp² orbitals overlaps with an sp² orbital of the second carbon to form a sigma bond. The other sp² orbitals of the two carbon atoms each overlaps with the Is orbital of a hydrogen atom, to form four sigma bonds. The unhybridized 2p orbitals of the carbon atoms now overlap above and below the

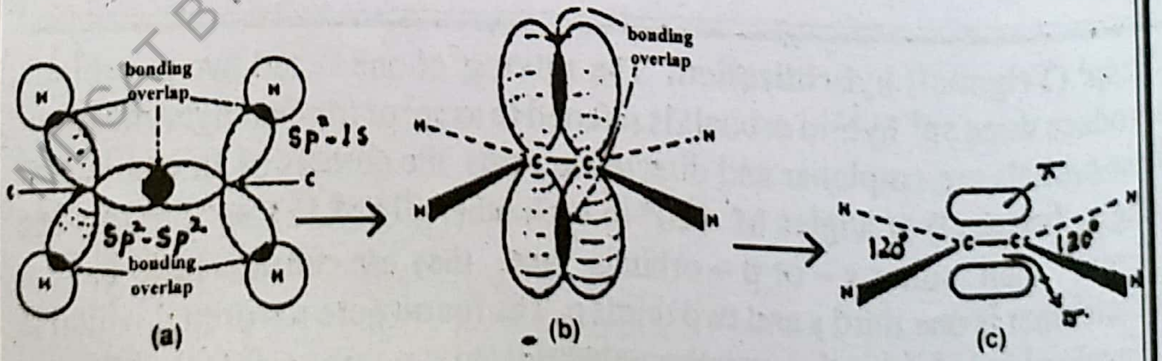
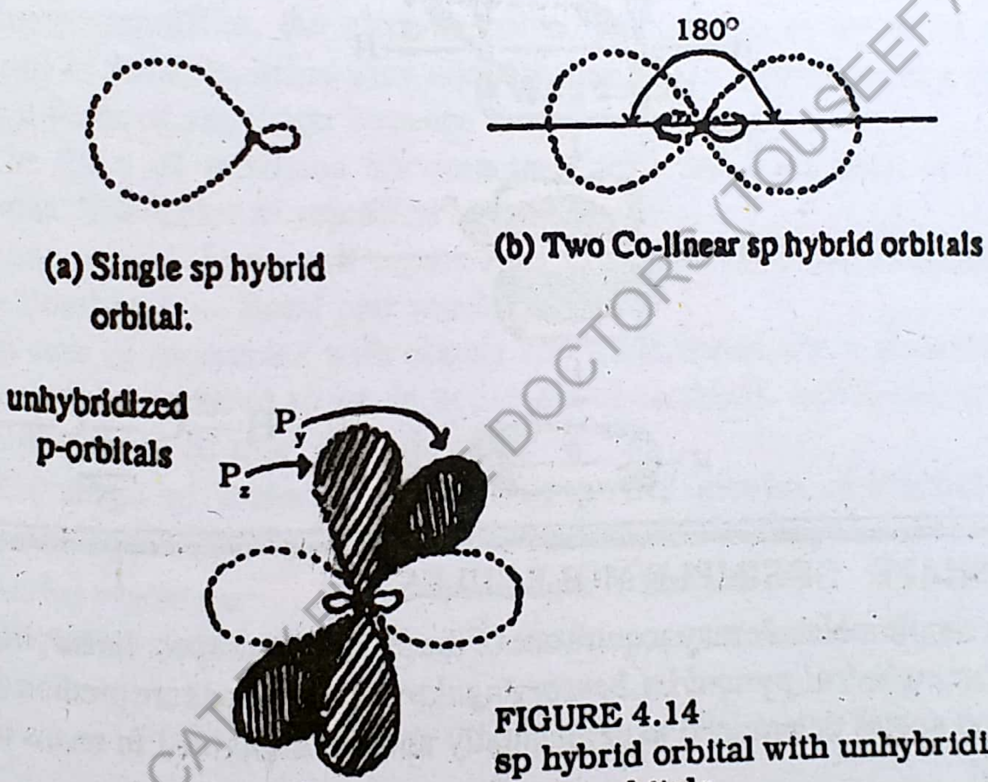


FIGURE 4.13
Molecular orbital diagram of Ethylene

plane to form a π bond (Fig. 4.13). Carbon-oxygen ($>C=O$), carbon-nitrogen ($>C=N-$) and other double bonds are formed in the same way. The two bonds (one sigma and one pi) making up the double bond are not equivalent to two single (sigma) bonds. It may be pointed out here that Boron also utilizes sp^2 orbitals for bond making (Section 4.9).

sp (diagonal) hybridization: The hybridization of an s- and a p- orbital leads to two hybrid orbitals known as sp orbitals. These orbitals are co-linear at an angle of 180° which provides maximum separation and overlap (Fig. 4.14). The unhybridized two p-orbitals ($2p_y$, $2p_z$) remain at right angles to the plane of the hybrid orbitals (Fig. 4.14).



(a) Single sp hybrid orbital:

(b) Two Co-linear sp hybrid orbitals

FIGURE 4.14
sp hybrid orbital with unhybridized P_y, P_z orbitals.

sp hybridization has been very useful in explaining the geometry of the molecules which contains carbon bonded to two other atoms or groups such as ethyne or acetylene (C_2H_2).

In ethyne molecule, one of the sp orbitals overlaps with one sp orbital of the second carbon to form a sigma bond, while the two remaining sp orbitals form sigma bonds with hydrogen atoms. The unhybridized p-orbitals overlap in parallel manner and two pi bonds are obtained in planes at right angles above below and on either side of the linear molecule (Fig. 4.15). like carbon, Beryllium utilizes sp^1 orbitals in bond making (Section 4.9).

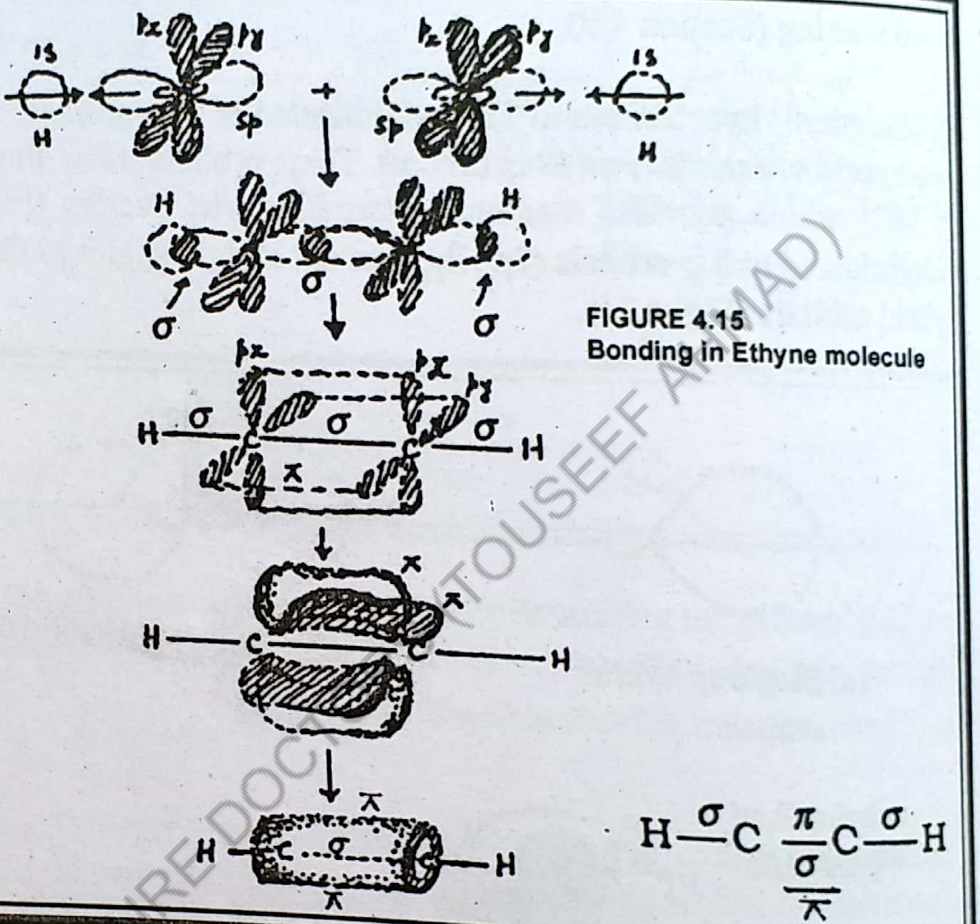


FIGURE 4.15
Bonding in Ethyne molecule

4.10 SHAPE. OF SIMPLE MOLECULES

A simple molecule may acquire one of the following shapes: *linear, trigonal planar, tetra hedral, pyramidal, bent or angular*. These shapes are predicted from the bond angles determined experimentally and are explained in terms of two models:

(i) Electron pair repulsion model (ii). Hybrid orbital model.

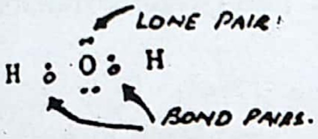
The assumptions of these models summarized below will serve as the guide lines to explain the shapes of molecules.

The electron pair repulsion model: This approach to the structure of a covalent molecule is due to SIGWICK and POWELL (1940).

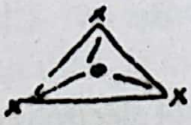
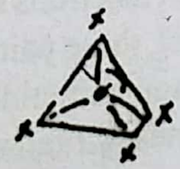
They pointed out that the shapes of molecules can be determined by the repulsion between the electron pairs present in valency shell of central atom.

The main postulates of this model or theory are:

1. There may be two types of electron pairs surrounding the central atom
   (a) Bond Pairs : These are the result of the sharing of unpaired electrons of central atom with unpaired electrons of surrounding atoms. These are also called ACTIVE SET OF ELECTRONS.
   (b) Lone Pairs : These are the paired electrons, which have not taken part in sharing. They are also called NON-BONDING PAIRS. They are also considered to be ACTIVE SET OF ELECTRONS.



2. Being similarly charged (i.e. negative) the bond pairs as well as the lone pairs repel each other.
3. Due to repulsion, the electron pairs of central atom try to be as far apart as possible, hence they orient themselves in space in such a manner that force of repulsion between them is minimized.
4. The force of repulsion between lone pairs and bond pairs is not the same. The order of repulsion is as follows:
   Lone pair — Lone pair repulsion > Lone pair — Bond pair repulsion > Bond pair — Bond pair repulsion.
5. In case of molecules with double and triple bonds, the π electron pairs are not considered to be an active set of electrons, hence not included in the count of total electron pairs.
6. The shape of molecule depends upon total number of electron pairs (bonding and lone pairs).It is summarized as follows.

Number of electron pairs around central atom		Geometry of Molecule	Bond Angle	Example
2	Linear		180°	BeCl$_2$; C$_2$H$_2$; CO$_2$; CS$_2$
3	Planar Trigonal		120°	BF$_3$; C$_2$H$_4$; SO$_2$; CO$_3^{-2}$
4	Tetrahedral		109°	CH$_4$; NH$_3$; H$_2$O CCl$_4$; CBr$_4$

Hybrid Orbital Model assumes that it is the nature of hybrid orbitals (i.e. hybridization) which determines the shape of a molecule.

sp-hybridization in the central atom gives linear molecule with an angle of 180°.

sp^2-hybridization in the central atom gives planar trigonal structure with an angle of 120°.

sp^3-hybridization with no lone pair or non-bonding orbital on the central atom gives tetrahedral geometry with bond angles of 109°. 28'.

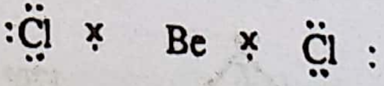
sp^3-hybridization with one nonbonding orbital (lone pair) gives pyramidal structure with an angle of 107°.

sp^3-hybridization with two non-bonding orbital on central atom gives bent or angular structure with bond angle of 104.5°.

The larger atoms of Groups VA and VIA such as phosphorus and sulphur do not use sp^3 hybrid orbitals in bond making, instead they utilize their p-orbitals which are mutually at right angles. Such elements form compounds with bond angles of about 90°.

Linear Molecules : All the diatomic molecules such as HF, HCl etc. are linear regardless of the number of active electron pairs surrounding the central atom. It is because, there are only two atoms in a diatomic molecule. Molecules containing more than two atoms can also have the linear shapes, for example, Beryllium Chloride ($BeCl_2$) is a triatomic linear molecule with the bond angle 180°.

The Lewis structure of $BeCl_2$ is represented as :


$$:\ddot{\underset{..}{Cl}}\ \times\ Be\ \times\ \ddot{\underset{..}{Cl}}\ :$$

Here there are two active sets of electrons surrounding the Beryllium atoms. In terms of electron repulsion model, these pairs must be arranged as far apart as possible, that is, the two chlorine atoms should be placed on the opposite side of beryllium which would give the linear structure of $BeCl_2$.

In terms of hybrid model, beryllium uses its sp-hybrid orbitals in bond making (i.e. beryllium is sp-hybridized).

$Be = 1s^2, 2s^2$ Excited $1s^2, 2s^1, 2p_x^1$ Hybridization Two sp^1 orbitals.

Both the sp^1 orbitals are arranged linearly at an angle of 180°. These orbitals overlap with $3p_x$ orbitals of the two chlorine atoms to form two sigma bonds, all the three atoms being in straight line (Fig. 4.16).

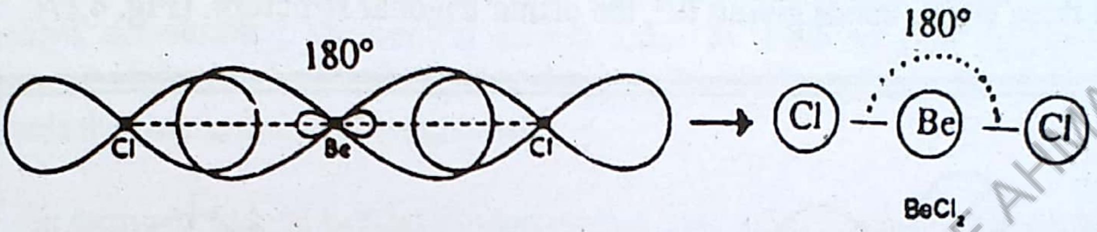


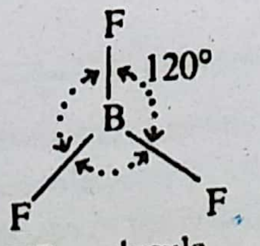
FIGURE 4.16
The formation of two a-bonds in $BeCl_2$ by overlap of $3p_x$ orbitals from two chlorine atom with two hybrid sp orbitals from a beryllium atom.

The linear structure of ethyne (H—C≡C—H) has already been discussed (Refer sp^1 hybridization). Likewise CO_2 and CS_2 are also linear molecules:

$$O = C = O \qquad S = C = S$$

(There are two electron pairs on the central atom carbon in each case)

Planar Trigonal Molecules : Boron trifluoride, BF_3, is a tetra-atomic planar trigonal molecule with the bond angles of 120°. The Lewis structure of BF_3 shows that there are three electron pairs surrounding the central Born atom. In terms of electron repulsion model, these electron pairs must be arranged as far apart as possible to minimize the repulsion, it is achieved by placing three fluorine atoms at the three corners of equilateral triangle in which each angle is of 120°.

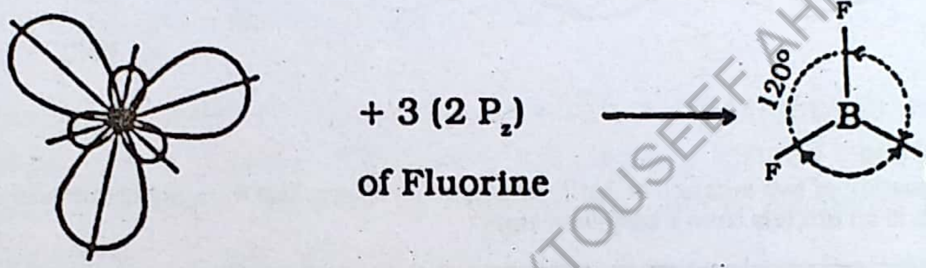


BF_3 molecule

In terms of the hybrid orbital model, boron atom undergoes sp² hybridization producing three sp² orbitals.

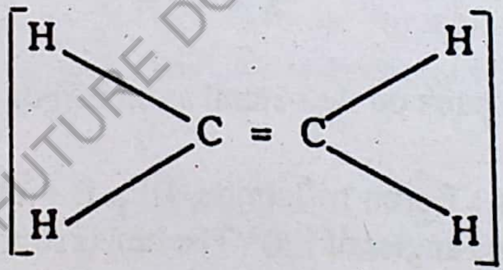
$B = 1s^2, 2s^2, 2p_x^1$ Excited $1s^2, 2s^1, 2p_x^1, 2p_y^1$ Hybridization Three sp² orbitals.

These orbitals are arranged trigonally in one plane (Coplanar) (Refer sp² hybridization). By overlapping with 2p orbitals of fluorine atoms, the sp² orbitals form three sigma bonds giving BF_3 the planar trigonal structure. (Fig. 4.17).

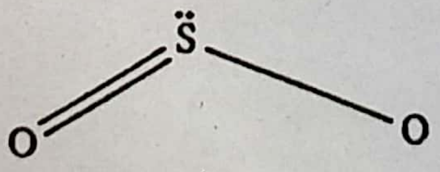


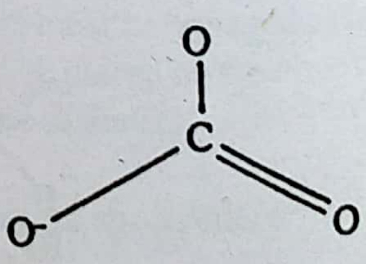
Three sp² orbitals of Boron.

FIGURE 4.17

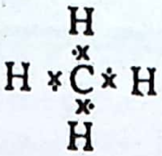


The planar trigonal geometry of Ethene has already been discussed in sp² hybridization. Sulphur dioxide, SO_2 and the carbonate ion, CO_3^{2-}, both have planar trigonal geometry because both S in SO_2 and C in CO_3^{2-} have three active sets of electrons surrounding them.





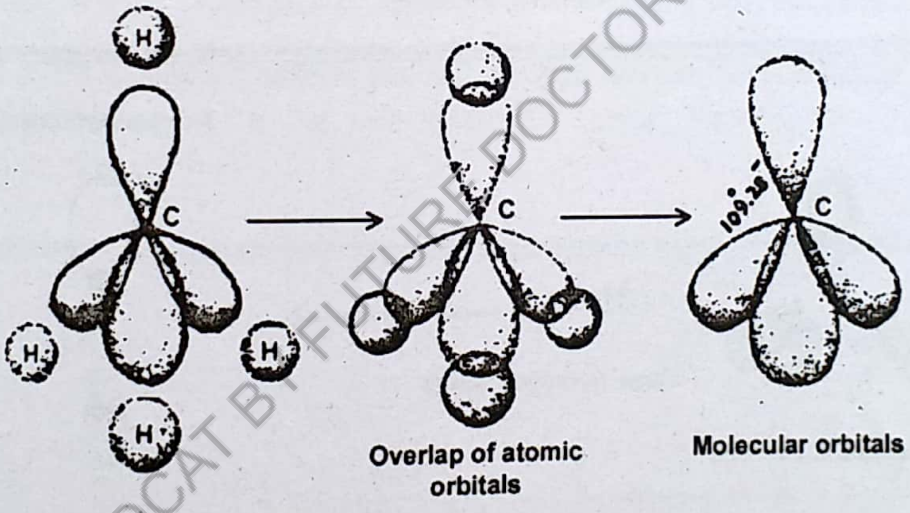
Tetrahedral Molecules : Methane, CH_4, is a tetrahedral molecule with bond angles 109°.28' (See Fig. 4.11) The Lewis structure of CH_4 is represented as :



$$\begin{array}{ccc} & H & \\ & \overset{\times}{\cdot} & \\ H \times\!\cdot & C & \cdot\!\times H \\ & \overset{\times}{\cdot} & \\ & H & \end{array}$$

In terms of electron pair repulsion model, there are four active sets of electrons surrounding the central carbon atom. In order to give maximum separation and minimum repulsion, the four hydrogen atoms must be directed towards the four corners of tetrahedron.

In terms of hybrid orbital model, carbon uses sp^3 orbitals to form sigma bonds with the hydrogen atoms as shown in the Fig. 4.18 (It has been discussed in sp^3 hybridization). Like wise all the compounds of CX_4 type such as CCl_4, CBr_4 etc. are tetrahedral with bond angles of 109°.28′



Overlap of atomic orbitals

Molecular orbitals

FIGURE 4.18
The structure of the methane molecule (the small lobes of the sp^3 orbitals have been omitted for simplicity).

Shape of Ammonia : The Lewis structure of NH_3 shows that the central atom nitrogen is surrounded by four electron pairs. In term of electron repulsions model, the tetrahedral structure gives the maximum separation as in the case of

CH_4. However, there is one lone pair electrons on nitrogen which repels the bonding pairs with the result that angle is reduced from 109° to 107°.

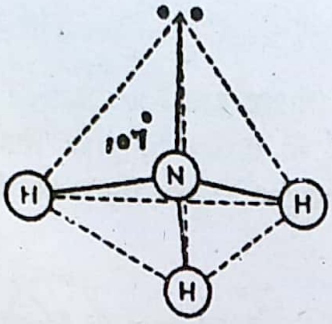


FIGURE 4.19
Shape of NH_3 molecule.

In term of hybrid orbital model, Nitrogen utilizes three of the four sp^3 orbitals to form sigma bonds with three hydrogen atoms having one non-bonding orbital on the nitrogen (Fig. 4.20). The deviation in the angle may be explained in terms of the non-bonding orbital.

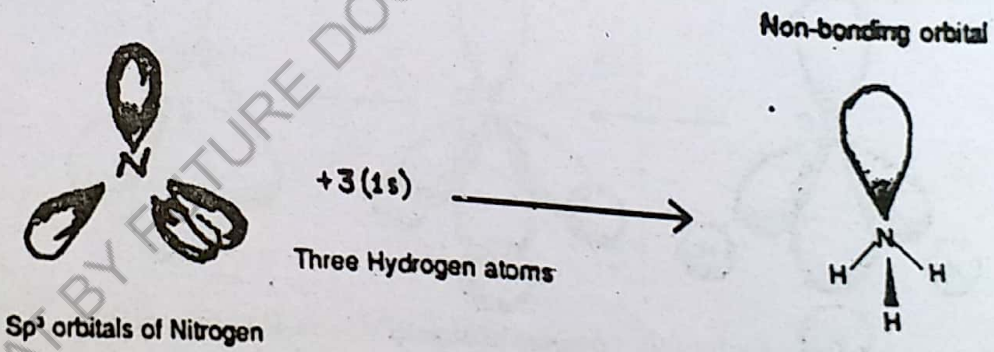


FIGURE 4.20
Shape of NH_3 molecule.

The electrons in the non-bonding orbital are associated with only one nucleus, and hence they are not held as tightly as the electrons in the bonding orbitals which are associated to two nuclei; consequently the non-bonding orbital occupies large volume of space. The larger orbital compresses the bonding orbitals slightly reducing the bond angle in the NH_3 to 107°

Shape of H_2O : As per Lewis Structure, the central atom oxygen is surrounded by the four active sets of electrons and according to the electron pair repulsion model, the tetrahedral arrangement would give maximum separation and minimum repulsion. However, the bond angle (H—O—H) is 104.5° (Fig. 4.21). The deviation in the angle is due to the presence of two lone pairs as explained in case of NH_3. The repulsion of the lone pairs and the bonded pairs reduces the angle from 109° to 104.5°.

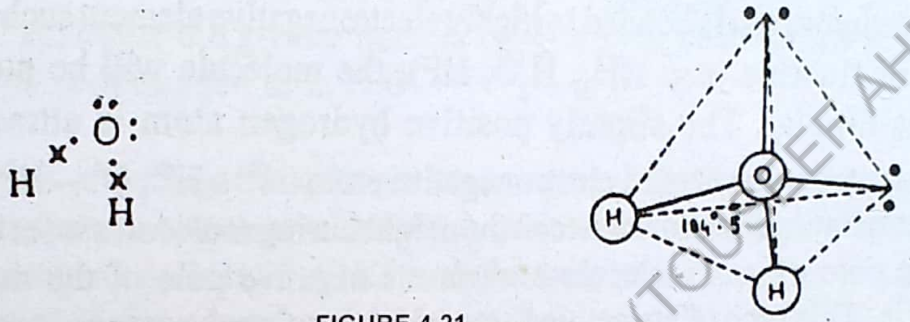


FIGURE 4.21
Shape of H_2O

In terms of hybrid orbital model, oxygen utilizes two of its sp^3 orbitals to form sigma bonds with the two hydrogen atoms, leaving two non-bonding orbitals on the oxygen.

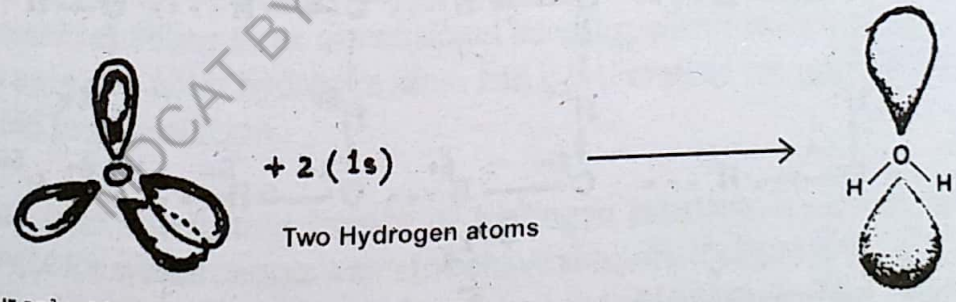


FIGURE 4.22
Shape of H_2O

As explained above, the non - bonding orbitals occupy the large volume of space, hence they compress the bonding orbitals and reduce the angle H–O–H in water to 104.5° giving angular or bent structure (Fig. 4.22).

Likewise, sulphur dichloride, SCl_2 is the angular molecule.

• 4.11 HYDROGEN BOND

Besides the ionic and covalent bonds which are the normal or primary bonds, there exists another type of bonding based on physical interaction of hydrogen atom called hydrogen bond.

When hydrogen is bonded to highly electronegative element such as nitrogen, oxygen or fluorine (e.g. NH_3, H_2O, HF), the molecule will be polarized and becomes dipolar. The slightly positive hydrogen atom is attracted by the slightly negatively charged electronegative atom ($N^{\delta-}-H^{\delta+}$, $O^{\delta-}-H^{\delta+}$, $F^{\delta-}-H^{\delta+}$). An electrostatic attraction between the neighbouring molecules is set up when the positive pole of one molecule attracts the negative pole of the neighbouring molecule. This type of attractive force which involves hydrogen is referred to as *hydrogen bond;* it is sometimes known as *protonic bridge*. To distinguish a hydrogen bond, it is best to write it as dotted line. The hydrogen bond causes the association of molecules as shown in fig. 4.23. Hydrogen fluoride and water, for instance are represented as $(HF)_x$ and $(H_2O)_x$.

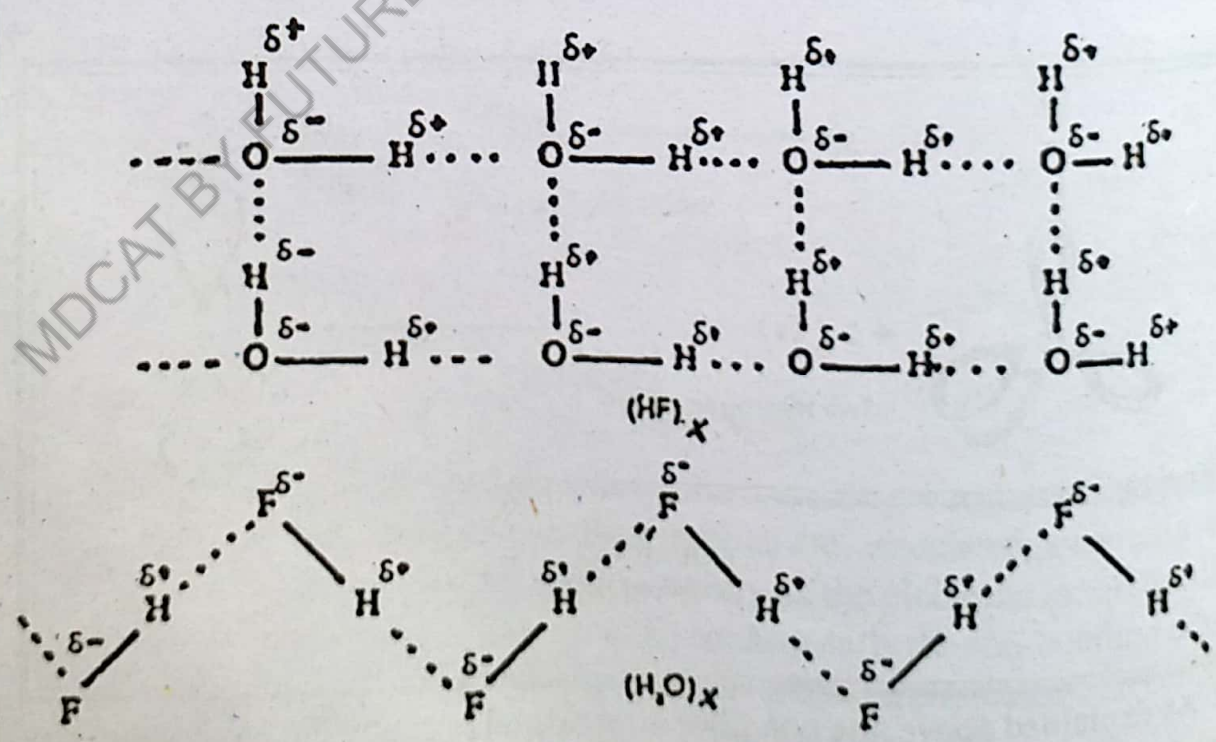


FIGURE 4.23
Association of HF and H_2O through hydrogen bonds.

Notice that within molecules, atoms are joined by strong covalent bonds but between the neighbouring molecules, hydrogen bonds exist. Thus hydrogen bonding is nothing but inter molecular attraction. The tendency to form hydrogen bonds increases rapidly from N–H through O–H to F–H and decreases from F–H to Cl–H and from O–H to S–H. Thus the tendency of a molecule to from hydrogen. bonds depends upon its ionic character which in turn depends upon the difference in electronegativity (ΔEN). Fluorine with the highest electronegativity forms the strongest hydrogen bonds. The bond strength (bond energy) of HF, H_2O and NH_3 (that is, for H......F, H......O and H......N) is 41.8, 29.4 and 8.4 KJ $mole^{-1}$ respectively. However the greater number of hydrogen bonds known are those which unite pairs of oxygen as in H_2O.

Although the hydrogen bonding is the strongest of the secondary bonds, it is still weaker than a normal covalent bond. It is evident from the fact that bond energy of hydrogen bonds is 20-40 KJ $mole^{-1}$ as compared to the bond energy of 150-500 KJ $mole^{-1}$ for normal covalent bonds.

The hydrogen bonding greatly affect the physical properties of molecules. For example, the first hydride in groups VA, VIA and VIIA of the periodic table (NH_3, H_2O and HF) have higher melting and boiling points than the other hydrides of these groups (e.g. PH_3, H_2S, HCl etc) as shown in the fig. 4.24.

Note that although fluorine is more electro negative than oxygen, water has a higher boiling point than hydrogen fluoride. This is because, the oxygen atom has two non-bonded pairs of electrons and there are two polar hydrogen atoms ($H^{\delta+}$) present enabling three dimensional bonding, where as in hydrogen fluoride, there is only one polar hydrogen atom and it is therefore only possible for chains of limited length to form.

The most interesting impact of hydrogen bonding is seen in the crystal structure of ice which causes water to behave abnormally from 0°C–4°C. Crystal structure of ice shows a tetrahedral arrangement of H_2O molecules. Each oxygen 'A' is surrounded tetrahedrally by four others, 1, 2, 3, 4. The hydrogen bonds shown by dotted lines (Fig. 4.25) link the pairs of oxygen atoms.

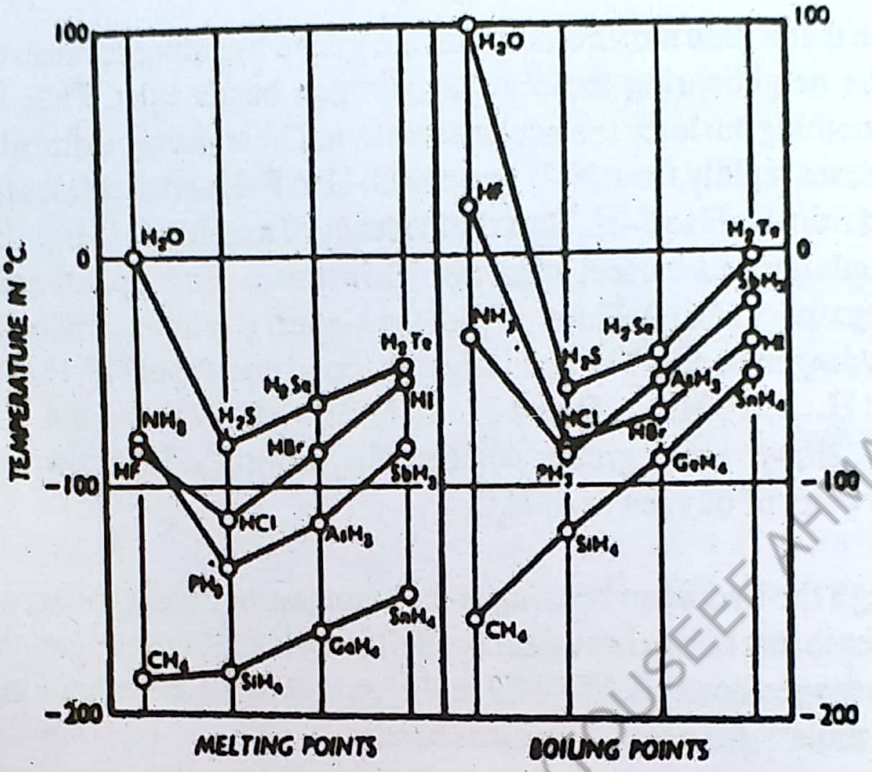


FIGURE 4.24
The abnormal melting and boiling points of water, hydrogen fluoride and ammonia.

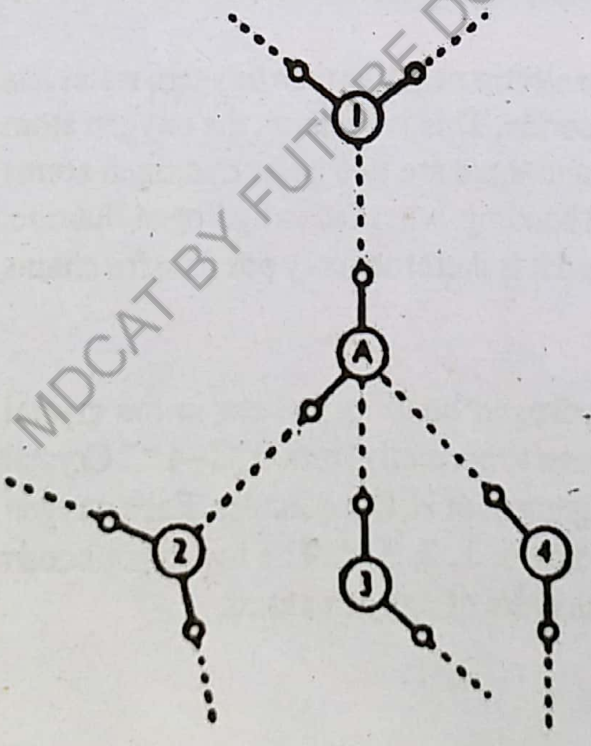


FIGURE 4.25
Crystal structure of ice.

The arrangement of the water molecules in ice is an open structure and due to larger volume, ice is less dense than liquid water. When ice melts some of the hydrogen bonds are broken and the molecules pack more closely together so that water has a higher density. This breaking down process is not complete until a temperature of 4°C is reached at which water has the maximum density. On these basis, the *anomalous* behaviour of water can be explained, that is, water when heated from 0° to 4°C contracts and when cooled from 4°C to 0°C, water expands (contrary to the behaviour of other liquids).

PROGRESS TEST 4

1. Describe the main types of bonds. What physical properties are associated with the molecules containing these bonds.
2. What is polar colvalent bond? Do all polar molecules contain polar covalent bonds? Do polar covalent bonds necessarily have polarity on a polar molecule as a whole? Support your answer with more specific examples.
3. Distinguish between the following:
   (i) Atomic orbital and molecular orbital.
   (ii) Sigma and pi bonds.
   (iii) Valence Bonds theory and Molecular orbital theory.
4. What do you understand by the term Dipole moment? Explain the significance of dipole moment.
5. What is meant by sp^3 hybrid orbitals? How do they differ from s - and p - orbitals?
6. Describe how electronegativity of atoms can be used to predict the nature of bond formed between two elements. Explain giving examples.
7. Write note on Bond energy.
8. What are the most important secondary bonds present in H_2O and HF molecules? How do they affect the physical properties of compound?
9. How can the theory of electron pair repulsion be used to rationalize the shapes of simple molecules.
10. Beryllium chloride has a linear shape where as water molecule has angular shape. Account for this difference in terms of electron pair repulsion model and hybrid orbital model.
11. Predict the shapes of the following molecules:
    PCl_3, PH_3, H_2S, SCl_2.

CHAPTER 5

ENERGETICS OF CHEMICAL REACTIONS

It is a matter of common observation that most of the things around us are in a continuous state of change or flux. These changes are important for all of us and we learn a great deal by looking at them and studying them carefully. One of the most observations is that all chemical changes are accompanied by important change in energy, that is energy is either absorbed or evolved. Heat energy is the most common form which is manifested in chemical reactions. Besides heat, other forms of energy are mechanical, electrical, chemical, radiant etc., which are stored in all substances.

A study based on the principle of conservation of energy is known as Thermodynamics. The laws of Thermodynamics are successfully used in Physics, Chemistry and Engineering.

Chemists are interested in the changes in materials and energy in the chemical reactions.

Chemical reactions which are accompanied by energy changes with the material changes, are generally known as Thermochemical reactions. In this chapter we are concerned with the energy changes taking place in chemical reactions in an elementary way. Thermochemical reactions are classified as (i) Exothermic reactions and (ii) Endothermic reactions.

(i) **Exothermic Reactions:** The chemical reactions which are accompanied by the liberation or emission of energy are called exothermic reactions. All combustion reactions are exothermic reactions.

e.g. $C + O_2 \longrightarrow CO_2 + \text{heat}$

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \text{heat}$

(ii) **Endothermic Reactions:** The chemical reactions are accompanied by the absorption of energy are called endothermic reactions.

e.g. $C + 2S + \text{heat} \longrightarrow CS_2$

$H_2 + I_2 + \text{heat} \longrightarrow 2H1$

The heat evolved or absorbed during chemical reactions depends upon (1) The amount of Chemical substances involved (2) The physical states of the substances involved (3) The temperature and (4) Whether the reaction occurs at constant pressure or constant volume.

5.1 THERMODYNAMIC TERMS (SYSTEM, SURROUNDINGS AND STATES)

The properties or changes of the matter are usually investigated by controlled experiments. Any real or imaginary portion of the universe or anything which is under examination or under consideration in the laboratory or elsewhere is called a system. The environments of a system or all the remaining portion of the universe which may act on the system are known as surroundings. The system and surroundings are separated from each other by real or imaginary boundries. For instance, when the hydrolysis of an ester is carried out in a reaction flask, placed in a thermostat then the contents of the flask is the system, the flask is the real boundry and the thermostat is the surrounding.

The properties of a system in bulk, rather than that of the part of the system, which are easily measurable are known as the macroscopic properties e.g. Pressure, temperature, volume, composition etc.

The properties of a system may be divided into two main groups (a) Intensive properties and (b) Extensive properties.

(a) **Intensive Properties :** It is a characteristic property of the system and is independent of the amount of material concerned. Density, pressure, temperature, viscosity, surface tension, refractive index, melting point, boiling point etc are the examples of Intensive properties.

(b) **Extensive Properties :** It is the property that depends upon the amount of the substance present in the system. The change in the extensive property is proportional to the change in the quantity of the material in the system. If the matter in a given system at a given condition is divided into two equal parts, the values of the extensive properties will become half of the original values. Mass, volume, Mole numbers, the Enthalpy, the entropy, the internal energy, the Gibb's free energy etc are the examples of extensive properties.

These Macroscopic properties give description of materials under a given set of experimental conditions. A system is said to be in a definite state when each of its properties has a definite value and thus the system is completely defined. The description of the system before it suffers any change is called as the initial state of the system while the description of the system after it undergoes a change is known as final state of the system. Changes in the system, therefore will be described by comparing the final and the initial states of the system. In other words, the change in state of a system is completely defined when its initial and final states are specified. For example if T_1 is the condition of temperature at the initial state and T_2 is the condition of temperature at the final state, then

$T_2 — T_1 = \Delta T$ which is the change in temperature of the system. Similarly, $V_2 - V_1 = \Delta V$ is the change in volume, $E_2 - E_1 = \Delta E$ is the change in the internal energy of the system and so on.

Thus,

Change in the property of a system = value of a property in the final state - value of the same property in the initial state.

5.2 FIRST LAW OF THERMODYNAMIC (ENERGY CONSERVATION)

First law of Thermodynamics was enunciated by Helmholtz in 1847. It states that energy can neither be created nor destroyed, although it may change from one form to another, in other words the total energy of a system and its surrounding must remain constant.

For the mathematical derivation of First law of Thermodynamics, imagine a system whose internal energy in the initial state is E_1, let a quantity of heat 'q' from the surroundings be absorbed by the system and does some work 'W' on the surroundings while the internal energy changes to E_2, due to heat and work operations, then the change in the internal energy $(E_2 - E_1)$, according to First law of thermodynamics is given by

$$E_2 - E_1 = \Delta E = q - W \quad \text{.......................(i)}$$

This is the mathematical statement of first law of thermodynamics. ΔE depends only on the initial and final states of the system.

Pressure – Volume Work : Consider a cylinder of a gas having an area of cross-section 'A' fitted with a frictionless and weight less piston (Fig. 5.1). If the pressure on the piston is P, then the total force 'f' acting on the piston would be PA, since pressure is the force per unit area (P=f/A). If the piston goes up through a small distance 'dl', then the workdone δW is given by as,

$$\delta W = f \times dl = PAdl = Pdv$$

$$\text{where } Adl = dv$$

$$\text{Thus } W = P\Delta V$$

The value of workdone 'W' is substituted in eq (1), the equation of First law of Thermodynamics becomes as

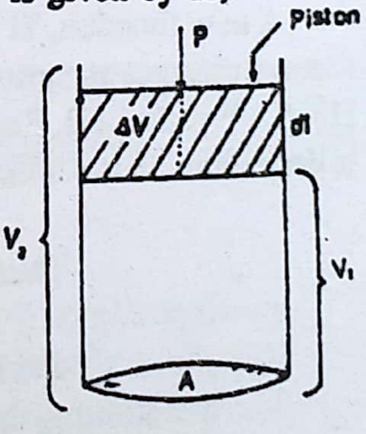


FIGURE 5.1

$$\Delta E = q - P\Delta V$$

or

$$q = \Delta E + P\Delta V \quad \text{----------------} \quad (2)$$

The absorption or evolution of heat during chemical reactions may take place (a) at constant volume and (b) at constant pressure. Let us consider these processes in some details.

(a) Process at Constant Volume : Let q_v be the heat absorbed at constant volume and at constant volume $\Delta V = 0$, So $P\Delta V$ also becomes zero, hence

$$q_v = \Delta E \quad \text{------------------------------} \quad (3)$$

Thus in the process carried at constant volume, the heat absorbed or evolved is equal to the energy change i.e., ΔE.

(b) Process at Constant Pressure : Since most of the chemical reactions in the laboratory are carried out in open vessels, so chemists are more interested in the processes that take place at constant pressure.

Let q_p be the heat absorbed at constant pressure, then the eq. (2) remains same i.e.

$$q_p = \Delta E + P\Delta V$$

We know that $\Delta E = E_2 - E_1$ and $\Delta V = V_2 - V_1$, so

$$q_p = (E_2 - E_1) + P(V_2 - V_1)$$
$$= E_2 + PV_2 - (E_1 + PV_1) \quad \text{------------} \quad (4)$$

A new function, 'H' called enthalpy (Heat content) is introduced to express thermal changes at constant pressure. This function is mathematically defined as $H = E + PV$. Since E, P and V are state functions, so 'H' is also state function and is dependent on the initial and final states.

Thus

$$E_2 + PV_2 = H_2$$

and $E_1 + PV_1 = H_1$

Substituting the values in eq. (4), we get

$$q_p = H_2 - H_1 = \Delta H \quad \text{---------} \quad (5)$$
$$\therefore \Delta H = \Delta E + P\Delta V \quad \text{---------} \quad (6)$$

5.3 Sign of ΔH

ΔH is the change in enthalpy. ΔH is the characteristic property of a system and depends on the initial and final states of a system and not on the means by which the changes are brought. For all exothermic processes, ΔH would be negative and for all endothermic process, ΔH is positive.

e.g. $C + O_2 \rightarrow CO_2$ $\quad \Delta H = -394\ KJ\ mol^{-1}$

$C + 2S \rightarrow CS_2$ $\quad \Delta H = +\ 117.6\ KJ\ mol^{-1}$

A summary of exothermic and endothermic reactions explained in terms of heat content is diagrammatized as follows:

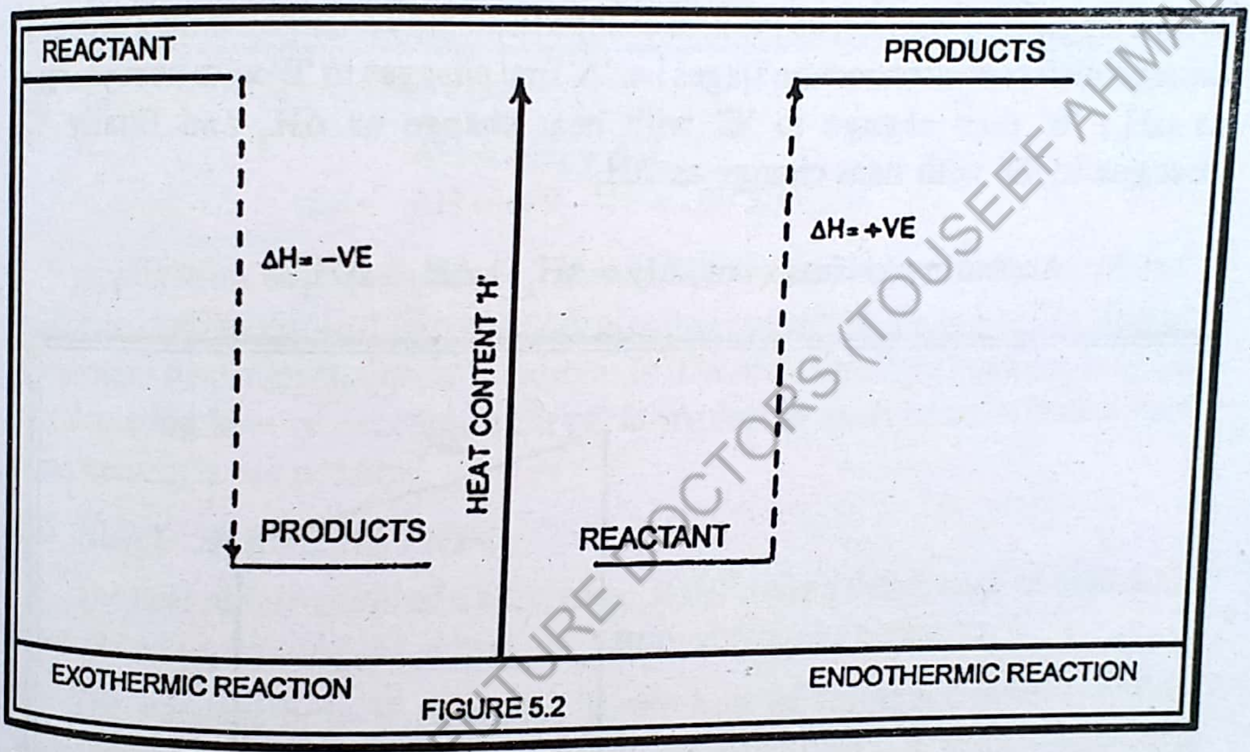


FIGURE 5.2

5.4 THERMOCHEMISTRY

The specific application of the first law of themodynamics is the study of chemical reactions is referred to as thermochemistry. Thermochemistry deals with the measurement or calculation of heat absorbed or given out in chemical reactions. The unit of energy is calorie and kilocalorie. The S.I units are however Joules and kilo joules.

(1 cal = 4.184J or 1Joule = 0.239 cal)

5.5 HESS'S LAW OF CONSTANT HEAT OF SUMMATION

G. H. HESS (1840) discovered a very important generalization which is known as Hess's law. It states that the heat evolved or absorbed in a given reaction must be independent of the particular manner in which the reaction takes place. It depends only on the initial and final states of the system. In other words, if a chemical reaction is made to take place in two or more different ways, whether in one or several steps, the amount of the total enthalpy change will be same, no matter by which method the change is brought about.

Consider a chemical reaction in which reactant 'A' changes to the product 'D' in a single step with ΔH as the heat change (Enthalpy change). It may proceed through different intermediate stages i.e. 'A' first changes to 'B' with heat change as ΔH_1, 'B' then change to 'C' with heat change as ΔH_2 and finally 'C' changes to 'D' with heat change as ΔH_3.

According to Hess's law, $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

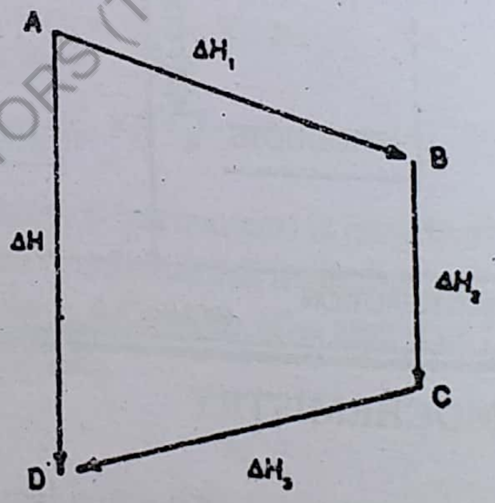


FIGURE 5.3

Illustration of the law is given by the following example :

Carbon dioxide gas reacts with excess of sodium hydroxide solution to give sodium carbonate with enthalpy or heat change about –90 KJ/mole. This reaction may easily be carried out via sodium bicarbonate formation in two steps. In the first step the enthalpy change is –49 KJ/mole and in the second step, the enthalpy change is –41 KJ/mole. It is given as follows:

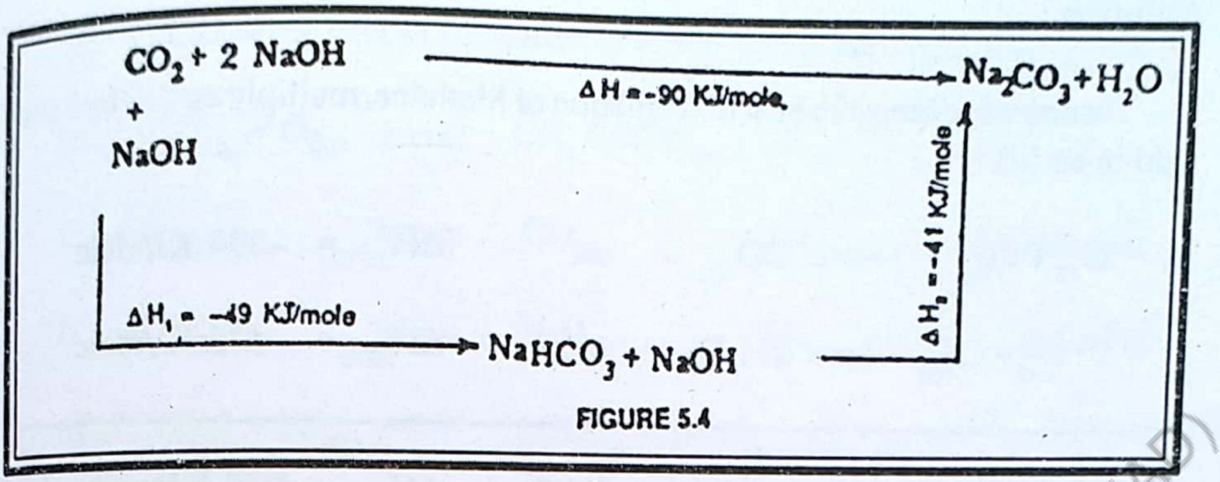


FIGURE 5.4

Hence according to Hess's law

$$\Delta H = \Delta H_1 + \Delta H_2$$

i.e. $\Delta H = -49 - 41 = -90$ KJ/mole

Application of Hess's law:- Thermochemical equations may be added, subtracted and multiplied like ordinary algebraic equation, therefore Hess's law of constant heat summation is important in Thermochemistry because it helps in calculating heat of reaction, heat of formation in such cases where direct measurement is not possible.

5.6 HEAT OF FORMATION

The heat of formation of a compound is defined as the change of enthalpy when one gram mole of the substance is formed from its elements.

The standard heat of formation is the heat of formation when all the substances involved in the reaction are each at unit activity (i.e. at 25°C and one atmospheric pressure).

The heat of formation is generally represented by ΔH_F. For example, the heat of formation of CH_4 $(C + 2H_2)$ is –74.9 KJ/mole. It can be calculated from the following data:

(i) $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ $\quad \Delta H_{25°C} = ?$

(ii) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\quad \Delta H_{25°C} = -394$ KJ/mole

(iii) $H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$ $\quad \Delta H_{25°C} = -286$-KJ/mole

(iv) $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$ $\quad \Delta H_{25°C} = -890.34$ KJ/mole

Solution :

In order to obtain the heat of formation of Methane, multiply eg (iii) by 2 and add in eq (ii)

$$C_{(S)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_{25°C} = -394 \text{ KJ/mole}$$

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(1)} \qquad \Delta H_{25°C} = -572 \text{ KJ/mole}$$

$$C \quad + 2H_{2(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(1)} \qquad \Delta H_{25°C} = -966 \text{ KJ/mole—(v)}$$

Finally subtracting eq (iv) from eq (v), we obtain

$$C + 2H_2 + \cancel{2O_2} \rightarrow \cancel{CO_2} + \cancel{2H_2O} \qquad \Delta H_{25°C} = -966 \text{ KJ/mole}$$

$$\underset{-}{CH_4} + \underset{-}{\cancel{2O_2}} \rightarrow \underset{-}{\cancel{CO_2}} + \underset{-}{\cancel{2H_2O}} \qquad \Delta H_{25°C} = -890.34 \text{ KJ/mole}$$

$$C + 2H_2 \rightarrow CH_4 \qquad \Delta H_{25°C} = -75.66 \text{ KJ/mole}$$

This is the heat of formation of CH_4 which we can not measure directly.

PROGRESS TEST 5

1. What do you understand by the terms: system, surroundings and states? Illustrate with an example

2. (a) What are intensive and extensive properties of a system?
   (b) Catagorise the following properties of a system into extensive and intensive properties.
   Free energy, Vapour pressure. Temperature, Surface tension, Mass. Internal energy, Melting point

3. State the First law of Thermodynamics and also give its mathematical statement, $\Delta E = q - w$.

4. (a) State and explain Hess's law of constant heat summation. Give its applications.

(b) Calculate the heat of formation of acetic acid from the following data.

$2C_{(S)} + 2H_{2(g)} + O_{2(g)} = CH_3COOH_{(l)} \quad \Delta H_f = ?$ — (1)

$C_{(S)} + O_{2(g)} = CO_{2(g)} \quad \Delta H_{25°C} = -394$ KJ/mole (2)

$H_{2(g)} + {}^1/_2O_{2(g)} = H_2O_{(l)} \quad \Delta H_{25°C} = -286$ KJ/mole (3)

$CH_3COOH_{(l)} + 2O_{2(g)} = 2CO_{2(g)} + 2H_2O_{(l)} \quad \Delta H_{25°C} = -870.8$ KJ/mole(4)

(Ans: –489.2 KJ/mole)

5. (a) Define and explain the terms (i) Exothermic process (ii) Endothermic process (iii) Heat of formation.

(b) Calculate the heat of formation of Ethane at 25°C from the following data

(i) $2C_{(S)} + 3H_{2(g)} = C_2H_{6(g)} \quad \Delta H_F = ?$
(ii) $C_{(S)} + O_{2(g)} = CO_{2(g)} \quad \Delta H = -394.00$ KJ/mole
(iii) $H_{2(g)} + {}^1/_2O_{2(g)} = H_2O(l) \quad \Delta H = -286.0$ KJ/mole
(iv) $C_2H_{6(g)} + {}^7/_2O_{2(g)} = 2CO_{2(g)} + 3H_2O(l) \quad \Delta H = -1560.632$ KJ/mole

(Ans: –85.368 KJ/ mole)

6. (a) Show that the product of pressure and volume, PV has the dimension of energy.

(b) In a certain process 848J of heat is absorbed by a system, while 394J of work is done on the system. What is the change in the internal energy for the process ? (Ans: 1242J)

7. (a) If 1800 cals, of heat is added to a system while system does work equivalent to 2800 cals by expanding against the surrounding. What is the value of ΔE for the system? (Ans: –1000 cals).

(b) In a certain process, 500J of work is done on a system which gives off 200J of heat. What is the value of ΔE for the process ? (Ans: 300J)

CHAPTER-6

CHEMICAL EQUILIBRIUM

6.1 EXTENT TO WHICH REACTIONS PROCEED·

All the chemical reactions do not proceed to the same extent, some proceed to completion and some never go to completion. The reactions which proceed to completion in a definite direction are called 'irreversible' or 'One way' reactions. For example,

$$\underset{\text{Reactants}}{NaCl + Ag\,NO_3} \longrightarrow \underset{\text{Products}}{NaNO_3 + AgCl_{(s)}}$$

In these reactions, the reactants are completely converted into products.

There is vast number of reactions which never proceed to completion and are called 'reversible' or 'both way' reactions. For such reactions under the same conditions, both the forward and reverse reactions can occur at the same time if all the reactants and products are present in one container.

$$\text{Reactants} \rightleftharpoons \text{Products}$$

The double arrow ($\rightleftharpoons$) indicates that the reaction is reversible and that both the forward (left to right) and reverse (right to left) reactions can occur simultaneously. Some examples of reversible reactions are given below :

(i) Formation of Ethyl acetate (ester).

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(ii) Dissociation of Hydrogen iodide.

$$2HI \rightleftharpoons H_2 + I_2$$

(iii) Dissociation of Phosphorus pentachloride

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

(iv) Hydrolysis of Bismuth chloride

$$BiCl_3 + H.OH \rightleftharpoons BiOCl + 2HCl$$

(v) Synthesis of ammonia by Haber process

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

6.2 EQUILIBRIUM STATE

In a reversible reaction, both the changes, forward and the reverse occur simultaneously. Under these circumstances, a reaction might come to some kind of 'balance' in which the forward and reverse reactions occur at the same rate. Consider, for example, the following homogeneous reaction (i.e. entirely liquid or entirely gaseous).

$$A + B \rightleftharpoons C + D$$

In the beginning, forward reaction predominates, but as soon as C and D are formed, the reverse reaction 'builds up' until equilibrium position is reached where the forward as well as the reverse change proceeds with the same rate.

The equilibrium state of a chemical reaction, however, differs from these physical examples. The children on a see saw or a note book on a table are in a state of 'static' equilibrium, but the chemical equilibrium is 'dynamic', that is, it is an equilibrium involving the constant inter change of particles in motion (as it involves the balancing of two reactions occurring simultaneously). In static equilibrium, we can observe the fact that the children or the book are in equilibrium, but in dynamic equilibrium we can't observe the individual particles involved.

Although the idea of reactants and products is confusing in a reversible reaction, at equilibrium point, all the substances involved are present. That is to say that an equilibrium mixture is formed. The composition of this mixture remains constant due to same rate of forward and backward change. At this point, it apparently appears as if the reaction has stopped because we don't see an increase in the amount of products. But as mentioned earlier, a reversible reaction never stops – it is dynamic. The equilibrium state does not change with the lapse of time.

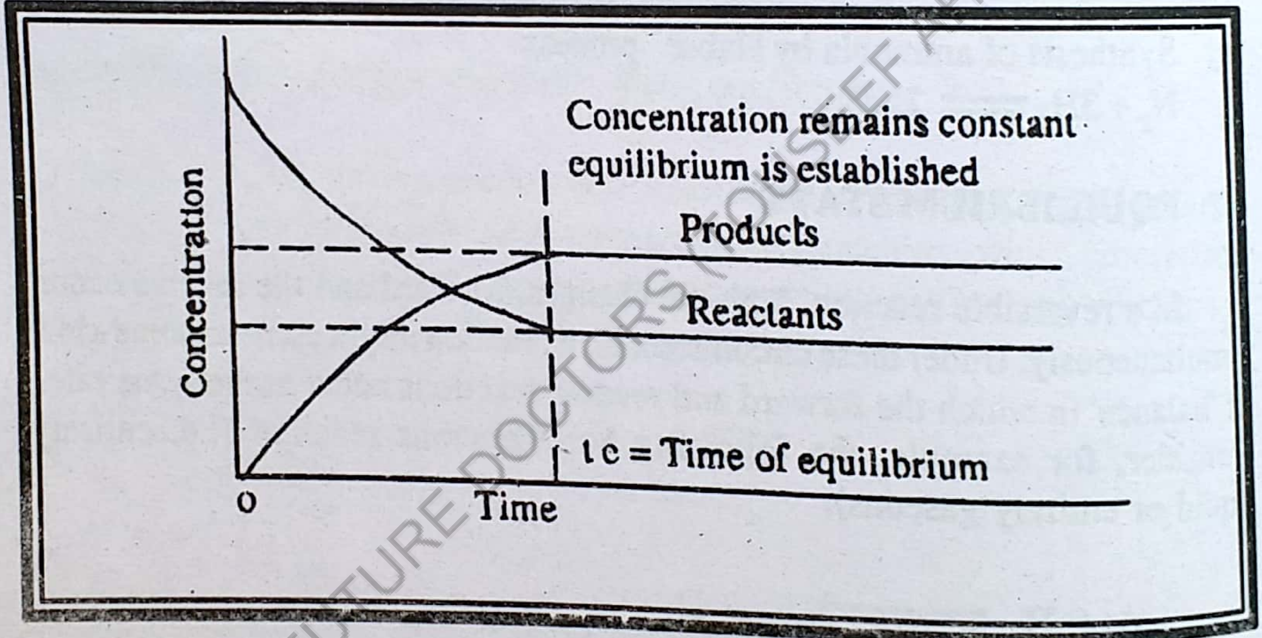


Fig.6.1

6.3 THE LAW OF MASS ACTION (EQUILIBRIUM LAW)

In 1864, the Scandinavian scientists, Guldberg and Waage formulated a generalization regarding the effect of concentration on reversible reactions in equilibrium. It is known as the law of mass action or law of equilibrium. It states that:

> "The rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is proportional to the product of the active masses of reactants."

The term active mass' means the concentration in terms of moles/dm³ (moles/litre). For example, the active mass of 4 gm H_2 is 2 moles/dm³ and it is represented by means of square brackets such as $[H_2]$ = active mass of H_2

To derive the expressions of Equilibrium Constant, K_c. In order to find out the influence of concentration on chemical equilibrium, it is essential to derive the expression of its equilibrium constant which is denoted by K_c or K_p. Let us, for instance, apply the law of mass action to the following general reversible reaction in which 'm' moles of A and 'n' moles of B react to give 'x' moles of C and 'y' moles of D.

$$\boxed{mA + nB \rightleftharpoons xC + yD}$$

Rate of Forward reaction $\propto [A]^m \; [B]^n$

$= K_1 [A]^m [B]^n$ .... (i)

Rate of reverse reaction $\propto [C]^x [D]^y$

$= K_2 [C]^x [D]^y$.....(ii)

Since, at equilibrium state,

Rate of forward reaction = Rate of reverse reaction

∴ (i) = (ii)

$$K_1 \; [A]^m \; [B]^n = K_2 [C]^x \; [D]^y$$

Or
$$\frac{K_1}{K_2} = \frac{[C]^x \; [D]^y}{[A]^m \; [B]^n}$$

Or
$$K_c = \frac{[C]^x \; [D]^y}{[A]^m \; [B]^n}$$

This is the expression of K_c, in which active masses of products are placed in the numerator while the active masses of reactants are placed in the denominator. In other words, equilibrium constant is the ratio of active masses of products and reactants at equilibrium. Thus, for the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$$K_c = \frac{[PCl_3] \; [PCl_2].}{[PCl_5]}$$

In case of gaseous equilibrium, a partial pressure is used instead of concentration because at a given temperature, partial pressure of a gas is proportional to its concentration. In this case, the equilibrium constant is expressed as K_p instead of K_c, for example, consider the following gaseous equilibrium.

$$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$$

$$K_p = \frac{[P_C][P_D]}{[P_A][P_B]},$$ where P_A, P_B, P_C, P_D are the partial pressures of gases A, B, C and D respectively.

Relation between K_c and K_p:

(i) $K_p = K_c$ in these cases where there is no change in volume such as

$$\underset{1\ \text{Vol.}}{H_{2(g)}} + \underset{1\ \text{Vol.}}{I_{2(g)}} \rightleftharpoons \underset{2\ \text{Vol.}}{2HI_{(g)}}$$

(ii) $K_p > K_c$ when reactions occur with increase in volume such as $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$

(iii) $K_p < K_c$ when there is decrease in volume on the product side such as $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

6.4 DETERMINATION OF EQUILIBRIUM CONSTANT

The value of equilibrium constant K_c does not depend upon the initial concentration of reactants. In order to find out the value of K_c, we have to find out the equilibrium concentration of reactants and products. Consider the following examples:

1. Ethyl Acetate Equilibrium :

Acetic acid (an organic acid) reacts with ethyl alcohol to form ethyl acetate (an ester) and water.

$$CH_3COOH + C_2H_5OH \underset{\text{Hydrolysis}}{\overset{\text{Esterification}}{\rightleftharpoons}} CH_3COO\,C_2H_5 + H_2O$$

Known masses of acetic acid and ethyl alcohol are taken in a stoppered flask. Let it be 'a' moles/dm^3 acetic acid and 'b' moles/dm^3 ethyl alcohol when equilibrium establishes after some time, the contents of the flask are cooled or 'quenched' by adding crushed ice to 'fix' the equilibrium. Since equilibrium mixture consists of unused reactants as well as the products, hence the amount of the acid left at equilibrium is determined by titrating it against standard solution of sodium hydroxide. Suppose the amount of acetic acid consumed at equilibrium is x moles/dm^3 which means the acid left at equilibrium is $(a-x)$ mole/dm^3. Note in the above equation there is 1 molecule of acid, one molecule of alcohol which react to form 1 molecule of ester and one molecule of water. In this case, therefore, the amount of acid used up must be equal to the amount of alcohol used, which means at equilibrium, the amount of acid left = $(a-x)$ moles/dm^3, alcohol = $(b-x)$ moles/dm^3, ester formed = x moles/dm^3 and water produced = x moles/dm^3.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
No. of moles at initial state =	a	b	Nil	Nil
No. of moles at equilibrium state =	$(a-x)$	$(b-x)$	x	x
Concentration at equilibrium state =	$\frac{(a-x)}{V}$	$\frac{(b-x)}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

On applying the law of mass action, we get:

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3\,COOH]\,[C_2H_5OH]}$$

$$K_c = \frac{\frac{(x)}{V} \times \frac{(x)}{V}}{\frac{(a-x)}{V}\frac{(b-x)}{V}} = \frac{x^2}{(a-x)\;(b-x)}$$

In separate experiments, different amounts of acetic acid and ethyl alcohol were made to react at constant temperature. Analysis of the equilibrium mixture gave the following results:

Equilibrium Conc : (Moles/dm³)

Acetic Acid	Ethyl alcohol	Ethyl acetate	Water	$K_c = \frac{[CH_3COOC_2H_5]\ [H_2O]}{[CH_3COOH]\ [C_2H_5OH]}$
18×10^{-3}	22×10^{-3}	40×10^{-3}	40×10^{-3}	4.04
63×10^{-3}	23×10^{-3}	75×10^{-3}	75×10^{-3}	3.88
75×10^{-3}	80×10^{-3}	160×10^{-3}	160×10^{-3}	4.26
28×10^{-3}	96×10^{-3}	105×10^{-3}	105×10^{-3}	4.10

For this system, the value of equilibrium constant, K_c is almost constant which averages to 4.

2. Hydrogen Iodide Equilibrium

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

To start with, suppose there are 'a' moles/dm³ of hydrogen and 'b' moles/dm³ of iodine which react in sealed bulbs at 444°C in the boiling sulphur for some length of time. In order to 'fix' the equilibrium, the equilibrium mixture is cooled. The bulbs are opened in the solution of sodium hydroxide which absorbs hydrogen iodide and iodine leaving behind hydrogen. Let the amount of hydrogen consumed at equilibrium be 'x' moles/dm³ which means the amount of hydrogen left at equilibrium is (a–x) moles/dm³. Since 1 mole of hydrogen reacts with 1 mole of iodine to form two moles of hydrogen iodide, hence the amount of iodine used is also 'x' moles/dm³. Thus 2x' moles/dm³ of hydrogen iodide are present at equilibrium. The equilibrium constant K_c is then calculated:

	$H_{2(g)}$ +	$I_{2(g)}$ $\rightleftharpoons$	$2HI_{(g)}$
No. of moles at initial state	a	b	Nil
No. of moles at equilibrium state	(a–x)	(b–x)	2x
Concentration at equilibrium state	$\frac{(a-x)}{V}$	$\frac{(b-x)}{V}$	$\frac{2x}{V}$

Applying the law of mass action

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\frac{(a-x)}{V}\frac{(b-x)}{V}} = \frac{4x^2}{(a-x)(b-x)}$$

In separate experiments different amounts of hydrogen and iodine were made to react at constant temperature. Analysis of the equilibrium mixture gave the following results:

Equilibrium Amounts (Moles/dm³)

Hydrogen	Iodine	Hydrogen Iodide	$K_c = \frac{[HI]^2}{[H_2][I_2]}$
0.00456	0.00074	0.01354	54.3
0.00356	0.00125	0.01559	54.6
0.00225	0.00234	0.01685	53.9
0.00048	0.00048	0.00353	54.1

For this system K_c averages to 54.

EXAMPLE 1. 4.6 gm of ethyl alcohol and 6.0 gm of acetic acid kept at constant temperature until equilibrium was established. 2.0 gm of unused acid were present. Calculate K_c.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

No. of moles at initial state $\frac{6.0}{60} = 0.1$ $\quad \frac{4.6}{46} = 0.1$ $\quad$ NIL $\quad$ NIL

Suppose no. of moles at equilibrium $\quad (0.1-x) \quad (0.1-x) \quad x \quad x$

During the reaction 2 gms. of acetic acid were left which is $\frac{2}{60} = 0.033$ mole

or $0.1-x = 0.033$ mole

or $x = 0.1-0.033 = 0.067$ mole:

Therefore 0.067 mole of acetic acid and 0.067 mole of ethyl alcohol must have reacted. Hence 0.067 mole of each product (ethyl acetate and water) are formed.

∴ No. of moles at equilibrium state	0.033	0.033	0.067	0.067
Conc. at equilibrium state	$\frac{0.033}{V}$	$\frac{0.033}{V}$	$\frac{0.067}{V}$	$\frac{0.067}{V}$

$$K_c = \frac{[CH_3COOC_2H_5]\ [H_2O]}{[CH_3COOH]\ [C_2H_6OH]} = \frac{\frac{0.067}{V} \times \frac{0.067}{V}}{\frac{0.033}{V} \times \frac{0.033}{V}} = \frac{0.067 \times 0.067}{0.033 \times 0.033} = 4.0$$

EXAMPLE 2. 9.2 gm of ethyl alcohol, 3.6 gm of acetic acid, 1.1 gm of ethyl acetate and 9.0 gm of water were mixed and allowed to attain equilibrium. If $K_c = 4$, what was the concentration of the resulting mixture?

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

No. of moles at initial state $\frac{3.6}{60} = 0.06,\ \frac{9.2}{46} = 0.2,\ \frac{1.1}{88} = 0.0125,\ \frac{9.0}{18} = 0.5$

If x mole of acetic acid and x mole of ethyl alcohol react, then additional x mole of each product (ethylacetate and water) are formed.

No. of moles at initial state	−n	−n	+n	+n
No. of moles at equilibrium state	0.06−n	0.2−n	0.0125+n	0.5+n
Concentration at equilibrium state	$\frac{0.06-n}{V}$	$\frac{0.2-n}{V}$	$\frac{0.0125+n}{V}$	$\frac{0.5+n}{V}$

$$K_c = \frac{[CH_3COOC_2H_5]\ [H_2O]}{[CH_3\ COOH]\ [C_2H_5OH]}$$

$$K_c = \frac{\left(\frac{0.0125+x}{V}\right)\left(\frac{0.5+x}{V}\right)}{\left(\frac{0.06-x}{V}\right)\left(\frac{0.2-x}{V}\right)}$$

$$3x^2 - 1.5525\,x + 0.04175 = 0$$

solving by the formula $ax^2 + bx + C = 0$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$x = 0.49$ or $x = 0.029$ moles

Since the initial amounts of acetic acid and ethyl alcohol are less than 0.49 moles, hence $x = 0.49$ is ruled out. In other words $x = 0.029$ moles. Thus the equilibrium concentration of the mixture is given below:

Acetic acid = $0.06 - 0.029$ = 0.031 mole/dm^3
Ethyl alcohol = $0.2 - 0.029$ = 0.171 mole/dm^3
Ethyl acetate = $0.0125 + 0.029$ = 0.0415 mole/dm^3
Water = $0.5 + 0.029$ = 0.529 mole/dm^3

EXAMPLE 3. In a reaction $A + B \rightleftharpoons 2C$, when equilibrium was attained, the concentration was $[A] = [B] = 4$ moles/dm^3, $[C] = 6$ moles/dm^3. Calculate the equilibrium constant K_c and the initial concentrations of A and B.

Solution.

(a) The equilibrium constant of the above reaction is given by,

$$K_c = \frac{[C]^2}{[A]\,[B]}$$

$$K_c = \frac{(\frac{6}{V})^2}{(\frac{4}{V})\cdot(\frac{4}{V})} = \frac{36}{16} = 2.25$$

(b) Since one mole of A and one mole of B react to form two mole of C, hence 6 moles of C are produced from 3 moles of A and 3 moles of B. Thus the initial concentration of $A = B = 4 + 3 = 7$ moles/dm^3 each.

6.5 APPLICATIONS OF THE LAW OF EQUILIBRIUM

The law of equilibrium is used to calculate the equilibrium constant of a reversible reaction. The study of equilibrium expression and its constant K_c is very important to a chemist or to a manufacturer. Some valuable predictions can be made about a reaction. In fact, a chemist can control the direction and the extent of a chemical reaction by changing the conditions through the knowledge of K_c. Below are given the important applications of equilibrium constant:

(i) K_c is used to predict the direction of a reaction.
(ii) It is also used to predict the extent to which a reaction occurs.

(1) To predict the direction of a Reaction :

The value of equilibrium constant K_c is a valuable aid in predicting the direction in which a reaction will shift in order to achieve the equilibrium, provided the initial concentration of the reagents involved is known.

$$\text{Reactants} \rightleftharpoons \text{Products.}$$

As regards to the ratio of the initial concentration of the reagents $\frac{[\text{Products}]_{\text{Initial}}}{[\text{Reactants}]_{\text{Initial}}}$, there are three possible cases.

(i) It is greater than K_c (ii) It is less than K_c (iii) It is equal to K_c.

(i) In the first case, when

$\frac{[\text{Products}]_{\text{Initial}}}{[\text{Reactants}]_{\text{Initial}}} > K_c$, the reaction will shift towards the reverse direction where less quantity of products is obtained and the ratio decreases to the value of K_c.

(ii) In the second case when

$$\frac{[\text{Products}]_{\text{Initial}}}{[\text{Reactants}]_{\text{Initial}}} < K_C,$$ the reaction will shift towards right where more quantity of products is formed and the ratio increases to the value of K_C.

(iii) In the Third case, when

$$\frac{[\text{Products}]_{\text{Initial}}}{[\text{Reactants}]_{\text{Initial}}} = K_C,$$ according to the law of mass action, equilibrium has been attained and there is no shifting of the reaction provided conditions are not changed.

EXAMPLE 4. The K_c for the dissociation of hydrogeniodide at 356°C is 1.3×10^{-2}. If there are 0.5 moles/dm³ Hydrogen, 1.5 moles/dm³ iodine and 5 moles/dm³ Hydrogeniodide, predict the direction in which the reaction moves so as to achieve the equilibrium.

The dissociation of Hydrogeniodide is represented by the equation,

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)} \quad K_C = 1.3 \times 10^{-2}$$

According to the law of mass action,

$$K_{\text{Initial}} = \frac{[H_2]_{\text{Initial}}\,[I_2]_{\text{Initial}}}{[HI]^2_{\text{Initial}}} = \frac{(0.5).(1.5)}{(5)^2} = \frac{0.75}{25} = 3\times 10^{-2}$$

Since the calculated value of the ratio of the concentrations of the reagents is 3×10^{-2} which is greater than the actual value of K_C, hence the reaction will shift towards the reverse direction.

EXAMPLE 5. K_C for the reaction $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$ at 448°C is 0.0194. If one litre vessel contains 0.2 moles. Hydrogen, 12 moles iodine and 15 moles Hydrogen iodide, predict the direction of reaction.

According to the law of mass action,

$$K_{Initial} = \frac{[H_2]_{Initial}\,[I_2]_{Initial}}{[HI]^2_{Initial}} = \frac{0.2 \times 12}{(15)^2} = \frac{2.4}{225} = 0.0106$$

Since the calculated ratio of the concentration of the products and reactants is less than the actual value, hence the reaction will move towards right i.e. towards the forward direction.

(2). To Predict the Extent of Reaction :

From the value of K_c, we can predict the extent to which a reaction will occur.

In the first case, when the value of K_c is very large, it is predicted that the forward reaction is almost complete. That is to say, the reactant is unstable. for example ozone, an allotropic form of oxygen, quickly decomposes to oxygen $2O_3 \rightleftharpoons 3O_2$. Its K_c is very large (10^{55}).

In the second case, when the value of K_c is very low, it is predicted that the forward reaction proceeds with negligible speed. That is to say, the reactant is fairly stable. For example, hydrogen fluoride unlike other hydrogen halides (HCl, HBr, HI) is very stable. Its dissociation in water is only 8%. That's why K_c for the reaction $2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)}$ is very low (10^{-13}).

In the third case, when the value of K_c is moderate – neither very high nor very low, the reaction occurs in both the directions and equilibrium will be attained after certain period of time. For example, K_c for the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is 10.

6.6 FACTORS AFFECTING BALANCE OF CHEMICAL EQUILIBRIUM (Le Chatelier's Principle).

The balance of a chemical equilibrium is disturbed by changing factors such as concentration, temperature and pressure. Le Chatelier's principle enables qualitative predictions to be made about the effects of the above mentioned factors on equilibrium position. This principle was enunciated in 1884 by Le-Chatelier.

"When a constraint or stress in a direction is applied to a system in equilibrium, the equilibrium position changes so as to undo the constraint"

By the term constraint we mean the changes concentration, pressure or temperature. According to this principle, if one of the factors involved in a chemical equilibrium is altered, the equilibrium shifts towards right or left in order to restore the balance of equilibrium.

1. Effect of Concentration Change :

By increasing the concentration of any substance present in the equilibrium mixture, the balance is disturbed, and the equilibrium moves away from that substance in order to decrease the concentration of the added substance. This is in accordance with the Le Chatelier's principle for the reaction $A + B \rightleftharpoons C + D$.

$$K_c = \frac{[C]\,[D]}{[A]\,[B]}$$

Without changing the other conditions, K_c is constant. If, for instance, the concentration of 'A' is increased, K_c decreases. To keep K_c constant, the concentration of 'C' and 'D' increases. Thus to get high yield of products, the concentration of cheaper reactant may be greatly increased.

Change in concentration	Effect on equilibrium position $A + B \rightleftharpoons C + D$
Increase in conc. of A or B	Equilibrium shifts to right and yield of products increases.
Increase in conc. of C or D	Equilibrium shifts to left i.e. more of A and B is formed.

2. Effect of Temperature Change :

For an exothermic reaction, K_c decreases with the rise of temperature. That is to say the concentration of products decreases. For an endothermic reaction, the rise of temperature favours the high yield of products. The effect of temperature on equilibrium can be explained in the light of Le Chatelier's principle.

In an exothermic reaction, heat is evolved in going from reactants to products. Increasing the temperature is a constraint to the equilibrium which is removed by absorbing heat in going from products to the reactants. In an endothermic reaction, heat is absorbed in going from reactants to the products. Increasing the temperature is the stress to the equilibrium which is nullified by absorbing heat in going from left towards right, i.e., from reactants to the products.

Nature of Reaction $A + B \rightleftharpoons C + D$	Change in Temperature	Effect on Equilibrium
Exothermic, eg. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$	Increase	Equilibrium shifts to left i.e. more NO and O_2 are formed.
	Decrease	Equilibrium shifts towards right and more products are formed (yield of NO_2 increases).
Endothermic, e.g. $N_{2(g)}+O_{2(g)} \rightleftharpoons 2NO$	Increase	Equilibrium moves towards right to give high yield of products (NO)
	Decrease	Equilibrium is driven towards left and more N_2 and O_2 are present in equilibrium mixture.

/

3. Effect of Pressure Change :

Change of pressure is related to the change of volume. Since solids and liquids are almost incompressible, hence their volumes are very little affected by the changes in pressure. In other words, pressure will only affect gaseous equilibria in which there is a volume change. If volume is same on both sides, pressure will have no effect on equilibrium.

If a reaction proceeds with increase in volume, $(2NH_3 \rightleftharpoons N_2 + 3H_2)$ the increase of pressure (constraint) shifts the equilibrium towards reactant side to remove the constraint of increased pressure. This is in accordance with the Le Chatelier's principle.

If a reaction proceeds with decreasing volume (e.g. $PCl_3 + Cl_2 \rightleftharpoons PCl_5$), the increase of pressure forces the equilibrium to be driven to right hand side.

Volume involved $mA + nB \rightleftharpoons xC + yD$	Change in pressure	Effect on equilibrium position
(i) If $x + y > m + n$ volume of products is greater than reactants e.g. $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$	Increase	Equilibrium moves towards left i.e., more O_3 is present in equilibrium mixture.
	Decrease	Equilibrium position moves towrds right, i.e. more O_2 is present in the equilibrium mixture.
(ii) If $x + y < m + n$ volume of products is less than the reactants. e.g. $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$	Increase	Equilibrium position is driven towards right, i.e. yield of N_2O_4 increases.
	Decrease	Equilibrium shifts towards left, i.e. N_2O_4 dissociates more and more NO_2 is present in the equilibrium mixture.
(iii) If $x + y = m + n$	No effect	

4. Effect of Catalyst on Equilibrium :

A catalyst has no effect on the equilibrium position, but it enables equilibirum to be reached more quickly by decreasing the 'energy of activation'. In fact a catalyst affects forward and reverse rates equally.

6.7 IMPORTANT INDUSTRIAL APPLICATIONS OF LE CHATELIER'S PRINCIPLE

A Chemist or a manufacturer is always ambitious in getting maximum yield of his products in the shortest possible time. For this purpose he uses the knowledge of equilibrium constant and Le Chatelier's principle to sort out the most suitable and favourable conditions under which the reaction is to be carried.

How far this knowledge is useful in various industries, is described with special reference to the synthesis of Ammonia by Haber's process and the manufacture of sulphuric acid by contact process.

EXAMPLES :

1. The Haber's Process:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad (\Delta H = -46.2\ KJ/mole)$$

1 Vol 3 Vol 2 Vol.

The reaction between nitrogen and hydrogen to produce ammonia is accompanied by decrease in volume and it is exothermic.

(i). Effect of concentration. If more nitrogen is added at equilibrium, according to Le-Chatelier's principle, the equilibrium is forced towards right in order to reduce the concentration of nitrogen. This increases the yield of NH_3. In actual practice, however, there is no practical advantage in using excess nitrogen or hydrogen. The two gases are mixed in the theoretical ratio of 1:3 by volume.

(ii). Effect of Temperature. Synthesis of ammonia is exothermic, that is, heat is liberated in the forward reaction. If, at equilibrium, temperature is kept low, according to Le-Chatelier's principle, the equilibrium shifts to right where heat is liberated; in this way balance of equilibrium position is maintained. In other words, the low temperature favours the formation of ammonia. The high temperature, at equilibrium, would obviously favour the reverse reaction. In actual practice, the reaction is carried out at high temperature of 450°C – 500°C which produces reduced yield at much higher rate. A catalyst of finely divided iron is used.

(iii). Effect of Pressure : The formation of ammonia proceeds with the reduction in volume (4 volumes on the reactant side and 2 volumes on the product side). The reaction, is therefore, carried out under high pressure, the equilibrium is forced to right as the formation of ammonia lowers the volume and by Le-Chatelier's principle, relieves the pressure. The pressures vary from 400 to 1000 atmospheres.

2. **Contact Process :** In Pakistan, sulphuric acid is manufactured largely by the Contact process in which the most important step is the oxidation of sulphur dioxide to sulphur trioxide in presence of catalyst vanadium pentoxide.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad (\Delta H = -395 \text{ KJ/mole})$$

2 Vol 1 Vol 2 Vol

This oxidation process is exothermic and occurs with the reduction of volume. In order to sort out suitable conditions under which high yield of SO_3 is produced, Le-Chatelier's principle is applied.

(i). Effect of Concentration: If at equilibrium position, the concentration of oxygen is increased, the Le-Chatelier's principle requires the system to react to oppose this change, that is, to reduce the concentration of oxygen. This is done with the conversion of more SO_2 to SO_3.

(ii). Effect of Temperature : If, at equilibrium, the temperature is decreased, according to Le-Chatelier's principle, the system tends to react so as to oppose the change, that is, to raise the temperature. This is achieved when more of SO_3 is produced. In actual practice, the reaction is carried out at 450°C (since a fast rate is more important than a high yield). A catalyst such as V_2O_5 is also added to speed up the reaction.

(iii). Effect of Pressure: Increasing yield of SO_3 is favoured by increased pressure (since the volume of products is less than the reactants). In practice, the reaction is carried out at one atmospheric pressure (since the volume is not large enough to justify the expense of high pressure vessel).

6.8 SOLUBILITY PRODUCT

When a saturated solution of sparingly or slightly soluble salt is in contact with undissolved salt, an equilibrium is established between the dissolved ions and the ions in the solid phase of the undisssolved salt. For example, AgCl is only very slightly soluble in water and the following equilibrium exists.

$$\underset{\text{Undissolved}}{AgCl_{(s)}} \rightleftharpoons \underset{\text{Dissolved}}{Ag^{+}_{(aq)} + Cl^{-}_{(aq)}}$$

According to the equilibrium law (law of mass action),

$$K_c = \frac{[Ag^+][Cl^-]}{[AgCl_{(s)}]}$$

But at saturation, the concentration of the solid AgCl is constant

$$K_c = \frac{[Ag^+]\,[Cl^-]}{K'}$$

$$K_c \times K' = [Ag^+]\,[Cl\ ]$$

$$K_{sp} = [Ag^+]\,[Cl^-]$$

K_{sp} is termed as the solubility product. It is the product of ionic concentration of the dissolved ions and it varies with the temperature. Similarly. For CaF_2:

$$K_{SP} = [Ca^{2+}]\,[F^-]^2$$

The solubility product is expressed in the chemical units of concentration i.e. molar concentration.

Calculation of solubility product from the solubility.

Solubilities are normally given in grams per cubic decimetre (g/dm^3) which are the physical units of concentration. The solubility of AgCl is 1.4×10^{-3} g/dm^3 at 25°C. Since the molecular mass of AgCl is 143.5, hence its solubility in terms of molarity is calculated:

$$\text{Molarity} = \frac{1.4 \times 10^{-3}}{143.5} = 0.98 \times 10^{-5} \quad \text{mole dm}^{-3}$$

Hence the concentration of Ag^+ is 0.98×10^{-5} moles dm^{-3}, the concentration of the Cl^- is also 0.98×10^{-5} mole dm^{-3} because there is one Cl^- ion for each Ag^+ ion. Now,

$$K_{sp}\,AgCl = [Ag^+]\,[Cl^-] = 0.98 \times 10^{-5}\ \text{mole dm}^{-3} \times 0.98 \times 10^{-5}\ \text{mol dm}^{-3}$$
$$K_{sp}\,AgCl = 0.96 \times 10^{-10} = 9.6 \times 10^{-11}\ \text{mol}^2\,\text{dm}^{-6}$$

Solubility products of some salts are given in the following table:

Table 6.1 Solubility products of salts at 18° – 25°C.

Compound	Formula	Solubility product
Lead chloride	$PbCl_2$	1×10^{-4} mole^3 dm^{-9}
Lead sulphide	PbS	8.4×10^{-28} mole^2 dm^{-6}
Nickel sulphide	NiS	1.8×10^{-21} mole^2 dm^{-6}
Mercuric sulphide	HgS	3.5×10^{-52} mole^2 dm^{-6}
Copper sulphide	CuS	8.7×10^{-36} mole^2 dm^{-6}
Cobalt sulphide	CoS	3.0×10^{-26} mole^2 dm^{-6}
Calcium carbonate	$CaCO_3$	1.0×10^{-8} mole^2 dm^{-6}
Barium sulphate	$BaSO_4$	1.0×10^{-10} mole^2 dm^{-6}

Calculation of Solubility from Solubility product :

If we know the value of solubility product, we can calculate the solubility of salt. For example, the solubility product of lead iodide (PbI_2) at 25°C is 1.00×10^{-9} mol^3 dm^{-9}

$$\underset{\text{undissolved}}{PbI_{2(S)}} \rightleftharpoons \underbrace{Pb^{2+}_{(aq)} + 2I^-_{(aq)}}_{\text{Dissolved}}$$

$$K_{SP} = [Pb^{2+}][I^-]^2 = 1.00 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$$

If x moles per dm^3 of PbI_2 dissolve (i.e ionize),

$[Pb^{2+}] = x$ and $[I^-] = 2x$

$K_{SP} = [Pb^{2+}][I^-]^2 = 1.00 \times 10^{-9}$ mol^3 dm^{-9}

or $(x)(2x)^2 = 1.00 \times 10^{-9}$ mol^3 dm^{-9}

$4x^3 = 1.00 \times 10^{-9}$ mol^3 dm^{-9}

$x = 0.63 \times 10^{-3}$ mol dm^{-3} PbI_2 dissolved.

Molecular mass of PbI_2 = 461 moles per dm^3 is converted into g/dm^3 (Chemical units into physical unit of concentration) as follows:

$$\text{Moles.} = \frac{\text{Mass in g}}{\text{molecular mass}}$$

$\therefore$ Mass in g = moles x molecular mass

$= 0.63 \times 10^{-3} \times 461$

$= 0.00063 \times 461$

$= 0.29$ g

Solubility of PbI_2 at 25°C = 0.29 g/dm^3.

Application of Solubility Product :

The solubility product (K_{SP}) is used to determine whether a precipitate should form from a solution of known ionic concentrations. The value of solubility product represents the equilibrium condition between the dissolved ions and undissolved solid phase of solute i.e. when a solution is saturated.

When the product of the ionic concentrations is equal to the solubility product, a saturated solution is said to exist. If the ionic product is less than the solubility product, the solution is not saturated i. e. more amount of the solute can go in to the solution. If the ionic product is larger than the solubility product, the solution is said to be super saturated and the excess of solute should precipitate so as to restore the equilibrium conditions. For example, the solubility product of calcium sulphate solution is 2.4 x 10^{-5} mole/dm^3.

$$CaSO_{4(S)} \rightleftharpoons Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

$$K_{SP} = [Ca^{2+}][SO_4^{2-}] = 2.4 \times 10^{-5}$$

If,

$$[Ca^{2+}][SO_4^{2-}] > 2.4 \text{ X } 10^{-5}$$

$CaSO_4$ would form precipitates so as to reach the value of 2.4 x 10^{-5}. If, on the other hand,

$[Ca^{2+}][SO_4^{2-}] < 2.4 \times 10^{-5}$ it means the solution is not saturated and more solute could go into the solution till the product becomes equal to 2.4 x 10^{-5}.

Problem :

Should $PbCrO_4$ precipitate from a solution prepared by mixing 100 cm^3 of 2.5 x 10^{-4} M $Pb(NO_3)$ and 300 cm^3 of 1.5 x 10^{-8} M K_2CrO_4? (K_{SP} of $PbCrO_4$ = 1.8 x 10^{-14}).

Solution:

The equation for the equilibrium is:

$$\underset{\text{Undissolved}}{PbCrO_{4(S)}} \rightleftharpoons \underbrace{Pb^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)}}_{\text{Dissolved}}$$

$$K_{SP} = [Pb^{2+}][CrO_4^{2-}] = 1.8 \times 10^{-14}$$

Total volume of the solution = 100 cm³ + 300 cm³ = 400 cm³. This volume contains the equivalent of 100 cm³ $Pb(NO_3)_2$ and 300 cm³ of K_2CrO_4. The concentration of each ion is calculated:

$$[Pb^{2+}] = \left(\frac{100cm^3\ Pb(NO_3)_2}{400\ cm^3\ \text{Total solution}}\right) \times 2.5 \times 10^{-4} M = 6.25 \times 10^{-5} M$$

$$[CrO_4^{2-}] = \left(\frac{300Cm^3\ K_2CrO_4}{400\ cm^{-3}\ \text{Total solution}}\right) \times 1.5 \times 10^{-8}\ M = 1.125 \times 10^{-8}\ M$$

The ionic product of $PbCrO_4$ is:
$[Pb^{2+}]\,[CrO_4^{2-}] = (6.25 \times 10^{-5})\ (1.125 \times 10^{-8}) = 7.03 \times 10^{-13}$

Since the ionic product (7.03×10^{-13}) is larger than the solubility product (1.8×10^{-14}), hence $PbCrO_4$ should precipitate out from the solution.

6.9 COMMON ION EFFECT

The equilibrium law can be applied to sparingly soluble salts such as AgCl. It is very slightly soluble in water and the following equilibrium exists between the solid ionic salt and its ions in the aqueous phase.

$$\underset{\text{Undissolved}}{AgCl_{(s)}} \rightleftharpoons \underset{\text{dissolved}}{Ag^{+} +_{(aq)}} + Cl^{-}_{(aq)}$$

The decrease in the solubility of the salt in a solution that already contains an ion common to that salt, is called common ion effect.

$$K_c = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

Since the concentration of solid AgCl is constant in its saturated solution, hence

$$K_c[AgCl] = K_{sp} = [Ag^+][Cl^-]$$

K_{sp} is known as the solubility product which is equal to the product of the ionic concentration. Similarly, for magnesium chloride ($MgCl_2$).

$$K_{sp} = [Mg^{2+}][Cl^{1-}]^2$$

Precipitation of an electrolyte is caused when the concentration of its ions exceeds the solubility product. It is achieved by increasing the concentration of any one of the ions. That is to say, by adding common ion, solubility product can be exceeded. For example, precipitation of AgCl is caused by adding Cl^- as common ion in the shape of NaCl. With the addition of common ion, either Cl^- or Ag^+, the ionization of AgCl is suppressed and it forms precipitate. This is known as common ion effect.

$$\left.\begin{aligned} AgCl_{(S)} &\rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)} \\ KCl_{(S)} &\rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)} \end{aligned}\right\} \text{ Common ion } (Cl^-)$$

Common ion effect finds useful application in qualitative salt analysis.

EXAMPLE : Cations of II and IV groups are precipitated as sulphides but under different conditions due to their different solubility products. In fact the solubility product of IV group sulphides is higher than that of II group sulphides.

TABLE – SOLUBILITY PRODUCTS AT 18°C

SULPHIDES OF II GROUP	SULPHIDES OF IV GROUP
PbS 3.4×10^{-28}	MnS 1.4×10^{-16}
CdS 3.6×10^{-29}	ZnS 1.2×10^{-23}
CuS 8.5×10^{-45}	NiS 1.4×10^{-24}
HgS 4.1×10^{-54}	CoS 3×10^{-26}

In order to precipitate the sulphides of II group, H_2S is passed through the original solution (O.S.) in presence of HCl.

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

HCl furnishes H^+ as common ions which shift the above equilibrium to left according to Le-Chatelier's principle. In other words, addition of HCl suppresses the ionization of H_2S there by lowering the concentration of sulphide ion (S^{2-}) which is however just enough to exceed the solubility product of II group sulphides. In this way group II cations are precipitated such as CuS, PbS, CdS etc.

IV group sulphides having higher solubility product are precipitated by H_2S in presence of NH_4OH. The OH^- of NH_4OH combines with H^+ of H_2S to form H_2O ($H^+ + OH^- \rightarrow H_2O$). The removal of H^+ from the product side shifts the equilibrium to right ($H_2S \rightleftharpoons 2H^+ + S^{2-}$). In this way, the concentration of sulphide ion (S^{2-}) increases which is enough to exceed the solubility product for the precipitation of sulphides, e.g. CoS, NiS, ZnS.

Group III cations are precipitated as hydroxides by NH_4OH in presence of NH_4Cl. The common ion in this case is NH_4^+ which suppresses the ionization of NH_4OH

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Thus with the addition of common ion (NH_4^+) the equilibrium is shifted towards left and the concentration of OH^- decreases. Under these conditions, the solubility product of the hydroxides of Al, Fe and Cr is only exceeded due to which they are precipitated. The hydroxides of other cations such as Zn, Ni, Co etc. are not precipitated due to their higher solubility product.

In addition to salt analysis, common ion effect is very useful in industries also. Chemical yields in manufacturing processes can be controlled and greatly increased by making use of common ion effect.

The common ion effect changes the equilibrium point of a reaction from a less to a more favourable position.

PROGRESS TEST 6

1. What are reversible and irreversible changes? Describe an experiment to demonstrate a reversible change.

2. (a) State and explain the law of equilibrium. Describe its applications.
   (b) What do you understand by K_C and K_p? Describe their relationship.

3. What is meant by solubility product and the common ion effect. Discuss the application of common ion effect in the qualitative salt analysis.

4. How is the balance of chemical equilibrium influenced? Explain giving examples.

5. For the gaseous equilibrium $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$; $\Delta H = 87.9$ KJ/mole, explain the effect upon the material distribution of (a) increased temperature (b) increased pressure (c) higher concentration of Cl_2 (d) higher concentration of PCl_5 (e) presence of a catalyst.

6. A quantity of PCl_5 was heated in a 12 dm^3 vessel at 250°C.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

At equilibrium, the vessel contains 0.21 mole PCl_5, 0.32 mole PCl_3 and 0.32 mole Cl_2. Compute the equilibrium constant K_C. ($K_C = 0.040$) Ans.

7. Consider the following equilibria:

(i) $3O_{2(g)} \rightleftharpoons 2O_{3(g)}$ $\quad \Delta H =$ positive

(ii) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ $\quad \Delta H =$ positive

(iii) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ $\quad \Delta H =$ negative

(a) Write the equilibrium constant expressions.
(b) In which direction will each equilibrium change as the temperature is raised?
(c) Which of the equilibria will not be affected by change in total pressure?

8. One mole of HI is introduced into a vessel held at constant temperature. When equilibrium is reached, it is found that 0.1 mole of I_2 have been formed. Calculate the equilibrium constant K_C. ($K_C = 0.0125$) Ans.

9. What effect on the position of equilibrium $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ for which $\Delta H = +176$ KJ/mole, does each of the following changes have: (a), adding $CaCO_3$ (b), adding CaO (c), decreasing the volume of the container (d), raising the temperature (e) removing CO_2.

10. State Le-Chatelier's principle. What are its industrial applications?

11. Write note on : (i) Reversibility of a chemical change (ii) dynamic equilibrium (iii), K_C and K_P.

12. When 1 mole of pure ethyl alcohol (C_2H_5OH) is mixed with 1 mole of acetic acid (CH_3COOH) at room temperature, the equilibrium mixture contains $^2/_3$ mole each of ester ($CH_3COOC_2H_5$) and water. (a), What is the equilibrium constant K_C, (b) how many moles of ester are formed at equilibrium when 3 moles of alcohol are mixed with 1 mole of acid? All substances are liquids at room temperature. (a) Kc = 4; (b) ester = 0.9 moles Ans.

solution for (b) Let x = no. of moles of alcohol reacting.

	Alcohol	+	Acid	$\rightleftharpoons$	Ester	+	water
No. of moles at initial state	3		1		NIL		NIL
Change by reaction	$-x$		$-x$		$+x$		$+x$
No. of moles at equilibrium state	$(3-x)$		$(1-x)$		x		x
Concentration at equilibrium state	$\frac{(3-x)}{V}$		$\frac{(1-x)}{V}$		$\frac{x}{V}$		$\frac{x}{V}$

$$K_c = 4 = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{3-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2}{3-4x+x^2}$$

$x^2 = 4(3-4x+x^2)$ or $3x^2 - 16x + 12 = 0$. Solving by quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{+16 \pm \sqrt{(-16)^2 - 4(3)(12)}}{2\,(3)} = \frac{16 \pm 10.6}{6}$$

$x = 4.433$ or $x = 0.9$

In the problem we started with 3 moles alcohol and one mole acid, hence we cannot form more than one mole ester even if all the acid is used up. Therefore correct root of quadratic is 0.9, that is, 0.9 mole ester is produced.

13. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Calculate the number of moles of Cl_2 produced at equilibrium when one mole of PCl_5 is heated at 250°C in a vessel having a capacity of 10 dm^3. At 250°C, $K_c = 0.041$ for the dissociation.
(0.465 moles) Ans.

14. (a) What is meant by the equilibrium constant and how it is determined experimentally?

(b) To determine the value of K_c for the reaction $CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$ 1 mole of CH_3COOH and 1 mole of C_2H_5OH in 1 dm^3 of solution in an inert solvent containing a small amount of acid catalyst were warmed until no further change occurred. At equilibrium, 0.667 mole of water was present. Calculate the value of K_c.
($K_c = 4$) Ans.

15. "At equilibrium all processes come to a halt." What is wrong with this statement when applied to chemical systems?

16. (a) What is meant by the solubility product? Give its uses.
(b) What is the solubility of lead chromate in moles per dm^3 at 25°C. K_{sp} for $PbCrO_4 = 2.8 \times 10^{-13}$ mole/dm^3

17. (a) Will Cadmium hydroxide precipitate from 0.01M solution of $CdCl_2$ at pH 9. K_{sp} of $Cd(OH)_2 = 2.5 \times 10^{-14}$ mole²/dm⁶. (Since ionic product of $Cd(OH)_2$ is greater than K_{sp} so it will precipitate).
(b) The solubility of $Mg(OH)_2$ at 25°C is 0.00764 g/dm^3. What is the solubility product of $Mg(OH)_2$? ($K_{sp} = 9.0 \times 10^{-12}$ mole²/dm²) Ans.

Should AgCl precipitate from a solution prepared by mixing 400 ml of 0.1M NaCl and 600 ml of 0.03 M $AgNO_3$?
K_{sp} of $AgCl = 1.6 \times 10^{-10}$ moles/dm^3. (Ionic product is larger than K_{sp} AgCl will precipitate). Ans.

CHAPTER - 7

SOLUTIONS AND ELECTROLYTES

INTRODUCTION

Solutions play an important role in many processes. Nutrients are carried in water solution to all parts of a plant; the body fluids of animals are water solutions of numerous substances. The ocean is a vast water solution containing compounds extracted from the minerals of the earth's crust. Medicines and drugs are frequently aqueous or alcoholic solutions of physiological active compounds.

Definition : *"A solution is a homogeneous mixture or single phase mixture of the molecules, atoms or ions of two or more components"* The component that predominates in the solution is usually referred to as the ***solvent***. Since there are three states of matter. There are nine types of solutions: ***three gaseous solutions, three liquid solutions***, and ***three solid solutions***.

7.1 CONCENTRATION OF SOLUTIONS

Concentrations are either expressed in physical units or chemical units. In the former, concentration is expressed in physical units; for example 20 grams of

NaOH per cubic decimetre (dm^3) of solution; a 10% aqueous solution of NaCl contains 10 g NaCl per 100 g solution i.e. 10 g NaCl mixed with 90 g water. What is of interest here that the concentrations expressed in chemical units are more common and frequently used which are discussed below:

Molar Concentration : *"The molar concentration (M) is the number of moles of the solute contained in one cubic decimetre (dm^3) or litre of solution"*. For example, a 0.5 molar solution of Na_2CO_3 contains 53g of Na_2CO_3 per cubic decimetre of solution, since 53 is half of the molecular mass of Na_2CO_3, 106. A one molar (1M) solution contains 106 g Na_2CO_3 per dm^3 of solution. The term molarity is often used to refer to molar concentration.

Molal Concentration : *"A molal concemtration (m) is the number of moles of the solute per kilogram of solvent.* For example, a molal solution (1 m) of Na_2CO_3 contains 106 g Na_2CO_3 dissolved in 1000 g of water, since 106 is the molar mass of Na_2CO_3. 0.5 molal solution contain 53 g Na_2CO_3 per kg of water. The term molality is often used to refer to molal concentration.

7.2 HYDRATION

Water is a universal solvent and its polar nature plays very important part in dissolving substances. It dissolves ionic compounds readily because of the *hydration* of their ions. A hydrated ion is the ion which is surrounded by water molecules. The clustering of ion with water molecules is due to the attraction of a positive ion for the negative end of water molecule, or of a negative ion for the positive end. In solution, the number of water molecules which surround the ions is indefinite. Very often when a water solution of a salt is evaporated, the salt crystallizes with a precise number of water molecules called water of crystallization. Such crystallized salts contain a definite amount of water of crystallization for example, when magnesium chloride is recrystallized from water, the crystallized salt has the composition $MgCl_2.6H_2O$. That is, each magnesium ion in the crystal is surrounded by six water molecules (Fig: 7.1). It is interesting to note that although hydrated salt like $MgCl_2$ $6H_2O$ has water molecule attached to its crystals, yet it appears dry.

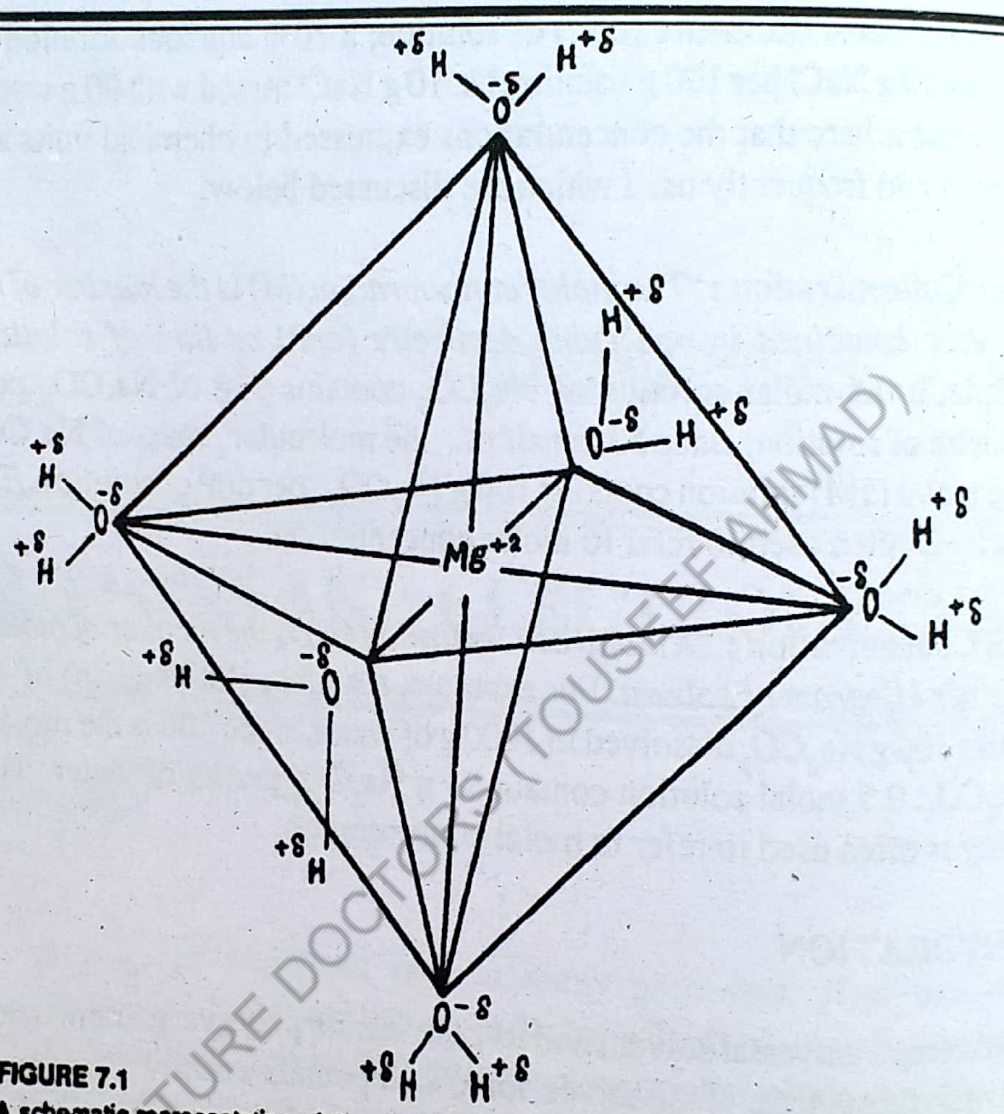


FIGURE 7.1

A schematic representation of the shape of a $[Mg(H_2O)^{2+}_6$ ion, (octahedral). The distance between the metal and oxygen have been exaggerated to show better the special relationship

The ability of an ion to form hydrate depends upon the charge density, that is, size of the ion and its charge. Smaller the size and greater the charge, greater would be the charge density. For example, Al^{+3} has greater charge density than Br because the former is smaller with greater charge than Br^-. Thus small positive ions with multiple charges such as Cu^{2+}, Al^{3+}, Cr^{3+} possess great attraction for water molecules as compared to large negative ions with a single charge such as Br^- or I^-. It is found that usually the water of crystallization is associated with positive ions. For example copper chloride is crystallized with the composition $CuCl_2.4H_2O$, and four water molecules are associated with Cu^{2+} in square planar fashion (Fig. 7.3).

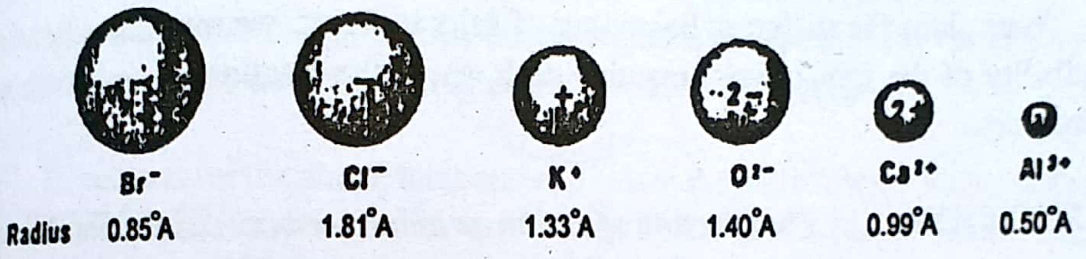


FIGURE 7.2
An arrangement of six ions in the order of their increasing charge density. The large bromide ion with a single charged has the least, the small triply charged aluminium ion the greatest charge density.

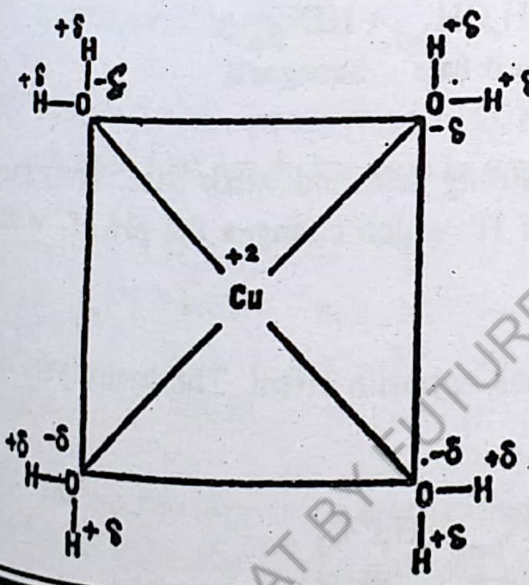


FIGURE 7.3
A Schematic representation of the shape of a $[Cu(H_2O)_4]^{2+}$ ion (square planer).

Many hydrated salts decompose upon heating to give the anhydrous salts.

$$\underset{\text{Pentahydrate}}{CuSO_4.5H_2O_{(s)}} \xrightarrow{\text{Heat}} \underset{\text{Anhydrous salt}}{CuSO_{4(s)}} + 5H_2O_{(g)}\uparrow$$

7.3 HYDROLYSIS

Aqueous solutions of normal salts may be neutral, acidic or alkaline,.

depending on the nature of the salt. For example, an aqueous solution of NH_4Cl is acidic, a Na_2CO_3 solution is alkaline while NaCl solution is neutral.

To explain the different behaviour of salts in water, we must consider the possibility of the ions of salts reacting with water, the reaction being known as hydrolysis.

DEFINITION : *"The reaction of cation or anion (or both) with water so as to change its pH is known as hydrolysis".*

It is interesting here to note that the hydrolysis occurs only when a change in pH takes place. For example, the aqueous solution of NH_4Cl turns blue litmus red because it is acidic in nature:

$$NH_4Cl_{(aq)} + HOH_{(l)} \longrightarrow \underset{\text{Weak base}}{NH_4OH_{(aq)}} + \underset{\text{Strong acid}}{HCl_{(aq)}}$$

In aqueous solution, NH_4Cl forms strong acid and weak base. Thus the solution contains higher concentration of H^+ which changes the pH of water toward acidic.

The aqueous solution of Na_2CO_3 has opposite effect. The hydrolysis is represented by the following equation:

$$Na_2CO_{3(s)} + 2HOH_{(l)} \longrightarrow \underset{\text{Strong base}}{2NaOH_{(aq)}} + \underset{\text{Weak acid}}{H_2CO_{3\,(aq)}}$$

It may be pointed out, the hydrolysis does not occur in case of NaCl because it does not change the pH of water. The aqueous solution of NaCl is, therefore, essentially neutral.

7.4 THEORY OF IONIZATION

The behaviour of the aqueous solutions of electrolytes was found to be quite different than that of non-electrolytes. For example, the electrolytic solutions conduct electricity and the different solutions of acids, bases and salts have different abilities to conduct electricity. Properties like elevation of boiling point, depression of freezing point, osmotic pressure and saturated vapour pressure show marked deviation than similar solutions of the other substances. A relation between the deviation in properties and electrical conductance was also noted. In general, greater the deviation, greater the electrical conductance.

To account for the above facts and to explain the phenomena of electrolysis, the IONIC THEORY was put forward by the Swedish Chemist Svante August Arrhenius about 1880.

(a) The substances called electrolytes are believed to contain electrically charged particles called ions. These charges are positive for H^+ ion or ions derived from metals and negative for the ions derived from non-metals. Number of electrical charges carried by an ion is equal to the valency of corresponding atom.

(b) Molecules of electrolytes (acids, bases and salts) dissociate into oppositely charged ions on dissolution in water, e.g.

$$H_2SO_4 = 2H^+ + SO_4^{2-}$$
$$NaCl = Na^+ + Cl^-$$
$$HCl = H^+ + Cl^-$$
$$NaOH = Na^+ + OH^-$$

(c) The number of positive and negtive charges on the ions must be equal so that the solution as a whole remains neutral.

(d) In solution, the ions are in state of disorderly motion. Upon colliding they may combine to give unionized molecules. Thus ionization is a reversible process in which the solution contains ions of electrolyte together with unionized molecules.

$$H_2SO_{4(aq)} \rightleftharpoons 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$$

(e) The extent of ionization or to say the degree of ionization depends upon the nature of electrolyte. Strong electrolytes such as NaCl, HCl, etc ionize completely in water. Weak electrolytes such as AgCl, acetic acid (CH_3 COOH) ionize only slightly. For example in 2M solution, only 4 molecules out of 1000 molecules of acetic acid are ionized which mean 996 molecules remain unionized.

(f) Ionization is not affected by electric current. When electric current is passed through an electrolytic solution, the ions begin to migrate towards the opposite electrodes, i.e. positive ions towards negative electrode (cathode) and negative ions towards positive electrode (anode). The ions which are attracted towards cathode are called Cations such as Na^+, H^+ etc., the ions which are attracted towards anode are called Anions, e.g. Cl^-, SO_4^{2-} etc. On reaching the electrodes, the ions lose their charge and change into neutral species (atoms or molecules) by the gain or loss of electrons.

Arrhenius Theory clarified many peculiarities in the behaviour of electrolytic solutions. The presence of ions affords a simple explanation of the deviation in freezing point, boiling point and Osmotic pressure. Since 1 mole of NaCl yields 1 mole of Na^+ (6.02×10^{23} ions) and 1 mole of Cl^- (6.02×10^{23}), the number of these ions is twice that of NaCl. Hence Osmotic pressure must also increase two fold. This is because such properties depend upon the number of particles and not on the nature of compound (colligative properties). However according to the Arrhenius ionic theory, an electrolytic solution is regarded as mechanical mixture of solvent molecules and ions. In no way, it reflected the interaction between these particles. Further development suggested that the ions can interact with water to form *hydrates*. (According to Arrhenius, ions are free to move like isolated atoms).

Despite the good agreement of the electrolytic dissociation theory with facts, it was at first not universally accepted. This was simply due to the concept of atom as being indivisible particle and as such the distinction between atom and ion could not be explained.

(g) The dissociation of electrolyte depends upon (i) nature of electrolyte (ii) degree of dilution (iii) temperature.

(h) The electrical conductivity depends upon (i) the number of ions present in the solution (ii) speed of ions.

7.5 CONDUCTANCE OF ELECTRIC CURRENT THROUGH SOLUTIONS

The existence of ions in solutions of electrolytes was postulated to account for the ability of certain solutions to conduct the electric current. One expects the conductance of an electrolytic solution to vary with (i), dilution (ii), absolute velocities of ions (iii) degree of ionization (iv), temperature (v), pressure etc.

In a concentrated solution, the number of ions per unit volume of solution increases and the distance between ions decreases causing stronger inter ionic attractions. As a result, migration of ions becomes more difficult and the conductance decreases with increase in concentration. As the solution is diluted the inter ionic attraction decreases and the migration of ions becomes easier. As a consequence, the conductance increases with dilution.

As the conduction of electric current is related to the movement of ions, it is obvious that conductance increases with the increase of absolute velocities of ions in solution.

On the basis of electro conductance data, electrolytes are broadly classified into two groups, strong electrolytes and weak electrolytes. The strong electrolytes such as HCl, NaCl etc. show larger conductance which is due to higher degree of ionization ($\propto$)

$$\propto = \frac{\text{Number of dissociated molecules}}{\text{Total molecules dissolved}}$$

Weak electrolytes like CH_3COOH show low conductance due to their low degree of ionization. In both cases, however, conductance increases rapidly with dilution. In fact, the strong electrolytes are almost completely ionized in dilute solutions.

Conductance of an electrolytic solution is also influenced by the temperature. On raising the temperature by 1°C, conductance increases by 2 to 2.5% which is due to reduced hydration of ions and lower viscosity of solutions.

Pressure has no noticeable effect on conductance. Large increase in pressure will cause a considerable fall in conductance. On raising the pressure to 2000 atmospheres, the electro conductance of acetic acid falls to 0.6% of its original value.

Conductance of a solution plays an important part in the industrial application of electrolysis since it determines to a considerable degree the consumptions of energy in the electrolytic process. Electro-conductivity determinations find extensive use in the control laboratory. Thus the salt contents in various solutions on vaporization of water (for example, in boiler water or on condensing milk) is determined from conductivity measurements.

Electrolysis : As described under the ionization theory, a solution of an electrolyte contains oppositely charged ions. When no electric current is passing, the ions are wandering randomly about in the solution. When electric current is passed through the electrolytic solution, movement of the ions towards their opposite electrodes takes place where they are eventually discharged. "The movement of anions and cations towards their respective electrodes accompanying all chemical changes in an electrolytic solution under the influence of electric current is known as electrolytic conduction of electrolysis".

Electrolysis is performed in what is called an electrolytic cell (see figure 7.4). The essential parts of an electrolytic cell are the positive and negative electrodes which are connected to a source of electricity. The positive electrode is termed an anode and the negative electrode is as cathode. Whether the anode is positive or negative depends upon the definition. The definition we will follow is "The anode is the electrode at which oxidation occurs; the cathode is the electrode where reduction occurs". In electrolytic cell as shown in the diagram anode is positive and cathode is negative. However, in electrochemical or galvanic cell such as battery, the anode is negative and the cathode is positive. The electric current flows into and out of the solution via electrodes. Conventially, the current (flow of electrons) enters the cell at cathode and leaves at anode.

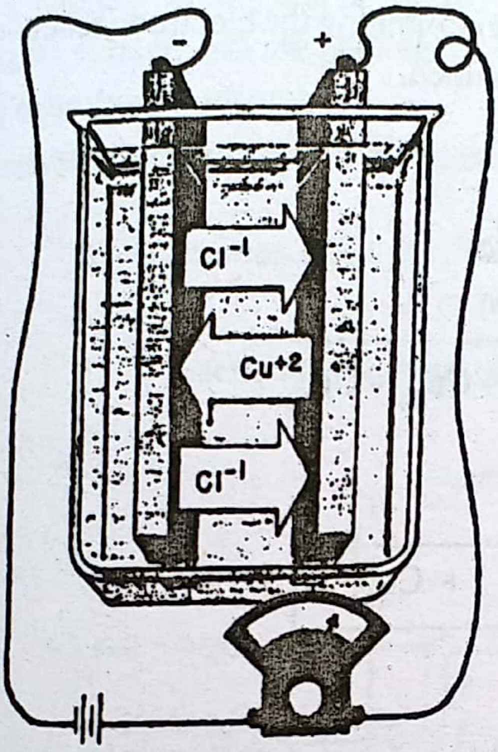


FIGURE 7.4
Electrolysis of Cupric Chloride.

The electrolysis of a moderately concentrated solution of cupric chloride ($CuCl_2$) is illustrated in the fig 7.4. As we are aware of the fact, $CuCl_2$, is composed of ions, it may precisely be represented as Cu^{2+}, Cl^-, Cl^-. On dissolving in water, these ions are separated.

$$CuCl_{2(aq)} \rightleftharpoons Cu^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

These ions are free to move around randomly among water molecules when no electric current is passing. As soon as the electric current is passed, the movement of these ions begins to take place. Cu^{2+} ions migrate towards cathode and Cl^- ions towards anode. At cathode, Cu^{2+} ions are discharged as copper atoms by the gain of electrons (reduction)

$Cu^{2+}_{(aq)} + 2e \longrightarrow Cu_{(s)}$ ... Reduction at cathode

At anode, Cl^- ions are discharged as Cl_2 gas by the loss of electrons (Oxidation).

$2Cl^-_{(aq)} - 2e \longrightarrow Cl_{2(g)}$ .... Oxidation at anode

Thus the reactions taking place in the electrolytic cell are oxidation - reduction reactions or redox reactions. By combining the electrode reactions, the over all reaction of the electrolysis is obtained.

$$\begin{array}{l} Cu^{2+}_{(aq)} + 2\cancel{e} \rightarrow Cu_{(S)} \\ 2Cl^-_{(aq)} - 2\cancel{e} \rightarrow Cl_{2(g)} \\ \hline Cu^{2+}_{(aq)} + 2Cl^-_{(aq)} \rightarrow Cu_{(S)} + Cl_{2(g)} \end{array}$$

$$\boxed{CuCl_{2(aq)} \rightarrow Cu_{(s)} + Cl_{2(g)}}$$

When the ions originally present have been changed to neutral particles, the current can no longer flow.

7.6 ELECTRODE POTENTIAL

The electric current producing appliance known as the Voltaic cell consists of two half cells. In each half cell a metal plate is placed in the solution of its ions.

"The difference of potential created between a metal and solution of its salt is called Electrode potential of the metal". It is the measure of tendency of an electrode to lose (or gain) electrons or to say it serves as a measure of chemical activity during reaction taking place in solution.

Since absolute electrode potential can not be measured, hence it is determined by comparing with the hydrogen electrode which is the reference electrode. Arbitrarily hydrogen electrode has been assigned a potential of 0.000 volts.

A hydrogen electrode consists of a platinum plate immersed in 1 molar solution of sulphuric acid. A current of pure H_2 is passed continuously through the solution under the pressure of 1 atm . (See figure 7.5). The platinum adsorbs H_2 gas on its surface and the platimun coated with hydrogen behaves as if it were made entirely of hydrogen.

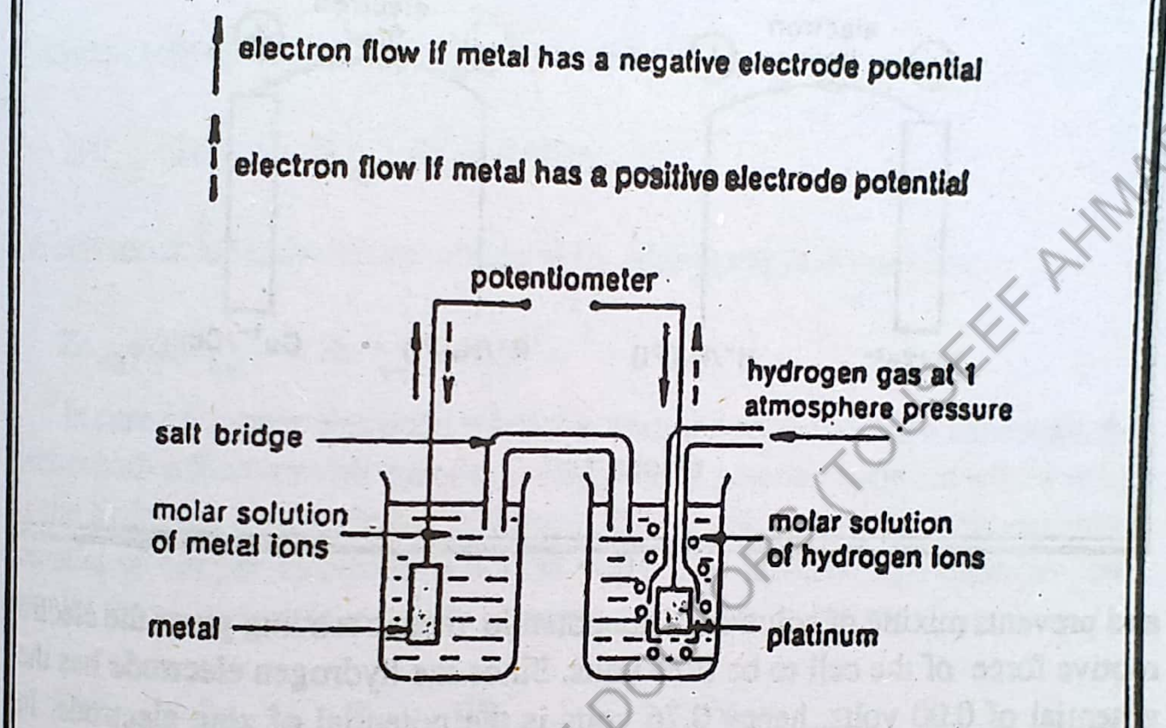


FIGURE 7.5

Since temperature and concentration influence the voltage, these variables are held constant for the comparison. The temperature is held at 25°C, the concentration of ions in contact with elemental electrode is held at 1 molar and the gas pressure at 1 atmosphere. Electrode maintained under these conditions is called standard electrode and its potential as *standard electrode potential*. It is designated as E°. For the purpose of uniformity, since 1953, standard electrode potentials have been expressed in terms of reduction reactions and they are referred to as standard reduction potentials E° Reduction. From these values, standard oxidation potentials are obtained by just reversing their sign.

$$E^\circ_{\text{Reduction}} = -E^\circ_{\text{oxidation}}$$

To illustrate the method of determining the standard electrode potential, we pick up the example of zinc electrode. For this purpose, we have to construct a voltaic cell made up of zinc (a strip of zinc immersed in IM$ZnSO_4$) and hydrogen electrodes. Salt bridge is made of KCl jelly completes the circuit between half cell

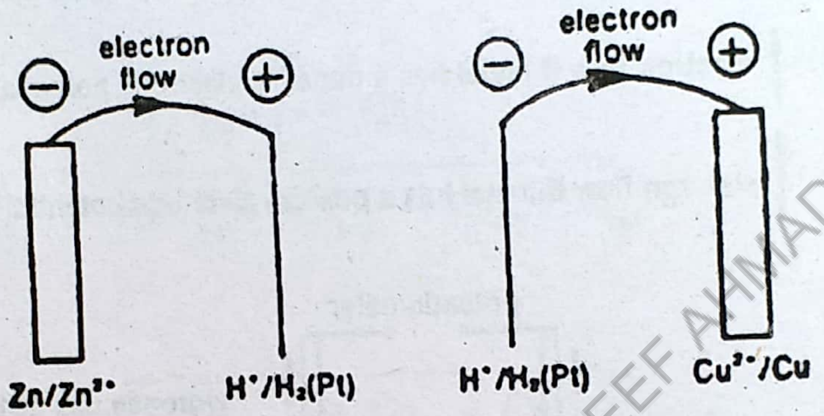


FIGURE 7.6

and prevents mixing of solutions. The potentio metric reading gives the electromotive force of the cell to be 0.76 volts. Since the hydrogen electrode has the potential of 0.00 volts, hence 0.76 volts is the potential of zinc electrode. In external circuit it is observed that flow of electrons takes place from zinc to hydrogen electrode (See fig. 7.6).

$$Zn;\ Zn^{2+}_{(aq)}\ (1.0M) \overset{e^-}{\rightarrow}\Vert\ H^+_{(aq)}\ (1.0M)\ ;\ H_{2(g)}\ (1\ atom);\ Pt.$$

Thus it is believed that electrons must have originated at zinc i.e. it is oxidized, is the anode and is negative with respect to hydrogen electrode. Thus the standard reduction potential of zinc electrode is – 0.76 V.

$$Zn^{2+}_{(aq)} + 2e \rightarrow Zn_{(S)}\ ;\ E^\circ_{Reduction} = -0.76V$$

The standard oxidation potential of zinc is therefore + 0.76 V.

$$E^\circ_{Reduction} = E^\circ_{Oxidation}$$
$$-0.76\ V = +0.76\ V$$

The negative sign signifies that actually the reaction at zinc electrode occurs in the opposite direction, i.e., it is the oxidation rather than reduction which occurs at zinc.

$$Zn_{(s)} - 2e \rightarrow Zn^{2+}_{(aq)} \; ; \; E^\circ_{Oxidation} = 0.76\ V$$

Reduction takes place at Hydrogen electrode:

$$2H^+_{(aq)} + 2e \rightarrow H_{2(g)} \; ; E^\circ = 0.00V$$

The cell reaction is, therefore, obtained by adding the half reaction:

$$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$$

In case of copper electrode when it is coupled with hydrogen electrode, the electromotive force or voltage of the cell given by potentio meter is + 0.34 volts. As the hydrogen electrode has potential of 0.00 volts, therefore, the electrode potential of copper electrode is + 0.34 volts. The positive sign indicates that actually the reduction takes place at copper electrode as written:

$$Cu^{2+}_{(aq)} + 2e \rightarrow Cu_{(s)} \; ; E^\circ_{Reduction} = +0.34\ V$$

From this we predict the oxidation potential to be – 0.34 V

$$E^\circ_{Reduction} = -E^\circ_{Oxidation}$$

$$+0.34\ V = -0.34\ V$$

In case of copper electrode (a strip of copper immersed in IM Cu SO_4) coupled with hydrogen electrode, the electrons originate at hydrogen electrode i.e. flow of electrons takes place from hydrogen to copper electrode (see fig. 7.6)

$$Cu^{2+}_{(1M)} \quad Cu_{(s)} \underset{||}{\xleftarrow{e^-}} H_2\ (1\ atm) \; ; 2H^+_{(aq)} \; ; Pt.$$

$$Pt, H_{2(g)} \; ; H^+_{(1M)} \underset{||}{\xrightarrow{e^-}} Cu^{2+}_{(1)} \; ; Cu_{(s)}$$

Thus copper electrode being cathode, is reduced and is positive with respect to hydrogen as shown above.

Table 7.1 list of more standard reduction potentials at 25°C.

ELECTRODE	HALF-REACTION	E^0 (V)	ELECTRODE	HALF-REACTION	E^0(V)
Li^+/Li	$Li^+ + e^- \rightarrow Li$	– 3.05	$Ag(NH_3)_2^+/Ag$	$Ag(NH_3)_2^+ + e \rightarrow Ag + 2NH_3$	+ 0.37
K^+/K	$K^+ + e^- \rightarrow K$	– 2.93	O_2/OH^-	$O_2 + 2H_2O + 4e \rightarrow 4OH$	+ 0.40
Ba^{2+}/Ba	$Ba^{2+} + 2e^- \rightarrow Ba$	– 2.90	$NiO_2/Ni(OH)_2$	$NiO_2 + 2H_2O + 2e \rightarrow Ni(OH)_2 + 2OH$	+ 0.49
Ca^{2+}/Ca	$Ca^{2+} + 2e^- \rightarrow Ca$	– 2.87	Cu^+/Cu	$Cu^+ + e^- \rightarrow Cu$	+ 0.52
Na^+/Na	$Na^+ + e^- \rightarrow Na$	– 2.71	I_2/I^-	$I_2 + 2e^- \rightarrow 21$	+ 0.54
Mg^{2+}/Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	– 2.37	O_2/H_2O_2	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	+ 0.68
Al^{3+}/Al	$Al^{3+} + 3e^- \rightarrow Al$	– 1.66	Fe^{3+}/Fe^{2+}	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+ 0.77
$Fe(OH)_2/Fe$	$Fe(OH)_2 + 2e^- \rightarrow Fe + 2OH^-$	– 0.88	Hg_2^{2+}/Hg	$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	+ 0.79
H_2O/H_2	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	– 0.83	Ag^+/Ag	$Ag^+ + e^- \rightarrow Ag$	+ 0.80
$Cd(OH)_2/Cd$	$Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$	– 0.81	O_2/H_2O(pH7)	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+ 0.82
Zn^{2+}/Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	– 0.76	Hg^{2+}/Hg	$Hg^{2+} + 2e \rightarrow Hg$	+ 0.85
Cr^{3+}/Cr	$Cr^{3+} + 3e^- \rightarrow Cr$	– 0.74	NO_3^-/NO	$NO_3^- + 4H^+ + 3e \rightarrow NO + 2H_2O$	+ 0.96
Fe^{2+}/Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	– 0.44	Br_2/Br^-	$Br_2 + 2e^- \rightarrow 2Br^-$	+ 1.07
H_2O/H_2 (pH 7)	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	– 0.42*	O_2/H_2O	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+ 1.23
Cd^{2+}/Cd	$Cd^{2+} + 2e^- \rightarrow Cd$	– 0.40	MnO_2/Mn^{2+}	$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	+ 1.28
$Ag(CN)_2^-/Ag$	$Ag(CN)_2^- + e^- \rightarrow Ag + 2CN^-$	– 0.40	$Cr_2O_7^{2-}/Cr^{3+}$	$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow$	+ 1.33
$PbSO_4/Pb$	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	– 0.36		$2Cr^{3+} + 7H_2O$	
Ni^{2+}/Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	– 0.25	Cl_2/Cl^-	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+ 1.36
Sn^{2+}/Sn	$Sn^{2+} + 2e^- \rightarrow Sn$	– 0.14	PbO_2/Pb^{2+}	$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	+ 1.46
Pb^{2+}/Pb	$Pb^{2+} + 2e^- \rightarrow Pb$	– 0.13	MnO_4^-/Mn^{2+}	$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$	+ 1.51
Fe^{3+}/Fe	$Fe^{3+} + 3e^- \rightarrow Fe$	– 0.036	$PbO_2/PbSO_4$	$PbO_2^+ + 4H^+ + SO_4^{2-} + 2e^- \rightarrow$	+ 1.69
H^+/H_2	$2H^+ + 2e^- \rightarrow H_2$	0.000		$PbSO_4 + 2H_2O$	
$AgCl/Ag$	$AgCl + e^- \rightarrow Ag + Cl^-$	+ 0.22	H_2O_2/H_2O	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	+ 1.78
Hg_2Cl_2/Hg	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	+ 0.27	$S_2O_8^{2-}/SO_4^{2-}$	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	+ 2.00
Cu^{2+}/Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34	F_2/F^-	$F_2 + 2e^- \rightarrow 2F^-$	+ 2.87

*The potential at pH 7 is not E^0

This is known as electro chemical series or E.C.S.

Few important facts about the electrochemical series are summarized as :

(i) Metals above hydrogen in ECS undergoes oxidation in the comparison cell i.e. they are anodes. Metals placed below hydrogen undergoes reduction i.e. they are cathodes.

(ii) Whether or not the electrode reaction will occur spontaneously when electrode is connected to hydrogen electrode can be inferred from the sign of electrode potential. If it is positive, the reaction will occur as written and the electrode will act as anode. If the sign is negative, the reverse reaction will occur and it will be cathode and hydrogen electrode as anode.

(iii) In the ECS, there is decreasing tendency from top to bottom to lose electrons (undergo oxidation) and increasing tendency to gain electrons (undergo reduction). In other words, the reducing strength decreases and the oxidizing strength increases from top to bottom. Thus lithium is the strongest reducing agent and F_2 the strongest oxidizing agent.

(iv) In E.C.S, the metals are placed in the order of reactivity and shows the displacement order. Metals displace metals lying below them in the list from solution of their salts. All metals above hydrogen have negative electrode potentials.

7.7 OXIDATION NUMBER (O.N.)

Definition :

"The formal charge (i.e. not real) on the atom in the compound or ion under consideration is known as oxidation number or state."

In defining the oxidation number, the term 'formal charge' is used which means it is not the actual charge on the atom in a molecule or ion. While using the concept of O.N., all the compounds (including all the covalent compounds) are imagined to be completely ionic, although no compound, is completely ionic. In covalent compounds, therefore, the bonding electrons (that are present in a bond) are considered to be "owned" by the more electronegative atom e.g. in $H:\underset{..}{\ddot{O}}:H$, oxygen is more electronegative than hydrogen, therefore two electrons, one from each hydrogen, are considered to be owned by oxygen giving rise to two negative charges on oxygen. Therefore, oxidation number of oxygen in water would be 2^- Each hydrogen is considered to have lost one electron giving rise to one positive charge on each hydrogen. Therefore, oxidation number of hydrogen would be 1^+.

Guiding rules that have been established to determine the oxidation number of atoms are mentioned below :

1. The oxidation number of all the elements in free state is zero.

$$Br^{\circ}_2,\ Na^{\circ},\ H_2^{\circ},\ P^{\circ},\ O_2^{\circ}\ ,\ N^{\circ}_2$$

2. In a compound, the more electronegative elements are assigned negative oxidation numbers, and the less electronegative elements are assigned the positive oxidation numbers.

$$Cl^{1+}F^{1-},\ H^{1+}Cl^{1^-}$$

3. In a neutral species, the sum of oxidation numbers is Zero:

$$^{2+}NO^{2^-}\quad,\quad ^{1+}HBr^{1^-}\quad,\quad ^{4+}SO_2{}^{(2^-)}{}_2$$

4 The oxidation number of oxygen in most of its compounds is 2 .

$$^{2+}SrO^{2-}\quad,\quad ^{(1+)2}H_2O^{2^-}\quad,\quad ^{4+}CO_2{}^{(2-)}{}_2$$

The exceptions are few :

$$^{(1+)2}OF_2^{(1-)_2}\quad,\quad ^{(1-)2}Na_2O_2{}^{(1-)}{}_2\quad,\quad ^{1+}KO_2^{(1/2-)_2}$$

Oxygcn is less E.N.

per oxide
(0-0 bond)

super oxidc.

5. The oxidation number of hydrogen when combined with a non-metal is 1⁺.

$\overset{4-}{C}\overset{(1+)_4}{H_4}$, $\overset{3-}{N}\overset{(1+)_3}{H_3}$, $\overset{1+}{H}\overset{1-}{F}$

When combined with a metal of lower E.N, O.N of Hydrogen is 1⁻.

$^{1+}NaH^{1-}$, $^{2+}CaH_2^{(1-)}{}_2$, $^{1+}KH^{1-}$

This is due to the electronegativity of hydrogen being intermediate between metals and non-metals.

6. The oxidation number of fluorine in its compounds is always 1⁻ because it is the most electronegative element and can not form more than one bond.

$^{2+}OF_2^{(1-)2}$, $^{6+}SF_6^{(1-)}{}_6$, $^{1+}ClF^{1-}$

The oxidation number of the other halogens in binary compounds is usually 1⁻

$\overset{1+}{K}\overset{1-}{Br}$, $\overset{1+}{Na}\overset{1-}{Cl}$, $\overset{2+}{Mg}\overset{(1-)}{Cl_2}{}^{2}$

Few exceptions are there

$\overset{1+}{H}\overset{2-}{O}\overset{1+}{Cl}$,	$\overset{1+}{H}\overset{3+}{Cl}\overset{(2-)}{O_2}{}^{2}$,	$\overset{1+}{H}\overset{5+}{Cl}\overset{(2-)_3}{O_3}$,	$\overset{1+}{H}\overset{7+}{Cl}\overset{(2-)_4}{O_4}$
Hypochlorous acid	Chlorous acid	Chloric acid	perchloric acid

7. In polyatomic ions, the sum of the oxidation states of all the atoms present in them equals the ionic charge:

$\overset{5+}{P}\overset{(2-)_4}{O_4^{3-}}$, $\overset{4+}{C}\overset{(2-)_3}{O_3^{2-}}$, $\overset{6+}{S}\overset{(2-)_4}{O_4^{2-}}$

8. Group I, II and III elements show the oxidation state of 1+, 2 + and 3+ respectively in their compounds:

$$\underset{\text{I group}}{\underset{\uparrow}{\overset{1+}{K}\overset{1-}{Cl}}} \quad , \quad \underset{\text{II group}}{\underset{\uparrow}{\overset{2+}{Ca}\overset{(1-)_2}{F_2}}} \quad , \quad \underset{\text{III group}}{\underset{\uparrow}{\overset{3+}{Al}\overset{(1-)_3}{Br_3}}}$$

It may be pointed out that the oxidation number is simply an imaginary number and it reflects the extent to which an element has been oxidized or reduced. In an oxidized form of the element, the O.N. is more positive, and in reduced form, it is more negative.

Example 1. Give the oxidation number of tin in $SnCl_2$ and $SnCl_4$.

Solution: Since oxidation number of each chlorine atom is 1^-, hence total negative charge in $SnCl_2$ is 2–. To balance the negative and positive oxidation number, the O.N. of Sn must be 2+.

$$\overset{2+}{Sn}\overset{(1-)_2}{Cl_2} \qquad \therefore \quad Sn = 2+$$

Similarly in $SnCl_4$, the O.N. of Sn = 4+

$$\overset{4+}{Sn}\overset{(1-)_4}{Cl_4} \qquad \therefore \quad Sn = 4+$$

Example 2. Give the oxidation number of Nitrogen in HNO_3.

Solution: In HNO_3, each of the three oxygen has O.N.=2^-, for a total of 6^-. Since hydrogen is 1^+, therefore O.N. of Nitrogen is 5^+.

$$\overset{1+}{H}\overset{5+}{N}\overset{(2-)_3}{O_3} \qquad N = 5+$$

Example 3. Determine the oxidation number of S in SO_3^{2-}

Solution: The total oxidation number of the three oxygen atoms, is 6⁻. 2⁻ is to be left as the charge on the whole ion. Therefore, the oxidation number of sulphur is 4+ $\left[\overset{4+}{S}\overset{(2-)_3}{O_3}\right]^{2-}$.

7.8 OXIDATION AND REDUCTION REACTIONS

Definition I : Oxidation is a chemical change in which electrons are lost by an atom or group of atoms, and reduction is a chemical change in which electrons are gained by an atom or group of atoms. Consider the following examples.

$$Fe^{\circ} \rightarrow Fe^{2+} + 2\bar{e} \quad \text{(Oxidation)}$$

In this reaction neutral iron atom has lost 2 electrons and has changed to ferrous ion, so it is oxidation.

$$Cl_2 + 2e \rightarrow 2\,Cl \qquad \text{(Reduction)}$$

In this reaction, Cl_2 gains two electrons and charges to Cl^- ions, it is therefore reduction. These definitions of oxidation and reduction are based on electron transfer.

Definition II : The most comprehensive definitions of oxidation and reduction are in terms of oxidation numbers:

Odixation is a process in which the oxidation number of an element is increased: reduction is a process in which the oxidation number of an element is decreased. For example $C^{\circ} + O^{\circ}_2 \rightarrow C^{4+}O_2{}^{(2-)}{}_2$ is an oxidation of carbon, since its oxidation number increases from zero to 4^+ (Total change of four units).

Similarly, $H_2{}^{\circ} + Br^{\circ}_2 \longrightarrow 2H^{+}Br^{-1}$ is the reduction of bromine as its oxidation number decreases from O to 1–. It may be pointed out that oxidation and reduction occur simultaneously and such reactions are referred to as redox reactions.

Oxidation number is the concept that is helpful in diagnosing quickly the state of oxidation or reductions of particular atoms in various compounds.

7.9 BALANCING OXIDATION-REDUCTION EQUATIONS (ION-ELECTRON METHOD)

In this method of balancing the redox equations, only those reactants and products are balanced that contain the elements undergoing a change in oxidation state. That is to say, only those reactants and products are balanced which are actually oxidized or reduced. For this purpose it is important to transform molecular equation into ionic equation. Following key points must be kept in mind while writing down an ionic equation:

(a) Ionic substances are written in the ionic form only if the ions are separated from each other in the reaction medium. For example solid NaCl, Na^+ and Cl^- are not written because these ions are held together in its crystal. When present in solution, however, NaCl would be indicated by Na^+ and Cl^-, or either of these ions alone if only the sodium or the chlorine undergoes a change in oxidation state. Insoluble salts such as $BaSO_4$ are always written in the neutral form.

(b) Partially ionized substances are written in the ionic form only if the extent of ionization is appreciable. Thus water which is very little ionized, is written as H_2O. Strong acids such as HCl, HNO_3, are written in the ionized form but weak acids such as nitrous acid, sulphurous acid (HNO_2, H_2SO_3) are always written in the molecular form. Strong bases such as NaOH, KOH may be written in the ionic form as Na^+ and OH^- or K^+ and OH^-. A weak base like NH_3 is written as NH_3.

(c) Complex ions such as ferrocyanide $[Fe(CN)_6]^{4-}$ or ferricyanide, $[Fe(CN)_6]^{3-}$ which are stable and are written as such and never as separate ions like Fe^{3+} and CN^-.

Rules for Balancing by Ion-Electron Method :

1. Write a skeleton equation which includes those reactants and products that contain the elements undergoing a change in oxidation state.
2. Transform the molecular skeleton equation into ionic form. If the given equation is already in the ionic form, then this step is omittted.

3. The ionic equation is split in to two partial equations i.e. the oxidation and reduction equation.

4. Balance each partial equation in terms of atoms. In neutral or acidic medium, H_2O and H^+ are added for balancing oxygen and hydrogen respectively. The oxygen atoms are balanced first.

   In case of basic medium, OH^- and H_2O are added to balance oxygen and hydrogen respectively.

5. Balance the charge in each partial equation by adding electrons to either the left or right side of the equation. It will be found that electrons are added to the left in the partial equation for the reduction equation and to the right in the partial equation for oxidation reaction.

6. Multiply each partial equation by a number so that the electrons in both the partial equations become equal in number.

7. Add the two partial equations after cancelling the electrons. In the sum equation, cancel out any species common to both sides.

Example 1. Balance the oxidation of H_2S with HNO_3 by ion electron method.

Step 1 :- Write the skeleton equation

$$HNO_3 + H_2S \longrightarrow NO + S + H_2O$$

Step 2 :- Transform the molecular equation into ionic form:

$$NO^-_3 + H_2S \longrightarrow NO + S$$

The oxidizing agent is the nitrate ion, NO^-_3, since its Nitrogen changes the oxidation state (undergoes decrease in oxidation state). The reducing agent is H_2S, since sulphur undergoes an increase in oxidation state. It could have been written as sulphide ion (S^{2-}), but H_2S is preferable because of the very slight degree of ionization of the acid in nitric acid solution.

Step 3:- Split the ionic equation into two partial equations (Oxidation, reduction).

$\overset{5+}{N}O_3 \longrightarrow \overset{2+}{N}O$ ... Reduction (Nitrogen from 5+to 2^+)

$H_2S^{2-} \longrightarrow S^{\circ}$ ... Oxidation (Sulphur from 2^- to O)

Step 4 :- Balance the partial equations. Since the medium is acidic, oxygen and hydrogen atoms are balanced by adding H_2O and H .

In the first partial equation, 2 H_2O must be added to the right side to balance the oxygen atoms. Then $4H^+$ are added to the left to balance Hydrogen.

$$NO_3^- + 4H^+ \longrightarrow NO + 2H_2O$$

In the second partial equation, $2H^+$ are added to the right to balance two hydrogen atoms on the left:

$$H_2S \longrightarrow S + 2H^+$$

Step 5 :- Charge is balanced in the partial equations by adding electrons. In the first equation, the net charge on the left is 4+ (1–) = 3 + and on the right it is zero. Hence 3 electrons are added to the left side:

$$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$$

In the second equation, the net charge on the right is 2+, hence 2 electrons are added to make it zero as on the left:

$$H_2S \longrightarrow S + 2H^+ + 2e^-$$

Step 6 :- In order to equate the electrons lost and gained, first partial equation is multiplied by 2 and the second by 3 (cross multiplied):

$$2NO_3^- + 8H^+ + 6e \longrightarrow 2NO + 4H_2O$$

$$3H_2S \longrightarrow 3S + 6H^+ + 6e^-$$

Step 7 :- Cancel out the electrons and add the partial equations:

$$2NO_3^- + 3H_2S + 8H^+ \longrightarrow 2NO + 3S + 4H_2O + 6H^+$$

Since $6H^+$ are common to both sides, hence they are cancelled

$$2NO_3^- + 3H_2S + 2H^+ \longrightarrow 2NO + 3S + 4H_2O \text{ (Balanced)}$$

This equation may be converted back to molecular form by combining NO_3^- and H^+.

$$\underline{\overline{2HNO_3 + 3H_2S \longrightarrow 2NO + 3S + 4H_2O}}$$

This is properly balanced equation.

Example 2: The oxidation of $FeSO_4$ by $KMnO_4$ in acidic solution

Step 1 :- The skeleton equation:

$$KMnO_4 + H_2SO_4 + FeSO_4 \rightarrow MnSO_4 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$$

Step 2 :- Transform into ionic form:

$$MnO_4^- + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+}$$

Step 3 :- Make partial equations :

$$MnO_4^- \longrightarrow Mn^{2+}$$

$$Fe^{2+} \longrightarrow Fe^{3+}$$

Step 4 :- Balance the partial equations :

$$MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

$$Fe^{2+} \longrightarrow Fe^{3+}$$

Step 5 :- Balance the charge by adding electrons.

$$MnO_4^- + 8H^+ + 5\bar{e} \longrightarrow Mn^{2+} + 4H_2O$$

$$Fe^{2+} \longrightarrow Fe^{3+} + 1\bar{e}$$

Step 6 :- To equate the electrons lost and gained, multiply second equation by 5:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
$$5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$$

Step 7 :- After cancelling electrons, add the two partial equations:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O \text{ (Balanced)}$$

To convert back to the molecular form:

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O$$

7.10 INDICATORS

The end point of an acid-base titration is often detected by means of an indicator. Indicators are complex molecules that are themselves weak acids or weak bases.

A large number of indicators are known and each undergoes its colour change over a particular pH range. The following table lists some of the common indicators along with their colour change:

Table 7.2 colours of some indicators in acid, base and neutral condition.

Indicator	Colour in acid	Colour in base	Colour when neutral
Litmus	Red	Blue	Purple
Methyl orange	Red	yellow	Orange
Phenolphthalein	Colourless	pink	Colourless
Universal Indicator	Red	Purple	Green

For a strong acid and weak base, methyl orange is often used. For a strong base and weak acid, Phenolphthalein is commonly chosen.

The behaviour of indicators can be explained by the fact that the unionized molecule of an indicator and its anion possess different colours. Alternatively, one may be coloured and the other colourless. The indicator HIn, for instance, dissociates to give its anion In^- as shown by the following equilibrium.

$$\underset{\text{(Red)}}{HIn} \rightleftharpoons \underset{\text{(Yellow)}}{H^+ + In^-}$$

The undissociated molecule HIn, say is red and the anion In^- yellow. It can be seen that the equilibrium position of the indicator will be affected by the hydrogen ion concentration $[H^+]$. If the hydrogen ion concentration, is high, the equilibrium will move to the left and the undissociated HIn will predominate the solution will be red. If a base is added which reduces the hydrogen ion concentration, the equilibrium position will move to the right and the solution will become yellow. When there is equal concentration of HIn and In^-, the indicator will be in its neutral position and it will give mixture of red and yellow and it will appear orange.

7.11 STRENGTH OF ACIDS AND BASES

All the acids and bases, according to the Arrhenius, ionize in aqueous solutions to yield H^+ and OH^- respectively. The extent to which these substances ionize, is however, not same in all the cases. The extent of ionization is expressed in terms of degree of dissociation or percentage dissociation.

The degree of dissociation (∝) is the ratio of the number of molecules ionized to the total number of dissolved molecules.

$$\propto \;=\; \frac{\text{Number of molecules dissociated}}{\text{Total number of dissolved molecules.}}$$

This ratio when multiplied by 100 gives the percentage dissociation. For example, the degree of dissociation of HCl is 0.9 – 0.95 and its percentage dissociation is 90–95% i.e. out of every 100 molecule, 90–95 molecules of HCl get ionized in equeous solution. The acids and bases having high percentage dissciations are strong and those with low percentage dissociation are weak. The following table 7.3 lists some strong and weak acids and base alongwith their percentage dissociation.

Table 7.3 Some strong and weak acids

Acids		Bases	
Strong	**Weak**	**Strong**	**Weak**
HCl 90-95%	H_2S 0.1%	NaOH 90-95%	NH_4OH 1.4%
HNO_3 90-95%	CH_3COOH 1.4%	KOH 90-95%	
H_2SO_4 60% (1 stage)	H_2CO_3 0.17%	$Ba(OH)_2$ 77% (1 stage)	

Thus strong acids or bases ionize almost completely and the weak acid or bases ionize partially in aqueous solutions.

According to Bronsted-Lowry theory, an acid is a proton donor and a base is a proton acceptor.

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \bar{A}_{(aq)}$$

The formation of acid-base theory in terms of equilibrium suggests a way of measuring the strength of acids and bases. For the above equilibrium the dissociation constant (Ka) of the acid HA is given by:

$$Ka = \frac{[H_3O^+_{(aq)}]\,[\bar{A}_{(aq)}]}{[HA_{(aq)}]\;[H_2O]}$$

Larger the value of dissociation constant (Ka), stronger is the acid. Same is true for bases. Some typical dissociation constants for acids are given in the following table 7.4

Table 7.4 Some typical dissociation constants for acids

Acid	Ka(mol dm^{-3}) at 298°K.
Hydrocyanic acid	4.8×10^{-10}
Formic acid	1.8×10^{-4}
Acetic acid	1.8×10^{-5}
Chloroacetic acid	1.4×10^{-3}

Thus chloroacetic acid is stronger than formic acid which in turn is stronger than acetic acid.

In term of pH, acids with-low pH values, such as hydrochloric acid, nitric acid and sulphuric acid are strong acids. Similarly bases with high pH values such as solution of potassium hydroxide, sodium hydroxide are strong alkalis. These substances are strong electrolytes and are nearly completely ionized in aqueous solutions. Weak acids and bases have pH value nearer to 7, they are partially ionized in aqueous solution and are weak electrolytes. Example are acetic acid and ammonia solution (NH_4OH).

7.12 pH

The small values of the concentration of hydrogen ion(H^+) that we have encountered with solutions of slightly dissociated acid led Sorensan in 1909 to introduce the conception of pH.

Water acts as an acid as well as a base. For example, if we add NH_3 to H_2O, water acts as a proton donor or acid forming NH^+_4. It also acts a proton acceptor or base forming H_3O^+, if an acid is added to it :

$$H_2O + \ddot{N}H_3 \longrightarrow NH^+_4 + OH^-$$
$$H_2O + H^{\delta+} - Cl^{\delta-} \longrightarrow H_3O^+ + Cl^-$$

Careful measurements have shown that pure water ionizes slightly to produce ions of H_3O^+ and OH^-. Electrical conductance measurements of water at 25°C has indicated the concentration of 1.0×10^{-7} M each of H^+ and OH^- The ionic product of water is therefore

$$K_w = [H_3^+O]\,[OH^-] = 1.0 \times 10^{-14} M$$

In acidic solution, the concentration of H_3O^+ is always greater than that of OH^- and in basic solutions, the concentration of H_3O^+ is less than that of OH^-

pH is a convenient way of expressing the acidity and basicity of dilute aqueous solutions.

The pH of a solution is the negative logarithm of the hydrogen ion concentration:

$$pH = -\log\,[H^+] = \log\,\frac{1}{[H^+]}$$

Thus for water in which $[H^+] = 1 \times 10^{-7}$,
$pH = -\log\,(10^{-7}) = (-\log 1.0) + (-\log 10^{-7})$
$= 0.00 + 7.00 = 7.00$

The pH of 7.00 represents the point of neutrality. Clearly acidic solutions will have pH values which are low i.e. less than 7, basic solutions will have pH values which are high i.e. greater than 7.

Table : pH Scale

$[H^+]$	10^{0}	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14} mol dm^{-3}
pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

← Acidic ← Neutral → Basic →

Thus acidity is measured on a scale from O (very acidic) to 14 (very alkaline). This is the pH scale. pH scale should be thought of simply as numbers which indicate acidity.

pH of a solution is determined using universal indicator. By mixing together various indicators which change colour at slightly different acidities, chemical manufacturers have developed a universal indicator which goes through a spectrum of colours as the acidity changes. pH numbers are related to universal indicator colours as follows :

Red	Orange	yellow	Green	Blue	Deep blue	Purple
0	3	6	7	8	10	14

pH of a solution can be determined by adding a few drops of universal indicator solution, the reading off the pH number from the corresponding colour. Colour charts are provided by the manufacturer for this purpose.

For more precise measurements, pH meters are available. These are used with a delicate glass electrode which, when dipped into a solution, will give a direct reading of pH on the meter.

Below is given the chart which gives the pH of some common matter:

1.0	1.2	2.9	6.6	7.0	7.3	7.9-8.4	10.5	11.6	13
HCl	H_2SO_4	CH_3COOH	Milk	Distilled water	Blood	Sea Water	Milk of Magnesia	Na_2CO_3	NaOH

← Acidic — **Neutral** — Basic →

Worked Example 1: What is the pH of 0.004 mol dm^{-3} HCl (fully dissociated) at 25°C.

Solution: The fully dissociated HCl has $[H^+] = 4.0 \times 10^{-3}$ mol dm^{-3}, so

$$\begin{aligned} pH &= -\log(4.0 \times 10^{-3}) \\ &= (-\log 4.0) + (-\log 10^{-3}) \\ &= -0.60 + 3 = 2.40 \end{aligned}$$

Worked Example 2: The pH of a solution is 9.63. Compute its hydrogen ion concentration.

Solution: The pure exponential number is $10^{-9.63}$. Converting this number to a mixed number, we have,

$$\begin{aligned} 10^{-9.63} = 10^{0.63} \times 10^{9} &= 10^{0.37} \times 10^{10} \\ &= 2.34 \times 10^{-10} \end{aligned}$$

Therefore the concentration of hydrogen ion in this solution is 2.34×10^{-10} mol dm^{-3}.

7.13 BUFFERS

Normally the pH of a solution does not remain essentially constant: for example the pH of distilled water is 7. This pH of water alters either by absorbing CO_2 from atmosphere (forming H_2CO_3) or by absorbing silicates of glass.

The control of pH in living systems is essential for health. It is found, for instance, that the blood has a pH of about 7.3. The pH remains constant although the concentration of carbon dioxide and hence carbonic acid, varies considerably. If acid is added to a sample of blood its pH is found to change very little unless an excess of acid is added.

A solution which tends to resist changes in pH is called a buffer solution.

Buffer solutions of specified pH values are prepared easily by half neutralizing a solution of a weak acid with a strong base, or a weak base with a strong acid. An example of buffer solution is acetic acid (a weak acid) mixed with sodium acetate (its salt with strong base). Similarly ammonia solution, NH_4OH (a weak base) mixed with ammonium chloride (its salt with strong acid) is another example of buffer solution.

$$CH_3\,COOH_{(aq)} + CH_3\,COO^-\ Na^+\,(aq) = \text{Buffer solution}$$

$$NH_4OH_{(aq)} + \overset{+}{NH_4}\overset{-}{Cl}_{(aq)} = \text{Buffer solution.}$$

In practice, more sophisticated buffer solutions have been developed for use, particularly in the field of Bio-chemistry. The buffer in blood is the carbonic acid, it self a weak acid, in conjuction with protein molecules. We can illustrate the functioning of a buffer system by the dissociation equilibrium of a weak acid.

$$CH_3\,COOH_{(aq)} \rightleftharpoons CH_3\,COO^-_{(aq)} + H^+_{(aq)}$$

The buffer also contains the salt sodium acetate which is fully dissociated to furnish acetate ions.

$$CH_3\,CO\bar{O}Na^+_{(aq)} \rightleftharpoons CH_3\,COO^-_{(aq)} + Na^+_{(aq)}$$

Due to the increase in the concentration of acetate ions, the acetic acid equilibrium is pushed to the left there by reducing the H^+ concentration and forming undissociated acetic acid. Thus there is no appreciable change in pH. Even if small amount of acid or alkali are added, there is very little change in pH of the mixture. In case of added acid, the additional H^+ in the solution will combine with CH_3 COO to produce undissociated acetic acid.

$$CH_3\,COO^-_{(aq)} + H^+_{(aq)} \longrightarrow CH_3COOH_{(aq)}$$

and the pH will remain at about original level.

Small amounts of base (NaOH) added to the buffer solution will be neutralized by reactions with weak acid.

$$OH^-_{(aq)} + CH_3\,COOH_{(aq)} \rightleftharpoons H_2O_{(l)} + CH_3\,COO^-_{(aq)}$$

7.14 NEUTRALIZATION

When two substances (acid and base) having opposed properties are allowed to react, salt and water are produced. The reaction is known as neutralization.

$$\text{Acid} + \text{Base} \longrightarrow \text{Salt} + \text{Water}$$

For example, Hydrochloric acid is completely neutralized by sodium hydroxide.

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

In this reaction strong acid neutralizes strong alkali. Instead of complete neutralization, there may be partial neutralization; for example sulphuric acid reacts with sodium hydroxide to form sodium hydrogen sulphate:

$$H_2SO_{4(aq)} + NaOH_{(aq)} \longrightarrow NaHSO_{4(aq)} + H_2O_{(aq)}$$

In this reaction, only one hydrogen ion of sulphuric acid is neutralized by sodium hydroxide.

In all these neutralization reactions, hydrogen ion of the acid combines with hydroxide ion of base to form water.

The reaction in which hydrogen ion of acids and hydroxide ions of alkalis to produce water is known as Neutralization.

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$$

It may be pointed out that the salts formed as a result of complete neutralization are normal and those produced by partial neutralization are either acidic or basic.

$NaCl$	$NaHSO_4$	$Mg(OH)Cl$
Normal salt	Acidic salt	Basic salt

PROGRESS TEST 7

1(a) "The ability of an ion depends upon its charge density". Comment on the statement.

(b) What is essential difference between hydration and hydrolisis.

2. What is ionization theory? How does it explain the conductance of electric current through solutions?

3. What is electrolysis? Explain by giving the example of $CuCl_2$. Give all necessary electrode reactions.

4. Write detailed note on Electrode potential. What do you infere from the Electro chemical series?

5.(a) Define oxidation number; oxidation, reduction.

(b) Give the oxidation number of:

(i) Cr in $K_2Cr_2O_7$ (ii) S in $Na_2S_2O_3$ (iii) C in C_2H_6O (iv) Mn in MnO^-_4

(v) N in NCl_3. (vi) O in OF_2

6. Enumerate the rules for balancing the Redox equations by Ion Electron method.

7. Balance the following equations by ion electron method.

(i) $Cr_2O_7^{2-} + \overset{+}{H} + I_2 \longrightarrow Cr^{3+} + I\bar{O}_3 + H_2O$

(ii) $MnO_4^{-1} + SO_3^{2-} + \overset{+}{H} \longrightarrow Mn^{+2} + SO_4^{2-}$

(iii) $Cr(OH)_3 + SO_6^{2-} \longrightarrow CrO_4^{2-} + SO_3^{2-}$ (Basic)

(iv) Oxidation of Cl^{-1} by MnO_4^{-1} in acid solution

($KMnO_4 + KCl + H_2SO_4 \rightarrow MnSO_4 + K_2SO_4 + H_2O + Cl_2$)

(v) $MnO_4^- + SO_3^{2-} + OH^- \rightarrow Mn^{2+} + SO_4^{2-}$

8. What are the indicators? How can you explain their behaviour?

9. Write notes on:

(i) pH (ii) Neutralization (iii) Buffers

10. Define pH? What is pH of 0.1M HCl at 25°C?

11. What are strong and weak acids and bases? Give appropriate examples.

CHAPTER 8

INTRODUCTION TO CHEMICAL KINETICS

INTRODUCTION

The word Kinetic is derived from a Greek word "kinetic" which means "moving". Hence chemical kinetics is that branch of chemistry which deals with the study of:

(i) Rates of chemical reactions
(ii) Factors affecting rate
(iii) The mechanism through which the reaction proceeds
(iv) Optimum conditions for the maximum yield of a product

8.1 RATE AND VELOCITY OF REACTION

During the course of a chemical reaction, the molar concentration of reactants gradually decreases, whereas that of products increases. Consider a general chemical reaction: $A \longrightarrow B$

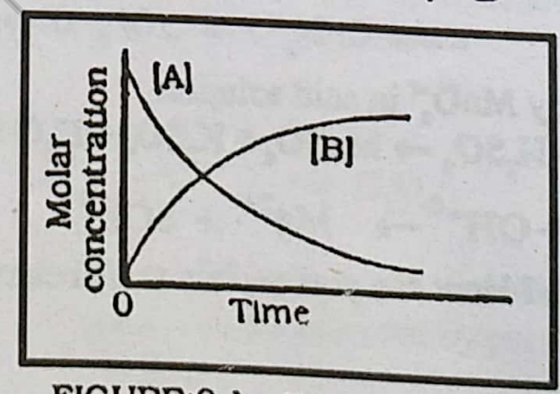


FIGURE:8.1 Reaction profile

Rate of reaction:– It is defined as the quantity of a reactant consumed or the quantity of a product formed per unit time i.e.

$$\text{Rate} = \frac{\text{Increase in concentration of products or decrease in concentration reactants}}{\text{Time taken for change}}$$

The graph clearly shows that the rate of reaction is not uniform and it changes with time. Initially the rate of disappearance of reactant [A] is fast and it tappers out gradually. Similarly the initial rate of formation of product [B] is fast but falls of latter on. Hence the overall rate of reaction as defined above is actually the Average Rate of Reaction.

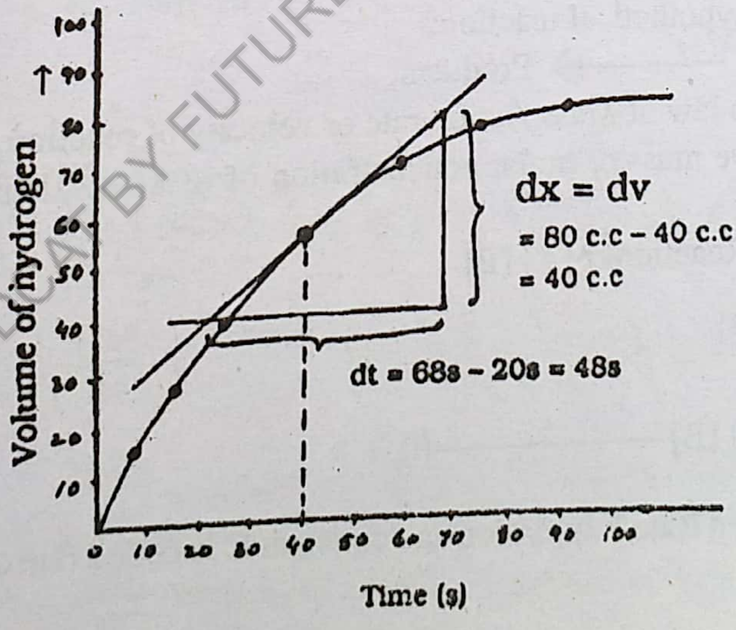
Velocity of reaction:– It is defined as the rate of a reaction at a particular given moment i.e. at a specific time. If we consider a very small interval of time "dt" in which the change in concentration (dx) is taken to be nearly constant then velocity of reaction is given by the expression:

$$\text{Velocity of reaction} = \frac{dx}{dt}$$

Velocity of reaction may also be termed as Instantaneous Rate of Reaction.

Instantaneous rate is the slope of the tangent to the curve at that time. Consider the reaction between Mg and HCl:

$$Mg_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_{2(g)}$$



Graph of rate of reaction

FIGURE.8.2

Reaction is followed by measuring the volume of H_2 gas evolved at regular interval of time. The results are plotted and a rate curve is obtained (Fig: 8.2).

To calculate velocity of reaction, say at 40s, the tangent to the curve at 40s is shown in the graph.

Now velocity of reaction at 40s=slope of tangent

$$=\frac{dx}{dt}=\frac{dv}{dt}=\frac{40c.c}{48s}=0.83c.c/s$$

Thus rate of production of H_2 at 40s is $0.83\,cm^3/s$

For the purpose of simplicity in future discussion, we will not differentiate between rate and velocity of reaction and will be frequently using the symbol $\frac{dx}{dt}$ for rate as well.

Unit of rate of reaction:– The concentration is usually expressed in moles/dm^3 and time in seconds, hence

$$\text{Rate of reaction}=\frac{\text{Change in concentration}}{\text{Time taken for change}}$$

$$=\frac{mole/dm^3}{s}=\frac{mole}{dm^3}\times\frac{1}{s}=mole(dm^3)^{-1}s^{-1}$$

8.2 RATE CONSTANT AND RATE EXPRESSION

Consider a hypothetical reaction:

$$A+B \longrightarrow \text{Products}$$

According to law of Mass Action rate or velocity of reaction is directly proportional to active mass or molar concentration of reactants, hence for the above reaction or

Velocity of Reaction α [A] [B]

$$\frac{dx}{dt}\ \alpha\ [A]\ [B]$$

$$\frac{dx}{dt}=K\ [A]\ [B] \text{ ——————(i)}$$

Expression (i) is called Rate Expression and constant K is called rate or velocity constant.

When the concentration of each reactant is unity i.e. 1 mole/dm^3 then K is called specific rate constant i.e. substituting the values in expression (i).

$$\frac{dx}{dt}=K[1]\,[1]$$

$$\therefore \quad \frac{dx}{dt}=K$$

Hence specific rate constant at a given temperature, may be defined as the rate of reaction when the molar concentration of each reactant is unity.

Example 1:– **Writing rate expression**

Problem: Write rate expression for the following reactions:

(a) $PCl_5 \longrightarrow PCl_3 + Cl_2$

(b) $2NO + O_2 \longrightarrow 2NO_2$

(c) $H_2SeO_3 + 6I^- + 4H^+ \longrightarrow Se + 3I_2 + 3H_2O$

Solution:

(a) Rate of reaction α $[PCl_5]$

$$\frac{dx}{dt} = K[PCl_5]$$

(b) Rate of reaction α $[NO]^2[O_2]$

$$\frac{dx}{dt} = K[NO]^2[O_2]$$

(c) Rate of reaction α $[H_2SeO_3]\,[I^{\ominus}]^6\,[H^{\oplus}]^4$

$$\frac{dx}{dt} = K[H_2SeO_3]\,[I^{\ominus}]^6\,[H^{\oplus}]^4$$

Example 2:– **Significance of plus and minus sign.**

Problem: For a chemical reaction $A \longrightarrow B$, the rate of reaction is denoted by:

$\frac{-dA}{dt}$ or $\frac{+dB}{dt}$. State the significance of plus and minus signs.

Solution: $\frac{-dA}{dt}$ represents the rate of reaction in terms of decrease in concentration of reactant A.

$\frac{+dB}{dt}$ represents the rate of reaction in terms of increase in concentration of product B.

Example3:– Calculating rate of disappearance

Problem: For a chemical reaction $C_2H_{2(g)} + 2H_{2(g)} \longrightarrow C_2H_{6(g)}$, the rate of appearance of C_2H_6 is 0.25 mole/dm^3.s. What is the rate of disappearance of C_2H_2 and H_2?

Solution:

Rate of disappearance of $C_2H_2 = 0.25 \text{mole/dm}^3.s$

Rate of disappearance of $H_2 = 0.25 \times 2 = 0.5 \text{ mole / dm}^3.s$

Example 4:– Calculating rate constant

Problem: For a chemical reaction $A + B \longrightarrow AB$. Calculate:

(a) Rate constant when initial concentration of both the reactants is 0.1 moles/dm^3 each and rate of reaction is 3.02×10^{-4} moles/dm^3

(b) Rate constant if initial concentration of A or B is doubled.

Solution:

(a) For this reaction

Rate of reaction α [A] [B]

$$\frac{dx}{dt} = K[A][B]$$

$$3.02 \times 10^{-4} \text{moles/dm}^3.s = K(0.1 \text{ mole/dm}^3)(0.1 \text{ mole/dm}^3)$$

$$\therefore K = \frac{3.02 \times 10^{-4} \text{ mole / dm}^3.s}{(0.1 \text{ mole / dm}^3)(0.1 \text{ mole / dm}^3)}$$

$$K = \frac{3.02 \times 10^{-4} \text{dm}^3}{0.01 \text{ mole.s}}$$

$$K = 3.02 \times 10^{-2} \text{dm}^3 \text{ / mole.s}$$

(b) Let concentration of B is doubled

As [A] =0.1 mole/dm^3

$\therefore$ [B]=0.1×2=0.2 mole/dm^3

Since concentration of [B] is doubled, the rate of reaction will also become double i.e.

$$\text{Rate} = 3.02 \times 10^{-4} \times 2 = 6.04 \times 10^{-4} \text{ mole/dm}^3.s$$

Now

$$\text{Rate} = K\,[A]\,[B]$$

$$6.04\times10^{-4}\,\text{mole}/\text{dm}^3.\text{s} = K\left(0.1\text{mole}/\text{dm}^3\right)\left(0.2\text{mole}/\text{dm}^3\right)$$

$$\therefore \quad K = \frac{6.04\times10^{-4}\,\text{mole}/\text{dm}^3\text{s}}{\left(0.1\text{mole}/\text{dm}^3\right)\left(0.2\text{mole}/\text{dm}^3\right)}$$

$$K = 3.02\times10^{-2}\,\text{dm}^3\,/\,\text{mole.s}$$

Characteristics of K:

(i) It has a fixed value at a particular temperature.

(ii) Its value varies with temperature.

(iii) Its value at a temperature remains unchanged when the concentration of either or of all reactants is changed.

8.3 TYPES OF REACTIONS BASED ON REACTION VELOCITY

If we happen to observe many chemical reactions that are part of our daily life, we note that different reactions take different amount of time for completion. For example combustion of gasoline is very fast, cooking of food takes moderate time, but rusting of iron is a very very slow process. Hence we may classify the reactions with respect to their rates as follows:

(i) Reactions proceeding at a very slow speed:– These are the reactions which proceed at extremely slow speed and take very long time for completion. It is difficult to determine experimentally velocity of such reactions. Examples are: rusting of iron, radioactive decay of elements and formation of diamond from carbon in earth crust.

(ii) Reactions proceeding at a very fast speed:– These reactions are instantaneous reactions i.e. they are so fast that they are completed in very small time of the order of 10^{-6}s. All ionic reactions are of this type. It is impossible to determine rates of such reactions.

Examples:

(a) $\overset{+}{H}\overset{-}{Cl} + \overset{+}{Na}\overset{-}{OH} \longrightarrow \overset{+}{Na}\overset{-}{Cl} + H_2O$

(Acid) (Base)

(b) $\overset{+}{Ag}\overset{-}{NO_3}{}_{(aq)} + \overset{+}{Na}\overset{-}{Cl}_{(aq)} \longrightarrow AgCl + \overset{+}{Na}\overset{-}{NO_3}{}_{(aq)}$

(iii) Reactions proceeding at moderate speed:– These are the reactions which proceed at experimentally measurable rate i.e. they have limited speed and are completed at the most in few hours. Generally reactions of organic and covalent compounds are of such type.

Examples are:

(a) $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

Sucrose Glucose Fructose

(b) $CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$

Acetic acid Ethyl alcohol Ester

Why some reactions are fast and others slow ?

Concept of activation energy:– A reaction takes place when molecules of reacting substances collide together. But all the collisions are not effective i.e. do not lead to the formation of product. It has been found that only those collisions are effective in which the colliding molecules possess a minimum amount of energy called Threshold energy.

Before collision the molecules of reactants in their normal state do possess their respective internal energy, but their average internal energy is less than threshold energy. Now the molecules must acquire the difference of energy, in order that their collisions be effective. The excess energy that the reactant molecules, having average energy less than the threshold energy, must acquire in order to react and change into products is called Activation Energy.

Thus:

Activation Energy=Threshold Energy–Average Internal Energy of molecules

A relation between these energies is shown in the graph (Fig:8.3)

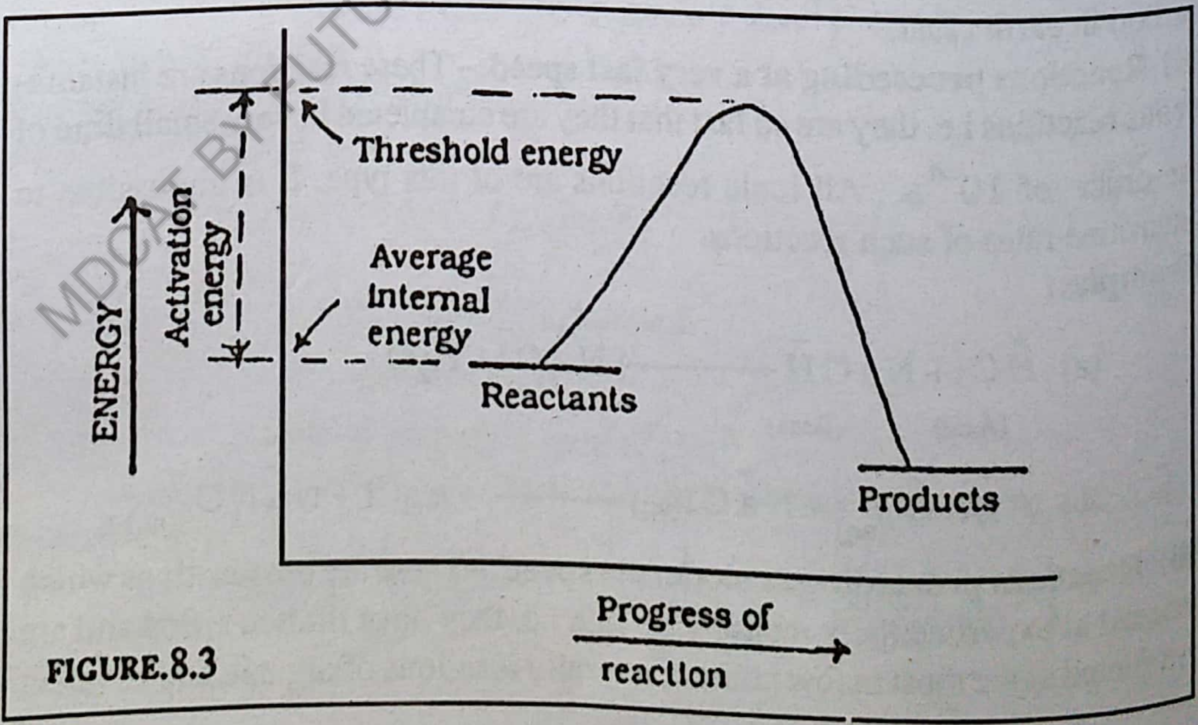


FIGURE.8.3

The speed of a reaction depends upon the activation energy of molecules. The reactions which have low values of activation energy are fast reactions and those which proceed slowly or moderately have comparatively high value of energy of activation.

Fast reactions can be slowed down and the slow reactions can be spedup by controlling the activation energy.

Example 5:– Calculating activation energy

Problem: For a chemical reaction $A \longrightarrow B$, the threshold energy of reaction is 31 K.J/mole. The average internal energy of A is 12 K.J/mole. Calculate activation energy of A.

Solution: Activation Energy=Threshold energy–Average internal energy
= 31 K.J/mole–12 K.J/mole
Activation Energy of A=19 K.J/mole.

8.4 DETERMINATION OF RATE OF REACTION

Two methods are employed for the determination of rate of a chemical reaction.

These are: (a) Physical methods (b) Chemical methods

(a) Physical methods:– In these methods the reaction is followed by measuring change in some physical property of reactants or products. Following are the methods generally employed:

	Name of physical methods	Observed physical property
(i)	Refractometric method	Change in refractive index.
(ii)	Spectroscopic method	Absorption of ultraviolet or infrared radiations.
(iii)	Calorimetric method	Change in colour intensity
(iv)	Conductivity method	Change in electrical conductivity
(v)	pH Method	Change in pH is observed
(vi)	Polarimetric method	Change in optical rotation of plane polarized light

(b) Chemical methods:– When physical methods are not available or suitable then a proper chemical method is used.

In a chemical method generally samples are drawn from the reacting vessel at regular intervals of time. Reaction is stopped at that particular moment by suddenly chilling the sample adding it to a suitable chemical. The amount of a reactant or product present at that time is generally found by titrating the sample against a proper reagent.

An example is the hydrolysis of methyl acetate (CH_3COOCH_3) in acidic medium.

$$CH_3COOCH_3 + H_2O \xrightleftharpoons{H^+} CH_3COOH + CH_3OH$$

Reaction is followed by measuring the amount of acetic acid (CH_3COOH) formed at regular interval by titrating the chilled samples against standard alkali (NaOH). With the passage of time more and more acetic acid is formed till reaction goes to completion.

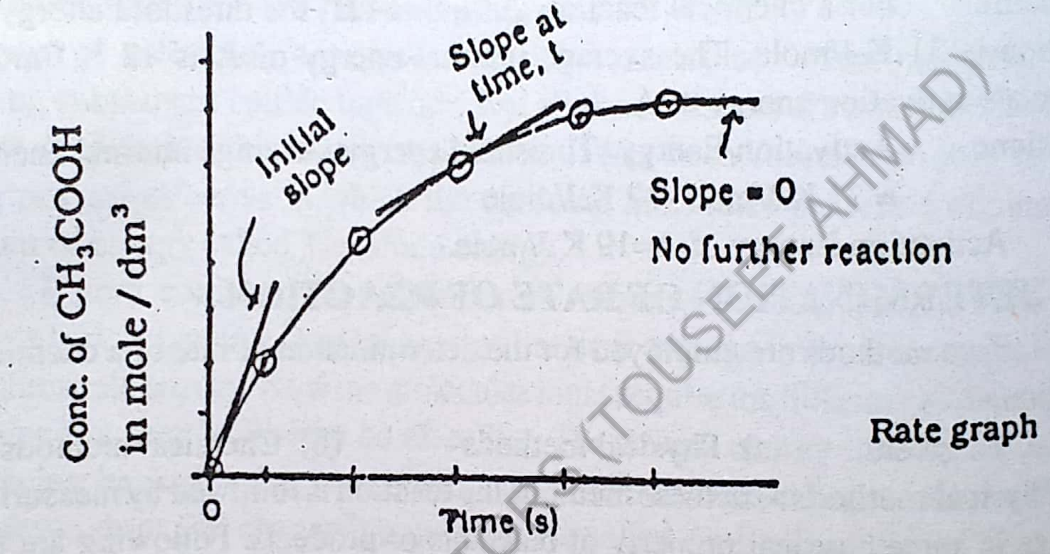


FIGURE.8.4

The results are plotted as a graph and rate curve is obtained.

The slope of rate curve at different times gives the rate of reaction $\left(\frac{dx}{dt}\right)$ at that moment; as discussed in section 8.1.

8.5 FACTORS AFFECTING RATE OF REACTION

The rate of a reaction involving collisions of molecules is influenced by many factors, enlisted below:

(i) Concentration of reactants
(ii) Nature of reactants
(iii) Temperature
(iv) Presence of catalyst
(v) Surface area of reactants (heterogeneous reactions)
(vi) Radiation

(i) Concentration of reactants:– Concentration is defined as number of moles or molecules of a substance per unit volume.

Rate of reaction varies with the concentration of reactants. According to law of mass action, the rate of a reaction is directly proportional to the concentration of reactants. The greater the concentration the greater the rate of reaction. This is because with the increase in concentration, the number of molecules of reactants also increases. There is now more crowding of molecules so frequency of collisions between them increases, resulting in the increase in rate of formation of products.

Consider a general reaction

$$xA + yB \longrightarrow C$$

Rate of reaction $\alpha[A]^x[B]^y$

$$\frac{dx}{dt} = K[A]^x[B]^y$$

In this rate expression the sum of exponents of concentration i.e. (x+y) is called Order of Reaction.

Order of chemical reaction: The relation between the rate and the concentration of the reactants taking part in the reaction can be described by the following reaction:

$$A + B \rightarrow \text{Product}$$

rate of reaction i.e. $\frac{dx}{dt} \alpha\ [A][B]$

or $\frac{dx}{dt} = K[A][B]$ ----(1)

Similarly for the reaction

$$A + 2B \rightarrow \text{Product}$$

$$\frac{dx}{dt} = K[A][B]^2 \text{ ---- (2)}$$

The equation of this type which describes the relationship between the concentrations of the reacting substances involved in the reaction and the rate, is called "rate expression". It is the rate expression which leads to the concept of order of reaction.

The order of reaction is defined as sum of all the exponents of the concentration in terms of the reactants involved in the rate equation.

Thus in rate equation (2)

Order of reaction (n)=1+2=3 (Third order reaction).

Consider the following examples:

(i) $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_{2(g)}$

$\frac{dx}{dt} = K[N_2O_5]$ The reaction is of the first order.

(ii) $2CH_3CHO \rightarrow 2CH_4 + 2CO$

$\frac{dx}{dt} = K[CH_3CHO]^2$ The reaction is of second order.

(iii) $2NO + O_2 \rightarrow 2NO_2$

$\frac{dx}{dt} = K\ [NO]^2\ [O_2]$ The reaction is of third order.

The order of reaction is assigned to a reaction only on the basis of experimental measurement and not by seeing the total nmber of molecules present in the reaction because there are reactions which contain more reacting molecules but the concentrations of only one or two molecules may alter during the reactions. For a reaction, minimum order of reaction may be of zero order and maximum upto third order.

Example 6:– Predicting effect of concentration on rate

Problem: The rate of a chemical reaction for the reaction:

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

was found experimentally to be represented by the expression

$$Rate = K[NO]^2[O_2]$$

What will be the effect on rate if

(a) Concentration of NO is doubled

(b) Concentration of NO is halved

(c) Concentration of O_2 is doubled

Solution: (a) As Rate $\alpha[NO]^2$, hence if concentration of NO is doubled, the rate will increase by $[2]^2 = 4$ times.

(b) If concentration of NO is halved the rate will be decreased by $\left[\frac{1}{2}\right]^2 = \frac{1}{4}$ times.

(c) As Rate $\alpha[O_2]$ hence if concentration of O_2 is doubled the rate will also be doubled.

Example 7:– **Predicting effect of concentration on rate constant**

Problem: For a chemical reaction at 450°C

$$2NH_3 \xrightarrow{\qquad} N_2 + 3H_2$$

$$\text{Rate} = K[NH_3]^2$$

What will be the effect on rate constant if concentration of NH_3 is increased four times ?

Solution: Now $K = \dfrac{\text{Rate}}{[NH_3]^2}$

The value of K will remain constant for either increasing or decreasing rate with reference to the ammonia concentration. K remains constant because as concentration of NH_3 is increased four times, the rate also increases by that factor.

(ii) Nature of reactants:– The nature of the reactants also affects the rate because activation energy for effective collision is different for different reacting substances.

Consider the following two reactions in which the collision probabilities are same, even then their rates are not equal.

$$2NO + O_2 \xrightarrow{\qquad} 2NO_2 \text{ Fast}$$

$$2CO + O_2 \xrightarrow{\qquad} 2CO_2 \text{ Slow}$$

Reaction between NO and O_2 is fast while that for CO and O_2 is slow. This is because activation energy for CO is higher than that of NO; as shown in Fig.8.5.

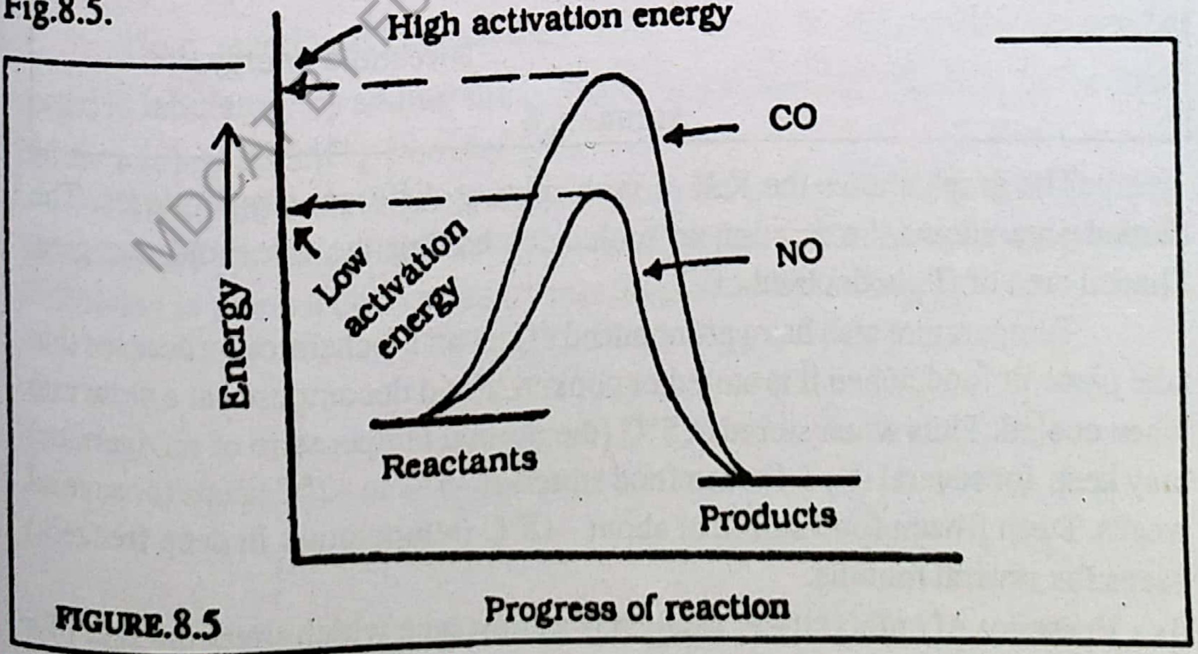


FIGURE.8.5

(iii) Temperature:– The rates of reaction are greatly influenced by the temperature at which the reaction is carried out. For example H_2 and O_2 do not combine at ordinary temperature, but combine very rapidly at high temperature.

As a general rate of thumb, the rate of reaction doubles for every 10°K rise in temperature. The reasons are:

(i) As temperature increases the velocity of molecules also increases, this results in the increase of frequency of collisions.

(ii) The rise in temperature raises the kinetic energy of each molecule. It has been found by raising the temperature by 10°C, the fraction of molecules possessing Threshold or activation energy becomes double, as a result number of effective collisions is also doubled, hence rate is doubled.

Effect of temperature on kinetic energy

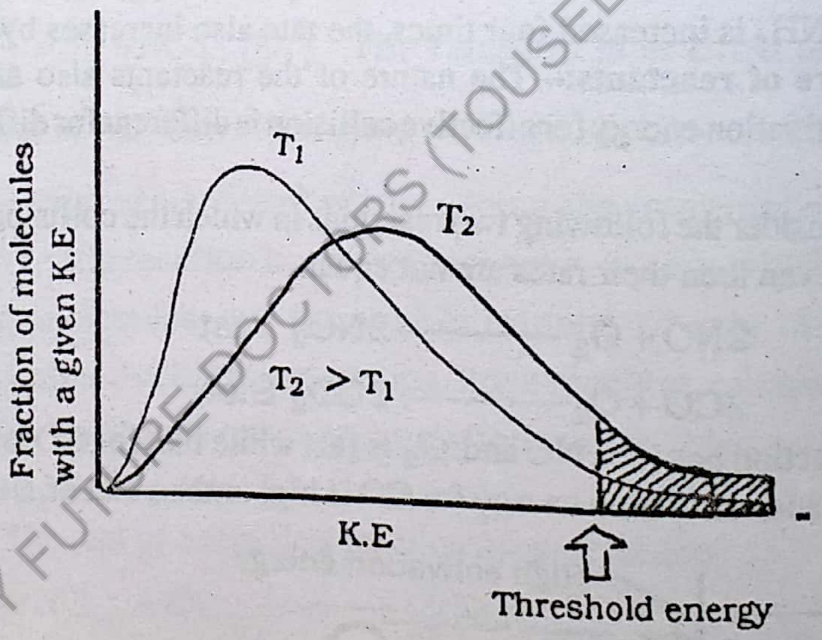


FIGURE.8.6

The graph shows the K.E of molecules at different temperatures. The shaded area shows the fraction of molecules having the threshold energies. Shaded area of T_2 is doubled of T_1.

Temperature also has a pronounced effect on biochemical processes that take place in food, when it is stored or cooked. Food decomposes at a slow rate when cooled. Thus when stored at 5°C (the normal temperature of refrigerator) may keep for several days. Frozen food stored at –5°C to –2°C keeps for several weeks. Deep frozen food stored at about –18°C (temperature in deep freezers) keeps for several months.

(iv) Presence of catalyst:– A catalyst is a substance which alters the rate of a chemical reaction without itself being consumed in the process. Basically they may be classified as:

(i) Positive catalysts:– They increase the rate of a chemical reaction.

For example: MnO_2 is a positive catalyst for decomposition of H_2O_2

$$2H_2O_{2(aq)} \xrightarrow{Mn\,O_2} 2H_2O_{(l)} + O_{2(g)}$$

Positive catalysts function by providing an alternate path to the reaction. The activation energy of this alternative route is lower as a result more reactants molecules possess the energy required for a successful collision. The total number of effective collisions per unit time increases and thus the rate of reaction increases.

(ii) Negative catalysts:– They decrease the rate of a chemical reaction. They are also called Inhibitors. For example glycerine is an inhibitor for the above decomposition of H_2O_2.

Negative catalysts on the other hand do not lower the activation energy rather they combine with reactant molecules, thus decreasing the number of colliding reactant molecules. This decreases the effective collisions, hence rate.

Some times one of the products of reaction acts as catalyst, such a process is called Auto catalysts. Initial rate of such reactions is slow but later on increases as the product concerned is formed. Example is Redox titration between $KMnO_4$ and oxalic acid.

$$2KMnO_{4(aq)} + 5H_2C_2O_{4(aq)} + 3H_2SO_{4(aq)} \longrightarrow 2MnSO_{4(aq)} + 10CO_{2(g)} + 8H_2O_{(l)} + K_2SO_4$$

Here reaction is catalysed by Mn^{+2} ion of $MnSO_4$. This fact can be tested in laboratory by adding some Mn^{+2} ions in form of $MnSO_4$ in the flask before adding $KMnO_4$ from burette.

There are certain catalysts known as Biocatalysts. These are enzymes. Enzymes are proteins which catalyse the chemical reactions in living systems. Following is given a chart of some reactions and their catalysts:

CHART

Reaction	Catalyst	Nature of catalysts
1. Synthesis of Ammonia by Haber's process $N_2 + 3H_2 \rightleftharpoons 2NH_3$	Reduced iron powder and small amount of Al_2O_3 or K_2O as .promoter	Positive
2. Conversion of SO_2 to SO_3 $2SO_2 + O_2 \rightleftharpoons 2SO_3$	V_2O_5 or Pt in finely divided form	Positive
3. Decomposition of laughing gas N_2O $2N_2O \overset{1000°K}{\rightleftharpoons} 2N_2 + O_2$	Traces of Cl_2	Positive
4. Decomposition of H_2O_2 $2H_2O_2 \longrightarrow 2H_2 + O_2$	(i) Glycerine (ii) MnO_2	Negative Positive
5. Oxidation of chloroform $(CHCl_3)$ to form poisonous gas Phosgene $(COCl_2)$ $CHCl_3 + \frac{1}{2}O_2 \longrightarrow COCl_2 + HCl$	2% Ethyl alcohol	Negative

(v) Surface area of reactants:– In case of heterogeneous reactions in which the reacting species are in different physical states, the surface area of solid reactant plays an important role with respect to rate of reaction. Greater the surface area, the higher is the rate of reaction. For example reaction between a piece of marble $(CaCO_3)$ and an acid is slow.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

But finally divided marble reacts vigorously because the powdered marble offers greater surface area for HCl to act upon. Similarly for the same reason amorphous boron is much more reactive than crystalline boron.

In case of liquid, the greater surface area, increases their rate of evaporation. For this reason spilled milk or a liquid evaporates faster than present in a glass or cup.

(vi) Radiation:– Some chemical reactions proceed only under the influence of light. These are called Photochemical Reaction: The concentration of reactants does not influence rate of such reactions, so they are Zero Order Reaction. Examples are:

(i) Reaction between H_2 and Cl_2

$$H_2 + Cl_2 \xrightarrow[\text{Bright sunlight}]{} 2HCl$$

(ii) Reaction between CH_4 and Cl_2

$$CH_4 + Cl_2 \xrightarrow[\text{Sunlight}]{} CH_3Cl + HCl$$

Radiation or light consists of photons. When photons strike the reactant molecule, they provide the necessary activation energy to the reactant molecules to react.

Example 8:– Determining order of reaction

Problem: A certain reaction $A + 2B \longrightarrow C + D$ gave the following data:

	Initial Concentration mole / dm^3		Initial rate of Reaction mole / dm^3.s
No:	A	B	
1.	0.1	0.1	3×10^{-3}
2.	0.2	0.1	6×10^{-3}
3.	0.1	0.2	9×10^{-6}

What is rate law and order of reaction?

Solution: Rate expression based on experimental data is called Rate law. According to data:

(a) When concentration of A is doubled, the rate is also doubled; hence

$$\text{Rate} \ \alpha [A] \text{———} (1)$$

(b) When concentration of B is doubled, rate increases by square i.e. from 3×10^{-3} to 9×10^{-6} i.e. $(3)^2 \times 10^{-6}$; hence

$$\text{Rate} \ \alpha [B]^2 \text{———} (2)$$

(c) Now combining (1) and (2), we have

$$\text{Rate} \ \alpha [A]\,[B]^2$$

or $Rate = K[A][B]^2$

This is Rate Law for the given reaction.

Now Order of Reaction=Sum of exponents of concentration in rate law.

Order of Reaction=1+2=3

Example 9:– Estimating value of K with change in temperature

Problem: As a rule of thumb rate, hence rate constant of a reaction increases by a factor of 2 for each 10°C rise in temperature, although the actual amount of increase differs from one reaction to another. Consider a reaction $A \longrightarrow B$, for which at 400°C, rate constant K, has a value of $3 \times 10^{-12}\ s^{-1}$. What can be the possible value of K at 450°C.

Solution: Temperature increases from 400°C to 450°C. Thus rise in temperature = 50°C. For each 10°C, K is more or less doubled. Hence value of K will increase 5 times i.e.

$$K = (3 \times 10^{-12}\ .s^{-1}) x 5$$

$$K = 15 \times 10^{-12}\ .s^{-1}$$

PROGRESS TEST 8

1. Only some collisions between molecules are effective in producing chemical reaction. Explain why?
2. Explain the concept of activation energy and the variation of reaction rate with temperature.
3. Distinguish between:
   (a) Rate and velocity of a reaction (b) Rate and rate constant (c) Positive catalyst and Inhibitor.
4. Give one example each for the following:
   (a) Rate of reaction (b) Velocity of reaction (c) Rate equation (d) Specific rate constant.
5. For the reaction $2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$, the rate equation is $\frac{dx}{dt} = K[NO]^2[O_2]$. What is the effect on the rate of the reaction when (a) the concentration of NO is redaced by one half (b) the concentraation of O_2 Is doubled (c) a catalyst is added to the reaction mixture.
6. The decomposition of formic acid is catalyzed by strong acids.

$$HCOOH_{(l)} \xrightarrow{H^+} CO_{(g)} + H_2O_{(l)}$$

(a) Write its rate expression (b) What is the effect on its rate if the acid concentration is doubled.

7. Write note on: Slow and fast reactions.

8. Among the factors that influence reaction rates, which are involved in each of the following:

   (i) Milk sours more rapidly in summar than in winter.

   (ii) Powdered zinc reacts more rapidly with water than the chunks of metallic zinc.

   (iii) Combustion of gasoline occurs more rapidly in an internal combustion engine than in an open container.

   (iv) Unless ignited, hydrogen does not react with oxygen of the air but a stream of hydrogen passed over platinum gauze bursts into flame.

9. Make a list of factors which affect the rates of chemical reactions. Describe the way in which each factor affects the rate of reaction. For each factor, mention whether it is specific to a certain type of reaction, or whether it is general.

10. Describe the rate of a chemical reaction as a change of concentration with time.

11. The reaction rate, R, for reaction $2A + B \longrightarrow A_2B$ was found experimentally to be given by the expression.

$$R = K[A]^2[B]$$

   (a) Will K increase, decrease or remain unchanged if the concentration of A is doubled? If the concentration of B is doubled?

   (b) Will R increase, decrease or remain unchanged, if the concentration of A is doubled? If the concentration of B is doubled?

12. For the decomposition of ethyl chlorocarbonate $(ClCO_2C_2H_5)$

$$ClCOOCH_2CH_3 \longrightarrow CO_2 + ClCH_2CH_3$$

$K = 1.3 \times 10^{-3} s^1$ at 200°C. What is the initial rate when the initial concentration of $ClCOOCH_2CH_3$ is 0.25 M?

Ans:– $(3.25 \times 10^4 Ms^1)$

Hint: Rate $K[ClCOOCH_2CH_3]$

$$= (1.3 \times 10^{-3} \quad s^1)(0.25M) = 3.25 \times 10^{-4} Ms^1$$

13. The rate constant for decomposition of nitrogen dioxide

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

is $1.8\times10^3\,dm^3mole^{-1}s^{-1}$. What is the initial rate when the initial concentration of NO_2 is 0.50 M?

(Hint: Rate = $K[NO_2]^2$, Ans:– 4.5×10^9 mole dm^{3}s^1)

or $(4.5\times10^9\,Ms^{-1})$

14. Following is given a data for the reaction $A + B \longrightarrow C$. Find order of reaction?

No.	Concentration (mole / dm^3) A	Concentration (mole / dm^3) B	Rate of Reaction
1.	0.1	0.1	8×10^{-4}
2.	0.2	0.1	16×10^{-4}
3.	0.1	0.2	16×10^{-4}

(Ans:– Order of reaction=2)

15. For the reaction $2H_2 + O_2 \xrightarrow{Pt} 2H_2O$.

$$Rate = \frac{dx}{dt} = [H_2]^2[O_2]$$

Fill in the following blanks:

No.	Conc. of $[H_2]$	Conc. of $[O_2]$	Rate at 25°
1.	1 mole / dm^3	1 mole / dm^3	5×10^6 mole / dm^3.s
2.	2 mole / dm^3	1 mole / dm^3	________
3.	1 mole / dm^3	3 mole / dm^3	________

Answer: (2) 25×10^{12} mole / dm^3.s

(3) 15×10^6 mole / dm^3.s

16. Write rate expression for the following reactions:

(i) $CH_2 = CH_2 + CH_2 \longrightarrow CH_3 - CH_3$

(ii) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$

(iii) $C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$

17. Draw energy diagrams for:

(a) an endothermic reaction

(b) an exothermic reaction in the presence and absence of a catalyst.

Multiple choice questions

1. Which of the following are best to explain the action of catalyst in speeding up a chemical reaction:

(A) It increases the equilibrium constant for the reaction.

(B) It increases the kinetic energy of reacting molecules.

(C) It prevents reverse reaction from occurring.

(D) It decreases energy of activation for the reaction.

(E) It decreases the enthalpy change for the reaction.

2. Which of the following are best to explain the rapid increase in the rate of a chemical reaction as the temperature rises:

(A) The collisions frequency of molecules increases.

(B) The collisions become more violent.

(C) A considerably higher proportion of molecules has the necessary minimum energy to react.

(D) The bonds in reacting molecules are more easily broken.

3. The energy of activation for the reaction $2H_2O_2 \xrightarrow{P_t} 2H_2O + O_2$ in absence of catalyst is 75 $K.Jmole^{-1}$.

The most likely value for the energy of activation in presence of catalyst is: (A) 53 $K.Jmole^{-1}$ (B) 75 $K.Jmole^{-1}$ (C) 98 $K.Jmole^{-1}$

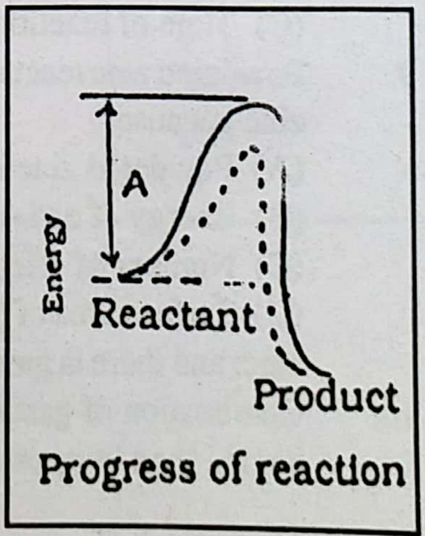
4. The energy profile diagrams for the reaction in presence and absence of a catalyst are shown below. In these profile A represents:

(A) Threshold Energy

(B) Energy of activation in absence of catalyst

(C) Average internal energy of reactants

(D) Energy of activation in presence of catalyst



5. The acid–catalysed reaction of an organic compound propanone (CH_3COCH_3) with iodine may be represented by the equation.

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_2ICOCH_3 + H^+ + I^-$$

other conditions remaining same, what will be the effect on initial rate of reaction if the concentrations of propanone, iodine and acid, all are doubled ?

(A) 2x (B) 4x (C) 6x (D) 8x

6. The decomposition of dinitrogen pentoxide in a suitable solvent may be represented by the equation:

$$2N_2O_5 \longrightarrow 4NO_2 + O_{2(g)}$$

The measurements of which are of the following physical quantities could not be used to determine the rate of this reaction:

(A) Volume of oxygen evolved.
(B) Electrical conductivity of solution.
(C) Absorbance of solution using calorimeter.
(D) Mass of reacting mixture.
(E) Pressure of oxygen evolved.

7. Which of the following statements for the reaction between H_2 and Cl_2 in presence of sunlight is correct ?

(A) Rate = $K[H_2][Cl_2]$
(B) The light lowers the energy of activation .
(C) Rate is independent of concentration of hydrogen and chlorine.

8. Rate constant of a reaction depends upon:

(A) Temperature (B) Initial concentration of reactants
(C) Time of reaction (D) Extent of reaction

9. Powdered zinc reacts more rapidly with water than the chunks of metallic zinc because:

(A) Powdered zinc is more reactive
(B) Energy of activation is lowered.
(C) Number of effective collisions has increased.
(D) Surface area of powdered zinc is much more than that of chunks of zinc: and there is greater contact between individual reacting molecules.

10. Combustion of gasoline occurs more rapidly in an internal combustion engine than in open air because:

(A) Number of molecules per unit volume increases
(B) Number of molecules per unit volume increases hence there is more collisions between the molecules
(C) There are more effective collisions
(D) In internal combustion engine, the temperature is higher than in open air. There is more collision among molecules, moreover the fraction of molecules possessing activation energy, increases.

Key:

1.	D	6.	B
2.	C	7.	C
3.	B	8.	A
4.	B	9.	D
5.	B	10.	D

UNITS OF MEASUREMENT AND SOME IMPORTANT CONSTANTS

Table 1
S.I BASE UNITS.

Physical Quantity	Name of unit	Symbol
Length	metre	m
Mass	kilogram	Kg
Time	second	s
Temperature	kelvin	K
Amount of substance	mole	mol
Electric current	ampere	A

Table 2
DERIVED S.I. UNITS

Physical quantity	S.I. name or special name	S.I symbol
Area	square metre	m^2
Volume	cubic metre, cubic decimetre	$m^3; dm^3$
Density	kilogram per cubic metre	$kg\ m^{-3}$
Velocity	metre per second	$m\,s^{-1}$
Force	newton	$N\ (kg\ m\ s^{-2} = Jm^{-1})$
Pressure	newton per square metre *(Force per unit area)*	$Nm^{-2}\left(kgm^{1}s^{-2} = Pa\right)$
Energy: Work	Joule	$J\left(kg\ m^2s^{-2} = Nm\right)$
Electric charge	Coulomb (C)	C(A.h.)
Quantity of heat	Joule	J
Heat capacity	Joule per Kelvin	$J\ K^{-1}$
Electric potential difference	Volt	$V\left(JA^{-1}s^{-1} = JC^{-1}\right)$
Electromotive force	Volt	V
Frequency	Hertz	Hz

Table 3
NON-S.I.UNITS

Physical quantity	Name and symbol	S.I. equivalent
Length	Angstrom (A°), Inch (In)	10^{-10} m; 10^{-8} cm; 0.0254 m; 2.54 cm.
Volume	Litre (L)	10^{-3} m^3 : 1 dm^3
Mass	Pound (lb)	0.4536 kg
Pressure	Atmosphere (atm), torr (m.m.Hg)	101,325 Nm^{-2}, 133.322 Nm^{-2}
Force	Dyne (dyn)	10^{-5} N
Energy	erg, calorie (cal), electron volt (ev).	10^{-7} J, 4.184 J, 1.6021×10^{-19} J.
Viscosity	Poise	10^{-1} kg $m^{-1}s^{-1}$
Surface Tension	dyne cm^{-1}	10^{-3} Nm^{-1}
Dipole moment	Debye	3.338×10^{-30} mC

Table 4
S.I. PREFIXES

Multiple	Prefix	Symbol
10^{15}	peta	P
10^{12}	tera	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	K
10^{2}	hecto	h
10	deka	da
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f

Table 5
CONVERSION FACTORS

1 a.m.u = 1.6605×10^{-27} kg

1 °A = 10^{-10} m = 10^{-8} cm

1 Litre (L) = 1 dm^3 = 10^{-3} m^3

1 atm = 101 325 Nm^{-2} = 1.01325×10^{5} Pa = 760 torr

1 erg = 10^{-7} J = 1kg.m^2.s^{-2}

1 cal = 4.1840 J

1 e.v = 1.6022×10^{-19} J = 23k cals / mol.

Table 6
PHYSICAL CONSTANTS

Avogadro's number	$N_A = 6.022\times10^{23}$ / mol
Electron rest mass	$m_e = 9.11\times10^{-31}$ kg
Faraday constant	$F = 96485$ C / mol
Molar gas constant	$R = 0.0821$ L(dm^3).atm, mol^{-1}k^{-1} $= 8.3145$ J.mol^{-1}k^{-1} $= 1.9872$ cal.mol^{-1}k^{-1}
Ideal gas molar volume at S.T.P	$= 22.414$ L(dm^3) / mol $V_m = 0.0224$ m^3 / mol
Planck's Constant	$h = 6.6261\times10^{-34}$ Js $= 2.179874\times10^{-18}$ J
Rydberg Constant for H–atom	$R_H = 1.09678\times10^{5}$ cm^{-1}
Absolute Zero	0 K = –273.16°C
Boltzman's Constant	$K = 1.381\times10^{-23}$ Jk^{-1}
Proton rest mass	$m_p = 1.673\times10^{-27}$ kg

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