

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

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.

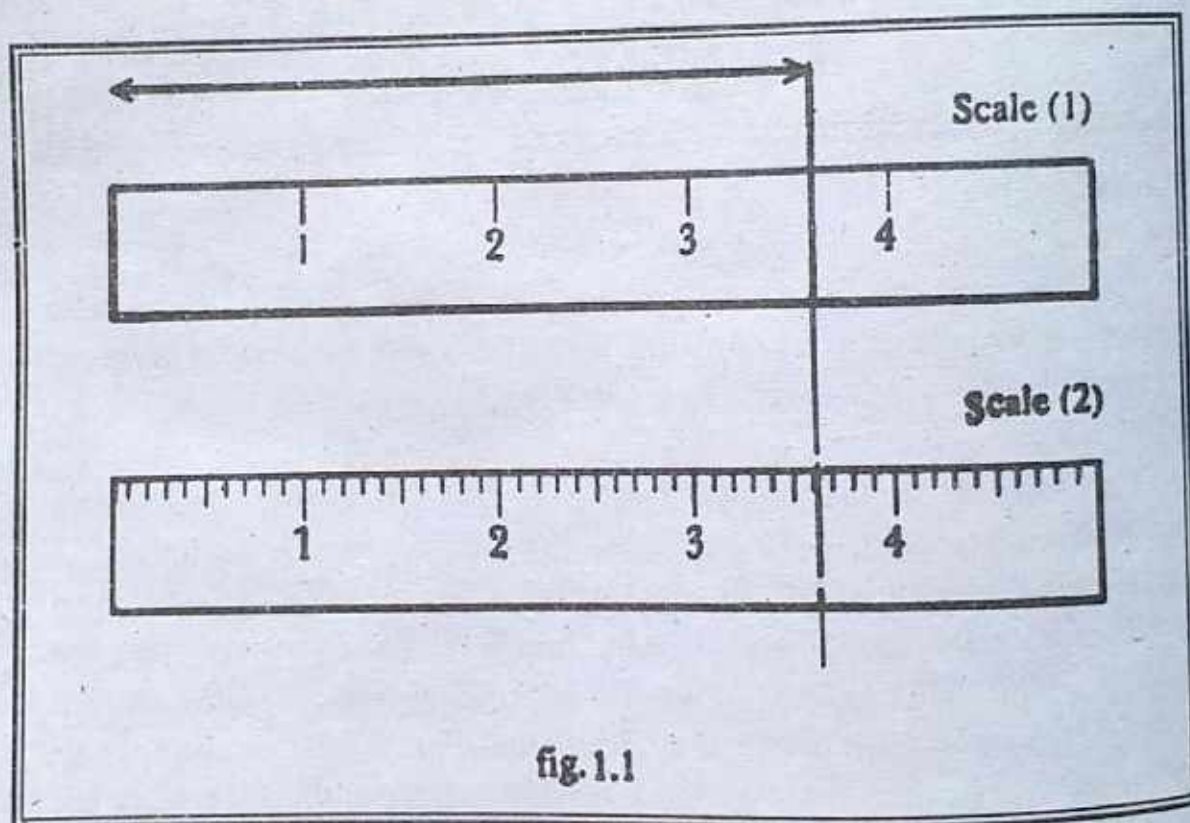


fig. 1.1

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 shows 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 significant 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 significant 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 $0.0112 \pm 0.0001\text{g}$ or as $11.2 \pm 0.1 \text{ mg}$.

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.

$$\begin{array}{rclcl} 1.31 + 2.1 & = & 3.41 & = & 3.4 \\ 8.741 - 5.31 & = & 3.431 & = & 3.43 \end{array}$$

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}

$$\begin{array}{rcl} \text{Solution :} & 5.00 \times 10^{-3} & \\ & 0.775 \times 10^{-3} & \\ & 0.0001 \times 10^{-3} & \\ \text{Total} & 5.7751 \times 10^{-3} & \\ \text{(Round up)} & 6.0 \times 10^{-3} & \end{array}$$

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.

$$\begin{array}{rcl} 15.5 \text{ m} & = & 15.5 \text{ m} \\ 651.8 \text{ cm} & = & 6.518 \text{ m} \\ 4291 \text{ m.m} & = & 4.291 \text{ m} \\ \\ \text{Total} & = & 26.309 \text{ m} \\ \text{(Round up)} & = & 26.3 \text{ m} \end{array}$$

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;

$$\begin{aligned}(1.32) \times (4.421) &= 5.84 \\ 15.88 + 7.95 &= 1.997 = 2.00\end{aligned}$$

$$\begin{array}{r} 31.23 \times 4.5 \\ \hline 9.41395 \end{array} = 15$$

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

Simplify

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

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

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

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 computations and aids in minimization of errors. For example suppose you wish to divide 0.00016 by 80,000. This may be written as :

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

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

$$\frac{(0.00042)(560)}{(84,000)(0.007)} = \frac{(4.2 \times 10^{-4})(5.6 \times 10^2)}{(8.4 \times 10^4)(7 \times 10^{-3})} = \frac{4.2 \times 5.6}{8.4 \times 7} \times \frac{10^{-4} \times 10^2}{10^4 \times 10^{-3}}$$
$$= 0.4 \times \frac{10^{-2}}{10^1} = 0.4 \times 10^{-3} = 4.0 \times 10^{-4}$$

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 positive 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.

$$\begin{aligned}\log ab &= \log a + \log b \\ \log a/b &= \log a - \log b \\ \log (a)^n &= n \log a\end{aligned}$$

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

Examples :

$$\begin{aligned}\text{(i) } \log (450 \times 566) &= \log 450 + \log 566 \\ &= 2.6532 + 2.7528 \\ &= 5.4060\end{aligned}$$

Antilog of 5.4060 = 25470

since the characteristics is 5

Antilog 0.4060 = 254200

$$\begin{aligned}
 \text{(ii) } \log(878 \div 122) &= \log 878 - \log 122 \\
 &= 2.9435 - 2.0864 \\
 &= 0.8571
 \end{aligned}$$

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

$$\begin{aligned}
 \text{(iii) } \log(68)^{1/8} &= \frac{1}{8} \log 68 = \frac{1}{8} (1.8325) \\
 &= 0.2290
 \end{aligned}$$

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

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 50cm³ 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 (Na^+) and chloride ions (Cl^-) 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 atoms (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:

$$\text{Mass of the sample of magnesium oxide} = 2.4 \text{ g Mg} + 1.6 \text{ g O} = 4.0 \text{ g}$$

Now, 4.0 g of the compound contain 2.4 g Mg

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

$$\therefore \text{Mg} = 60.0\%$$

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

$$\text{O} = 40.0\%$$

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.

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

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

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

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 CO₂ and 1.640 g H₂O. What is its empirical formula?

Solution : The masses of CO₂ and H₂O are used to find out the masses of carbon and hydrogen:

$$\begin{aligned}\text{Mass of C} &= \frac{1 \text{ mole C}}{1 \text{ mole CO}_2} \times 3.002 \text{ g CO}_2 = \frac{12 \text{ g C}}{44 \text{ g CO}_2} \times 3.002 \text{ g CO}_2 \\ &= 0.819 \text{ g C} \\ \text{Mass of H} &= \frac{2 \text{ moles H atoms}}{1 \text{ mole H}_2\text{O}} \times 1.640 \text{ g H}_2\text{O} = \frac{2 \text{ g H}}{18 \text{ g H}_2\text{O}} \times 1.640 \\ &= 0.18 \text{ g H}\end{aligned}$$

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

$$\begin{aligned}1.367 \text{ g compound contain} & \quad 0.819 \text{ g C} \\ 100 \text{ g compound contain} & \quad \frac{0.819 \text{ g} \times 100 \text{ g}}{1.367 \text{ g}} = 59.9 \text{ g} \\ & \quad \text{C} = 59.9\%\end{aligned}$$

$$\begin{aligned}1.367 \text{ g compound contain} & \quad 0.18 \text{ g H} \\ \therefore 100 \text{ g compound contain} & \quad \frac{0.18 \text{ g} \times 100 \text{ g}}{1.367 \text{ g}} = 13.16 \text{ g H} \\ & \quad \therefore \text{H} = 13.16\%\end{aligned}$$

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

$$\begin{aligned}\% \text{ O} &= 100 - 59.9 - 13.16 = 26.94 \% \\ & \quad \text{O} = 26.94\%\end{aligned}$$

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

$$\begin{aligned}\text{C} &= \frac{59.9}{12} = 5 \\ \text{H} &= \frac{13.16}{1} = 13.6\end{aligned}$$

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

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

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

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

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

Thus the empirical formula of the compound = $\text{C}_3 \text{H}_8 \text{O}$

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 $\text{C}_6 \text{H}_6$. 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 $(\text{CH}_2\text{O})_n$. Thus molecular formula of Glucose = $(\text{CH}_2\text{O})_6 = \text{C}_6\text{H}_{12}\text{O}_6$. 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. $\text{Na}_2 \text{S}_4\text{O}_6$ is not represented as $\text{Na S}_2\text{O}_3$ 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 $\text{S}_4\text{O}_6^{2-}$. 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,

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

Now the molecular formula of glucose is $(\text{CH}_2\text{O})_6$ or $\text{C}_6\text{H}_{12}\text{O}_6$.

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 :

$$\text{Mass of carbon} = \frac{1 \text{ mole C}}{1 \text{ mole CO}_2} \times 3.03 \text{ g CO}_2 = \frac{12 \text{ g}}{44 \text{ g}} \times 3.03 = 0.83 \text{ g C}$$

$$\text{Mass of Hydrogen} = \frac{2 \text{ mole H}}{1 \text{ mole H}_2\text{O}} \times 1.55 \text{ g H}_2\text{O} = \frac{2 \text{ g}}{18 \text{ g}} \times 1.55 \text{ g} = 0.17 \text{ g H}$$

(ii) To calculate percentage of carbon and hydrogen:

$$\begin{aligned} & 1.0 \text{ g of the compound contain } 0.83 \text{ g C} \\ \therefore & 100 \text{ g of the compound contain } 0.83 \text{ g} \times \frac{100 \text{ g}}{1.0 \text{ g}} = 83 \% \text{ C} \end{aligned}$$

Since butane contains only carbon and hydrogen, hence :

$$\text{Percentage of Hydrogen} = 100 - 83 = 17\% \text{ H}$$

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

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

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

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

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

$$\text{C} = 1 \times 2 = 2 ; \text{H} = 2.5 \times 2 = 5$$

Thus the empirical formula of the compound = C_2H_5 .

$$\begin{aligned} \text{The empirical formula mass of } \text{C}_2\text{H}_5 &= (12)2 + (1)5 \\ &= 24 + 5 = 29 \end{aligned}$$

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

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

$$\begin{aligned} \text{Molecular formula} &= (\text{Empirical formula})_n \\ &= (\text{C}_2\text{H}_5)_2 \\ &= \text{C}_4\text{H}_{10} \end{aligned}$$

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

$$= 1 \text{ g} = 6.02 \times 10^{23} \text{ atoms}$$

A mole of hydrogen molecule

$$= 2 \text{ g} = 6.02 \times 10^{23} \text{ molecules}$$

A mole of NaCl

$$= 58.5 \text{ g} = 1 \text{ mole } Na^+ + 1 \text{ mole } Cl^- \\ = 6.02 \times 10^{23} Na^+ + 6.02 \times 10^{23} Cl^-$$

$$\text{A mole of } H_2O = 18 \text{ g} = 6.02 \times 10^{23} \text{ molecules}$$

$$2 \text{ moles of } H_2O = 36 \text{ g} = 2 \times 6.02 \times 10^{23} = 1.204 \times 10^{24} \text{ molecules}$$

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,



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.

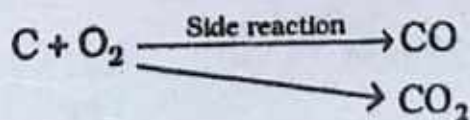
Suppose we want to calculate the mass of carbon dioxide formed when a given mass of carbon burns in air, we know the equation for the reaction i.e.



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.



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 :

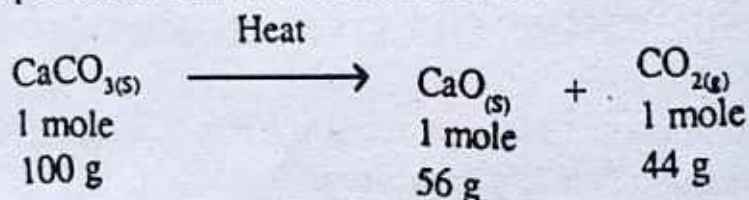
In such relationships, we can determine the unknown mass of a reactant or product from a given mass of the substance in a chemical reaction with the help of balanced chemical equation. Actually from a balanced chemical equation we get the exact relationships between the masses of the reactants and products.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

**Method - I**

$$\text{No. of moles in 25 g of CaCO}_3 = \frac{25}{100} = 0.25 \text{ mole}$$

$$\begin{array}{lcl} 1 \text{ mole of CaCO}_3 \text{ yields} & & 1 \text{ mole of CO}_2 \\ \therefore 0.25 \text{ mole of CaCO}_3 \text{ yields} & & 0.25 \text{ mole of CO}_2 \\ & = & 0.25 \text{ mole of CO}_2 \\ \therefore \text{Mass of CO}_2 \text{ in 0.25 mole} & = & 0.25 \times 44 \\ & = & 11 \text{ g} \end{array}$$

$$\begin{array}{lcl} 1 \text{ mole of CaCO}_3 \text{ yields} & & 1 \text{ mole of CaO} \\ \therefore 0.25 \text{ mole of CaCO}_3 \text{ yields} & & 0.25 \text{ mole of CaO} \\ & = & 0.25 \text{ mole of CaO} \end{array}$$

$$\begin{array}{lcl} \therefore \text{mass of CaO in 0.25 mole} & = & 0.25 \times 56 \\ & = & 14 \text{ g.} \end{array}$$

Method - II

$$\begin{array}{ll} 100 \text{ g of CaCO}_3 \text{ yield} & 44 \text{ g of CO}_2 \\ 1 \text{ g of CaCO}_3 \text{ yields} & \frac{44 \text{ g of CO}_2}{100} \end{array}$$

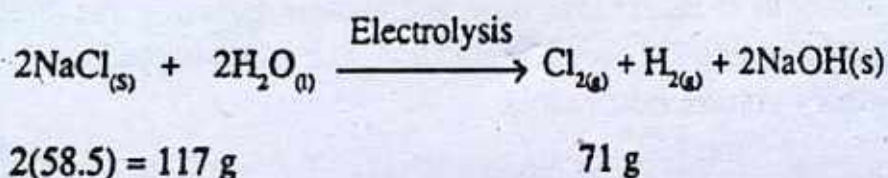
$$\begin{aligned}
 \therefore 25 \text{ g of CaCO}_3 \text{ yield } & \frac{44 \text{ g} \times 25 \text{ g}}{100 \text{ g}} = 11 \text{ g of CO}_2 \\
 100 \text{ g of CaCO}_3 \text{ yield } & 56 \text{ g of CaO} \\
 1 \text{ g of CaCO}_3 \text{ yields } & \frac{56 \text{ g}}{100} \text{ of CaO} \\
 \therefore 25 \text{ g of CaCO}_3 \text{ yield } & \frac{56 \text{ g} \times 25 \text{ g}}{100 \text{ g}} = 14 \text{ g of CaO}
 \end{aligned}$$

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:

**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

$$\begin{aligned}
 \therefore 142 \text{ g of Cl}_2 \text{ are produced by } & \frac{117 \text{ g}}{71 \text{ g}} \times 142 \text{ g} \\
 & = 234 \text{ g of NaCl.}
 \end{aligned}$$

Method - II

$$\begin{aligned}
 \text{No. of g moles of Cl}_2 \text{ in } 142 \text{ g} &= \frac{142 \text{ g of Cl}_2}{71 \text{ g Cl}_2} \\
 &= 2 \text{ g moles of Cl}_2
 \end{aligned}$$

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 $= 4 \times 58.5$
 $= 234 \text{ g of NaCl.}$

(b) Mass - Volume Relationships

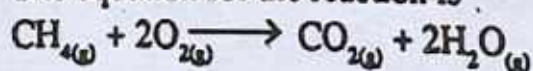
The molar quantities of gases can be expressed in terms of volumes as well as weights (Mass). According to Avogadro, one gram mole of any gas at standard temperature (0°C) and standard pressure (1 Atm. or 760 mm Hg) occupies a volume 22.4dm^3 . It is a mathematical coincidence that one ounce mole of 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



Method - 1

$$\text{No. of moles of CH}_4 \text{ in 20grams} = \frac{\text{Given mass of CH}_4}{\text{Molar mass of CH}_4}$$

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

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 $22.4 \times 1.25 = 28 \text{ dm}^3$

Method-II

Molecular weight (mass) of $\text{CH}_4 = 16$

Molecular weight (mass) of $\text{CO}_2 = 44$

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 $\frac{44 \text{ g}}{16 \text{ g}} \times 20 \text{ g} = 55 \text{ grams of } \text{CO}_2$

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

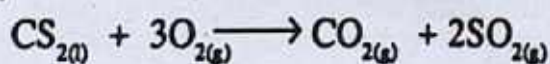
1 gram of CO_2 at S.T.P. occupies a volume $\frac{22.4}{44} \text{ dm}^3$

55 grams of CO_2 at S.T.P. occupy a volume $\frac{22.4 \text{ dm}^3}{44 \text{ g}} \times 55 \text{ g}$
 $= 28 \text{ dm}^3$

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:



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
 $\therefore$ 2 moles of CS_2 react with $3 \times 2 = 6$ moles of O_2
 $\therefore$ Volume of 6 moles of O_2 at S.T.P. = 6×22.4
 $= 134.4 \text{ dm}^3$

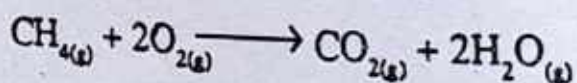
1 mole of CS_2 gives 1 mole of CO_2
 $\therefore$ 2 moles of CS_2 give 2 mole of CO_2

$$\therefore \text{Volume of 2 moles of } \text{CO}_2 = 2 \times 22.4 \text{ dm}^3 \\ = 44.8 \text{ dm}^3$$

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 $\text{SO}_2 = 4 \times 22.4 \text{ dm}^3 \\ = 89.6 \text{ dm}^3$

(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:



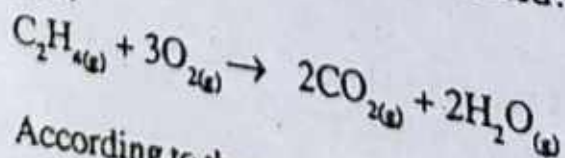
One volume of CH_4 gas reacts with two volumes of O_2 gas to give one volume of CO_2 gas and two volumes of water vapours. The co-efficients of the formulae give the volume relationships. We already know that one mole of any gas at S.T.P. occupies a volume of 22.4 dm^3 . Thus in the above equation we 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:



According to the equation one dm^3 of C_2H_4 will require three dm^3 of oxygen gas. So,

1 dm³ of Ethene (C₂H₄) requires 3 dm³ of O₂

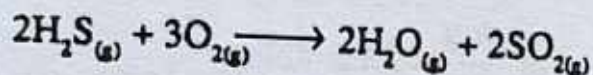
∴ 500 dm³ of Ethene require 3 x 500
= 1500 dm³ of O₂

1 dm³ of Ethene (C₂H₄) produces 2 dm³ of CO₂

∴ 500 dm³ of Ethene produce 2 x 500 = 1000 dm³ of CO₂

Example -2

Hydrogen sulphide burns in oxygen according to the equation.



Calculate the volume of O₂ at S.T.P. required to burn 900 dm³ of H₂S and also find the volume of SO₂ gas produced.

According to equation:

Solution:

2 dm³ of H₂S gas require 3 dm³ of O₂ for combustion

1 dm³ of H₂S gas requires $\frac{3}{2}$ dm³ of O₂ for combustion

∴ 900 dm³ of H₂S gas require $\frac{3}{2} \times 900 = 1350$ dm³ of O₂

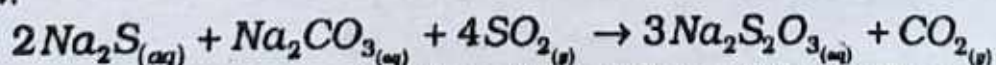
2 dm³ of H₂S gas give 2 dm³ of SO₂

∴ 900 dm³ of H₂S gas give 900 dm³ of SO₂ = 900 dm³ of SO₂

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, until 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 (Na₂S₂O₃) can be prepared by the reaction given below:



How many grams of sodium thiosulphate will be produced when 200g each of the three reagents Na₂S, Na₂CO₃ and SO₂ 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 $\text{Na}_2\text{S}_2\text{O}_3$.

According to balanced chemical equation:

4 moles of SO_2 produce 3 moles of $\text{Na}_2\text{S}_2\text{O}_3$

1 mole of SO_2 produces $\frac{3}{4}$ moles of $\text{Na}_2\text{S}_2\text{O}_3$

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

Amount in grams = $2.34 \times 158 = 369.72 \text{ g}$

(Molecular mass of $\text{Na}_2\text{S}_2\text{O}_3 = 158 \text{ g}$)

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 ($\text{C}_6\text{H}_{12}\text{O}_6$).

[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: $\text{C}_3\text{H}_4\text{N}$]

(ii) Find the Molecular formula of the compound. [Ans: $\text{C}_6\text{H}_8\text{N}_2$]

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) $\frac{31.23 \times 4.56}{9.41395}$ [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 (e) 0.00000067

[Ans: (a) 6.782×10^3 (b) 5.652×10^2 (c) 1.9×10^{-4} (d) 7×10^4 (e) 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) $\frac{57 \times 365 \times (566)^{1/2}}{78 \times 221 \times (356)^{2/3}}$

[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

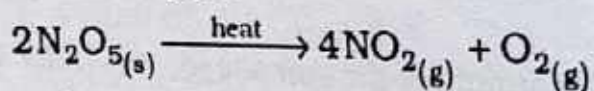
8. Acetic acid contains carbon, hydrogen and oxygen. 4.24g of sample of acetic acid on complete combustion gave 6.21g of CO_2 and 2.54 of H_2O . The molecular mass of acetic acid is 60. Find (i) Empirical formula of acetic acid and (ii) Molecular formula of acetic acid.

[Ans: (i) CH_2O (ii) $\text{C}_2\text{H}_4\text{O}_2$]

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) $\text{C}_2\text{H}_6\text{O}_2$]

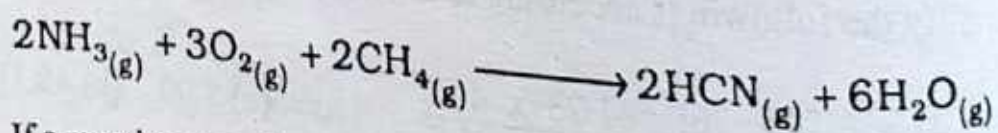
10. When dinitrogen pentoxide (N_2O_5), a white solid is heated, it decomposes to nitrogen dioxide and oxygen.



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 $\text{NO}_2 = 22.4\text{dm}^3$ (ii) Volume of $\text{O}_2 = 5.6\text{dm}^3$]

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



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 $\text{O}_2 = 100.8\text{dm}^3$ (iii) Volume of $\text{CH}_4 = 67.8\text{dm}^3$]

12. Ammonia gas can be produced by heating together the solid NH_4Cl and $\text{Ca}(\text{OH})_2$. 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.

