

## 2. Introduction to analytical chemistry

**2.1 Intrduction :** Analytical chemistry facilitates investigation chemical composition of substances. It uses the instruments and methods to separate, identify and quantify the matter under study. The analysis thus provides chemical or physical information about a sample. Analysis may be qualitative or quantitative. Qualitative analysis is concerned with the detection of the presence or absence of elements in compounds and of chemical compounds in mixtures. Quantitative analysis deals with the determination of the relative proportions of elements in compounds and of chemical compounds in mixtures.



### Remember

The branch of chemistry which deals with the study of separation, identification, qualitative and quantitative determination of the compositions of different substances, is called analytical chemistry.

### Importance of analytical chemistry :

The course of analytical chemistry extends the knowledge acquired by the students in studying general, inorganic and organic chemistry. Chemical analysis is one of the most important methods of monitoring the composition of raw materials, intermediates and finished products, and also the composition of air in streets and premises of industrial plants. In agriculture, chemical analysis is used to determine the composition of soils and fertilizers; in medicine, to determine the composition of medicinal preparations. Analytical chemistry has applications in forensic science, engineering and industry. Industrial process as a whole and the production of new kinds of materials are closely associated with analytical chemistry. Analytical chemistry consists of classical, wet chemical methods and modern instrumental methods.

**2.2 Analysis :** Analysis is carried out on a small sample of the material to be tested, and not on the entire bulk. When the amount of a solid or liquid sample is a few grams, the analysis is called semi-microanalysis. It is of two types : **qualitative and quantitative**. Classical qualitative analysis methods include separations such as precipitation, extraction and distillation. Identification may be based on differences in colour, odour, melting point, boiling point, and reactivity. Classical quantitative methods consist of volumetric analysis, gravimetric analysis, etc.

**2.2.1 Chemical methods of qualitative analysis :** Chemical analysis of a sample is carried out mainly in two stages : by the dry method in which the sample under test is not dissolved and by the wet method in which the sample under test is first dissolved and then analyzed to determine its composition. The dry method is usually used as preliminary tests in the qualitative analysis.

The semi-micro qualitative analysis is carried out using apparatus such as : test tubes, beakers, evaporating dish, crucible, spot plate, watch glass, wire gauze, water bath, burner, blow pipe, pair of tongs, centrifuge, etc.

The qualitative analysis of **organic** and **inorganic** compounds involves **different** types of **tests**. The majority of organic compounds are composed of a relatively small number of elements. The most important ones are : carbon, hydrogen, oxygen, nitrogen, sulphur, halogen, phosphorus. Elementary qualitative analysis is concerned with the detection of the presence of these elements. The identification of an organic compound involves tests such as detection of functional group, determination of melting/ boiling point, etc. The qualitative analysis of simple inorganic compounds involves detection and confirmation of cationic

and anionic species (basic and acidic radical) in them.

**2.2.2 Chemical methods of quantitative analysis :** Quantitative analysis of organic compounds involves methods such as (i) determination of percentage constituent element, (ii) concentrations of a known compound in the given sample, etc. Quantitative analysis of simple inorganic compounds involves methods based on (i) decomposition reaction (gravimetric analysis), and (ii) the progress of reaction between two solutions till its completion (titrametric or volumetric analysis), etc. The quantitative analytical methods involve measurement of quantities such as mass and volume, by mean of some equipment/ apparatus such as weighing machine, burette.

### 2.3 Mathematical operation and error analysis :

The accuracy of measurement is of a great concern in analytical chemistry. Also there can be intrinsic errors in the analytical measurement. The numerical data, obtained experimentally, are treated mathematically to reach some quantitative conclusion. Therefore, an analytical chemist has to know how to report the quantitative analytical data, indicating the extent of the accuracy of measurement, perform the mathematical operation and properly express the quantitative error in the result. In the following subsection we will consider these aspects related to measurements and calculation.

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above values as  $6.022 \times 10^{23}$  and  $1.66 \times 10^{-24}$  g. The number 123.546 becomes  $1.23546 \times 10^2$ , in scientific notation. Note that while writing it, we have moved the decimal to the left by two places and same is the exponent (2) of 10 in the scientific notation. Similarly, 0.00015 can be written as  $1.5 \times 10^{-4}$ .

**Problem 2.1 :** For adding  $5.55 \times 10^4$  and  $6.95 \times 10^3$ , first the exponent is made equal. Thus  $5.55 \times 10^4 + 0.695 \times 10^4$ . Then these numbers can be added as follows :  $(5.55 + 0.695) \times 10^4 = 6.245 \times 10^4$

**Problem 2.2 :** The subtraction of two numbers can be done as shown below:

$$\begin{aligned} & 3.5 \times 10^{-2} - 5.8 \times 10^{-3} \\ &= (3.5 \times 10^{-2}) - (0.58 \times 10^{-2}) \\ &= (3.5 - 0.58) \times 10^{-2} \\ &= 2.92 \times 10^{-2} \end{aligned}$$

Here the decimal has to be moved four places to the right and (-4) is the exponent in the scientific notation. Now let us perform mathematical operations on numbers expressed in scientific notation.

**Problem 2.3 :**  $(5.6 \times 10^5) \times (6.9 \times 10^8)$   
 $= (5.6 \times 6.9) (10^{5+8})$   
 $= (5.6 \times 6.9) \times 10^{13}$   
 $= 38.64 \times 10^{13}$   
 $= 3.864 \times 10^{14}$

**Problem 2.4 :**  $(9.8 \times 10^{-2}) \times (2.5 \times 10^{-6})$   
 $= (9.8 \times 2.5) (10^{-2 + (-6)})$   
 $= (9.8 \times 2.5) \times (10^{-2-6})$   
 $= 24.50 \times 10^{-8}$   
 $= 2.45 \times 10^{-7}$

**Addition and subtraction :** To perform addition operation, first the numbers are written in such a way that they have the same exponent. The coefficients are then added. (Problems 2.1 and 2.2)

**Multiplication :** The rule for the multiplication of exponential numbers can be well explained from the solved problems 2.3 and 2.4.

### 2.3.2 Precision and accuracy of measurement

Aim of any measurement is to get the actual value called true value or accepted value of a quantity. Nearness of the measured value to the true value is called the accuracy of measurement. Larger the accuracy smaller the error. Accuracy depends upon the sensitivity or least count (the smallest quantity that can be measured) of the measuring equipment. consider, for example, a burette reading of 10.2 mL. For all the three situations in the Fig. 2.1 the reading would be noted is 10.2 mL. It means that there is an uncertainty about the digit appearing after the decimal point in the reading 10.2 mL. This is because the least count of the burette is 0.1 mL. The meaning of the reading 10.2 mL is that the true value of the reading lies between 10.1 mL and 10.3 mL. This is indicated by writing  $10.2 \pm 0.1$  mL. Here, the burette reading has an error of  $\pm 0.1$  mL (Fig. 2.1).

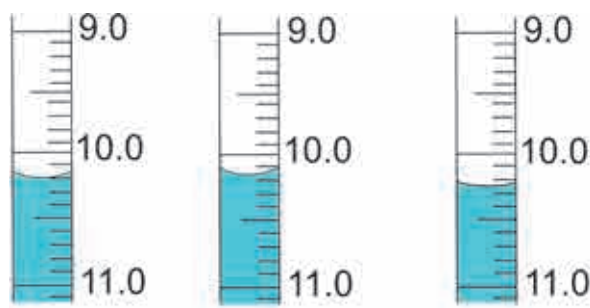
Errors may be expressed as **absolute** or **relative error**.

Absolute error = Observed value - True value

Relative error is generally a more useful quantity than absolute error. Relative error is the ratio of an absolute error to the true value. It is expressed as a percentage.

$$\text{Relative error} = \frac{\text{Absolute error}}{\text{True value}} \times 100 \%$$

There can be error in a measurement due to a number of reasons including inefficiency of the person doing measurement.



**Fig. 2.1 : Three possibilities of a burette reading 10.2 mL**

Multiple readings of the same quantity are noted to minimize the error. If the readings match closely, they are said to have high precision. High precision implies reproducibility of the readings. **High precision is a prerequisite for high accuracy.** Precision is expressed in terms of deviation. An absolute deviation is the modulus of the difference between an observed value and the arithmetic mean for the set of several measurements made in the same way. It is a measure of absolute error in the repeated observation.

$$\text{Absolute deviation} = |\text{Observed value} - \text{Mean}|$$

Arithmetic mean of all the absolute deviations is called the mean absolute deviation in the measurements. The ratio of mean absolute deviation to its arithmetic means is called relative deviation.

Relative deviation

$$= \frac{\text{Mean absolute deviation}}{\text{Mean}} \times 100 \%$$

**Problem 2.5 :** In laboratory experiment, 10 g potassium chlorate sample on decomposition gives following data ; The sample contains 3.8 g of oxygen and the actual mass of oxygen in the quantity of potassium chlorate is 3.92 g. Calculate absolute error and relative error.

**Solution :** The observed is 3.8 g and accepted value is 3.92 g

$$\begin{aligned} \text{Absolute error} &= \text{Observed value} \\ &\quad - \text{True value} \\ &= 3.8 - 3.92 = -0.12 \text{ g} \end{aligned}$$

The negative sign indicates that your experimental result is lower than the true value.

$$\begin{aligned} \text{The relative error} &= \frac{\text{Absolute error}}{\text{True value}} \times 100\% \\ &= \frac{-0.12}{3.92} \times 100\% \\ &= -3.06 \% \end{aligned}$$

**Problem 2.6 :** The three identical samples of potassium chlorate are decomposed. The mass of oxygen is determined to be 3.87 g, 3.95 g and 3.89 g for the set. Calculate absolute deviation and relative deviation.

**Solution :**

$$\text{mean} = \frac{3.87 + 3.95 + 3.89}{3} = 3.90$$

| Average deviation of a set of measurements |                |           |
|--------------------------------------------|----------------|-----------|
| Sample                                     | Mass of oxygen | Deviation |
| 1                                          | 3.87g          | 0.03g     |
| 2                                          | 3.95g          | 0.05g     |
| 3                                          | 3.89g          | 0.01g     |
| Mean absolute deviation                    |                | 0.03      |

Absolute deviation

$$= |\text{Observed value} - \text{Mean}|$$

∴ Mean absolute deviation =  $\pm 0.03$  g.

The relative deviation,

$$= \frac{\text{Mean absolute deviation}}{\text{Mean}} \times 100\%$$

$$= \frac{0.03}{3.9} \times 100\% = 0.8\%$$

**2.3.3 Significant Figures :** Uncertainty in measured value leads to uncertainty in calculated result. Uncertainty in a value is indicated by mentioning the number of significant figures in that value. Consider, the column reading  $10.2 \pm 0.1$  mL recorded on a burette having the least count of 0.1 mL. Here it is said that the last digit '2' in the reading is uncertain, its uncertainty is  $\pm 0.1$  mL. On the other hand, the figure '10' is certain. The significant figures in a measurement or result are the number of digits known with certainty plus one uncertain digit. In a scientific experiment a result is obtained by doing calculation in which values of a number of quantities measured with equipment of different least counts are used.

Following rules are to be followed during such calculation.

### 2.3.4 Rules for deciding significant figures :

1. All non zero digits are significant; e. g. 127.34 g contains five significant figures which are 1, 2, 7, 3 and 4.
2. All zeros between two non zero digits are significant e. g. 120.007 m contains six significant figures.
3. Zeroes on the left of the first non zero digit are not significant. Such a zero indicates the position of the decimal point. For example, 0.025 has two significant figures, 0.005 has one significant figure.
4. Zeroes at the end of a number are significant if they are on the right side of the decimal point. Terminal zeros are not significant if there is no decimal point. (This is because the least count of an instrument contains decimal point) For example 0.400 g has three significant figures. The measurements here indicates that it is made on a weighing machine having least count of 0.001 g. Significant figures are also indicated in scientific notation by means of decimal point. For example, the measurement 400 g has one significant figure. The measurement  $4.0 \times 10^2$  g has two significant figures, whereas the measurement  $4.00 \times 10^2$  g has three significant figures. The zeros after the decimal points in these cases indicates that the least counts of the weighing machines are 1 g, 0.1 g and 0.01 g, respectively.
5. In numbers written in scientific notation, all digits are significant. For example,  $2.035 \times 10^2$  has four significant figures, and  $3.25 \times 10^{-5}$  has three significant figures.

**Problem 2.7 :** How many significant figures are present in the following measurements ?

- a. 4.065 m      b. 0.32 g      c. 57.98 cm<sup>3</sup>  
 d. 0.02 s      e.  $4.0 \times 10^{-4}$  km  
 f. 604.0820 kg      g.  $307.100 \times 10^{-5}$  cm

**Ans. :** a. 4      b. 2      c. 4      d. 1  
             e. 2      f. 7      g. 6

In general, a quantity measured with an instrument of smaller least count will have more significant figures and will be more accurate than when measured with an instrument of larger least count.

### 2.3.5 Calculations with significant figures :

When performing calculations with measured quantities the rule is that the accuracy of the final result is limited to the accuracy of the least accurate measurement. In other words, the final result can not be more accurate than the least accurate number involved in the calculation.

**Rounding off :** The final result of a calculation often contains figures that are not significant. When this occurs the final result is rounded off. The following rules are used to round off a number to the required number of significant figures :

If the digit following the last digit to be kept is less than five, the last digit is left unchanged.

e.g. 46.32 rounded off to two significant figures is 46.

If the digit following the last digit to be kept is five or more, the last digit to be kept is increased by one. e.g. 52.87 rounded to three significant figures is 52.9.

**Problem 2.8 :** Round off each of the following to the number of significant digits indicated :

a. 1.223 to two digits   b. 12.56 to three digits   c. 122.17 to four digits   d. 231.5 to three digits.

**Ans. :** i. 1.2; the third digit is less than 5, so we drop it all the others to its right.

ii. 12.6; the fourth digit is greater than 5, so we drop it and add 1 to the third digit.

iii. 122.2; the fifth digit is greater than 5, so we do it and add 1 to the fourth digit.

iv. 232; the fourth digit is 5, so we drop it and add 1 to the third digit.

## 2.4 Determination of molecular formula :

Molecular formula of a compound is the formula which indicates the actual number of atoms of the constituent elements in a molecule. It can be obtained from the experimentally determined values of percent elemental composition and molar mass of that compound.

### 2.4.1 Percent composition and empirical formula :

Compounds are formed by chemical combination of different elements. Quantitative determination of the constituent element by suitable methods provides the percent elemental composition of a compound. If the percent total is not 100, the difference is considered as percent oxygen. From the percent composition, the ratio of the atoms of the constituent elements in the molecule is calculated. **The simplest ratio of atoms of the constituent elements in a molecule is called the empirical formula of that compound.** Molecular formula can be obtained from the empirical formula if the molar mass is known. The molar mass of the substance under examination is determined by some convenient method. The following example illustrates this sequence.

**Problem 2.9 :** A compound contains 4.07 % hydrogen, 24.27% carbon and 71.65 % chlorine by mass. Its molar mass is 98.96 g. What is its empirical formula ? Atomic masses of hydrogen, carbon and chlorine are 1.008, 12.000 and 35.453 u, respectively

#### **Solution :**

**Step I :** Check whether the sum of all the percentages is 100.

$$4.07 + 24.27 + 71.65 = 99.99 \approx 100$$

Therefore no need to consider presence of oxygen atom in the molecule.

**Step II :** Conversion of mass percent to grams. Since we are having mass percent, it is convenient to use 100 g of the compound as the starting material. Thus in the 100 g sample of the above compound, 4.07 g hydrogen 24.27 g carbon and 71.65 g chlorine is present..... Contd on next page

**Step III :** Convert into number/of moles of each element. Divide the masses obtained above by respective atomic masses of various elements.

$$\text{Moles of hydrogen} = \frac{4.07 \text{ g}}{1.008 \text{ g}} = 4.04$$

$$\text{Moles of carbons} = \frac{24.27 \text{ g}}{12.01 \text{ g}} = 2.0225$$

$$\text{Moles of chlorine} = \frac{71.65 \text{ g}}{35.453 \text{ g}} = 2.021$$

**Steps IV :** Divide the mole values obtained above by the smallest value among them.

Since 2.021 is smallest value, division by it gives a ratio of 2:1:1 for H:C:Cl.

In case the ratio are not whole numbers, then they may be converted into whole number by multiplying by the suitable coefficient.

**Step V :** Write empirical formula by mentioning the numbers after writing the symbols of respective elements.  $\text{CH}_2\text{Cl}$  is thus, the empirical formula of the above compound.

**Step VI :** Writing molecular formula

**a. Determine empirical formula mass :** Add the atomic masses of various atoms present in the empirical formula.

For  $\text{CH}_2\text{Cl}$ , empirical formula mass is  
 $12.01 + 2 \times 1.008 + 35.453$

$$= 49.48 \text{ g}$$

**b. Divide molar mass by empirical formula mass**

$$\therefore \frac{\text{Molar mass}}{\text{Empirical formula mass}} = \frac{98.96 \text{ g}}{49.48 \text{ g}}$$

$$\therefore r = 2$$

**c. multiply empirical formula by r obtained above to get the molecular formula.**

Molecular formula = r x empirical formula  
 molecular formula is 2 x  $\text{CH}_2\text{Cl}$  i.e.  $\text{C}_2\text{H}_4\text{Cl}_2$ .

**Problem 2.10 :** A compound with molar mass 159 was found to contain 39.62 % copper and 20.13 % sulfur. Suggest molecular formula for the compound (Atomic masses: Cu = 63, S = 32 and O = 16).

**Solution :**

$$\begin{aligned} \% \text{ copper} + \% \text{ sulfur} &= 39.62 + 20.13 \\ &= 59.75 \end{aligned}$$

This is less than 100 % Hence compound contains adequate oxygen so that the total percentage of elements is 100%.

$$\text{Hence \% of oxygen} = 100 - 59.75 = 40.25\%$$

$$\text{Moles of Cu} = \frac{\% \text{ of Cu}}{\text{Atomic mass of Cu}}$$

$$= \frac{39.62}{63} = 0.629$$

$$\text{Moles of S} = \frac{\% \text{ of S}}{\text{Atomic mass of S}}$$

$$= \frac{20.13}{32} = 0.629$$

$$\text{Moles of O} = \frac{\% \text{ of O}}{\text{Atomic mass of O}} = \frac{40.25}{16} = 2.516$$

Hence the ratio of number of moles of Cu:S:O is

$$\frac{0.629}{0.629} = 1 \quad \frac{0.629}{0.629} = 1 \quad \text{and} \quad \frac{2.516}{0.629} = 4$$

Hence empirical formula is  $\text{CuSO}_4$

Empirical formula mass

$$= 63 + 32 + 16 \times 4 = 159$$

Molar mass = Empirical mass (Since Molar mass = Molecular mass)

$$\therefore \text{Molecular formula} = \text{Empirical formula} = \text{CuSO}_4$$

## 2.5 Chemical reactions and stoichiometric calculations

Calculation based on a balanced chemical equations are known as stoichiometric calculations.

Balanced chemical equation is symbolic representation of a chemical reaction. It supplies the following information which is useful in solving problems based on chemical equations

- It indicates the number of moles of the reactants involved in a chemical reaction and the number of moles of the products formed.

- ii. It indicates the relative masses of the reactants and products linked with a chemical change, and
- iii. it indicates the relationship between the volume/s of the gaseous reactants and products, at STP.

### 2.5.1 Stoichiometric problems

Generally problems based on stoichiometry are of the following types :

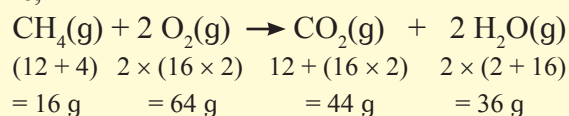
- a. Problems based on mass-mass relationship;
- b. Problems based on mass-volume relationship and
- c. Problems based on volume-volume relationship.

Steps involved in problems based on stoichiometric calculations :

1. Write down the balanced chemical equation representing the chemical reaction.
2. Write the number of moles and the relative masses or volumes of the reactants and products below the respective formulae.
3. Relative masses or volumes should be calculated from the respective formula mass referring to the condition of STP.
4. Apply the unitary method to calculate the unknown factor/s as required by the problem.

**Problem 2.11 :** Calculate the mass of carbon dioxide and water formed on complete combustion of 24 g of methane gas. (Atomic masses, C = 12 u, H = 1 u, O = 16 u)

**Solution :** The balanced chemical equation is,



Hence, 16 g of  $\text{CH}_4$  on complete combustion will produce 44 g of  $\text{CO}_2$

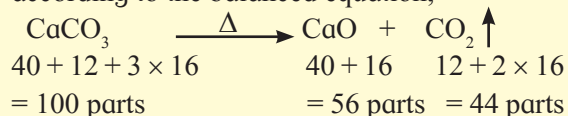
$$\therefore 24 \text{ g of } \text{CH}_4 = \frac{24}{16} \times 44 = 66 \text{ g of } \text{CO}_2$$

Similarly, 16 g of  $\text{CH}_4$  will produce 36 g of water.

$$24 \text{ g of } \text{CH}_4 = \frac{24}{16} \times 36 = 54 \text{ g water.}$$

**Problem 2.12 :** How much CaO will be produced by decomposition of 5g  $\text{CaCO}_3$  ?

**Solution :** Calcium carbonate decomposes according to the balanced equation,



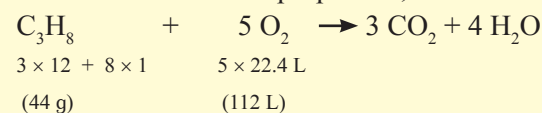
So, 100 g of  $\text{CaCO}_3$  produces 56 g of CaO

$\therefore$  5 g of  $\text{CaCO}_3$  will produce

$$= \frac{56 \text{ g}}{100 \text{ g}} \times 5 \text{ g} = 2.8 \text{ g of } \text{CaCO}_3$$

**Problem 2.13 :** How many litres of oxygen at STP are required to burn completely 2.2 g of propane,  $\text{C}_3\text{H}_8$  ?

**Solution :** The balanced chemical equation for the combustion of propane is,



(Where 1 mol of ideal gas occupies 22.4 L of volume)

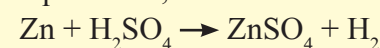
Thus 44 g of propane requires 112 litres of oxygen for complete combustion

$\therefore$  2.2 g of propane will require

$$\frac{112}{44} \times 2.2 = 5.6 \text{ litres of } \text{O}_2 \text{ at STP for complete combustion.}$$

**Problem 2.14 :** A piece of zinc weighing 0.635 g when treated with excess of dilute  $\text{H}_2\text{SO}_4$  liberated 200  $\text{cm}^3$  of hydrogen at STP. Calculate the percentage purity of the zinc sample.

**Solution :** The relevant balanced chemical equation is,



It indicates that 22.4 L of hydrogen at STP = 65 g of Zn.

(where Atomic mass of Zn = 65 u)

$\therefore$  0.200 L of hydrogen at STP

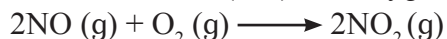
$$= \frac{65 \text{ g}}{22.4 \text{ L}} \times 0.200 \text{ L} = 0.58 \text{ g}$$

$$\therefore \text{percentage purity of Zn} = \frac{0.58}{0.635} \times 100 = 91.33 \%$$

## 2.6 Limiting reagent

When a chemist carries out a reaction, the reactants are not usually present in exact stoichiometric amounts, that is, in the proportions indicated by the balanced equation. Because the goal of a reaction is to produce the maximum quantity of a useful compound from the starting materials, frequently, a large excess of one reactant is supplied to ensure that the more expensive reactant is completely converted into the desired product. The reactant which is present in lesser amount gets consumed after some time and subsequently, no further reaction takes place, whatever be the amount left of the other reactant present. Hence, the reactant which gets consumed, limits the amount of product formed and is therefore, called the **limiting reagent**.

Consider the formation of nitrogen dioxide ( $\text{NO}_2$ ) from nitric oxide ( $\text{NO}$ ) and oxygen



Suppose initially we have 8 moles of  $\text{NO}$  and 7 moles of  $\text{O}_2$ . One way to determine which of the two reactants is the limiting reagent is to calculate the number of moles  $\text{NO}_2$  obtainable from the given initial quantities of  $\text{NO}$  and  $\text{O}_2$ .

From the preceding definition, we see that the limiting reagent will yield the smaller amount of the product. Starting with 8 moles of  $\text{NO}$ , we find the number of  $\text{NO}_2$  produced is

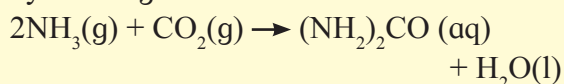
$$8 \text{ mol NO} \times \frac{2 \text{ mol NO}_2}{2 \text{ mol NO}} = 8 \text{ mol NO}_2$$

and starting with 7 moles of  $\text{O}_2$ , the number of moles  $\text{NO}_2$  formed is

$$7 \text{ mol O}_2 \times \frac{2 \text{ mol NO}_2}{1 \text{ mol O}_2} = 14 \text{ mol NO}_2$$

Because 8 moles  $\text{NO}$  result in a smaller amount of  $\text{NO}_2$ ,  $\text{NO}$  must be the limiting reagent, and  $\text{O}_2$  is the excess reagent, before reaction has started.

**Problem 2.15 :** Urea [ $(\text{NH}_2)_2\text{CO}$ ] is prepared by reacting ammonia with carbon dioxide.



In one process, 637.2 g of  $\text{NH}_3$  are

treated with 1142 g of  $\text{CO}_2$ . (a) Which of the two reactants is the limiting reagent ? (b) Calculate the mass of  $(\text{NH}_2)_2\text{CO}$  formed. (c) How much excess reagent (in grams) is left at the end of the reaction ?

**Solution :** (a) We carry out two separate calculations. First : If 637.2 g of  $\text{NH}_3$  reacts completely, calculate the number of moles of  $(\text{NH}_2)_2\text{CO}$ , that could be produced, by the following relation.

$$\begin{aligned} \text{mass of NH}_3 &\longrightarrow \text{moles of NH}_3 \\ &\longrightarrow \text{moles of } (\text{NH}_2)_2\text{CO} \\ \text{moles of } (\text{NH}_2)_2\text{CO} &= 637.2 \text{ g NH}_3 \\ &\times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} \times \frac{1 \text{ mol } (\text{NH}_2)_2\text{CO}}{2 \text{ mol NH}_3} \\ &= 18.71 \text{ moles } (\text{NH}_2)_2\text{CO} \end{aligned}$$

Second : The relation from 1142 g of  $\text{CO}_2$  :

$$\text{mass of CO}_2 \longrightarrow \text{moles of CO}_2 \longrightarrow \text{moles of } (\text{NH}_2)_2\text{CO}$$

The number of moles of  $(\text{NH}_2)_2\text{CO}$  that could be produced if all the  $\text{CO}_2$  reacted :

$$\begin{aligned} \text{moles of } (\text{NH}_2)_2\text{CO} &= 1142 \text{ g CO}_2 \\ &\times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{1 \text{ mol } (\text{NH}_2)_2\text{CO}}{1 \text{ mol CO}_2} \\ &= 25.95 \text{ mol } (\text{NH}_2)_2\text{CO} \end{aligned}$$

It follows, therefore, that  $\text{NH}_3$  must be the limiting reagent because it produces (a) smaller amount of  $(\text{NH}_2)_2\text{CO}$  (b) The molar mass of  $(\text{NH}_2)_2\text{CO}$  is 60.06 g. We use this as a conversion factor to convert from moles of  $(\text{NH}_2)_2\text{CO}$  to grams of  $(\text{NH}_2)_2\text{CO}$ .

$$\begin{aligned} \text{mass of } (\text{NH}_2)_2\text{CO} &= 18.71 \text{ mol } (\text{NH}_2)_2\text{CO} \\ &\times \frac{60.06 \text{ g } (\text{NH}_2)_2\text{CO}}{1 \text{ mol}} \\ \therefore &= 1124 \text{ g } (\text{NH}_2)_2\text{CO} \end{aligned}$$

(c) Starting with 18.71 moles of  $(\text{NH}_2)_2\text{CO}$ , we can determine the mass of  $\text{CO}_2$  that reacted using the mole ratio from the balanced equation and the molar mass of  $\text{CO}_2$  .....Contd. on next page

The conversion steps are  
 moles of  $(\text{NH}_2)_2\text{CO} \longrightarrow$  moles of  $\text{CO}_2$   
 $\longrightarrow$  grams of  $\text{CO}_2$

So that,

mass of  $\text{CO}_2$  reacted

$$= 18.71 \text{ mol } (\text{NH}_2)_2\text{CO}$$

$$\times \frac{1 \text{ mol } \text{CO}_2}{1 \text{ mol } (\text{NH}_2)_2\text{CO}} \times \frac{44.01 \text{ g } \text{CO}_2}{1 \text{ mol } \text{CO}_2}$$

$$= 823.4 \text{ g}$$

The amount of  $\text{CO}_2$  remaining (in excess) is the difference between the initial amount (1142 g) and the amount reacted (823.4 g):  
 mass of  $\text{CO}_2$  remaining = 1142 g - 823.4 g  
 = 318.6 g  $\approx$  319 g

**2.7 Concentration of solution :** A majority of reactions in the laboratory are carried out in solutions. Therefore, it is important to understand how the amount of substance is expressed when it is present in the form of a solution. The concentration of a solution or the amount of substance present in given volume of a solution can be expressed in any of the following ways :

1. Mass percent or weight percent (w/w %)
2. Mole fraction
3. Molarity (M)
4. Molality (m)

**2.7.1 Mass percent :** It is obtained by using following relation:

$$\text{Mass percent} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100 \%$$

**Problem 2.16 :** A solution is prepared by adding 2 g of a substance A to 18 g of water. Calculate the mass percent of the solute.

**Solution :** Mass percent of

$$A = \frac{\text{Mass of A}}{\text{Mass of solution}} \times 100$$

$$= \frac{2 \text{ g}}{2 \text{ g of A} + 18 \text{ g of water}} \times 100$$

$$= \frac{2 \text{ g}}{20 \text{ g}} \times 100 = 10 \%$$

## 2.7.2 Mole fraction

It is the ratio of number of moles of a particular component of a solution to the total number of moles of the solution. If a substance 'A' dissolves in substance 'B' and their number of moles are  $n_A$  and  $n_B$ , respectively, then the mole fraction of A and B are given as :

$$\text{Mole fraction of A} = \frac{\text{No. of moles of A}}{\text{No. of moles of solution}}$$

$$\therefore \text{Mole fraction of A} = \frac{n_A}{n_A + n_B}$$

$$\text{Mole fraction of B} = \frac{\text{No. of moles of B}}{\text{No. of moles of solution}}$$

$$= \frac{n_B}{n_A + n_B}$$

## 2.7.3 Molarity

It is the most widely used unit and is denoted by M. It is defined as the number of moles of the solute present in 1 litre of the solution. Thus,

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in litres}}$$

**Problem 2.17 :** Calculate the molarity of NaOH in the solution prepared by dissolving its 4 g in enough water to form 250 mL of the solution.

**Solution :**

Since molarity (M) =

$$\frac{\text{No. of moles of solute}}{\text{Volume of solution in litres}}$$

$$\therefore M =$$

$$\frac{\text{Mass of NaOH} / \text{Molar mass of NaOH}}{0.250 \text{ L}}$$

$$\therefore M = \frac{4 \text{ g} / 40 \text{ g}}{0.250 \text{ L}}$$

$$\therefore M = \frac{0.1 \text{ mol}}{0.250 \text{ L}}$$

$$\therefore M = 0.4 \text{ mol L}^{-1} = 0.4 \text{ M}$$

Note that molarity of a solution depends upon temperature because volume of a solution is temperature dependent.

### 2.7.4 Molality

It is defined as the number of moles of solute present in 1 kg of solvent. It is denoted by  $m$ .

$$\text{Molality (m)} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$$

Note that molality of a solution does not change with temperature since mass remains unaffected with temperature. Often in chemistry laboratory, a solution of desired concentration is prepared by diluting a solution of known higher concentration. The solution of higher concentration is also known as stock solution.

**Problem 2.18 :** The density of 3M solution of NaCl is  $1.25 \text{ g mL}^{-1}$ . Calculate molality of the solution.

**Solution :** Molarity =  $3 \text{ mol L}^{-1}$

Mass of NaCl in 1 L solution =  $3 \times 58.5$   
 $\therefore = 175.5 \text{ g}$

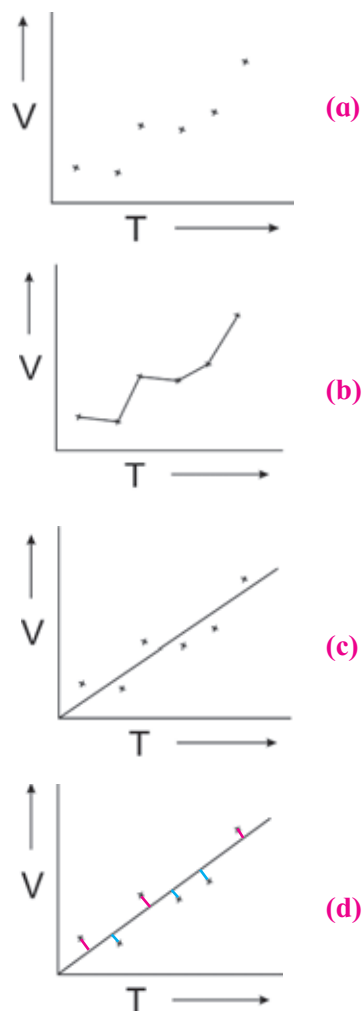
Mass of 1L solution =  $1000 \times 1.25 = 1250 \text{ g}$   
( $\because$  density =  $1.25 \text{ g mL}^{-1}$ )

Mass of water in solution =  $1250 - 175.5$   
 $\therefore = 1074.5 \text{ g}$

$$\begin{aligned}\text{Molality} &= \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}} \\ &= \frac{3 \text{ mol}}{1.0745 \text{ kg}} = 2.79 \text{ m}\end{aligned}$$

**2.8 Use of graph in analysis :** Analytical chemistry also involves deducing some relation, if any, between two or more properties of matter under study. One of the classic example in the relation between temperature and volume of a given amount of gas. A set of experimentally measured values of volume and temperature of a definite mass of a gas upon plotting on a graph paper appeared as in the figure (Fig. 2.2 (a)). When the points are directly connected, a zig zag pattern results (Fig. 2.2 (b)). From this pattern no meaningful result can be deduced. A zig zag pattern results due to many types of errors that incur in many measurements involved an experiment. Figure 2.2 (c) shows a smooth curve which may be called an average curve passing through these

points. In the above example it happens to be straight line and the inference is that  $V \propto T$ .



**Fig. 2.2 : Drawing an average curve through the points on graph**

While fitting it to a smooth curve, care is taken that the plotted points are evenly distributed about it. Mathematically 'even distribution' is understood as follows :

From each point draw a perpendicular to the curve. The perpendicular represents deviation of each point from the curve (Fig 2.2 (d)). The positive deviations are shown in red and negative deviations are shown in blue. Take sum of all the red perpendiculars and all the blue perpendiculars separately. If the two sums are equal (or nearly equal) the curve drawn shows the experimental points in the best possible representation.



## Exercises

### 1. Choose correct option

- A. The branch of chemistry which deals with study of separation, identification, and quantitative determination of the composition of different substances is called as .....  
a. Physical chemistry  
b. Inorganic chemistry  
c. Organic chemistry  
d. Analytical chemistry
- B. Which one of the following property of matter is Not quantitative in nature ?  
a. Mass                      b. Length  
c. Colour                    d. Volume
- C. SI unit of mass is .....  
a. kg                        b. mol  
c. pound                    d. m<sup>3</sup>
- D. The number of significant figures in  $1.50 \times 10^4$  g is .....  
a. 2                        b. 3  
c. 4                        d. 6
- E. In Avogadro's constant  $6.022 \times 10^{23}$  mol<sup>-1</sup>, the number of significant figures is .....  
a. 3                        b. 4  
c. 5                        d. 6
- F. By decomposition of 25 g of CaCO<sub>3</sub>, the amount of CaO produced will be .....  
a. 2.8 g                    b. 8.4 g  
c. 14.0 g                   d. 28.0 g
- G. How many grams of water will be produced by complete combustion of 12 g of methane gas  
a. 16    b. 27    c. 36                      d. 56
- H. Two elements A (At. mass 75) and B (At. mass 16) combine to give a compound having 75.8 % of A. The formula of the compound is  
a. AB                      b. A<sub>2</sub>B  
c. AB<sub>2</sub>                    d. A<sub>2</sub>B<sub>3</sub>
- I. The hydrocarbon contains 79.87 % carbon and 20.13 % of hydrogen. What is its empirical formula ?  
a. CH                      b. CH<sub>2</sub>  
c. CH<sub>3</sub>                    d. C<sub>2</sub>H<sub>5</sub>
- J. How many grams of oxygen will be required to react completely with 27 g of Al? (Atomic mass : Al = 27, O = 16)  
a. 8                        b. 16  
c. 24                      d. 32
- K. In CuSO<sub>4</sub>·5H<sub>2</sub>O the percentage of water is .....  
(Cu = 63.5, S = 32, O = 16, H = 1)  
a. 10 %                    b. 36 %  
c. 60 %                    d. 72 %
- L. When two properties of a system are mathematically related to each other, the relation can be deduced by  
a. Working out mean deviation  
b. Plotting a graph  
c. Calculating relative error  
d. all the above three

### 2. Answer the following questions

- A. Define : Least count
- B. What do you mean by significant figures? State the rules for deciding significant figures.
- C. Distinguish between accuracy and precision.
- D. Explain the terms percentage composition, empirical formula and molecular formula.
- E. What is a limiting reagent ? Explain.
- F. What do you mean by SI units ? What is the SI unit of mass ?
- G. Explain the following terms  
(a) Mole fraction  
(b) Molarity  
(c) Molality
- H. Define : Stoichiometry
- I. Why there is a need of rounding off figures during calculation ?
- J. Why does molarity of a solution depend upon temperature ?

M. Define Analytical chemistry. Why is accurate measurement crucial in science?

### 3. Solve the following questions

- A. How many significant figures are in each of the following quantities ?  
 a. 45.26 ft                      b. 0.109 in  
 c. 0.00025 kg                  d.  $2.3659 \times 10^{-8}$  cm  
 e. 52.0 cm<sup>3</sup>                      f. 0.00020 kg  
 g.  $8.50 \times 10^4$  mm              h. 300.0 cg
- B. Round off each of the following quantities to two significant figures :  
 a. 25.55 mL                      b. 0.00254 m  
 c.  $1.491 \times 10^5$  mg              d. 199 g
- C. Round off each of the following quantities to three significant figures :  
 a. 1.43 cm<sup>3</sup>                      b.  $458 \times 10^2$  cm  
 c. 643 cm<sup>2</sup>                      d. 0.039 m  
 e.  $6.398 \times 10^{-3}$  km  
 f. 0.0179 g                      g. 79,000 m  
 h. 42,150                      i. 649.85;  
 j. 23,642,000 mm  
 k. 0.0041962 kg
- D. Express the following sum to appropriate number of significant figures :  
 a.  $2.3 \times 10^3$  mL +  $4.22 \times 10^4$  mL +  $9.04 \times 10^3$  mL +  $8.71 \times 10^5$  mL;  
 b. 319.5 g - 20460 g - 0.0639 g - 45.642 g - 4.173 g

### 4. Solve the following problems

- A. Express the following quantities in exponential terms.  
 a. 0.0003498                      b. 235.4678  
 c. 70000.0                      d. 1569.00
- B. Give the number of significant figures in each of the following  
 a.  $1.230 \times 10^4$                       b. 0.002030  
 c.  $1.23 \times 10^4$                       d.  $1.89 \times 10^{-4}$
- C. Express the quantities in above (B) with or without exponents as the case may be.
- D. Find out the molar masses of the following compounds :  
 a. Copper sulphate crystal ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ )  
 (Ans.: 249.5 g/mol)

b. Sodium carbonate, decahydrate ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ )

(Ans.: 286 g/mol)

c. Mohr's salt [ $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ]

(Ans.: 392 g/mol)

(At. mass : Cu = 63.5; S = 32; O = 16; H = 1; Na = 23; C = 12; Fe = 56; N = 14)

E. Work out the percentage composition of constituents elements in the following compounds :

a. Lead phosphate [ $\text{Pb}_3(\text{PO}_4)_2$ ],

b. Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ),

c. Macrocosmic salt - Sodium ammonium hydrogen phosphate, tetrahydrate ( $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ )

(At. mass : Pb = 207; P = 31; O = 16; K = 39; Cr = 52; Na = 23; N = 14)

F. Find the percentage composition of constituent green vitriol crystals ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ). Also find out the mass of iron and the water of crystallisation in 4.54 kg of the crystals. (At. mass : Fe = 56; S = 32; O = 16)

(Ans.: mass of Fe = 0.915 kg, mass of  $7\text{H}_2\text{O}$  = 2.058 kg)

G. The red colour of blood is due to a compound called "haemoglobin". It contains 0.335 % of iron. Four atoms of iron are present in one molecule of haemoglobin. What is its molecular weight ? (At. mass : Fe 55.84)

(Ans.: 66674.6 g/mol)

H. A substance, on analysis, gave the following percent composition: Na = 43.4 %, C = 11.3 % and O = 45.3 %. Calculate the empirical formula. (At. mass Na = 23 u, C = 12 u, O = 16 u).

(Ans.:  $\text{Na}_2\text{CO}_3$ )

I. Assuming the atomic weight of a metal M to be 56, find the empirical formula of its oxide containing 70.0% of M.

(Ans.:  $\text{M}_2\text{O}_3$ )

J. 1.00 g of a hydrated salt contains 0.2014 g of iron, 0.1153 g of sulfur, 0.2301 g of oxygen and

0.4532 g of water of crystallisation.  
Find the empirical formula. (At. wt. : Fe = 56; S = 32; O = 16)

(Ans.:  $\text{FeSO}_4$ )

- K. An organic compound containing oxygen, carbon, hydrogen and nitrogen contains 20 % carbon, 6.7 % hydrogen and 46.67 % nitrogen. Its molecular mass was found to be 60. Find the molecular formula of the compound.

(Ans.:  $\text{CH}_4\text{N}_2\text{O}$ )

- L. A compound on analysis gave the following percentage composition by mass : H = 9.09; O = 36.36; C = 54.55. Mol mass of compound is 88. Find its molecular formula.

- M. Carbohydrates are compounds containing only carbon, hydrogen and oxygen. When heated in the absence of air, these compounds decompose to form carbon and water. If 310 g of a carbohydrate leave a residue of 124 g of carbon on heating in absence of air, what is the empirical formula of the carbohydrate ?

(Ans.:  $\text{CH}_2\text{O}$ )

- N. Write each of the following in exponential notation :

- a. 3,672,199      b. 0.000098  
c. 0.00461      d. 198.75

- O. Write each of the following numbers in ordinary decimal form :

- a.  $3.49 \times 10^{-11}$       b.  $3.75 \times 10^{-1}$   
c.  $5.16 \times 10^4$       d.  $43.71 \times 10^{-4}$   
e.  $0.011 \times 10^{-3}$       f.  $14.3 \times 10^{-2}$   
g.  $0.00477 \times 10^5$       h. 5.00858585

- P. Perform each of the following calculations. Round off your answers to two digits.

- a.  $\frac{1}{3.40 \times 10^{24}}$ ;      b.  $\frac{33}{9.00 \times 10^{-4}}$ ;  
c.  $\frac{1.4 \times 10^9}{(2.77 \times 10^3)(3.76 \times 10^5)}$ ;

d. 
$$\frac{(4 \times 10^{-3})(9.9 \times 10^{-7})}{(789)(1.002 \times 10^{-10})(0.3 \times 10^2)}$$

- Q. Perform each of the following calculations. Round off your answers to three digits.

a.  $(3.26 \ 104)(1.54 \ 106)$

b.  $(8.39 \ 107)(4.53 \ 109)$

c. 
$$\frac{8.94 \times 10^6}{4.35 \times 10^4}$$

d. 
$$\frac{(9.28 \times 10^9)(9.9 \times 10^{-7})}{(511)(2.98 \times 10^{-6})}$$

- R. Perform the following operations :

a.  $3.971 \times 10^7 + 1.98 \times 10^4$ ;

b.  $1.05 \times 10^{-4} - 9.7 \times 10^{-5}$ ;

c.  $4.11 \times 10^{-3} + 8.1 \ 10^{-4}$ ;

d.  $2.12 \times 10^6 - 3.5 \times 10^5$ .

- S. A 1.000 mL sample of acetone, a common solvent used as a paint remover, was placed in a small bottle whose mass was known to be 38.0015 g. The following values were obtained when the acetone - filled bottle was weighed : 38.7798 g, 38.7795 g and 38.7801 g. How would you characterise the precision and accuracy of these measurements if the actual mass of the acetone was 0.7791 g ?

(Ans.:  $\pm 0.07736\%$  0.1027%)

- T. Your laboratory partner was given the task of measuring the length of a box (approx 5 in) as accurately as possible, using a metre stick graduated in millimeters. He supplied you with the following measurements:

12.65 cm, 12.6 cm, 12.65 cm, 12.655 cm, 126.55 mm, 12 cm.

- a. State which of the measurements you would accept, giving the reason.

(Ans.: 12.6 cm)

- b. Give your reason for rejecting each of the others.

U. What weight of calcium oxide will be formed on heating 19.3 g of calcium carbonate ?

(At. wt. : Ca = 40; C = 12; O = 16)

(Ans. : 10.8 g)

V. The hourly energy requirements of an astronaut can be satisfied by the energy released when 34 grams of sucrose are “burnt” in his body. How many grams of oxygen would be needed to be carried in space capsule to meet his requirement for one day ?

(Ans. : 916.21 g)



#### Activity :

**Collect information about various apparatus/instruments used in chemistry laboratory and make presentation of it in science exhibition.**



#### Internet my friend

1. Error in chemical analysis

<https://chem.libretexts.org>...>chapters>

2. Collect information about Analytical chemistry.