Solution

We know that 1 in = 2.54 cm

From this equivalence, we can write

$$\frac{1\text{ in}}{2.54\text{ cm}} = 1 = \frac{2.54\text{ cm}}{1\text{ in}}$$

Thus, $\frac{1\text{ in}}{2.54\text{ cm}}$ equals 1 and $\frac{2.54\text{ cm}}{1\text{ in}}$ also equals 1. Both of these are called **unit factors**. If some number is multiplied by these unit factors (i.e., 1), it will not be affected otherwise.

Say, the 3 in given above is multiplied by the unit factor. So,

$$3\text{ in} = 3\text{ in} \times \frac{2.54\text{ cm}}{1\text{ in}} = 3 \times 2.54\text{ cm} = 7.62\text{ cm}$$

Now, the unit factor by which multiplication is to be done is that unit factor ($\frac{2.54\text{ cm}}{1\text{ in}}$ in the above case) which gives the desired units i.e., the numerator should have that part which is required in the desired result.

It should also be noted in the above example that units can be handled just like other numerical part. It can be cancelled, divided, multiplied, squared, etc. Let us study one more example.

Example

A jug contains 2L of milk. Calculate the volume of the milk in m^3.

Solution

Since 1 L = 1000 cm^3

and 1m = 100 cm, which gives

$$\frac{1\text{ m}}{100\text{ cm}} = 1 = \frac{100\text{ cm}}{1\text{ m}}$$

To get m^3 from the above unit factors, the first unit factor is taken and it is cubed.

$$\left(\frac{1\text{ m}}{100\text{ cm}}\right)^3 \Rightarrow \frac{1\text{ m}^3}{10^6\text{ cm}^3} = (1)^3 = 1$$

Now 2 L = 2 ×1000 cm^3

The above is multiplied by the unit factor

$$2 \times 1000\text{ cm}^3 \times \frac{1\text{ m}^3}{10^6\text{ cm}^3} = \frac{2\text{ m}^3}{10^3} = 2 \times 10^{-3}\text{ m}^3$$

Example

How many seconds are there in 2 days?

Solution

Here, we know 1 day = 24 hours (h)

$$\text{or } \frac{1\text{ day}}{24\text{ h}} = 1 = \frac{24\text{ h}}{1\text{ day}}$$

then, 1h = 60 min

$$\text{or } \frac{1\text{ h}}{60\text{ min}} = 1 = \frac{60\text{ min}}{1\text{ h}}$$

so, for converting 2 days to seconds,

i.e., 2 days – – – – – – = – – – seconds

The unit factors can be multiplied in series in one step only as follows:

$$2\text{ day} \times \frac{24\text{ h}}{1\text{ day}} \times \frac{60\text{ min}}{1\text{ h}} \times \frac{60\text{ s}}{1\text{ min}}$$

$$= 2 \times 24 \times 60 \times 60\text{ s}$$
$$= 172800\text{ s}$$

1.5 LAWS OF CHEMICAL COMBINATIONS

Antoine Lavoisier
(1743–1794)

The combination of elements to form compounds is governed by the following five basic laws.

1.5.1 Law of Conservation of Mass

This law was put forth by Antoine Lavoisier in 1789. He performed careful experimental studies for combustion reactions and reached to the conclusion that in all physical and chemical changes, there is no net change in mass duting the process. Hence, he reached to the conclusion that matter can neither be created nor destroyed. This is called 'Law of Conservation of Mass'. This law formed the basis for several later developments in chemistry. Infact, this was the result of exact measurement of masses of reactants and products, and carefully planned experiments performed by Lavoisier.

1.5.2 Law of Definite Proportions


Joseph Proust (1754–1826)

This law was given by, a French chemist, Joseph Proust. He stated that *a given compound always contains exactly the same proportion of elements by weight.*

Proust worked with two samples of cupric carbonate — one of which was of natural origin and the other was synthetic. He found that the composition of elements present in it was same for both the samples as shown below:

	% of copper	% of carbon	% of oxygen
Natural Sample	51.35	9.74	38.91
Synthetic Sample	51.35	9.74	38.91

Thus, he concluded that irrespective of the source, a given compound always contains same elements combined together in the same proportion by mass. The validity of this law has been confirmed by various experiments. It is sometimes also referred to as **Law of Definite Composition**.

1.5.3 Law of Multiple Proportions

This law was proposed by Dalton in 1803. According to this law, *if two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in the ratio of small whole numbers.*

For example, hydrogen combines with oxygen to form two compounds, namely, water and hydrogen peroxide.

Hydrogen + Oxygen $\rightarrow$ Water
2g 16g 18g

Hydrogen + Oxygen $\rightarrow$ Hydrogen Peroxide
2g 32g 34g

Here, the masses of oxygen (i.e., 16 g and 32 g), which combine with a fixed mass of hydrogen (2g) bear a simple ratio, i.e., 16:32 or 1: 2.

1.5.4 Gay Lussac's Law of Gaseous Volumes

This law was given by Gay Lussac in 1808. He observed that *when gases combine or are produced in a chemical reaction they do so in a simple ratio by volume, provided all gases are at the same temperature and pressure.*


Joseph Louis Gay Lussac

Thus, 100 mL of hydrogen combine with 50 mL of oxygen to give 100 mL of water vapour.

Hydrogen + Oxygen $\rightarrow$ Water
100 mL 50 mL 100 mL

Thus, the volumes of hydrogen and oxygen which combine (i.e., 100 mL and 50 mL) bear a simple ratio of 2:1.

Gay Lussac's discovery of integer ratio in volume relationship is actually the law of definite proportions by volume. The law of definite proportions, stated earlier, was with respect to mass. The Gay Lussac's law was explained properly by the work of Avogadro in 1811.

1.5.5 Avogadro's Law

In 1811, Avogadro proposed that *equal volumes of all gases at the same temperature and pressure should contain equal number of molecules.* Avogadro made a distinction between **atoms** and **molecules** which is quite understandable in present times. If we consider again the reaction of hydrogen and oxygen to produce water, we see that two volumes of hydrogen combine with one volume of oxygen to give two volumes of water without leaving any unreacted oxygen.

Note that in the Fig. 1.9 (Page 16) each box contains equal number of molecules. In fact, Avogadro could explain the above result by considering the molecules to be **polyatomic.** If hydrogen and oxygen were considered as **diatomic** as recognised now, then the above results are easily understandable. However, Dalton and others believed at that time that atoms of the same kind


Lorenzo Romano Amedeo Carlo Avogadro di Quareqa edi Carreto (1776–1856)

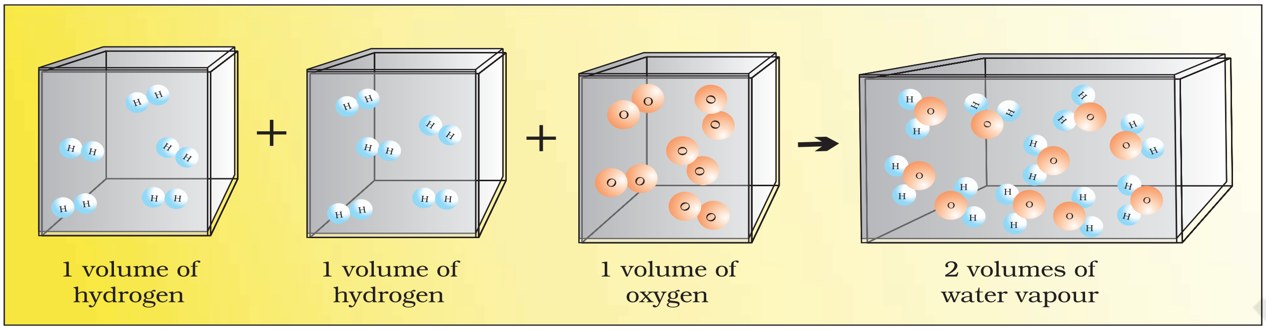


Fig. 1.9 *Two volumes of hydrogen react with one volume of oxygen to give two volumes of water vapour*

cannot combine and molecules of oxygen or hydrogen containing two atoms did not exist. Avogadro's proposal was published in the French *Journal de Physique*. In spite of being correct, it did not gain much support.

After about 50 years, in 1860, the first international conference on chemistry was held in Karlsruhe, Germany, to resolve various ideas. At the meeting, Stanislao Cannizaro presented a sketch of a course of chemical philosophy, which emphasised on the importance of Avogadro's work.

1.6 DALTON'S ATOMIC THEORY

Although the origin of the idea that matter is composed of small indivisible particles called *'a-tomio'* (meaning, *indivisible*), dates back to the time of Democritus, a Greek Philosopher (460–370 BC), it again started emerging as a result of several experimental studies which led to the laws mentioned above.

John Dalton
(1776–1884)

In 1808, Dalton published 'A New System of Chemical Philosophy', in which he proposed the following :

1. Matter consists of indivisible atoms.
2. All atoms of a given element have identical properties, including identical mass. Atoms of different elements differ in mass.
3. Compounds are formed when atoms of different elements combine in a fixed ratio.
4. Chemical reactions involve reorganisation of atoms. These are neither created nor destroyed in a chemical reaction.

Dalton's theory could explain the laws of chemical combination. However, it could not explain the laws of gaseous volumes. It could not provide the reason for combining of atoms, which was answered later by other scientists.

1.7 ATOMIC AND MOLECULAR MASSES

After having some idea about the terms atoms and molecules, it is appropriate here to understand what do we mean by atomic and molecular masses.

1.7.1 Atomic Mass

The atomic mass or the mass of an atom is actually very-very small because atoms are extremely small. Today, we have sophisticated techniques e.g., mass spectrometry for determining the atomic masses fairly accurately. But in the nineteenth century, scientists could determine the mass of one atom **relative** to another by experimental means, as has been mentioned earlier. Hydrogen, being the lightest atom was arbitrarily assigned a mass of 1 (without any units) and other elements were assigned masses relative to it. However, the present system of atomic masses is based on carbon-12 as the standard and has been agreed upon in 1961. Here, Carbon-12 is one of the **isotopes** of carbon and can be represented as ^{12}C. In this system, ^{12}C is assigned a mass of exactly 12 atomic mass unit (**amu**) and masses of all other atoms are given relative to this standard. One **atomic mass unit** is defined as a mass exactly equal to one-twelfth of the mass of one carbon – 12 atom.

And 1 amu = 1.66056×10^{-24} g

Mass of an atom of hydrogen

$$= 1.6736 \times 10^{-24} \text{ g}$$

Thus, in terms of amu, the mass

$$\text{of hydrogen atom} = \frac{1.6736 \times 10^{-24} \text{ g}}{1.66056 \times 10^{-24} \text{ g}}$$

$$= 1.0078 \text{ amu}$$

$$= 1.0080 \text{ amu}$$

Similarly, the mass of oxygen - 16 (^{16}O) atom would be 15.995 amu.

At present, **'amu'** has been replaced by **'u'**, which is known as **unified mass**.

When we use atomic masses of elements in calculations, we actually use *average atomic masses* of elements, which are explained below.

1.7.2 Average Atomic Mass

Many naturally occurring elements exist as more than one isotope. When we take into account the existence of these isotopes and their relative abundance (per cent occurrence), the average atomic mass of that element can be computed. For example, carbon has the following three isotopes with relative abundances and masses as shown against each of them.

Isotope	Relative Abundance (%)	Atomic Mass (amu)
^{12}C	98.892	12
^{13}C	1.108	13.00335
^{14}C	2×10^{-10}	14.00317

From the above data, the average atomic mass of carbon will come out to be:

(0.98892) (12 u) + (0.01108) (13.00335 u) + (2×10^{-12}) (14.00317 u) = 12.011 u

Similarly, average atomic masses for other elements can be calculated. In the periodic table of elements, the atomic masses mentioned for different elements actually represent their average atomic masses.

1.7.3 Molecular Mass

Molecular mass is the sum of atomic masses of the elements present in a molecule. It is obtained by multiplying the atomic mass of each element by the number of its atoms and adding them together. For example, molecular mass of methane, which contains one carbon atom and four hydrogen atoms, can be obtained as follows:

Molecular mass of methane,

(CH_4) = (12.011 u) + 4 (1.008 u)

= 16.043 u

Similarly, molecular mass of water (H_2O)

= 2 × atomic mass of hydrogen + 1× atomic mass of oxygen

= 2 (1.008 u) + 16.00 u

= 18.02 u

1.7.4 Formula Mass

Some substances, such as sodium chloride, do not contain discrete molecules as their constituent units. In such compounds, positive (sodium ion) and negative (chloride ion) entities are arranged in a three-dimensional structure, as shown in Fig. 1.10.

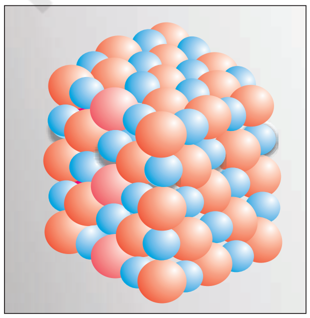


Fig. 1.10 *Packing of Na^+ and Cl^- ions in sodium chloride*

It may be noted that in sodium chloride, one Na^+ ion is surrounded by six Cl^- ion and *vice-versa*.

The formula, such as NaCl, is used to calculate the **formula mass** instead of molecular mass as in the solid state sodium chloride does not exist as a single entity.

Thus, the formula mass of sodium chloride is atomic mass of sodium + atomic mass of chlorine

= 23.0 u + 35.5 u = 58.5 u

Problem 1.1

Calculate the molecular mass of glucose ($C_6H_{12}O_6$) molecule.

Solution

Molecular mass of glucose ($C_6H_{12}O_6$)
= 6 (12.011 u) + 12 (1.008 u) + 6 (16.00 u)
= (72.066 u) + (12.096 u) + (96.00 u)
= 180.162 u

1.8 MOLE CONCEPT AND MOLAR MASSES

Atoms and molecules are extremely small in size and their numbers in even a small amount of any substance is really very large. To handle such large numbers, a unit of convenient magnitude is required.

Just as we denote one dozen for 12 items, score for 20 items, gross for 144 items, we use the idea of mole to count entities at the microscopic level (i.e., atoms, molecules, particles, electrons, ions, etc).

In SI system, **mole** (symbol, mol) was introduced as seventh base quantity for the amount of a substance.

The mole, symbol mol, is the SI unit of amount of substance. One mole contains exactly $6.02214076 \times 10^{23}$ elementary entities. This number is the fixed numerical value of the Avogadro constant, N_A, when expressed in the unit mol^{-1} and is called the Avogadro number. The amount of substance, symbol n, of a system is a measure of the number of specified elementary entities. An elementary entity may be an atom, a molecule, an ion, an electron, any other particle or specified group of particles. It may be emphasised that the mole of a substance always contains the same number of entities, no matter what the substance may be. In order to determine this number precisely, the mass of a carbon–12 atom was determined by a mass spectrometer and found to be equal to 1.992648×10^{-23} g. Knowing that one mole of carbon weighs 12 g, the number of atoms in it is equal to:

$$\frac{12\,\text{g}/\text{mol}\ ^{12}\text{C}}{1.992648 \times 10^{-23}\,\text{g}/^{12}\text{C atom}}$$

$$= 6.0221367 \times 10^{23}\ \text{atoms/mol}$$

This number of entities in 1 mol is so important that it is given a separate name and symbol. It is known as **'Avogadro constant'**, or Avogadro number denoted by N_A in honour of Amedeo Avogadro. To appreciate the largeness of this number, let us write it with all zeroes without using any powers of ten.

602213670000000000000000

Hence, so many entities (atoms, molecules or any other particle) constitute one mole of a particular substance.

We can, therefore, say that 1 mol of hydrogen atoms = 6.022×10^{23} atoms

1 mol of water molecules = 6.022×10^{23} water molecules

1 mol of sodium chloride = 6.022×10^{23} formula units of sodium chloride

Having defined the mole, it is easier to know the mass of one mole of a substance or the constituent entities. **The mass of one mole of a substance in grams is called its molar mass.** The molar mass in grams is numerically equal to atomic/molecular/ formula mass in u.

Molar mass of water = 18.02 g mol^{-1}

Molar mass of sodium chloride = 58.5 g mol^{-1}

1.9 PERCENTAGE COMPOSITION

So far, we were dealing with the number of entities present in a given sample. But many a time, information regarding the percentage of a particular element present in a compound is required. Suppose, an unknown or new compound is given to you, the first question

Fig. 1.11 *One mole of various substances*

you would ask is: what is its formula or what are its constituents and in what ratio are they present in the given compound? For known compounds also, such information provides a check whether the given sample contains the same percentage of elements as present in a pure sample. In other words, one can check the purity of a given sample by analysing this data.

Let us understand it by taking the example of water (H_2O). Since water contains hydrogen and oxygen, the percentage composition of both these elements can be calculated as follows:

Mass % of an element =

$$\frac{\text{mass of that element in the compound} \times 100}{\text{molar mass of the compound}}$$

Molar mass of water = 18.02 g

$$\text{Mass \% of hydrogen} = \frac{2 \times 1.008}{18.02} \times 100$$

= 11.18

$$\text{Mass \% of oxygen} = \frac{16.00}{18.02} \times 100$$

= 88.79

Let us take one more example. What is the percentage of carbon, hydrogen and oxygen in ethanol?

Molecular formula of ethanol is: C_2H_5OH

Molar mass of ethanol is:

$(2\times12.01 + 6\times1.008 + 16.00)$ g = 46.068 g

Mass per cent of carbon

$$= \frac{24.02\,g}{46.068\,g} \times 100 = 52.14\%$$

Mass per cent of hydrogen

$$= \frac{6.048\,g}{46.068\,g} \times 100 = 13.13\%$$

Mass per cent of oxygen

$$= \frac{16.00\,g}{46.068\,g} \times 100 = 34.73\%$$

After understanding the calculation of per cent of mass, let us now see what information can be obtained from the per cent composition data.

1.9.1 Empirical Formula for Molecular Formula

An **empirical formula** represents the simplest whole number ratio of various atoms present in a compound, whereas, the **molecular formula** shows the exact number of different types of atoms present in a molecule of a compound.

If the mass per cent of various elements present in a compound is known, its empirical formula can be determined. Molecular formula can further be obtained if the molar mass is known. The following example illustrates this sequence.

Problem 1.2

A compound contains 4.07% hydrogen, 24.27% carbon and 71.65% chlorine. Its molar mass is 98.96 g. What are its empirical and molecular formulas?

Solution

Step 1. Conversion of mass per cent to grams

Since we are having mass per cent, it is convenient to use 100 g of the compound as the starting material. Thus, in the 100 g sample of the above compound, 4.07g hydrogen, 24.27g carbon and 71.65g chlorine are present.

Step 2. Convert into number moles of each element

Divide the masses obtained above by respective atomic masses of various elements. This gives the number of moles of constituent elements in the compound

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

$$\text{Moles of carbon} = \frac{24.27\,g}{12.01\,g} = 2.021$$

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

Step 3. Divide each of the mole values obtained above by the smallest number amongst them

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

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

Step 4. Write down the empirical formula by mentioning the numbers after writing the symbols of respective elements

CH_2Cl is, thus, the empirical formula of the above compound.

Step 5. Writing molecular formula

(a) Determine empirical formula mass by adding the atomic masses of various atoms present in the empirical formula. For CH_2Cl, empirical formula mass is
$12.01 + (2 \times 1.008) + 35.453$
$= 49.48$ g

(b) Divide Molar mass by empirical formula mass

$$\frac{\text{Molar mass}}{\text{Empirical formula mass}} = \frac{98.96\,\text{g}}{49.48\,\text{g}}$$
$$= 2 = (n)$$

(c) Multiply empirical formula by n obtained above to get the molecular formula

Empirical formula = CH_2Cl, $n = 2$. Hence molecular formula is $C_2H_4Cl_2$.

1.10 STOICHIOMETRY AND STOICHIOMETRIC CALCULATIONS

The word 'stoichiometry' is derived from two Greek words — *stoicheion* (meaning, *element*) and *metron* (meaning, *measure*). Stoichiometry, thus, deals with the calculation of masses (sometimes volumes also) of the reactants and the products involved in a chemical reaction. Before understanding how to calculate the amounts of reactants required or the products produced in a chemical reaction, let us study what information is available from the **balanced** chemical equation of a given reaction. Let us consider the combustion of methane. A balanced equation for this reaction is as given below:

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(g)$$

Here, methane and dioxygen are called *reactants* and carbon dioxide and water are called *products*. Note that all the reactants and the products are gases in the above reaction and this has been indicated by letter (g) in the brackets next to its formula. Similarly, in case of solids and liquids, (s) and (l) are written respectively.

The coefficients 2 for O_2 and H_2O are called stoichiometric coefficients. Similarly the coefficient for CH_4 and CO_2 is one in each case. They represent the number of molecules (and moles as well) taking part in the reaction or formed in the reaction.

Thus, according to the above chemical reaction,

- One **mole** of CH_4(g) reacts with two **moles** of O_2(g) to give one **mole** of CO_2(g) and two **moles** of H_2O(g)
- One **molecule** of CH_4(g) reacts with 2 **molecules** of O_2(g) to give one **molecule** of CO_2(g) and 2 molecules of H_2O(g)
- 22.7 L of CH_4(g) reacts with 45.4 L of O_2 (g) to give 22.7 L of CO_2 (g) and 45.4 L of H_2O(g)
- 16 g of CH_4 (g) reacts with 2×32 g of O_2 (g) to give 44 g of CO_2 (g) and 2×18 g of H_2O (g).

From these relationships, the given data can be interconverted as follows:

mass
mass $\rightleftharpoons$ moles $\rightleftharpoons$ no. of molecules

$$\frac{\text{Mass}}{\text{Volume}} = \text{Density}$$

1.10.1 Limiting Reagent

Many a time, reactions are carried out with the amounts of reactants that are different than the amounts as required by a balanced chemical reaction. In such situations, one reactant is in more amount than the amount required by balanced chemical reaction. The reactant which is present in the least amount gets consumed after sometime and after that further reaction does not take place whatever be the amount of the other reactant. Hence, the reactant, which gets consumed first, limits the amount of product formed and is, therefore, called the **limiting reagent**.

In performing stoichiometric calculations, this aspect is also to be kept in mind.

1.10.2 Reactions in Solutions

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

1. Mass per cent or weight per cent (w/w %)
2. Mole fraction
3. Molarity
4. Molality

Let us now study each one of them in detail.

Balancing a chemical equation

According to the law of conservation of mass, a balanced chemical equation has the *same number of atoms of each element on both sides* of the equation. Many chemical equations can be balanced by *trial and error*. Let us take the reactions of a few metals and non-metals with oxygen to give oxides

$4\,Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$ (a) balanced equation

$2\,Mg(s) + O_2(g) \rightarrow 2MgO(s)$ (b) balanced equation

$P_4(s) + O_2(g) \rightarrow P_4O_{10}(s)$ (c) unbalanced equation

Equations (a) and (b) are balanced, since there are same number of metal and oxygen atoms on each side of the equations. However equation (c) is not balanced. In this equation, phosphorus atoms are balanced but not the oxygen atoms. To balance it, we must place the coefficient 5 on the left of oxygen on the left side of the equation to balance the oxygen atoms appearing on the right side of the equation.

$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$ balanced equation

Now, let us take combustion of propane, C_3H_8. This equation can be balanced in steps.

Step 1 Write down the correct formulas of reactants and products. Here, propane and oxygen are reactants, and carbon dioxide and water are products.

$C_3H_8(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$ unbalanced equation

Step 2 *Balance the number of C atoms:* Since 3 carbon atoms are in the reactant, therefore, three CO_2 molecules are required on the right side.

$C_3H_8(g) + O_2(g) \rightarrow 3CO_2(g) + H_2O(l)$

Step 3 *Balance the number of H atoms:* on the left there are 8 hydrogen atoms in the reactants however, each molecule of water has two hydrogen atoms, so four molecules of water will be required for eight hydrogen atoms on the right side.

$C_3H_8(g) + O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

Step 4 *Balance the number of O atoms:* There are 10 oxygen atoms on the right side (3 × 2 = 6 in CO_2 and 4×1= 4 in water). Therefore, five O_2 molecules are needed to supply the required 10 CO_2 and 4×1= 4 in water). Therefore, five O_2 molecules are needed to supply the required 10 oxygen atoms.

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

Step 5 *Verify that the number of atoms of each element is balanced in the final equation.* The equation shows three carbon atoms, eight hydrogen atoms, and 10 oxygen atoms on each side.

All equations that have correct formulas for all reactants and products can be balanced. Always remember that subscripts in formulas of reactants and products cannot be changed to balance an equation.

Problem 1.3

Calculate the amount of water (g) produced by the combustion of 16 g of methane.

Solution

The balanced equation for the combustion of methane is :

CH_4 (g) + $2O_2$ (g) $\rightarrow$ CO_2 (g) + $2H_2O$ (g)

(i) 16 g of CH_4 corresponds to one mole.

(ii) From the above equation, 1 mol of CH_4 (g) gives 2 mol of H_2O (g).

2 mol of water (H_2O) = 2×(2+16)
= 2×18 = 36 g

$$1 \text{ mol } H_2O = 18 \text{ g } H_2O \Rightarrow \frac{18\text{ g } H_2O}{1\text{ mol } H_2O} = 1$$

$$\text{Hence, } 2 \text{ mol } H_2O \times \frac{18\text{ g } H_2O}{1\text{ mol } H_2O}$$

$$= 2\times18 \text{ g } H_2O = 36 \text{ g } H_2O$$

Problem 1.4

How many moles of methane are required to produce 22g CO_2 (g) after combustion?

Solution

According to the chemical equation,

CH_4 (g) + $2O_2$ (g) $\rightarrow$ CO_2 (g) + $2H_2O$ (g)

44g CO_2 (g) is obtained from 16 g CH_4 (g).

[$\therefore$ 1 mol CO_2(g) is obtained from 1 mol of CH_4(g)]

Number of moles of CO_2 (g)

$$= 22 \text{ g } CO_2 \text{ (g)} \times \frac{1\text{ mol } CO_2\text{ (g)}}{44\text{ g } CO_2\text{ (g)}}$$

= 0.5 mol CO_2 (g)

Hence, 0.5 mol CO_2 (g) would be obtained from 0.5 mol CH_4 (g) or 0.5 mol of CH_4 (g) would be required to produce 22 g CO_2 (g).

Problem 1.5

50.0 kg of N_2 (g) and 10.0 kg of H_2 (g) are mixed to produce NH_3 (g). Calculate the amount of NH_3 (g) formed. Identify the limiting reagent in the production of NH_3 in this situation.

Solution

A balanced equation for the above reaction is written as follows :

$$N_2\text{ (g)} + 3H_2\text{ (g)} \rightleftharpoons 2\ NH_3\text{ (g)}$$

Calculation of moles :

Number of moles of N_2

$$= 50.0\text{ kg } N_2 \times \frac{1000\text{ g } N_2}{1\text{ kg } N_2} \times \frac{1\text{ mol } N_2}{28.0\text{ g } N_2}$$

= 17.86×10^2 mol

Number of moles of H_2

$$= 10.00\text{ kg } H_2 \times \frac{1000\text{ g } H_2}{1\text{ kg } H_2} \times \frac{1\text{ mol } H_2}{2.016\text{ g } H_2}$$

= 4.96×10^3 mol

According to the above equation, 1 mol N_2 (g) requires 3 mol H_2 (g), for the reaction. Hence, for 17.86×10^2 mol of N_2, the moles of H_2 (g) required would be

$$17.86\times10^2 \text{ mol } N_2 \times \frac{3\text{ mol } H_2\text{ (g)}}{1\text{ mol } N_2\text{ (g)}}$$

= 5.36×10^3 mol H_2

But we have only 4.96×10^3 mol H_2. Hence, dihydrogen is the limiting reagent in this case. So, NH_3(g) would be formed only from that amount of available dihydrogen *i.e.*, 4.96×10^3 mol

Since 3 mol H_2(g) gives 2 mol NH_3(g)

$$4.96 \times10^3 \text{ mol } H_2\text{ (g)} \times \frac{2\text{ mol } NH_3\text{ (g)}}{3\text{ mol } H_2\text{ (g)}}$$

= 3.30×10^3 mol NH_3 (g)

3.30×10^3 mol NH_3 (g) is obtained.

If they are to be converted to grams, it is done as follows :

1 mol NH_3 (g) = 17.0 g NH_3 (g)

$$3.30 \times10^3 \text{ mol } NH_3\text{ (g)} \times \frac{17.0\text{ g } NH_3\text{ (g)}}{1\text{ mol } NH_3\text{ (g)}}$$

$= 3.30 \times 10^3 \times 17$ g NH_3 (g)
$= 56.1 \times 10^3$ g NH_3
$= 56.1$ kg NH_3

1. *Mass per cent*

It is obtained by using the following relation:

$$\text{Mass per cent} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

Problem 1.6

A solution is prepared by adding 2 g of a substance A to 18 g of water. Calculate the mass per cent of the solute.

Solution

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

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

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

$$= 10\%$$

2. *Mole Fraction*

It is the ratio of number of moles of a particular component 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 fractions of A and B are given as:

Mole fraction of A

$$= \frac{\text{No. of moles of A}}{\text{No. of moles of solutions}}$$

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

Mole fraction of B

$$= \frac{\text{No. of moles of B}}{\text{No. of moles of solutions}}$$

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

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 in 1 litre of the solution. Thus,

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

Suppose, we have 1 M solution of a substance, say NaOH, and we want to prepare a 0.2 M solution from it.

1 M NaOH means 1 mol of NaOH present in 1 litre of the solution. For 0.2 M solution, we require 0.2 moles of NaOH dissolved in 1 litre solution.

Hence, for making 0.2M solution from 1M solution, we have to take that volume of 1M NaOH solution, which contains 0.2 mol of NaOH and dilute the solution with water to 1 litre.

Now, how much volume of concentrated (1M) NaOH solution be taken, which contains 0.2 moles of NaOH can be calculated as follows:

If 1 mol is present in 1L or 1000 mL solution

then, 0.2 mol is present in

$$\frac{1000\text{ mL}}{1\text{ mol}} \times 0.2\text{ mol solution}$$

$= 200$ mL solution

Thus, 200 mL of 1M NaOH are taken and enough water is added to dilute it to make it 1 litre.

In fact for such calculations, a general formula, $M_1 \times V_1 = M_2 \times V_2$ where M and V are molarity and volume, respectively, can be used. In this case, M_1 is equal to 0.2M; $V_1 = 1000$ mL and, $M_2 = 1.0$M; V_2 is to be calculated. Substituting the values in the formula:

$0.2\text{ M} \times 1000\text{ mL} = 1.0\text{ M} \times V_2$

$$\therefore V_2 = \frac{0.2\text{ M} \times 1000\text{ mL}}{1.0\text{ M}} = 200\text{ L}$$

Note that the **number of moles of solute** (NaOH) was 0.2 in 200 mL and *it has remained the same*, i.e., 0.2 even after dilution (in 1000 mL) as we have changed just the amount of solvent (i.e., water) and have not done anything with respect to NaOH. But keep in mind the concentration.

Problem 1.7

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)

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

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

$$= \frac{4\,\text{g} / 40\,\text{g}}{0.250\,\text{L}} = \frac{0.1\,\text{mol}}{0.250\,\text{L}}$$

$$= 0.4\,\text{mol}^{-1}$$

$$= 0.4\,\text{M}$$

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

4. *Molality*

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

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

Problem 1.8

The density of 3 M solution of NaCl is 1.25 g mL^{-1}. Calculate the molality of the solution.

Solution

M = 3 mol L^{-1}

Mass of NaCl
in 1 L solution = 3 × 58.5 = 175.5 g

Mass of
1L solution = 1000 × 1.25 = 1250 g
(since density = 1.25 g mL^{-1})
Mass of water in solution = 1250 –75.5
= 1074.5 g

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

$$= \frac{3\,\text{mol}}{1.0745\,\text{kg}} = 2.79\ \text{m}$$

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

SUMMARY

Chemistry, as we understand it today is not a very old discipline. People in ancient India, already had the knowledge of many scientific phenomenon much before the advent of modern science. They applied the knowledge in various walks of life.

The study of chemistry is very important as its domain encompasses every sphere of life. Chemists study the properties and structure of substances and the changes undergone by them. All substances contain matter, which can exist in three states – solid, liquid or gas. The constituent particles are held in different ways in these states of matter and they exhibit their characteristic properties. Matter can also be classified into elements, compounds or mixtures. An **element** contains particles of only one type, which may be **atoms** or **molecules**. The compounds are formed where atoms of two or more elements combine in a fixed ratio to each other. Mixtures occur widely and many of the substances present around us are mixtures.

When the properties of a substance are studied, measurement is inherent. The quantification of properties requires a system of measurement and units in which the quantities are to be expressed. Many systems of measurement exist, of which the English and the Metric Systems are widely used. The scientific community, however, has agreed to have a uniform and common system throughout the world, which is abbreviated as SI units (International System of Units).

Since measurements involve recording of data, which are always associated with a certain amount of uncertainty, the proper handling of data obtained by measuring the quantities is very important. The measurements of quantities in chemistry are spread over a wide range of 10^{-31} to 10^{+23}. Hence, a convenient system of expressing the numbers in **scientific notation** is used. The uncertainty is taken care of by specifying the number of **significant figures,** in which the observations are reported. The **dimensional analysis** helps to express the measured quantities in different systems of units. Hence, it is possible to interconvert the results from one system of units to another.

The combination of different atoms is governed by basic laws of chemical combination — these being the **Law of Conservation of Mass, Law of Definite Proportions, Law of Multiple Proportions, Gay Lussac's Law of Gaseous Volumes** and **Avogadro Law**. All these laws led to the **Dalton's atomic theory,** which states that atoms are building blocks of matter. The **atomic mass** of an element is expressed relative to ^{12}C isotope of carbon, which has an exact value of 12u. Usually, the atomic mass used for an element is the **average atomic mass** obtained by taking into account the natural abundance of different isotopes of that element. The **molecular mass** of a molecule is obtained by taking sum of the atomic masses of different atoms present in a molecule. The **molecular formula** can be calculated by determining the mass per cent of different elements present in a compound and its molecular mass.

The number of atoms, molecules or any other particles present in a given system are expressed in the terms of **Avogadro constant** (6.022×10^{23}). This is known as **1 mol** of the respective particles or entities.

Chemical reactions represent the chemical changes undergone by different elements and compounds. A **balanced** chemical equation provides a lot of information. The coefficients indicate the molar ratios and the respective number of particles taking part in a particular reaction. The quantitative study of the reactants required or the products formed is called **stoichiometry**. Using stoichiometric calculations, the amount of one or more reactant(s) required to produce a particular amount of product can be determined and vice-versa. The amount of substance present in a given volume of a solution is expressed in number of ways, e.g., mass per cent, mole fraction, molarity and molality.

EXERCISES

1.1 Calculate the molar mass of the following:

(i) H_2O (ii) CO_2 (iii) CH_4

1.2 Calculate the mass per cent of different elements present in sodium sulphate (Na_2SO_4).

1.3 Determine the empirical formula of an oxide of iron, which has 69.9% iron and 30.1% dioxygen by mass.

1.4 Calculate the amount of carbon dioxide that could be produced when

(i) 1 mole of carbon is burnt in air.

(ii) 1 mole of carbon is burnt in 16 g of dioxygen.

(iii) 2 moles of carbon are burnt in 16 g of dioxygen.

1.5 Calculate the mass of sodium acetate (CH_3COONa) required to make 500 mL of 0.375 molar aqueous solution. Molar mass of sodium acetate is 82.0245 g mol^{-1}.

1.6 Calculate the concentration of nitric acid in moles per litre in a sample which has a density, 1.41 g mL^{-1} and the mass per cent of nitric acid in it being 69%.

1.7 How much copper can be obtained from 100 g of copper sulphate ($CuSO_4$)?

1.8 Determine the molecular formula of an oxide of iron, in which the mass per cent of iron and oxygen are 69.9 and 30.1, respectively.

1.9 Calculate the atomic mass (average) of chlorine using the following data:

	% Natural Abundance	**Molar Mass**
^{35}Cl	75.77	34.9689
^{37}Cl	24.23	36.9659

1.10 In three moles of ethane (C_2H_6), calculate the following:

(i) Number of moles of carbon atoms.

(ii) Number of moles of hydrogen atoms.

(iii) Number of molecules of ethane.

1.11 What is the concentration of sugar ($C_{12}H_{22}O_{11}$) in mol L^{-1} if its 20 g are dissolved in enough water to make a final volume up to 2L?

1.12 If the density of methanol is 0.793 kg L^{-1}, what is its volume needed for making 2.5 L of its 0.25 M solution?

1.13 Pressure is determined as force per unit area of the surface. The SI unit of pressure, pascal is as shown below:

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

If mass of air at sea level is 1034 g cm^{-2}, calculate the pressure in pascal.

1.14 What is the SI unit of mass? How is it defined?

1.15 Match the following prefixes with their multiples:

	Prefixes	**Multiples**
(i)	micro	10^6
(ii)	deca	10^9
(iii)	mega	10^{-6}
(iv)	giga	10^{-15}
(v)	femto	10

1.16 What do you mean by significant figures?

1.17 A sample of drinking water was found to be severely contaminated with chloroform, $CHCl_3$, supposed to be carcinogenic in nature. The level of contamination was 15 ppm (by mass).

(i) Express this in per cent by mass.

(ii) Determine the molality of chloroform in the water sample.

1.18 Express the following in the scientific notation:

(i) 0.0048

(ii) 234,000

(iii) 8008

(iv) 500.0

(v) 6.0012

1.19 How many significant figures are present in the following?

(i) 0.0025

(ii) 208

(iii) 5005

(iv) 126,000

(v) 500.0

(vi) 2.0034

1.20 Round up the following upto three significant figures:

(i) 34.216

(ii) 10.4107

(iii) 0.04597

(iv) 2808

1.21 The following data are obtained when dinitrogen and dioxygen react together to form different compounds:

	Mass of dinitrogen	Mass of dioxygen
(i)	14 g	16 g
(ii)	14 g	32 g
(iii)	28 g	32 g
(iv)	28 g	80 g

(a) Which law of chemical combination is obeyed by the above experimental data? Give its statement.

(b) Fill in the blanks in the following conversions:

(i) 1 km = ... mm = ... pm

(ii) 1 mg = ... kg = ... ng

(iii) 1 mL = ... L = ... dm^3

1.22 If the speed of light is 3.0×10^8 m s^{-1}, calculate the distance covered by light in 2.00 ns.

1.23 In a reaction

$A + B_2 \rightarrow AB_2$

Identify the limiting reagent, if any, in the following reaction mixtures.

(i) 300 atoms of A + 200 molecules of B

(ii) 2 mol A + 3 mol B

(iii) 100 atoms of A + 100 molecules of B

(iv) 5 mol A + 2.5 mol B

(v) 2.5 mol A + 5 mol B

1.24 Dinitrogen and dihydrogen react with each other to produce ammonia according to the following chemical equation:

$N_2 (g) + H_2 (g) \rightarrow 2NH_3 (g)$

(i) Calculate the mass of ammonia produced if 2.00×10^3 g dinitrogen reacts with 1.00×10^3 g of dihydrogen.

(ii) Will any of the two reactants remain unreacted?

(iii) If yes, which one and what would be its mass?

1.25 How are 0.50 mol Na_2CO_3 and 0.50 M Na_2CO_3 different?

1.26 If 10 volumes of dihydrogen gas reacts with five volumes of dioxygen gas, how many volumes of water vapour would be produced?

1.27 Convert the following into basic units:

(i) 28.7 pm

(ii) 15.15 pm

(iii) 25365 mg

1.28 Which one of the following will have the largest number of atoms?

(i) 1 g Au (s)
(ii) 1 g Na (s)
(iii) 1 g Li (s)
(iv) 1 g of Cl_2(g)

1.29 Calculate the molarity of a solution of ethanol in water, in which the mole fraction of ethanol is 0.040 (assume the density of water to be one).

1.30 What will be the mass of one ^{12}C atom in g?

1.31 How many significant figures should be present in the answer of the following calculations?

(i) $\dfrac{0.02856 \times 298.15 \times 0.112}{0.5785}$ (ii) 5×5.364

(iii) $0.0125 + 0.7864 + 0.0215$

1.32 Use the data given in the following table to calculate the molar mass of naturally occuring *argon* isotopes:

Isotope	**Isotopic molar mass**	**Abundance**
^{36}Ar	35.96755 g mol^{-1}	0.337%
^{38}Ar	37.96272 g mol^{-1}	0.063%
^{40}Ar	39.9624 g mol^{-1}	99.600%

1.33 Calculate the number of atoms in each of the following (i) 52 moles of Ar (ii) 52 u of He (iii) 52 g of He.

1.34 A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide, 0.690 g of water and no other products. A volume of 10.0 L (measured at STP) of this welding gas is found to weigh 11.6 g. Calculate (i) empirical formula, (ii) molar mass of the gas, and (iii) molecular formula.

1.35 Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction, $CaCO_3$ (s) + 2 HCl (aq) → $CaCl_2$ (aq) + CO_2(g) + H_2O(l)

What mass of $CaCO_3$ is required to react completely with 25 mL of 0.75 M HCl?

1.36 Chlorine is prepared in the laboratory by treating manganese dioxide (MnO_2) with aqueous hydrochloric acid according to the reaction

4 HCl (aq) + MnO_2(s) → $2H_2O$ (l) + $MnCl_2$(aq) + Cl_2 (g)

How many grams of HCl react with 5.0 g of manganese dioxide?

11082CH02

UNIT 2

STRUCTURE OF ATOM

Objectives

After studying this unit you will be able to

- know about the discovery of electron, proton and neutron and their characteristics;
- describe Thomson, Rutherford and Bohr atomic models;
- understand the important features of the quantum mechanical model of atom;
- understand nature of electromagnetic radiation and Planck's quantum theory;
- explain the photoelectric effect and describe features of atomic spectra;
- state the de Broglie relation and Heisenberg uncertainty principle;
- define an atomic orbital in terms of quantum numbers;
- state aufbau principle, Pauli exclusion principle and Hund's rule of maximum multiplicity; and
- write the electronic configurations of atoms.

"The rich diversity of chemical behaviour of different elements can be traced to the differences in the internal structure of atoms of these elements."

The existence of atoms has been proposed since the time of early Indian and Greek philosophers (400 B.C.) who were of the view that atoms are the fundamental building blocks of matter. According to them, the continued subdivisions of matter would ultimately yield atoms which would not be further divisible. The word 'atom' has been derived from the Greek word *'a-tomio'* which means 'uncut-able' or 'non-divisible'. These earlier ideas were mere speculations and there was no way to test them experimentally. These ideas remained dormant for a very long time and were revived again by scientists in the nineteenth century.

The atomic theory of matter was first proposed on a firm scientific basis by John Dalton, a British school teacher in 1808. His theory, called **Dalton's atomic theory**, regarded the atom as the ultimate particle of matter (Unit 1). Dalton's atomic theory was able to explain the law of conservation of mass, law of constant composition and law of multiple proportion very successfully. However, it failed to explain the results of many experiments, for example, it was known that substances like glass or ebonite when rubbed with silk or fur get electrically charged.

In this unit we start with the experimental observations made by scientists towards the end of nineteenth and beginning of twentieth century. These established that atoms are made of sub-atomic particles, i.e., electrons, protons and neutrons — a concept very different from that of Dalton.

2.1 DISCOVERY OF SUB-ATOMIC PARTICLES

An insight into the structure of atom was obtained from the experiments on electrical discharge through gases. Before we discuss these results we need to keep in mind a basic rule regarding the behaviour of charged particles : "Like charges repel each other and unlike charges attract each other".

2.1.1 Discovery of Electron

In 1830, Michael Faraday showed that if electricity is passed through a solution of an electrolyte, chemical reactions occurred at the electrodes, which resulted in the liberation and deposition of matter at the electrodes. He formulated certain laws which you will study in Class XII. These results suggested the particulate nature of electricity.

In mid 1850s many scientists mainly Faraday began to study electrical discharge in partially evacuated tubes, known as **cathode ray discharge tubes**. It is depicted in Fig. 2.1. A cathode ray tube is made of glass containing two thin pieces of metal, called electrodes, sealed in it. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages. The pressure of different gases could be adjusted by evacuation of the glass tubes. When sufficiently high voltage is applied across the electrodes, current starts flowing through a stream of particles moving in the tube from the negative electrode (cathode) to the positive electrode (anode). These were called **cathode rays or cathode ray particles**. The flow of current from cathode to anode was further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material zinc sulphide. When these rays, after passing through anode, strike the zinc sulphide coating, a bright spot is developed on the coating [Fig. 2.1(b)].

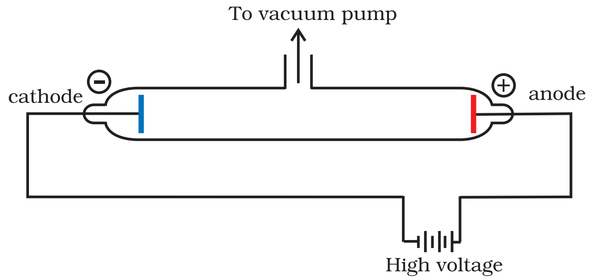


Fig. 2.1(a) *A cathode ray discharge tube*

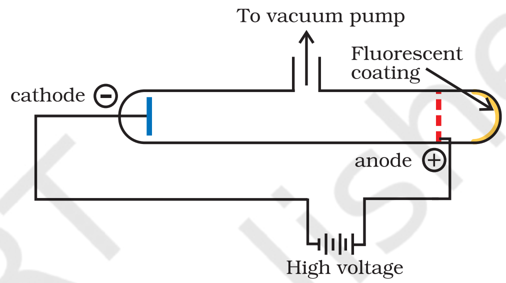


Fig. 2.1(b) *A cathode ray discharge tube with perforated anode*

The results of these experiments are summarised below.

(i) The cathode rays start from cathode and move towards the anode.

(ii) These rays themselves are not visible but their behaviour can be observed with the help of certain kind of materials (fluorescent or phosphorescent) which glow when hit by them. Television picture tubes are cathode ray tubes and television pictures result due to fluorescence on the television screen coated with certain fluorescent or phosphorescent materials.

(iii) In the absence of electrical or magnetic field, these rays travel in straight lines (Fig. 2.2).

(iv) In the presence of electrical or magnetic field, the behaviour of cathode rays are similar to that expected from negatively charged particles, suggesting that the cathode rays consist of negatively charged particles, called **electrons.**

(v) The characteristics of cathode rays (electrons) do not depend upon the material of electrodes and the nature of the gas present in the cathode ray tube.

Thus, we can conclude that electrons are basic constituent of all the atoms.

2.1.2 Charge to Mass Ratio of Electron

In 1897, British physicist J.J. Thomson measured the ratio of electrical charge (e) to the mass of electron (m_e) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons (Fig. 2.2). When only electric field is applied, the electrons deviate from their path and hit the cathode ray tube at point A (Fig. 2.2). Similarly when only magnetic field is applied, electron strikes the cathode ray tube at point C. By carefully balancing the electrical and magnetic field strength, it is possible to bring back the electron to the path which is followed in the absence of electric or magnetic field and they hit the screen at point B. Thomson argued that the amount of deviation of the particles from their path in the presence of electrical or magnetic field depends upon:

(i) the magnitude of the negative charge on the particle, greater the magnitude of the charge on the particle, greater is the interaction with the electric or magnetic field and thus greater is the deflection.

(ii) the mass of the particle — lighter the particle, greater the deflection.

(iii) the strength of the electrical or magnetic field — the deflection of electrons from its original path increases with the increase in the voltage across the electrodes, or the strength of the magnetic field.

By carrying out accurate measurements on the amount of deflections observed by the electrons on the electric field strength or magnetic field strength, Thomson was able to determine the value of e/m_e as:

$$\frac{e}{m_e} = 1.758820 \times 10^{11}\ \text{C kg}^{-1} \qquad (2.1)$$

Where m_e is the mass of the electron in kg and e is the magnitude of the charge on the electron in coulomb (C). Since electrons are negatively charged, the charge on electron is $-e$.

2.1.3 Charge on the Electron

R.A. Millikan (1868-1953) devised a method known as oil drop experiment (1906-14), to determine the charge on the electrons. He found the charge on the electron to be -1.6×10^{-19} C. The present accepted value of electrical charge is $-1.602176 \times 10^{-19}$ C. The mass of the electron (m_e) was determined by combining these results with Thomson's value of e/m_e ratio.

$$m_e = \frac{e}{e/m_e} = \frac{1.602176 \times 10^{-19}\text{C}}{1.758820 \times 10^{11}\text{C kg}^{-1}}$$

$$= 9.1094 \times 10^{-31}\ \text{kg} \qquad (2.2)$$

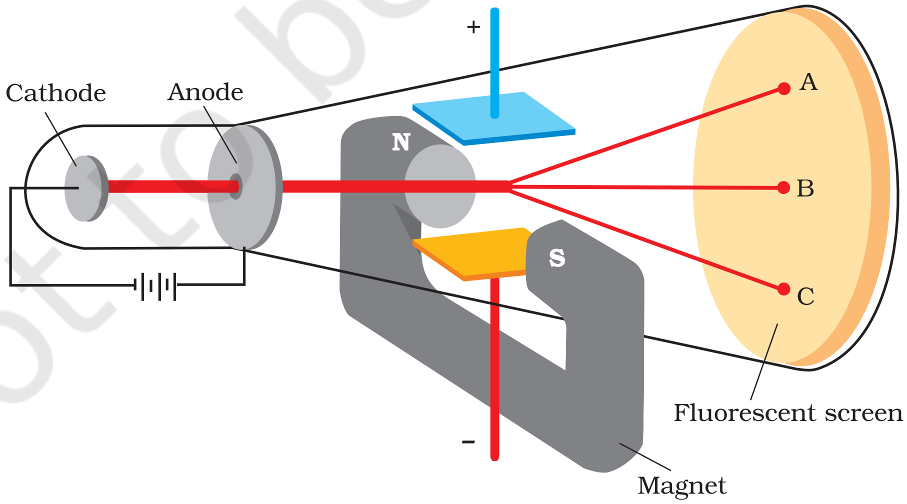


Fig. 2.2 *The apparatus to determine the charge to the mass ratio of electron*

2.1.4 Discovery of Protons and Neutrons

Electrical discharge carried out in the modified cathode ray tube led to the discovery of **canal rays** carrying positively charged particles. The characteristics of these positively charged particles are listed below.

(i) Unlike cathode rays, mass of positively charged particles depends upon the nature of gas present in the cathode ray tube. These are simply the positively charged gaseous ions.

(ii) The charge to mass ratio of the particles depends on the gas from which these originate.

(iii) Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge.

(iv) The behaviour of these particles in the magnetic or electrical field is opposite to that observed for electron or cathode rays.

The smallest and lightest positive ion was obtained from hydrogen and was called **proton**. This positively charged particle was characterised in 1919. Later, a need was felt for the presence of electrically neutral particle as one of the constituent of atom. These particles were discovered by Chadwick (1932) by bombarding a thin sheet of beryllium by α-particles. When electrically neutral particles having a mass slightly greater than that of protons were emitted. He named these particles as **neutrons**. The important properties of all these fundamental particles are given in Table 2.1.

2.2 ATOMIC MODELS

Observations obtained from the experiments mentioned in the previous sections have suggested that Dalton's indivisible atom is composed of sub-atomic particles carrying positive and negative charges. The major problems before the scientists after the discovery of sub-atomic particles were:

- to account for the stability of atom,
- to compare the behaviour of elements in terms of both physical and chemical properties,
- to explain the formation of different kinds of molecules by the combination of different atoms and,
- to understand the origin and nature of the characteristics of electromagnetic radiation absorbed or emitted by atoms.

Millikan's Oil Drop Method

In this method, oil droplets in the form of mist, produced by the atomiser, were allowed to enter through a tiny hole in the upper plate of electrical condenser. The downward motion of these droplets was viewed through the telescope, equipped with a micrometer eye piece. By measuring the rate of fall of these droplets, Millikan was able to measure the mass of oil droplets. The air inside the chamber was ionized by passing a beam of X-rays through it. The electrical charge on these oil droplets was acquired by collisions with gaseous ions. The fall of these charged oil droplets can be retarded, accelerated or made stationary depending upon the charge on the droplets and the polarity and strength of the voltage applied to the plate. By carefully measuring the effects of electrical field strength on the motion of oil droplets, Millikan concluded that the magnitude of electrical charge, q, on the droplets is always an integral multiple of the electrical charge, e, that is, $q = n$ e, where n = 1, 2, 3... .

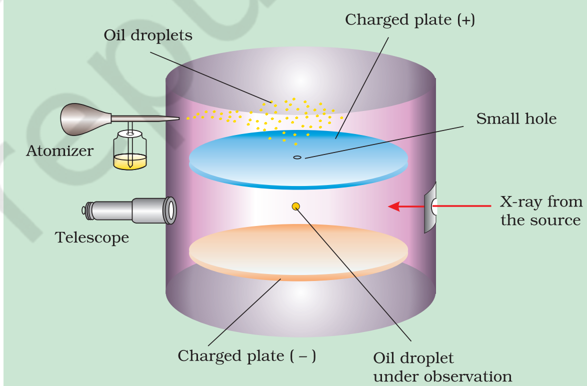


Fig. 2.3 *The Millikan oil drop apparatus for measuring charge 'e'. In chamber, the forces acting on oil drop are: gravitational, electrostatic due to electrical field and a viscous drag force when the oil drop is moving.*

Table 2.1 Properties of Fundamental Particles

Name	Symbol	Absolute charge/C	Relative charge	Mass/kg	Mass/u	Approx. mass/u
Electron	e	-1.602176×10^{-19}	–1	9.109382×10^{-31}	0.00054	0
Proton	p	$+1.602176\times10^{-19}$	+1	1.6726216×10^{-27}	1.00727	1
Neutron	n	0	0	1.674927×10^{-27}	1.00867	1

Different atomic models were proposed to explain the distributions of these charged particles in an atom. Although some of these models were not able to explain the stability of atoms, two of these models, one proposed by J.J. Thomson and the other proposed by Ernest Rutherford are discussed below.

2.2.1 Thomson Model of Atom

J. J. Thomson, in 1898, proposed that an atom possesses a spherical shape (radius approximately 10^{-10} m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement (Fig. 2.4). Many different names are given to this model, for example, **plum pudding, raisin pudding or watermelon**. This model

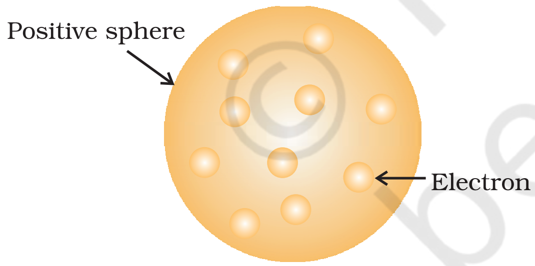


Fig.2.4 *Thomson model of atom*

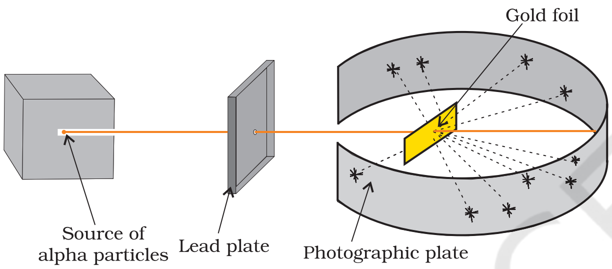
can be visualised as a pudding or watermelon of positive charge with plums or seeds (electrons) embedded into it. *An important feature of this model is that the mass of the atom is assumed to be uniformly distributed over the atom.* Although this model was able to explain the overall neutrality of the atom, but was not consistent with the results of later experiments. Thomson was awarded Nobel Prize for physics in 1906, for his theoretical and experimental investigations on the conduction of electricity by gases.

In the later half of the nineteenth century different kinds of rays were discovered, besides those mentioned earlier. Wilhalm Röentgen (1845-1923) in 1895 showed that when electrons strike a material in the cathode ray tubes, produce rays which can cause fluorescence in the fluorescent materials placed outside the cathode ray tubes. Since Röentgen did not know the nature of the radiation, he named them X-rays and the name is still carried on. It was noticed that X-rays are produced effectively when electrons strike the dense metal anode, called targets. These are not deflected by the electric and magnetic fields and have a very high penetrating power through the matter and that is the reason that these rays are used to study the interior of the objects. These rays are of very short wavelengths (~0.1 nm) and possess electro-magnetic character (Section 2.3.1).

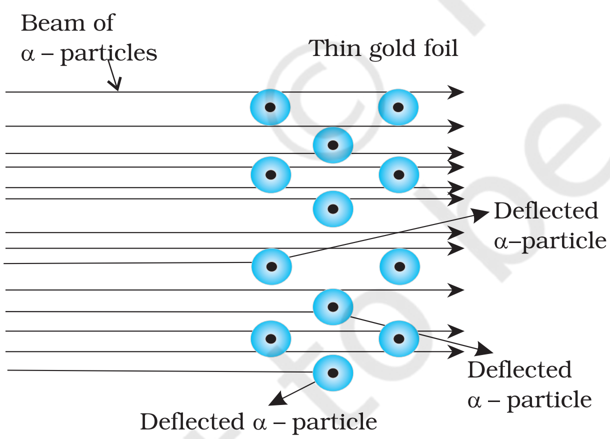
Henri Becqueral (1852-1908) observed that there are certain elements which emit radiation on their own and named this phenomenon as **radioactivity** and the elements known as **radioactive elements.** This field was developed by Marie Curie, Piere Curie, Rutherford and Fredrick Soddy. It was observed that three kinds of rays i.e., α, β- and γ-rays are emitted. Rutherford found that α-rays consists of high energy particles carrying two units of positive charge and four unit of atomic mass. He concluded that α- particles are helium nuclei as when α-particles combined with two electrons yielded helium gas. β-rays are negatively charged particles similar to electrons. The γ-rays are high energy radiations like X-rays, are neutral in nature and do not consist of particles. As regards penetrating power, α-particles are the least, followed by β-rays (100 times that of α–particles) and γ-rays (1000 times of that α-particles).

2.2.2 Rutherford's Nuclear Model of Atom

Rutherford and his students (Hans Geiger and Ernest Marsden) bombarded very thin gold foil with α–particles. Rutherford's famous **α–particle scattering experiment** is represented in Fig. 2.5. A stream of high energy α–particles from a radioactive source was directed at a thin foil (thickness ~ 100 nm) of gold metal. The thin gold foil had a circular fluorescent zinc sulphide screen around it. Whenever α–particles struck the screen, a tiny flash of light was produced at that point.



A. *Rutherford's scattering experiment*



B. *Schematic molecular view of the gold foil*

Fig. 2.5 *Schematic view of Rutherford's scattering experiment. When a beam of alpha (α) particles is "shot" at a thin gold foil, most of them pass through without much effect. Some, however, are deflected.*

The results of scattering experiment were quite unexpected. According to Thomson model of atom, the mass of each gold atom in the foil should have been spread evenly over the entire atom, and α–particles had enough energy to pass directly through such a uniform distribution of mass. It was expected that the particles would slow down and change directions only by a small angles as they passed through the foil. It was observed that:

(i) most of the α–particles passed through the gold foil undeflected.

(ii) a small fraction of the α–particles was deflected by small angles.

(iii) a very few α–particles (~1 in 20,000) bounced back, that is, were deflected by nearly 180°.

On the basis of the observations, Rutherford drew the following conclusions regarding the structure of atom:

(i) Most of the space in the atom is empty as most of the α–particles passed through the foil undeflected.

(ii) A few positively charged α–particles were deflected. The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had presumed. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α–particles.

(iii) Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The radius of the atom is about 10^{-10} m, while that of nucleus is 10^{-15} m. One can appreciate this difference in size by realising that if a cricket ball represents a nucleus, then the radius of atom would be about 5 km.

On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom. According to this model:

(i) The positive charge and most of the mass of the atom was densely concentrated in extremely small region. This very small portion of the atom was called **nucleus** by Rutherford.

(ii) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called **orbits**. Thus, Rutherford's model of atom resembles the solar system in which the nucleus plays the role of sun and the electrons that of revolving planets.

(iii) Electrons and the nucleus are held together by electrostatic forces of attraction.

2.2.3 Atomic Number and Mass Number

The presence of positive charge on the nucleus is due to the protons in the nucleus. As established earlier, the charge on the proton is equal but opposite to that of electron. The number of protons present in the nucleus is equal to atomic number (Z). For example, the number of protons in the hydrogen nucleus is 1, in sodium atom it is 11, therefore their atomic numbers are 1 and 11 respectively. In order to keep the electrical neutrality, the number of electrons in an atom is equal to the number of protons (atomic number, Z). For example, number of electrons in hydrogen atom and sodium atom are 1 and 11 respectively.

Atomic number (Z) = number of protons in the nucleus of an atom
= number of electrons in a nuetral atom (2.3)

While the positive charge of the nucleus is due to protons, the mass of the nucleus, due to protons and neutrons. As discussed earlier protons and neutrons present in the nucleus are collectively known as **nucleons**. The total number of nucleons is termed as **mass number (A)** of the atom.

mass number (A) = number of protons (Z) + number of neutrons (n) (2.4)

2.2.4 Isobars and Isotopes

The composition of any atom can be represented by using the normal element symbol (X) with super-script on the left hand side as the atomic mass number (A) and subscript (Z) on the left hand side as the atomic number (i.e., ${}^{A}_{Z}X$).

Isobars are the atoms with same mass number but different atomic number for example, ${}^{14}_{6}C$ and ${}^{14}_{7}N$. On the other hand, atoms with identical atomic number but different atomic mass number are known as **Isotopes**. In other words (according to equation 2.4), it is evident that difference between the isotopes is due to the presence of different number of neutrons present in the nucleus. For example, considering of hydrogen atom again, 99.985% of hydrogen atoms contain only one proton. This isotope is called **protium (${}^{1}_{1}H$)**. Rest of the percentage of hydrogen atom contains two other isotopes, the one containing 1 proton and 1 neutron is called **deuterium** (${}^{2}_{1}D$, 0.015%) and the other one possessing 1 proton and 2 neutrons is called **tritium (${}^{3}_{1}T$)**. The latter isotope is found in trace amounts on the earth. Other examples of commonly occuring isotopes are: carbon atoms containing 6, 7 and 8 neutrons besides 6 protons (${}^{12}_{6}C$, ${}^{13}_{6}C$, ${}^{14}_{6}C$); chlorine atoms containing 18 and 20 neutrons besides 17 protons (${}^{35}_{17}Cl$, ${}^{37}_{17}Cl$).

Lastly an important point to mention regarding isotopes is that *chemical properties of atoms are controlled by the number of electrons, which are determined by the number of protons in the nucleus.* Number of neutrons present in the nucleus have very little effect on the chemical properties of an element. Therefore, all the isotopes of a given element show same chemical behaviour.

Problem 2.1

Calculate the number of protons, neutrons and electrons in $^{80}_{35}Br$.

Solution

In this case, $^{80}_{35}Br$, Z = 35, A = 80, species is neutral

Number of protons = number of electrons = Z = 35

Number of neutrons = 80 – 35 = 45, (equation 2.4)

Problem 2.2

The number of electrons, protons and neutrons in a species are equal to 18, 16 and 16 respectively. Assign the proper symbol to the species.

Solution

The atomic number is equal to number of protons = 16. The element is sulphur (S).

Atomic mass number = number of protons + number of neutrons

= 16 + 16 = 32

Species is not neutral as the number of protons is not equal to electrons. It is anion (negatively charged) with charge equal to excess electrons = 18 – 16 = 2. Symbol is $^{32}_{16}S^{2-}$.

Note : Before using the notation $^{A}_{Z}X$, find out whether the species is a neutral atom, a cation or an anion. If it is a neutral atom, equation (2.3) is valid, i.e., number of protons = number of electrons = atomic number. If the species is an ion, determine whether the number of protons are larger (cation, positive ion) or smaller (anion, negative ion) than the number of electrons. Number of neutrons is always given by A–Z, whether the species is neutral or ion.

2.2.5 Drawbacks of Rutherford Model

As you have learnt above, Rutherford nuclear model of an atom is like a small scale solar system with the nucleus playing the role of the massive sun and the electrons being similar to the lighter planets. When classical mechanics* is applied to the solar system, it shows that the planets describe well-defined orbits around the sun. The gravitational force between the planets is given by the expression $\left(G.\frac{m_1m_2}{r^2}\right)$ where m_1 and m_2 are the masses, r is the distance of separation of the masses and G is the gravitational constant. The theory can also calculate precisely the planetary orbits and these are in agreement with the experimental measurements.

The similarity between the solar system and nuclear model suggests that electrons should move around the nucleus in well defined orbits. Further, the coulomb force (kq_1q_2/r^2 where q_1 and q_2 are the charges, r is the distance of separation of the charges and k is the proportionality constant) between electron and the nucleus is mathematically similar to the gravitational force. However, when a body is moving in an orbit, it undergoes acceleration even if it is moving with a constant speed in an orbit because of changing direction. So an electron in the nuclear model describing planet like orbits is under acceleration. According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation (This feature does not exist for planets since they are uncharged). Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink. Calculations show that it should take an electron only 10^{-8} s to spiral into the nucleus. But this does not happen. Thus, the Rutherford model cannot explain the stability of an atom. If the motion of an electron is described on the basis of the classical mechanics and electromagnetic theory, you may ask that since the motion of electrons in orbits is leading to the instability of the atom, then why not consider electrons as stationary

* *Classical mechanics is a theoretical science based on Newton's laws of motion. It specifies the laws of motion of macroscopic objects.*

around the nucleus. If the electrons were stationary, electrostatic attraction between the dense nucleus and the electrons would pull the electrons toward the nucleus to form a miniature version of Thomson's model of atom.

Another serious drawback of the Rutherford model is that it says nothing about distribution of the electrons around the nucleus and the energies of these electrons.

2.3 DEVELOPMENTS LEADING TO THE BOHR'S MODEL OF ATOM

Historically, results observed from the studies of interactions of radiations with matter have provided immense information regarding the structure of atoms and molecules. Neils Bohr utilised these results to improve upon the model proposed by Rutherford. Two developments played a major role in the formulation of Bohr's model of atom. These were:

(i) Dual character of the electromagnetic radiation which means that radiations possess both wave like and particle like properties, and

(ii) Experimental results regarding atomic spectra.

First, we will discuss about the duel nature of electromagnetic radiations. Experimental results regarding atomic spectra will be discussed in Section 2.4.

2.3.1 Wave Nature of Electromagnetic Radiation

In the mid-nineteenth century, physicists actively studied absorption and emission of radiation by heated objects. These are called thermal radiations. They tried to find out of what the thermal radiation is made. It is now a well-known fact that thermal radiations consist of electromagnetic waves of various frequencies or wavelengths. It is based on a number of modern concepts, which were unknown in the mid-nineteenth century. First active study of thermal radiation laws occured in the 1850's and the theory of electromagnetic waves and the emission of such waves by accelerating charged particles was developed in the early 1870's by James Clerk Maxwell, which was experimentally confirmed later by Heinrich Hertz. Here, we will learn some facts about electromagnetic radiations.

James Maxwell (1870) was the first to give a comprehensive explanation about the interaction between the charged bodies and the behaviour of electrical and magnetic fields on macroscopic level. He suggested that when electrically charged particle moves under accelaration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves called **electromagnetic waves** or **electromagnetic radiation**.

Light is the form of radiation known from early days and speculation about its nature dates back to remote ancient times. In earlier days (Newton) light was supposed to be made of particles (corpuscules). It was only in the 19th century when wave nature of light was established.

Maxwell was again the first to reveal that light waves are associated with oscillating electric and magnetic character (Fig. 2.6).

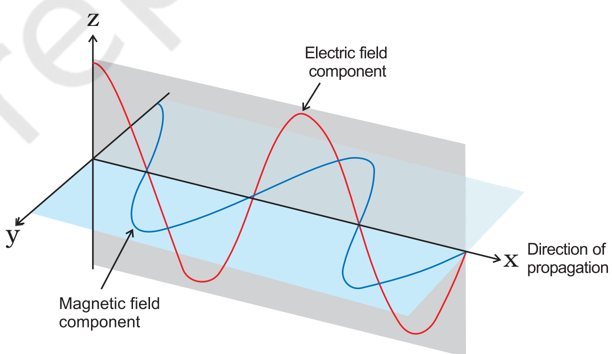


Fig.2.6 *The electric and magnetic field components of an electromagnetic wave. These components have the same wavelength, frequency, speed and amplitude, but they vibrate in two mutually perpendicular planes.*

Although electromagnetic wave motion is complex in nature, we will consider here only a few simple properties.

(i) The oscillating electric and magnetic fields produced by oscillating charged particles are perpendicular to each other and both are perpendicular to the direction of propagation of the wave. Simplified picture of electromagnetic wave is shown in Fig. 2.6.

(ii) Unlike sound waves or waves produced in water, electromagnetic waves do not require medium and can move in vacuum.

(iii) It is now well established that there are many types of electromagnetic radiations, which differ from one another in wavelength (or frequency). These constitute what is called **electromagnetic spectrum** (Fig. 2.7). Different regions of the spectrum are identified by different names. Some examples are: radio frequency region around 10^6 Hz, used for broadcasting; microwave region around 10^{10} Hz used for radar; infrared region around 10^{13} Hz used for heating; ultraviolet region around 10^{16}Hz a component of sun's radiation. The small portion around 10^{15} Hz, is what is ordinarily called **visible light**. It is only this part which our eyes can see (or detect). Special instruments are required to detect non-visible radiation.

(iv) Different kinds of units are used to represent electromagnetic radiation.

These radiations are characterised by the properties, namely, frequency (ν) and wavelength (λ).

The SI unit for frequency (ν) is hertz (Hz, s^{-1}), after Heinrich Hertz. It is defined as the number of waves that pass a given point in one second.

Wavelength should have the units of length and as you know that the SI units of length is meter (m). Since electromagnetic radiation consists of different kinds of waves of much smaller wavelengths, smaller units are used. Fig. 2.7 shows various types of electro-magnetic radiations which differ from one another in wavelengths and frequencies.

In vaccum all types of electromagnetic radiations, regardless of wavelength, travel at the same speed, i.e., 3.0×10^8 m s^{-1} (2.997925×10^8 ms^{-1}, to be precise). This is called **speed of light** and is given the symbol 'c'. The frequency (ν), wavelength (λ) and velocity of light (c) are related by the equation (2.5).

$$c = \nu \lambda \tag{2.5}$$

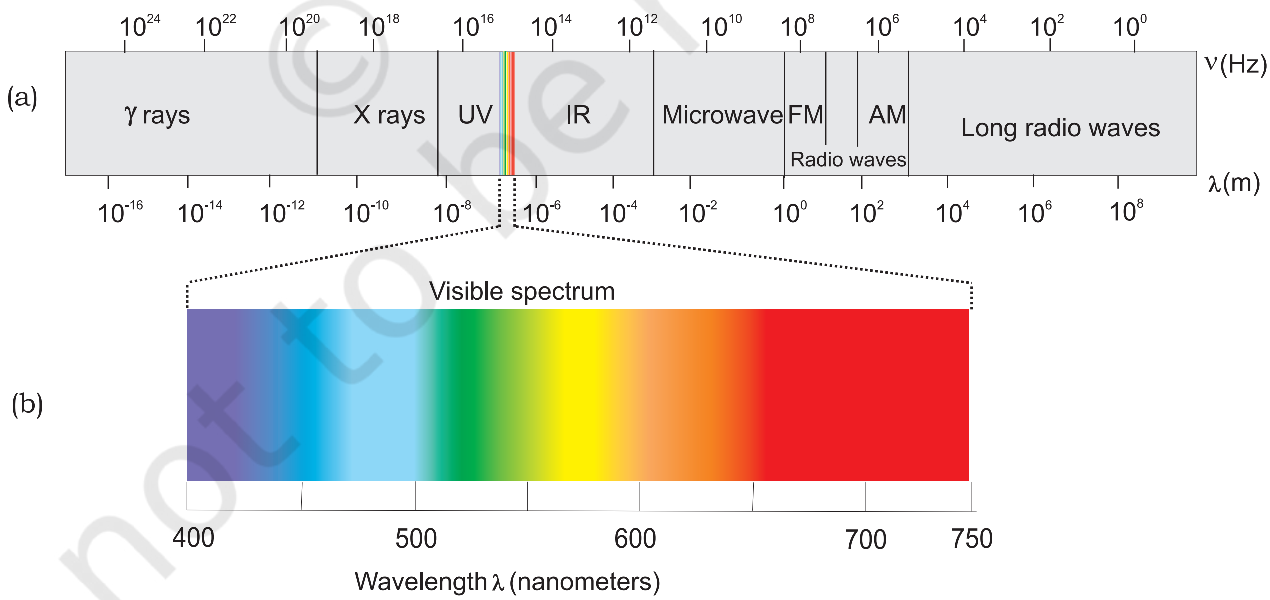


Fig. 2.7 *(a) The spectrum of electromagnetic radiation. (b) Visible spectrum. The visible region is only a small part of the entire spectrum.*