

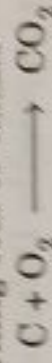




elements in the same proportion. This law is sometimes referred to as law of **definite composition** or **definite proportion**.

Similarly, carbon dioxide can be obtained by a number of methods, such as

(i) By burning coal or candle



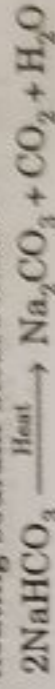
(ii) By heating limestone ( $CaCO_3$ )



(iii) By the action of dilute hydrochloric acid on marble pieces.



(iv) By heating sodium bicarbonate.

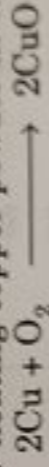


It has been observed that each sample of carbon dioxide contains carbon and oxygen elements in the ratio of 3 : 8 by weight.

Similarly, pure water can be obtained from many sources. Irrespective of the source, water always contains hydrogen and oxygen elements combined together in the ratio of 1 : 8 by weight.

**Experimental verification of the law.** The law can be easily verified in the laboratory. For example, copper oxide (CuO) can be prepared by the following methods :

(i) by heating copper powder in oxygen :



Copper powder

(ii) by heating copper carbonate :



Copper carbonate

(iii) by heating copper nitrate :



Copper nitrate

The weighed quantities of three samples of copper oxide as obtained above were reduced to copper separately in a current of hydrogen :



The weight of copper left behind in each case is noted. From the weight of copper left behind, the weight of oxygen in the samples of copper oxides was calculated.

It was observed that in all the samples, the ratio of copper and oxygen by weight has been found to be the same i.e., 4 : 1. This illustrates the law of constant composition.

#### Limitations of Law of Constant Composition

(i) The law of constant composition does not hold good when a compound is obtained by using different isotopes of the combining elements. For example, when  $CO_2$  is formed from C-12 the ratio between C and O is 12 : 32. But when  $CO_2$  is formed from C-14 isotope, the ratio of C : O is 14 : 32. Thus, *different isotopes of the same element give different mass ratio between combining atoms.*

(ii) The elements may combine in the same ratio but the compounds formed may be different.

## Recent Position of the Law in the Light of Recent Developments

It may be noted that the law of conservation of mass is not strictly valid for nuclear reactions.

According to Einstein theory of relativity, mass and energy are interconvertible. The mass ( $m$ ) and energy ( $E$ ) are related as,  $E = mc^2$  where  $c$  is the velocity of light ( $3 \times 10^8$  m/sec). We know that chemical reactions are generally accompanied by liberation of energy. Since energy and mass are related to each other, this means that the energy must be coming from the reactants. As a result, there should be decrease in mass of the reactants. However, the mass changing into energy for ordinary chemical reactions (according to relation  $m = E/c^2$ ) is extremely small because the value of  $c$  is very large and, therefore, there is no measurable change in mass during chemical processes. However, in case of **nuclear reactions** and **radioactive disintegrations**, the change in mass is quite significant because tremendous amount of energy is released during these reactions. Therefore, the law of conservation of mass does not hold good. In these reactions, some mass gets converted into energy. In such cases, mass and energy is totally conserved though mass and energy are not separately conserved. Thus, law of conservation of mass is modified and the modified law is known as **law of conservation of mass-energy** which states that **mass and energy are interconvertible, but the total mass and energy of the system remains constant.**

## 2. Law of Constant Composition or Definite Proportions

The law of constant composition deals with the composition of various elements present in a compound. It was stated by a French chemist, Joseph Proust, in 1799. Law of constant composition states that

**a pure chemical compound always contains same elements combined together in the same definite proportion by weight.**

Proust worked with two samples of cupric carbonate; one of which was naturally occurring cupric carbonate and other was prepared in the laboratory. He found that the composition of the elements present in two samples of cupric carbonate was same as shown below :

	Percentage	
	Cu	O
Naturally occurring cupric carbonate	51.35	38.91
Cupric carbonate prepared in laboratory	51.35	38.91

The above results show that irrespective of the source, a given compound always contains same



For example, in the compounds  $C_2H_6OH$  and  $CH_3OCH_3$  (both have same molecular formula  $C_2H_6O$ , known as isomers) the ratio of C : H : O is 24 : 6 : 16 or 12 : 3 : 8. Thus, the inverse of the law is not correct.

### 3. Law of Multiple Proportions

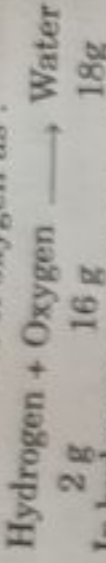
This law was proposed by Dalton in 1803. Law of multiple proportions states that

*when two elements combine to form more than one compound, then the masses of one of the elements which combine with a fixed mass of the other element are in a simple whole number ratio.*

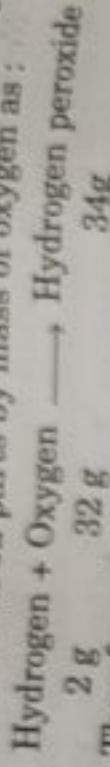
The law may be illustrated by the following examples :

(i) Hydrogen combines with oxygen to form two compounds namely *water* and *hydrogen peroxide*.

In water 2 parts by mass of hydrogen combine with 16 parts by mass of oxygen as :



In hydrogen peroxide, 2 parts by mass of hydrogen combines with 32 parts by mass of oxygen as :



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

(ii) Nitrogen and oxygen combine to form five oxides namely nitrous oxide ( $N_2O$ ), nitric oxide ( $NO$ ), nitrogen trioxide ( $N_2O_3$ ), nitrogen tetroxide ( $N_2O_4$ ) and nitrogen pentoxide ( $N_2O_5$ ). The different weights of oxygen which combine with the fixed weight of nitrogen in all these oxides are calculated.

Oxide	Number of parts by weight of nitrogen	Number of parts by weight of oxygen	Fixed weight of nitrogen (14 parts)	Number of parts by weight of oxygen combining with 14 parts by weight of nitrogen
$N_2O$	28	16	14	8
$NO$	14	16	14	16
$N_2O_3$	28	48	14	24
$N_2O_4$	28	64	14	32
$N_2O_5$	28	80	14	40

The ratio between the different weights of oxygen in different compounds which combine with the same weight of nitrogen (14 parts) is :

$$8 : 16 : 24 : 32 : 40$$

$$\text{or } 1 : 2 : 3 : 4 : 5$$

This is a simple whole number and hence, supports the law.

### Experimental Verification of Law of Multiple Proportions

Copper forms two oxides cuprous oxide ( $Cu_2O$ ) and cupric oxide ( $CuO$ ). 1.00 gm of each oxide of copper ( $CuO$  and  $Cu_2O$  respectively) is heated in a current of hydrogen. Both the oxides react with hydrogen producing metallic copper. From the weight of copper obtained, the respective weights of oxygen in the two compounds are obtained. Then, the different weights of oxygen which combine with the same weight of copper in the two compounds are calculated. These weights are found to bear a simple whole number ratio. Thus, the law has been verified.

### 4. Law of Reciprocal Proportions or Law of Equivalent Proportions

This law was put forward by Richter in 1792. It states that

*when two different elements combine separately with a fixed mass of a third element, the ratio in which they do so will be the same or some simple multiple of the ratio in which they combine with each other.*

In other words, the mass ratio of two elements A and B which combine with the fixed mass of C separately, is either the same or some simple whole number multiple of the mass ratio in which A and B combine together. This law may be illustrated by the following examples :

Consider three elements sulphur, oxygen and hydrogen. Both sulphur and oxygen separately combine to form hydrogen sulphide ( $H_2S$ ) and water ( $H_2O$ ) respectively. They also combine with each other to form sulphur dioxide ( $SO_2$ ) as shown.

According to the law, the ratio of weights of S and O which combine with the same weight of H will either be same or a simple multiple of the ratio in which S and O combine with each other. This may be verified as :

In *hydrogen sulphide* ( $H_2S$ ), 2 parts by weight of hydrogen combine with 32 parts by weight of sulphur.



In water molecule ( $H_2O$ ), 2 parts by weight of hydrogen combine with 16 parts by weight of oxygen.

The ratio of the weights of sulphur and oxygen which, combine separately with the fixed weight (= 2 parts) of hydrogen is,

$$32 : 16 \text{ or } 2 : 1 \quad \dots(i)$$

Now, let us calculate the ratio of sulphur and oxygen in  $SO_2$ .

In sulphur dioxide ( $SO_2$ )

Sulphur and oxygen combine in the ratio of 32 : 32 or 1 : 1...*(ii)*

The two ratios *(i)* and *(ii)* are related to each other as

$$\frac{2}{1} : \frac{1}{1} \text{ or } 2 : 1$$

which are simple multiple of each other.

However, sulphur and oxygen also react to form sulphur trioxide ( $SO_3$ ) which is also in accordance with the law.

In sulphur trioxide ( $SO_3$ )

Sulphur and oxygen combine in the weight ratio of 32 : 48 or 2 : 3

The two ratios *(i)* and *(iii)* are also related to each other as

$$\frac{2}{1} : \frac{2}{3} \text{ or } 3 : 1 \quad \dots(iii)$$

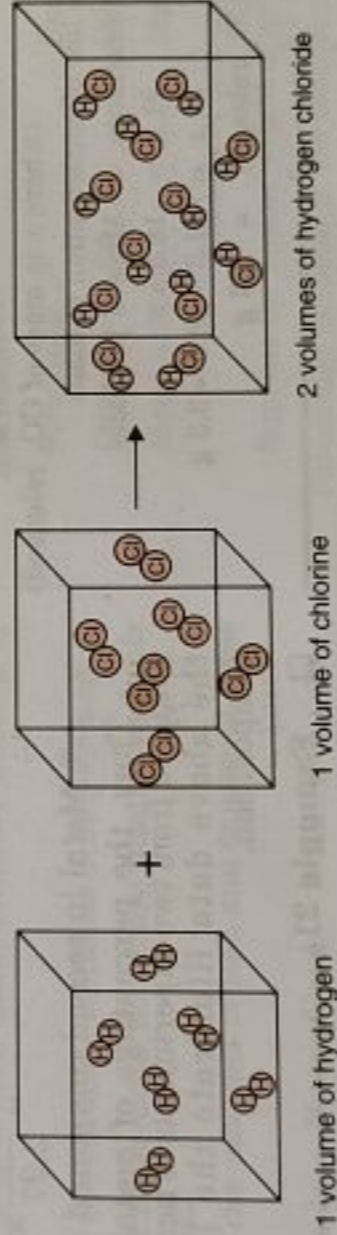
which are simple multiple of each other.

### 5. Gay Lussac's Law of Combining Volumes

Gay Lussac performed a number of experiments on reactions involving gases and found that some regularity exists between the volumes of the gaseous reactants and products. In 1808, he put forward a generalisation known as **Gay Lussac's law of combining volumes**. It states that

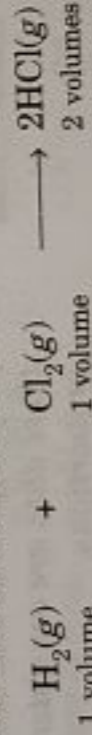
**when gases react together or produced in a chemical reaction, they do so in a simple ratio by volume to one another and to the volumes of the products (if these are also gases) provided all gases are at the same temperature and pressure.**

This law may be illustrated by the following examples :

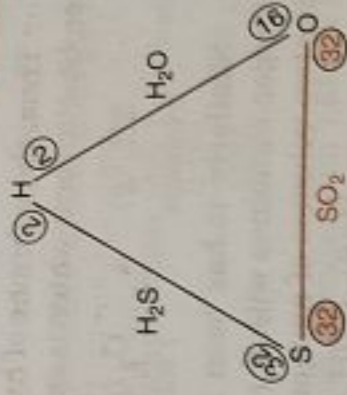
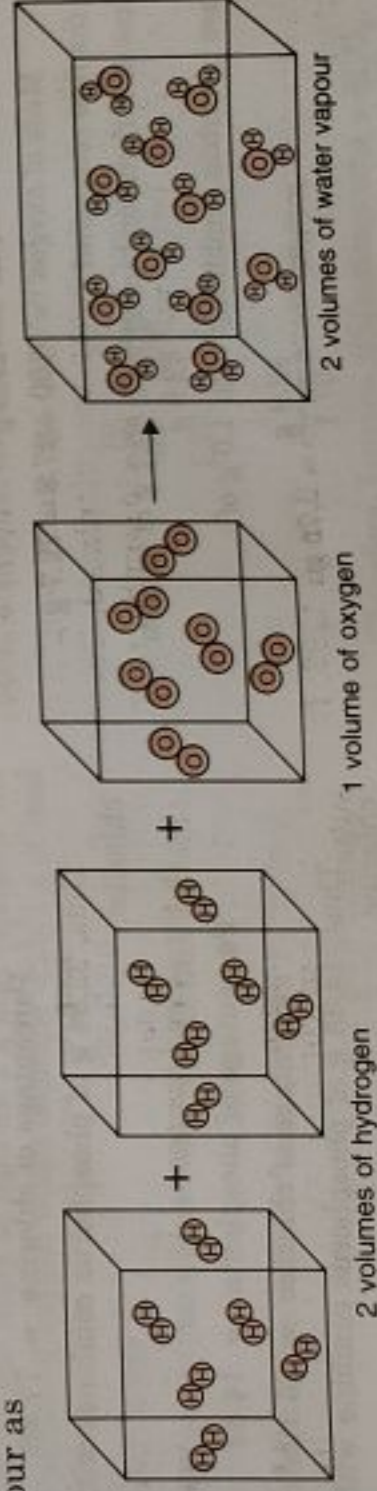


It has been experimentally found that 1 volume of hydrogen reacts with 1 volume of chlorine to give 2 volumes of hydrogen chloride as :

Thus, the volume ratio of hydrogen : chlorine : hydrogen chloride is 1 : 1 : 2. This is a simple whole number ratio and is also in agreement with their molar ratios when they are involved in the reaction.

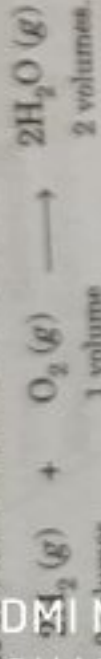


For example, 100 mL of hydrogen combine with 100 mL of chlorine to give 200 mL of hydrogen chloride. Similarly, we observe that 2 volumes of hydrogen combine with 1 volume of oxygen to give 2 volumes of water vapour as

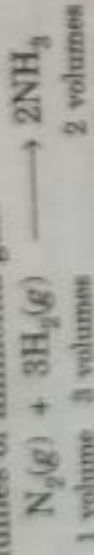




Thus, the volumes of hydrogen and oxygen which combine to form water is in the ratio : 2 : 1 : 2.



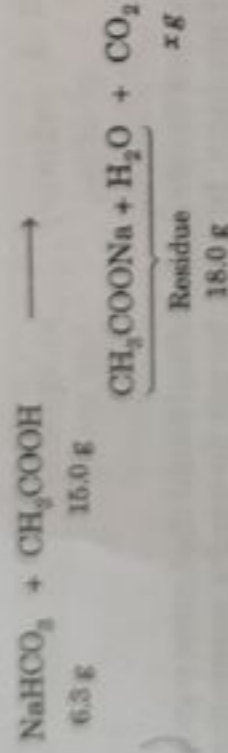
Similarly, it has been found that one volume of nitrogen combines with three volumes of hydrogen to give two volumes of ammonia gas.



**SOLVED EXAMPLES**

**Example 18.** If 6.3 g of  $\text{NaHCO}_3$  are added to 15.0 g of  $\text{CH}_3\text{COOH}$  solution, the residue is found to weigh 18.0 g. What is the mass of  $\text{CO}_2$  released in the reaction?

**Solution:**



$$\begin{aligned} \text{Sum of the mass of reactants} &= \text{Mass of NaHCO}_3 + \text{Mass of CH}_3\text{COOH} \\ &= 6.3 + 15.0 = 21.3 \text{ g} \\ \text{Sum of the mass of products} &= \text{Mass of residue} + \text{Mass of CO}_2 \\ &= (18.0 + x) \text{ g} \end{aligned}$$

According to law of conservation of mass  
(where x is mass of  $\text{CO}_2$  released)

$$\begin{aligned} \text{Mass of reactants} &= \text{Mass of products} \\ 21.3 &= 18.0 + x \\ \text{or } x &= 21.3 - 18.0 = 3.3 \text{ g} \\ \therefore \text{Mass of CO}_2 \text{ released} &= \mathbf{3.3 \text{ g}} \end{aligned}$$

**Example 19.** Carbon and oxygen are known to form two compounds. The carbon content in one of these compounds is 42.9% while in the other, it is 27.3%. Show that the data are in the agreement with the law of multiple proportions.

**N.C.E.R.T.**

**Solution:** In the first compound,

$$\begin{aligned} \text{Mass of carbon} &= 42.9 \text{ g} \\ \text{Mass of oxygen} &= 100 - 42.9 = 57.1 \text{ g} \end{aligned}$$

In the second compound,

$$\begin{aligned} \text{Mass of carbon} &= 27.3 \text{ g} \\ \text{Mass of oxygen} &= 100 - 27.3 = 72.7 \text{ g} \end{aligned}$$

In the first compound,

$$\begin{aligned} \text{Mass of carbon combining with 57.1 g of oxygen} \\ &= 42.9 \text{ g} \end{aligned}$$

Mass of carbon combining with 1.0 g of

$$\text{oxygen} = \frac{42.9 \text{ g}}{57.1} = 0.75 \text{ g}$$

In the second compound,

$$\text{Mass of carbon combining with 72.7 g of oxygen} = 27.3 \text{ g}$$

Mass of carbon combining with 1.0 g of

$$\text{oxygen} = \frac{27.3}{72.7} = 0.375 \text{ g}$$

The ratio of mass of carbon combining with fixed mass of oxygen (i.e., 1 g) is

$$0.75 : 0.375 \text{ or } 2 : 1.$$

This is a simple ratio and therefore, illustrates the law of multiple proportions.

**Example 20.**

2.0 g of a metal burnt in oxygen gave 3.2 g of its oxide. 1.42 g of the same metal heated in steam gave 2.27 g of its oxide. Which law is shown by this data?

**Solution:** In the first compound,

3.2 g of metal oxide contained 2.0 g of metal  
100 g of metal oxide contained metal

$$= \frac{2.0}{3.2} \times 100 = 62.5 \text{ g}$$

$\therefore$  % Metal in first compound = 62.5%

In the second compound,

2.27 g of metal oxide contained metal = 1.42 g  
100 g of metal oxide contained metal

$$= \frac{1.42}{2.27} \times 100 = 62.55 \text{ g}$$

$\therefore$  % Metal in second compound = 62.55%

Thus, the percentage of metal in metal oxide obtained from two experiments is nearly same. Hence, the above data illustrate the law of constant composition.

**Example 21.**

Phosphorus and chlorine form two compounds. The first compound contains 22.54% by mass of phosphorus and 77.46% by mass of chlorine. In the second compound the percentages are 14.88 for phosphorus and 85.12 for chlorine. Show that these data are consistent with the law of multiple proportions.

**Solution:** In the first compound,

$$\text{Percentage of phosphorus} = 22.54$$

$$\text{Percentage of chlorine} = 77.46$$

Thus, 22.54 g of phosphorus combines with 77.46 g of chlorine.

In the second compound,

$$\text{Percentage of phosphorus} = 14.88$$

$$\text{Percentage of chlorine} = 85.12$$

Thus, 14.88 g of phosphorus combine with 85.12 g of chlorine.



Let us fix the mass of phosphorus as 1 g and find the different masses of chlorine which combine with 1 g of phosphorus in two compounds.

*In the first compound,*

Mass of chlorine which combines with 22.54 g of phosphorus = 77.46 g

The mass of chlorine which combines with 1 g of

$$\text{phosphorus} = \frac{77.46}{22.54} = 3.44 \text{ g}$$

*In the second compound,*

Mass of chlorine which combines with 14.88 g of phosphorus = 85.12 g

Mass of chlorine which combines with 1 g of phosphorus

$$= \frac{85.12}{14.88} = 5.72$$

The ratio of the masses of chlorine which combines with the fixed mass of phosphorus (1 g) in the two compounds is

$$3.44 : 5.72$$

$$1 : 1.66 \text{ or } 3 : 5 \text{ (approximately)}$$

This is a simple whole number ratio. Therefore, the data is in agreement with the **law of multiple proportions**.

□ **Example 22**

Three oxides of lead on analysis were found to contain lead as under :

(i) 3.45 g of yellow oxide contains 3.21 g of lead.

(ii) 1.195 g of brown oxide contains 1.035 g of lead.

(iii) 1.77 g of red oxide contains 1.61 g of lead.

Show that these data illustrate law of multiple proportions.

**Solution:** The amounts of lead and oxygen in three oxides are :

$$\begin{aligned} \text{(i) Yellow oxide : Mass of lead} &= 3.21 \text{ g} \\ \text{Mass of oxygen} &= 3.45 - 3.21 \\ &= 0.24 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{(ii) Brown oxide : Mass of lead} &= 1.035 \text{ g} \\ \text{Mass of oxygen} &= 1.195 - 1.035 \\ &= 0.160 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{(iii) Red oxide : Mass of lead} &= 1.61 \text{ g} \\ \text{Mass of oxygen} &= 1.77 - 1.61 \\ &= 0.16 \text{ g} \end{aligned}$$

Let us fix the mass of lead as 1 g and calculate the different weights of oxygen which combine with 1 g of lead in these oxides.

(i) *Yellow oxide*

Mass of oxygen which combines with 3.21 g of lead = 0.24 g

Mass of oxygen which combines with 1 g of lead =  $\frac{0.24}{3.21} = 0.075 \text{ g}$

(ii) *Brown oxide*

Mass of oxygen which combines with 1.035 g of lead = 0.160 g

Mass of oxygen which combines with 1 g of lead =  $\frac{0.160}{1.035} = 0.15 \text{ g}$

(iii) *Red oxide*

Mass of oxygen which combines with 1.61 g of lead = 0.16 g

Mass of oxygen which combines with 1 g of lead

$$= \frac{0.16}{1.61} = 0.10 \text{ g}$$

The ratio of different masses of oxygen which combine with same mass of lead (1 g) in these oxides is :

$$0.075 : 0.15 : 0.10$$

$$3 : 6 : 4$$

This is a simple ratio.

Hence, the data illustrate the law of multiple proportions.

□ **Example 23**

Two oxides of a metal contain 27.6% and 30% of oxygen respectively. If the formula of the first compound is  $M_3O_4$ , find the formula of the second compound.

**Solution:**

First oxide	Second oxide
Oxygen = 27.6%	Oxygen = 30%
Metal = 72.4%	Metal = 70%

Formula of first oxide =  $M_3O_4$

Suppose the atomic weight of metal =  $x$

Percentage of metal in the compound  $M_3O_4$

$$= \frac{3x}{3x + 64} \times 100$$

$$\therefore \frac{3x}{3x + 64} \times 100 = 72.4$$

$$\text{or } 300x = 217.2x + 4633.6$$

$$\text{or } 82.8x = 4633.6 \text{ or } x = 56$$

Now in the second oxide, metal and oxygen are 70% and 30%. Therefore, their atomic ratio will be

M : O

$$\frac{70}{56} : \frac{30}{16}$$

$$1.25 : 1.875$$

$$\text{or } 1 : 1.5$$

$$\text{or } 2 : 3$$

Therefore, formula of the compound =  $M_2O_3$ .