Chapter: Chemicals Arithmetic

Atoms, Molecules and Mole concept

(Skills developed in this Chapter may be tested in examinations. Details of specific methods may be left out)

How do we go about finding the composition of chemical substances or how do we calculate the quantities of chemicals required to produce a certain mass of a substance?

If we mix 1 g of hydrogen with 1 g of oxygen, we would get 2 g of a mixture. This is simple arithmetic. But if we now pass an electric spark through the mixture, a chemical reaction takes place and water is formed. We now have a few questions to answer e.g.

1. What amount of water is produced?
2. Is anything left from the original gases? If so, what is left and how much?

Answers to such questions and many others which are routinely provided by chemists do not come from simple arithmetic but from chemical arithmetic which is a combination of simple arithmetic and chemical logic.

Initial efforts in quantitative analysis of reactions led to various laws of chemical combinations which in turn led to Dalton's atomic theory. This theory gave us a method to analyse the composition of substances and their reactions, in terms of the number of atoms and molecules involved by using molecular formulae and balanced chemical equations.

However, there were two problems (i) Atoms and molecules are so small that they cannot be counted or weighed and (ii) the number of atoms and molecules involved in a reaction is so large that expressing them in actual numbers becomes extremely inconvenient.

The first problem was solved by assuming that the mass of a single hydrogen atom is 1 amu. Thus, the mass of all other atoms could be expressed in amu, without knowing their absolute mass. The present standard is ^{12}C atom which is defined as having a mass of 12 amu and mass of all other atoms are expressed relative to it.

The second problem of number of atoms and molecules involved in a reaction was solved by the mole concept (evolved by Avogadro) which defines one mole as the number of atoms in 12.0000 g of $^{12}_{6}C$.

Combining these two approaches, we have a very convenient method of converting the number of atoms and molecules into their masses and vice versa.

Note that for the purpose of this conversion, we do not need to know how many are actually present in 12.0000 g of ^{12}C. It is simply expressed as one mole (a unit for numbers such as 'dozen' is for 12). Similarly we do not need to know what the actual mass of an atom is. It is simply expressed in amu (a unit for mass such as 'g' or

'ounce'). All that we know is
1 amu $\times$ 1 mol (N_A) = 1 g
and this conversion factor gives us a powerful tool for counting and weighing atoms and molecules without actually seeing them.

Reverting now to the original problem raised here, we know that 1 g of oxygen is only $\frac{1}{16}$ mole of oxygen atoms and 1 g of hydrogen is 1 mole of hydrogen atoms while water has hydrogen and oxygen in a 2:1 ratio of atoms. Thus, $\frac{1}{16}$ mole of oxygen atoms could only combine with $2\times\frac{1}{16}=\frac{1}{8}$ moles of hydrogen atoms or $\frac{1}{8}$ g of hydrogen forming $(1+\frac{1}{8})$ g water. $\frac{7}{8}$ g of hydrogen will remain unreacted.

With respect to 1 amu equaling $\frac{1}{12}$ the mass of a $^{12}_{6}C$ as the IUPAC standard, the mole or Avogadro's number is 6.023 x 10^{23} mol^{-1} i.e. the number of $^{12}_{6}C$ atoms in 12.000 g of $^{12}_{6}C$.

1. Atomic Mass

The mass of an atom compared to $\frac{1}{12}$ the mass of a $^{12}_{6}C$ isotope is the atomic mass expressed in amu .

It is also the mass of Avogadro's number (N_A = 6.023 $\times$ 10^{23}) of atoms.

Note that 1 g atom for different elements mean different mass in grams corresponding to their atomic mass e.g.

1 g atom of C = 12 g ; 1 g atom of O = 16 g

1 g atom of Mg = 24 g ; 1 g atom of K = 39 g, etc.

Remember that one gram atom of any element contains Avogadro's number of atoms. From this it is possible to calculate the mass of a single atom. Thus for ^{12}C, 6.023 $\times 10^{23}$ atoms weigh 12 g

$$\therefore \text{1 atom of carbon weighs} = \frac{12\times1}{6.02\times10^{23}} \text{ g}$$
$$= 1.9924 \times 10^{-23} \text{ g}$$

Determination of atomic mass

i) Dulong and Petit's method

For solid elements,

$$\text{atomic mass} \times \text{specific heat} = 6.4$$

Hence by knowing the specific heat of a solid element, its approximate atomic mass can be calculated.

ii) Methods based on vapour density

In this method the vapour density of a volatile chloride is determined and the following formula applied

$$\text{molecular mass} = 2 \times \text{vapour density}$$

Suppose the valency of element *A* is *x*. Then the formula of its chloride will be ACl_x. If the equivalent mass of element *A* is known then the molecular mass of its chloride would be given by

$$\begin{aligned} \text{molecular mass} &= x \times \text{equivalent mass} + x \times 35.5 \\ &= 2 \times \text{vapour density} \end{aligned}$$

Hence *x* can be found from which it follows that

$$\text{atomic mass} = x \times \text{equivalent mass}$$

iii) For gaseous elements - from molecular mass and atomicity

Atomicity is the number of atoms present in a molecule and can be found by C_p/C_v ratio and

$$\text{molecular mass} = \text{atomicity} \times \text{atomic mass}$$

The molecular mass of gaseous elements may be determined by using Graham's law of diffusion.

2. Molar Mass

The amount of substance that contains the mass in grams numerically equal to its formula weight in amu contains 6.023×10^{23} formula units, or one mole of the substance. Molar mass is numerically equal to the formula weight of the substance and has units g mol^{-1}.

Determination of masses of molecules

i) For gases

a. Methods based on molar volume or vapour density

The volume occupied by one mole or one gram mole of any gas or vapours is called Molar Volume and is 22.4 litres at STP.

In Regnault's method we measure vapour density as

$$\text{Vapour density} = \frac{\text{mass of known volume of gas}}{\text{mass of same volume of hydrogen under identical conditions}}$$

and molar mass = 2 $\times$ vapour density

b. Diffusion method
Using Graham's law of diffusion

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

where
r_A = rate of diffusion of gas A
r_B = rate of diffusion of gas B
M_A = Molar mass of A
M_B = Molar mass of B

ii) For volatile liquids

The following methods are used to determine molecular mass in the case of volatile liquids:

a. Dumas method
b. Hofmann method
c. Victor-Meyer method

All these methods are based on determination of molar volume (or vapour density) of vapours (or gas) produced on heating a volatile liquid. Alternatively, in Victor-Meyer method the volume of air displaced by vapours obtained on heating a known mass of volatile liquid is taken as the volume of vapours.

iii) For non-volatile but soluble substances

Molecular mass of such substances is determined with the help of colligative properties.

a. Osmotic pressure method (Berkeley-Hartley Method, Morse-Fraser Method)

$\Pi = CRT$ where
Π = Osmotic pressure
C = Concentration in mol L^{-1}
R = Solution constant (same as gas constant)
T = Temperature in K

b. Relative lowering of vapour pressure method (Ostwald-Walker Method)

$$\frac{p - p_s}{p} = \frac{m_2/M_2}{m_2/M_2 + m_1/M_1}$$

where p = vapour pressure of solvent

p_s = vapour pressure of solution

m_2 = mass of solute

M_2 = molar mass of solute

m_1 = mass of solvent

M_1 = molar mass of solvent

c. Elevation of boiling point method (Landsberger method)

$$M_2 = \frac{k_b m_2}{m_1 \Delta T_b}$$

where M_2 = molar mass of solute

m_2 = mass of solute

m_1 = mass of solvent

ΔT_b = Elevation in boiling point

k_B = molal elevation or ebulioscopic constant

d. Depression of freezing point method (Beckmann method and Rast Camphor method)

$$M_2 = \frac{k_f m_2}{m_1 \Delta T_f}$$

where M_2 = molar mass of solute

and m_2 = mass of solute

m_1 = mass of solvent

ΔT_f = Depression in freezing point

K_f = Molal depression point or cryoscopic constant

iv) For non-volatile and insoluble substances

The molecular masses of substances like polymers, proteins, etc. which have a very high molecular mass and are non-volatile and insoluble, cannot be determined by any of the above methods.

For these substances approximate molecular mass is determined by the Sedimentation Method which is based on the fact that rate of settling of particles is dependent on their mass.

Operational Skills:

1. Counting atoms

Example

Calculate the total number of atoms present in each of the following cases:

a. 150 g Na_2CO_3
b. 8.8×10^4 amu of CO_2
c. One litre of a mixture of C_3H_8 and C_2H_4 at STP in 1:1 molar ratio
[Note: One mole of any gas at STP occupies 22.4 litre (molar volume)]

Answer

a. Molar mass of $Na_2CO_3 = 2 \times 23 + 12 + 3 \times 16 = 106\ g\ mol^{-1}$

$$150\ g\ Na_2CO_3 \times \frac{1\ mol\ Na_2CO_3}{106\ g\ Na_2CO_3} = 1.415\ mol\ Na_2CO_3$$

Atoms of Na

$= 2 \times 1.415 \times 6.02 \times 10^{23} = 1.704 \times 10^{24}$

Atoms of C

$= 1.415 \times 6.02 \times 10^{23} = 0.8518 \times 10^{24}$

Atoms of O

$= 3 \times 1.415 \times 6.02 \times 10^{23} = 2.555 \times 10^{24}$

Total Atoms

$= (1.704 + 0.8518 + 2.555) \times 10^{24} = 5.1108 \times 10^{24}$ atoms

b. 8.8×10^4 amu CO_2 (molar mass of CO_2 = 44 g mol^{-1})

$$8.8 \times 10^4\ amu \times \frac{1\ molecule\ CO_2}{44\ amu\ CO_2} \times \frac{3\ atoms}{1\ molecule\ CO_2}$$

$= 0.6 \times 10^4$ atoms

c.

$$\text{Number of moles of } C_3H_8 = \frac{1}{2} \times \frac{1}{22.4} = \frac{1}{44.8}$$

One molecule of C_3H_8 has 3C + 8H = 11 atoms

$$\text{Number of atoms in } C_3H_8 = \frac{1}{44.8} \times 11 \times 6.02 \times 10^{23}$$

$$\text{Number of moles of } C_2H_4 = \frac{1}{2} \times \frac{1}{22.4} = \frac{1}{44.8}$$

One molecule of C_2H_4 has 2C + 4H = 6

$$\text{Number of atoms from } C_2H_4 = 6 \times \frac{1}{44.8} \times 6.02 \times 10^{23}$$

$$\text{Total number of atoms} = \frac{(6 + 11) \times 6.02}{44.8} \times 10^{23} = 2.28 \times 10^{23} \text{ atoms}$$

atoms