Empirical and Molecular Formulae

(Skills developed in this Chapter may be tested in examinations)

The simplest formula that expresses the relative number of atoms of different elements in a compound is called its empirical formula.
Thus, for glucose (molecular formula $C_6H_{12}O_6$), the empirical formula is CH_2O and for borane (molecular formula B_2H_6) the empirical formula is BH_3 and for sand it is SiO_2.
Empirical formula of a compound is determined from the mass composition data of all the elements present in it.

Molecular Formula

Molecular formula of a compound shows the exact number of atoms of various elements present in it. If atomic masses of all atoms constituting the compound are added, we get the molecular mass (it is an additive property).
Molecular mass is always a simple whole number multiple of empirical formula.

molecular formula = $n \times$ empirical formula and

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

For compounds like $FeSO_4.7H_2O$ or aluminum, etc. it is not proper to use the molecular mass because there is no molecule as such. A better term is 'formula mass' which is commonly used for such inorganic compounds.

Determining Empirical Formula from Composition of a Compound

If we know the mass of different elements in a given sample of a compound and we also know the atomic mass of the element, then we can find the respective number of their moles in the sample. The ratio of their moles gives us the empirical formula of the sample.

Example
A compound contains 43.4% sodium, 11.3% carbon and rest oxygen. Find its empirical formula.

Element	%	Atomic mass	Relative number of atoms	Simplest ratio
Sodium	43.4	23	$\frac{43.4}{23} = 1.887$	$\frac{1.887}{0.94} = 2$
Carbon	11.3	12	$\frac{11.3}{12} = 0.94$	$\frac{0.94}{0.94} = 1$
Oxygen	100-(43.4 + 11.3)	16	$\frac{45.3}{16} = 2.83$	$\frac{2.83}{0.94} = 3$

Simplest ratio Na : C : O : : 2 : 1 : 3
Hence, empirical formula is Na_2CO_3

Note:
If the simplest ratio is not a whole number e.g. 2.06, then it may be taken as 2 but if it is 2.48 or so, then the entire ratio must be multiplied by a suitable factor (in this case 2) to make it nearer to a whole number. Why? Because atoms always combine in whole numbers and not in fractions.

Example
A 4.679 g sample of pure compound contains 2.65×10^{22} atoms of carbon, 0.132 mol of oxygen atom and the rest sodium. Calculate the empirical formula of the compound.
Answer

$$2.65\times10^{22}\text{ atoms of C} \times \frac{1\text{ mol C}}{6.02\times10^{23}\text{ atoms C}} \times \frac{12\text{ g C}}{1\text{ mol C}} = 0.528\text{ g C}$$

$$0.132\text{ mol O} \times \frac{16\text{ g O}}{1\text{ mol O}} = 2.112\text{ g O}$$

$$\text{mass of Na} = \text{mass of sample} - \text{mass of C} - \text{mass of O}$$
$$= 4.679 - (0.527 + 2.112) = 2.04\text{ g Na}$$

Element	Mass in 4.679 g	Atomic mass	Relative number of atoms	Simplest ratio
Na	2.04	23	$\frac{2.04}{23} = 0.086$	$\frac{0.086}{0.044} = 2$
C	0.527	12	$\frac{0.527}{12} = 0.044$	$\frac{0.044}{0.044} = 1$
O	2.112	16	$\frac{2.112}{16} = 0.132$	$\frac{0.132}{0.044} = 3$

Hence empirical formula is Na_2CO_3

Determination of Relative Atomic Mass from Composition of the Compound

If we know the composition (i.e. mass of different elements in a sample) of a compound and we know the atomic mass of all but one element, we can calculate the unknown atomic mass.

Example
A compound XY_3 contains 0.9677 g of Y and 10.0 g of X. If the atomic mass of Y is 1 amu, find the atomic mass of X.

Answer

Element	Percentage	Atomic mass	Relative no. of atoms	Simplest ratio
X	$\frac{10.0 \times 100}{10.9677} = 91.1768$	x	$\frac{91.1768}{x}$	1
Y	$\frac{0.9666 \times 100}{10.9677} = 8.8232$	1	$\frac{8.8232}{1}$	$\frac{8.8232}{91.1768} = 31$

Hence, x = 31

Determination of Empirical Formula of a Compound from Mass of Reactants and Products in a Chemical Reaction

Example.
When 5.56 g of a sample of $FeSO_4.x\ H_2O$ was mildly heated, 3.04 g of anhydrous $FeSO_4$ was obtained. On heating the anhydrous salt strongly, 1.6 g of a brown residue Fe_pO_q was obtained. Calculate *x*, *p* and *q*.
Answer:

We have $FeSO_4.xH_2O \rightarrow FeSO_4 \rightarrow Fe_pO_q$

5.56 g 3.04 g 1.6 g

Formula mass of $FeSO_4 = 56 + 32 + 4 \times 16 = 152$

Number of moles of $FeSO_4$ in 5.56 g $FeSO_4 . x\ H_2O$

= Number of moles of $FeSO_4$ in 3.04 g

$$= \frac{3.04\ g}{152\ g\ mol^{-1}} = 0.02\ mol$$

Mass of water = 5.56 - 3.04 = 2.52 g

$$\therefore \text{Moles of } H_2O = \frac{2.52\ g}{18\ g\ mol^{-1}} = 0.14\ mol$$

Thus, in the hydrated salt
Moles $FeSO_4$: Moles $H_2O \equiv 1 : x \equiv 0.02 : 0.14 \equiv 1:7$
Thus $x = 7$ and formula is $FeSO_4.7H_2O$
For the empirical formula of Fe_pO_q

We have $n_{Fe} = n_{FeSO_4} = 0.02$

$\therefore$ Mass of iron $= 0.02 \times 56 = 1.12$ g
Thus in 1.6 g of Fe_pO_q we have 1.12 g Fe and (1.6 - 1.12) = 0.48 g O.

Element	Mass in 1.6 g sample	Number of moles in 1.6 g sample	Relative number of moles of atoms
Fe	1.12	$\frac{1.12}{56} = 0.02$	2
O	0.48	$\frac{0.48}{16} = 0.03$	3

Hence $p : q = 2 : 3$ or $p = 2$ and $q = 3$. Formula of oxide is Fe_2O_3

Determination of Atomic Mass from Mass of Reactants and Products in a Chemical Reaction

Just as we can use composition data to determine empirical formula or atomic mass, we can also use data on mass of reactants and products to the same effect. If atomic mass is known, we can find empirical formula and if the empirical formula is known, then we can find atomic mass.

Example

1.12 g of a sample of M_2O_3 was obtained on roasting (heating in air) 1234 g of MS. Find the atomic mass of M.

Answer

Suppose atomic mass of M is x.

$$2\,MS + \frac{7}{2}\,O_2 \rightarrow M_2O_3 + 2SO_2$$

2 (x + 32) (2x + 3 $\times$ 16) Formula mass

$$\frac{\text{Formula mass of MS}}{\text{Formula mass of } M_2O_3} = \frac{\text{mass of MS}}{\text{mass of } M_2O_3}$$

$$\text{or } \frac{2(x+32)}{2x + 3 \times 16} = \frac{1.234}{1.12}$$

2.24x + 71.68 = 2.468x + 59.232

or 0.228x = 12.448

x = 54.596 amu

Example

A pure sample of $NaClO_3$ weighing 5.325 g was heated to get 2.925 g NaCl. This NaCl was dissolved in 100 mL water and 50 mL of this solution was treated with excess $AgNO_3$ to get 3.5875 g precipitate of AgCl. This AgCl, when ignited alone, left a residue of 2.7 g Ag. If the atomic mass of O is 16, what is the atomic mass of Na, Ag and Cl?

Answer

The reaction is $2NaClO_3 \xrightarrow{\Delta} 2NaCl + 3O_2$

Mass loss on heating

5.325 - 2.925 = 2.4 g (which must be due to loss of oxygen).

Atomic mass of oxygen is known. Hence, moles of O_2 (molar mass = 32 g mol^{-1}) formed = $\frac{2.4\text{ g}}{32\text{ g mol}^{-1}} = 0.075$ mol

From the equation, it is clear that 2 mol NaCl is also formed when 3 mol O_2 is formed.

So, moles of NaCl = $\frac{2}{3} \times 0.075$ mol = 0.05 mol

and in reaction

$$NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl$$

$$2\,AgCl \rightarrow 2Ag + Cl_2$$

So relation between moles of NaCl, AgCl and Ag

mol NaCl mol AgCl mol Ag

Out of total NaCl formed and dissolved in 100 mL, only 50 mL is taken for obtaining AgCl.

$\therefore$ mol NaCl $= \frac{0.05}{2} - 0.025 \equiv 0.025$ mol AgCl $\equiv$ 0.025 mol Ag

and moles $= \frac{\text{mass}}{\text{molar mass}}$

For Ag,

Atomic mass of Ag $= \frac{\text{mass}}{\text{Moles}}$

$= \frac{2.7\text{g}}{0.025 \text{ mol}} = 108 \text{ g mol}^{-1}$

$\therefore$ Atomic mass of Cl = 143.5 - 108 = 35.5 g mol^{-1}

For NaCl, molar mass

$= \frac{\text{mass}}{\text{moles}} = \frac{2.925}{2} \times \frac{1}{0.025} = 58.5 \text{ g mol}^{-1}$

$\therefore$ Atomic mass of Na

$= 58.5 - 35.5 = 23 \text{ g mol}^{-1}$

Determination of Empirical Formula of a Metallic Compound from Composition and Specific Heat of the Metal

The specific heat of the metal tells us its approximate atomic mass. Using this data, we get an approximate ratio of moles. Since actual ratio must be simple whole numbers, we can round up the fractional approximate number to the nearest whole number to obtain the correct formula.

Example

Specific heat of a metallic element is 0.2667. If its nitride contains 28% nitrogen find its atomic mass and the formula of nitride.

Atomic mass $\times$ Specific Heat $\simeq 6.4$

Atomic mass $\simeq \frac{6.4}{0.2667} \simeq 23.997$

If nitrogen is 28% then metal is 72% in nitride.

Simplest formula ratio of elements is given by $\frac{\text{percentage}}{\text{atomic mass}}$

For N, $= \frac{28}{14} = 2$

For Metal, $= \frac{72}{23.997} = 3$

Hence formula is M_3N_2.

Using the Mole Concept to Determine Molecular Mass

Example:

The average iron content in human blood protein haemoglobin is 0.333 %. If the number of iron atoms in one molecule of haemoglobin is four, find its molecular mass (Atomic mass of Fe = 56)

Answer:
Since the haemoglobin molecule contains 4 atoms of Fe, the minimum mass of iron in one molecule should be 4 × 56 = 224 g
When 0.333 g Fe is present in 100 g haemoglobin

224 g Fe should be present in $\frac{100 \times 224}{0.333}$ = 6.72 × 10^4 of haemoglobin.

Using Rate of Diffusion Data to Determine Atomic Mass

Example
A gaseous element was found to diffuse four times slower as compared to hydrogen under identical conditions. If the C_p/C_v = 1.4 for the gaseous element, find its atomic mass.
Answer
The ratio C_p/C_v= 1.4 suggests it to be diatomic.
From Graham's law of diffusion

$$\frac{r_x}{r_{H_2}} = \sqrt{\frac{M_{H_2}}{M_x}} \quad \text{or} \quad \frac{1}{4} = \sqrt{\frac{2}{M_x}}$$

So M_x = 32 g mol^{-1}
Since its atomicity is 2
∴ Atomic mass = 16 amu

Using the Concept of Molar Volume to Determine Molecular Mass

Example
In Victor Meyer's method 0.1884 g of a volatile organic compound displaced 55.2 mL of air at 22°C and 750 mmHg pressure. If the aqueous tension of water at 22°C is 20 mm, calculate the molecular mass of the organic compound. If the compound contains 69.77% C, 11.63% H and rest oxygen, find its molecular formula.

Answer
Volume of moist air = 55.2 mL
First calculate volume of dry air at STP applying

$$\frac{P_0V_0}{T_0} = \frac{P_1V_1}{T_1} \text{ or } \frac{760\,\text{mmHg}\ V_0}{273\ \text{K}} = \frac{(750-20)\text{mmHg} \times 55.2\ \text{mL}}{295\ \text{K}}$$

V_0 = 49.07 mL (Volume of dry air)

Mass of substance that will displace 22.4 L of air at STP

$$= \frac{0.1884\text{g} \times 22400\ \text{mL}}{49.07\ \text{mL}} = 86\ \text{g}$$

∴ molar mass of compound is 86 g mol^{-1}.

Element	Atomic mass	%	Relative number of atoms	Atomic ratio	Simple atomic ratio

Carbon	12	69.77	$\frac{69.77}{12} = 5.814$	$\frac{5.814}{1.1625} = 5.001$	5
Hydrogen	1	11.63	$\frac{11.63}{1} = 1$	$\frac{11.63}{1.1625} = 10.004$	10
Oxygen	16	(100 - 96.77 - 11.63) = 18.6	$\frac{18.6}{16} = 1.1625$	$\frac{1.1625}{1.1625} = 1$	1

$\because$ Empirical formula = $C_5H_{10}O$
and Empirical formula mass = $(5 \times 12) + (10 \times 1) + 16 = 86$
It is the same as molar mass.
Hence, the molecular formula is the same as the empirical formula = $C_5H_{10}O$.