TOPIC 8.

CHEMICAL CALCULATIONS II: % composition, empirical formulas.

Percentage composition of elements in compounds.
In Topic 1 it was stated that a given compound always has the same composition by weight regardless of how it was produced. The reason for this is that each compound has a fixed chemical formula which specifies the number of atoms of each of its component elements. For example, the compound glucose of formula $C_6H_{12}O_6$ always has 6 C atoms, 12 H atoms and 6 O atoms in every one of its molecules. Using the mole concept, if the formula of the compound is known, then from the atomic weights of the component elements, the % by weight for each element in the compound can be calculated.
Using glucose as an example,

Molecular formula: $C_6H_{12}O_6$.

Each glucose molecule contains:

6 carbon atoms 12 hydrogen atoms 6 oxygen atoms

∴ an Avogadro number of glucose molecules (1 mole of glucose) contains

6 × Avogadro number (= 6 moles) of C atoms and

12 × Avogadro number (= 12 moles) of H atoms and

6 × Avogadro number (= 6 moles) of O atoms.

1 mole of glucose has a mass (its gram formula weight or molar mass) which is the sum of the gram atomic weights of all of the constituent atoms.

i.e. mass of 1 mole of glucose, $C_6H_{12}O_6 = (6 \times 12.01 + 12 \times 1.01 + 6 \times 16.00)$ g

= 180.18 g (using atomic weight data to 2 decimals)

1 mole of carbon atoms weighs 12.01 g and there are 6 moles of C atoms in 1 mole of glucose, so the mass of carbon in 1 mole of glucose = 6 × 12.01 g = 72.06 g.

and % carbon in $C_6H_{12}O_6 = \frac{72.06}{180.18} \times 100\% = 40.0\%$ by mass.

Similarly, the percentage of hydrogen and oxygen can be calculated as follows:

1 mole of H atoms weighs 1.01 g and there are 12 moles of H atoms in 1 mole of glucose, so the mass of hydrogen in 1 mole of glucose = 12 × 1.01 g = 12.12 g.

% hydrogen $= \frac{12.12}{180.18} \times 100\% = 6.7\%$ by mass.

1 mole of O atoms weighs 16.00 g and there are 6 moles of O atoms in 1 mole of glucose, so the mass of oxygen in 1 mole of glucose = 6 × 16.00 g = 96.00 g.

$$\% \text{ oxygen} = \frac{96.00}{180.18} \times 100\,\% = 53.3\,\% \text{ by mass.}$$

[Note that the sum of the % of all the elements must add up to 100 %.]

Thus the % composition of glucose by mass is

carbon 40.0 % oxygen 53.3 % hydrogen 6.7 %

In this way, the % composition by mass of any compound can be calculated provided that its formula is known.

Example: Calculate the % composition by mass of chloride ion in sodium chloride.

The molar mass of NaCl = 22.99 + 35.45 g = 58.44 g.

From the formula of sodium chloride,

1 mole of NaCl (58.44 g) contains 1 mole of Cl^- (35.45 g).

$$\text{Therefore } \% \text{ by mass of } Cl^- = \frac{35.45}{58.44} \times 100\,\% = 60.67\,\%$$

Determination of empirical formulas of compounds.

Recall that the empirical formula of a compound is the simplest integer ratio of the elements in that compound. The empirical formula of any pure compound can be determined from analytical data giving the percentage composition by mass of the elements present. The calculations involved are simply the reverse of those just done above where, from the empirical or molecular formula, the % by weight of its component elements was deduced. Now, given the % by weight of the component elements, the empirical formula will be deduced. This is best shown by some examples.

Example 1. Analysis of a compound returns the following data for % by mass:

iron (Fe): 63.5 % sulfur (S): 36.5 %

From the data, in 100.0 g of compound there would be 63.5 g of iron combined with 36.5 g of sulfur. The empirical formula expresses the simplest ratio of the relative number of **atoms** of Fe and S present and as one mole of atoms of any element contains N_A atoms of that element, this will be the same as the relative number of **moles** of Fe and S atoms present in the compound. To calculate the number of moles of Fe and of S atoms present in the compound, divide the mass of each of these two constituent elements by their **atomic weights**.

Moles of Fe = mass / atomic weight of Fe = 63.5/55.85 = 1.14 mole of Fe atoms

Moles of S = mass / atomic weight of S = 36.5/32.07 = 1.14 mole of S atoms

Thus the ratio of moles of Fe to moles of S in the compound is

1.14 moles of Fe atoms : 1.14 moles of S atoms.

i.e. $1.14 \times N_A$ Fe atoms: $1.14 \times N_A$ S atoms which on dividing by N_A gives

1.14 Fe atoms:1.14 S atoms.

However, the empirical formula must have integer quantities for all the numbers of atoms in it. In this example, it is obvious that, within the usual allowable experimental error in analytical data of about 0.3 %,
ratio of atoms of Fe : atoms of S = 1.00 : 1.00 and the empirical formula is FeS.

The above calculation is illustrated in the following flow diagram.

iron 63.5 % by mass
= 63.5 g in 100 g of compound

sulfur 36.5 % by mass
= 36.5 g in 100 g of compound

Calculate moles of Fe and S atoms:

63.5 / 55.85 moles of Fe atoms
= 1.14 moles Fe

36.5 / 32.07 moles of S atoms
= 1.14 moles S

As ratio of moles =
ratio of atoms,

$Fe_{1.14}S_{1.14}$

Simplify:

FeS

Example 2. Analysis returns the following data for an unknown compound:

nitrogen: 26.2 % chlorine: 66.4 % hydrogen: 7.5 % by mass.

Determine its empirical formula.

[Note that these percentages add up to 100 %, within the experimental error. If they do not add up to 100 %, the difference is attributed to oxygen for which normally there is no analytical data available.]

In 100.0 g of compound there are 26.2 g of nitrogen, 66.4 g of chlorine and 7.5 g of hydrogen.

To convert to moles of N, Cl and H **atoms**, divide each mass by the **atomic weight of each element**. [A common error is to divide by the molecular weight for species such as N, Cl, O and H which occur in nature as diatomic molecules.]

Moles of N atoms = 26.2/14.01 = 1.87 mole of N **atoms**

Moles of Cl atoms = 66.4/35.45 = 1.87 mole of Cl **atoms**

Moles of H atoms = 7.5/1.008 = 7.4 mole of H **atoms**

$\therefore$ ratio of the number of atoms of N : Cl : H in the compound is 1.87 : 1.87 : 7.4

This time, in order to convert these numbers to integers they must be divided by the highest common factor. A good starting point is to divide each by the smallest number, in this case 1.87.

This provides N : Cl : H = 1.00 : 1.00 : 4.0

Thus the empirical formula is $NClH_4$.

Molecular formulas.
In an earlier Topic, the molecular formula was shown to be a simple multiple of the empirical formula. Once the empirical formula has been deduced, the molecular formula for a compound that exists as molecules can be determined provided that the molecular weight which can also be obtained by experiment is known. Dividing the molecular weight by the empirical formula weight gives the integer by which the empirical formula must be multiplied to obtain the molecular formula. This is illustrated in the next example which also includes the situation where the total of the percentage compositions does not add up to 100 %.

Example 3. An unknown compound whose molecular weight has been determined to be 120 provided the following analytical results:

carbon: 40.0 %   hydrogen: 6.7 %

Determine the empirical and molecular formulas for this compound.

As the total % composition data given = 46.7 %, it is assumed that the balance of the mass is oxygen = (100 – 46.7) % = 53.3 %.

In 100.0 g of compound there would be 40.0 g of carbon, 6.7 g of hydrogen and 53.3 g of oxygen atoms in combination.

The amount of each element present expressed as moles of **atoms** would be

$$C = \frac{40.0}{12.01} = 3.33 \text{ mole of C atoms}$$

$$H = \frac{6.7}{1.008} = 6.6 \text{ mole of H atoms}$$

$$O = \frac{53.3}{16.00} = 3.33 \text{ mole of O atoms}$$

Therefore the ratio of atoms of C : H : O = 3.33 : 6.6 : 3.33

Dividing each by 3.33, the empirical formula is CH_2O.

The empirical formula weight of $CH_2O = 12.01 + 2 \times 1.008 + 16.00 = 30$.

As the experimentally determined molecular weight is 120, then the empirical formula must be multiplied by 120/30 = 4 to obtain the molecular formula.

i.e. the molecular formula is $C_4H_8O_4$.

[Note the use of the word "amount" in these examples. By definition, "amount" is a measure of the quantity of a given substance expressed in moles. This could be compared with, say, "mass" which is a measure of quantity expressed for example in grams, or "time" which is measured for example in seconds]

Test your understanding of this section.
Why aren't the percentages by mass of the constituent elements in a compound related as simple integers?
In determining the empirical formula for a compound containing hydrogen, why is the mass of hydrogen present divided by its atomic weight rather than its molecular weight?
What information is needed in order to deduce the molecular formula of a compound?

Objectives of this Topic.
When you have completed this Topic, including the tutorial questions, you should have achieved the following goals:

1. Understand the basis for calculating the percentage composition of compounds from their molecular formulas and the reverse process, the deduction of molecular formulas from experimentally obtained percentage composition data.

2. Be able to calculate the percentage composition by mass of any compound from its formula.

3. Be able to calculate the empirical formula of a compound from the experimentally derived percentage composition by mass data.

4. Be able to determine the molecular formula for a compound from its empirical formula and its molecular weight.

SUMMARY

The formula for any given compound always has the same number of atoms of each of its constituent elements combined in simple integer ratios. As the atoms of each element always have their own characteristic mass, then it follows that any given compound always has the same percentage composition of each element by mass although, as seen in Topic 7, the masses of each element in the compound are not in simple numerical ratios. Thus for any compound whose empirical formula is known, the percentage composition by mass of each of its constituent elements can be deduced.
Using this process in reverse, if the percentage composition of a compound is available from experiment, then the empirical formula for the compound can be deduced by converting this mass data into relative numbers of moles of each element in the compound. This is done by dividing the mass of each element present in a given mass of compound by that element's gram atomic weigh. The relative number of moles of each element in the compound is the same as the relative number of atoms of each, which when reduced to the simplest integer ratio, is the empirical formula of the compound.
For molecular compounds, the molecular formula is a simple multiple of the empirical formula. If the molecular weight is also available from experiment, then the molecular formula can be deduced by comparing the empirical formula weight with the molecular weight to obtain the required multiple.

TUTORIAL QUESTIONS - TOPIC 8.

1. Determine the percentage by mass of:
   (i) bromide ion in potassium bromide
   (ii) carbon in carbon dioxide
   (iii) sulfur in lead(II) sulfate
   (iv) hydrogen in methane (CH_4)
   (v) hydrogen in ethane (C_2H_6).
   (vi) carbon in carbon monoxide
   (vii) oxide ion in copper(I) oxide
   (viii) oxide ion in copper(II) oxide

2. (i) A compound of molar mass 62 g mol^{-1} contains C, H and O only. Analysis gives 38.7 % carbon and 9.8 % hydrogen by mass.
   Determine (a) the empirical and (b) the molecular formula of the compound.

   (ii) A compound is found to contain the following weight percentages of each element:
   carbon = 52.1 %, hydrogen = 4.4 %, boron = 7.8 %, nitrogen = 10.1 %, chlorine = 25.6 %.
   What is the empirical formula of the compound?

   (iii) (a) What is the empirical formula of a compound containing 40 % sulfur and 60 % oxygen by weight?

   (b) What is its molecular formula if its molecular weight is 240?

   (iv) Derive the empirical formulas of substances having the following percentage compositions by weight:

   (a) Iron 63.5 %; sulfur 36.5 %
   (b) Iron 46.5 %; sulfur 53.4 %
   (c) Iron 53.7 %; sulfur 46.3 %

   (v) A compound is shown to be ionic as it is soluble in water, providing a solution that conducts electricity. Analysis of the compound gave the following percentage composition by weight:
   sodium = 32.4 %; sulfur = 22.6 %; oxygen (by difference) = 45.0 %.
   Derive the empirical formula for this compound.

   (vi) A gas formed by the reaction of N_2F_4 and $S_2O_6F_2$, is found to contain nitrogen 9.5 %, sulfur 20.9 %, and fluorine 38.0 %;
   The remainder was assumed to be oxygen.
   What is the empirical formula of the gas?

3. An iron supplement is used to treat anaemia and 50 mg (i.e. 50×10^{-3} g) of Fe^{2+} is required per tablet. If the iron compound used in the tablet is $FeSO_4.6H_2O$, what mass of this compound would be required per tablet to provide the desired mass of Fe^{2+}?

4. [For those who fancy a challenge.]
The Law of Multiple Proportions states: *"If two elements combine to form two or more compounds, the various weights of one element which combine with a fixed weight of the other element are in a simple ratio of whole numbers."*
The five oxides of nitrogen contain respectively, 63.64 %, 46.67 %, 36.84 %, 30.44 % and 25.93 % by weight of nitrogen. Show that these numbers are in accord with the above law.

ANSWERS TO TUTORIAL TOPIC 8

1. (i) 67.14 %
   (ii) 27.29 %
   (iii) 10.57 %
   (iv) 25.13 %
   (v) 20.11 %
   (vi) 42.88 %
   (vii) 11.19 %
   (viii) 20.11 %

Explanations and Partial Solutions.

(i) Molar mass of KBr = 119.0 g mol^{-1}
Molar mass of Br = 79.90 g mol^{-1}
There is only one Br in the formula for potassium bromide,
$\therefore$ % Br in KBr = (79.90 / 119.0) × 100 = 67.14 %
Note the importance of having the correct formula for the compound, potassium bromide.

(ii) Molar mass of CO_2 = 44.01g mol^{-1}

(iii) Molar mass of $PbSO_4$ = 303.3 g mol^{-1}

(iv) Molar mass of CH_4 = 16.04 g mol^{-1}
Molar mass of H = 1.008 g mol^{-1}
There are four H atoms in each CH_4 molecule,
$\therefore$ % H in methane = [(4 × 1.008) / 16.04] × 100 = 25.13 %

(v) Molar mass of C_2H_6 = 30.07 g mol^{-1}

(vi) Molar mass of CO = 28.01 g mol^{-1}

(vii) Molar mass of Cu_2O = 143.1 g mol^{-1}

(viii) Molar mass of CuO = 79.55 g mol^{-1}

2. (i) (a) CH_3O (b) $C_2H_6O_2$

Worked Solution.

In 100 g compound, mass of carbon = 38.7 g, mass of hydrogen = 9.8 g and mass of oxygen = (100.0 – 38.7 – 9.8) = 51.5 g.
Moles of C atoms = 38.7 / 12.01 = 3.22 mol
Moles of H atoms = 9.8 / 1.008 = 9.72 mol [Note the use of the atomic weight for H as it is the number of moles of H atoms that is required.]
Moles of O atoms = 51.5 / 16.00 = 3.22 mol [Likewise, the atomic weight of O is used so that moles of O atoms is obtained]
∴ ratio of moles of C:H:O = 3.22 : 9.72 : 3.22 = ratio of atoms of C:H:O
Reducing these ratios to integers gives the empirical formula with the ratios of C:H:O = 1.00 : 3.02 : 1.00, which within the allowable error for analysis (0.3%), is CH_3O
The formula mass of $CH_3O = 12.01 + 3 \times 1.008 + 16.00 = 31.0$
Molar mass of the compound is 62 which corresponds to twice the empirical formula mass. ∴ molecular formula is $C_2H_6O_2$.

(ii) C_6H_6BNCl

(iii) (a) SO_3 (b) S_3O_9

(iv) (a) FeS (b) FeS_2 (c) Fe_2S_3

(v) Na_2SO_4

(vi) NSF_3O_3

3. 0.23 g

Worked Solution.

One mole of $FeSO_4.6H_2O$ contains one mole of Fe^{2+}.
∴ moles of $FeSO_4.6H_2O$ = moles of Fe^{2+} required.
Moles $Fe^{2+} = 50 \times 10^{-3} / 55.85 = 8.95 \times 10^{-4}$ mol.
Molar mass of $FeSO_4.6H_2O$ = 260.0 g mol^{-1}.
Mass of $FeSO_4.6H_2O$ required = $8.95 \times 10^{-4} \times 260.0 = 0.23$ g.

4. Take an amount of each compound such that there would be exactly 1.0 g of nitrogen present in each sample. For each compound, calculate the mass of compound taken and thence by difference, the mass of oxygen present.

If 63.64 % is nitrogen, then mass of compound = $\frac{100}{63.64} \times 1.0$ g = 1.57 g
and mass of oxygen = 1.57 − 1.0 = 0.57 g

If 46.67 % is nitrogen, then mass of compound = $\frac{100}{46.67} \times 1.0$ g = 2.14 g
and mass of oxygen = 2.14 − 1.0 = 1.14 g

If 36.84 % is nitrogen, then mass of compound = $\frac{100}{36.84} \times 1.0$ g = 2.71 g
and mass of oxygen = 2.71 − 1.0 = 1.71 g

If 30.44 % is nitrogen, then mass of compound = $\frac{100}{30.44} \times 1.0$ g = 3.29 g
and mass of oxygen = 3.29 − 1.0 = 2.29 g

If 25.93 % is nitrogen, then mass of compound = $\frac{100}{25.93} \times 1.0$ g = 3.86 g
and mass of oxygen = 3.86 − 1.0 = 2.86 g

Thus the ratios of N:O in the various compounds are
0.57 : 1.14 : 1.71 : 2.29 : 2.86
which simplifies to
1 : 2 : 3 : 4 : 5