EMPIRICAL / MOLECULAR FORMULA DETERMINATIONS

These calculations usually centre around the combustion of a fuel containing carbon C, hydrogen H, and oxygen O. The products being carbon dioxide CO_2, and water H_2O. Other **variations** may occur but, essentially, the following steps remain the same.

Volumes of products may be given at non Standard conditions and will either need to be converted to Standard conditions and then to number of moles **or** directly to number of moles using the following relationships.

PV = nRT		n = V / 22.71 @ STP	
P = pressure	kPa	n = no. of moles	
V = volume of gas	Litres	V = volume of gas	Litres
n = no. of moles		STP = standard temperature and pressure	
R= Universal gas constant	8.314	Temperature	^{0}C or 273.1 K
T = temperature	Kelvin (^{0}C + 273.1)	Pressure	100 kPa at STP

STEPS

1. Convert mass of CO_2 to mass of C by multiplying it by mass of C in CO_2 i.e. multiplying by 12.01/(12.01+ 2(16)) i.e. 12.01/44.01

2. Convert mass of H_2O to mass of H by multiplying it by mass of H in H_2O i.e. multiplying by 2(1.008)/(2(1.008) + 16) i.e. 2.016/18.016

3. Subtract the combined mass of C + H from the mass of the fuel to obtain the mass of O i.e. m(O) =m (C, H, O) − m (C, H)

4. Convert mass of C to moles of C. (/12.01 i.e. n =m/M)

5. Convert mass of H to moles of H. (/1.008 i.e. n=m/M)

6. Convert mass of O to moles of O. (/16.00 i.e. n=m/M)

7. Determine the empirical formula by dividing each of the above molar ratios by the smaller of them to give a ratio compared to 1.

   [if decimals such as 0.25 (1/4), 0.33 (1/3), 0.5 (1/2), 0.66 (2/3) or 0.75 (3/4), appear here, be aware that you will need to get rid of these fractions by multiplying, usually, by the denominator to obtain the **smallest whole number ratio**].

8. The molecular formula is a multiple (1x, 2x, 3x etc.) of the empirical formula. This multiple is obtained by dividing the molecular (formula) mass by the empirical formula mass.

Caution: In many of these problems 2 samples of different masses are used. Consequently the number of moles in the two samples will be different. However if you convert the masses of the elements to % mass, then the % mass in both samples will be the same.

Apart from C, H and O many of these compounds will also contain another element such as N, S, Cl, P, Fe etc. These will generally be analysed as follows.

N in the compound may be converted to NH_3 and then reacted with HCl.
$N \rightarrow NH_3 + HCl_{(aq)} = NH_4Cl_{(aq)}$

S in the compound may be converted to $SO_4^{2-}{}_{(aq)}$ and then reacted with Ba^{2+} ions to form $BaSO_{4(s)}$.
$S \rightarrow SO_4^{2-}{}_{(aq)} + Ba^{2+}{}_{(aq)} = BaSO_{4(s)}$

Cl in the compound may be converted to $AgCl_{(s)}$ by reacting it $AgNO_{3(aq)}$
$Cl \rightarrow Cl^-{}_{(aq)} + Ag^+{}_{(aq)} = AgCl_{(s)}$

P in the compound may be converted to $PO_4^{3-}{}_{(aq)}$ and then precipitated as a phosphate or converted to phosphoric acid and then reacted with a base such as NaOH.

Fe might be converted to $Fe^{2+}{}_{(aq)}$ and then reacted with acidified $KMnO_4$ or acidified $K_2Cr_2O_7$.

Worked Example

A 0.5064 g sample of a liquid known to contain only carbon, hydrogen, sulfur and oxygen was thoroughly burned in excess oxygen. The resultant carbon dioxide and water were separated and their mass determined. The sulfur dioxide was catalytically converted into sulfur trioxide which was dissolved in excess aqueous barium chloride precipitating the sulfur as barium sulfate. The mass of carbon dioxide was found to be 0.5702 g, that of the water was 0.3501, and that of the precipitated barium sulfate was 1.5120 g.

Calculate the empirical formula of the compound analysed.

[C, H, O, S] →	CO_2 +	H_2O
0.5064 g	0.5702 g	0.3501g

$m(C)_{\text{in } 0.5064g} = 0.5702 \times 12.01 \div 44.01 = 0.1556$ g
$m(H)_{\text{in } 0.5064g} = 0.3501 \times 2(1.008) \div 18.016 = 0.03917$ g

[C, H, O, S] + $Ba^{2+}{}_{(aq)}$ →	$BaSO_{4(s)}$
0.5064 g	1.512 g

$m(S)_{\text{in } 0.5064g} = 1.512 \times 32.061 \div 233.36 = 0.2077$ g

m(O) = m[C,H,O,S] – m[C,H,S] = 0.5064 – (0.1556+ 0.03917 + 0.2077) g
= 0.10393 g

	C	H	O	S
m =	0.1556	0.03917	0.10393	0.2077
n = m/M	0.1556/12.01	0.03917/1.008	0.10393/16	0.2077/32.06
n =	0.01295	0.03885	0.006495	0.006478
÷ 0.006478	1.99 ≈ 2	5.99 ≈ 6	1	1
Formula	2	6	1	1

Empirical formula = C_2H_6OS

SET 3 Formulae Determinations

1. An organic compound consisting of carbon, hydrogen and oxygen was analysed by combustion. Complete combustion of 0.290 g of the compound gave 0.660 g of carbon dioxide and 0.270 g of water. Calculate the empirical formula of the compound.

2. Citric acid, an alkanoic (carboxylic) acid responsible for the sour taste of lemon juice, contains only carbon hydrogen and oxygen.
   1.383 g of anhydrous citric acid is burned in dry oxygen to give 1.900 g of CO_2 and 0.518 g of H_2O.

   A. Calculate the empirical formula of citric acid.
   B. The molecular mass of citric acid is 192.1. What is its molecular formula?

3. On complete combustion 0.270 g of an alkanone (ketone), a compound of C, H and O, gave 0.612 g of CO_2 and 0.251 g of H_2O.
   Find the empirical formula of the alkanone.

4. A 1.728 g sample of a compound containing magnesium, carbon and oxygen decomposes upon heating, giving gaseous CO_2 and a 0.821 g residue of magnesium oxide. Determine the empirical formula of this compound.

5. Ethylene glycol, the common antifreeze, contains 38.7 % carbon and 9.7 % hydrogen with the balance being oxygen. Calculate the empirical formula. An estimate of the molecular mass can be obtained by determining the lowering of the freezing point of water caused by a measured quantity of the compound; the approximate molecular mass thus determined was 59.
   Determine the molecular formula and the exact molecular mass/draw a possible structure.

6. A white crystalline compound containing only carbon, hydrogen and oxygen was analysed as follows. A 2.76 g sample of the compound when burned in excess oxygen produced 1.93 g of carbon dioxide and 1.18 g of water.

   A. Calculate the empirical formula of the compound.

   B. From further analysis it was established that the molecular mass of the compound was 126.0. What is the compound's molecular formula?

7. Burning a compound of calcium, carbon and nitrogen in oxygen in a combustion train generates calcium oxide (CaO), carbon dioxide (CO_2), nitrogen dioxide (NO_2), and no other substances. A small sample gives 2.389 g of CaO, 1.876 g of CO_2, and 3.921 g of NO_2. Determine the empirical formula of the compound.

8. A sample of 1.000 g of a compound containing carbon and hydrogen reacts with oxygen at elevated temperature to yield 0.692 g of H_2O and 3.381 g of CO_2.

   A. Calculate the masses of C and H in the sample.
   B. Does the compound contain any other elements?
   C. What are the mass percentages of C and H in the compound?
   D. What is the empirical formula of the compound?

SET 4 Formulae Determinations

1. Carminic acid, a naturally occurring red pigment extracted from the cochineal insect, contains only carbon, hydrogen and oxygen. It was commonly used as a dye in the first half of the nineteenth century.

   Carminic acid is 53.66% C and 4.09% H by mass. Its molar mass is 492.34 g. What is the molecular formula of carminic acid?

2. Isobutylene is a hydrocarbon used in the manufacture of synthetic rubber. When 0.847 g isobutylene was analysed by combustion, the gain in mass of the CO_2 absorber was 2.657 g and that of the H_2O absorber was 1.089 g. What is the empirical formula of isobutylene?

3. A white crystalline compound containing only carbon, hydrogen and oxygen was analysed as follows. A 2.76 g sample of the compound when burned in excess oxygen produced 1.93 g of carbon dioxide and 1.18 g of water.

   A. Calculate the empirical formula of the compound.

   C. From further analysis it was established that the molecular mass of the compound was 126.0. What is the compound's molecular formula?

4. A compound contains only carbon, hydrogen, nitrogen and oxygen. Combustion of 0.157 g of the compound produces 0.213 g CO_2 and 0.0310 g H_2O. In another experiment, it is found that 0.103 g of the compound produces 0.0230 g NH_3. What is the empirical formula of the compound?

5. Thiophene is a liquid compound of the elements C, H and S.
   A sample of thiophene weighing 7.96 g was burned in oxygen, giving 16.65 g CO_2.
   Another sample was subjected to a series of reactions that transformed all of the sulphur in the compound to barium sulfate. If 4.31 g of thiophene gave 11.96 g of barium sulfate, what is the empirical formula of thiophene?
   Its molecular mass is 84 amu. What is its molecular formula?
   Given that thiophene is a ring or cyclic compound, draw a possible structural formula.

6. When 1.5173 g of an organic iron compound containing Fe, C, H and O was burned in oxygen, 2.838 g of CO_2 and 0.8122 g of H_2O were produced.
   In a separate experiment to determine the mass % of iron, 0.3355 g of the compound yielded 0.0758 g of Fe_2O_3.
   What is the empirical formula of the compound?

7. An organometallic compound containing nickel, carbon, hydrogen and oxygen was analysed as follows
   A 3.45 g sample of the compound was combusted in excess oxygen.
   It produced 3.44 g of carbon dioxide and 1.06 g of water.
   A second sample of the compound, with a mass of 2.33 g, was treated with H_2S and 1.20 g of nickel sulphide was precipitated.

   A. Determine the empirical formula of the compound.

   B. 5.32 g of the compound was found to be 3.00×10^{-2} mol. Determine the molecular formula of the compound.

SET 5 Formulae Determinations

1. Carminic acid, a naturally occurring red pigment extracted from the cochineal insect, contains only carbon, hydrogen and oxygen. It was commonly used as a dye in the first half of the nineteenth century.

   A. A titration required 18.02 mL of 0.0406 mol L^{-1} NaOH to neutralise 0.3602 g carminic acid.
   Assuming there is only one acidic hydrogen per molecule, what is the molecular mass of carminic acid?

   B. Carminic acid is 53.66% C and 4.09% H by mass.
   What is the molecular formula of carminic acid?

2. Citric acid, an alkanoic (carboxylic) acid responsible for the sour taste of lemon juice, contains only carbon hydrogen and oxygen.
   1.383 g of anhydrous citric acid is burned in dry oxygen to give 1.900 g of CO_2 and 0.518 g of H_2O.

   A. Calculate the empirical formula of citric acid.
   B. The molecular mass of citric acid is 192.1. What is its molecular formula?
   C. Given that one mole of citric acid reacts with three moles of potassium hydroxide, suggest (draw) a structural formula for citric acid.

3. Compound X, a brownish solid, was once considered as an additive in place of lead in petrol. The compound contains carbon, hydrogen, oxygen and iron.

   1.3270 g of X is burned in dry oxygen to give 3.037 g of CO_2, 0.615 g of H_2O and 0.392 g of Fe_2O_3.

   A. Calculate the empirical formula of X.
   B. When 0.375 g of X was decomposed the gas product occupied 71 mL at 30 ^{0}C and 98 kPa. When this decomposition occurs 1 mole of X is known to produce 2 moles of gas. Calculate the molecular mass of X.
   C. What is the molecular formula of X?

4. 24.9g of a hydrated metal sulfate ($M_xSO_4.yH_2O$) are heated to remove all of the water of crystallisation. The mass of this water is 9.00g.

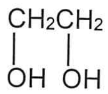
   The remaining 15.9g of M_xSO_4 is dissolved in water and the sulphate is precipitated as $PbSO_4$. This has a mass of 30.3g.

   A. What is the mass of the metal ion, (M)?
   B. If the metal ion and the sulphate ion are combined in the same stoichiometric ratio, what is the metal ion?
   C. What is the empirical formula of the compound $M_xSO_4.yH_2O$?

Formulae Determinations

Answers to SET 3

1. C_3H_6O
2. $C_6H_8O_7$; $C_6H_8O_7$
3. C_3H_6O
4. $MgCO_3$
5. CH_3O $C_2H_6O_2$ 62.068



6. CH_3O_3 $C_2H_6O_6$
7. $CaCN_2$
8. A: 0.923 g C, 0.077 g H
   B: No
   C: 92.3% C, 7.7% H
   D: CH

Answers to SET 4

1. $C_{22}H_{20}O_{13}$
2. CH_2
3. CH_3O_3 $(CH_3O_3)_2$ or $C_2H_6O_6$
4. $C_7H_5N_3O_6$
5. C_4H_4S, C_4H_4S
6. $C_{15}H_{21}O_6Fe$
7. A: $C_4H_6O_4Ni$ B; $C_4H_6O_4Ni$ since $M_r = 177$ = Empirical formula mass

Answers to SET 5

1. 492.34g $C_{22}H_{20}O_{13}$
2. $C_6H_8O_7$; $C_6H_8O_7$; 3 x –COOH groups as 3 moles of OH^- required for neutralisation. Each –COOH group is attached to 3 C singly bonded carbons atoms, an –OH group is attached to the middle C of the 3 singly bonded C atoms. All other bonds are taken up by H's.
3. $C_{14}H_{14}O_2Fe$
4.