Section 003

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Section 006

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The reverse calculations yield the formula of a compound from the % compositions given by experiment

Worked Example:
Calculate the molecular formula of a compound that is 58.77% C, 13.81% H, and 27.40% N, and whose molar mass = 204.4 g mol^{-1}

Assume 100 g of compound

∴ Mass of C = 58.77 g: n(C) = 58.77g/12.01 g mol^{-1} = 4.893 mol

∴ Mass of H = 13.81 g: n(H) = 13.81/1.008 = 13.70 mol

∴ Mass of N = 27.40 g: n(N) = 27.40/14.01 = 1.956 mol

Simplest molar ratio C: H: N = 4.893: 13.70: 1.956

= 2.502: 7.004: 1.000

Making all the numbers into integers:
C:H: N = 5.004: 14.008: 2.000 ~ 5: 14: 2

∴ Empirical formula = $C_5H_{14}N_2$

Molar mass of the empirical formula = 5(12.0) + 14(1.01) +2(14.0) ~ 102 g mol^{-1}

Since the molar mass of the sample = 204.4 g mol^{-1}

∴ Molecular formula = (empirical formula) x 2

∴ Molecular formula = $C_{10}H_{28}N_4$

Empirical Formulas by Experiment

The most common experimental method of obtaining empirical formulas is by **combustion analysis** where every element is converted to is most stable oxide on combustion

$C + O_2 \rightarrow CO_2$

$2H + ½O_2 \rightarrow H_2O$

$S + O_2 \rightarrow SO_2$

Except for N which is converted to N_2

For example: $C_5H_6NO_2 + O_2 \rightarrow CO_2 + H_2O + N_2$

Balanced: $C_5H_6NO_2 + (11/2)O_2 \rightarrow 5CO_2 + 3H_2O + ½N_2$

By weighing the combustion products, one can determine the masses of the elements and the empirical formula of a compound

**** Worked Example**:

A 3.10 g sample of a compound containing C, H, and O only yielded 4.40 g CO_2 and 2.70 g of H_2O. What is the empirical formula?

Mass fraction of C in CO_2: $= m(C)/m(CO_2) = 12.0/44.0$

$\therefore$ mass C in compound = (12.0/44.0)x 4.40 g =1.20 g C

Mass fraction of H in H_2O = $2m(H)/m(H_2O)$ = 2.02/18.0

$\therefore$ mass of H in compound = (2.02/18.0)x2.70 g = 0.303g H

The mass of O in compound can be obtained by the difference: 3.10 -1.2 -0.30 = 1.60 g

$\therefore$ in the unknown compound: # moles C = 1.20/12.0 = 0.1

mole H = 0.303/1.01 = 0.3

moles O = 1.6/16.0 = 0.1

$\therefore$ $C_{0.1}H_{0.3}O_{0.1} = CH_3O$

Chemical Analysis

If a substance does **not** burn in oxygen, then the content of each element in a mixture can be determined by converting each element to a known compound whose mass can be measured

Worked Example:

A gold ring, known to be alloy of Cu and Au weighs 20.0 g.
If all the Cu is converted to 17.8 g $CuCl_2$ what is the % by mass of Au in the ring?

Mass fraction of Cu in $CuCl_2$ = $m(Cu)/m(CuCl_2)$=63.5/136.5

$\therefore$ mass of Cu in 17.8 g $CuCl_2$ = (63.5/136.5)x17.8g = 8.28 g

$\therefore$ mass of Au in the ring = 20.0 – 8.28 = 11.7 g

$\therefore$ % Au = (11.7/20.0) x 100% = 58.5% The ring is 14K gold

The Balanced Equation

A chemical equations indicates the **products** formed from **reactants**

For example:

Na +	Cl_2	→ NaCl
sodium	chlorine	sodium chloride (table salt)

The exact mass consequences of such a reaction can only be calculated if the **number of moles** of all reactants and products are equal

i.e.	2Na	+	Cl_2	→	2 NaCl
mass	2(23.0)		2(35.5)		2(23.0 + 35.5)
		117			117

Calculations based on the mass relationship of **balanced** equations is termed **stoichiometry**

Balancing simple chemical equations is simply a trial-and-error process of balancing individual atoms

1.) balance subscripts of highest subscripts first on the product side
2.) balance the rest of the atoms

For example: $C_4H_8SO_2 + 6\ O_2 \rightarrow 4\ CO_2 + 4\ H_2O + 1\ SO_2$

** Only balanced equations yield correct stoichiometric results

Mass relationships

A correctly balanced equation relates the # molecules, # moles, and the masses of products to reactants

For example:
the combustion of natural gas, methane, CH_4

$$\begin{array}{llll} CH_4 & + \; 2O_2 & \rightarrow \; CO_2 & + \; 2H_2O \\ 16.0 & 2x(32) = 64 & 44 & 2x(18) = 36 \\ & 80.0 & & 80.0 \end{array} \quad \equiv \text{mass balance}$$

The numbers in red are the **ideal combining masses**, that is,
16.0 g CH_4 will react **completely** with 64.0 g of O_2 to yield 44.0 g CO_2 and 36.0 g H_2O

If the masses differ from ideal masses, one can calculate the extent of the reaction

Example:
if 34.0 g CH_4 is burned in an excess of O_2 what is the mass of H_2O produced?

There are **two** general ways of solving stoichiometry problems

i) The mole method

moles CH_4 —2.)→ # moles H_2O

1.) ↑ (from mass CH_4 given) 3.) ↓ (to mass H_2O?)

CH_4 + $2O_2$ → CO_2 + $2H_2O$
mass CH_4 given — mass H_2O?

1.) # moles CH_4 present = 34.0/16.0 = 2.125 mol

2.) # moles H_2O present: $\frac{CH_4}{H_2O} \xrightarrow{\text{ideal ratio}} \frac{1}{2} \xrightarrow{\text{actual}} \frac{2.125}{x}$

x = 4.25 moles H_2O produced

3.) mass H_2O = 4.25 mol x 18.0 g mol^{-1} = 76.5 g

ii) The direct mass method

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Here we determine mass H_2O directly from the mass CH_4

$$\frac{CH_4}{H_2O} \xrightarrow{\text{ideal mass ratio}} \frac{16.0}{36.0} \qquad \xrightarrow{\text{actual}} \frac{34.0}{x}$$

x = 76.5 g

The direct method is quicker for calculations requiring mass calculations, but the mole method is OK too (and it always works)
Both must be done **properly**

Limiting Reagent

Under most real conditions one reactant runs out before the other – termed the limiting reagent (L.R.)

The mass of the L. R. then determines the masses of all the species used/produced.

For example: 4 wagon frames + 12 wheels → 3 wagons. L. R. ≡ wheels

Per Cent Yield

Under experimental conditions the mass of the product is usually less than the theoretical maximum.
The actual yield is expressed as:

$$\%\,\text{yield} = \frac{\text{actual yield}}{\text{maximum yield}} \times 100\%$$

Example:
In the combustion of 34.0 g CH_4 with 100 g O_2 a student collected 48.6 g H_2O. What is the percent yield of this experiment?

1.) Begin with a balanced equation:

	CH_4	+	$2O_2$	→	CO_2	+	$2H_2O$
2.) Ideal combining masses:	**16.0**		**64.0**		**44.0**		**36.0**

3.) Determine which reactant is **limiting**

$$\text{ideal mass ratio} = \frac{CH_4}{O_2} = \frac{16.0}{64.0} = \frac{1}{4.0}$$

$$\text{actual mass ratio} = \frac{CH_4}{O_2} = \frac{34.0}{100.0} = \frac{1}{2.94}$$

Since 2.94 < 4.00, O_2 is the L.R.

4.) Now calculate the maximum possible yield of H_2O based on O_2 as L. R.

$$\frac{O_2}{H_2O} = \frac{64.0}{36.0} = \frac{100}{x}$$

ideal **actual**

→ x = 56.3 g

∴ 56.3 g H_2O is the maximum possible mass of H_2O that the conditions can yield

5.) Now calculate % yield:

$$\frac{\text{actual yield}}{\text{maximum yield}} = \frac{48.6}{56.3} \times 100\% = 86.3\%$$

Reactions in Aqueous Solution

An aqueous solution of cations and anions will conduct electricity and is termed an **electrolyte**

The solubility of ionic compounds, in g per 100 mL, varies widely, but the following generalities are useful:

Very Soluble

Top Group I: Na^+, K^+, NH_4^+ salts

Group VII: F^-, Cl^-, Br^-, I^- salts

Strong acid anions: NO_3^-, ClO_3^-, SO_4^{2-}

Poorly Soluble

Bottom Group II: Ca^{2+}, Sr^{2+}, Ba^{2+}

Weak acid anions: CO_3^{2-}, PO_4^{3-}, $C_2O_4^{2-}$, CrO_4^{2-}

Sulfides*: S^{2-}

Oxides and hydroxides*: O^{2-}, OH^-

*Soluble if attached to Na^+, K^+, NH_4^+ (Group I cations)
These soluble ions are often **spectator ions** in redox reactions (later)

Ionic Equations

Often two ionic compounds will react with each other to produce a new ionic compound of low solubility.
This new compound will precipitate out of solution

Example:

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + NaCl$$

$$\downarrow \qquad \downarrow$$

$$Ca^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + CO_3^{2-}(aq)$$

insol. sol. sol. insol.

The anions and cations that constitute the insoluble pair produce a net **ionic equation**:

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3\downarrow$$

The remaining soluble ions (Na^+, Cl^-) are ignored as spectator ions

Most Common Chemical Reactions

1.) Oxidation reactions (≡ combustion)

Most elements react with O_2 to give stable oxides

For example: $3Fe + 2O_2 \rightarrow Fe_3O_4$

They occur because the products are more stable than the reactants

Very exothermic reactions accompanied by heat/light (fire) = combustion

For example: $C + O_2 \rightarrow CO_2$

Exchange Reactions

These proceed by the exchange of anion/cation pairs
- also know as **double replacement**

Commonly used to prepare desired compounds from more readily available ones

There are two major types:

a) Precipitation Reactions

In these the most soluble compounds form and precipitate from solution as in ionic equations

For example:

$$CaCl_2(aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + 2NaCl(aq)$$

b) acid-base reactions

For example:

$$Na^+OH^- + H^+Cl^- \rightarrow Na^+Cl^- + H_2O$$

base **acid** **salt** **water**

In acid-base reactions, the **acid** supplies **H^+** to a **proton acceptor**, the **base** (here OH^-);
the remaining anion joins with the cation of the base to form a **salt**

Note:
There are 6 strong acids (complete dissociation):
HCl, HBr, HI, HNO_3, $HClO_4$, H_2SO_4

All others are weak acids (partial dissociation): much more later

c) Gas-forming Reactions

For example:
all metal carbonates

i) Lose CO_2 on heating (symbol = Δ)

Example: $CaCO_3 \xrightarrow{\Delta} CaO + CO_2(g)$
"quick lime"

ii) React with acids

Example:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + [H_2CO_3] \rightarrow H_2O + CO_2(g)\uparrow$$

Gas evolution drives the reactions completely to the right; that is, they are not reversible