Chapter 1

Stoichiometry

1.1 The mole concept and Avogadro's constant

You should know (1.1.1) that the *amount of substance* is measured in moles and the units for this are 'mol'. L is Avogadro's constant $= 6.023 \times 10^{23}\text{mol}^{-1}$. You should be able to convert between the amount of substance and the number of particles (1.1.2).

- 12 g of ^{12}C $= 6.023 \times 10^{23}$ atoms $= 1$ mole
- 6.023×10^{23} of any particle $= 1$ mole

$$\text{Number of moles}(n) = \frac{\text{Number of particles}}{6.023 \times 10^{23}} \tag{1.1}$$

Try exercise 1.2 on page 7 of G&D, questions 1, 2, 5, 7, 8.

1.2 Formulas

Define molar mass (M), and calculate the mass of one mole of a species (1.2.1). You should be able to distinguish between atomic mass, molecular mass and formula mass (1.2.2). Molar mass (M) can be used for all three. Empirical and molecular formulae should be familiar from your work at GCSE, although we have covered them again now.

Chemical formulae of compounds should be familiar to you. There are only two types of compound - covalent and ionic. The formulae can be deduced using electronic structures, but we normally memorise covalent formulae (or work them out from the given name) and deduce ionic formulae from our knowledge of ions. Remember that compounds containing non-metal atoms only will be covalent, whereas those containing both metal and non-metal atoms will be ionic.

There are some simple rules for **naming compounds**:

- 'ide' at the end means only two elements are in the compound, such as iron (II) sulphide - FeS
- 'ate' at the end means that two elements *and* oxygen are present, such as in iron (II) sulphate - $FeSO_4$
- 'mono', 'di', 'tri' and 'tetra' prefixes indicate one, two, three or four of something: CO is carbon monoxide, CO_2 is carbon dioxide, SO_3 is sulphur trioxide, CCl_4 is carbon tetrachloride

Molar mass

The relative atomic mass, A_r, is the weighted mean of all the naturally occurring isotopes of the element relative to an atom of carbon-12. A_r has no units.

The relative molecular mass, M_r, is the total mass of all the atoms in the molecule relative to an atom of ^{12}C. Again, it has no units.

Atomic mass is the mass of one of atoms of an element **in grams**. For instance, the atomic mass of magnesium is 24.31 g mol^{-1}.

Molecular mass, or formula mass, is the mass of one mole of molecules or the mass of one mole of the atoms in the formula.

The molar mass M can be used for atomic mass, molecular mass and formula mass and therefore has units of g mol^{-1}.

Moles and mass

$$n = \frac{m}{M} \tag{1.2}$$

where n = amount of substance (number of moles, units: mol)
m = mass (units: g)
M = molar mass (units: g mol^{-1})

For example, how many moles of fluorine atoms have a mass of 76 g?

$$n = \frac{m}{M} = \frac{76\text{g}}{19\text{gmol}^{-1}} = 4 \text{ mol} \tag{1.3}$$

Percentage composition by mass

What is the % oxygen by mass in CO_2?
Answer: $M = 12.01 + 2 \times 16 = 44.01$
There are 2 O atoms in CO_2 so % oxygen is
$\frac{32}{44.01} \times 100 = 72.71\%$

Empirical formula

The empirical formula of a compound is the simplest whole number ratio of the atoms in the compound.

2.476 of an oxide of copper is found to contain 2.199 of copper. What is its empirical formula?

	Cu	O
m(g)	2.199 g	$(2.476 - 2.199) = 0.277$ g
M(g mol^{-1})	63.55 g mol^{-1}	16.00 g mol^{-1}
$n = \frac{m}{M}$	$\frac{2.199}{63.55} = 0.03460$ mol	$\frac{0.277}{16.00} = 0.1731$ mol
simplest ratio (divide by smallest)	$\frac{0.03460}{0.01731} = 2$	$\frac{0.01731}{0.01731} = 1$

Empirical formula = Cu_2O

Molecular formula

The molecular formula gives the actual number of atoms of each type in the molecule and is a multiple of the empirical formula. If the molar mass in the previous example was 286.2 then the molecular formula would be Cu_4O_2.

1.3 Chemical equations

You should be familiar with balancing chemical equations from GCSE. You need to be able to use *state symbols*. All ionic compounds are solids (s). Some are soluble in water and you need to learn the **solubility rules**:

- All group 1 and ammonium compounds are soluble

- All nitrates are soluble
- All ethanoates are soluble
- All chlorides are soluble except lead (Pb) and silver (Ag)
- Most sulphates are soluble except lead, barium and calcium
- All carbonates are insoluble except sodium, lithium, potassium and ammonium
- Most hydroxides are insolube except sodium, lithium, potassium and ammonium. Calcium hydroxide is slightly / sparingly soluble

Metals are solids except mercury, Hg. Non-metals are gases, except bromine which is a liquid and boron, carbon, silicon, phosphorus, sulphur, iodine, astatine, arsenic and tellurium which are solids. Covalent compounds don't follow simple rules - you just have to learn them as you go along.

HONIFBrCl reminds us which non-metallic elements are diatomic (H_2 for example). Ionic equations show us what ions are reacting and miss out spectator ions - normally those which stay in solution.

$$\mathrm{Pb(NO_3)_2\,_{(aq)} + 2NaCl\,_{(aq)} \longrightarrow PbCl_2\,_{(s)} + 2NaNO_3\,_{(aq)}} \tag{1.4}$$

becomes

$$\mathrm{Pb^{2+}\,_{(aq)} + 2Cl^-\,_{(aq)} \longrightarrow PbCl_2\,_{(s)}} \tag{1.5}$$

1.4 Mass relationships

Calculations involving masses rely on the fact that mass is conserved during chemical reactions - that's why you have to balance equations in the first place.

What mass of sodium hydrogen carbonate must be heated to give 8.80 g of carbon dioxide?

$$\begin{aligned}
&\mathrm{2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O}\\
&\text{2 moles } \mathrm{NaHCO_3} \longrightarrow \text{1 mole } \mathrm{CO_2}\\
&n(\mathrm{CO_2}) = \frac{8.80}{44.01} = 0.20 \text{ mol}\\
&\text{Thus } n(\mathrm{NaHCO_3}) = 0.40 \text{ mol}\\
&\text{rearrange } n = \frac{m}{M} \text{ to give } m = nM\\
&= 0.40 \text{ mol} \times (22.99 + 1.01 + 12.01 + 48) = 33.6 \text{ g}
\end{aligned}$$

Limiting reagent

In most of the chemical reactions we carry our there is an excess of reagents (reactants) except one, which is therefore the *limiting reagent* because it determines the amount of product formed. The limiting reagent can be identified by calculating the amount in moles of each reagent and then dividing by the stoichiometric equation. The smallest number then identifies the limiting reagent, as there is not enough of it to react with all of the other things present.

Consider the reaction

$$H_2O_{2\,(aq)} + 2KI_{\,(aq)} + H_2SO_{4\,(aq)} \longrightarrow I_{2\,(s)} + K_2SO_{4\,(aq)} + 2H_2O_{\,(l)} \tag{1.6}$$

What mass of iodine is produced when 100 g of KI is added to 12 g of H_2O_2 and 50 g H_2SO_4?

	H_2O_2	KI	K_2SO_4
mole ratio in equation	1	2	1
number of moles	$\frac{12}{34.02}$	$\frac{100}{166}$	$\frac{50}{98.08}$
	0.3527	0.6024	0.5098
divide by stoichiometric coefficient	0.3527	0.3012	0.5098

This tells us that KI is the limiting reagent. We know from the equation that two moles of KI produce one mole of I_2, so 0.6024 moles KI produce 0.3012 moles I_2. The mass of this I_2 is

$0.3012 \times (126.9 + 126.9)g = 76.44$ g

In practice 76.44 g is never going to be achieved because of impurities in reactants, side reactions and so on. We can compare our actual yield with this theoretical maximum to calculate our *percentage yield*. If 62.37 g were actually produced the yield would be

$\frac{62.37}{76.44} \times 100 = 81.59\%$

1.5 Concentration

Calculations involving concentrations will be practised plenty over the two years of the course. You need to remember

$$c = \frac{n}{V} \tag{1.7}$$

Make sure that your units are always consistent - volumes in dm^3.

Titration calculations

In simple titration calculations you will need to find out the concentration of an unknown when you're given the concentration of something else and a couple of volumes.

Example a: 10 cm^3 of 0.200 mol dm^{-3} $Na_2CO_{3\,(aq)}$ requires 25.00 cm^3 of HCl $_{(aq)}$ to neutralise it. What is the concentration of the hydrochloric acid?

$$2\ HCl_{(aq)} + Na_2CO_{3\,(aq)} \longrightarrow 2\ NaCl_{(aq)} + CO_{2\,(g)} + H_2O_{(l)} \qquad (1.8)$$

$$\begin{aligned} n(Na_2CO_3) &= cV = 0.2 \times \tfrac{10}{1000} \\ &= 2 \times 10^3 \text{ mol} \\ n(HCl) &= 2 \times (2 \times 10^{-3}) = 4 \times 10^{-3} \text{ mol} \\ [HCl] &= \tfrac{n}{V} = \tfrac{4\times10^{-3}}{\frac{25}{1000}} = 0.160 \text{ mol dm}^{-3} \end{aligned}$$

Example b: 10 cm^3 of I_2 solution, concentration 0.131 mol dm^{-3} reacts with 20.4 cm^3 of $Na_2S_2O_{3\,(aq)}$ of concentration 0.128 mol dm−3. Calculate the stoichiometry of the reaction (the 'big numbers' in the equation).

$$\begin{aligned} n(I_2) &= cV = 0.131 \times \tfrac{10}{1000} \\ &= 1.31 \times 10^{-3} \\ n(Na_2S_2O_3) &= 0.128 \times \tfrac{20.4}{1000} \\ &= 2.61 \times 10^{-3} \end{aligned}$$

The stoichiometry of the reaction is given by the ratio of the numbers of moles: 2($Na_2S_2O_3$):1(I_2). The equation for the reaction would be:

$$I_{2\,(aq)} + 2Na_2S_2O_{3\,(aq)} \longrightarrow 2NaI_{(aq)} + Na_2S_4O_{6\,(aq)} \qquad (1.9)$$

Back Titration

Back titrations normally involve finding the purity of a sample of the number of moles of water of crystallisation in a mole of sample.

Example: 0.5214 g of impure calcium hydroxide was dissolved in 50.00 cm^3 of 0.2500 mol dm^{-3} $HCl_{(aq)}$. 33.64 cm^3 of 0.1108 mol dm^{-3} $NaOH_{(aq)}$ was then required to just neutralise the remaining acid. Assuming the impurities do not react, what percentage of the sample was calcium hydroxide?
50.00 cm^3 of 0.2500 mol dm^{-3} of acid is
$n = cV = 0.2500 \times \frac{50}{1000} = 0.0125$ mol
The amount of acid which reacted with the sodium hydroxide can be calculated from the equation.

$$NaOH + HCl \longrightarrow NaCl + H_2O \tag{1.10}$$

33.64 cm^3 of 0.1108 sodium hydroxide is
$n = cV = (0.1108 \times \frac{33.64}{1000})$ mol $= 3.7273 \times 10^{-3}$ mol
Therefore the number of moles of acid which reacted with $Ca(OH)_2$
$= 0.0125 - 0.0037273 = 0.008773$ mol

$$2HCl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O \tag{1.11}$$

so the number of moles of calcium hydroxide is half the number of moles of acid
$= \frac{1}{2}(0.008773) = 0.004386$ mol
Now we work out the number of moles of $Ca(OH)_2$ in the original sample using $n = \frac{m}{M}$
$m = nM = (0.004386 \times 74.10) = 0.325$ g
The purity of $Ca(OH)_2 = \frac{0.325}{0.5214} \times 100 = 62.33\%$

1.6 Scientific notation

You should be able to use scientific notation in your numerical answers. This is really useful as you can ensure that you always use a sensible numbers of significant figures without worrying about zeros. Scientific notation is in the form $a \times 10^b$.

Significant figures

Significant figures show the limits of accuracy and where uncertainty begins.
Two significant figures
$1.4 = 1.4 \pm 0.05$ means between 1.35 and 1.45
Three significant figures
$1.42 = 1.42 \pm 0.005$ means between 1.415 and 1.425

Significant zeros

- Zeros preceding a non-zero digit are not significant. i.e. 0.00014 is to two s.f.
- Zeros between non-zero digits are significant. 103307 has six s.f., whereas 0.04403 has four s.f.
- Zeros after non-zero digits are ambiguous without a decimal point, and thus it is best to use scientific notation

  300 cm^3 is ? s.f.

  3×10^2 cm^3 is one s.f.

  3.00×10^2 cm^3 is three s.f.

In calculations you can only quote the answer to the same accuracy as the least accurate information you're given in the question. You should round off answers at the end of a calculation and not before - this means that you won't sacrifice accuracy.