UNIT 1

The core principles of chemistry

Topic 1.1

Formulae, equations and amount of substance

Introduction

The keys to this topic are:

- ★ to be able to calculate the number of moles from data
- ★ to set out calculations clearly

Things to learn

- ★ The Avogadro constant is the number of carbon atoms in exactly 12 g of the carbon-12 isotope. Its value is $6.02 \times 10^{23}\ mol^{-1}$.
- ★ The **relative atomic mass** of an element is the average mass of an atom of that element relative to $1/12^{th}$ the mass of a carbon-12 atom.
- ★ The **relative molecular mass** of an element or compound is the average mass of a molecule (or group of ions) of that element or compound relative to $1/12^{th}$ the mass of a carbon-12 atom.
- ★ One **mole** of a substance is the amount of that substance that contains 6.02×10^{23} particles of that substance. This means that one mole of a substance is its relative molecular mass expressed in grams.

> 1 mol of NaOH has a mass of 40.0 g.
> 1 mol of O_2 has a mass of 32.0 g.

- ★ The molar mass of a substance is the mass (in grams) of one mole.
- ★ Amount of substance is the number of moles of that substance.
- ★ The empirical formula is the simplest whole number ratio of the elements in the compound.

Things to understand

Calculation of empirical formulae from percentage data

This is best calculated using a table.

Element	%	% divided by r.a.m.	Divide by smallest
Carbon	48.7	48.7/12.0 = 4.1	4.1/2.7 = 1.5
Hydrogen	8.1	8.1/1.0 = 8.1	8.1/2.7 = 3
Oxygen	43.2	43.2/16.0 = 2.7	2.7/2.7 = 1

The final column gives the empirical formula. However, if any value in this column comes to a number ending in .5, .25, .33 or .67, you must multiply all the values by 2, 4 or 3 respectively to obtain integers. Here, the empirical formula is $C_3H_6O_2$.

Equations

Equations must balance. The number of atoms of an element on one side of the equation must be the same as the number of atoms of that element on the other side.

Ionic equations

Ionic equations must also balance for charge.

There are three rules:
- ★ Write the ions separately for *solutions* of ionic compounds (salts, strong acids and bases).
- ★ Write full 'molecular' formulae for solids and all covalent substances.
- ★ Spectator ions must be cancelled so that they do not appear in the final equation.

Moles

There are three ways of calculating the amount (in moles) of a substance:
- ★ For a pure substance X:

$$\textbf{amount (in moles) of X} = \frac{\textbf{mass of X (in grams)}}{\textbf{molar mass}}$$

Hint

Avoid writing mol = 0.061. Instead, state the name or formula of the substance, e.g. amount of H_2O = 0.061 mol.

Worked example

Calculate the amount of H_2O in 1.1 g of water

Answer

$1.1\ g/18.0\ g\ mol^{-1} = 0.061$ mol of H_2O

- ★ For gases:

$$\textbf{amount of gas (in moles)} = \frac{\textbf{volume (in dm}^3\textbf{)}}{\textbf{molar volume}}$$

The molar volume of a gas is $24\ dm^3\ mol^{-1}$, measured at room temperature and pressure (r.t.p.).

Worked example

Calculate the amount of H_2 in $3.2\ dm^3$ of $H_2(g)$ at r.t.p.

Answer

3.2/24 = 0.13 mol of $H_2(g)$

As volume in dm^3 = volume in $cm^3/1000$, the following formulae can be used:
moles = $M \times V/1000$
or
concentration = moles $\times 1000/V$
where M is the concentration in $mol\ dm^{-3}$ and V is the volume in cm^3

- ★ For solutions:

$$\textbf{amount of solute (in moles)} = \textbf{concentration (in mol dm}^{-3}\textbf{)} \times \textbf{volume (in dm}^3\textbf{)}$$

$$\textbf{concentration} = \frac{\textbf{moles}}{\textbf{volume in dm}^3}$$

Worked example

Calculate the amount of NaOH in $22.2\ cm^3$ of a $0.100\ mol\ dm^{-3}$ solution.

Answer

$0.100 \times 0.0222 = 2.22 \times 10^{-3}$ mol of NaOH

Calculation of number of particles

The number of particles can be calculated from the number of moles:
- ★ number of molecules = moles × Avogadro constant
- ★ number of ions = moles × Avogadro constant × number of those ions in the formula

Worked example

Calculate the number of carbon dioxide molecules in 3.3 g of CO_2.

Answer

amount of CO_2 = 3.3/44.0 = 0.075 mol

number of molecules = $0.075 \times 6.02 \times 10^{23} = 4.5 \times 10^{22}$

Calculate the number of sodium ions in 5.5 g of Na_2CO_3

Answer

amount of Na_2CO_3 = 5.5/106.0 = 0.0519 mol

number of Na^+ ions = $0.0519 \times 6.02 \times 10^{23} \times 2 = 6.2 \times 10^{22}$

Calculations based on reactions

These can only be carried out if a correctly balanced equation is used.

Reacting mass questions

First, write a balanced equation for the reaction.

Then follow the route:

$$\text{mass A} \xrightarrow{\text{step 1}} \text{moles A} \xrightarrow{\text{step 2}} \text{moles B} \xrightarrow{\text{step 3}} \text{mass B}$$

For steps 1 and 3 use the relationship:

amount of A or B (in moles) = mass/molar mass

For step 2 use the stoichiometric ratio from the equation:

moles of B = moles of A × ratio B/A

Worked example

Calculate the mass of sodium hydroxide required to react with 1.23 g of silicon dioxide.

Answer

Equation: $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$

Step 1: amount of SiO_2 = 1.23/60.1 = 0.0205 mol

Step 2: amount of NaOH = 0.0205 mol × 2/1 = 0.0410 mol

Step 3: mass of NaOH = 0.0410 × 40.0 = 1.64 g

In step 2, the stoichiometric ratio is 2:1 as there are 2NaOH to 1SiO_2 in the equation.

Concentration of solutions

There are three formulae involved here:

$$\frac{\textbf{amount of solute (in moles)}}{\textbf{volume of solution in dm}^3} \quad \textbf{units: mol dm}^{-3}$$

$$\frac{\textbf{amount of solute (in grams)}}{\textbf{volume of solution in dm}^3} \quad \textbf{units: g dm}^{-3}$$

$$\frac{\textbf{amount of solute (in grams)}}{\textbf{1 million grams of solute}} \quad \textbf{units: ppm}$$

Parts per million (ppm) is used for measuring the concentration of material present in small quantities, such as pollutants in the air or in water supplies.

Worked example

Calculate the concentration, in mol dm^{-3}, of a solution containing 2.22 g of sodium hydroxide in 200 cm^3 of solution.

Answer

amount of NaOH = 2.22/40.0 = 0.0555 mol
concentration = 0.0555/0.200 = 0.278 mol dm^{-3}

A water sample contained 0.0025 ppm of aluminium sulfate, $Al_2(SO_4)_3$. Calculate the mass of aluminium sulfate in 1 dm^3 of water.

Answer

mass of aluminium sulfate in 10^6 g of water = 0.0025 g
mass in 1000 g of water (1 dm^3) = 0.0025 × 1000/10^6 = 0.0000025 or 2.5×10^{-6} g

1 dm^3 of water has a mass of 1000 g.

Gas volume calculations

1 For reactions where a gas is produced from a solid or a solution, follow the scheme below.

$$\text{mass of A} \xrightarrow{\text{step 1}} \text{moles of A} \xrightarrow{\text{step 2}} \text{moles of gas B} \xrightarrow{\text{step 3}} \text{volume of gas B}$$

For step 1 use the relationship:

$$\textbf{moles of A} = \frac{\textbf{mass of A}}{\textbf{molar mass of A}}$$

For step 2 use the stoichiometric ratio from the equation:

moles of B = moles of A × ratio of B/A

For step 3 use the relationship:

volume of gas B = moles of B × molar volume

Worked example

Calculate the volume of carbon dioxide gas evolved at r.t.p. when 7.8 g of sodium hydrogen carbonate is heated. The molar volume of a gas is 24 dm^3 at the temperature and pressure of the experiment.

Answer

Equation: $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2(g)$
Step 1: amount of $NaHCO_3$ = 7.8/84.0 mol = 0.09286 mol
Step 2: amount of CO_2 = 0.09286 mol × 1/2 = 0.0464 mol
Step 3: volume of CO_2 = 0.0464 mol × 24 dm^3 mol^{-1} = 1.1 dm^3

In step 2, the stoichiometric ratio is 1:2 as there is $1CO_2$ to $2NaHCO_3$ in the equation.

2 For calculations involving gases only, a shortcut can be used. The volumes of the two gases are in the same ratio as their stoichiometry in the equation.

Worked example

What volume of oxygen is needed to completely burn 15.6 cm^3 of ethane?

Answer

Equation: $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$

Calculation: $$\frac{\text{volume of oxygen gas}}{\text{volume of ethane gas}} = \frac{7}{2} = 3.5$$

volume of oxygen (O_2) = 3.5 × 15.6 = 54.6 cm^3

Significant figures

★ You should always express your answer to the same number of significant figures as asked for in the question or as there are in the data.

Hint

If you cannot work this out in an exam, give your answer to 3 significant figures (or 2 decimal places for pH calculations), and you are unlikely to be penalised. Do not round up numbers in the middle of a calculation. Any intermediate answers should be given to at least 1 significant figure more than your final answer.

Percentage yield

First, calculate the theoretical yield from the equation using the reacting mass method as above (page 3).

The % yield is less than 100% because of competing reactions and handling losses.

$$\text{Then, the \% yield} = \frac{\text{actual yield in grams}}{\text{theoretical yield in grams}} \times 100\ \%$$

Atom economy

This can be obtained from the chemical equation where:

$$\text{atom economy} = \frac{\text{mass of atoms in the desired product} \times 100}{\text{mass of atoms of all the reactants}}$$

$$= \frac{\text{molar mass of product} \times \text{number of formulae of it in the equation} \times 100}{\text{sum of molar masses of all the reactants}}$$

Worked example

Calculate the atom economy of the production of silver from silver nitrate solution and copper.

$$2AgNO_3(aq) + Cu(s) \longrightarrow Cu(NO_3)_2(aq) + 2Ag$$

Answer

molar masses: $Ag = 107.9\ g\ mol^{-1}$

$AgNO_3 = 169.9\ g\ mol^{-1}$

$Cu = 63.5\ g\ mol^{-1}$

$$\text{atom economy} = \frac{107.9 \times 2 \times 100}{(169.9 \times 2) + 63.5} = \frac{21\,580}{403.3} = 53.5\%$$

Hint

Do not forget to multiply the molar masses of silver and silver nitrate by 2 as there are 2 mol of each in the equation.

Checklist

Before attempting questions on this topic, check that you can:

- ☐ calculate the empirical formula of a substance from the % composition
- ☐ write balanced ionic equations
- ☐ calculate the number of moles of a pure substance from its mass, of a solute from the volume and concentration of its solution, and of a gas from its volume
- ☐ calculate reacting masses and reacting gas volumes
- ☐ calculate the concentration of a solution in $mol\ dm^{-3}$ or ppm
- ☐ calculate the atom economy given the equation

Testing your knowledge and understanding

For the first set of questions, cover the margin, write down your answer, then check to see if you are correct.

The table below contains data that will help you.

Substance	Solubility
Nitrates	All soluble
Chlorides	All soluble, except for AgCl and $PbCl_2$
Sodium compounds	All soluble
Hydroxides	All insoluble, except for those of group 1 and barium

★ Write ionic equations for the reactions between solutions of:
- **a** lead nitrate and potassium chloride
- **b** magnesium chloride and sodium hydroxide
- **c** sodium chloride and silver nitrate
- **d** hydrochloric acid and sodium hydroxide

★ Calculate the amount (in moles) of:
- **a** Na in 1.23 g of sodium metal
- **b** NaCl in 4.56 g of solid sodium chloride
- **c** Cl_2 in 789 cm^3 of chlorine gas at room temperature and pressure
- **d** NaCl in 32.1 cm^3 of a 0.111 $mol\,dm^{-3}$ solution of sodium chloride

★ Calculate the volume of a 0.222 $mol\,dm^{-3}$ solution of sodium hydroxide, which contains 0.0456 mol of NaOH.

★ Calculate the number of water molecules in 1.00 g of H_2O.

★ Calculate the number of sodium ions in 1.00 g of Na_2CO_3.

★ 4.44 g of solid sodium hydroxide were dissolved in water and the solution made up to 250 cm^3. Calculate the concentration in:
- **a** $g\,dm^{-3}$
- **b** $mol\,dm^{-3}$

Answers

a $Pb^{2+}(aq) + 2Cl^-(aq) \longrightarrow PbCl_2(s)$
b $Mg^{2+}(aq) + 2OH^-(aq) \longrightarrow Mg(OH)_2(s)$
c $Cl^-(aq) + Ag^+(aq) \longrightarrow AgCl(s)$
d $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

a 1.23/23.0 = 0.0535 mol
b 4.56/58.5 = 0.0779 mol
c 0.789/24.0 = 0.0329 mol
d 0.111 × 0.0321 = 3.56×10^{-3} mol

0.0456/0.222 = 0.205 dm^3 = 205 cm^3

(1.00/18.0) × 6.02×10^{23} = 3.34×10^{22}

(1.00/106.0) × 2 × 6.02×10^{23} = 1.14×10^{22}

a 4.44g/0.250 dm^3 = 17.8 $g\,dm^{-3}$
b 4.44/40.0 = 0.111 mol
Therefore, 0.111 mol/0.250 dm^3 = 0.444 $mol\,dm^{-3}$

The **answers** to the **numbered questions** are on page 127

1 **a** An organic compound contains 82.76% carbon and 17.24% hydrogen by mass. Calculate its empirical formula.
b It was found to have a relative molecular mass of 58.0. Calculate its molecular formula.

2 Balance the following equations:
- **a** $NH_3 + O_2 \longrightarrow NO + H_2O$
- **b** $Fe^{3+}(aq) + Sn^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Sn^{4+}(aq)$

3 What mass of sodium hydroxide is needed to react with 2.34 g of phosphoric(v) acid, H_3PO_4, to form the salt Na_3PO_4?

4 When sodium chloride solution is added to lead nitrate solution, a precipitate of lead chloride is formed.

$$2NaCl(aq) + Pb(NO_3)_2(aq) \longrightarrow PbCl_2(s) + 2NaNO_3(aq)$$

- **a** Calculate the atom economy for the preparation of lead chloride by this method.
- **b** If hydrochloric acid was used instead of sodium chloride, would the atom economy be higher or lower? Justify your answer.

5 At r.t.p., what volume of hydrogen sulfide gas, H_2S, is required to react with 25 cm^3 of a 0.55 mol dm^{-3} solution of bismuth nitrate, $Bi(NO_3)_3$? The molar volume of a gas is 24 dm^3 mol^{-1} under these conditions. The reagents react according to the equation:

$$3H_2S(g) + 2Bi(NO_3)_3(aq) \longrightarrow Bi_2S_3(s) + 6HNO_3(aq)$$

6 What volume of hydrogen gas is produced by the reaction of 33 dm^3 of methane gas with steam, according to the equation:

$$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3H_2(g)?$$

7 Calculate the number of aluminium ions in 1.0 cm^3 of:

a a 0.030 ppm solution of aluminium sulfate, $Al_2(SO_4)_3(aq)$

b a 0.030 nmol dm^{-3} solution of aluminium sulfate

(molar mass of aluminium sulfate = 342.3 g mol^{-1}; Avogadro constant = 6.02×10^{23} mol^{-1}; 1 nmol (nanomole) = 10^{-9} mol)

8 Calculate the mass of sodium sulfate, Na_2SO_4, produced when 4.0 g of sodium hydroxide is mixed with a solution containing 5.0 g of sulfuric acid:

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

Topic **1.2**

Energetics

Introduction

★ State symbols should always be used in equations in this topic.

★ In definitions in this topic, there are three key points:
- the enthalpy change per mole
- the substance the mole refers to (for example, 1 mol of substance being formed/1 mol of atoms being produced/1 mol of substance being burnt).
- the standard conditions

★ It always helps to add an equation with state symbols as an example because this may gain marks lost by an omission in the definition.

Things to learn

★ An **exothermic reaction** produces heat, so that heat is then given out to the surroundings. For all exothermic reactions, ΔH is *negative* (see Figure 1.1). This means that chemical energy is being converted into thermal (heat) energy.

★ An **endothermic reaction** loses heat, so that heat is then taken in from the surroundings**.** For all endothermic reactions, ΔH is *positive* (see Figure 1.2).

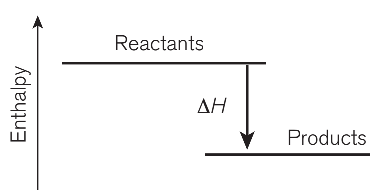

Figure 1.1 Enthalpy diagram for an exothermic reaction

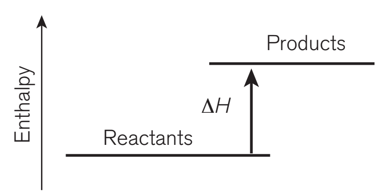

Figure 1.2 Enthalpy diagram for an endothermic reaction

★ Standard conditions are:
- a pressure of 1 atmosphere
- a stated temperature (usually 298 K)
- solutions, if any, at a concentration of 1.00 mol dm^{-3}

– substances in their most stable states, e.g. carbon as graphite not diamond, water at 298K as a liquid.

★ Standard **enthalpy of reaction**, $\Delta H_r^{\ominus}$, is the enthalpy change when the molar quantities as written in the equation react at 1 atm pressure and a stated temperature (usually 298 K). For example, $\Delta H_r^{\ominus}$ for sulfur dioxide reacting with oxygen according to the equation:

$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

is for 2 mol of SO_2 gas reacting with 1 mol O_2 gas to form 2 mol of SO_3 gas.

It follows from this definition that the enthalpy of formation of an element in its stable state is zero.

★ Standard **enthalpy of formation**, $\Delta H_f^{\ominus}$, is the enthalpy change when *one mole* of a compound is formed from its *elements* in their most stable states at 1 atm pressure and a stated temperature (usually 298 K). For example, $\Delta H_f^{\ominus}$ for ethanol is the enthalpy change for the reaction:

$2C(graphite) + 3H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l)$

★ Standard **enthalpy of combustion**, $\Delta H_c^{\ominus}$, is the enthalpy change when *one mole* of a substance is completely burned in oxygen at 1 atm pressure and a stated temperature (usually 298 K). For example, $\Delta H_c^{\ominus}$ for ethane is the enthalpy change for the reaction:

$C_2H_6(g) + 3\frac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

★ Standard **enthalpy of atomisation** of an element, $\Delta H_a^{\ominus}$, is the enthalpy change when *one mole* of a *gaseous atom* is formed from the element in its stable state at 1 atm pressure and a stated temperature (usually 298 K). For example, $\Delta H_a^{\ominus}$ for bromine is the enthalpy change for the reaction:

$\frac{1}{2}Br_2(l) \longrightarrow Br(g)$

Hint

You should always give an equation as an example for this and other enthalpy definitions.

★ Standard **enthalpy of neutralisation** $\Delta H^{\ominus}_{neut}$ of an acid is the enthalpy change when the acid is neutralised by a base and *one mole of water* is produced at 1 atm pressure and a stated temperature (usually 298 K). For example, $\Delta H^{\ominus}_{neut}$ for sulfuric acid, with sodium hydroxide solution, is the enthalpy change for the reaction:

$\frac{1}{2}H_2SO_4(aq) + NaOH(aq) \longrightarrow \frac{1}{2}Na_2SO_4(aq) + H_2O(l)$

For hydrochloric acid, it is for the reaction:

$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$

For any strong acid being neutralised by any strong base, it is for the reaction:

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad \Delta H^{\ominus}_{neut} = -57\,kJ\,mol^{-1}$

★ **Average bond enthalpy** is the *average* enthalpy change when *one mole* of that bond is broken into *separate gaseous atoms* of the elements concerned (at 1 atm pressure). It is *always* endothermic.

★ **Hess's law** states that the enthalpy change for a given reaction is independent of the route by which the reaction takes place, provided the states of the reactants and products are the same in both routes (see Figure 1.3). Thus, the enthalpy change proceeding *directly* from reactants to products is the same as the *sum* of the enthalpy changes of all the reactions for the change to be carried out in two or more steps.

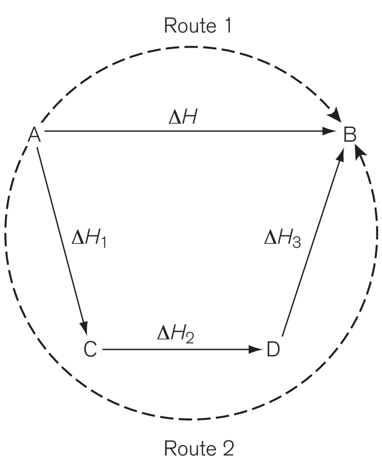

Figure 1.3 A reaction cycle

Things to understand

Calculation of ΔH_r from ΔH_f data

★ You can use the expression:

$$\Delta H_{reaction} = \text{the sum of } \Delta H_{formation} \text{ of products} - \text{the sum of } \Delta H_{formation} \text{ of reactants}$$

★ Remember that if you have two moles of a substance, you must double the value of ΔH_f.

★ The enthalpy of formation of an element (in its stable state) is zero.