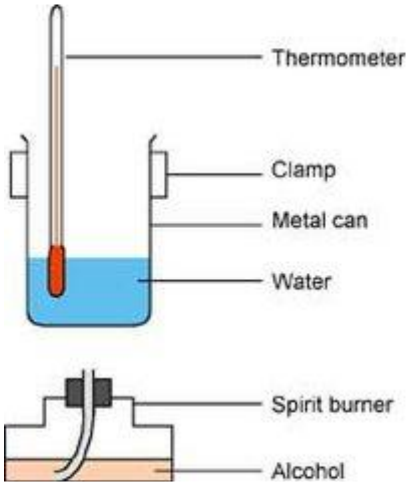
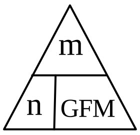
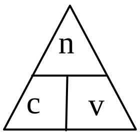
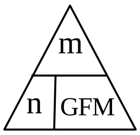
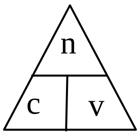
Cathkin High School
CfE Higher Chemistry

Unit 3:
Chemistry in Society



Getting the Most from Reactants

No.	Learning Outcome	Understanding?
1	**Getting the most from reactions** by considering: feedstock (cost & sustainability; energy requirements; recycling; uses of by-products; yield	
2	Use balanced equations to determine mole ratio(s) for reactions	
3	Calculations from balanced equations using 	
4	Calculations from balanced equations using 	
5	Calculations from balanced equations using both  	
6	Calculating Reacting Gas Volumes from balanced equations	
7	Calculating % yield	
8	Determining the limiting factors and the reactant in excess for reactions	
9	Understand what is meant by 'the atom economy'	
10	Explain the importance of 'the atom economy'	

Equilibria

No.	Learning Outcome	Understanding?
1.	Understand the use of ⇌ for reversible reactions	
2.	Explain what is meant by 'dynamic equilibrium'	
3.	Understand the term 'position of equilibrium'	
4.	Determine and explain the effect of altering concentration, temperature or pressure on the position of equilibrium	
5.	State the effect of a catalyst on an equilibrium mixture.	

Chemical Energy

No.	Learning Outcome	Understanding?
1.	Carry out $E = cm\Delta T$ calculations	
2.	Define 'Enthalpy of Combustion' and understand its use in the above calculations	
3.	Understand Hess's Law and the reasons for using it	
4.	Use Hess's Law to calculate enthalpy changes for reactions which cannot be measured directly.	
5.	Explain the difference between molar bond enthalpy and mean bond enthalpy	
6.	Enthalpy calculations using bond enthalpies	

Oxidising & Reducing Agents

No.	Learning Outcome	Understanding?
1.	Define the terms oxidising agent and reducing agent	☺ 😐 ☹
2.	Construct ion-electron ½ equations for complexes	☺ 😐 ☹
3.	Identify chemicals as being oxidising or reducing agents within a given reaction	☺ 😐 ☹
4.	Give uses for oxidising agents	☺ 😐 ☹
5.	Write ion-electron equations for oxidation, reduction and redox reactions	☺ 😐 ☹

Chemical Analysis

No.	Learning Outcome	Understanding?
1.	Explain why the technique 'liquid chromatography' is used	☺ 😐 ☹
2.	Explain why the technique 'gas chromatography' is used	☺ 😐 ☹
3.	Explain 'retention line' and its importance in identifying substances from chromatographic techniques	☺ 😐 ☹
4.	Explain why different compounds have different retention values in different solvents	☺ 😐 ☹

Chemical Industry

Importance of the Chemical Industry

- the Chemical Industry is one of the largest British industries.
- its products are indispensable to many aspects of modern life and many are used for the benefit of society
- it is the only manufacturing industry to export more than it imports and so earns a trade balance surplus from these exports for Britain
- also invisible trade balance surplus from selling licenses to use British processes abroad
- the chemical industry involves the investment of large sums of money but employs relatively few people making it a capital intensive and not a labour intensive industry.

Stages in the manufacture of a new product

The manufacture of a new product is a step-wise process from its discovery.

research and development	a new potentially useful chemical is prepared and patented. Some products are discovered by accident, but others as a result of long and expensive research.
laboratory process	small scale to review the production route
pilot study	the product is now required in larger amounts and will be manufactured in a pilot study using the route identified by the research group but in kilogram quantities. Product quality, health hazards, and production costs will be discussed.
scaling up	planning the scaling up from lab quantities to full scale production will have been going on from the pilot study stage.
Production	plant design, planning considerations, commissioning and start up
review	this will occur at each stage. All processes are reviewed and modifications are made.

Raw Materials and Feedstocks

A feedstock is a chemical from which other chemicals are manufactured. Feedstocks are made from raw materials; the basic resources that the earth supplies to us. They are:

- Fossil fuels–coal, oil and natural gas
- metallic ores–e.g. aluminium extracted from bauxite(Al_2O_3)
- minerals–chlorine from sodium chloride
- water and air – water in hydration of ethene to ethanol and nitrogen in the Haber Process, oxygen in the catalytic oxidation of ammonia
- organic materials–of plant and animal or vegetable oils and starch

Crude oil is a raw material from which naphtha is obtained by fractional distillation. Naphtha is a feedstock that can be cracked to produce ethene.

Batch and Continuous Processes

In a batch process the chemicals are loaded into the reaction vessel. The reaction is monitored and at the end of the reaction the product is separated and the reaction vessel cleaned out ready for the next batch.

In a continuous process the reactants are continuously loaded at one end of the reaction vessel and the products are removed at the other end. Each process has advantages and disadvantages.

Batch Process v Continuous Process

Process	Advantages	Disadvantages
Batch	• suited to smaller scale production up to 100 tons per annum • more versatile than continuous as they can be used form ore than one reaction more suited for multi step reactions or when reaction time is long	• possibility of contamination from one batch to the next • filling and emptying takes time during which no product, and hence no money, is being made
Continuous	• suited to large scale production >1000 tons per annum • suitable for fast single step processes • more easily automated using computer control	• very much higher capital cost before any production can occur • not versatile, can make only one product not cost effective when run below full capacity

	• smaller work force operates round the clock, 365 days per year • tend to operate with relatively low volumes of reactants allowing easy removal of excess heat energy	

In general products that are made on a very large scale will use a continuous process eg. sulphuric acid, ammonia, iron, ethene, poly(ethene)

Products made on a smaller scale or when a continuous process would be difficult to devise or operate will use a batch process eg. pharmaceuticals, dyes, copper refining by electrolysis

Factors Influencing the Choice of Synthetic Route

- Cost - availability of feedstocks
- Yield of the reaction – can unreacted starting materials be recycled, or sold?
- Difficulty and cost of waste disposal
- Energy consumption
- Emissions to the atmosphere

Economic Aspects

Operating Conditions

The conditions under which a chemical process operates are chosen to maximise economic efficiency. We have considered these in other topics but examples are:

- Raising the temperature may increase the rate of a reaction but it will increase energy costs so may not be economic
- Increasing the pressure may shift equilibrium in favour of the product but will mean using stronger reaction vessels and more powerful compressors and may not be economic.

Costs in the Chemical Industry

Costs come under 3 main categories – capital, fixed and variable costs.

Capital Costs:

These are incurred when building the plant. The life of a plant is assumed to be only about 10 years after which it is written off. The cost of this depreciation is recovered under fixed costs.

Fixed Costs

These are costs that are the same whether 1 ton or 1000 tons of product are made. The effect of the fixed cost decreases as the amount of product increases. They include:

- Depreciation of the plant
- Labour
- Land purchase

Variable Costs

These are directly related to output and include:

- Raw materials and energy
- Packaging
- Waste disposal and effluent treatment

Location of the Chemical Industry

Many locations are for historical and practical reasons. They had to be near:

- Water supply
- Raw materials
- Good communications; near ports, roads and rail
- Reliable energy supplies
- Available skilled labour

Safety and the Environment

The chemical industry is well aware of its environmental responsibilities and is acting accordingly.

- Power stations that burn fossil fuels must remove the sulphur dioxide from the gases before release to the atmosphere. The SO_2 is converted to H_2SO_4 , which is sold.
- Waste used to be dumped in quarries, rivers, the sea or stored in containers from which it could leak into streams. These methods are no longer acceptable and are increasingly becoming illegal. Waste must be treated and discharged only when it is not harmful to the environment – it must meet requirements of pH and metal ion content.
- Water containing organic waste must not be discharged into rivers or canals if it will reduce significantly the oxygen content of the water,

causing fish to die.

- Between 1990 and 1996 discharge of potentially harmful chemicals into UK rivers was reduced by 91 %.
- Plants have reduced accidents by 50% in the last decade.
- road and rail tankers that carry chemicals are constructed to withstand impact in accidents.
- Plants have their own fire fighting teams on site.
- Plants are designed with safety in mind. Chemicals are hazardous so the accident rate will never be zero but the aim is to learn from mistakes and reduce the rate to a minimum.

Calculations Based on Equations

Calculations Involving The Mole

One mole of a substance is the **gram formula mass** of the substance. The gram formula mass (gfm) can be determined from the **formula** of the substance.

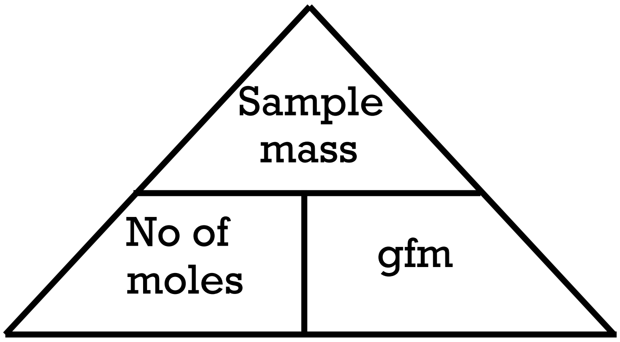
Calculate the mass of one mole of sodium hydroxide.

Formula (using the valency rule) = NaOH

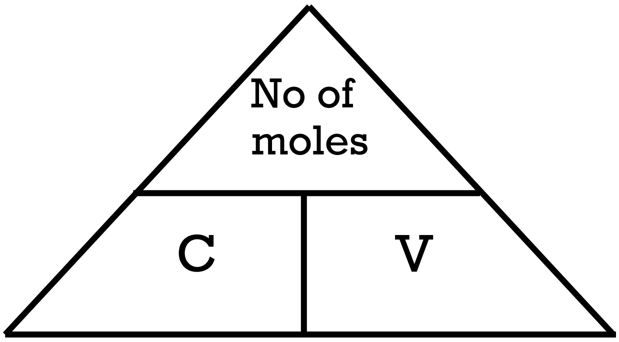
Formula Mass = (1 X Sodium) + (1 X Oxygen) + (1 X Hydrogen)
= 23 + 16 + 1
= 40g

So one mole of sodium hydroxide has a mass of 40g.

Simple mole calculations can be carried out for **SOLIDS** using the following mole triangle:



And simple mole calculations for **SOLUTIONS** can be carried out using the following mole triangle:



Calculations Based on Equations

A balanced equation is taken to give the relative number of moles of each reactant and product. Since the mass of one mole of any substance is expressed in grams, the masses involved can then be calculated as shown.

Worked Example

Calculate the mass of water produced on burning 1g of methane

$$\underset{\text{1 mole}}{CH_4} + O_2 \longrightarrow CO_2 + \underset{\text{2 moles}}{2H_2O}$$

It is not necessary to calculate the masses of carbon dioxide and oxygen – these substances are not included in the question.

Step 1 Convert moles to mass for the substances involved

CH_4	$2H_2O$
$12 + (4 \times 1)$	$2\,[\,(2 \times 1) + 16\,]$
16g	36g

Step 2 By proportion; determine the mass of water produced

$$16\text{g} \longrightarrow 36\text{g}$$
$$1\text{g} \longrightarrow \frac{36 \times 1}{16}$$
$$= \mathbf{2.25g}$$

The Idea of Excess

Reactants are needed for a chemical reaction to take place. When one of the reactants is used up the reaction will stop. Any reactant, which is left unreacted, is said to be “in excess”.

Worked Example 1

8g of methane is mixed with 16g of oxygen. A spark is applied to the mixture to start the reaction. Calculate the mass of carbon dioxide produced.

$$\begin{array}{ccccccc} CH_4 & + & 2O_2 & \longrightarrow & CO_2 & + & 2H_2O \\ \text{1 mole} & & \text{2 moles} & & \text{1 mole} & & \end{array}$$

Step 1 Calculate the number of moles of each reactant

$$\text{No. moles } CH_4 = \frac{\text{mass}}{\text{gfm}} = \frac{8}{16} = 0.5\text{moles}$$

$$\text{No. moles O} = \frac{\text{mass}}{\text{gfm}} = \frac{16}{32} = 0.5\text{moles}$$

Step 2 Use the balanced equation to determine the quantity of each reactant used in the reaction.

$$\begin{array}{ccc} CH_4 & + & 2O_2 \\ \text{1 mole} & & \text{2 moles} \end{array}$$

Therefore, for every 0.5 moles of methane 1 mole of oxygen would be required. Looking at the quantities of reactants from step 1 there is not enough oxygen to allow all of the methane to react therefore some methane will be left over at the end. The methane is said to be in excess and the oxygen will therefore determine the quantity of carbon dioxide produced.

Step 3 Convert moles to mass and carry out a proportion calculation to determine the mass of carbon dioxide produced.

$$\begin{array}{ccccccc} CH_4 & + & 2O_2 & \longrightarrow & CO_2 & + & 2H_2O \\ \text{1 mole} & & \textbf{2 moles} & & \textbf{1 mole} & & \end{array}$$

$$\begin{array}{ccc} 64g & \longrightarrow & 44g \\ 16g & \longrightarrow & \dfrac{44 \text{ x } 16}{64} \\ & = & \mathbf{11g} \end{array}$$

Worked Example 2

What mass of hydrogen gas is produced when 2.45g of magnesium is added to 100cm^3 of dilute hydrochloric acid, concentration 1 moll^{-1}?

$$\begin{array}{cccccc} Mg & + & 2HCl & \longrightarrow & MgCl_2 & + \; H_2 \\ \text{1 mole} & & \text{2 moles} & & \text{1 mole} & \end{array}$$

Step 1 Calculate the number of moles of each reactant

$$\text{No. moles Mg} = \frac{\text{mass}}{\text{gfm}} = \frac{2.45}{24.5} = 0.1 \text{ moles}$$

$$\text{No. moles HCl} = C \times V = 1 \times 0.1 = 0.1 \text{ moles}$$

Step 2 Use the balanced equation to determine the quantity of each reactant used in the reaction.

$$\begin{array}{lcccc} & Mg & + & 2HCl \\ & \text{1 mole} & & \text{2 moles} \\ \text{So} & \text{0.1 moles} & \text{requires} & \text{0.2 moles} \end{array}$$

From step 1 it can be seen that there is not enough acid to allow all of the Mg to react hence the Mg will be in excess and the acid will control the mass of hydrogen produced.

Molar Volume

The molar volume is the volume of which one mole of a gas occupies.

Worked Example 1

The volume of 8g of oxygen is 5.5 litres. Calculate the volume of 3 mol of oxygen.

gfm O_2 = 2 x 16 = 32g

$$\begin{array}{lcl} 8g & \longrightarrow & 5.5 \\ 96g & \longrightarrow & \dfrac{5.5 \times 96}{8} \\ & = & 66 \text{ litres} \end{array}$$

Worked Example 2

Calculate the volume of 0.14g of nitrogen. (**assume the molar volume of the gas is 23 litres mol^{-1}**)

gfm N_2 = 2 x 14 = 28g

$$28\text{g} \longrightarrow 23$$
$$0.14\text{g} \longrightarrow \frac{23 \times 0.14}{28}$$
$$= 0.115 \text{ litres } \textbf{or } 115\text{cm}^3$$

Worked example 3

Calculate the volume of hydrogen produced when 0.2g of zinc reacts with excess sulphuric acid. (Take the molar volume to be 22.2 litres mol^{-1})

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

1 mole → 1 mole

$$65\text{g} \longrightarrow 22.2\text{g}$$
$$0.2\text{g} \longrightarrow \frac{22.2 \times 0.2}{65}$$
$$= 0.068 \text{ litres}$$

Reacting Volumes

1 mole of any gas occupies roughly the same volume (at the same temperature and pressure).

This means that equal volumes of gases contain the same number of moles.

1 litre of O_2	1 litre of H_2	1 litre of CO_2

We already know that a balanced equation gives the same number of moles of reactants and products.

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

1mole 3moles 2moles

So.. 1litre 3litres $\longrightarrow$ 2litres
Or.. $10cm^3$ $30cm^3$ $\longrightarrow$ $20cm^3$
Or.. $1cm^3$ $3cm^3$ $\longrightarrow$ $2cm^3$

NOTE: liquid or solid reactants and products are not included in this calculation!

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$$
1mole 1mole 1mole

So.. not a gas 1litre $\longrightarrow$ 1litre
Or.. $10cm^3$ $\longrightarrow$ $10cm^3$
Or.. $1cm^3$ $\longrightarrow$ $1cm^3$

Worked Example 1

$30cm^3$ of methane is completely burned in $100cm^3$ of oxygen. What is the volume and composition of the gas at the end of the experiment? (All volumes are measured at atmospheric pressure and room temperature)

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$$
1mole 2moles 1mole

Step 1: from the balanced equation determine which reactant is in excess

1mole CH_4 reacts with 2moles of O_2
$30cm^3$ $\longrightarrow$ $60cm^3$

Since there is $100cm^3$ of O_2, O_2 is in excess by **$40cm^3$**

Step 2: since the oxygen is in excess the methane will be used up first and hence will control the volume of product.

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$$
1mole 1mole
$30cm^3$ $30cm^3$

So the total volume and composition of gas at the end of the experiment is:

$40cm^3$ of O_2 left unreacted and $30cm^3$ of CO_2 produced

NOTE: since the water is a liquid it is not considered.

Step 3: Carry out a proportion calculation to determine the mass of hydrogen produced.

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$

1 mole **2 moles** **1 mole**

2 moles ⟶ 2g

0.1moles ⟶ $\frac{0.1 \times 2}{2}$

= **0.1g**

Percentage Yield Calculations

The yield in a chemical reaction is the quantity of product obtained. The actual yield can be compared, as a percentage, with the theoretical.

Worked Example 1

5g of methanol reacts with excess ethanoic acid to produce 9.6g of methyl ethanoate. Calculate the percentage yield.

Step 1: determine the theoretical yield (the quantity expected from the balanced equation)

$$CH_3OH + CH_3COOH \longrightarrow CH_3OOCCH_3$$

1 mol 1 mol

32g ⟷ 74g

5g ⟶ $\frac{74 \times 5}{32}$

= 11.56g

Theoretical Yield = **11.56g**

Step 2: The actual yield is always given in the question.

Actual yield = **9.6g**

Step 3: Percentage yield = $\frac{9.6}{11.56} \times 100$

= **83%**

The percentage yield is a very important consideration for industrial chemists. They must take account of cost of raw materials, plant-running costs etc. If the yield of product is not sufficient enough to cover the costs of production then the process would not be considered to be economically viable.

Atom Economy

Atom economy is a measure of the proportion of reactant atoms which are incorporated into the desired product of a chemical reaction.

Calculation of atom economy therefore also gives an indication of the proportion of reactant atoms forming waste products.

$$\boxed{\%\ \text{atom economy} = \frac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100}$$

In developing an atom economical reaction pathway the industrial chemist may well prefer rearrangement and addition reactions over less environmental friendly substitution and elimination reactions.

Example 1: Addition reaction – halogenation of an alkene

(Z)-but-2-ene	Bromine	2,3-dibromobutane
C_4H_8	Br_2	$C_4H_8Br_2$
1mol	1mol	1mol
(12 x 4) + (8 x 1)	2 x 79.9	(12 x 4) + (8 x 1) + (79.9 x 2)
= 56g	= 159.8g	= 215.8g

Total mass of reactants = 56 g + 159.8 g = 215.8 g
(Note: Product mass is also 215.8 g)

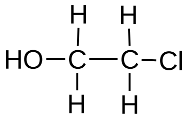
Mass of desired product (2,3-dibromobutane) = 215.8 g

$$\boxed{\%\ \text{atom economy} = \frac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100}$$

$$\%\ \text{atom economy} = \frac{215.8}{215.8} \times 100 = \mathbf{100\%}$$

This process is 100% atom efficient, with all the reactant atoms included within the desired product.

Example 2: Elimination reaction

2 

$HO-CH_2-CH_2-Cl$

+ $Ca(OH)_2$ ⟶

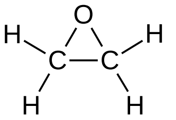
2-chloroethanol
C_2H_5OCl
2mol
2[(12 x 2) + (5 x 1) + 16 + 35.5]

= 161g

Calcium hydroxide
$Ca(OH)_2$
1mol
40 + 2(16 +1)

= 74g

Desired Product

2  +

ethylene oxide
C_2H_4O
2mol
2[(12 x 2) + (4 x 1) + 16]

= 88g

Waste Products

$CaCl_2$ + $2H_2O$

Calcium chloride
$CaCl_2$
1mol
40 + (2 x 35.5)

= 111g

Water
H_2O
2mol
2 [(2 x 1) + 16]

= 36g

Total mass of reactants = 161 g + 74 g = 235 g
(Note: Total product mass = 235 g)

Mass of desired product ethylene oxide = 88 g

$$\text{\% atom economy} = \frac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100$$

$$\text{\% atom economy} = \frac{88}{235} \times 100 = \mathbf{37.4\%}$$

This elimination reaction is therefore only 37.4% atom efficient, with the remaining 62.6% in the form of unwanted waste products (calcium chloride and water).

Equilibria

Reversible Reaction

In a reversible reaction, if the conditions are not altered a **balance** point will be reached. At this point the reaction is said to be in **equilibrium**. At equilibrium the reactants change into products at **exactly the same rate** at which the products change back into reactants.

Rate of change of reactants → **products** **=** **Rate of change of products** → **reactants**

At equilibrium the concentrations of the reactants and products remain **constant** but **not necessarily equal.**

$A \rightleftharpoons B$ **or** $A \rightleftharpoons B$

30% **70%** **50%** **50%**

The Position of Equilibrium

The position of equilibrium means the extent to which the reaction has taken place

$A \rightleftharpoons B$

20% 80%

The equilibrium in this case lies well to the right hand side. There is 80% conversion of A into B. Sometimes this is indicated by the size of the arrows.

A reaction written as;

would mean that the position of equilibrium lies to the left hand side.

For example:

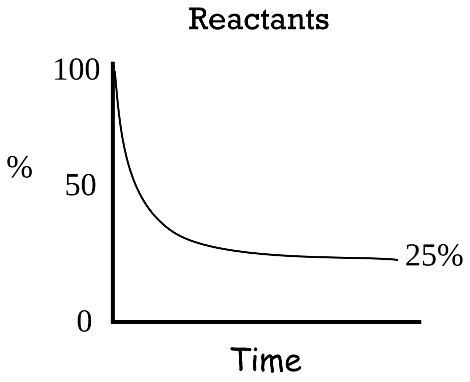
$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

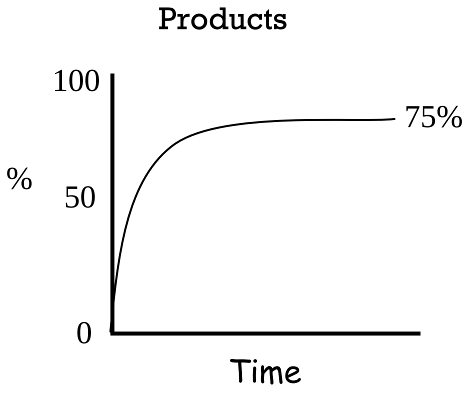
Mainly molecules — Few ions

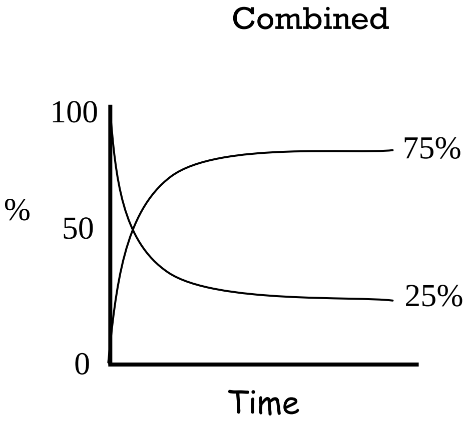
Products of an Equilibrium Reaction with Time

Reactants		**Products**
A + B	$\rightleftharpoons$	C + D
25%		**75%**

At the start of the reaction there will be 100% reactants. However, as the reaction proceeds the reactants will be used up and the products will be formed. Eventually the reaction will reach equilibrium. At this stage the concentration of both the reactants and products will remain constant.







In a reversible reaction when the curve levels off this indicates that the reaction has reached equilibrium. (it does not indicate that the reaction has stopped).

Shifting the Position of Equilibrium

If, once an equilibrium has been established the reaction conditions are changed then the position of equilibrium will be altered. If a new equilibrium is established where there is an increase in products we say the equilibrium has shifted to the right. If the new equilibrium results in an increased amount of reactants then we say the equilibrium has shifted to the left.

Changing reaction conditions such as concentration, temperature and pressure will cause a shift in equilibrium position.

Changing Concentration

Increasing the concentration of the reactants, or decreasing the concentration of the products shifts the position of equilibrium to the right hand side

Decreasing the concentration of the reactants or increasing the concentration of the products shifts the position of equilibrium to the left.

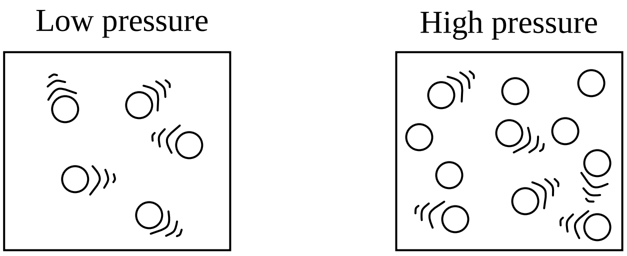
Changing Temperature

Increasing the temperature favours the endothermic reaction.

Decreasing the temperature favours the exothermic reaction.

Changing Pressure

In the gaseous state molecules have high energies and are fast moving. Pressure is the result of gas molecules bombarding the walls of the vessel in which the gas is contained. The greater the number of molecules in a given volume the greater the pressure.



$$C_{(g)} \rightleftharpoons 2D_{(g)}$$

The pressure on the right hand side is greater than the pressure on the left hand side because there are more molecules.

NOTE:

1. **Pressure** only affects the equilibrium of a system that involves **gases**.

2. A pressure change will alter equilibrium **only** if there are **different** numbers of **moles of gases** on each side.

$$\underbrace{A(g) + B(g)}_{\text{2 moles}} \rightleftharpoons \underbrace{C(g) + D(g)}_{\text{2 moles}}$$

Changing pressure will **not affect** this equilibrium since there are the **same number of moles** of gas on each side of the equation.

$$\underbrace{2A(g) + B(g)}_{\text{3 moles}} \rightleftharpoons \underbrace{C(g) + D(g)}_{\text{2 moles}}$$

Changing pressure **will affect** this equilibrium since there are **different numbers of moles** of gases on each side of the equation.

Increasing the pressure will favour the side with the lowest number of moles in the gas state.

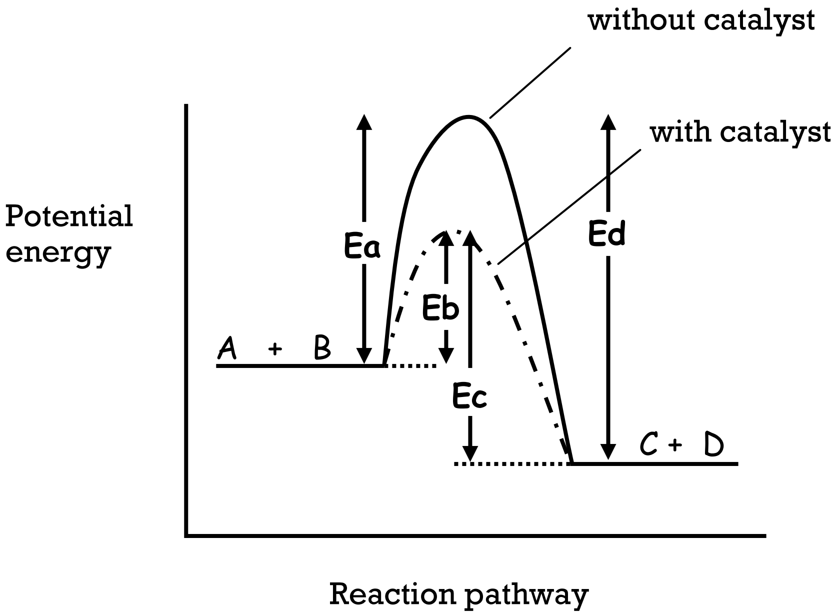
Decreasing the pressure will favour the side with the highest number of moles in the gas state.

Effect of a Catalyst

Consider the reversible reaction at equilibrium:

$$A + B \rightleftharpoons C + D$$

If a catalyst is added the rates of both the forward and backward reaction will be increased.



There is the **same decrease** in the **activation energies** of the **forward** and **backward** reactions and hence there is the same increase in their rates. Therefore, **a catalyst does not alter the position of equilibrium**. It does however, **speed up the rate at which equilibrium is attained.**

Equilibrium in Industry

The manufacture of ammonia is a very important reaction. Ammonia is made from nitrogen and hydrogen by the Haber Process. The reaction is reversible and if the conditions were kept constant equilibrium would be attained.

$$N_{2(g)} + H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -91 kJmol^{-1}$$

At equilibrium only 15% yield of ammonia is achieved however, the reaction conditions can be altered to increase the rate of the forward reaction to increase the yield of ammonia.

(a) Concentration

As a result of economic considerations, the Haber Process does not actually ever attain equilibrium. In a condenser, **the ammonia gas is cooled and the liquid ammonia piped off**. Constantly removing the ammonia gas decreases the rate of the backward reaction. In addition, the **unreacted nitrogen and hydrogen are recycled**. The increase in the concentrations of the reactant gases increases the rate of the forward reaction. The effect of both of these factors is a more economical production of ammonia.

(b) Pressure

Since the number of product molecules is less than the number of reactant molecules, increasing the pressure increases the rate of the forward reaction. The pressure chosen is about **200 atmospheres**. Beyond this pressure, the relative increase in the rate cannot justify the increased costs.

(c) Temperature

Since the reaction is exothermic, increasing the temperature decreases the percentage conversion of reactants to ammonia. However, if the temperature is too low the reaction is too slow. As a result, the Haber Process is carried out at a moderately high temperature of about **400°C.**

(d) Use of a catalyst

An **iron catalyst** is used in the Haber Process. The catalyst does not alter the position of equilibrium, it does however, allow the process to be carried out more efficiently at a lower temperature.

Chemical Energy

Enthalpy of Combustion

When 1 mole of a substance burns it releases a certain amount of energy which we call the enthalpy of combustion.

Definition of Enthalpy of Combustion:

The enthalpy of combustion is the energy released to the surroundings when one mole of a substance burns completely in oxygen.

When writing balanced equations for enthalpies of combustion it is important to ensure only 1 mole of the substance being burned is included in the equation:

- $C + O_2 \text{-->} CO_2$
- $H_2 + \frac{1}{2} O_2 \text{-->} H_20$
- $S + O_2 \text{-->} SO_2$
- $CO + \frac{1}{2} O_2 \text{-->} CO_2$
- $C_3H_8 + 5O_2 \text{-->} 3CO_2 + 4H_2O$

Enthalpy Calculations

There are two types of combustion calculations. In the first type the temperature difference is not mentioned and this calculation simply requires a proportion calculation to be carried out.

Worked example 1

When 1g of ethanol, gram formula mass 46g, is burned 30kJ of energy is released. Calculate the Enthalpy of Combustion for ethanol.

$$1\text{g} \longrightarrow 30\text{kJ}$$

$$46\text{g} \longrightarrow \frac{30 \times 46}{1}$$

$$1380\text{kJ}$$

This means that when 1 mole of ethanol burns it will produce 1380kJ. Since combustion is always an exothermic reaction the enthalpy of combustion is - 1380 **kJmol**$^{-1}$

Worked example 2

0.16g of methanol, CH_3OH is burned in a spirit burner. The heat from this combustion causes the temperature of 100g of water to be raised from 20°C to 27°C. Calculate the enthalpy of combustion of methanol.

Step 1

$$\begin{aligned} E_h &= c\,m\,\Delta T \\ &= 4.18 \times 0.1 \times 7 \\ &= 2.926\text{ kJ} \end{aligned}$$

Remember mass is always expressed in kg & 1cm^3 of water equals 1g

Step 2

$$0.16\text{g} \longrightarrow 2.926\text{kJ}$$

$$32\text{g} \longrightarrow \frac{2.926 \times 32}{0.16}$$

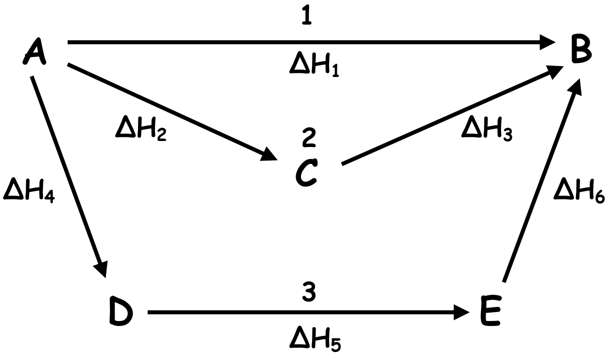
$$= 585.2\text{kJ}$$

So Enthalpy of Combustion, **ΔH = - 585.2 kJmol^{-1}**

Hess's Law

The Law of Conservation of Energy states that energy can neither be created nor destroyed, but that it can be changed from one form to another. This particular application of the **conservation of energy** law to **chemical reactions** is known as **Hess's Law**.

Hess's Law: the **enthalpy change** in converting reactants into products **is the same** regardless of the route by which the reaction takes place.



The total enthalpy change for route 1 = $\Delta \mathbf{H_1}$

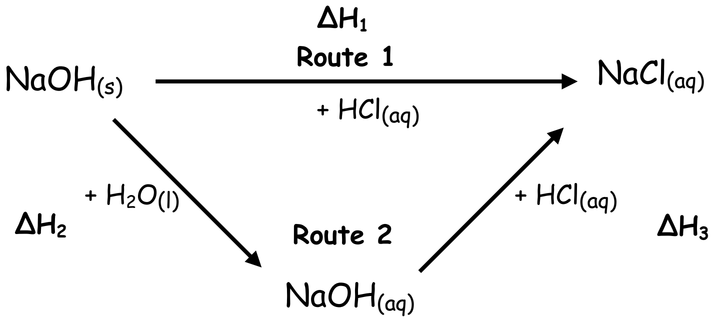
The total enthalpy change for route 2 = $\Delta \mathbf{H_2} + \Delta \mathbf{H_3}$

The total enthalpy change for route 3 = $\Delta \mathbf{H_4} + \Delta \mathbf{H_5} + \Delta \mathbf{H_6}$

According to Hess's Law the total enthalpy change for 1, 2 & 3 will be identical.

$$\Delta H_1 = \Delta H_2 + \Delta H_3 = \Delta H_4 + \Delta H_5 + \Delta H_6$$

The reaction can take place by two methods:



According to Hess's Law:

$$\boxed{\Delta \mathbf{H}_1 = \Delta \mathbf{H}_2 + \Delta \mathbf{H}_3}$$

Applications of Hess's Law

Hess's Law can be used to calculate enthalpy changes, which are difficult or impossible to determine, **by experiment.**

Enthalpy of Formation

Definition: The enthalpy of formation is the quantity of heat energy taken in or given out when **1 mole of a substance is formed from its elements in their normal state.**

Calculations

The information you need to tackle a calculation will either be given in the question or can be found in the data booklet.

Worked Example 1

Calculate the enthalpy of formation of ethane given that the enthalpies of combustion of carbon, hydrogen and ethane are -394kJmoll^{-1}, -286kJmoll^{-1} and -1560kJmol^{-1} respectively.

The first thing that you must do is write a balanced equation for the equation that you are required to calculate the enthalpy change for. This is called the Target Equation.

TE: $2C_{(s)} + 3H_{2(g)} \longrightarrow C_2H_{6(g)}$ $\Delta H = ?$

Next you need to construct balanced equations for each of the substances in your target equation, using the information given in the question.

(1) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -394$
(2) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$ $\Delta H = -286$
(3) $C_2H_{6(g)} + 3\frac{1}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\Delta H = -1560$

These equations can now be rearranged to give the target equation. Note that whatever change you make to the equation you must also make to the enthalpy value!

2 x (1) $2C_{(s)} + \cancel{2O}_{2(g)} \longrightarrow \cancel{2CO}_{2(g)}$ $\Delta H = -778$
3 x (2) $3H_{2(g)} + \cancel{1\frac{1}{2}O_{2(g)}} \longrightarrow \cancel{3H_2O}_{(l)}$ $\Delta H = -858$
reverse (3) $\cancel{2CO}_{2(g)} + \cancel{3H_2O}_{(l)} \longrightarrow C_2H_{6(g)} + 3\cancel{\frac{1}{2}O}_{2(g)}$ $\Delta H = +1560$

Once everything that appears on both the reactant side and the product side have been cancelled you should be left with your target equation!

$$2C_{(s)} + 3H_{2(g)} \longrightarrow C_2H_{6(g)} \qquad \Delta H = -76\text{kJmoll}^{-1}$$

Worked example 2

Use the enthalpies of combustion in your data booklet to find the enthalpy change for the reaction between ethyne and hydrogen to produce ethane.

TE: $C_2H_2 + 2H_2 \longrightarrow C_2H_6 \quad \Delta H = ?$

(1) $C_2H_2 + 2\frac{1}{2}O_2 \longrightarrow 2CO_2 + H_20 \quad \Delta H = -1300$
(2) $H_2 + \frac{1}{2}O_2 \longrightarrow H_20 \quad \Delta H = -286$
(3) $C_2H_6 + 3\frac{1}{2}O \longrightarrow 2CO + 3H_2O \quad \Delta H = -1560$

(1) $C_2H_2 + \cancel{2\frac{1}{2}O_2} \longrightarrow \cancel{2CO_2} + \cancel{H_20} \quad \Delta H = -1300$
2 x (2) $2H_2 + \cancel{O_2} \longrightarrow \cancel{2H_20} \quad \Delta H = -572$
reverse (3) $\cancel{2CO}_{2(g)} + \cancel{3H_2O}_{(l)} \longrightarrow C_2H_{6(g)} + \cancel{3\frac{1}{2}O}_{2(g)} \quad \Delta H = +1560$

$C_2H_2 + 2H_2 \quad C_2H_6 \quad \Delta H = -312 kJmoll^{-1}$

Bond Enthalpies

Bond enthalpies can be divided into two categories (see the Data Booklet).
The bond dissociation enthalpy is the energy required to break one mole of bonds and form two separate atoms, all species being in the gaseous state. These values are accurately known but it is only possible to calculate them for diatomic molecules, e.g.

$H_2(g) \rightarrow 2H(g) \quad +432\ kJ\ mol^{-1}$
$N_2(g) \rightarrow 2N(g) \quad +941\ kJ\ mol^{-1}$
$HCl(g) \rightarrow H(g) + Cl(g) \quad +428\ kJ\ mol^{-1}$

For molecules with more than two atoms, such as methane, it is only possible to calculate the mean bond enthalpy since the situation is much more complex with the C–H bonds breaking off one after the other to form a different fragment of the original molecule.

The removal of the first hydrogen atom from CH_4 does not require the same energy as the removal of the second hydrogen from the CH_3 fragment and so on. The value obtained is the average or mean bond enthalpy for C–H, i.e.

$$CH_4(g) \rightarrow C(g) + 4H(g) \qquad \Delta H = 4 \times C\text{–}H = 1656\ kJ\ mol$$

Therefore the mean bond enthalpy of C–H = 1656 / 4 = 414 kJ mol^{-1}

Mean bond enthalpies are quoted in data books for bonds of that type in any molecule but can also be calculated from other enthalpy changes, as shown in the following examples.

Example Question

Calculate the mean bond enthalpy of the C–H bond from the enthalpy of formation of methane and any other required data from the Data Booklet.

Step 1: **Write down the required equation:**

$CH_4 \rightarrow C(g) + 4H(g)$ $\Delta H = 4 \times$ C–H

Step 2: **Express all the information given in equation form:**

(1) $C(s) + 2H_2(g) \rightarrow CH_4(g)$ $\Delta H = –75$ kJ mol^{-1}
(2) $C(s) \rightarrow C(g)$ $\Delta H = + 715$ kJ mol^{-1}
(3) $H_2(g) \rightarrow 2H(g)$ $\Delta H = +432$ kJ mol^{-1}

Step 3: **Use the three equations to obtain the required balanced equation:**

(1) Reverse $CH_4(g) \rightarrow C(s) + 2H_2(g)$ $\Delta H = +75$ kJ mol^{-1}
(2) Nothing $C(s) \rightarrow C(g)$ $\Delta H = +715$ kJ mol^{-1}
(3) x2 $2H_2(g) \rightarrow 4H(g)$ $\Delta H = +864$ kJ mol^{-1}

Step 4**: Add the three equations to give the required equation and Δ*H*:**

$CH_4(g) \rightarrow C(g) + 4H(g)$ $\Delta H =$ 1654 kJ mol_{-1}

1654 kJ = 4 x C–H C–H = 1654 / 4

Mean bond enthalpy of C–H = 413.5 kJ mol_{-1}

REDOX Reactions

A REDOX reaction involves two **half** reactions - **oxidation** and **reduction**.

These half reactions can be written as **ion-electron** equations. Ion-electron equations are found on **page 11** of the Data Booklet.

Oxidation involves the **LOSS** of electrons **(OIL)**:

$Fe \longrightarrow Fe^{2+} + 2e$ $\qquad$ $Mg \longrightarrow Mg^{2+} + 2e$

The ion-electron equation for **oxidation** must be written in **reverse.**

Reduction involves the **GAIN** of electrons **(RIG):**

$Cu^{2+} + 2e \longrightarrow Cu$ $\qquad$ $Ag^{+} + e \longrightarrow Ag$

Remember, oxidation and reduction are **two halves** of the **same** chemical **reaction**. The combined reaction is called a **Redox** reaction.

To form the overall redox reaction, the ion-electron equations for the oxidation and reduction must be combined, ensuring that the electrons cancel.

Oxidation: $Mg_{(s)} \longrightarrow Mg^{2+} + 2e$

Reduction: $Ag^{+} + e \longrightarrow Ag_{(s)}$ (x2)

$Mg_{(s)} + 2Ag^{+} \longrightarrow Mg^{2+} + 2Ag_{(s)}$

Oxidation: $Al_{(s)} \longrightarrow Al^{3+} + 3e$ (x2)

Reduction: $2H^{+} + 2e \longrightarrow H_{2(g)}$ (x3)

$Mg_{(s)} + 2Ag^{+} \longrightarrow Mg^{2+} + 2Ag_{(s)}$

Oxidising and Reducing Agents

In a redox reaction the species that is oxidised is described as a **reducing agent** - a species that allows reduction to occur.

Similarly, a species which is reduced is described as an **oxidising agent** - a species that allows oxidation to occur.

eg.

$$\underset{\substack{\uparrow \\ \text{reducing agent}}}{Mg_{(s)}} \quad + \quad \underset{\substack{\uparrow \\ \text{oxidising agent}}}{2Ag^{+}} \quad \longrightarrow \quad Mg^{2+} \quad + \quad 2Ag_{(s)}$$

Using the Data Booklet

When writing redox equations you must first identify the oxidation and reduction half reactions and then combine them to give the redox reaction. Use the Electrochemical Series on page 12 of the data booklet.

Example:

Iron(II)sulphate solution is reacted with potassium permanganate solution until the first appearance of a permanent pink colour.

Step 1: What four ions are present in the two solutions?

Step 2: Write the ion-electron equation for the oxidation reaction.

Step 3: Write the ion-electron equation for the reduction reaction.

Step 4: Add the two half equations together to give the redox equation (remember to balance the electrons first)

To find the species being oxidised in the solution start at the top right and work your way down until you find the first atom or ion being oxidised from the solution. Highlight it when you find it.

$Li^{+}_{(aq)} + e^{-} \longrightarrow Li_{(s)}$

$Cs^{+}_{(aq)} + e^{-} \longrightarrow Cs_{(s)}$

$Rb^{+}_{(aq)} + e^{-} \longrightarrow Rb_{(s)}$

$K^{+}_{(aq)} + e^{-} \longrightarrow K_{(s)}$

$Sr^{2+}_{(aq)} + 2e^{-} \longrightarrow Sr_{(s)}$

$Ca^{2+}_{(aq)} + 2e^{-} \longrightarrow Ca_{(s)}$

$Na^{+}_{(aq)} + e^{-} \longrightarrow Na_{(s)}$

$Mg^{2+}_{(aq)} + 2e^{-} \longrightarrow Mg_{(s)}$

$Al^{3+}_{(aq)} + 3e^{-} \longrightarrow Al_{(s)}$

$Zn^{2+}_{(aq)} + 2e^{-} \longrightarrow Zn_{(s)}$

$Cr^{3+}_{(aq)} + 3e^{-} \longrightarrow Cr_{(s)}$

$Fe^{2+}_{(aq)} + 2e^{-} \longrightarrow Fe_{(s)}$

$Ni^{2+}_{(aq)} + 2e^{-} \longrightarrow Ni_{(s)}$

$Sn^{2+}_{(aq)} + 2e^{-} \longrightarrow Sn_{(s)}$

$Pb^{2+}_{(aq)} + 2e^{-} \longrightarrow Pb_{(s)}$

$Fe^{3+}_{(aq)} + 3e^{-} \longrightarrow Fe_{(s)}$

$2H^{+}_{(aq)} + 2e^{-} \longrightarrow H_{2(g)}$

$Sn^{4+}_{(aq)} + 2e^{-} \longrightarrow Sn^{2+}_{(aq)}$

$Cu^{2+}_{(aq)} + e^{-} \longrightarrow Cu^{+}_{(aq)}$

$SO_4{}^{2-}_{(aq)} + 2H^{+}_{(aq)} + 2e^{-} \longrightarrow SO_3{}^{2-}_{(aq)} + H_2O_{(l)}$

$Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)}$

$I_{2(s)} + 2e^{-} \longrightarrow 2I^{-}_{(aq)}$

$Fe^{3+}_{(aq)} + e^{-} \longrightarrow Fe^{2+}_{(aq)}$

$Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)}$

$Hg^{2+}_{(aq)} + 2e^{-} \longrightarrow Hg_{(s)}$

$Br_{2(l)} + 2e^{-} \longrightarrow 2Br^{-}_{(aq)}$

$O_{2(g)} + 4H^{+}_{(aq)} + 4e^{-} \longrightarrow 2H_2O_{(l)}$

$Cr_2O_7{}^{2-}_{(aq)} + 14H^{+}_{(aq)} + 6e^{-} \longrightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$

$Cl_{2(g)} + 2e^{-} \longrightarrow 2Cl^{-}_{(aq)}$

$MnO_4{}^{-}_{(aq)} + 8H^{+}_{(aq)} + 5e^{-} \longrightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$

$F_{2(g)} + 2e \longrightarrow 2F^{-}_{(aq)}$

To find the species being reduced in the solution start at the bottom left and work your way up until you find the first atom or ion from the solution. Highlight it when you find it.

More Complicated Half-Equations

There are some ion-electron equations that are not given in the data book. You must learn the rules to work them out for yourself.

Worked example

Write an ion-electron equation for the following reaction:

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$

Step 1: If necessary, balance the central atom / ion.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

Step 2: Add water (H_2O) if it is needed to balance the oxygen atoms.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

Step 3: Balance the hydrogen in the water by adding hydrogen ions.

$$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$

Step 4: Calculate the total electrical charge on each side of the equation.

$$\underbrace{Cr_2O_7^{2-} + 14H^+}_{(12+)} \longrightarrow \underbrace{2Cr^{3+} + 7H_2O}_{(6+)}$$

Step 5: Add electrons to balance the electrical charges.

$$\underbrace{Cr_2O_7^{2-} + 14H^+}_{(12+)} + \underbrace{6e^-}_{(6-)} \longrightarrow \underbrace{2Cr^{3+} + 7H_2O}_{(6+)}$$

Chemical Analysis

Chromatography

Chromatography is a method of separating and analysing a mixture of soluble chemical substances.
There are different types of Chromatography techniques. The most common is paper chromatography.

Diagram showing a paper chromatograph

Uses of Chromatography

Chromatography can be used to follow the course of a chemical reaction or to establish the products of a chemical reaction.

It can also be used to identify additives in foods, analyse fibres found at a crime scene and fingerprinting.

Paper Chromatography

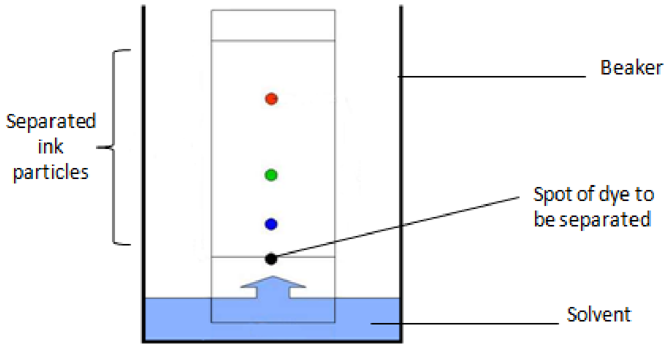
During paper chromatography a small sample of the mixture being tested is spotted onto the base line (a straight line usually drawn in pencil above the level of the solvent) on the filter paper. The filter paper is then placed in a solvent.

By capillary action the solvent moves up the paper. This is when different components of the mixture are separated.

Components can move quickly or slowly up the paper depending on the solvent used.

There are two stages in paper chromatography; the Mobile Phase and the Stationary Phase.

The solvent is the mobile phase in paper chromatography and the wet paper is the stationary phase.



Why does separation occur?

Separation of the mixture occurs due to the polarity and size of the molecules within the mixture. Depending on what solvent is used depends on how the molecules behave.

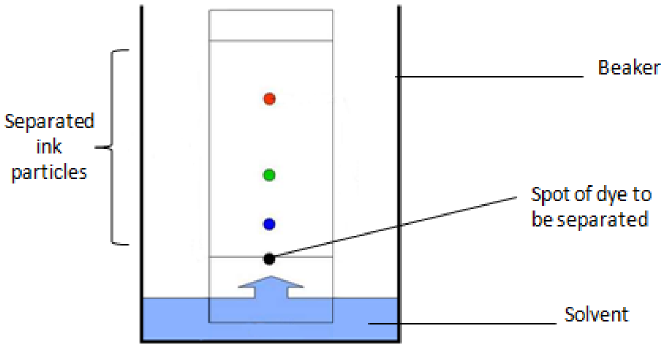
For example, if a mixture contains very polar molecules and non-polar molecules and a polar solvent, such as ethanol, is used the polar molecules move much quicker up the filter paper. This is because the less polar molecules will be more attracted to the mobile phase.
In terms of large and small molecules smaller molecules move much quicker and further up the filter paper compared to larger molecules.

The Retention Factor (Rf) Values

The Rf factor can be used to compare the different components found in a sample. The Rf values of a mixture being tested can be compared with known samples.

$$\boxed{\text{Rf} = \frac{\text{distance from the base line to the spot}}{\text{distance from the base line to the solvent front}}}$$

Note: if two substances on chromatography paper have the same Rf value it is likely that they are the same compound. If they do not have the same Rf value then they are definitely different compounds.



The Rf value of the red, green and blue particles can be measured and calculated to prove that certain molecules are present in the mixture.

Redox Titrations

As with volumetric titrations there has to be a way of determining the end-point of the reaction. For many reactions an **indicator** must be used however, for some redox reactions the end-point can be recognised from a colour change in one of the reactants, for example, when potassium permanganate solution (purple) reacts with iron(II) sulphate solution, the permanganate ions are reduced to colourless manganese ions. When a colour change involving one of the reactants is used to determine the end-point the reaction is said to be **self-indicating**.

Worked example:
20cm^3 of iron(II)sulphate were titrated with 0.01mol^{-1} potassium permanganate solution until a permanent pink colour was observed. If the volume of potassium permanganate used was 25.6cm^3, what is the concentration of the iron(II)sulphate solution?

Step 1: write the ion-electron equations and combine to give the redox equation.

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \qquad (x5)$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_20$$

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

mole ratio 5 : 1

Step 2: calculate the number of moles of the 'known' substance

Moles = c x v
MnO_4^- 0.01 x 0.0256
0.000256 moles

using the mole ratio: 5 : 1

0.00128 : 0.000256

Step 3: calculate the concentration of the iron(II)sulphate solution

$$C = \text{moles} / v$$
$$\frac{0.00128}{0.02}$$
$$= 0.064moll^{-1}$$

Word	Meaning
Atom Economy	The proportion of reactant atoms which are incorporated into the desired product of a chemical reaction. $\% \text{ atom economy} = \dfrac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100$
Batch processes	These involve mixing one batch of reactants in a vessel, allowing the reaction to complete, then removal of the products, before reloading with a fresh batch of reactants.
Bond Dissociation Enthalpy	Energy required to break one mole of bonds to form two separate atoms, all species being in the gaseous state.
Capital costs	Capital costs are incurred in the initial building of the plant and associated infrastructure.
Cash flow	Cash flow is the movement of money into and out of a business, and is a measure of profitability.
Continuous processes	These take place in a plant where reactants are fed in continuously at one end, and products are removed continuously from the other.
Chromatography	A method of separating and analysing a mixture of soluble chemical substances.
Dynamic equilibrium	A dynamic equilibrium is achieved when the rates of two opposing processes become equal, so that no net change results
Electrodes	The electrodes (one negative and one positive) dip into the electrolyte and form the connection to the electric wires. Any chemical reactions occur at their surfaces.
Electrolysis	Electrolytes are liquids containing ions which are free to move, and are therefore capable of conducting electricity.

Word	Meaning
Electrolyte	Electrolytes are liquids containing ions which are free to move, and are therefore capable of conducting electricity.
Electrolytic cell	An electrolytic cell is the equipment used to carry out electrolysis – oxidation occurs at the positive electrode and reduction at the negative electrode.
Equilibrium	Chemical equilibrium is the state reached by a reaction mixture when the rates of forward and reverse reactions have become equal
Excess	Reactant added which is not all used up in the reaction.
Feedstock	Feedstocks are the reactants from which other chemicals can be extracted or synthesised.
Fixed costs	Fixed costs are incurred irrespective of whether a plant is operating at maximum or only at partial capacity.
Hess's law	The enthalpy change for a chemical reaction is independent of the route taken, providing the starting point and finishing point is the same for both routes.
Molar Volume	The volume, in litres, occupied by one mole of gas under standard conditions of temperature and pressure.
Ion-electron equations	An ion-electron equation is a half-equation, either an oxidation or a reduction, which in combination of the opposite type, can be part of a complete redox equation.
Oxidation	An oxidation is a loss of electrons by a reactant in any reaction.
Oxidising agent	An oxidising agent is a substance which accepts electrons.
Pilot plant	A pilot plant is a small scale chemical plant, built with similar materials to a fullscale one, to investigate the chemical and engineering aspects of a process before a full-scale plant is

Word	Meaning
	built.
Raw materials	Raw materials are the initial starting materials from which the a process's feedstock is derived.
Reducing agent	A reducing agent is a substance which donates electrons.
Reduction	A reduction is a gain of electrons by a reactant in any reaction.
Stoichiometry	Stoichiometry means literally 'measuring elements' and is concerned with the quantities of substances reacting and the quantities of substances produced as derived from the balanced equation, i.e. it is concerned with mole relationships.
Variable costs	Variable costs are dependent on a plant's output.
Yield	Quantity of product obtained in a reaction, usually given as % yield = actual/theoretical x100.