AS
and A Level
Chemistry

STUDENT MATHS SUPPORT

PEARSON

Contents

Introduction

Congratulations on choosing A level chemistry!

Quite a few chemistry students are also very competent at maths but, if that's not you, don't worry! There's very little mathematics that you'll encounter in A level chemistry that you haven't yet seen in your Mathematics GCSE. Of course, you do need to be well practised in a few number-related skills to master chemistry, but most of these fall into the category of relatively simple calculations. You'll discover, as you practice more and more calculations over the next two years, that chemistry calculations at A level fall into one of a small number of types, and you'll soon pick up the necessary steps to work your way through.

Quite a lot of mathematics in chemistry is about one of three things: how much of a substance is involved in a reaction; how fast the reaction is going; and how far has a reaction gone. Two of these – calculations involving reacting quantities (or moles) and calculations involving reaction rates are ones that you'll have come across at GCSE. The last one – the idea of reactions at equilibrium – is an idea you may have seen at GCSE, but you've yet to put numbers into the idea.

So why do chemists use maths? Mostly, because it's good for describing patterns clearly and because it allows chemists to put a number on things: rather than saying something **increases** we'd like to be able to say by **how much**.

This might mean that you find your chemistry teachers look at equations and mathematics a bit differently than your maths teachers. This is partly because maths teachers see maths as a series of skills – which is why much of maths, especially at A level, uses letters rather than numbers. Chemists see mathematics as a tool to support the quantitative nature of the science. So, we're less concerned with a theoretical problem than we are with real life problems and situations.

Having said that, it is important that you have some understanding of the mathematical processes you'll use in different situations in Chemistry A level. Of course, it is simply possible to recognise which equation needs to be used in which chemical scenario, to substitute numbers, and to calculate a value. However, this approach lacks flexibility in dealing with questions where the data provided is a bit sneaky and different! Also, students who simply use equations with no idea of what they are doing often won't look at the answer and notice if the final result looks odd. For example, imagine you'd simply learned to put numbers into an equation to calculate the pH of an acidic solution (as you will in the second year of A level) and you came up with the answer 9.45. Someone that uses maths blindly would underline their answer and move on to the next question. A good chemist would spot the problem (an acidic solution with a pH greater than 7…), and go back and look at the numbers again and work out what had gone wrong.

The moral is – learn to use the maths, but don't forget the Chemistry!

How to use maths in chemistry

The better your ability to visualise patterns and understand equations in chemistry, the easier you will find it. This booklet aims to give you some pointers to and some practice in those bits of maths that come up frequently in A level Chemistry. It also shows you the calculating skills you need to practise so that you can find answers quickly and check they are reasonable. Chemistry calculations might seem daunting at first but don't be put off: like anything else that is worth doing, you will get good at them through practice.

You might find it useful to use this guide after attending lessons in a topic where you will see how most of the equations given can be derived.

Basic toolkit for all chemistry calculations

There are two ideas and techniques that come up very frequently in chemistry and it's worth looking at these before looking at more detailed techniques.

Simple proportions or ratios

Here's a simple question:

> John has a box of Mars bars. He places two Mars bars on a weighing balance and finds that they have a mass of 126 g. How much would three Mars bars weigh?

Hopefully you would answer this by thinking:

> One Mars bar must weigh $\dfrac{126\,g}{2}$ = 63 g.
>
> So three Mars bars weigh 63 g × 3 = 189 g.

You use exactly the same skills when you do a simple moles calculation in chemistry – using ratios within the chemical equation. The only difference is that you're dealing with atoms, not Mars bars; and different atoms all have different masses.

The idea of simple proportions is very important when it comes to looking at calculations involving solutions, which you'll encounter at the start of the A level course.

For example:

> Emily made a solution of copper sulfate by dissolving 6 g of copper sulfate into 25 cm^3 of water.
>
> She now wants to make 1000 cm^3 of copper sulfate solution of the same concentration. What mass of copper sulfate will she need?

As always, there are different ways of approaching this problem.

One method is:

> I need 6 g of copper sulfate to make 25 cm^3 of solution
>
> So to make 1 cm^3 of solution I'd need $\dfrac{6}{25}$ g of copper sulfate.
>
> And to make 1000 cm^3 of solution, I'll need $\dfrac{6}{25} \times 1000 = 240$ g.

Another method is:

> I want to scale up making this solution.
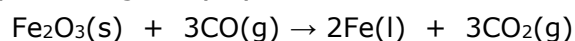> 25 cm^3 × 10 = 250 cm^3
> And 250 cm^3 × 4 = 1000 cm^3.
> So the mass of copper sulfate I'll need must be 6 × 10 × 4 = 240 g.

In many ways, the method doesn't matter – as long as you get the right answer! – but it is quite important to see **why** the calculation works. For this reason, don't rely on the 'equation triangles' that some people use.

Practice questions

1. Iron is made by reducing iron(III) oxide with carbon monoxide:
$$Fe_2O_3(s) \; + \; 3CO(g) \rightarrow 2Fe(l) \; + \; 3CO_2(g)$$
If we start with 10 moles of iron(III) oxide:

(a) how many moles of iron are produced?

(b) how many moles of carbon monoxide will be needed to reduce the iron(III) oxide?

2. A solution of sodium thiosulfate has a concentration of 37 g / l.

What mass of sodium thiosulfate is dissolved in 250 cm^3 of this solution?

(Hint: 1 litre = 1 dm^3 = 1000 cm^3)

Changing the subject of an equation

Let's remind you how changing the subject of an equation works by taking a simple example. In this case, we'll look at an example that isn't from chemistry, just to show that the principle is universal.

$$\text{speed}(s) = \frac{\text{distance}(d)}{\text{time}(t)}$$

Let's make time the subject of this equation. Firstly, we'll multiply each side by time (t):

$$s \times t = \frac{d \times t}{t}$$

On the right-hand side, the 't's cancel:

$$s \times t = d$$

And now we can divide both sides by s:

$$\frac{s \times t}{s} = \frac{d}{s}$$

And the 's's now cancel to give:

$$t = \frac{d}{s}$$

Where you can, think of a "sense check" you can do. Here, it's easy – imagine a car travelling at 50 miles per hour, and travelling 100 miles. How long will it take? Fairly obviously, it does 50 miles in the first hour, and another 50 miles in the second hour, so the answer is 2 hours.

Now look at our equation above: $t = \dfrac{d}{s} = \dfrac{100\,\text{miles}}{50\,\text{miles per hour}} = 2$ hours.

If you find this difficult, then it may be wise to learn the transformed formulae.

You could use the three-fold attack for learning any equation mentioned:
- learn the equation
- learn what each symbol stands for
- learn the units for each quantity.

The combination of these is most helpful, especially the units, as these will often inspire the correct equation, when read, in an examination question.

Maths Skills for Chemists

Mole calculations

There are three methods of measuring quantities:

- mass (in grams, g) for a solid, using a top pan balance
- volume (in cubic centimetres, cm^3) for a liquid or solution, using a burette, pipette, measuring cylinder or a volumetric flask
- counting.

Though we will often measure mass and volume, it is most convenient to always relate quantities in chemistry to each other by **counting actual particles** (atoms, molecules or ions as appropriate).

Because particles are so small, typically about one ten-millionth of a millimetre in diameter, we count in 'bundles' of approximately 6×10^{23} (Avogadro's number – the number of carbon atoms in 12 g of carbon, where the carbon is made up of atoms containing six protons and six neutrons).

- We call 6×10^{23} one **mole,** written **1 mol**.
- We need to specify the type of particles.

For example, 1 mol of hydrogen **atoms**, H, is different to 1 mol of hydrogen **molecules**, H_2 (which contains 2 mol of hydrogen **atoms**).

- To convert from moles to numbers, just multiply by 6×10^{23}.
- So number of atoms in a molecule = $n \times 6 \times 10^{23}$ where n is the number of atoms that makes up the molecule.

Worked example

How many atoms are in 1 mol of water, H_2O?

Answer

Number of atoms = 3 (two hydrogen atoms, one oxygen atom) $\times 6 \times 10^{23}$

$\qquad\qquad\qquad = 1.8 \times 10^{24}$

Practice question

The Avogadro constant is 6.0×10^{23} mol^{-1}.

The number of **atoms** in 1 mol of dinitrogen tetroxide, N_2O_4, is:

A 3.6×10^{24}
B 1.2×10^{24}
C 6.0×10^{23}
D 1.0×10^{23}

Interpretation of symbols, formulae & equations

- A **symbol** stands for one mole of atoms of an element.

  O stands for one mole of oxygen atoms.

- A **formula** stands for one mole of a compound, or element.

  $CaCl_2$ stands for one mole of calcium chloride which contains one mole of calcium ions and two moles of chloride ions.

  Cl_2 stands for one mole of chlorine gas which contains two moles of chlorine atoms.

- An **equation** is interpreted is the same way.

  $Zn(s) + 2HCl(aq) \rightarrow ZnSO_4(aq) + H_2(g)$ stands for one mole of atoms of zinc in the solid state **reacting with** two moles of hydrochloric acid in aqueous solution **to form** one mole of zinc sulphate in aqueous solution **and** one mole of molecules of hydrogen in the gaseous state.

You will find this useful in calculations based on equations.

To convert from a mass to a number of moles

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

where n = amount (mol); m = mass (g); M = molar mass (g mol^{-1}).

Learn:

1 the equation
2 what each symbol stands for
3 the units for each quantity.

You also need to be able to change the subject of this relationship:

$$m = n \times M \qquad M = \frac{m}{n}$$

If you find this difficult learn them separately.

Practice question

Copper(II) sulfate solution, $CuSO_4(aq)$, can be made by adding excess copper(II) oxide, CuO, to hot dilute sulfuric acid. This is an exothermic reaction. The balanced equation for this reaction is

$$CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$$
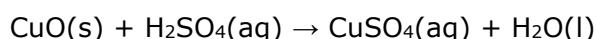
Calculate the mass of copper(II) oxide needed, if a 10% excess is required, when 0.020 mol of sulfuric acid is completely reacted.

[Relative atomic masses: Cu = 63.5 and O = 16.0]

Molar mass

The **molar mass** is the mass of one mole of a substance.

For atoms of an element this is called the relative atomic mass of the element, symbol A, still measured in g mol^{-1}.

For molecules or compounds this molar mass needs to be calculated. For example:

- H_2 has molar mass 2 g mol^{-1}
- $FeSO_4.7H_2O$ has molar mass
  $(56 \times 1) + (32 \times 1) + (16 \times 4) + [7 \times (1 \times 2 + 16)] = 278$ g mol^{-1}

g mol^{-1} means 'gram per mole'.

The '-1' is the mathematical way of writing 'per' – it literally means 'divided by'.

Practice question

Calculate the molar mass of copper(II) sulfate-5-water, $CuSO_4.5H_2O$.

Remember to include the appropriate units in your answer. You will need to use the Periodic Table as a source of data.

Amounts of gases

Amounts of gases are usually measured by volume, either in cm^3 if a gas syringe is being used, or in dm^3 (1 dm^3 = 1000 cm^3).

As gas molecules are very small compared to the volume they occupy, the volume of a gas depends only on the number of molecules of gas, or the number of moles of gas molecules.

At 298 K (25°C) and atmospheric pressure, one mole of any gas occupies approximately 24 dm^3 (this is called the molar volume of a gas – you will always be told the value).

To convert volumes to moles use:

$$n = \frac{V}{24}$$

where n = amount (mol); V = volume (dm^3).

As usual you should be able to find V given n using:

$$V = n \times 24$$

If you are given small volumes of gas (in cm^3), then you can adapt the equations here by using 24 000 cm^3 as the molar volume in place of 24 dm^3: the important thing is that the units for molar volume should be the same as the units for the volume of gas!

Practice question

The equation for the complete combustion of ethane is

$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$$
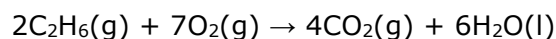
What volume of oxygen, measured at room temperature and pressure, is needed to completely burn 0.1 mol of ethane?

[The volume of 1 mol of any gas measured at room temperature and pressure is 24 dm^3]

A 2.4 dm^3

B 4.8 dm^3

C 8.4 dm^3

D 16.8 dm^3

Amounts of liquids

Amounts of liquids are usually measured by volume in cm^3 using a measuring cylinder, graduated pipette, or graduated syringe.

To convert volumes to moles a different method is needed.

First the mass, m, needs to be found using the relationship between mass, volume, V, and density, ρ (the Greek letter rho – pronounced 'row' as in rowing a boat).

$$\rho = \frac{m}{V} \qquad m = \rho V$$

Where m = mass (g); V = volume (cm^3); ρ = density (g cm^{-3}).

Amount in moles $n = \dfrac{\rho V}{M}$

Either be able to rearrange the equation or learn $V = \dfrac{nM}{\rho}$.

Practice question

Calculate the volume of 0.125 mol of butan-1-ol, in cm^3.

[Density of butan-1-ol = 0.81 g cm^{-3}]

Amounts of solutions

Do not confuse liquids and solutions.

$$n = \frac{V}{1000} \times c$$

Where n = amount of solute (mol); c = concentration (mol dm^{-3}); V = volume of solution (cm^3).

Note the use of 1000 here. This is used because V is measured in cm^3, but c is measured in mol dm^{-3}; so V is divided by 1000 to convert the volume from cm^3 into dm^3.

> **Practice question**
>
> How many moles of **ions** are present in 20 cm^3 of 0.050 mol dm^{-3} calcium chloride solution, $CaCl_2(aq)$?
>
> **A** 0.0050
>
> **B** 0.0030
>
> **C** 0.0020
>
> **D** 0.0010

Percentage yields

$$Percentage\ yield = \frac{actual\ amount\ formed\ (mol) \times 100}{expected\ amount\ (mol)}\%$$

It is also perfectly acceptable to work in quantities measured in grams.

The expected amount formed is found from the initial amount in moles of the reactant (the one that is **not** in excess) and the chemical equation for the reaction.

Note that questions will be set both on calculating yields and calculating initial amounts of chemicals required to produce a certain amount of product.

In a multi-step process percentage yields are multiplied together to give the overall yield for the process.

> **Practice question**
>
> Calculate the percentage yield if 2.7 g of copper(II) sulfate-5-water is obtained from reacting 0.020 mol of sulfuric acid with excess copper(II) oxid3.

Enthalpy changes

There are two keys to enthalpy calculations.

- Learn the definitions of the terms used.
- To avoid forgetting signs in calculations, write all numbers in brackets with their signs.

Enthalpy

Enthalpy is heat energy at constant pressure. It refers to the energy of the **chemicals**.

If a reaction is exothermic heat is given out so the sign of the enthalpy change is negative.

To indicate a 'standard' enthalpy change, we use a superscript after the ΔH sign – this is usually in the form of a degree symbol: $\Delta H°$ or a symbol similar to a Greek theta: $\Delta H^{\ominus}$.

Practice question

In an experiment to measure the enthalpy change of a reaction involving gases, which of the following conditions must always be kept constant?

A   Pressure

B   Temperature

C   Volume

D   Temperature and pressure

Standard enthalpy changes

Refer to the amounts in a chemical equation measured in moles. The enthalpy change is measured in kJ mol^{-1}.

Standard means measured under standard conditions i.e. atmospheric pressure (100 kPa) and temperature (298 K). All chemicals must be in their standard states.

Calculation of standard enthalpy changes

First use this equation:

$$Q = mc\Delta T$$

where Q = energy exchanged; m = mass; c = specific heat capacity (always given in questions); ΔT = change in temperature (final – initial).

Then use:

$$\Delta H = \frac{-Q}{n}$$

where ΔH = enthalpy change (J mol^{-1}); Q = energy exchanged (J); n = amount (mol).

NB If the temperature rises, the reaction is exothermic and ΔH is negative.

Standard states

Standard states are the most stable states under standard conditions, e.g. $H_2O(l)$, $CO_2(g)$, $Na(s)$.

However, note that for carbon, the most stable state is C(graphite).

Solutions are aqueous and concentrations are 1 mol dm^{-3}.

Standard enthalpy change of formation $\Delta_f H$

$\Delta_f H$ is the standard enthalpy change when 1 mol of compound:

- forms from its elements
- under standard conditions.

From this definition the standard enthalpy change of formation of an element is zero.

Calculation of enthalpy changes from $\Delta_f H$ values

$\Delta_f H$ = The sum of $\Delta_f H$ of products – the sum of $\Delta_f H$ of reactants.
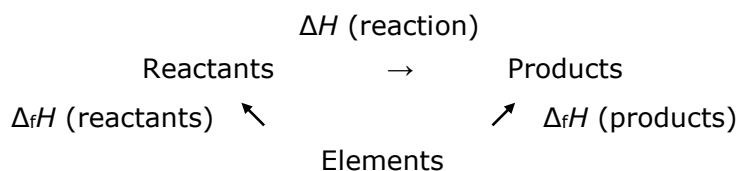
Each $\Delta_f H$ must be multiplied by the amount in front of the chemical in the chemical equation.

Hess's Law

Hess's Law is an application of the conservation of energy:

When there are two routes to the products from the same starting materials the total enthalpy change for each route is the same.

Hess's Law triangles

$$\Delta H \text{ (reaction)}$$

Reactants $\qquad \rightarrow \qquad$ Products

$\Delta_f H$ (reactants) ↘ $\qquad\qquad$ ↗ $\Delta_f H$ (products)

Elements

By Hess's Law:

$$\Delta_f H(\text{reactants}) + \Delta H(\text{reaction}) = \Delta H(\text{products})$$
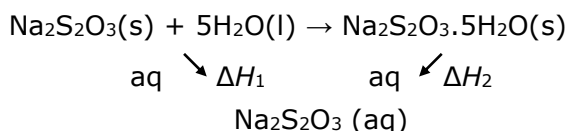
So:

$$\Delta H(\text{reaction}) = \Delta_f H(\text{products}) - \Delta_f H(\text{reactants})$$

Do not to forget to multiply by the numbers in the chemical equation.

Practice question

The enthalpy change for the reaction to form hydrated sodium thiosulfate crystals cannot be measured directly.
The following Hess's Law cycle can be used.

$$Na_2S_2O_3(s) + 5H_2O(l) \rightarrow Na_2S_2O_3.5H_2O(s)$$

aq $\searrow \Delta H_1$ aq $\nearrow \Delta H_2$

$$Na_2S_2O_3 \ (aq)$$

The enthalpy change for the reaction, $\Delta_r H$, is equal to:
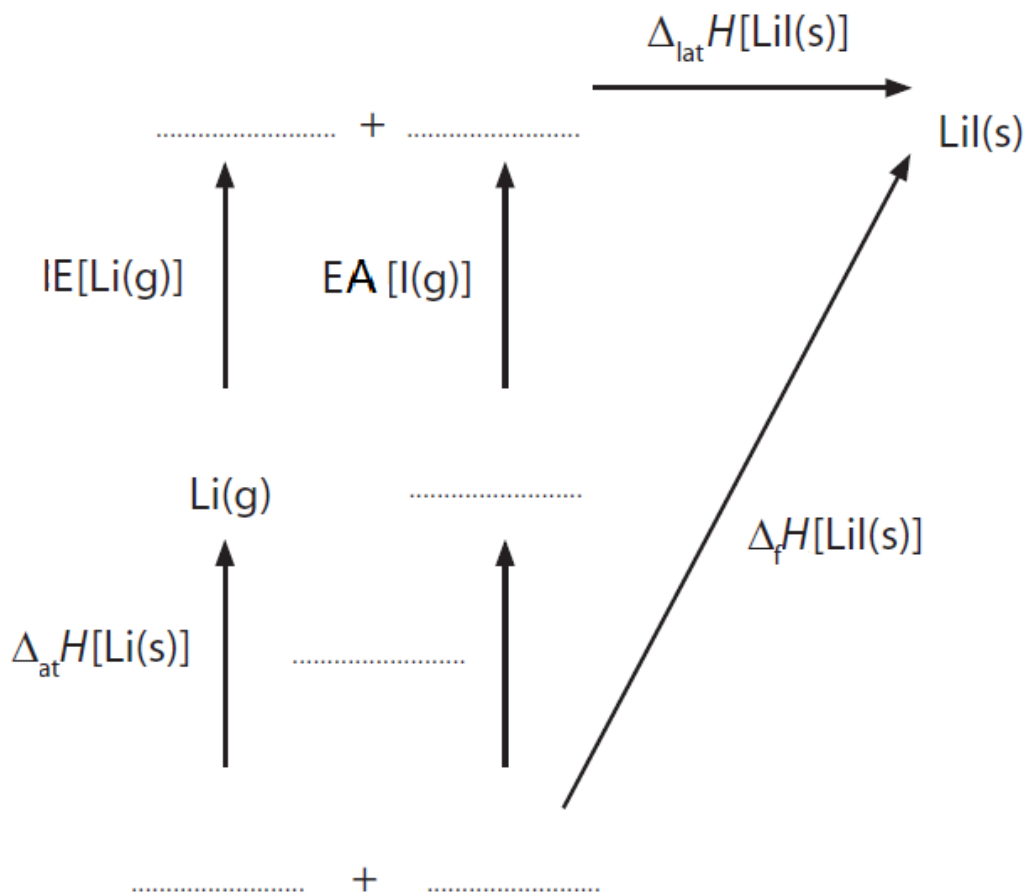
A $\Delta H_1 + \Delta H_2$

B $\Delta H_1 - \Delta H_2$

C $-\Delta H_1 - \Delta H_2$

D $-\Delta H_1 + \Delta H_2$

Other definitions

- **Standard enthalpy change of combustion**, $\Delta_c H$: the enthalpy change when one mole of a compound is completely burned in oxygen.

- **Standard enthalpy of atomisation**, $\Delta_{at} H$ of an element: the enthalpy change when one mole of atoms of an element are formed, e.g. $\frac{1}{2}H_2(g) \rightarrow H(g)$

- The **enthalpy change of neutralisation** of an acid, $\Delta_n H$: the enthalpy change when an acid is completely neutralised by an alkali to form 1 mole of water.

- The **first ionization energy** of an element is the enthalpy change when one mole of electrons are removed from one mole of atoms of the element, in the gaseous state, to form one mole of singly-charged positive ions in the gaseous state
e.g. $Na(g) \rightarrow Na^+(g) + e$ or $O(g) \rightarrow O^+(g) + e$

- The **second ionization energy** of an element is the enthalpy change when one mole of electrons are removed from one mole of singly-charged ions of the element, in the gaseous state, to form one mole of doubly-charged positive ions, in the gaseous state e.g. $Na^+(g) \rightarrow Na^{2+}(g) + e$
Note that $Mg(g) \rightarrow Mg^{2+}(g) + 2e$ is the sum of the 1st and 2nd IE for magnesium

- The **first electron affinity** of an element is the enthalpy change when one mole of electrons is gained by one mole of atoms of the element, in the gaseous state, to form one mole of singly negative ions in the gaseous state e.g. $Cl(g) + e \rightarrow Cl^-(g)$

- The **second electron affinity** of an element is the enthalpy change when one mole of electrons is gained by one mole of singly negative ions of the element, in the gaseous state, to form one mole of doubly negative ions in the gaseous state
e.g. e.g. $O^-(g) + e \rightarrow O^{2-}(g)$

- The **lattice energy** of an ionic compound is the enthalpy change when one mole of an ionic salt forms from its gaseous ions.

Practice question

a On the energy cycle below, fill in the missing formulae (including state symbols) and the missing enthalpy change.

$$\Delta_{lat}H[LiI(s)]$$

.... + ... $\longrightarrow$ LiI(s)

$IE[Li(g)]$ $EA [I(g)]$

Li(g)   ....

$\Delta_{at}H[Li(s)]$ .... $\Delta_f H[LiI(s)]$

.... + ...

b Calculate the electron affinity of iodine, EA[I(g)], using the data below.

	$\Delta H/kJ\ mol^{-1}$
Lattice energy for lithium iodide, $\Delta_{lat}H$	−759
Enthalpy change of atomization of lithium, $\Delta_{at}H$	+159
Enthalpy change of atomization of iodine, $\Delta_{at}H$	+107
First ionization energy of lithium, IE	+520
Enthalpy change of formation of lithium iodide, $\Delta_f H$	−270

Entropy

Entropy change of system, ΔS_{sys}

Just like enthalpy changes, you calculate entropy change of system by subtracting entropy values for the reactants from entropy values for the products.

Just like with enthalpy changes, remember to multiply by the coefficients in the chemical equation.

Unlike enthalpies, elements have non-zero entropy values.

Always give sign and units (J mol^{-1} K^{-1}).

Entropy changes of surroundings, ΔS_{surr}

$$\Delta S_{surr} = \frac{-\Delta H}{T}$$

To find entropy change of surrounding, use **minus** enthalpy change **in J** divided by temperature **in K**.

Remember sign, units and significant figures.

Total entropy change, ΔS_{tot}

The total entropy changes is the sum of entropy change of system and entropy change of surroundings i.e. $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$

If this is positive the reaction is spontaneous.

Practice question

Calculate the temperature for a reaction to be spontaneous if:

$\Delta S_{system} = +225$ J K^{-1} mol^{-1} and $\Delta H = +206.1$ kJ mol^{-1}
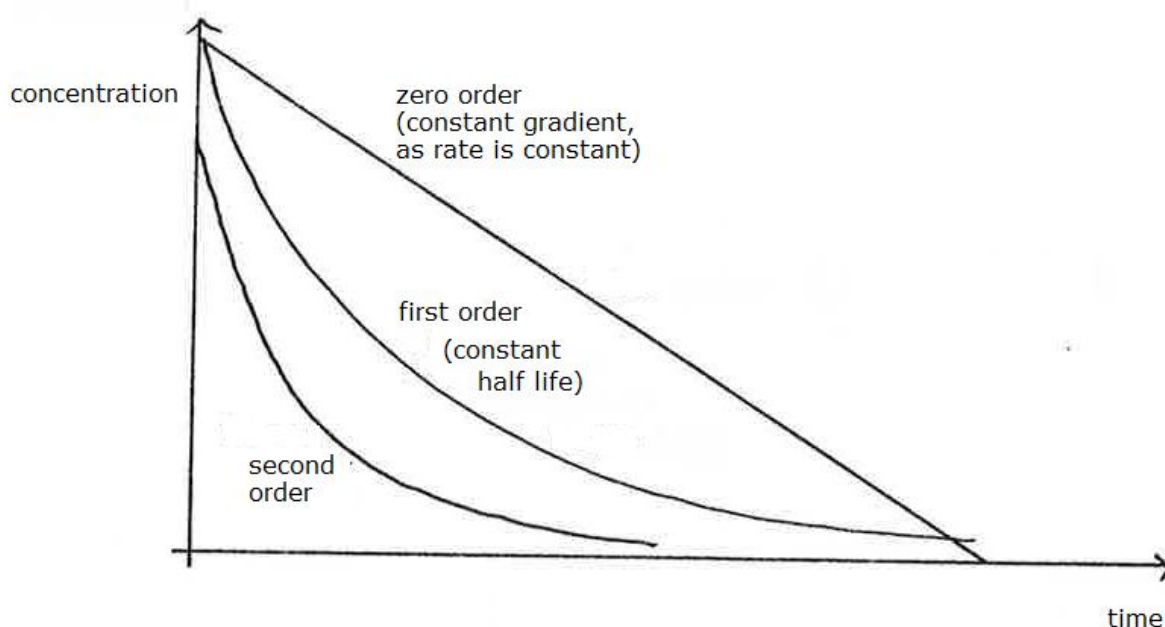

Reaction rates

There are nine graphs you should be familiar with:

- Three concentration against time graphs (for zero, first and second order reactions).
- Three rate against concentration graphs (also for zero, first and second order reactions) (less common).

To distinguish between the above, always check the units on the axes.

- ln(rate) against $\frac{1}{T}$, which has the gradient, $\frac{-E_a}{R}$.

- Number of molecules with energy E, against energy E.
- Energy against reaction path.

Concentration against time graphs

For these graphs you should know that the rate of a reaction is equal to the gradient of the graph at any point.

1 If the graph is a straight line the reaction is zero order.
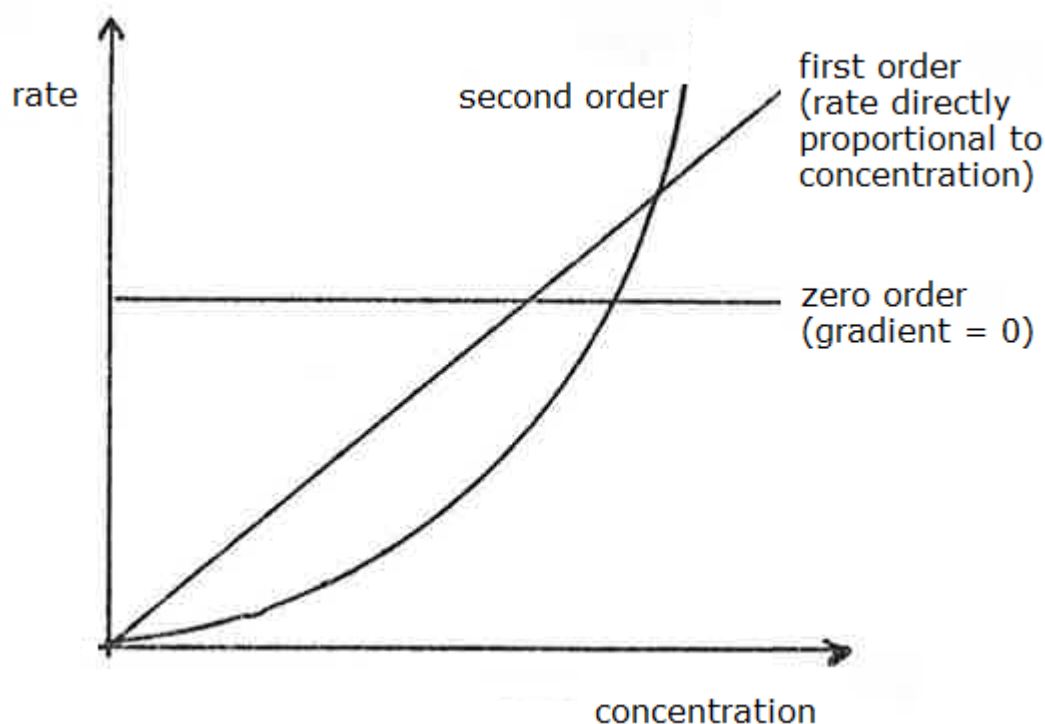
$$\text{rate} = k$$

2 If the graph is a curve with constant half life the reaction is first order.

$$\text{rate} = k[A]$$

3 If the graph is a curve with increasing (strictly doubling) half lives the reaction is second order.

$$\text{rate} = k[A]^2$$

Rate against concentration graphs

1 Horizontal line means zero order.

2 Straight line through the origin means first order (as rate is proportional to concentration) and the gradient is equal to the rate constant.

3 Curve means second order. If the graph is changed so that rate is plotted against the square of concentration, this would produce a straight line, with the gradient equal to the rate constant, *k*).

Practice question 1

Four sketch graphs are shown below.

A

B

C

D
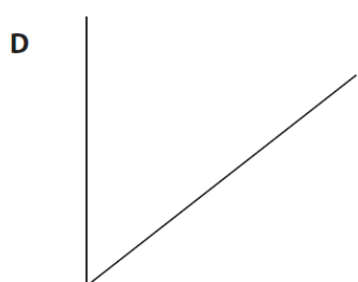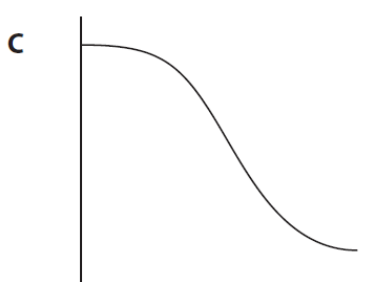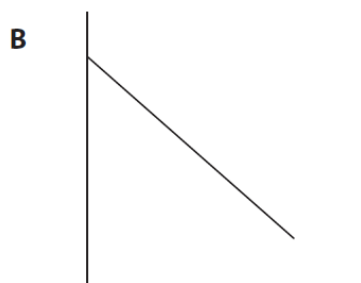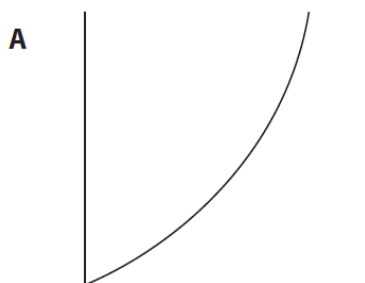
a Which could be a graph of the concentration of a reactant, on the vertical axis, against time for a **zero** order reaction?

A   **B**   **C**   **D**

b Which could be a graph of rate of reaction, on the vertical axis, against the concentration of a reactant for a **first** order reaction?

A   **B**   **C**   **D**

c Which could be a graph of rate of reaction, on the vertical axis, against the square of the concentration of a reactant for a **second** order reaction?

A   **B**   **C**   **D**

d Which could be a graph of the concentration of a reactant, on the vertical axis, against time for a reaction which is catalysed by a product?

A   **B**   **C**   **D**

Practice question 2

Persulfate ions, $S_2O_8^{2-}$, oxidise iodide ions in aqueous solution to form iodine and sulfate ions, SO_4^{2-}.

The effect of iodide ion concentration on the rate of this reaction was measured.

A few drops of starch solution and a small measured volume of sodium thiosulfate solution were added to a known volume of potassium persulfate solution.

Potassium iodide solution was then added and the time taken for the mixture to change colour was measured.

The reaction was repeated using different concentrations of potassium iodide, but the same volumes and concentrations of sodium thiosulfate solution and potassium persulfate solution.

The rates of the reaction were compared using the reciprocal of the time, T ($\frac{1}{T}$) for the mixture to change colour as a measure of the initial rate.

The results obtained were tabulated as follows.

[I⁻] /mol dm⁻³	Time /s	1/time /s⁻¹
0.0100	40.0	0.0250
0.0075	53.3	0.0188
0.0050	80.0	0.0125
0.0040	100.0	0.0100

a Plot a graph of $\frac{1}{T}$ on the vertical axis against concentration of iodide ions.

b $\frac{1}{T}$ is a measure of the initial rate of the reaction.

Deduce the order of reaction with respect to iodide ions. Justify your answer.

c The reaction is first order with respect to persulfate ions. Write the overall rate equation for the reaction and deduce the units for the rate constant.

Rate =

Units for the rate constant =

ln(rate) against $^1/_T$

In plotting these graphs it is usually best to draw the *x*-axis at the top of the graph as ln(rate) values are usually negative.

It is wise to label the *x*-axis as $\frac{1}{T}$ / K^{-1}, though strictly the correct label is K / *T*.

The scale should be numbered with each part '× 10^{-3}' then the factor of 1000 will not get lost!

Use this graph to find activation energy

$$E_a = -R \times \text{gradient}$$

You will always be told the value of *R*.

Watch out for factors of 1000. $\frac{1}{T}$ values are usually around 1×10^{-3} to 5×10^{-3}.

You should get an answer in J mol^{-1} or kJ mol^{-1}

Practice question 3

a The table shows the measurements of the rate constant, *k*, at different temperatures. Some of the corresponding values for reciprocal of temperature and ln *k* are also shown.

Complete the table by calculating the missing values.

T/K	k	$\frac{1}{T}$ / K^{-1}	ln k
280	3.80×10^{-6}	3.57×10^{-3}	-12.5
290	1.65×10^{-5}	3.45×10^{-3}	-11.0
300	6.87×10^{-5}	3.33×10^{-3}	-9.6
310	2.48×10^{-4}	3.23×10^{-3}	-8.3
320	8.65×10^{-4}		

b Plot a graph of ln *k* on the vertical axis against $\frac{1}{T}$ on the horizontal axis.

Calculate the gradient of your graph and use this to calculate the activation energy, E_a. Remember to include units with your answer, which should be given to three significant figures.

The Arrhenius equation can be expressed as ln k = $\frac{-E_a}{R} \times \frac{1}{T}$ + a constant

[Gas constant, R = 8.31 K-1 mol-1]

Number of molecules with energy *E* against energy, *E*

You will often need to draw two curves, one at lower temperature and one at higher temperature.

- Both start at the origin.
- Both approach the *x*-axis asymptotically.
- At higher temperature the peak is lower and further to the right.

The area under the graph from a particular energy, E_x, to the right-hand end of the *x*-axis is the fraction of molecules with energy greater than E_x

Often you will be asked to label the activation energy, and show how at higher temperature the fraction of molecules increases dramatically

Energy against reaction path

Energy against reaction paths are often two curves: one for catalysed, one for uncatalysed (higher activation energy).

Both start at same value and finish at same value. The start and finish values depend on the sign of the enthalpy change.

Activation energy is from initial energy to height of curve

Equilibrium constants, K_c

K_c is $\dfrac{\text{product concentratons, raised to power of number in equation, multiplied together.}}{\text{reactant concentratons, raised to power of number in equation, multiplied together}}$.

Concentrations must be measured at equilibrium.

Equilibrium constants are constant at a particular temperature.

Model for calculations involving K_c

Though this model is not needed for many calculations it will always work!

The reason this is seen to be the hardest topic for many students is that they are not sufficiently on top of the section on moles – it is a good idea to revise this before starting this topic.

- Write the equation for the reaction across the top of the calculation
- Under the equation, label three rows:
    - Initial amounts / mol
    - Equilibrium amounts / mol
    - Equilibrium concentrations.
- These can be used to calculate the equilibrium constant.

Practice question

This question is about an experiment to determine the equilibrium constant, K_c, for the reaction between ethanoic acid and ethanol to form ethyl ethanoate and water.

Two sealed test tubes were prepared.

The first test tube contained 0.0400 mol ethanoic acid, 0.0400 mol of ethanol and 0.20 cm³ of concentrated hydrochloric acid.

The second test tube contained 0.0400 mol ethyl ethanoate, 0.0400 mol of water and 0.20 cm³ of concentrated hydrochloric acid.

After standing at 25°C for two weeks, to ensure equilibrium is reached, the contents of each test tube were separately titrated with 0.200 mol dm⁻³ sodium hydroxide solution.

0.20 cm³ of concentrated hydrochloric acid was also titrated with the same sodium hydroxide solution.

In this experiment, the following titres were obtained.

Titration	Volume of 0.200 mol dm⁻³ sodium hydroxide/cm³
Contents of first test tube	77.10
Contents of second test tube	77.05
0.20 cm³ of concentrated hydrochloric acid	11.70

cont.

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a Write the equation for the reaction between ethanoic acid and ethanol to form ethyl ethanoate and water, using structural formulae.

b Calculate the number of moles of ethanoic acid present at equilibrium in the first test tube.

c Deduce the number of moles of ethanol present at equilibrium in the first test tube.

d Calculate the number of moles of ethyl ethanoate formed at equilibrium in the first test tube.

e Write an expression for the equilibrium constant, K_c, for the reaction.

Assuming the number of moles of water and ethyl ethanoate present at equilibrium are the same, calculate the equilibrium constant, K_c.

Equilibrium constants, K_p

The only difference between K_p and K_c is that partial pressures replace concentrations.
To find partial pressures, mole fractions, X_i, are needed
For reactant A, the mole fraction, X_a, is given by

$$X_a = \frac{n_a}{n_a + n_b}$$

where n_a = number of moles of A; $n_a + n_b$ = total number of moles of all reactants.

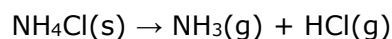To find the p_a i.e. the partial pressure of A, use the equation $p_a = X_a P$
where P is the total pressure.

The following point is most frequently unfamiliar to students:
- Notice the sum of the mole fraction in a mixture is equal to 1.
- So for a two-reactant mixture of A and B, $X_b = 1 - X_a$

Practice question 1

Ammonium chloride decomposes on heating:

$$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$$

The equilibrium constant, K_p, for this reaction equals:

A $pNH_3 \times pHCl$

B $\dfrac{1}{(pNH_3 \times pHCl)}$

C $\dfrac{pNH_3 \times pHCl}{pNH_4Cl}$

D $\dfrac{pNH_4Cl}{pNH_3 \times pHCl}$

Practice question 2

The equation for the synthesis of methanol is:

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$$
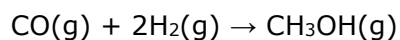
At equilibrium, when the temperature is 340 K, the total pressure is 20 atm.
The number of moles of each component present at equilibrium are shown in the table below.

Formula	Equilibrium moles / mol	Mole fraction
CO	0.15	0.23
H_2	0.32	
CH_3OH	0.18	0.28

a The mole fraction of hydrogen in the equilibrium mixture is:

A 0.23
B 0.46
C 0.49
D 0.92

b The numerical value for the equilibrium partial pressure of the carbon monoxide, in atmospheres, is:

A 3.0
B 4.6
C 5.0
D 9.2

c Units for the equilibrium constant, K_p, for this reaction are:

A no units
B atm
C atm^{-1}
D atm^{-2}

Acid–base equilibria and pH calculations

It is important to spend time practising some simple calculations using your own calculator in this topic.

- Definition: $pH = -lg[H^+(aq)]$

- Strong acid: $pH = -lg\ c$

  where c is the concentration of the acid

- Weak acid: $pH = -lg\ \sqrt{(K_a c)}$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

  Assumptions in pH equation:

  - [HA] at equilibrium = concentration of acid, c (i.e. degree of dissociation is small)
  - The only source of H^+ is the weak acid (i.e. ignore contribution made by ionization of water).

- Strong alkali $pH = -lg\ K_w/c$

  where $K_w = [H^+(aq)][OH^-(aq)] = 1.0 \times 10^{-14}$ mol^2 dm^{-6}

  and c is concentration of alkali

- For a buffer solution:

$$K_a = \frac{[H^+][Base]}{[Acid]}$$

  So $pH = pK_a + lg\dfrac{[Base]}{[Acid]}$ or $pH = pK_a - lg\dfrac{[Acid]}{[Base]}$

- To calculate ratios of acid to base:

$$\frac{K_a}{[H^+]} = \frac{[Base]}{[Acid]}$$

Practice question 1

Select the correct pH for each of the following solutions.

a 2 mol dm^{-3} nitric acid.

  A -2   **B** -0.3   **C** +0.3   **D** +2

b 0.10 mol dm^{-3} barium hydroxide, Ba(OH)$_2$. $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}.
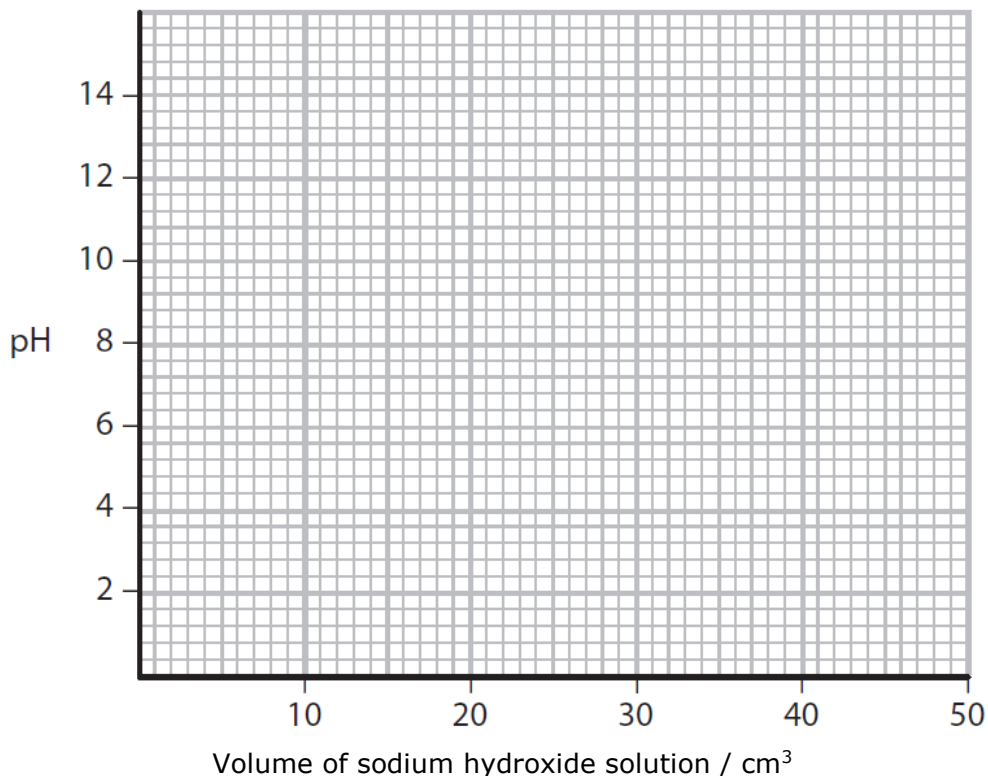
  A 13.0   **B** 13.3   **C** 13.7   **D** 14.3

c A mixture of 20 cm^3 of 1.0 mol dm^{-3} hydrochloric acid and 10 cm^3 of 1.0 mol dm^{-3} sodium hydroxide.

  A 0   **B** 0.30   **C** 0.48   **D** 7

Practice question 2

Sketch the titration curve obtained when 50 cm^3 of 0.10 mol dm^{-3} sodium hydroxide solution is added to 25 cm^3 of 0.10 mol dm^{-3} butanoic acid.

Volume of sodium hydroxide solution / cm^3

Reversing a logarithm

If   pH = 4 i.e. -lg[H$^+$(aq)] = 4

To get rid of lg raise both sides of equation to powers of 10.

This gives   [H$^+$(aq)] = 10^{-pH} = 10^{-4} = 0.0001 mol dm^{-3}

To find K_a given the pH of a weak acid of concentration c, use $K_a = \dfrac{10^{-2pH}}{c}$.

Practice question 3

A shampoo is buffered by the addition of a mixture of methanoic acid and sodium methanoate.

The pH of this shampoo is 4.9. Calculate the hydrogen ion concentration in the shampoo, and hence the ratio of methanoate ions to methanoic acid.

Electrode potentials

Standard electrode potentials, symbol $E^\ominus$, are simply a way of measuring **oxidising power**. Here are three examples:

- $Ag^+(aq) \,|\,Ag(s)$ +0.80 V
- $Cu^{2+}(aq)|Cu(s)$ +0.34 V
- $Zn^{2+}(aq)|Zn(s)$ -0.76 V

Notice that the values give us the correct order of oxidising power of the first ion.

The sign is a quick indication of the nature of the entity. A positive value indicates that the ion is an oxidising agent; a negative value that the metal is a potential reducing agent

More complex oxidising agents

These electrode potentials are measured against the hydrogen electrode as metal ion electrode potentials.

Here are the electrode potentials for some common oxidising agents:

- $Cl_2(aq), 2Cl^-(aq)|Pt$ +1.36 V
- $[Cr_2O_7^{2-}(aq)+14H^+(aq)],[2Cr^{3+}(aq)+7H_2O(l)]|Pt$ +1.33 V
- $[O_2(g)+2H_2O(l)],4OH^-(aq)|Pt$ +0.40 V

Uses of standard electrode potentials

To calculate e.m.f.s of cells

$E_{cell} = E^\ominus$(Right side electrode) – $E^\ominus$(Left side electrode)

The entities with the more positive electrode potential will form the positive side of the cell.

Example for a copper zinc cell:

- $Zn(s)|Zn^{2+}(aq)::Cu^{2+}(aq)|Cu(s)$

    E_{cel} = (+0.34) – (-0.76)

        = +1.10 V

As with enthalpy changes, it is helpful to write numbers with signs in brackets so that they do not get lost in calculations. It is essential to include the sign and the unit in your answer.

Predicting reactions

Write down the reaction in the form of two electrode systems giving the most negative first and the most positive second.

The reaction will go anti-clockwise.

For example: will acidified dichromate(VI) oxidise iron(II) to iron(III)?

- $Fe^{3+}(aq),Fe^{2+}(aq)|Pt$ +0.77 V
- $[Cr_2O_7^{2-}(aq) + 14H^+(aq)],[2Cr^{3+}(aq) + 7H_2O(l)]|Pt$ +1.33 V

For the reaction to go anti-clockwise the second reaction must go to the right and the first to the left, so acidified dichromate(VI) **will** oxidise iron(II) to iron(III).

To write the equation for a predicted reaction use the following steps

Write the equation for each half reaction, including the appropriate number of electrons. You may need to work out the oxidation numbers of some entities to do this.

Balance the two equations so that there is no overall gain or loss of electrons.
Then combine the two equations.

For the example above:

- Fe^{2+} (aq) $- e^- \rightarrow Fe^{3+}$(aq)
- $Cr_2O_7^{2-}$(aq) $+ 14H^+$(aq) $+ 6e^- \rightarrow 2Cr^{3+}$(aq) $+ 7H_2O$(l)
- 2(6+)   2(3+)

In this case we need to take six electrons from the first reaction so we must multiply the equation by six. This gives:

- $6Fe^{2+}$(aq) $+ 6e^- \rightarrow 6Fe^{3+}$(aq)

Now it is easy to add the equations together:

- $6Fe^{2+}$(aq) $+ Cr_2O_7^{2-}$(aq) $+ 14H^+$(aq) $\rightarrow 6Fe^{3+}$(aq) $+ 2Cr^{3+}$(aq) $+ 7H_2O$(l)
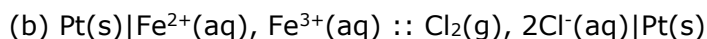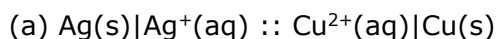

It is important to remember that though a reaction can be predicted using electrode potentials, or entropy changes, the reaction may not take place at an appreciable rate.

This final point applies to all methods of predicting the spontaneity of reactions and is frequently examined.

We can predict if a reaction is possible or 'spontaneous', but **not** how fast it will go.

Practice question

Calculate the emfs of the following cells:

(a) Ag(s)|Ag^+(aq) :: Cu^{2+}(aq)|Cu(s)

(b) Pt(s)|Fe^{2+}(aq), Fe^{3+}(aq) :: Cl_2(g), $2Cl^-$(aq)|Pt(s)

Data:

Cu^{2+}(aq)|Cu(s) = +0.34V

Fe^{3+}(aq),Fe^{2+}(aq)|Pt = +0.77V

Ag^+(aq) |Ag(s) = +0.80V

Cl_2(aq), $2Cl^-$(aq)|Pt = +1.36V