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INTERNATIONAL ADVANCED LEVEL

CHEMISTRY

TEACHER MATHEMATICS SUPPORT

Pearson Edexcel International Advanced Subsidiary in Chemistry (XCH11)
Pearson Edexcel International Advanced Level in Chemistry (YCH11)
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Pearson

Contents

Introduction

As well as the content requirements in terms of chemistry subject knowledge, the subject criteria for A level Chemistry, also contain a series of mathematical requirements. The nature of the mathematical skills that accompany the new International Advanced Level Chemistry is given in detail in the new chemistry specification in *Appendix 6: Mathematical skills and exemplifications*.

Although these skills are not new for A level Chemistry, the new International Advanced levels now have a requirement, to ensure comparability with the GCE A Level Chemistry, for these skills to be routinely tested. This means that, both for IAS and IAL, at least 20% of marks on examination papers will assess mathematical skills, within the context of the relevant chemistry.

In order to be able to develop their skills, knowledge and understanding, students need to have been taught, and to have acquired competence in, the appropriate areas of mathematics relevant to chemistry.

It is important to stress that the inclusion of a list of mathematical skills within the International A level Chemistry is not new – and teachers should avoid the idea that delivering Chemistry A level requires large-scale treatment of mathematics in isolation. Students should be encouraged to see mathematical skills – almost all of which are mathematical ideas that they are familiar with from International GCSE/GCSE – as tools that can be applied in different chemical situations.

The Student Guide for mathematics contains notes summarising the essential mathematical parts of the Chemistry specification. These are included in this guide, along with answers to the questions in the Student Guide and some additional tips.

The Student Guide covers selected topics which students find difficult. These are:

- Mole calculations
- Enthalpy changes
- Reaction rates
- Equilibrium calculations
- Acid base equilibria and pH calculations
- Electrode potentials

They should be used after showing students how most of the equations given can be derived. For example, any of the mole equations are derived by considering simple proportions.

Answers to questions

All the questions included are practice questions selected from past papers. The answers are adapted from published mark schemes and are not given in the student guide.

Further help with mathematics

A number of other resources exist to help students and teachers with mathematics. On the Edexcel website, there is a free student workbook: "*Moles, Formulae and Equations*".

Other useful resources include:

Calculations in AS/A level Chemistry by Jim Clark

Calculations for A level Chemistry by EN Ramsden

Maths Skills for A level Chemistry by Dan McGowan and Emma Poole

Basic toolkit for all chemistry calculations

Simple proportions or ratios

Tip: As simple proportion makes up so much of chemical calculations, it is worth spending time ensuring this concept is understood. Simple examples outside chemistry – such as proportions in which ingredients might be mixed in a recipe – help reinforce the idea.

As an example of this, consider the question 'If two oranges cost six pence, how much do three oranges cost?' Students can apply the same mathematical steps they would use in answering this simple maths problem when finding the number of moles from the mass of solid element. The reasoning for this goes:

If **two** oranges cost **six** pence.	If a mass of an element, ***M***, measured in grams contains exactly **1** mol of an element.
Then one orange costs $\frac{6}{2}$ pence.	Then 1 g contains $\frac{1}{M}$ of the element.
So three oranges cost $\frac{6 \times 3}{2}$ pence.	So m g contains $\frac{m}{M}$ mol.

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?

$Fe_2O_3(s) \rightarrow 2Fe(l)$, so 10 moles of iron(III) oxide produce 20 moles of iron.

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

$Fe_2O_3(s)$ reacts with $3CO(g)$, so 10 moles of iron(III) oxide require 30 moles of carbon monoxide.

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)

37 g in 1000 cm^3, so in 250 cm^3 there are 37 x 250/1000 = 9.25 g

Re-arranging equations

Another area is to practice is changing the subject of an equation.

If weaker students cannot do this then it may be easiest to learn the transformed formulae. In the example above, this means learning

$$\text{Number of moles, } n\text{, } = \frac{m}{M}$$

$$m = n \times M$$

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

The simple three-fold attack for learning any equation is:

- 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.

Tip: Do not encourage an over-reliance on calculation 'triangles': students who use these cannot answer questions when data is presented in different units, for example.

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) $\times 6 \times 10^{23}$

$= 1.8 \times 10^{24}$

Practice question

The Avogadro constant is $6.0 \times 10^{23}\ mol^{-1}$.

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}

Answer

A 3.6×10^{24}

Interpretation of symbols, formulae & equations

Tip: Take this opportunity to reinforce the difference between atoms and molecules.

- 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}).

Tip: The learning of equations like this is best emphasised as follows.

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.
Give your answer to an appropriate number of significant figures.

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

Answer

$$\text{Mass} = (79.5 \times 0.02 \times \frac{110}{100}\ \underline{110}\ = 1.749 =)\ 1.75\ g = 1.7\ g$$

An answer of 1.74 or 1.8 would lose 1 mark for incorrect rounding and 1.749 would lose one mark for too many significant figures.
Also: incorrect mass x 1.1 could score 1 mark if working is given and the correct answer to this calculation is given with the unit.

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_r, 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
  $(55.8 \times 1) + (32.1 \times 1) + (16 \times 4) + [7 \times (1 \times 2 + 16)] = 277.9$ g mol^{-1}

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

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

Tip: The term "relative molecular mass" is often used. Note that the Edexcel specification uses the term "molar mass", which has units. Use of the units in calculations encourages students to consider dimensions so that, for example, a mass is given in kg rather than g, they are likely to spot this and adjust accordingly.

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.

Answer

249.6 g mol^{-1}

1 mark would be awarded for the vale, one mark for correct units.

159.6 g mol^{-1} (omits water of crystallization) can still get unit mark.

249 g mol^{-1} (incorrect rounding) can also still get unit mark.

While g/mol may be allowed for the unit g/mol^{-1} is incorrect.

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!

Tip: The molar volume of gas will be provided in question papers.

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

Answer

C 8.4 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 $n = \frac{\rho V}{M}$

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

Practice question

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

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

Answer

$74 \times 0.125 = 9.25\ g$

$\frac{9.25}{0.81} = 11.4\ cm^3$

11 cm^3 would be acceptable if the question required "appropriate number of significant figures" because the data is to 2 and 3SF.

11.42 or 11.420 would also be acceptable values if SF is not a consideration

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.

Tip: A variety of questions can be asked in this area, so students should be familiar with techniques, including:

- interconverting between $g\ dm^{-3}$ and $mol\ dm^{-3}$
- simple titrations
- titrations involving dilutions in a volumetric flask
- "back" titrations

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

Answer

B 0.0030

Percentage yields

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

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 0.020 mol of sulfuric acid with excess copper(II) oxide.

Answer

Maximum yield = 249.6 × 0.02 = 4.992 (g)

Percentage yield = $\frac{2.7 \times 100}{4.992}$ = (54.0865) = 54%

Or $\frac{2.7}{249.6}$ = 0.01082

Percentage yield = 0.01082 × $\frac{100}{0.02}$ 100/0.02 = 54%

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 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

Answer

B Temperature

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 $\Delta_f H^\ominus$

$\Delta_f H^\ominus$ 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 $\Delta_f H^\ominus$ values

$\Delta_f H$ = The sum of $\Delta_f H$ of products – the sum of $\Delta_f H^\ominus$ 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

$$\begin{tikzcd}
\text{Reactants} \arrow[rr, "\Delta H\text{ (reaction)}"] & & \text{Products} \\
& \text{Elements} \arrow[ul, "\Delta_f H^\ominus\text{ (reactants)}"] \arrow[ur, "\Delta_f H^\ominus\text{ (products)}"'] &
\end{tikzcd}$$

By Hess's Law:

$$\Delta_f H^\ominus(\text{reactants}) + \Delta H^\ominus(\text{reaction}) = \Delta_f H^\ominus(\text{products})$$

So:

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

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

Tip: Remember to reinforce with students the idea that elements have a value of $\Delta_f H^\ominus$ which is 0.

This idea may become confused when students move on to consider entropy.

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 ↘ ΔH_1 aq ↙ ΔH_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 $-\Delta H_1 + \Delta H_2$

Answer
B $\Delta H_1 - \Delta H_2$

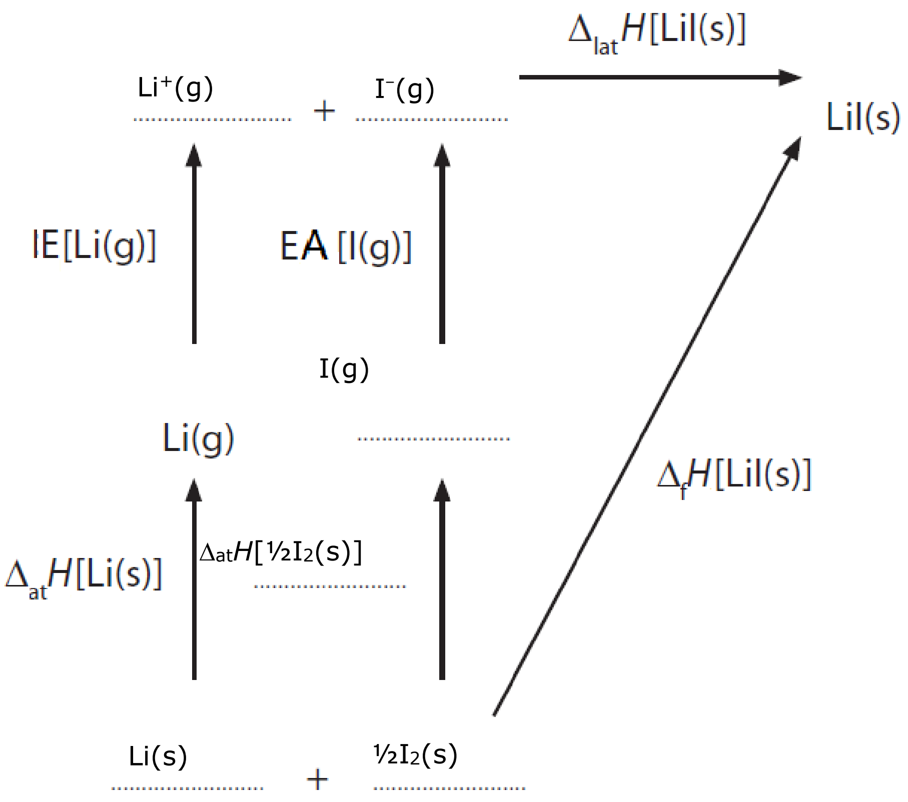
Other definitions

- **Standard enthalpy change of combustion**, $\Delta_c H^{\ominus}$: the enthalpy change when one mole of a compound is completely burned in oxygen.
- **Standard enthalpy of atomisation**, $\Delta_{at} H^{\ominus}$ 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, $\Delta_n H^{\ominus}$: the enthalpy change when an acid is completely neutralised by an alkali to form 1 mole of water.
- The **first ionisation 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 ionisation 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.



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

	ΔH/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

Answer

-270 = + 159 + 107 + 520 + electron affinity – 759

Or Electron affinity = -270 – (159 + 520 + 107 – 759)

Or Electron affinity = -270 – 159 – 520 – 107 + 759

So Electron affinity = -297 (kJ mol^{-1})

Entropy

Tip: Introduce entropy as disorder by asking students about domestic tensions over their bedrooms. The vast majority will admit to chaos, showing that natural processes lead to disorder.

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.

Tip: One of the biggest sources of errors in examination papers is the failure to convert ΔH from kJ mol^{-1} into J mol^{-1} before calculating ΔS_{surr}

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 to for a reaction to be spontaneous if

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

Answer

$$0 = (+225) + \frac{(-206.1 \times 103)}{T}$$

So T = 916 K

Reaction rates

There are nine graphs you should be familiar with:

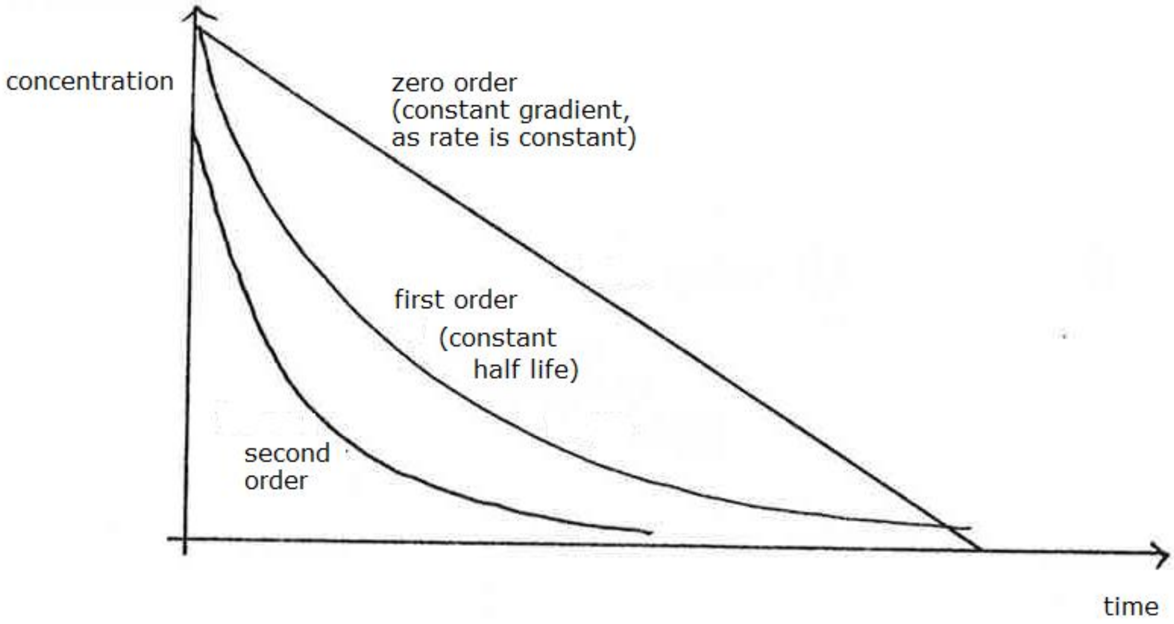
- Three concentration against time graphs (for zero, first and second order reactions).
- Three rate against concentration graphs (also for zero, first and second order reactions) (less common).

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.

Tip: Get students to sketch each of the nine graphs as a revision exercise.

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.

$$\text{rate} = k$$

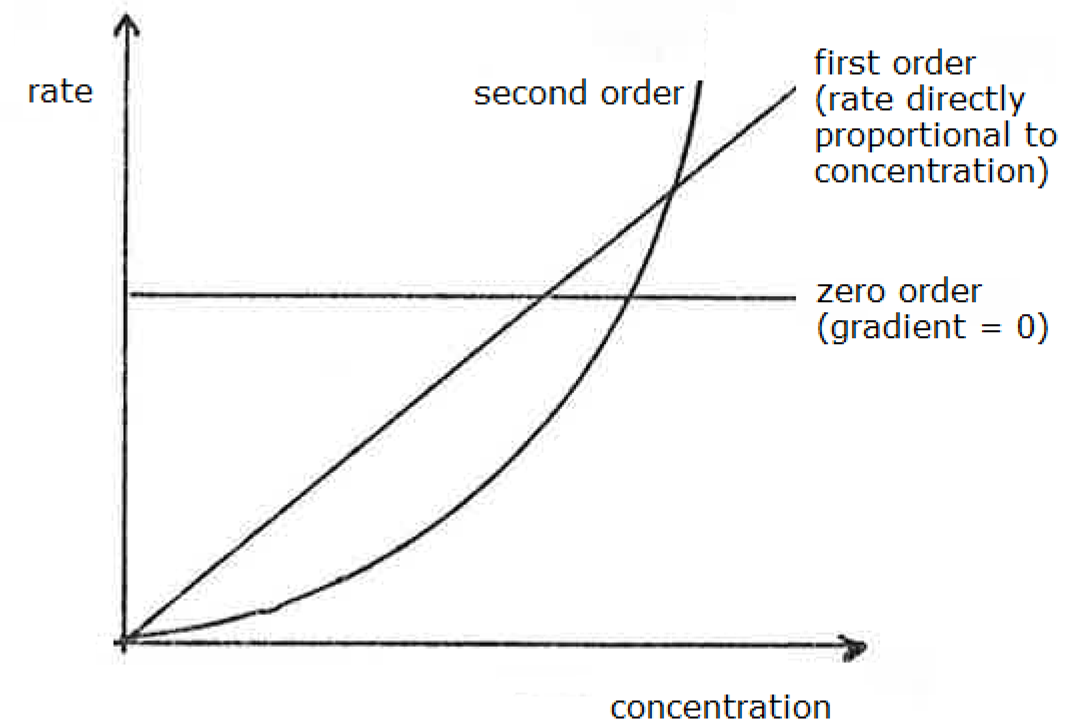
2 If the graph is a curve with constant half life the reaction is first order.

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

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*).

Tip: Students who are good A level mathematicians might like to do some further work in this area, linking chemistry to maths. Areas for them to explore might include:

1. how does half-life for a 1st order reaction relate to the rate constant, *k*.

[They may need to be given the reaction for 1st order kinetics, unless they have seen it in Physics, $[A] = [A]_0\ e^{-kt}$

2. working out which graphs to plot in order to find a value for the rate constant, *k*.

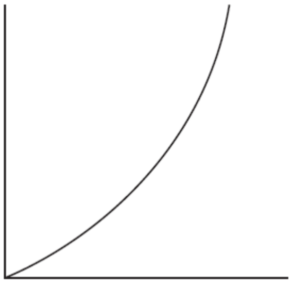
[In this case, they would start with the idea that rate = $k[A]^n$

and use the idea that rate = - d[A]/dt to integrate the rate equations]

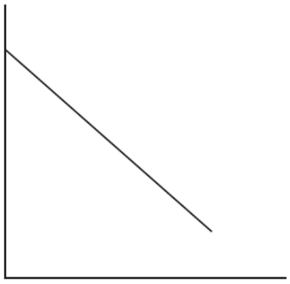
Practice question 1

Four sketch graphs are shown below.

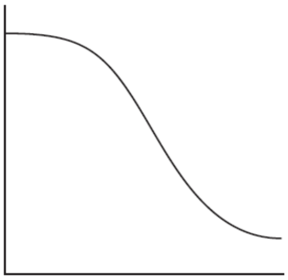
A



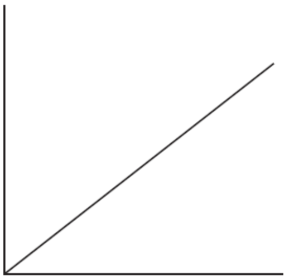
B



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?

Answer: B

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?

Answer: 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?

Answer: 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?

Answer: C

Practice question 2

Persulfate ions, $S_2O_8^{2-}$, oxidize 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.

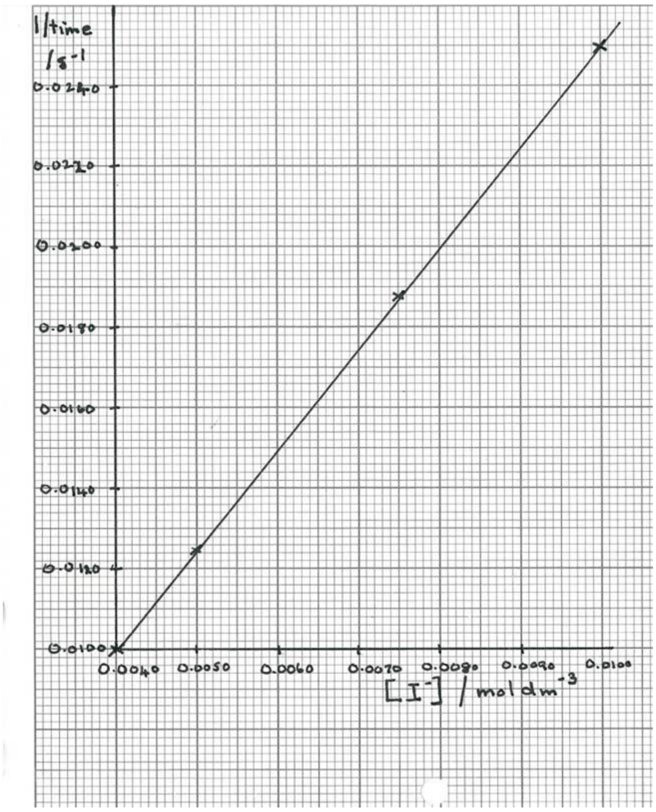
The reaction was repeated using different concentrations of potassium iodide, but the same volumes and concentrations of sodium thiosulfate solution and potassium persulfate solution.

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.



contd.

Answer

Correct graph of rate *v*. concentration, with axes correct and values increasing on both axes labelled with quantity and units would gain one mark.

For the second mark, sensible scales to use at least half the graph paper but allow graphs starting at the origin and points cover two by two big squares. Linear scales. All points reasonably correct with straight line drawn.

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.

Answer

Because the graph is a straight line (through the origin) / rate is proportional to $[I^-]$.

Or: As concentration increases by (factor of) 2 rate increases by 2 (or any other numbers).

Or: Rate increases linearly.

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 = $k[S_2O_8^{2-}][I^-]$

Units for the rate constant = $dm^3\ mol^{-1}\ s^{-1}$

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}		

Answer

$\frac{1}{T}$: 3.13 × 10^{-3} or 3.125 × 10^{-3} ln *k*: -7.1 or -7.05 or -7.0528

Note that 3.12 × 10^{-3} and -7.0 would not be acceptable as these are incorrectly rounded.

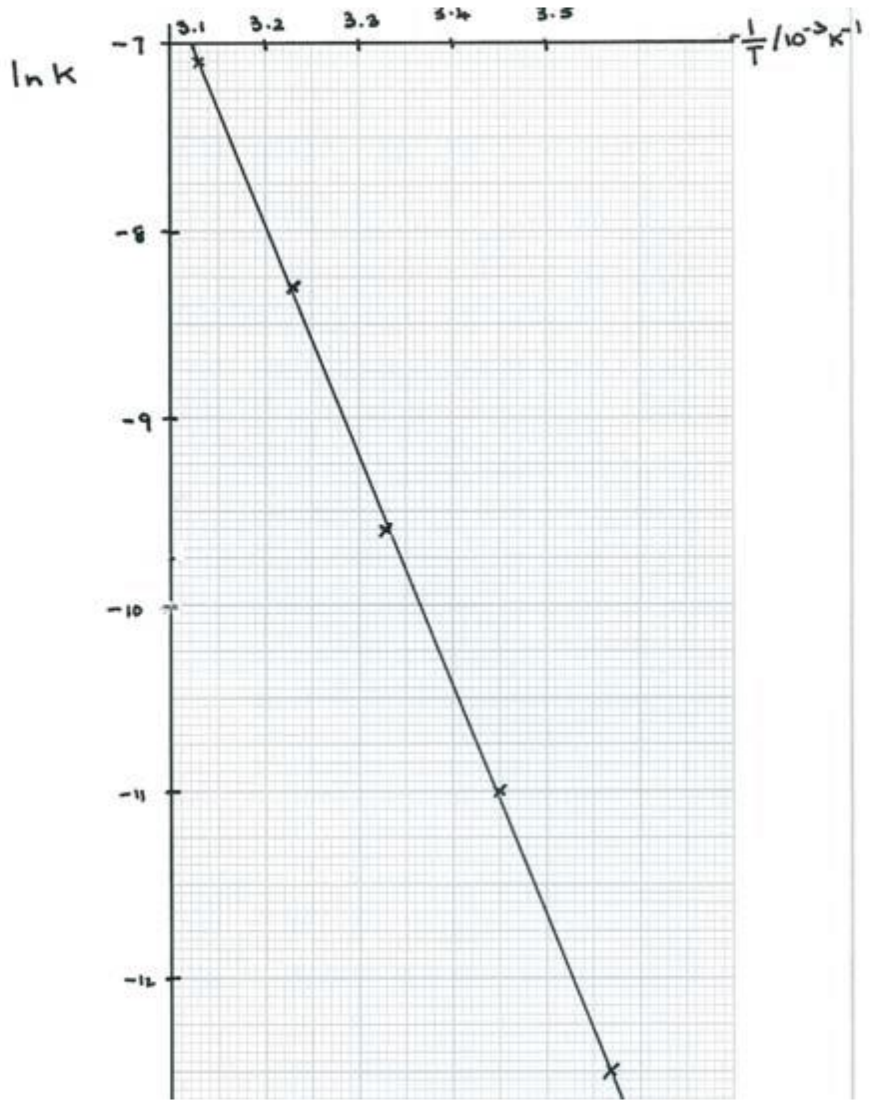
contd.

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, $R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$]



One mark would be given for correct axes with sensible scales i.e. points/line covering at least 3 large squares on the x-axis and 5 on the y-axis, with ln k values becoming more negative down the axis and the negative signs shown.

A second mark would be given for having both axes labelled, with units on x-axis and no units on y-axis.

x-axis: 3.1-3.5 $1/T\ /10^{-3}\ K^{-1}$ or 3.1-3.5 $1/T \times 10^{3}\ /K^{-1}$

Or: 0.0031-0.0035 or 3.1×10^{-3}/-3.5×10^{-3} $1/T\ /K^{-1}$

A third mark would be given for points correctly plotted and straight line drawn. *contd.*

Two marks would be given for the gradient – this may be shown on the graph.

gradient = -11 550 to -12 760 (K)

Two marks would be given for the calculation.

E_a = (+)96.0 to (+)106 kJ mol^{-1} or (+)96000 to (+)106000 J mol^{-1} would be awarded both marks.

If E_a was in this range but not given to 3 sf, or the units were incorrect or missing, one mark would be awarded.

Or: If not, E_a = -8.31 × their gradient or gradient = $\frac{-E_a}{R}$ would be awarded one mark, and having the value to 3 sf and units **and** consequential sign if negative would receive the second mark.

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 forms 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.

Tip: Using these graphs to explain why catalyst increase the reaction rate is a common question. Students should be able to use the graph to provide this explanation.

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

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

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.

Tip: Within the confines of the A level specification, both K_c and K_p have units – students should be able to calculate these for any equilibrium reaction.

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 cm^3 of concentrated hydrochloric acid.

The second test tube contained 0.0400 mol ethyl ethanoate, 0.0400 mol of water and 0.20 cm^3 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 cm^3 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/cm^3
Contents of first test tube	77.10
Contents of second test tube	77.05
0.20 cm^3 of concentrated hydrochloric acid	11.70

cont.

a Write the equation for the reaction between ethanoic acid and ethanol to form ethyl ethanoate and water, using structural formulae. State symbols are not required.

Answer

$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$

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

Answer

Volume of alkali reacting with ethanoic acid = 77.1 − 11.7 = 65.4 cm^3

$$\text{Moles of ethanoic acid} = \frac{65.4 \times 0.200}{1000}$$

$$= 0.01308 \text{ or } 1.308 \times 10^{-2} \text{ (mol)}$$

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

Answer

Number of moles of ethanol = 0.01308 or 1.308×10^{-2} (mol)

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

Answer

Number of moles of ethyl ethanoate = 0.0400 − 0.01308 = 0.02692 (mol)

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.

Answer

$$K_c = \frac{[CH_3CO_2CH_2CH_3][H_2O]}{[CH^3CO_2H][CH_3CH_2OH]}$$

$$= \frac{0.02692 \times 0.02692}{0.01308 \times 0.01308}$$

$$= 4.23579 = 4.24$$

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, $X_b = 1 - X_a$

Tip: In K_p calculations, students often miss out a step: usually the conversion of mole fractions to partial pressures.

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 $\frac{1}{(pNH_3 \times pHCl)}$

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

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

Answer

A $pNH_3 \times pHCl$

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

Answer: C 0.49

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

Answer: B 4.6

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

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

Answer: D atm^{-2}

Acid-base equilibria and pH calculations

It is important to spend a lesson practising some simple calculations with student using their own calculators in this topic.

- Definition: $\mathrm{pH} = -\log[\mathrm{H+(aq)}]$
- Strong acid: $\mathrm{pH} = -\log c$

  where c is the concentration of the acid
- Weak acid: $\mathrm{pH} = -\log \sqrt{(K_a c)}$

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

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 $\mathrm{pH} = -\log K_w/c$

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

  and c is concentration of alkali
- For a buffer solution:

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

So $\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{Base}]}{[\mathrm{Acid}]}$ or $\mathrm{pH} = \mathrm{p}K_a - \log\frac{[\mathrm{Acid}]}{[\mathrm{Base}]}$

Tip: Students frequently mis-remember these forms of the Henderson-Hasselbach equation. It is usually easier, in an examination, for students to simply work from the K_a expression.

- To calculate ratios of acid to base:

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

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 **Answer: B**

b 0.10 mol dm^{-3} barium hydroxide, $Ba(OH)_2$. $K_w = 1.0 \times 10^{-14}\ \mathrm{mol^2\,dm^{-6}}$.

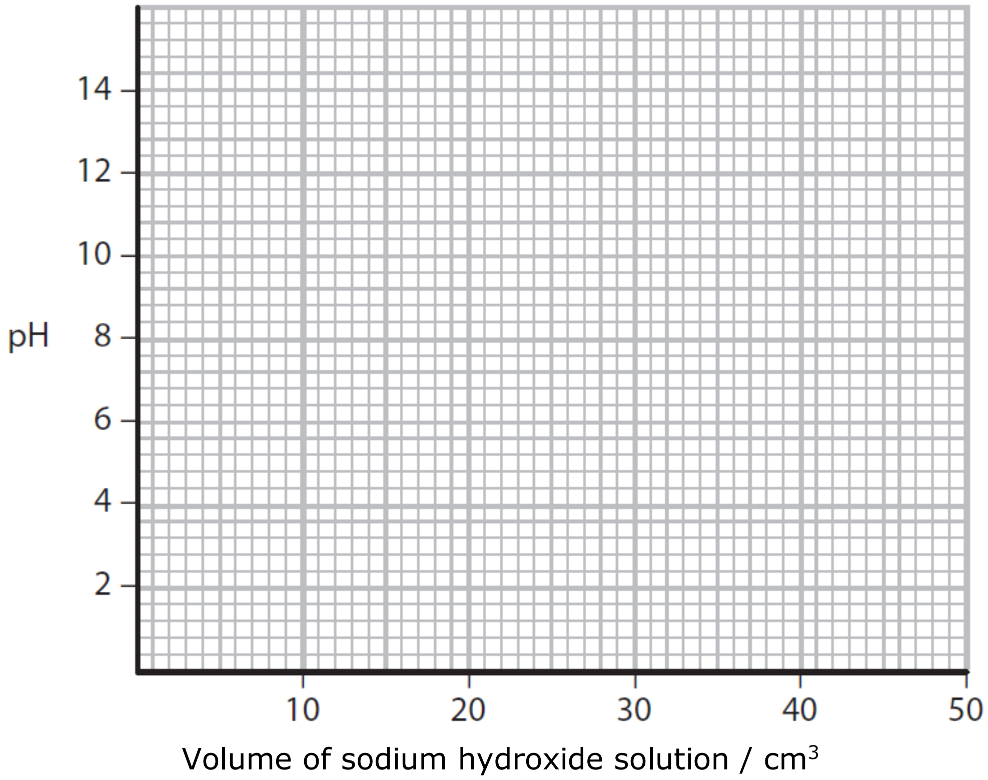
A 13.0 **B** 13.3 **C** 13.7 **D** 14.3 **Answer: B**

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 **Answer: C**

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.



Answer

Start pH at 2.9 (allow between 2 and 4).

Initial sharp rise to buffer region then vertical section at 25 cm^3.

Vertical within pH range 6–11 and 2.5–4 units long.

End pH value in range 12–13.

$p_a = X_a \times P$

P = total pressure (usually in atmospheres).

Reversing a logarithm

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

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

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

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

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.

pH = 4.9 so $[H^+] = (1.2589254 \times 10^{-5}) = 1.259 \times 10^{-5}$

$$\frac{K_a}{[H^+]} = \frac{[HCOO^-]}{[HCOOH]}$$

$$= \frac{1.6 \times 10^{-5}}{1.259 \times 10^{-5}}$$

= 12.7 (:1) or 13(:1) ($HCOO^-$ per HCOOH or base : acid)

Electrode potentials

Tip: Many teachers find this the hardest topic to teach.

One simple way to approach the topic is to consider metal / metal ion half-cells only, and to consider the value of the electrode potential in terms of the simple reactivity series which students learned at KS3.

So, zinc is more reactive than copper i.e. zinc has a greater tendency to lose electrons and turn into zinc ions compared to copper losing electrons to form copper ions. So, zinc is more readily oxidised – it more readily loses electrons – so its half-cell value is more negative.

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

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

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

Tip: The method given below seems easiest for most students. It is a good "rule of thumb", but care should be taken in referring to this as "the anticlockwise rule".

One useful idea for students to consider – especially if they are also physicists – is that the more negative cell is the one that will be electron releasing.

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:

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

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

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

(a) $E_{cell} = E_R - E_L = +0.34 - (+0.80) = -0.46V$

(b) $E_{cell} = E_R - E_L = +1.36 - (+0.77) = +0.59V$

Reaction (a) is, therefore, not feasible. Students should know this, as silver is less reactive that copper, so silver could not reduce copper(II) ions to copper.

Reaction (b) is feasible. Students are likely to have come across the oxidation of iron(II) to iron(III), if not by chlorine then by aerial oxidation.