A level

Topic 16

Nearly there



Exam skills 11

This exam-style question uses knowledge and skills you have already revised. Have a look at pages II5–II7 for a reminder about **reaction rates** and **order of reaction**.

Worked example

Hydrogen peroxide reacts with iodide ions to form iodine. If thiosulfate ions, $S_2O_3^{2-}$, are also present, they react with the iodine formed. Once all these ions have reacted, iodine is no longer reduced. The appearance of iodine is detected by starch solution.

(a) Describe the final colour of the reaction mixture.

Blue-black.

(b) The concentration of I⁻ ions was varied while keeping the concentrations and volumes of the other reagents the same and the time for the mixture to change colour was recorded.

[I ⁻]/ mol dm ⁻³	time/ s	1/time/ s ⁻¹
0.040	16.5	0.0606
0.030	22.4	0.0446
0.016	41.7	0.0239
0.008	85.2	0.0117

(i) Complete the table, and plot a graph of 1/time on the vertical axis against [I⁻]. (3 marks)



(ii) 1/time is a measure of the initial rate of reaction. Deduce the order of reaction with respect to iodide ions, and justify your answer. (2 marks)

The reaction is first order with respect to iodide ions because the rate is proportional to $[I^-]$. The graph is a straight line (it has a constant gradient).

(iii) Describe a way in which the experiment could be improved, without changing the method, measuring apparatus or the solutions used.

(1 mark)

You could repeat the experiment.

This describes a version of the 'iodine clock experiment':

- I. $H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$
- 2. $I_2 + 25_2O_3^{2-} \rightarrow 5_4O_6^{2-} + 2I^{-}$
- Sulfuric acid is added to provide H⁺ ions.

Practical Skills Water is usually added before the reactants are mixed together so that the total volume remains the same.

Laboratory digital stop clocks often time to ± 0.01 s, but this precision is unnecessary when you have to judge when to stop the clock.

Practical skills Make sure you can recall colours and colour changes from practical activities.

'Purple' would not be correct here.

When you plot a graph, you need to make sure you:

- choose sensible scales on which the plotted points occupy at least half of the grid supplied
- use linear scales
- plot points accurately draw a line of best fit.

• araw a nine or bos

- You should also: • make sure you have your axes the right way round
 - label each axis with the quantity and unit.

Command word: Deduce

If a question asks you to **deduce** something, it means you need to reach a conclusion from the information given.

Command word: Justify

If a question asks you to **justify** something, it means you need to give evidence to prove something.

Practical Since temperature is one of the factors that determines the rate of a reaction, the experiment should be repeated at the same temperature. This could be done using a thermostatic water bath.

120

A level

Had a look Topic 18

Methods in organic chemistry 2

Nearly there Nailed it!





(a) involves continuous evaporation and condensation?

(1 mark)

(b) is suitable for separating limonene, an insoluble liquid that boils at 176°C, from water? (1 mark)

identity and purity of the liquid if, for example:

· your thermometer is incorrectly calibrated the liquid shares the same boiling temperature

with another liquid.

A level

Topic 12



Nearly there Nailed it!





You can calculate the pH of a strong base if you take into account the ionic product of water, K_{w} .

Ionic product of water, K _w	
Water reacts with itself in an acid-base reaction:	skills
$H_2O(I) + H_2O(I) \Longrightarrow H_3O^+(aq) + OH^-(aq)$	In pure, neutral water, $[H^+(aa)] = [OH^-(aa)]$
This can be simplified to:	This means that:
$H_2O(I) \rightleftharpoons H^+(aq) + OH^-(aq)$	• $K_w = [H^+(aq)]^2$
You can write an expression for K_c but for water	• $[H^+(aq)] = \sqrt{K_w}$
this is called the ionic product of water:	You can calculate the pH of water at 298 K:
$\mathcal{K}_{w} = [H^{+}(aq)][OH^{-}(aq)] \qquad \qquad [H_{2}O(l)] \text{ is a constant} \\ and is not included in \\ \end{cases}$	$pH = -log_{10}(\sqrt{(1.00 \times 10^{-14})}) = 7.00$
For pure water at 298 K: the expression.	The dissociation of water is endothermic.
• $K_{\rm w} = 1.00 \times 10^{-14} {\rm mol}^2 {\rm dm}^{-6}$	This means that as the temperature increases:
In the same way that $pK_a = -\log_{10}K_a$:	\mathcal{K}_{w} increases
$pK_{w} = -\log_{10}K_{w}$	✓ pK _w decreases
For pure water at 298 K,	\checkmark the pH of pure water decreases.
• $pK_w = 14.0$	Neutral pH is only 7.00 at 298 K.

Worked example

(a) Explain why sodium hydroxide, NaOH, is a strong base. (1 mark)

It is fully dissociated in aqueous solution:

NaOH(aq)
$$\rightarrow$$
 Na⁺(aq) + OH⁻(aq)

(b) Calculate the hydrogen ion concentration in $0.250 \text{ mol dm}^{-3}$ sodium hydroxide at 298 K. $(K_{\rm w} = 1.00 \times 10^{-14} \,{\rm mol}^2 \,{\rm dm}^{-6})$ (1 mark)

 $K_w = [H^+(aq)][OH^-(aq)]$

 $50 [H^+(aq)] = \frac{1}{[OH^-(aq)]}$ K, $[H^+(aq)] = \frac{(1.00 \times 10^{-14})}{(1.00 \times 10^{-14})}$ 0.250 $= 4.00 \times 10^{-14} \, \text{mol} \, \text{dm}^{-3}$

(c) Calculate the pH of this solution at 298 K. Express your answer to 2 decimal places.

(1 mark)

 $pH = -log_{10}(4.00 \times 10^{-14}) = -(-13.40)$ = 13.40

Enthalpy changes of neutralisation

Strong acids are fully dissociated in solution and have the greatest magnitude of ΔH_{neut}^{Θ} . Weak acids are partially dissociated in solution:

- Energy is needed to dissociate them.
- The magnitudes of their ΔH^{Θ}_{neut} are lower.

Strong bases are fully dissociated in solution. They include KOH and $Ca(OH)_2$ (a dibasic base). Weak bases are only partially dissociated in solution. Ammonia is a weak base.

The temperature is quoted because the value for K_{w} varies with temperature.

When you calculate [OH-(aq)]:

- [OH-(aq)] = [monobasic strong base]
- [OH⁻(aq)] = 2 × [dibasic strong base]

You may have to calculate the pH of a strong base from its concentration. The steps are:

- I. Calculate [OH⁻(aq)] from [base] (see above).
- **2.** Calculate $[H^+(aq)]$ from K_w and $[OH^-]$
- 3. Calculate pH using [H+(aq)].

Now try this

Calculate the pH of these strong bases at 298 K. Express your answers to one decimal place.

- (a) $0.500 \text{ mol } \text{dm}^{-3}$ sodium hydroxide. (2 marks)
- (b) $0.500 \text{ mol } \text{dm}^{-3}$ calcium hydroxide, Ca(OH)₂.

(2 marks)



Vanadium can be reduced from oxidation number +5 to +2 by zinc in acidic solution.

Colours of vanadium compounds and the oxidation number of vanadium

The table summarises the colours of solutions containing vanadium ions.

Oxidation number	+5	+4	+3	+2		
Formula	VO ₂ +	VO ²⁺	V ³⁺	V ²⁺		
Name	dioxovanadium(V)	oxovanadium(IV)	vanadium(III)	vanadium(II)	Be careful! You need	
Colour of solution	vellow	blue	areen	purple	to know these colours. Take care not to confuse VO_2^+ with VO^{2+} .	
	yenew	DIOC	green	Pupic		
Reduction from V(V) to V(II) This can be reduced to vanadium(II) using:						

Ammonium trioxovanadate(V), NH_4VO_3 , is a soluble vanadium(V) compound. In acidic conditions, it forms the

dioxovanadium(V) ion, VO_2^+ .

Had a look

This can be reduced to vanadium(II) using:
• zinc with sulfuric or hydrochloric acid.
You see a change in colour during the reaction:
I. yellow to blue (+3 to +4)
2. blue to green (+4 to +5)
3. green to purple $(+3 \text{ to } +2)$

Explaining reduction using E^{Θ} values

The table summarises, in terms of standard electrode potentials, why these reactions happen.

1.

Change	Oxidation (left)	Reduction (right)	$E_{cell}^{\Theta} = E_{right}^{\Theta} - E_{left}^{\Theta}$	Overall
+5	_		+100 - (-0.76)	$2VO_2^+ + 4H^+ + Zn$
to +4	$Zn \rightleftharpoons Zn^{2+} + 2e^{-}$	$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	= +1.76 V	\downarrow 2VO ²⁺ + 2H ₂ O + Zn ²⁺
+4 to	$Zn \rightleftharpoons Zn^{2+} + 2e^{-}$	$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34 - (-0.76)	2VO ²⁺ + 4H ⁺ + Zn
+3			= +1.10 V	$2V^{3+} + 2H_2O + Zn^{2+}$
+ 3 to	$Zn \rightleftharpoons Zn^{2+} + 2e^{-}$	$\vee^{3+} + e^- \rightleftharpoons \vee^{2+}$	-0.26 - (-0.76) = +0.50 V	2V ³⁺ + Zn ↓
+2			· 5.5 6 V	$2V^{2+} + Zn^{2+}$

Notice that all three E_{cell}^{Θ} values are positive, so the reactions are feasible.

Worked example

Explain why V²⁺ ions cannot be reduced to vanadium using acidified zinc. (2 marks)

$$E_{cell}^{\Theta} = E_{right}^{\Theta} - E_{left}^{\Theta} = -1.18 - (-0.76)$$
$$= -0.42 V$$

As E_{cell}^{Θ} is negative, the reaction is not feasible.

Now try this

An excess of acidified potassium manganate(VII) solution, $KMnO_4(aq)/H^+(aq)$ was added to a solution containing $V^{2+}(aq)$ ions. Identify the vanadium species present when the reaction is complete and write the half-equation for its formation. (2 marks)

 $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O, E^{\Theta} = +1.51 V$

The Data Book shows you that, for the reaction: $V^{2+} + 2e^{-} \rightleftharpoons V, E^{\Theta} = -1.18 V$

The overall reaction required would be: $V^{2+} + Zn \rightarrow V + Zn^{2+}$

Since this is not feasible, the reduction reactions described above do not continue to vanadium.

Right hand electrode system	E^{Θ}/V
$Zn^{2+} + 2e^{-} \rightleftharpoons Zn$	-0.76
$V^{3+} + e^- \rightleftharpoons V^{2+}$	-0.26
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00

Data booklet

Physical constants

Avogadro constant (L)	$6.02 \times 10^{23} \mathrm{mol}^{-1}$
Elementary charge (e)	$1.60 \times 10^{-19} \mathrm{C}$
Gas constant (<i>R</i>)	$8.31 \text{ J mol}^{-1} \text{ K}^{-1}$
Molar volume of ideal gas:	
at s.t.p.	$22.4 \text{ dm}^3 \text{ mol}^{-1}$
at r.t.p.	$24.0 \text{ dm}^3 \text{ mol}^{-1}$
Specific heat capacity of water	$4.18 \text{ J g}^{-1} \text{ K}^{-1}$
Ionic product of water (K_w)	$1.00 \times 10^{-14} \text{mol}^2 \text{dm}^{-6}$
$1 \text{ dm}^3 = 1\ 000 \text{ cm}^3 = 0.001 \text{ m}^3$	

Correlation of infrared absorption wavenumbers with molecular structure

Group	Wavenumber range/cm ⁻¹
C—H stretching vibrations	
Alkane	2962–2853
Alkene	3095–3010
Alkyne	3300
Arene	3030
Aldehyde	2900–2820 and 2775–2700
C—H bending variations	
Alkane	1485–1365
Arene 5 adjacent hydrogen atoms	750 and 700
4 adjacent hydrogen atoms	750
3 adjacent hydrogen atoms	780
2 adjacent hydrogen atoms	830
1 adjacent hydrogen atom	880
N—H stretching vibrations	
Amine	3500-3300
Amide	3500-3140
O—H stretching vibrations	
Alcohols and phenols	3750–3200
Carboxylic acids	3300-2500
C=C stretching vibrations	
Isolated alkene	1669–1645
Arene	1600, 1580, 1500, 1450
C=O stretching vibrations	
Aldehydes, saturated alkyl	1740–1720
Ketones alkyl	1720–1700
Ketones aryl	1700–1680
Carboxylic acids alkyl	1725–1700
aryl	1700–1680
Carboxylic acid anhydrides	1850–1800 and 1790–1740
Acyl halides chlorides	1795
bromides	1810
Esters, saturated	1750–1735
Amides	1700–1630
Triple bond stretching vibrations	
CN	2260–2215
CC	2260-2100



Exam skills 6

Nearly there

This exam-style question uses knowledge and skills you have already revised. Have a look at pages 60 and GI for a reminder about oxidation of alcohols and halogenoalkanes from alcohols.

Worked example

- (a) Ethanal can be made from ethanol.
 - (i) State the names or formulae of the two substances needed to make ethanal from ethanol. (2 marks)

Potassium dichromate(VI), acidified with dilute sulfuric acid.

(ii) Draw a diagram to show the laboratory apparatus needed to make ethanal from ethanol and to collect the ethanal. (2 marks)



(iii) Describe what would be seen when ethanol and ethanal are warmed separately with Tollens' reagent. (1 mark)

There would be no visible change with ethanol but a silver mirror would form with ethanal.

- (b) Phosphorus(V) chloride, PCl₅, reacts with ethanol.
 - (i) Describe what would be seen during the reaction. (1 mark)

Steamy fumes are produced.

(ii) Write an equation for the reaction. (1 mark)

$CH_3CH_2OH + PCI_5 \rightarrow CH_3CH_2CI + POCI_3 + HCI_3$

(c) A mixture of ethanol and water can be distilled to separate some of the ethanol. Name a suitable drying agent to absorb remaining water in the distilled ethanol and describe how you would produce dry ethanol using it. (2 marks)

Use anhydrous calcium oxide. Mix it with the distilled ethanol, then filter the mixture to remove the solid.

'Potassium dichromate' would not be enough - you need to include the oxidation number of chromium in K2Cr2O7. Similarly, 'acid' would not be enough for H_2SO_4 – you need to state its name or formula.

Nailed it!

Practical skills

You need to draw apparatus for heating under distillation conditions. If you showed apparatus for reflux instead, further oxidation to ethanoic acid would occur if this apparatus was used.

Make sure you show that heat is needed (a labelled arrow is enough). Take care that your drawing shows:

- the still head sealed so that the vapours could not escape without entering the condenser
- the condenser open at one end so that the apparatus would not explode.

Make sure you can recall the expected observations when experiments are carried out.

The answer describes the expected observations for both compounds.

Command word: Describe If a question asks you to **describe** something, it means you need to:

- give an account of something
- link statements if necessary.

You do not need to:

include a justification or reason.

The organic reactant and product are shown using structural formulae rather than molecular formulae.

Ethanol and water can be separated from each other by distillation because they have different boiling points.

Anhydrous sodium sulfate or anhydrous magnesium sulfate could be used instead. You could decant the mixture instead of filtering it (the solid would stay behind).

AS & A level

Topic 2



Nearly there Nailed it!

Shapes of molecules and ions

Valence shell electron pair repulsion (VSEPR) theory lets you predict shapes of molecules and ions.

Predicting a shape			
Use a dot and cross diagram to find the number of pairs of electrons around the central atom.	The effect of lone pairs The arrangement of electron pairs around the central atom keeps repulsion to a minimum.		
This gives you the basic shape (see table below).			
	lone pair-lone pair most repulsion		
Multiple bonds	lone pair-bond pair		
Treat these as single bonds.	bond pair-bond pair least repulsion		
For example, $O=C=O$ and $H-C\equiv C-H$ are linear	Each lone pair of electrons		
molecules with a bond angle of 180°.	reduces the bond angle by		
	about 2.5°. For example, NH_3		
Maths Make sure you can visualise the skills angles and shapes in regular 2D and	is trigonal pyramidal,		
3D shapes and can draw them.	107° 109.5° if it were tetrahedral).		

Shapes and angles

Bond pairs	Lone pairs	Shape	Example		Bond pairs	Lone pairs	Shape	Example	
2	0	linear	I80° CI-Be-CI	-Beryllium is in Group 2.	5	0	trigonal bipyramidal		A dashed line shows a bond going into the plane of the paper.
3	0	trigonal planar	CI IS 120° CI CI CI	- Boron is in Group 3.	6	0	octahedral		A wedge shows a bond coming out of the plane of the paper.
4	0	tetrahedral	109.5° H С''нн H	An ordinary line shows a bond in the plane of the paper.			1		

Worked example

Draw the shape of a water molecule, including its bond angle. (1 mark) There are two bonding pairs and two lone pairs around the O atom, so the basic shape is tetrahedral.

Repulsion by the two lone pairs reduces the bond angle by about 5°, producing a V-shaped (or bent line) molecule.

Now try this

- 1 Predict the bond angles in the following molecules and ions.
 - (a) CHCl₃ (b) NH_4^+ (c) NH_2^- (d) BeF_2 (e) PF_5 (5 marks)

Carbon is the central atom in CHCl₃.

- 2 Predict the bond angles in BH₃ and PH₃. Explain the difference between them.
 - (3 marks)
- 3 Sulfur trioxide, SO_3 , has three triple bonds around the central atom and no lone pairs. Name the shape of the SO₃ molecule and suggest its bond angle. (2 marks)





Sub-shells and orbitals

have the letters s, p or d.

Each shell contains one or more **sub-shells**, which

S

2

 \checkmark An orbital is a region around the nucleus where there is a high probability of finding an electron. An orbital can hold up to two electrons with

Each sub-shell contains different numbers of orbitals.

P

3

6

AS & A level

Topic 1

f

7

14

d

5

10

Shells, sub-shells and orbitals

Sub-shell

Number of orbitals

opposite spins.

Number of electrons

Electrons surround the nucleus of an atom and are arranged in orbitals, sub-shells and shells.

Ouantum shells

Electrons in atoms exist in energy levels called quantum shells.



Worked example

Draw diagrams to show the shape of an s-orbital and of a p-orbital. (2 marks)



The arrows represent the three axes in space x, y and z. The p-orbital could have been drawn in one of the other two orientations instead.



You must show an s-orbital as a circle. You do not need to know the shape of d- or f-orbitals.

Electrons in shells

You need to know the maximum number of electrons in the first four quantum shells.

Shell	Sub-shell(s)	Maximum number of electrons
4	4s 4p 4d 4f	2 + 6 + 10 + 14 = 32
3	35 3p 3d	2 + 6 + 10 = 18
2	25 2p	2 + 6 = 8
	ls	2

The 4d and 4f sub-shells are included here only so you can see why the fourth shell can contain up to 32 electrons.

Now try this

- 1 (a) Explain what is meant by the term orbital. (2 marks)
 - (b) Draw the shapes of an s-orbital and a p-orbital. (2 marks)

Electrons in orbitals

Electrons have a property called **spin**. The electrons in an orbital have opposite spins.

$4p$ $1 \downarrow 1 \downarrow 1 \downarrow$	
	3d is higher
4s ≬ ↓	than 4s
3p 11111	_
3₅ _↑↓	
2p 1111 -	$2p_x 2p_y 2p_z$
25 ∱↓	arrows represent
ls 🚺 <	electrons with
	opposite spin

2 State the maximum number of electrons that can occupy: (a) an s-, a p- and a d-sub-shell (1 mark)

boxes.

- (b) each of the first four quantum shells. (1 mark)
- 3 Explain why electrons may be represented as arrows in

(2 marks)



Stability of carbonates and nitrates

Nearly there

Group I and 2 carbonates and nitrates may undergo thermal decomposition, reactions in which heat is used to break down a reactant into two or more products.

Carbonates

Had a look

Many, but not all, Group I and 2 carbonates decompose to form metal oxides and carbon dioxide.

Li ₂ CO ₃	decomposes	BeCO ₃		
Na ₂ CO ₃		MgCO ₃	decompose	
K ₂ CO ₃	do not	CaCO ₃	with	
Rb ₂ CO ₃	decompose	SrCO ₃	difficulty	
C52CO3		BaCO ₃	Villeology W	

In Group I, only lithium carbonate decomposes at Bunsen burner temperatures:

$$Li_2CO_3(s) \rightarrow Li_2O(s) + CO_2(g)$$

Going down Group 2, the carbonates become more stable and need higher temperatures to decompose them. In general:

 $MCO_3(s) \rightarrow MO(s) + CO_2(g)$

Worked example

The diagram shows apparatus that can be used to investigate the thermal stability of Group 2 carbonates. The time taken for the limewater to turn cloudy is measured for each carbonate.



State three factors to control so a fair comparison can be made. (3 marks)

Explaining trends

Cations (positively charged ions) can affect anions such as CO_3^{2-} and NO_3^{-} .

They can lower the energy needed to break a C-O bond or N-O bond.

This effect increases:

- the smaller the cation
- the greater the cation's charge.
- Li⁺ ions and Group 2 ions can cause:
- CO_3^{2-} ions to decompose to O^{2-} and CO_2 .
- NO_3^- ions to decompose to O^{2-} , NO_2 and O_2 .

Nitrates

Group I and 2 nitrates decompose to form different products, depending on their stability.

LiNO ₃	Li ₂ O NO ₂ O ₂	$Be(NO_3)_2$	
NaNO ₃		$Mg(NO_3)_2$	
KNO3	MNO ₂	$Ca(NO_3)_2$	$MO NO_2$
RbNO ₃	O ₂	Sr(NO ₃) ₂	\cup_2
CsNO ₃		Ba(NO ₃) ₂	

Here are three example equations:

- $4LiNO_3(s) \rightarrow 2Li_2O(s) + 4NO_2(q) + O_2(q)$
- $2RbNO_3(s) \rightarrow 2RbNO_2(s) + O_2(g)$
- $2Mg(NO_3)_2 \rightarrow 2MgO(s) + 4NO_2(g) + O_2(g)$

Going down Groups I and 2, nitrates become more stable. Higher temperatures are needed to decompose them.

The same number of moles of carbonate should be used each time. The size of the flame and its distance to the boiling tube should be the same.



Other factors include the volume of limewater and the particle size of the carbonates. There should also be a way to standardise the measurement of cloudiness, such as a black cross drawn on the opposite side of the tube.

Practical skills

You need to understand experimental procedures to show patterns in the thermal decomposition of Group I and 2 nitrates and carbonates.

Now try this

Lithium nitrate behaves differently from other Group 1 nitrates.

- (a) Describe, with the help of equations, the differences in the thermal decomposition of lithium nitrate and potassium nitrate. (4 marks)
- (b) Explain the difference in observed thermal stability of these two nitrates. (2 marks)