



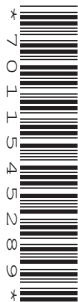
Oxford Cambridge and RSA

A Level Chemistry A

H432/03 Unified chemistry

Wednesday 20 June 2018 – Morning

Time allowed: 1 hour 30 minutes



You must have:

- the Data Sheet for Chemistry A
(sent with general stationery)

You may use:

- a scientific or graphical calculator



First name										
Last name	StemUp Model Solution									
Centre number						Candidate number				

INSTRUCTIONS

- Use black ink. You may use an HB pencil for graphs and diagrams.
- Complete the boxes above with your name, centre number and candidate number.
- Answer **all** the questions.
- Write your answer to each question in the space provided. If additional space is required, use the lined page(s) at the end of this booklet. The question number(s) must be clearly shown.
- Do **not** write in the barcodes.

INFORMATION

- The total mark for this paper is **70**.
- The marks for each question are shown in brackets [].
- Quality of extended responses will be assessed in questions marked with an asterisk (*).
- This document consists of **16** pages.

Answer **all** the questions.

1 This question refers to the elements in the first three periods (H→Ar) of the Periodic Table.

(a) Select an element from the first three periods that fits each of the following descriptions.

(i) The element that forms a 1– ion with the same electron configuration as helium.

hydrogen, H [1]

(ii) The element with the highest first ionisation energy.

helium, He [1]

(iii) The element in Period 3 which has the successive ionisation energies shown below.

Ionisation number	1st	2nd	3rd	4th
Ionisation energy/kJ mol ⁻¹	738	1451	7733	10541

magnesium, Mg [1]

(iv) The element which forms a compound with fluorine that has octahedral molecules.

sulfur, S [1]

(v) An element which reacts with water to form an acidic solution.

chlorine, Cl [1]

(vi) The element **X**, which forms a compound with hydrogen, **XH₃**, with a molar mass of 34.0 g mol⁻¹.

phosphorus, P [1]

(vii) An element which forms a compound with hydrogen in which the element has an oxidation number of –4.

carbon, C [1]

(viii) The element which has a density of 1.33 × 10⁻³ g cm⁻³ at room temperature and pressure.

oxygen, O [1]

(b) Table 1.1 shows some properties of Period 3 chlorides.

Group		1	2	14 (4)	15 (5)	16 (6)
Chloride		NaCl	MgCl ₂	SiCl ₄	PCl ₃	SCl ₂
Electrical conductivity	Solid	poor	poor	poor	poor	poor
	Liquid	good	good	poor	poor	poor
Melting point		high	high	low	low	low

Table 1.1

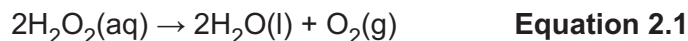
Explain the properties shown in Table 1.1 in terms of bonding and structure.

NaCl and MgCl₂ have giant ionic lattice structures, with strong electrostatic attraction between oppositely charged ions (ionic bonds).
In the solid the ions are fixed in the lattice so conductivity is poor, but in the liquid the ions are mobile and can carry charge, so they conduct well.
Their melting points are high because a large amount of energy is needed to break the strong ionic bonds.
SiCl₄, PCl₃ and SCl₂ are simple molecular (simple covalent) substances, with no mobile ions or electrons, so they are poor conductors as solid and liquid.
Only weak London forces (induced dipole-dipole interactions) act between the molecules, which need little energy to overcome, so melting points are low. Ionic bonds are much stronger than London forces.

[5]

2 This question looks at reactions of hydrogen peroxide and of cobalt(II) ions.

(a) Aqueous hydrogen peroxide decomposes as shown in **equation 2.1**.



The reaction is catalysed by manganese(IV) oxide, MnO_2 .

A student investigates the decomposition of a hydrogen peroxide solution as outlined below.

- The student adds 50.00 cm^3 of $\text{H}_2\text{O}_2(\text{aq})$ to a conical flask.
- The student adds a small spatula measure of MnO_2 and quickly connects the flask to a gas syringe.
- The student measures the volume of oxygen every 200 seconds.

Results

Time/s	Volume of O_2/cm^3
0	0
200	15
400	28
600	36
800	41
1000	46
1200	48
1400	50

(i) Process the results as outlined below.

- On page 5, plot a graph of **volume of O_2** against **time**.
- Use your graph to find the rate of the reaction, in cm^3s^{-1} , at $t = 500\text{ s}$.

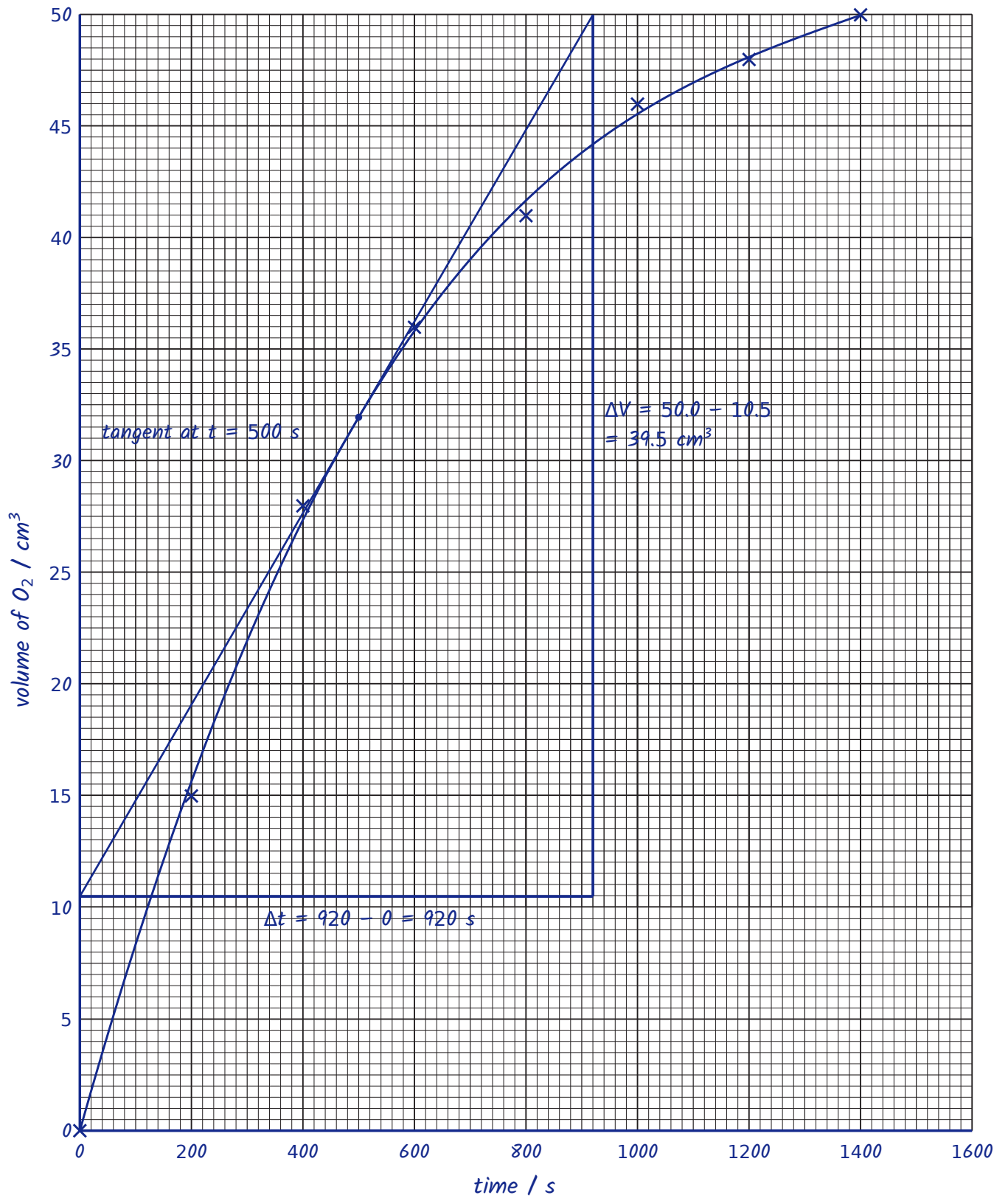
Show your working on the graph and in the space below.

The tangent is drawn to the curve at $t = 500\text{ s}$ (see graph).

$$\text{gradient} = \Delta V / \Delta t = (50.0 - 10.5) / (920 - 0)$$

$$= 39.5 / 920 = 0.0429\text{ cm}^3\text{ s}^{-1}$$

$$\text{rate} = \dots\dots\dots 0.043 \dots\dots\dots \text{cm}^3\text{s}^{-1} \quad [5]$$



- (ii) The student allows the reaction in **equation 2.1** to proceed until no more gas is evolved. The volume of O_2 in the syringe is now 55 cm^3 , measured at RTP.

Calculate the initial concentration of the H_2O_2 .

Give your answer to **two** significant figures.

$$n(O_2) = 55/24000 = 2.29 \times 10^{-3} \text{ mol}$$

$$n(H_2O_2) = 2 \times 2.29 \times 10^{-3} = 4.58 \times 10^{-3} \text{ mol}$$

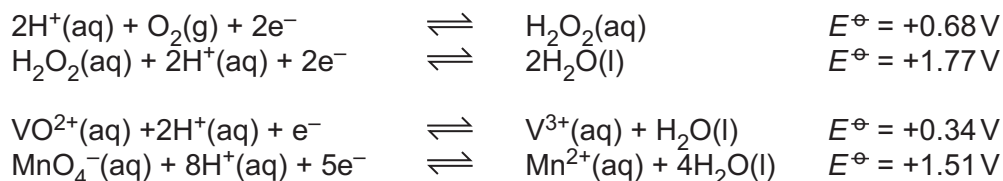
$$[H_2O_2] = 4.58 \times 10^{-3} \times 1000/50.00 = 0.0917 \text{ mol dm}^{-3}$$

$$= 0.092 \text{ mol dm}^{-3} \text{ (2 s.f.)}$$

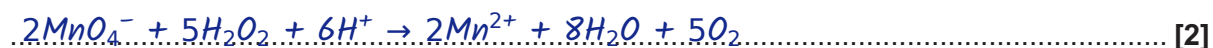
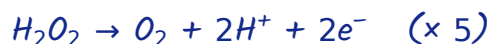
initial concentration of H_2O_2 = ... 0.092 mol dm^{-3} [3]

- (b) Hydrogen peroxide can act as an oxidising agent or as a reducing agent.

Some standard electrode potentials are shown below.



Use this information to write an equation for a reaction in which hydrogen peroxide acts as a reducing agent.



(c) Cobalt(II) forms complex ions with water ligands and with chloride ligands.

- With water ligands, cobalt(II) forms a pink octahedral complex ion, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.
- With chloride ligands, cobalt(II) forms a blue tetrahedral complex ion.

A student dissolves cobalt(II) sulfate in water in a boiling tube. A pink solution forms.

Experiment 1

The student places the boiling tube in a water bath at 100°C .

Concentrated hydrochloric acid is added dropwise.

The colour of the solution changes from pink to blue.

Experiment 2

The student places the boiling tube from **experiment 1** in an ice/water bath at 0°C .

The colour of the solution changes from blue to pink.

- (i) Write the equilibrium equation for the reaction that takes place when the colour of the solution changes.



- (ii) Explain the observations and predict whether the formation of the blue colour is exothermic or endothermic.

At 100°C (high temperature) the equilibrium shifts to the right, forming.....

blue $[\text{CoCl}_4]^{2-}$; the extra Cl^- from conc. HCl also shifts it to the right......

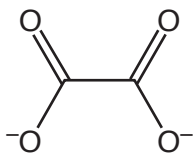
At 0°C (low temperature) the equilibrium shifts to the left, re-forming.....

pink $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$

So the forward reaction forming the blue colour is endothermic...... [2]

3 This question is about ethanedioic acid, $(\text{COOH})_2$, and ethanedioate ions, $(\text{COO}^-)_2$.

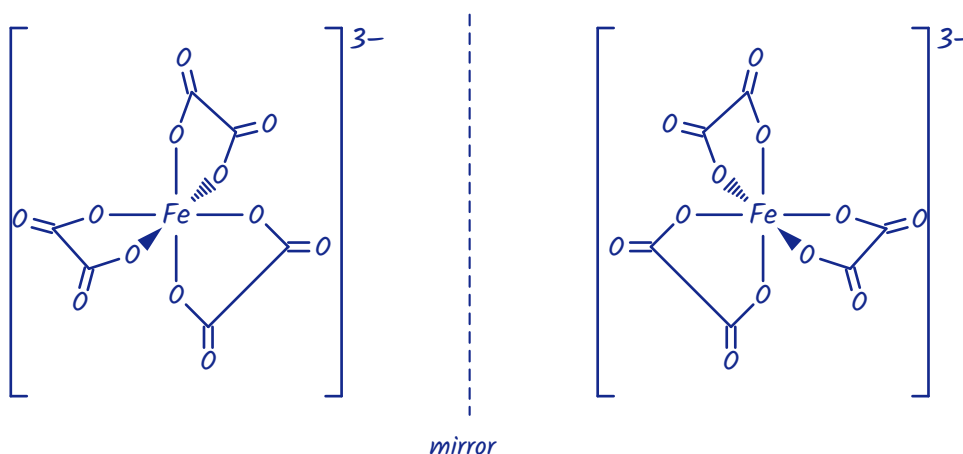
(a) The ethanedioate ion, shown below, can act as a bidentate ligand.



Fe^{3+} forms a complex ion with three ethanedioate ions.
The complex ion has two optical isomers.

Draw the 3D shapes of the optical isomers.

In your diagrams, show the structure of the ethanedioate ligands and any overall charge.



[3]

(b) Ethanedioic acid, $(\text{COOH})_2$, is present in rhubarb leaves.

A student carries out a redox titration using aqueous cerium(IV) sulfate, $\text{Ce}(\text{SO}_4)_2(\text{aq})$, to determine the percentage, by mass, of ethanedioic acid in rhubarb leaves.

In the titration, $\text{Ce}^{4+}(\text{aq})$ ions oxidise ethanedioic acid in hot acid conditions:



$\text{Ce}^{4+}(\text{aq})$ ions have a yellow colour. $\text{Ce}^{3+}(\text{aq})$ ions are colourless.

The student weighs 82.68 g of rhubarb leaves and extracts ethanedioic acid from the leaves.

The ethanedioic acid is added to dilute sulfuric acid to form a colourless solution which is made up to 250.0 cm^3 with distilled water.

The student heats 25.00 cm^3 of this solution to 70°C and titrates this volume with $0.0500 \text{ mol dm}^{-3}$ $\text{Ce}(\text{SO}_4)_2$ from the burette.

The student repeats the titration to obtain concordant (consistent) titres.

Titration results

The trial titre has been omitted.

	1	2	3
Final reading/cm ³	24.30	47.80	23.65
Initial reading/cm ³	1.05	24.30	0.50

- (i) This titration is self-indicating and the student does not need to add an indicator.

What colour change would the student observe at the end point?

Colour change from *colourless* to *yellow* [1]

- (ii) Calculate the percentage, by mass, of ethanedioic acid in the rhubarb leaves.

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

titres: 23.25, 23.50, 23.15 cm³

concordant titres are 23.25 and 23.15 cm³

mean titre = (23.25 + 23.15)/2 = 23.20 cm³

$n(\text{Ce}^{4+}) = 0.0500 \times 23.20/1000 = 1.16 \times 10^{-3} \text{ mol}$

$n((\text{COOH})_2) \text{ in } 25.00 \text{ cm}^3 = 1.16 \times 10^{-3}/2 = 5.80 \times 10^{-4} \text{ mol}$

$n((\text{COOH})_2) \text{ in } 250.0 \text{ cm}^3 = 5.80 \times 10^{-4} \times 10 = 5.80 \times 10^{-3} \text{ mol}$

$M((\text{COOH})_2) = 90.0 \text{ g mol}^{-1}$

mass of $(\text{COOH})_2 = 5.80 \times 10^{-3} \times 90.0 = 0.522 \text{ g}$

percentage = $0.522/82.68 \times 100 = 0.631\%$ (3 s.f.)

percentage of ethanedioic acid = *0.631* % [6]

4 This question is about two compounds used in medicine.

(a) *Cis-platin*, $\text{PtCl}_2(\text{NH}_3)_2$, is a complex of platinum which is used in cancer treatment.

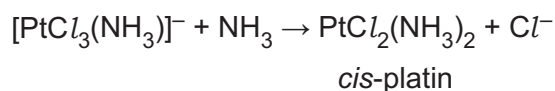
(i) What is the oxidation number of platinum in *cis-platin*?

+2.....

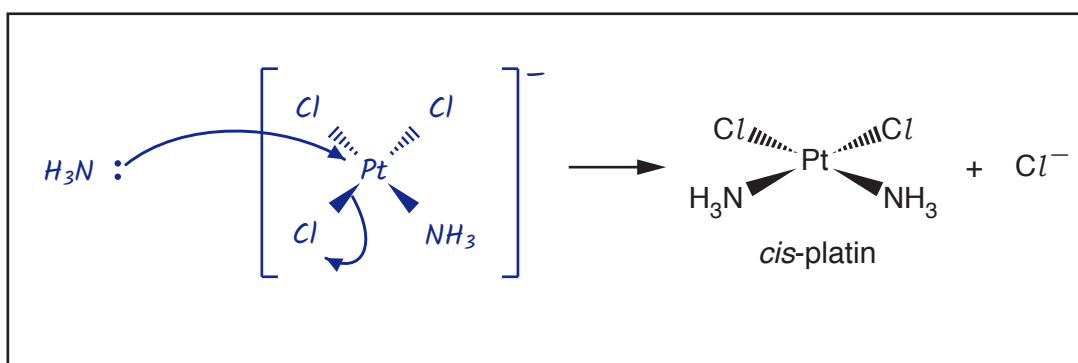
[1]

(ii) *Cis-platin* is prepared in a ligand substitution reaction which takes place in multiple steps.

The equation for the final step forming *cis-platin* is shown below.

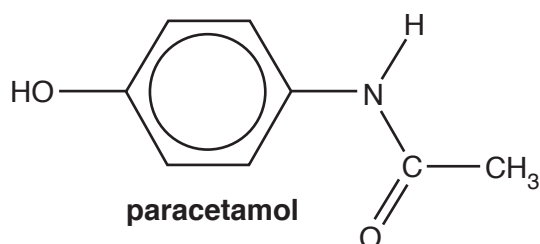


In the box, outline the mechanism for the formation of *cis-platin* from $[\text{PtCl}_3(\text{NH}_3)]^-$. Use curly arrows and lone pairs where appropriate.



[2]

(b) Paracetamol is a solid organic compound used in tablets as a painkiller.



(i) Name the functional groups present in paracetamol.

phenol.....

amide.....

[2]

(ii)* A chemist prepares a pure solid sample of paracetamol from 4-nitrophenol in two stages:



Describe a two-stage synthesis of 5.00g of pure paracetamol from 4-nitrophenol. The overall percentage yield of paracetamol from 4-nitrophenol is 40.0%.

In your answer, include the mass of 4-nitrophenol required, the reagents and intermediate, and details of the purification of paracetamol. [6]

$M(\text{paracetamol}, \text{C}_8\text{H}_9\text{NO}_2) = 151.0 \text{ g mol}^{-1}$, so $n(\text{paracetamol}) =$

$5.00/151.0 = 0.0331 \text{ mol}$. With a 40.0% overall yield, $n(4\text{-nitrophenol})$

$\text{needed} = 0.0331 \times 100/40.0 = 0.0828 \text{ mol}$.

$M(4\text{-nitrophenol}, \text{C}_6\text{H}_5\text{NO}_3) = 139.0 \text{ g mol}^{-1}$, so mass of 4-nitrophenol =

$0.0828 \times 139.0 = 11.5 \text{ g}$.

Stage 1: reduce the NO_2 group by heating under reflux with tin (Sn) and concentrated HCl, then add NaOH(aq). The intermediate is 4-aminophenol,

$\text{HOC}_6\text{H}_4\text{NH}_2$.

Stage 2: react 4-aminophenol with ethanoyl chloride, CH_3COCl ; the NH_2 group forms the amide (paracetamol) and HCl is given off.

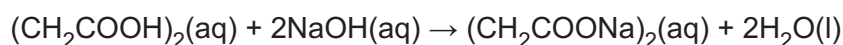
Purification (recrystallisation): dissolve the impure solid in the minimum volume of hot solvent (e.g. water) and filter hot to remove insoluble impurities. Cool slowly so paracetamol crystallises (scratch with a glass rod if needed) while soluble impurities stay in solution. Filter under reduced pressure (Buchner funnel), wash the crystals with a little cold solvent and

Additional answer space if required.

dry them. Check purity: a sharp melting point equal to the data book value.

- 5 A student carries out two experiments in the laboratory based on succinic acid (butanedioic acid), $(\text{CH}_2\text{COOH})_2$.

(a) Aqueous succinic acid can be neutralised by aqueous sodium hydroxide, $\text{NaOH}(\text{aq})$:



This reaction can be used to determine a value for the enthalpy change of neutralisation, $\Delta_{\text{neut}}H$.

The student follows this method:

- Add 50.0 cm^3 of 0.400 mol dm^{-3} succinic acid to a polystyrene cup.
- Measure out 50.0 cm^3 of 1.00 mol dm^{-3} $\text{NaOH}(\text{aq})$, which is in excess.
- Measure the temperature of both solutions.
- Add the $\text{NaOH}(\text{aq})$ to the aqueous succinic acid in the polystyrene cup, stir the mixture, and record the maximum temperature.

Temperature readings

Maximum temperature of mixture/ $^{\circ}\text{C}$	26.5
Initial temperature of both solutions/ $^{\circ}\text{C}$	21.5

Calculate a value for the enthalpy change of neutralisation, $\Delta_{\text{neut}}H$, in kJ mol^{-1} .

Assume that the density of all solutions and the specific heat capacity, c , of the reaction mixture are the same as for water.

$$n(\text{succinic acid}) = 0.400 \times 50.0/1000 = 0.0200\text{ mol}$$

$$q = mc\Delta T = 100.0 \times 4.18 \times 5.0 = 2090\text{ J} = 2.090\text{ kJ}$$

$$\text{per mol succinic acid: } 2.090/0.0200 = 104.5\text{ kJ}$$

$$n(\text{H}_2\text{O}) \text{ formed} = 2 \times 0.0200 = 0.0400\text{ mol}$$

$$\Delta_{\text{neut}}H = -2.090/0.0400 = -52.25\text{ kJ mol}^{-1}$$

$$= -52.3\text{ kJ mol}^{-1} \text{ (exothermic)}$$

$$\Delta_{\text{neut}}H = \dots\dots\dots -52.3 \dots\dots\dots \text{ kJ mol}^{-1} \text{ [4]}$$

- (b) Succinic acid is esterified by ethanol, $\text{C}_2\text{H}_5\text{OH}$, in the presence of an acid catalyst to form an equilibrium mixture.

The equilibrium constant, K_c , for this equilibrium can be calculated using the amounts, in moles, of the components in the equilibrium mixture, using **expression 5.1**.

$$K_c = \frac{n(\text{CH}_2\text{COOC}_2\text{H}_5)_2 \times n(\text{H}_2\text{O})^2}{n(\text{CH}_2\text{COOH})_2 \times n(\text{C}_2\text{H}_5\text{OH})^2} \quad \text{Expression 5.1}$$

A student carries out an experiment to determine the value of K_c for this equilibrium.

- The student mixes together 0.0500 mol of succinic acid and 0.150 mol of ethanol, with a small amount of an acid catalyst.
- The mixture is allowed to reach equilibrium.
- The student determines that 0.0200 mol of succinic acid are present in the equilibrium mixture.

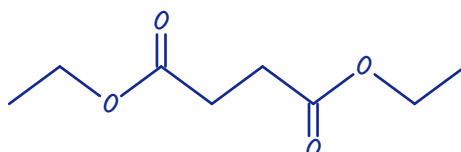
- (i) Which technique could be used to determine the equilibrium amount of succinic acid?

titration with standard NaOH(aq) [1]

- (ii) Write the equation for the equilibrium reaction that takes place.

$(\text{CH}_2\text{COOH})_2 + 2\text{C}_2\text{H}_5\text{OH} \rightleftharpoons (\text{CH}_2\text{COOC}_2\text{H}_5)_2 + 2\text{H}_2\text{O}$ [1]

- (iii) Draw the skeletal formula of the ester present in the equilibrium mixture.



[1]

- (iv) K_c is the equilibrium constant in terms of equilibrium concentrations.

Why can **expression 5.1** be used to calculate K_c for this equilibrium?

The total moles on each side of the equation are the same (3 and 3), so the volume cancels in K_c [1]

- (v) Calculate the value of K_c for this reaction.

Show your working.

$$n(\text{ester}) = 0.0500 - 0.0200 = 0.0300 \text{ mol}$$

$$n(\text{H}_2\text{O}) = 2 \times 0.0300 = 0.0600 \text{ mol}$$

$$n(\text{C}_2\text{H}_5\text{OH}) = 0.150 - 0.0600 = 0.0900 \text{ mol}$$

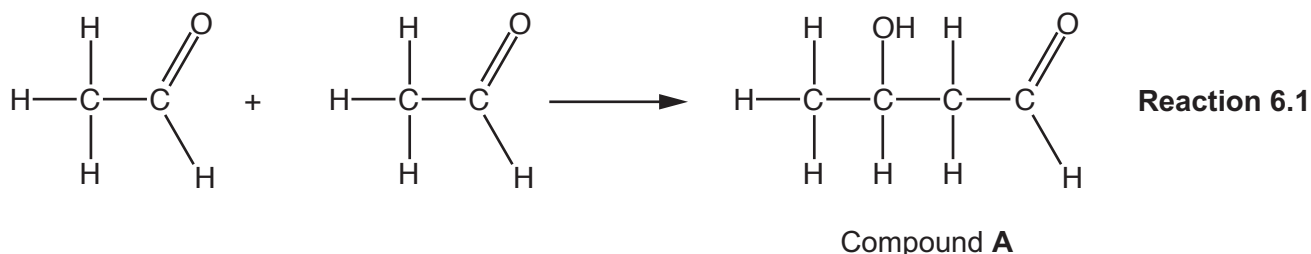
$$K_c = (0.0300 \times 0.0600^2) / (0.0200 \times 0.0900^2) = 0.667$$

$$K_c = \dots\dots\dots 0.667 \dots\dots\dots [3]$$

6 This question is about organic reactions.

(a) Compound **A** is formed when ethanal is mixed with $\text{OH}^-(\text{aq})$ ions, which act as a catalyst.

The balanced equation is shown in **reaction 6.1** below.



(i) Give the systematic name for compound **A**.

3-hydroxybutanal [1]

(ii) What type of reaction has taken place?

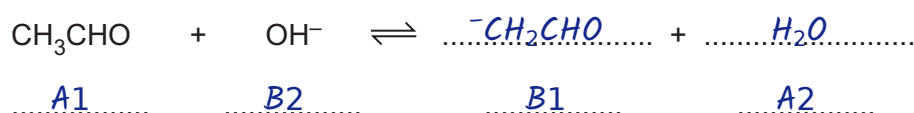
addition [1]

(iii) **Reaction 6.1** takes place in two steps. OH^- ions act as a catalyst.

In **step 1**, ethanal reacts with OH^- ions to set up an acid–base equilibrium.

In **step 2**, compound **A** is formed.

- Complete the equilibrium for **step 1** and label the conjugate acid–base pairs as: **A1**, **B1** and **A2**, **B2**.



- Suggest the equation for **step 2**.



[3]

(iv) A similar reaction takes place when propanone, $(\text{CH}_3)_2\text{CO}$, is mixed with $\text{OH}^-(\text{aq})$ ions.

Draw the structure of the organic product of this reaction.



[1]

(b)* Many organic reactions use electrophiles as reagents.

Explain the role of electrophiles in organic chemistry.

Your answer should include **one** reaction of an aliphatic compound and **one** reaction of an aromatic compound, including relevant mechanisms. [6]

An electrophile is an electron pair acceptor. It is attracted to a region of high electron density, such as the C=C π -bond in an alkene or the delocalised π -electrons of benzene, and accepts a pair of electrons to form a new covalent bond.

Aliphatic: ethene + Br₂ → 1,2-dibromoethane, electrophilic addition at room temperature. The π -electrons of C=C induce a dipole in Br₂ (Br δ^+ -Br δ^-). A pair of electrons from the π -bond moves to Br δ^+ and the Br-Br bond breaks heterolytically, giving a carbocation and Br $^-$. The Br $^-$ lone pair then bonds to C $^+$ (mechanism 1, page 16). With propene and HBr the major product, 2-bromopropane, comes from the more stable secondary carbocation (Markownikoff).

Aromatic: nitration of benzene, electrophilic substitution, with conc. HNO₃ and conc. H₂SO₄ at 50 °C. Electrophile: HNO₃ + H₂SO₄ → NO₂ $^+$ + HSO₄ $^-$ + H₂O. A pair of π -electrons from the ring bonds to NO₂ $^+$, giving an intermediate with the delocalisation partly broken. The C-H bond electrons return to the ring, so

Additional answer space if required.

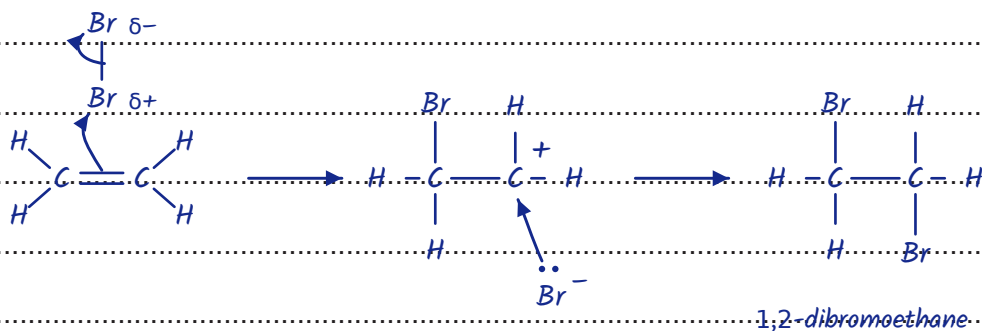
the stable delocalised ring is restored (substitution, not addition), giving nitrobenzene. H $^+$ + HSO₄ $^-$ → H₂SO₄ regenerates the catalyst (mechanism 2, page 16).

END OF QUESTION PAPER

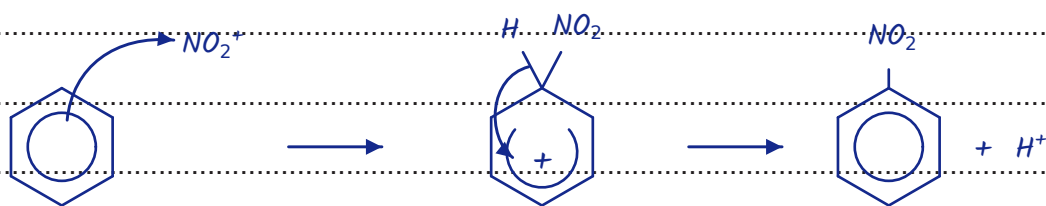
ADDITIONAL ANSWER SPACE

If additional space is required, you should use the following lined page(s). The question number(s) must be clearly shown in the margin(s).

6(b)

mechanism 1: electrophilic addition of Br₂ to ethene

mechanism 2: nitration of benzene (electrophilic substitution)



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