OCR
Oxford Cambridge and RSA

A Level Chemistry A

H432/03 Unified chemistry

Wednesday 20 June 2018 – Morning

Time allowed: 1 hour 30 minutes

7011545289

You must have:
- the Data Sheet for Chemistry A (sent with general stationery)

You may use:
- a scientific or graphical calculator

H432/03

First name									
Last name									
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.

H gaining an electron

.....H..... [1]

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

He ionisation energy increases from the bottom left to top right of the periodic table

.....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

period 3 group 2 large jump meaning 2+ charge

.....Mg..... [1]

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

.....S..... [1]

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

.....Cl or F..... forms HCl, HOCl HF, HOF [1]

(vi) The element **X**, which forms a compound with hydrogen, $\mathbf{X}H_3$, with a molar mass of 34.0 g mol^{-1}.

$x = 34 - 3 = 31$ ↑ RFM of x

.....P..... [1]

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

group 4

.....C..... [1]

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

$1.33 \times 10^{-3} \times 24000$ cm^3 [1]

$= 32$ ↑ RFM of element

24000 cm^3 volume at RTP

(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 + $MgCl_2$:
giant ionic lattice, ions are mobile in liquid state so are better electrical conductors

$SiCl_4$, PCl_3, SCl_2:
simple molecular so held together by london forces of attraction

ionic bonds are stronger than london forces hence NaCl and $MgCl_2$ have higher melting points. **[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**.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g) \qquad \textbf{Equation 2.1}$$

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 $H_2O_2(aq)$ 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.

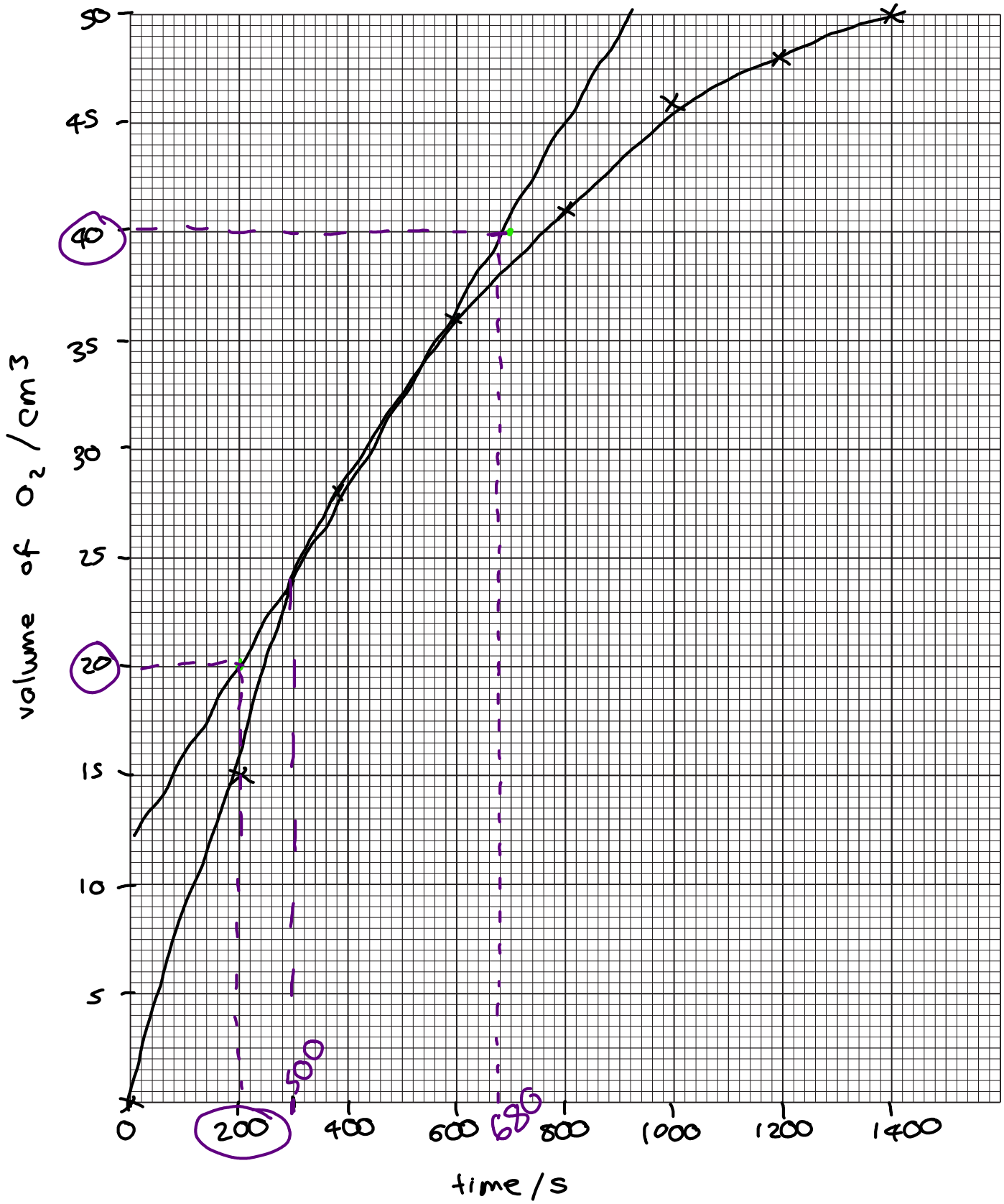
- On page 5, plot a graph of **volume of O_2** against **time**.
- Use your graph to find the rate of the reaction, in $cm^3 s^{-1}$, at t = 500 s.

tangent at 500 s

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

$$\frac{40-20}{680-200} = 0.042\ cm^3 s^{-1}$$

rate = ... 0.042 ..... $cm^3 s^{-1}$ **[5]**


volume of O_2 / cm^3
50
45
40
35
30
25
20
15
10
5
0
200
400
600
800
1000
1200
1400
time / s
500
680

(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.

volume / molar volume (24000 cm^3) = mol

$\frac{55}{24000} = 2.29 \times 10^{-3}$ mol

1 : 2 molar ratio

$2.29 \times 10^{-3} \times 2 = 4.58 \times 10^{-3}$ mol of H_2O_2

n = V x C

$4.58 \times 10^{-3} \div 50 \times 10^{-3} = 0.092$ mol dm^{-3}

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.

$2H^+(aq) + O_2(g) + 2e^-$	$\rightleftharpoons$	$H_2O_2(aq)$	$E^\ominus = +0.68\,V$
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$2H_2O(l)$	$E^\ominus = +1.77\,V$
$VO^{2+}(aq) + 2H^+(aq) + e^-$	$\rightleftharpoons$	$V^{3+}(aq) + H_2O(l)$	$E^\ominus = +0.34\,V$
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\rightleftharpoons$	$Mn^{2+}(aq) + 4H_2O(l)$	$E^\ominus = +1.51\,V$

+7 → +2 reduction

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

oxidisation

$5H_2O_2 \rightarrow 2H^+ + 5O_2 + 2e^-$ (×10)

$2MnO_4^- + 8H^+ + 5e^- \rightarrow 2Mn^{2+} + 4H_2O$ (×8, ×10)

$5H_2O_2 + 2MnO_4^- + 16H^+ + 10e^- \rightarrow 10H^+ + 5O_2 + 10e^- + 2Mn^{2+} + 8H_2O$

$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O$ **[2]**

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

- With water ligands, cobalt(II) forms a pink octahedral complex ion, $[Co(H_2O)_6]^{2+}$.
- 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.

ligand substitution

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

$[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$ **[1]**

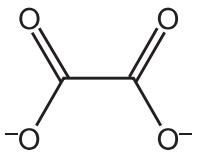
(ii) Explain the observations and predict whether the formation of the blue colour is exothermic or endothermic.

equilibrum shifts right at 100°c and shifts left at 0°c so endothermic.

[2]

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

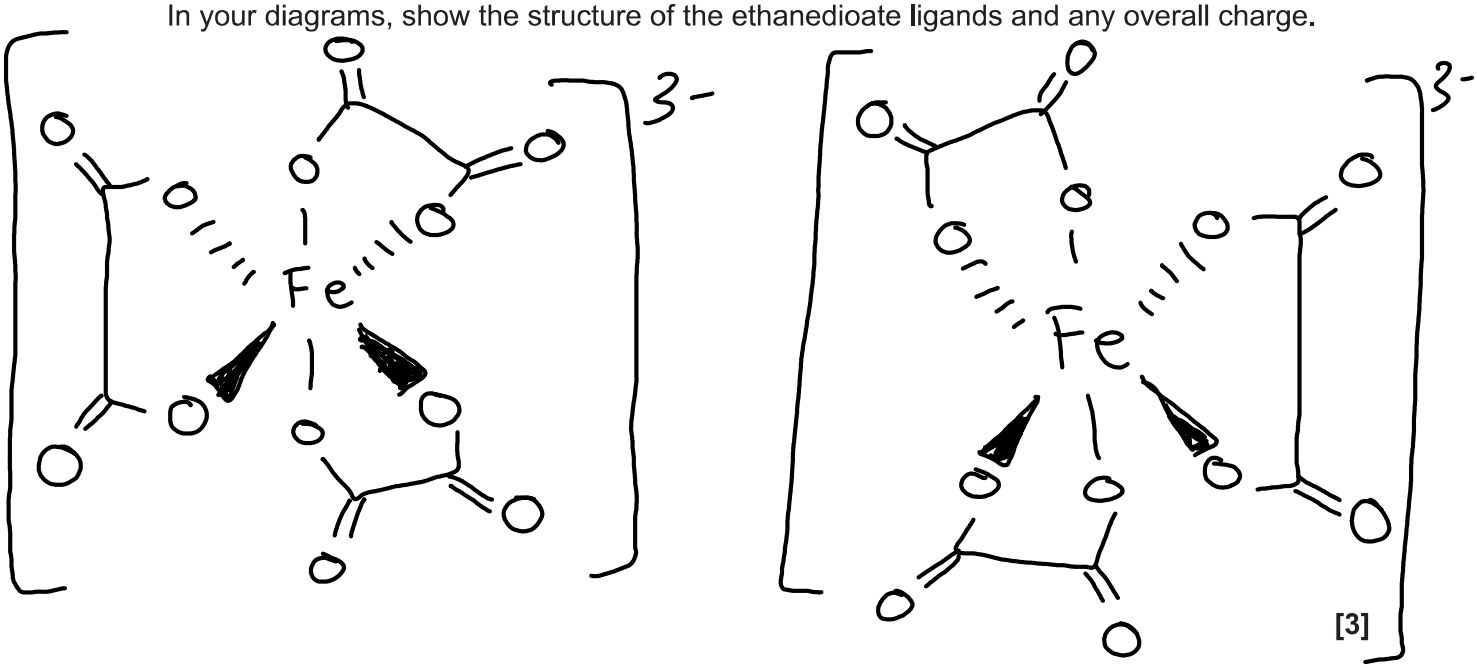
(a) The ethanedioate ion, shown below, can act as a bidentate ligand.



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, $(COOH)_2$, is present in rhubarb leaves.

A student carries out a redox titration using aqueous cerium(IV) sulfate, $Ce(SO_4)_2(aq)$, to determine the percentage, by mass, of ethanedioic acid in rhubarb leaves.

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

$$2Ce^{4+}(aq) + (COOH)_2(aq) \rightarrow 2Ce^{3+}(aq) + 2CO_2(g) + 2H^+(aq)$$

$Ce^{4+}(aq)$ ions have a yellow colour. $Ce^{3+}(aq)$ 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 mol dm^{-3} $Ce(SO_4)_2$ 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
titre / cm^3	23.25	23.50	23.15

(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.

mean titre: $\frac{23.25 + 23.15}{2} = 23.20$ cm^3

n = V x C

$23.20 \times 10^{-3} \times 0.05 = 1.16 \times 10^{-3}$ mol of Ce^{4+}

$\frac{1.16 \times 10^{-3}}{2} = 5.80 \times 10^{-4}$ mol of $(COOH)_2$ in 25cm^3

$5.80 \times 10^{-4} \times 10 = 5.80 \times 10^{-3}$ mol of $(COOH)_2$ in 250cm^3

m = mol x RFM

$5.80 \times 10^{-3} \times ((12 + ((16 \times 2) + 1) \times 2)$

$= 0.522$g

$\frac{0.522}{82.68} \times 100 = 0.631$ % (3SF.)

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

4 This question is about two compounds used in medicine.

(a) *Cis*-platin, $PtCl_2(NH_3)_2$, is a complex of platinum which is used in cancer treatment.

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

All compounds must have an oxidation number of 0

Pt +2
Cl_2 $-1 \times 2 = -2$
$(NH_3)_2$ $0 \times 2 = 0$

.....+2..... **[1]**

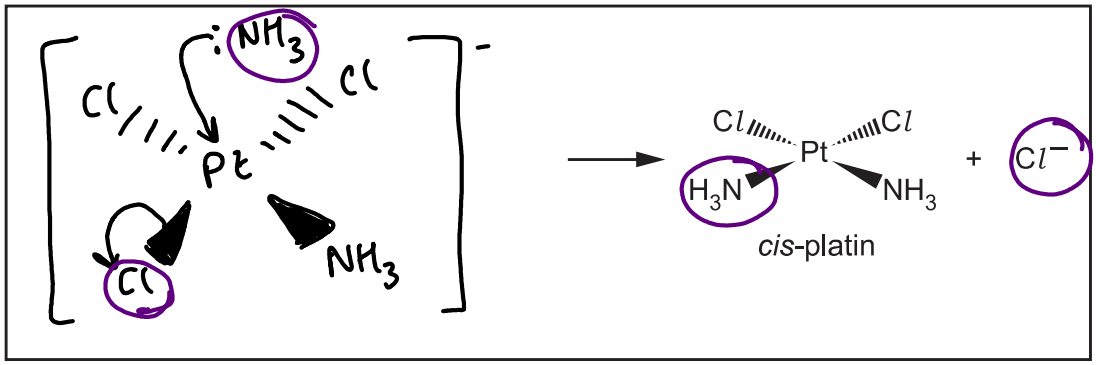
(ii) *Cis*-platin is prepared in a ligand substitution reaction which takes place in multiple steps.

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

$$[PtCl_3(NH_3)]^- + NH_3 \rightarrow PtCl_2(NH_3)_2 + Cl^-$$

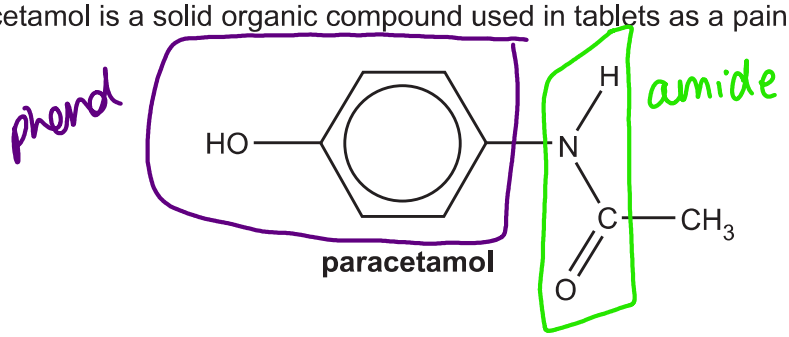
cis-platin

In the box, outline the mechanism for the formation of *cis*-platin from $[PtCl_3(NH_3)]^-$.
Use curly arrows and lone pairs where appropriate.



[2]

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



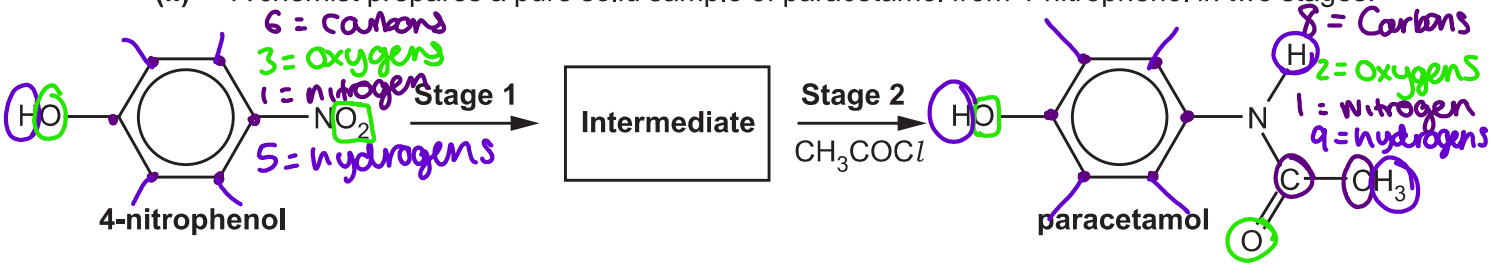
(i) Name the functional groups present in paracetamol.

phenol.....

amide..... **[2]**

11

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



Describe a two-stage synthesis of 5.00 g 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]**

mass of 4-nitrophenol:

mass / mol x RFM

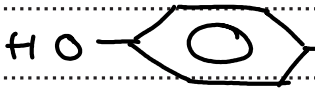
$\frac{5}{(12\times8)+(16\times2)+14+9} = 0.0331$ mol of paracetamol

$0.0331 \times \frac{100}{40} = 0.0828$ mol of 4-nitrophenol

$0.0828 \times ((12\times6)+((6\times3)+14+5) = 11.50\,g$

intermidiate: 4-aminophenol

reagents: Sn, Conc. HCl



• dissolve impure solid in minimum volume of hot solvent

• cool solution and filter solid

• scratch with glass rod

Additional answer space if required.

• wash with cold solvent and dry

5 A student carries out two experiments in the laboratory based on succinic acid (butanedioic acid), $(CH_2COOH)_2$.

(a) Aqueous succinic acid can be neutralised by aqueous sodium hydroxide, NaOH(aq):

$$(CH_2COOH)_2(aq) + 2NaOH(aq) \rightarrow (CH_2COONa)_2(aq) + 2H_2O(l)$$

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

energy released to produce 1 mol of water there are (2) so ÷ by 2 at the end of the calculation

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} NaOH(aq), which is in excess.
- Measure the temperature of both solutions.
- Add the NaOH(aq) to the aqueous succinic acid in the polystyrene cup, stir the mixture, and record the maximum temperature.

Temperature readings

Maximum temperature of mixture/°C	26.5
Initial temperature of both solutions/°C	21.5

Calculate a value for the enthalpy change of neutralisation, $\Delta_{neut}H$, 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 = V × C

$50 \times 10^{-3} \times 0.4 = 0.02$ mol

$Q = mc\Delta T$ ← $26.5 - 21.5 = 5$ °C

4.18

100 cm^3

$100 \times 4.18 \times 5 = 2090$ J $= 2.090$ kJ

$\frac{2.090}{0.02} = \pm 104.5$ kJ mol^{-1}

$\frac{104.5}{2} = \pm 52.3$ kJ mol

enthalpy change of neutralisation is -ve

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

(b) Succinic acid is esterified by ethanol, C_2H_5OH, 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**.

$$K_c = \frac{n((CH_2COOC_2H_5)_2) \times n(H_2O)^2}{n((CH_2COOH)_2) \times n(C_2H_5OH)^2}$$

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.

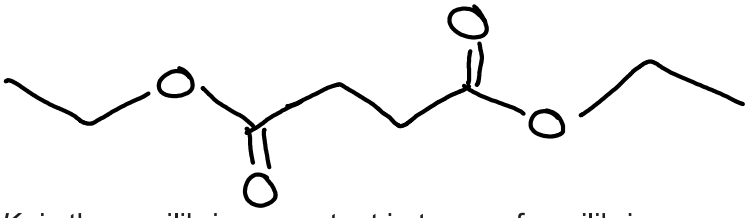
(i) Which technique could be used to determine the equilibrium amount of succinic acid?

titration ..... **[1]**

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

$(CH_2COOH)_2 + 2C_2H_5OH \rightleftharpoons (CH_2COOC_2H_5)_2 + 2H_2O$ ..... **[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?

volumes cancel out / same number of moles on each side of the equation ..... **[1]**

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

Show your working.

	$(CH_2COOH)_2$	C_2H_5OH	$(CH_2COOC_2H_5)_2$	H_2O
I	0.05	0.15	0	0
C	−0.03	−0.06	+0.03	+0.06
E	0.02	0.09	0.03	0.06

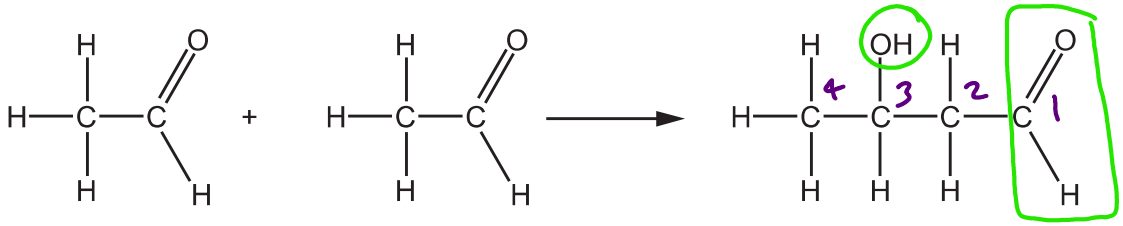
K_c = 0.67 ..... **[3]**

$$K_c = \frac{0.03 \times 0.06^2}{0.02 \times 0.09^2} = 0.67$$

6 This question is about organic reactions.

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

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



Reaction 6.1

Compound **A**

(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**.

CH_3CHO + OH^- $\rightleftharpoons$ CH_3CO^- + H_2O

A1 B2 B1 A2

Acids are proton donors

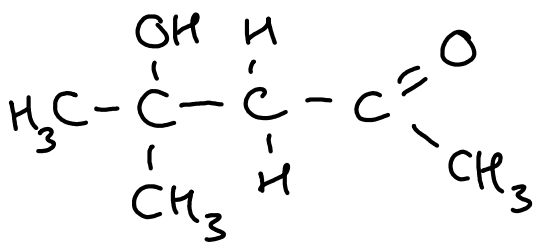
- Suggest the equation for **step 2**.

$CH_3CHO + {}^-CH_2CHO + H_2O \rightarrow CH_3CHOHCH_2CHO + OH^-$

[3]

(iv) A similar reaction takes place when propanone, $(CH_3)_2CO$, is mixed with OH^-(aq) ions.

Draw the structure of the organic product of this reaction.



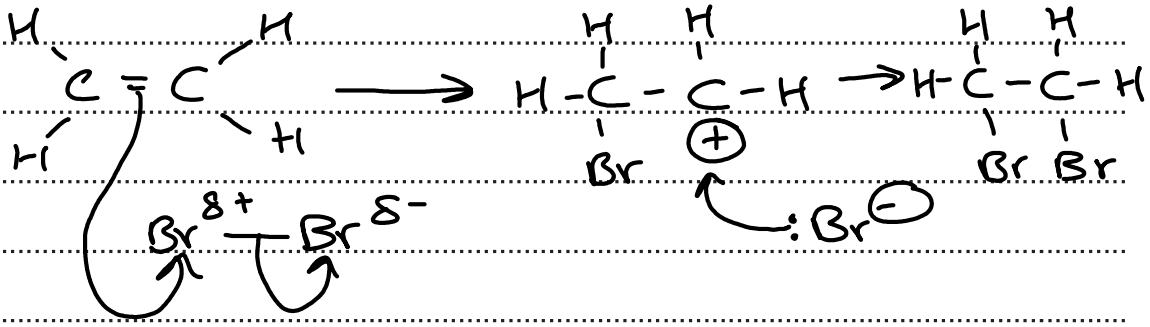
[1]

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

Explain the role of electrophiles in organic chemistry.

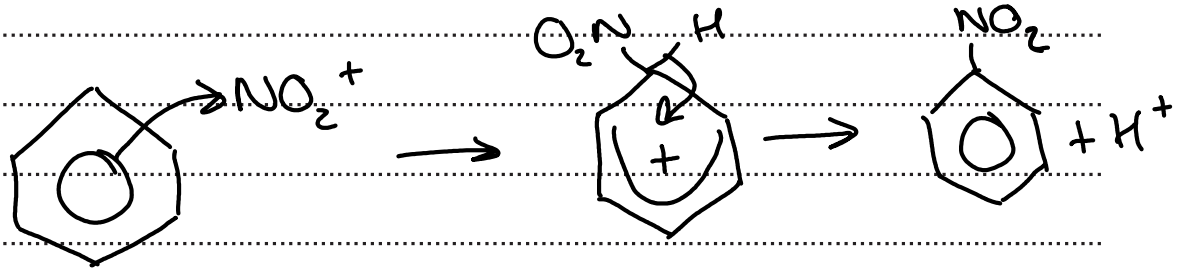
Your answer should include **one** reaction of an aliphatic compound and **one** reaction of an aromatic compound, including relevant mechanisms. **[6]**

electrophilic addition:



electrophilic substitution:

$H_2SO_4 + HNO_3 \rightarrow NO_2^+ + H_2O + HSO_4^-$



$H^+ + HSO_4^- \rightarrow H_2SO_4$

Additional answer space if required.

electrophiles act as electron pair acceptors.

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).