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

(a) Write the ionic equation for this reaction. State symbols are not required.

(1)

(b) 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 (1/time) for the mixture to change colour as a measure of the initial rate.

(i) What is the final colour of the reaction mixture?

(1)

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(ii) What would be observed if the reaction was carried out without the addition of sodium thiosulfate?

(1)

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(iii) Explain why the concentration of iodide ions remains constant until the mixture changes colour.

(1)

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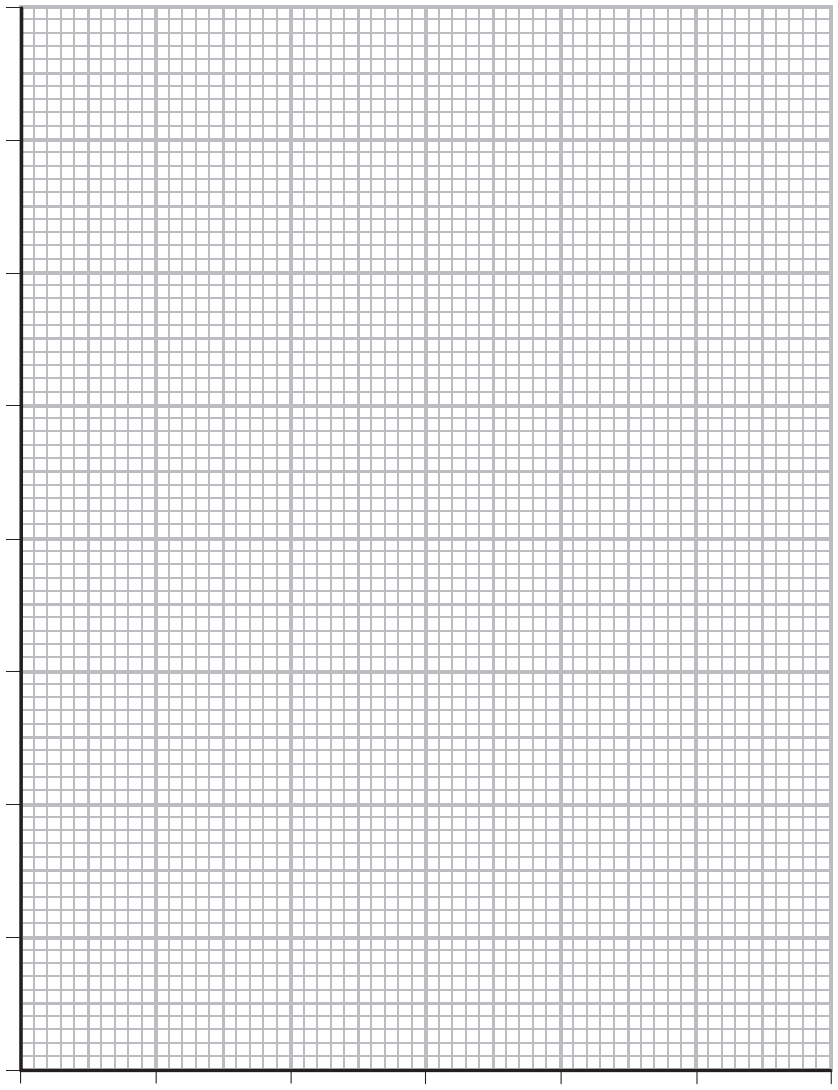
.....

(c) 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

(i) Plot a graph of 1/time on the vertical axis against concentration of iodide ions.

(2)



(ii) 1/time is a measure of the initial rate of the reaction.

Deduce the order of reaction with respect to iodide ions.

Justify your answer.

(2)

.....

.....

(iii) 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.

(2)

Rate =

Units for the rate constant.....

(d) The reaction in part (b) is repeated at two different temperatures, keeping the initial volumes and concentrations of the solutions constant.

T (Temperature) /K	1/time /s^{-1}	1/T /K^{-1}	ln(1/time)
293	0.0215	3.31×10^{-3}	–3.84
303	0.0430	3.20×10^{-3}	–3.15

(i) Calculate, without drawing a graph, the activation energy of the reaction. Remember to give a sign and units with your answer.

$$\ln(1/\text{time}) = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \qquad [R = 8.31 \text{ J mol}^{-1}\text{K}^{-1}]$$

(3)

(ii) Suggest how the reliability of the activation energy determination could be improved, without changing the apparatus, solutions or method.

(1)

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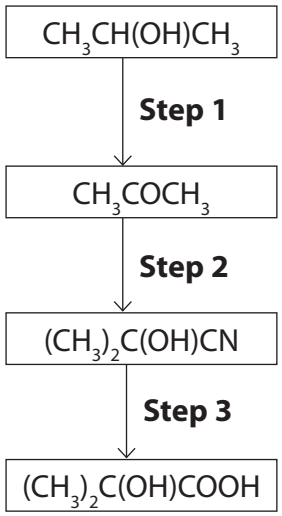
(Total for Question = 14 marks)

2 A flow chart for making 2-hydroxy-2-methylpropanoic acid from propan-2-ol is shown below.



(a) (i) Give the reagents and conditions for **Step 1**.

(2)

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.....

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(ii) Propanone is formed in **Step 1**.
Give a chemical test to identify the carbonyl group and a further test to show the presence of the $H_3C–\overset{\overset{O}{\|}}{C}–$ group.

For both tests, give the observations that you would make.

(4)

Carbonyl group.....

.....

$H_3C–\overset{\overset{O}{\|}}{C}–$ group.....

(b) (i) In **Step 2**, propanone undergoes an addition reaction with HCN in the presence of CN^- ions.
Give the mechanism for this reaction.

(3)

(ii) Explain why this reaction would not take place at either a very low or very high pH.

(2)

Low pH.....

.....

High pH.....

.....

(c) (i) The reaction in **Step 3** forms 2-hydroxy-2-methylpropanoic acid, $(CH_3)_2C(OH)COOH$.
Suggest the type of reaction occurring in **Step 3**.

(1)

(ii) Explain why the presence of the alcoholic hydroxyl group cannot be confirmed in the infrared spectrum of 2-hydroxy-2-methylpropanoic acid.

(1)

(iii) The hydrogen of the alcohol group in 2-hydroxy-2-methylpropanoic acid can be identified by a single peak in the nmr spectrum.

Give the chemical shift you would expect for this peak.

(1)

.....

(iv) How many peaks would you expect in a high resolution nmr spectrum for 2-hydroxy-2-methylpropanoic acid, $(CH_3)_2C(OH)COOH$?

(1)

.....

(v) Explain why, in high resolution nmr, the peak due to the hydrogens of the 2-methyl group in 2-hydroxy-2-methylpropanoic acid is a singlet.

(1)

.....

.....

(vi) Would you expect 2-hydroxy-2-methylpropanoic acid to have optical isomers? Justify your answer.

(1)

.....

.....

(d) (i) Molecules of 2-hydroxy-2-methylpropanoic acid react together to form a condensation polymer.

Draw a **displayed** formula for this polymer, showing two repeating units.

(2)

(ii) Give the name of the functional group that links the two molecules in the polymer.

(1)

.....

(Total for Question = 20 marks)

3 Two organic compounds, **X** and **Y**, both with the molecular formula C_4H_8O, contain a carbonyl group.

(a) Describe what you would see when 2,4-dinitrophenylhydrazine is added to either of these compounds.

(1)

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(b) It is suspected that **X** is a ketone and **Y** is an aldehyde. Outline a chemical test you could carry out to confirm this, describing the results in each case.

(3)

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(c) (i) Give the structural formulae of the two possible isomers of **Y** which are aldehydes.

(1)

(ii) Name the technique you would use to purify the product of the test with 2,4-dinitrophenylhydrazine.

(1)

.....

(iii) Other than by spectroscopic techniques, how would you use the purified product to identify compound **Y**? [Practical details are not required.]

(2)

(Total for Question 8 marks)