RAFFLES INSTITUTION
2013 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CHEMISTRY 9647/03

Paper 3 Free Response **24 September 2013**

Candidates answer on separate paper. **2 hours**

Additional Materials: Writing Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

DO NOT open this question booklet until you are told to do so.

Write your name, class and index number in the spaces provided on the cover page.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
Begin each question on a fresh sheet of paper.
A Data Booklet is provided. Do not write anything on it.
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.
At the end of the examination, fasten all your work securely together, with the cover page on top.

Answer any **four** questions.
Begin each question on **a fresh sheet of paper**.

1 Esters are sweet-smelling organic compounds that have been used as flavourings in food and perfumes. For example, ethyl propanoate is an ester with pineapple-like smell.

(a) Explain why the rate of the following reaction gradually increases at first and then decreases.

$$CH_3CH_2COOCH_2CH_3 + H_2O \longrightarrow CH_3CH_2COOH + CH_3CH_2OH$$

ethyl propanoate

[2]

(b) The kinetics of the hydrolysis of ethyl propanoate in the presence of aqueous sodium hydroxide solution at T K was studied.

Two separate experiments were carried out with different concentrations of aqueous sodium hydroxide solution. For each experiment, the concentration of ethyl propanoate was determined at regular time intervals as the reaction progressed.

The graph on **page 13** shows the results of Experiment 1 with [NaOH] = 2.0 mol dm^{-3}.
The results of Experiment 2 with [NaOH] = 1.0 mol dm^{-3} are shown below.

Time / min	Experiment 2 with [NaOH] = 1.0 mol dm^{-3} $[CH_3CH_2COOCH_2CH_3]$ / mol dm^{-3}
0	0.0200
25	0.0152
50	0.0115
75	0.0088
100	0.0067
125	0.0051

1 **(i)** Using the same axes on **page 13**, plot the graph for Experiment 2.

3 **(ii)** Use the two graphs to determine the order of reaction with respect to $CH_3CH_2CO_2CH_2CH_3$ and to NaOH, showing your working clearly.

1 **(iii)** Hence write the rate equation for the above reaction.

2 **(iv)** Calculate the initial rate from Experiment 1, and use it, together with your rate equation, to calculate the rate constant for the reaction.

1 **(v)** In a third experiment, 0.0100 mol dm^{-3} of ethyl propanoate was reacted with 2.0 mol dm^{-3} of sodium hydroxide.

On the same axes given on **page 13**, sketch the graph expected for this experiment, indicating clearly two half-lives.

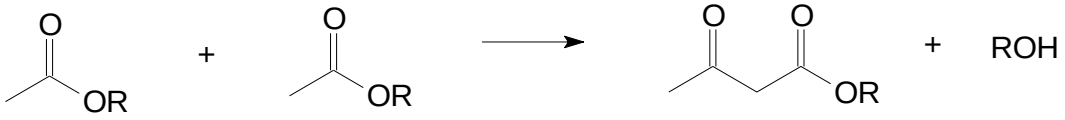
(vi) The hydrolysis of ethyl propanoate by sodium hydroxide is known to occur as follows:

- The first step involves a nucleophilic attack of the hydroxide ion on the carboxyl carbon to form a tetrahedral intermediate.
- The second step involves formation of a carbon–oxygen π bond and the leaving of an ethoxide ion.
- The third step involves the protonation of the ethoxide ion by propanoic acid.

Using curly arrows, describe the mechanism for the hydrolysis of ethyl propanoate by sodium hydroxide.

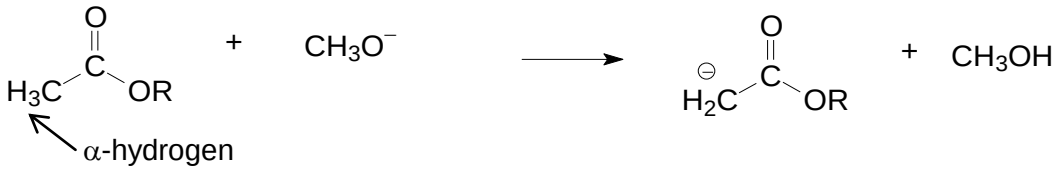
[11]

(c) The Claisen condensation of esters involves the formation of a new carbon-carbon bond between two esters. The products are a keto-ester and an alcohol. The reaction takes place in the presence of a strong base e.g. CH_3O^-.



a keto-ester

(i) The first step in Claisen condensation involves the strong base CH_3O^- removing an α-hydrogen atom (i.e. the hydrogen atom bonded to the carbon atom next to the carbonyl carbon atom) in an acid-base reaction as shown below.



Suggest a reason why the α-hydrogen atom of the ester is acidic.

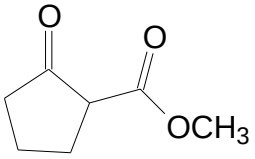
(ii) With reference to the acid-base reaction mentioned in **(i)**, explain why each of the following reactions does not take place in the presence of CH_3O^-.

(1) $CH_3CH_3 \longrightarrow {}^-CH_2CH_3$

(2) $CH_3COOH \longrightarrow {}^-CH_2COOH$

(iii) Draw the structures of all the keto-esters formed when a mixture of $CH_3CO_2CH_2CH_3$ and $CH_3CH_2CO_2CH_2CH_3$ undergo the Claisen condensation.

(iv) Draw the structure of the reactant that can be used to prepare the following compound by the Claisen condensation.



[7]

[Total: 20]

[Turn over

2 Nickel is a typical transition element in the d-block of the Periodic Table. It is commonly used as a catalyst and as an alloying ingredient.

(a) Explain why nickel is regarded as a *transition element*.

[1]

(b) In an experiment to study the reaction between nickel and the metal ion, $M^{2+}(aq)$, an electrochemical cell was set up using the Ni^{2+}/Ni and M^{2+}/M half-cells at 298 K.

During the experiment, the concentration of Ni^{2+} ions in the Ni^{2+}/Ni half-cell was kept at 1.0 mol dm^{-3} but the concentration of M^{2+} ions in the M^{2+}/M half-cell was changed. The e.m.f. of the cell was measured with each change of solution in the M^{2+}/M half-cell, and the results obtained are tabulated below.

$[M^{2+}]$ / mol dm^{-3}	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
e.m.f. / V	0.091	0.061	0.032	0.002	–0.028	–0.057
lg $[M^{2+}]$	–1.0	–2.0	–3.0	–4.0	–5.0	–6.0

(i) Plot a graph of e.m.f. against lg $[M^{2+}]$.

(ii) With the aid of the graph plotted and relevant data from the *Data Booklet*, determine the standard electrode potential of the M^{2+}/M half-cell.

(iii) The above electrochemical cell is 'dead' when the overall cell reaction reaches equilibrium. With the aid of the graph plotted, calculate the equilibrium constant, K_c, for the cell reaction shown below at 298 K.

$$Ni(s) + M^{2+}(aq) \rightleftharpoons Ni^{2+}(aq) + M(s)$$

(iv) Using your answer from **(ii)** and relevant data from the *Data Booklet*, predict what might be observed when a rod of metal M is dipped into an aqueous copper(II) nitrate(V) solution.

[8]

(c) Nickel forms many hydrated salts such as $NiCl_2.6H_2O$ and $NiSO_4.7H_2O$. When some $NiCl_2.6H_2O$ is dissolved in water, a green solution containing $[Ni(H_2O)_6]^{2+}$ ions forms. Addition of excess aqueous ammonia to this green solution results in a blue solution containing $[Ni(NH_3)_6]^{2+}$ ions.

(i) State and explain whether the H–O–H bond angle in H_2O in an isolated gaseous H_2O molecule is larger or smaller than that in the $[Ni(H_2O)_6]^{2+}$ ion.

(ii) Explain briefly why the two nickel(II) ion-containing solutions have different colours.

[4]

(d) Nickel is able to form neutral complexes. One such complex, tetracarbonylnickel(0), $Ni(CO)_4$, was first prepared in 1888 by passing carbon monoxide over finely divided nickel. This complex is a colourless liquid at room temperature.

(i) Draw the displayed formula of tetracarbonylnickel(0), showing clearly all the dative covalent bonds.

(ii) Define the term *bond energy*.

(iii) With the aid of a labelled energy level diagram incorporating the data below, determine the carbon–nickel bond energy in tetracarbonylnickel(0).

	ΔH / kJ mol^{-1}
Enthalpy change of formation of liquid tetracarbonylnicke(0), ΔH_1	–636
Enthalpy change of formation of gaseous carbon monoxide, ΔH_2	–111
Enthalpy change of vapourisation of tetracarbonylnickel(0), ΔH_3	+29
Enthalpy change of atomisation of nickel, ΔH_4	+431

[7]

[Total: 20]

3 This question is mainly about the chemistry of inorganic elements and compounds.

(a) Silicon, phosphorus and sulfur are Period 3 elements.

Arrange these three elements in order of decreasing melting point and account for the order in terms of structure and bonding.

[4]

(b) Compound **A** is an oxide of a Period 3 element and compound **B** is a chloride of another Period 3 element.

In an experiment, **A** was dissolved in water to form a 100 cm^3 solution of pH 13.70 at 298 K. When **B** was next added, a white precipitate formed together with some steamy fumes observed. The resultant solution was found to be acidic.

(i) Identify **A** and hence calculate the amount of **A** used in the experiment.

(ii) Identify **B** and write an equation, with state symbols, for the reaction between **B** and water.

[4]

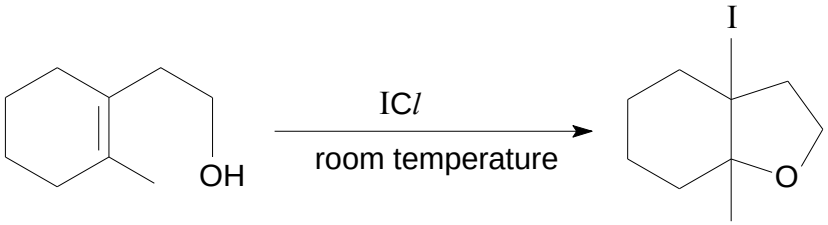
(c) Halogens form many interhalogen compounds. Examples include iodine pentafluoride and iodine monochloride.

(i) Iodine pentafluoride (IF_5) is a liquid at room temperature. It can undergo self-ionisation to give IF_x^+ ions and pentagonal pyramidal IF_y^- ions.

Deduce the values of *x* and *y*. Hence predict, with reasoning, the shape of the IF_x^+ ion.

(ii) Iodine monochloride (IC*l*) reacts with alkenes in a way similar to the reaction between Cl_2 and propene.

Describe the mechanism for the following reaction involving iodine monochloride.



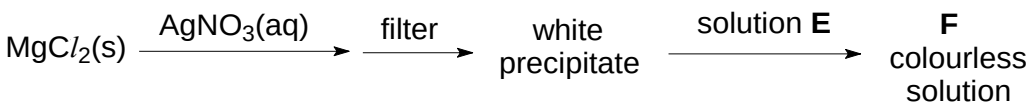
[6]

(d) Aqueous potassium iodide is added to a solution of bromine in hexane in a test-tube and the mixture is shaken.

Describe and explain the observations in the above experiment.

[2]

(e) The reaction scheme below shows how a sample of anhydrous magnesium chloride is converted into a solution containing compound **F**.



Upon analysis, **F** is found to contain the following percentage composition by mass:

Ag, 52.6%; C*l*, 17.3%; N, 13.6%; C, 11.7%; H, 4.8%.

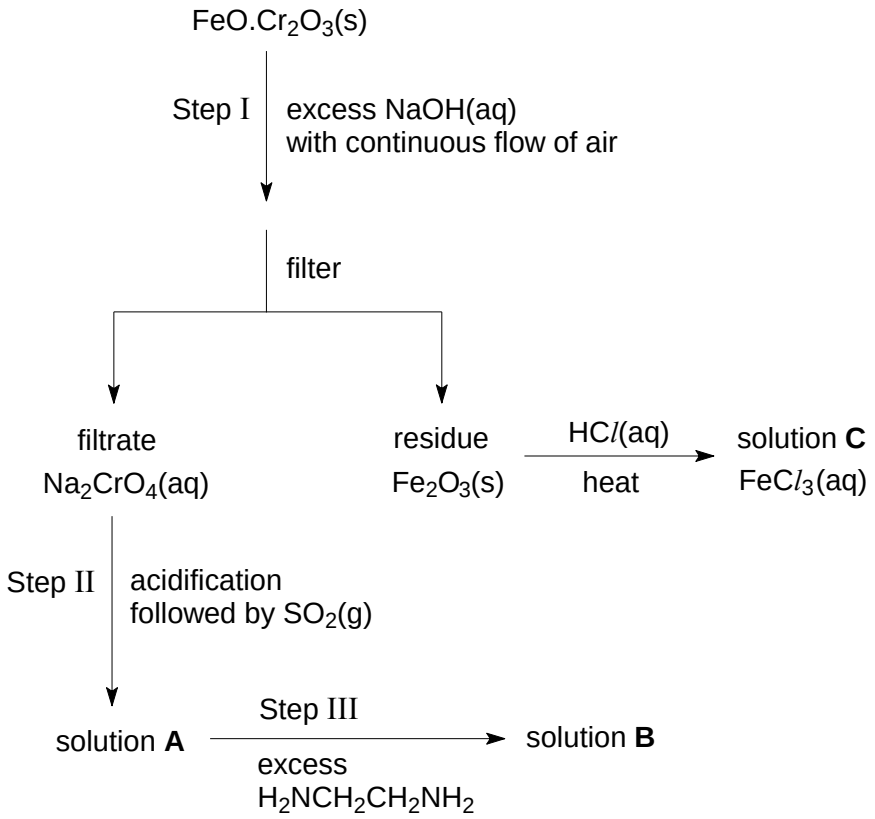
(i) Determine the empirical formula of **F** and hence suggest a suitable identity for **F**.

(ii) State the observation when dilute nitric acid is added to **F** and write a balanced equation for this reaction.

[4]

[Total: 20]

4 **(a)** Chromite, $FeO.Cr_2O_3$, is the chief source of chromium. The reaction scheme below shows the conversion of chromite into two chromium(III) complex ions in solutions **A** and **B**.



(i) With the aid of the *Data Booklet*, write a balanced equation for the reaction involving Cr_2O_3 in Step I.

(ii) Identify the complex ion in **A.**

(iii) Draw the structure of the complex ion in **B**, showing its shape.

(iv) State the series of colour changes that occur in Step II.

(v) Suggest a simple chemical test which can be used to distinguish between the cations in solutions **A** and **C**.

[6]

(b) The compounds **P** and **Q** are isomers with the molecular formula $C_9H_8O_2$.

P liberates carbon dioxide with sodium hydrogencarbonate but **Q** does not. **Q** reacts with ammoniacal solution of silver nitrate to give **R** and a grey precipitate.

Upon oxidation with hot acidified potassium manganate(VII), 1 mole of **P** gives 2 moles of carbon dioxide and 1 mole of benzoic acid while 1 mole of **Q** gives 1 mole of carbon dioxide and 1 mole of a compound, $C_8H_6O_5$.

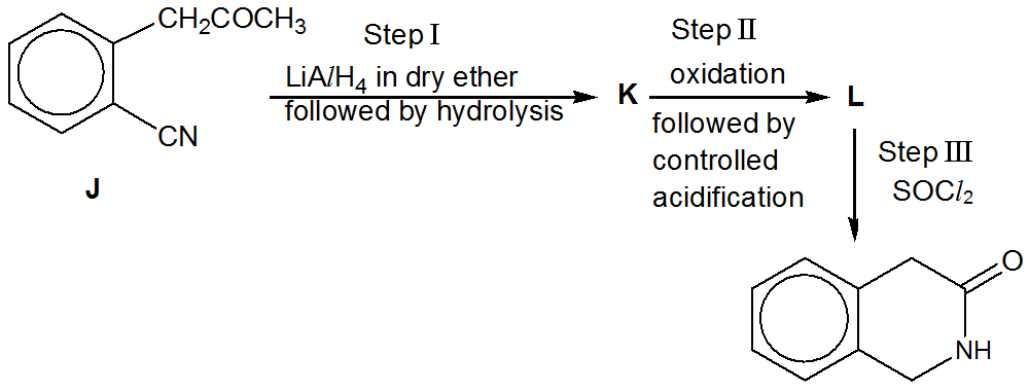
P decolourises aqueous bromine in the dark to form **S**, $C_9H_9O_3Br$ while **Q** reacts with aqueous bromine to form a white precipitate **T**, $C_9H_6O_3Br_4$.

P is reacted with a stoichiometric amount of aqueous potassium hydroxide and the resultant solution is heated before it is added to **T**. The compound **U** that is formed has a molecular formula of $C_{18}H_{13}O_5Br_3$.

Deduce the structures of all the lettered compounds (**P** to **U**) and explain the chemistry of the reactions described.

[11]

(c) A cyclic amide can be synthesised from compound **J** as shown below.



(i) Draw the structure of **L**.

(ii) A student suggests the use of hot, acidified potassium manganate(VII) as the oxidising agent in Step II.

Explain why this choice of reagent is inappropriate and suggest a suitable alternative.

[3]

[Total: 20]

[Turn over

5 *Lingzhi* (*Ganoderma lucidum)* is a medicinal mushroom that has been used in Chinese medicines for more than 2000 years due to its numerous health benefits. It is rich in proteins which enhance the immune system and polysaccharides such as β-glucans, which possess anti-tumour properties.

(a) A peptide chain made of 10 amino acid residues, isolated from a protein in *Lingzhi*, can be hydrolysed into the following tripeptides:

val-ser-gly, leu-gly-val, ser-gly-arg, val-ala-val, arg-asn-leu, ala-val-ser

Deduce the primary structure of this peptide chain.

[1]

(b) The following table shows six α-amino acids found in a segment of a protein in *Lingzhi*.

α-amino acid	**formula of side chain (R in $RCH(NH_2)CO_2H$)**
glutamic acid	$-CH_2CH_2CO_2H$
lysine	$-(CH_2)_4NH_2$
valine	$-CH(CH_3)_2$
glutamine	$-CH_2CH_2CONH_2$
phenylalanine	$-CH_2C_6H_5$
serine	$-CH_2OH$

Describe two types of side-chain interaction, illustrating your answer with suitable pairs of amino acid residues from the table above.

[2]

(c) The enthalpy change associated with the folding of a protein chain into its tertiary structure is –585 kJ mol^{-1}. The numerical value for the entropy change associated with this folding is 1740 J mol^{-1} K^{-1}.

(i) Explain whether the entropy change for this process is positive or negative.

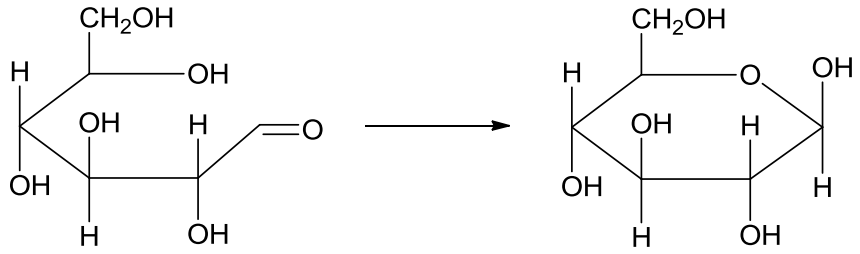
(ii) Hence calculate the Gibbs free energy change at 298 K for the folding of the protein chain into its tertiary structure.

(iii) A change in temperature can cause this tertiary protein structure to unfold. Determine the temperature at which this protein structure begins to unfold, stating any assumptions made.

[4]

(d) β-Glucans, isolated from *Lingzhi,* are made up of D-glucose molecules joined by β-glycosidic linkages. The D-glucose molecules can exist as α- and β-forms.

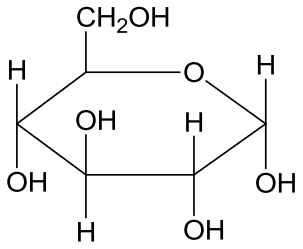
Each β-glucose molecule is formed from the cyclisation of an open-chain glucose molecule as shown below:



open-chain glucose β-glucose

(i) State the type of reaction involved in the cyclisation.

(ii) In addition, the open-chain glucose molecule also cyclises to form an α-glucose molecule as shown below.



α-glucose

Suggest why it is possible for open-chain glucose molecules to form both α- and β-glucose molecules.

[2]

(e) Both α-glucose and β-glucose are optically active compounds. A 1.0 mol dm^{-3} α-glucose solution has an optical rotation angle of $+113.4^{o}$ while a 1.0 mol dm^{-3} β-glucose solution has an optical rotation angle of $+19.0^{o}$ at 298 K.

These two forms of glucose can exist in equilibrium as shown below.

$$\beta\text{-glucose(aq)} \rightleftharpoons \alpha\text{-glucose(aq)}$$

If an aqueous solution of either 1.0 mol dm^{-3} β-glucose or α-glucose is allowed to stand, the optical rotation changes until it reaches $+52.2^{o}$.

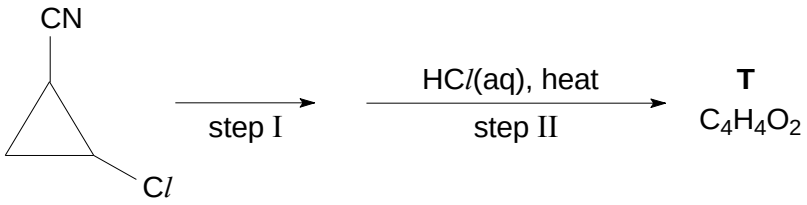
(i) Calculate the mole fraction of β-glucose in the equilibrium mixture.

(ii) Calculate the value of the equilibrium constant, K_c, for the above reaction.

[3]

(f) *Russula subnigricans* is another species of mushroom found in China. Unlike *Lingzhi* which has medicinal value, *Russula subnigricans* is highly poisonous. Ingestion of this mushroom causes rapid breakdown of muscle fibres and can lead to death. Scientists recently isolated the toxin **T** from this deadly mushroom (reported in *Nature Chemical Biology*, 2009).

T has a structure in which three of its four carbon atoms are in the same plane. It was proposed that **T** could be synthesised from a nitrile as shown in the reaction scheme below.

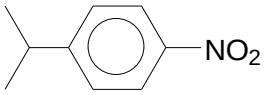


(i) Suggest a suitable structural formula for **T**.

(ii) Hence suggest suitable reagent and condition for step I.

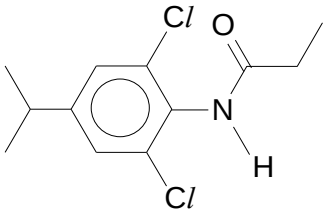
[2]

(g) Phenylalanine is an α-amino acid with molecular formula, $C_9H_{11}NO_2$. Unlike phenylalanine which is amphoteric, compound **U**, an isomer of phenylalanine, is neutral.



compound **U**

(i) Compound **U** can be converted into compound **V** shown below in three steps. Suggest suitable reagents and conditions for this conversion.



compound **V**

(ii) One of the three steps in **(g)(i)** involves an electrophilic substitution reaction. Write a balanced equation for this reaction.

(iii) Explain why compound **V** is not basic despite the presence of a lone pair of electrons on the nitrogen atom.

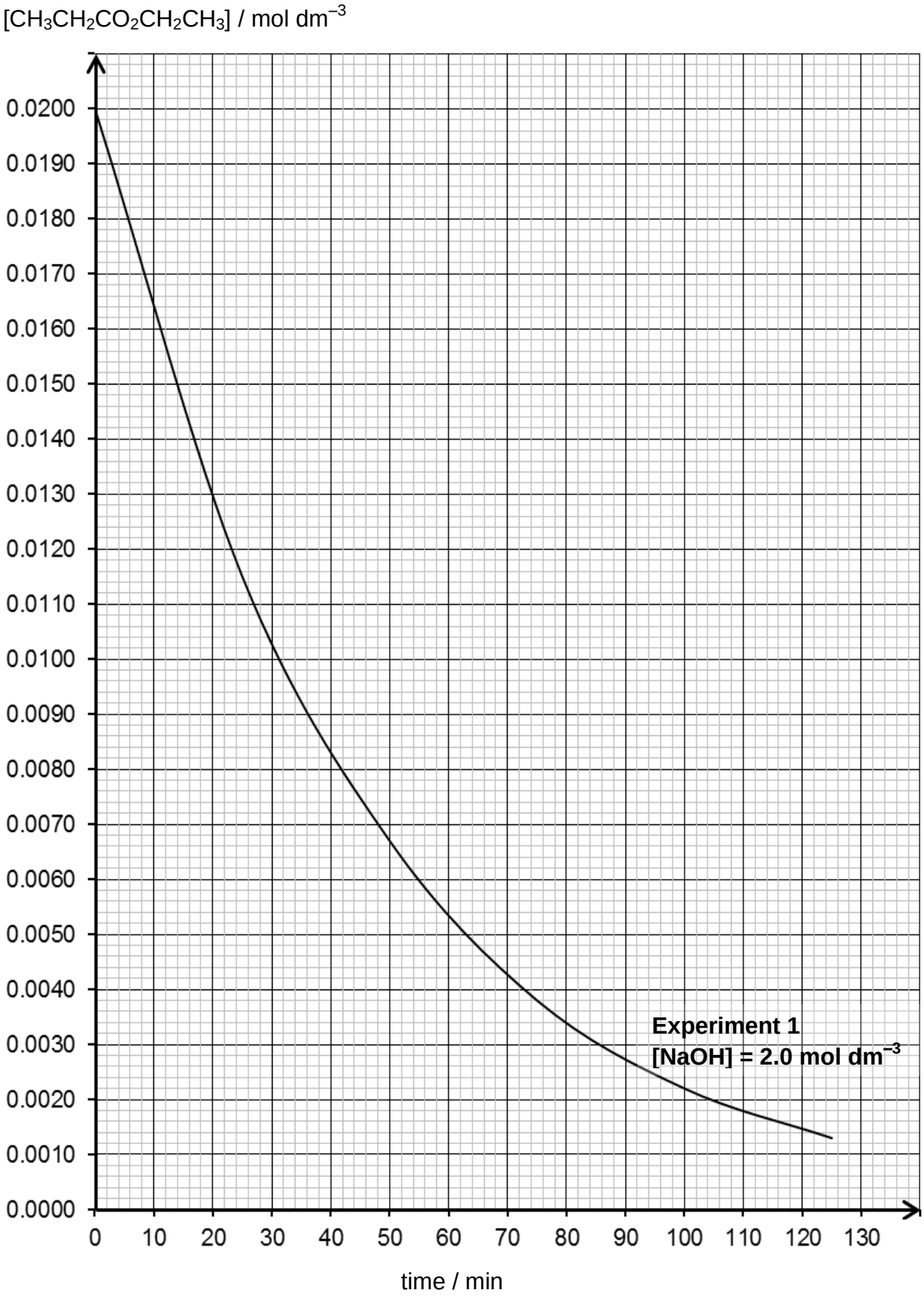
(iv) Compound **W** is another isomer of phenylalanine. Part of its structure includes a nitro group attached to a benzene ring. When reacted with chlorine in the presence of ultraviolet light, **W** forms only two mono-chlorinated products in the molar ratio of 1:2.

Suggest a suitable structural formula for **W**.

[6]

[Total: 20]

Graph for Question 1(b)


[CH3CH2CO2CH2CH3] / mol dm–3
0.0200
0.0190
0.0180
0.0170
0.0160
0.0150
0.0140
0.0130
0.0120
0.0110
0.0100
0.0090
0.0080
0.0070
0.0060
0.0050
0.0040
0.0030
0.0020
0.0010
0.0000
0
10
20
30
40
50
60
70
80
90
100
110
120
130
time / min
Experiment 1
[NaOH] = 2.0 mol dm–3