Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination 2015
Year 6

H2 CHEMISTRY 9647/02

Paper 2 Structured Questions

16 September 2015

2 hours

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.

2 Answer **all** questions.

3 Write your answers in the spaces provided on the Question Paper.

4 The use of an approved scientific calculator is expected, where appropriate.

4 A Data Booklet is provided.

5 The number of marks is given in brackets [ ] at the end of each question or part question.

Question No.	1 (P)	2	3	4	5	6	7	Total	%
Marks	12	15	15	6	9	10	5	[72]	

This document consists of **19** printed pages and **1** blank page.

Answer **all** the questions in the spaces provided.

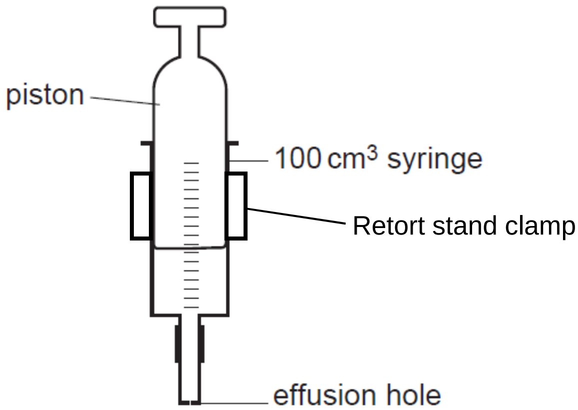
1 **Planning (P)**

(a) *Part* **(a)** *is on the rate of effusion of gas*.

If a container of gas has a tiny hole in it, the gas will gradually escape through the hole. This process is called effusion and the rate at which it occurs is called the rate of effusion.

A student has carried out a series of preliminary experiments to investigate how the rate of effusion depends on the relative molecular mass, M_r, of a gas. She found that the rate of effusion is halved when the M_r of a gas is doubled.

(i) Using the apparatus shown below, plan a laboratory experiment to verify the student's findings. The experiment will involve using different gases where their rate of effusion will be determined, bearing in mind that temperature will also affect the effusion rate of the gas.



In addition to the standard apparatus present in a laboratory you are provided with the following:

- access to samples of hydrogen, butane, oxygen, carbon dioxide and chlorine gases

Your plan should include:

- brief, but specific, details of the apparatus you would use;
- how you ensure the syringe only contain the gas you are investigating;
- how you would measure the effusion time;
- how you produce *reliable* results;
- steps taken to ensure other factors are controlled;
- a table with appropriate headings to show the data you would record when carrying out your experiment and the values you would calculate in order to construct a graph to support or reject the statement. The headings must include the appropriate units.

Table [You need **not** use all the columns in the following table.]

(ii) Sketch a graph you would plot using your measured or calculated data obtained in **(a)(i)** and describe how you would use the graph to determine the effusion rate of nitrogen gas (M_r = 28.0). You may assume that the student's findings is accurate.

[8]

(b) *Part* **(b)** *is on the synthesis of an inorganic compound*.

The compound, $Cu(NH_3)_4SO_4$, can be synthesised in the laboratory by gradually adding aqueous ammonia to an aqueous solution of copper(II) sulfate. The blue solution will turn a deeper blue colour. The mixture should be allowed to stand for about 15 minutes. Deep blue crystals will be deposited by addition of cold acetone (an organic solvent) and the mixture be allowed to stand in cold for another 15 minutes.

$$Cu(H_2O)_6^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+} + 6H_2O$$

You may assume that you are provided with the following chemicals:

- 60 cm^3 aqueous solution of copper(II) sulfate, of concentration 0.50 mol dm^{-3};
- aqueous ammonia, of concentration 2.0 mol dm^{-3}
- 50 cm^3 acetone

(i) Calculate the minimum volumes of:

- copper(II) sulfate solution;
- aqueous ammonia;

required for the preparation of 5 g of $Cu(NH_3)_4SO_4$ (M_r = 227.6).

(ii) Write a plan for the preparation of approximately 5 g of $Cu(NH_3)_4SO_4$.

In your plan you should give a full description of the procedures you would use to prepare and purify the product. Details on confirming the identity of the product are **not** required.

[4]

[Total: 12]

2 **(a)** Pure unsymmetrical dimethylhydrazine (UDMH), $(CH_3)_2N_2H_2$ can be used as a rocket fuel. It is typically mixed with dinitrogen tetraoxide, N_2O_4.

The equation for the reaction of the UDMH with dinitrogen teraoxide is given below.

$$\Delta S^{\ominus} = +844 \text{ J mol}^{-1} \text{ K}^{-1}$$
$$\Delta G^{\ominus} = -2107 \text{ kJ mol}^{-1}$$

$$(CH_3)_2N_2H_2(l) + 2N_2O_4(l) \longrightarrow 2CO_2(g) + 4H_2O(g) + 3N_2(g)$$

In the ascent stage of a lunar module, the total mass of propellant (UDMH and N_2O_4) used in the thruster rockets was 244 kg.

(i) Calculate the total volume of product gases formed from the complete reaction of UDMH at a temperature of –10 °C and a pressure of 0.6 kPa, assuming that the UDMH and dinitrogen tetroxide were mixed in the molar ratio 1 : 2.

The table below shows some other relevent thermodynamic data.

substance	$\Delta H_f^{\ominus}$(298 K) / kJ mol^{-1}
$(CH_3)_2N_2H_2(l)$	***x***
$CO_2(g)$	–394
$H_2O(g)$	–242
$N_2O_4(l)$	+9.0

(ii) Define the term standard enthalpy change of formation of $(CH_3)_2N_2H_2$.

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....

(iii) Determine the value of ***x*** at 298 K.

[6]

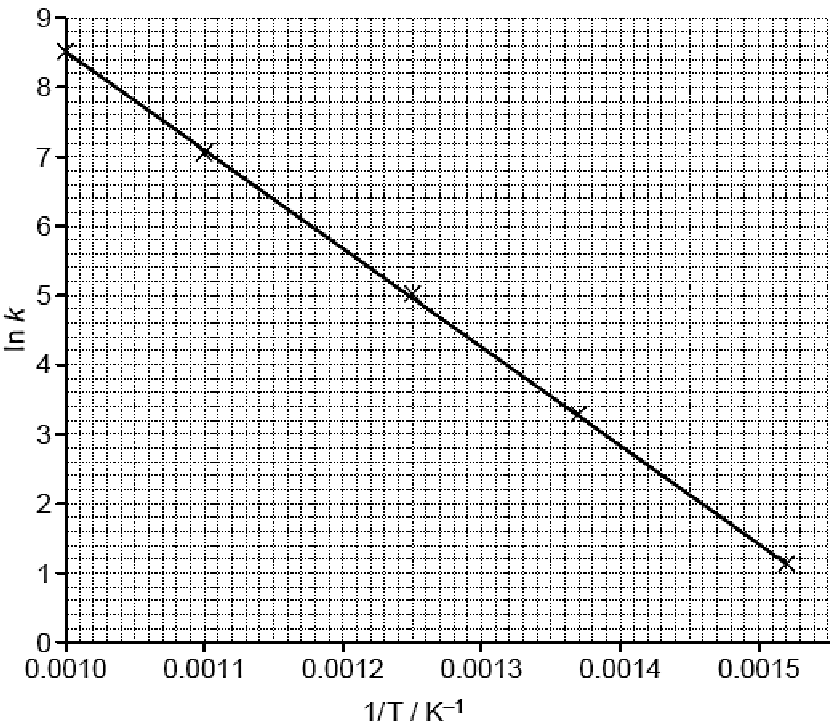
(b) Dinitrogen tetroxide exists in equilibrium with nitrogen dioxide. Nitrogen dioxide itself can be decomposed into nitrogen monoxide and oxygen as shown below.

$$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$$

The rate equation for this thermal decomposition is as follows.

$$\text{Rate} = k\,[NO_2]^2$$

The rate constant, k, for the thermal decomposition was measured at five different temperatures and the results were used to plot the graph shown below.



The Arrhenius equation is $k = \mathrm{A}e^{-\frac{E_a}{RT}}$, where k is the rate constant, A is the Arrhenius constant, E_a is the activation energy, R is the molar gas constant, and T is the thermodynamic temperature in Kelvins.

The Arrhenius equation may also be expressed in the following form:

$$\ln k = \ln \mathrm{A} - \frac{E_a}{RT}$$

(i) Use the graph to calculate the activation energy, E_a, for the decomposition of nitrogen dioxide, stating its units.

(ii) A 3.0 dm^3 vessel is filled with 6.0 mol of NO_2 at a temperature of 650 K.

The rate constant, *k*, at this temperature is 3.16 $dm^3\ mol^{-1}\ s^{-1}$.

Calculate the initial rate of decomposition for the reaction at this temperature, stating its units.

[4]

(c) The first ever rocket-power fighter plane, the Messerschmitt Me 163, was powered by the reaction between a hydrazine-methanol mixture and hydrogen peroxide.

(i) When hydrazine reacts with hydrogen peroxide, chemically stable products are formed.

Suggest an equation for the reaction between hydrazine and hydrogen peroxide and state the change in oxidation state of the oxidised species.

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(ii) In a proposed electrochemical cell, hydrogen peroxide oxidises the methanol to carbon dioxide in acidic medium.

Write a balanced equation for the reaction occuring at the anode and cathode.

Anode : ....

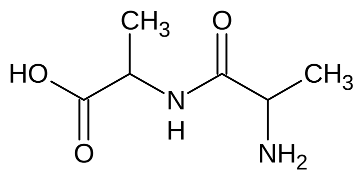
Cathode : ....

(iii) Given that the cell is capable of producing an e.m.f. of 1.75 V. By using suitable data from the *Data Booklet*, calculate the standard reduction potential for the anode reaction.

[5]

[Total: 15]

3 This question is about calcium and nitrogen containing organic compounds. Calcium oxalate (CaC_2O_4) is a sparingly soluble salt but the solubility of calcium oxalate is increased by the addition of alanyl-alanine. Alanyl-alanine is a dipeptide of alanine with the structure given below.



alanyl-alanine

(a) Write a balanced equation with state symbols between the reaction of calcium and water.

.... [1]

(b) (i) Write the expression of the solubility product of calcium oxalate and express the solubility of calcium oxalate, ***z***, in terms of the solubility product.

(ii) In 1942, Wilbur *et al* reported in the *Journal of American Chemical Society* the effect of pH on the solubility of calcium oxalate. Wilbur proposed that the solubility of calcium oxalate in any solution, in the absence of excess calcium or oxalate ions, should follow the equation below.

$$s = \sqrt{K_{sp}\left(\frac{[H^+]+K_2}{K_2}\right)} \qquad \text{where } K_2 = \frac{[H^+][C_2O_4^{2-}]}{[HC_2O_4^-]}$$

Explain and account for the difference in the expression of solubility for calcium oxalate obtained in **(b)(i)** and that proposed by Wilbur. You must explain why the inclusion of some terms was necessary in Wilbur's equation.

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(iii) Hence, state and explain the effect of decreasing pH on the solubility of calcium oxalate.

(iv) Identify a potential problem, in the determination of the solubility of calcium oxalate at high pH, when sodium hydroxide is directly added to a solution of calcium oxalate.

[9]

(c) Alanine is a commonly obtained amino acid resulting from the hydrolysis of proteins. In the human body, alanine undergoes biological oxidation to give carbon dioxide, water and urea ($CO(NH_2)_2$).

(i) Write a balanced equation for the biological oxidation of one mole of alanine.

(ii) When nitrogen containing organic compounds are burnt in calorimetric experiments, the nitrogen they contained is transformed to nitrogen molecules. Using this information as well as the standard enthalpy changes of combustion given in the table below,

compound	$\Delta H_{combustion}$ / kJ mol^{-1}
alanine(s)	–1577
urea(l)	–632

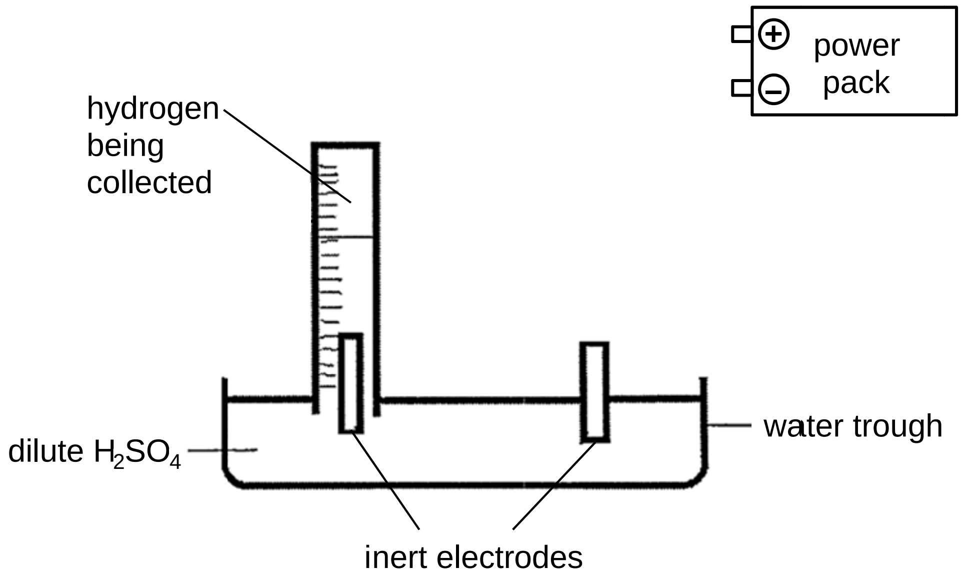
construct an energy cycle and calculate the energy that can be obtained from the biological oxidation of 1.00 g of alanine at standard conditions.

[5]

[Total: 15]

4 *Use of the Data Booklet is relevant to this question.*

A student decided to determine the value of the Avogadro constant, **L**, by an electrolysis experiment. The following incomplete diagram shows the apparatus that was used.



(a) Complete the diagram above, showing additional equipment connected in the circuit, and showing the powerpack connected to the correct electrodes. [1]

(b) List the measurements the student would need to make in order to use the results to calculate a value for the Faraday constant.

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.... [1]

(c) 210 cm^3 of hydrogen gas was collected on the inert electrode by passing a current of 5.6 A for 5 minutes at room temperature and pressure. Calculate the quantity of charge required to deposit one mole of hydrogen gas.

[2]

(d) One mole of hydrogen contains 2**L** atoms and each electron carries a charge of ***e*** coulombs. Using your answer in **(c)** and the value of ***e*** given in the *Data Booklet*, determine the value of the Avogadro constant, **L**.

[1]

(e) Suggest a reason for the difference between the value obtained in **(d)** and the theoretical value.

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[1]

[Total: 6]

5 **(a)** Some of the common Period 3 compounds are named as hydroxides and some as acids:

Compound	*Common Name*
NaOH	sodium hydroxide
$Mg(OH)_2$	magnesium hydroxide
$Al(OH)_3$	aluminium hydroxide
$Si(OH)_4$	silicic acid (usually written as H_4SiO_4)
$P(OH)_3$	phosphorous(III) acid (usually written as H_3PO_3)
$S(OH)_2$	not known; unable to exist

(i) State and explain two factors which determine the systematic variation in the acid–base behaviour of these compounds.

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(ii) Complete the missing row in the table on Page **13**.

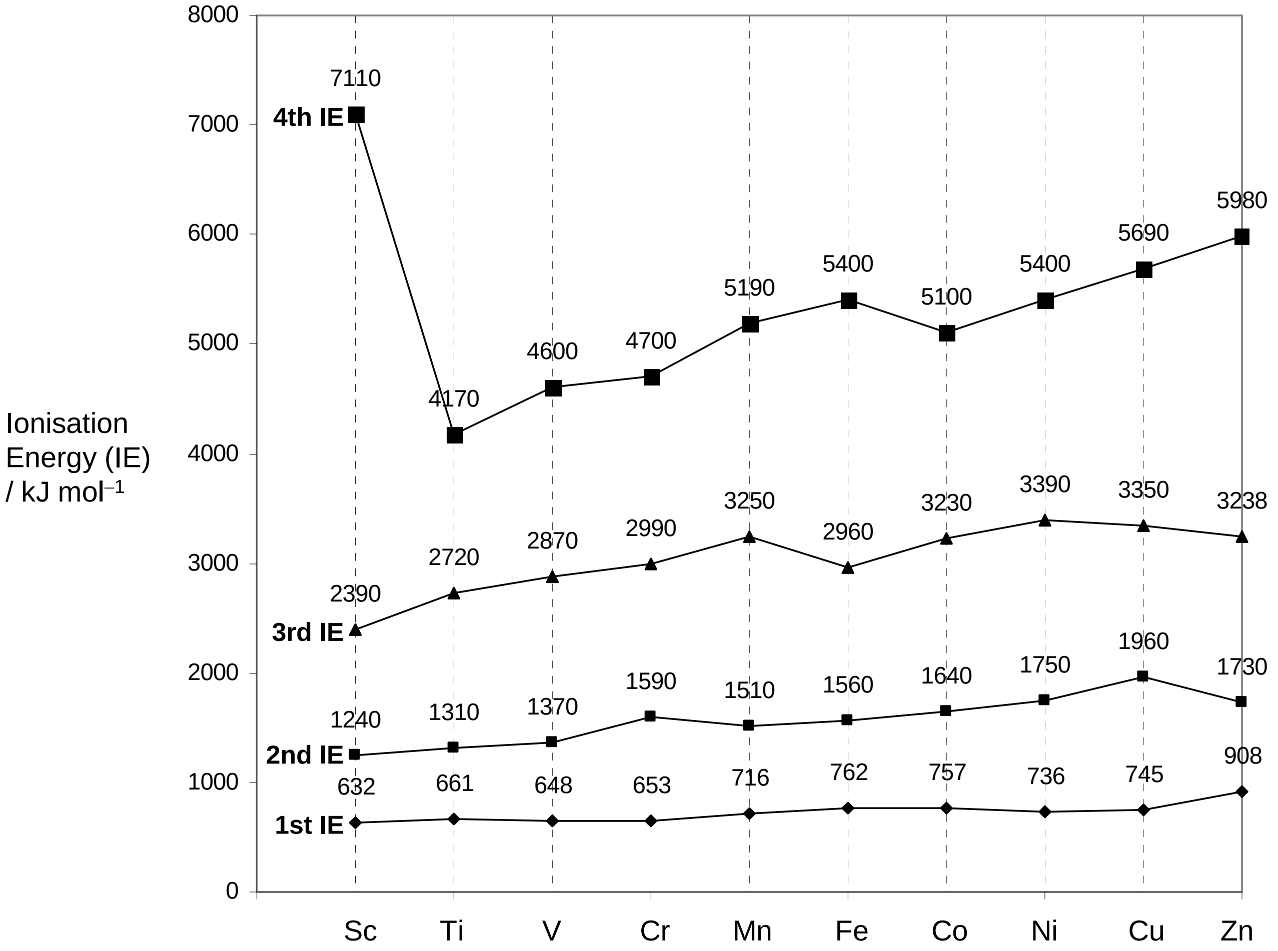
[4]

(b) A student treated 2 separate samples of 1–chlorobut–2–ene and 2–chlorobut–2–ene with warm aqueous sodium hydroxide, followed by an excess of dilute nitric acid and aqueous silver nitrate.

A white precipitate is observed for only one of the samples. Explain the observations.

[2]

(c) The graph below shows the variation of the first to fourth ionisation energies for the first row d-block elements scandium to zinc.



(i) Give an equation that represents the second ionisation energy of copper.

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(ii) Why is the second ionisation energy of copper higher than that of zinc?

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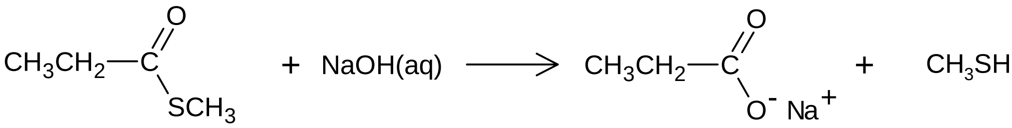
[3]

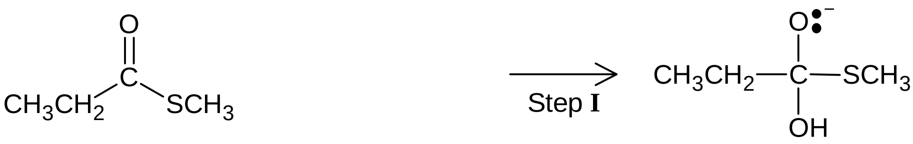
[Total: 9]

6 **(a)** The flavor of strong-smelling blue cheese is largely due to S-methyl thiopropanoate, which can be hydrolysed to form methanethiol under alkaline conditions.

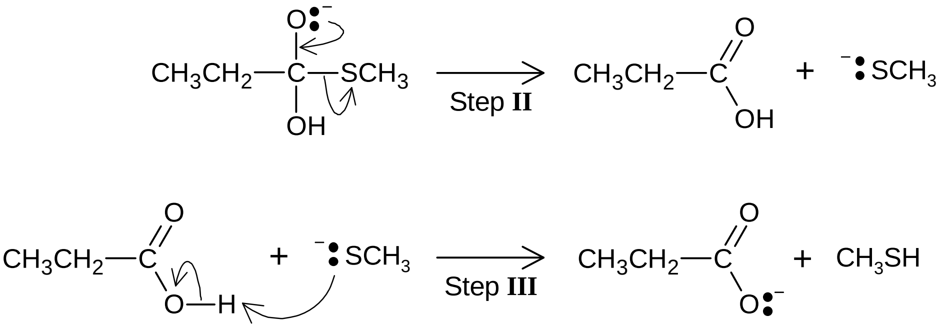


S-methyl thiopropanoate **methanethiol**

The mechanism for this hydrolysis involves three steps, as shown below. Step **I** is **not** complete.



tetrahedral intermediate



(i) Identify the nucleophile in this reaction.

Hence, complete the mechanism in Step **I** above to show how the tetrahedral intermediate is formed. Your drawing should show the movement of electrons clearly.

Nucleophile is ....

(ii) Name the type of reaction that has occurred in Step **III**.

....,

[3]

(b) Data concerning methanethiol and two of its analogues are given in the table below.

compound	M_r	atomic radius of atom **Z** in CH_3**Z**H / nm	dipole moment / D	boiling point / °C	pK_a
CH_3OH	32.0	0.073	1.7	65	15.5
CH_3SH	48.1	0.102	1.5	6	10.4
CH_3SeH	95.0	0.116	1.3	25	≈ 5

No calculation is required.

(i) Explain the differences in boiling points of the three compounds.

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(ii) Arrange the three compounds in order of **decreasing** acidity and suggest a reason for this trend.

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[5]

(c) When each of the three compounds has dissolved, each molecule is surrounded by water molecules. Draw simple diagrams to show how a water molecule interacts with a CH_3SH molecule and with a CH_3OH molecule. Label each diagram to show the type of interaction involved.

CH_3SH	CH_3OH

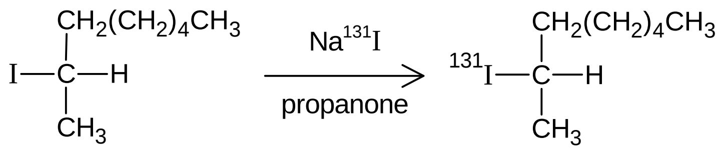
[2]

[Total: 10]

7 Chemists can follow the incorporation of an atom into a molecule by using a radioactively labelled element.

A pure optical isomer of 2-iodooctane is added to a solution of sodium iodide in propanone solvent. The sample of sodium iodide used in this reaction is made with ^{131}I, a radioactive isotope of iodine.

The 2-iodooctane undergoes nucleophilic substitution reaction with $^{131}I^-$ to slowly become a mixture of equal amounts of two optical isomers, and so loses its optical activity.



2-iodooctane

2-iodooctane labelled with ^{131}I

The table below records the extent in which optical activity is lost and the corresponding extent in which ^{131}I is incorporated as the reaction progresses.

% loss in optical activity	% incorporation of ^{131}I
20	10
40	20
60	30
80	40
100	50

(a) From the data above, deduce whether 2-iodooctane has undergone an S_N1 or S_N2 reaction. Explain your answer from a mechanistic perspective.

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.... [3]

(b) Based on your deduction in **(a)**, draw the mechanism of the radioactive labelling of 2-iodooctane by $^{131}I^{-}$. You are **not** required to use wedge and dash bonds to illustrate optical isomerism.

[2]

[Total: 5]

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