ST ANDREW'S JUNIOR COLLEGE

JC2 Preliminary Examinations

Higher 2

CANDIDATE NAME

CLASS | 2 | 0 | S | | |

CHEMISTRY

9729/02

Paper 2 Structured Questions

1 September 2021

2 hours

Candidate answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the **spaces provided** on the Question Paper.

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

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

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

For Examiner's Use		
Q1		9
Q2		9
Q3		24
Q4		20
Q5		13
Total		75

This document consists of ___ printed pages.

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

1 (a) Fig. **1.1** shows a sketch of the logarithm of the first ten ionisation energies, log (IE), of element **A** against the number of electrons removed.
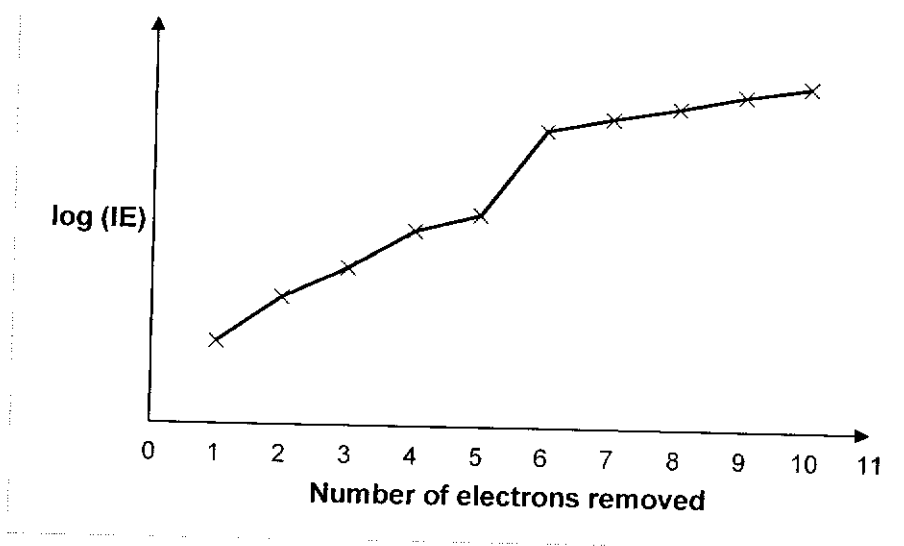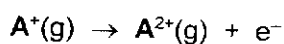

Fig. 1.1

(i) Write an equation for the *second ionisation energy* of element **A**.   **[1]**

$A^+(g) \rightarrow A^{2+}(g) + e^-$

Must have state symbols

(ii) Explain the following features of Fig. 1.1.

- the general trend in ionisation energy shown in the graph
- the significant jump in values from the 5th to the 6th ionisation energy   **[4]**

Ionisation energies <u>increased</u> as more electrons were removed. The <u>nuclear charge remained the same</u>, but it attracted <u>a decreasing number of electrons</u>. This led to <u>an increase in the attractive forces</u> on the remaining electrons and hence <u>more energy was required to remove the next electron</u>.
OR

Successive IE <u>increases</u> as <u>remaining electrons</u> will be <u>attracted more strongly</u> to <u>increasingly positively charged ion</u> and hence <u>more energy was required to remove the next electron</u>

The 6th electron is from the <u>inner quantum shell</u>. The <u>decrease in distance</u> of this electron (6th electron) from the nucleus, and <u>less shielding</u> resulted in <u>a</u>

stronger attraction to nucleus, significant increase in the energy required to remove this electron /more difficult to remove this inner shell electron.

(iii) Element **A** is in Period 3.

Identify element **A** using information from Fig. 1.1 and complete its electronic configuration. [1]

Element **A** is phosphorus / P.

$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^3$
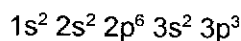
(b) Sulfur is another element in Period 3. It forms covalent bonds with other elements in covalent compounds such as SO_2, SO_3, SCl_2.

(i) Describe a covalent bond. [1]

A covalent bond is the electrostatic attraction between a shared / bonding pair of electrons and two positively charged nuclei.

(ii) Predict the intermolecular force which exists between SO_3 molecules. Explain how this force arises. You may use diagrams where appropriate to illustrate your answer. [2]

The SO_3 molecules are held together by instantaneous dipole-induced dipole (id-id) attractions.

In each electron cloud, electrons are constantly moving. The electron density of a cloud can be unsymmetrical at any moment, resulting in an instantaneous dipole.

This dipole can induce a dipole in the neighbouring electron cloud, causing an attraction between them.

OR
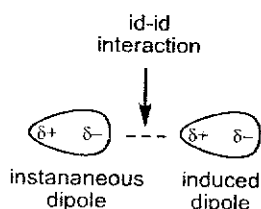
Diagram marks depend on labels used

Label for id-id

Uneven electron cloud

Labels for instantaneous dipole and induced dipole

Two electron clouds with different labels

2 Esters are commonly used as artificial flavourings in food products such as cakes and sweets. However, the shelf life of acidic foods containing esters are relatively short as esters are prone to acid-catalysed hydrolysis.

The kinetics of the acid-catalysed hydrolysis of the ester, methyl propanoate, $CH_3CH_2CO_2CH_3$, was investigated in an experiment.

(a) Write a balanced equation for the hydrolysis of methyl propanoate. [1]

$CH_3CH_2CO_2CH_3 + H_2O \rightarrow CH_3CH_2CO_2H + CH_3OH$
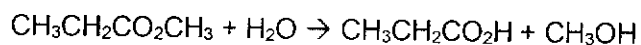
(b) 0.200 mol of ester was hydrolysed by heating with water and hydrochloric acid catalyst in a 1 dm^3 mixture. In a second experiment, hydrochloric acid was replaced with sulfuric acid of the same concentration. When the reaction is complete, 0.200 mol of propanoic acid is obtained.

The following results were obtained.
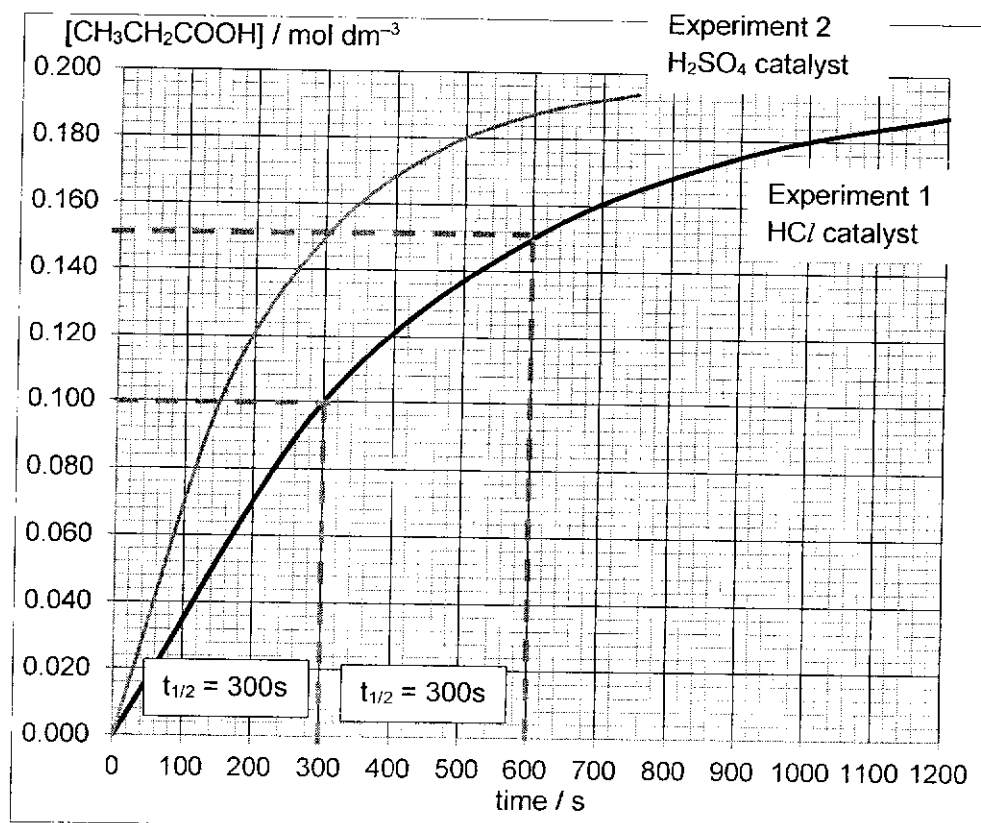
(i) Based on the results obtained, show that the reaction is first order with respect to the ester and first order with respect to H^+ ions. **[4]**

$[CH_3CH_2COOH]_{max} = 0.200$ mol dm^{-3}

Show 2 half life on the graph (either experiment 1 or 2) correctly e.g.

- from $0 \rightarrow 0.100$
- from $0.100 \rightarrow 0.150$
- does not have to be successive (one after the other e.g. 0.02 -> 0.11)

Since **half life is constant at 300 s (experiment 1) / 150 s (experiment 2)**, reaction is first order with respect to [ester].

Show **2 tangent to curve at t=0** clearly and **calculate gradient** of both tangent to curve

When [H⁺] x 2, initial rate x 2, reaction is 1st order with respect to [H⁺]

OR

Show **2 half life of the other experiment** on the graph clearly

rate = k[ester][H⁺]

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[H^+]}$$

When [H⁺] x 2, half life x ½
Reaction is 1st order with respect to H⁺

(ii) State the units of the rate constant, k. **[1]**

Units of rate constant k = mol^{-1} dm^3 s^{-1}

(c) With the aid of a sketch of the Boltzmann distribution, explain how an increase in temperature changes the rate of ester hydrolysis. **[3]**

No. of molecules
with energy, E
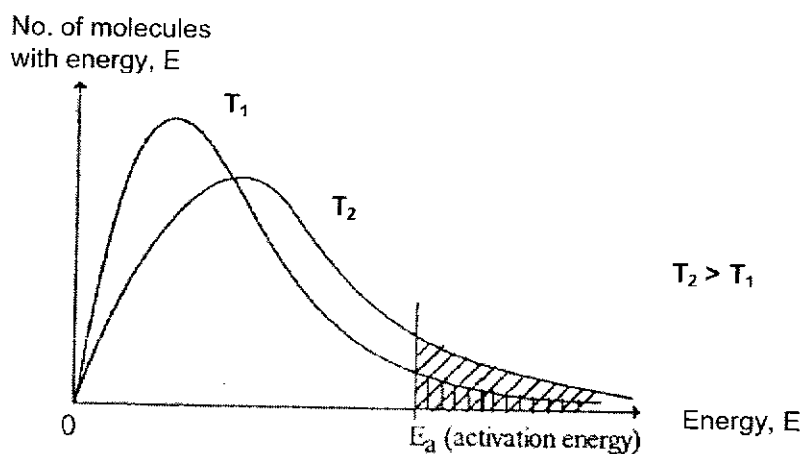
Note: E_a does not shift as temperature changes.

When temperature is increased, the **molecules gain kinetic energy and move about faster**. This **increases the number of molecules having energy greater than or equal to activation energy**. As a result, the **frequency of effective collisions increases**. **Reaction rate thus increases**.

[Total: 9 marks]

3 Scuba diving is an extreme sport where divers carry their own source of breathing gas to explore the open sea.

Table **3.1** lists the compositions by volume of two breathing gases used by scuba divers.

Table 3.1

Mixture	Composition by volume
Nitrox	32% oxygen, 68% nitrogen
Heliox	21% oxygen, 79% helium

(a) (i) State one assumption of the kinetic theory as applied to an ideal gas. Hence, deduce, with reasons, whether Nitrox or Heliox shows greater deviation from ideal gas behaviour. **[2]**

The intermolecular forces between the gas particles are negligible/insignificant.

Nitrox shows greater deviation as nitrogen has a larger electron cloud size than helium, so its intermolecular forces/ id-id are less negligible /more significant.

OR

The particle size/volume is negligible as compared to the size/volume of the container.

Nitrox shows greater deviation as <u>nitrogen molecule is larger</u> than helium atom, so its particle size/volume is less negligible/ more significant.

(ii)   Use of the *Data Booklet* is relevant to this question.

A canister of breathing gas has a density of 435 g m^{-3} at standard temperature and pressure (s.t.p). Calculate the average molar mass of the mixture.

Hence, with reference to Table 3.1, deduce the identity of the breathing gas.   **[3]**

$pV = nRT$

$$pV = \frac{m}{M}RT$$

$$M = \frac{mRT}{pV} = \frac{\rho RT}{p} = \frac{(435)(8.31)(273)}{10^5}$$

= 9.87 g mol^{-1}

The breathing gas is Heliox.

(b) At sea level, the atmospheric pressure is 1 atm. In the sea, there is an increase in pressure of 1 atm for every 10 m of depth below the surface. For example, at 10 m, the pressure on the diver's body is 2 atm and at 20 m, the corresponding pressure is 3 atm.

When a diver inhales from the gas canister, the air that enters the diver's lungs is at the surrounding pressure.

For safety reasons, divers should not inhale oxygen at partial pressures greater than 1.3 atm, as this may lead to oxygen toxicity, causing seizures and death.

(i)   A scuba diver takes a deep breath from his oxygen gas canister to fill up his lungs to 6 dm^3 at a depth of 15 m. Calculate the volume that will be occupied in   **[2]**
his lungs by this amount of air at the surface.

Pressure at 15 m = 2.5 atm

Amount of air remains constant.

$p_1V_1 = p_2V_2$, where p_2 is 1 atm

$(2.5)(6) = (1)(V_2)$

$V_2 = 15$ dm^3

(ii) "Never hold your breath when surfacing" is a fundamental rule of scuba diving. **[1]** With reference to your answer in **(b)(i)**, explain why.

The <u>volume of air in the lungs increases</u> greatly when he surfaces (from 6 to 15 dm^3, hence he must exhale or the pressure increase results in lung damage). (in their own words)

(iii) A scuba diver uses Nitrox for a dive. Calculate the total pressure of the Nitrox mixture that corresponds to oxygen at a partial pressure of 1.3 atm. Hence, determine the maximum depth the diver can descend to safely. **[2]**

Partial pressure of oxygen = 1.3 atm

Total pressure = 1/0.32 x 1.3 = 4.0625 atm

Maximum depth = (4.0625 – 1) x 10 = 30.6 m

(iv) State an assumption that you have made in your calculations for **(b)(i)** and **(b)(iii)**. **[1]**

Temperature remains constant.

Or These gases behave as ideal gases.

(c) Diving suits are commonly made of neoprene, a synthetic polymer that is waterproof and a good insulator.
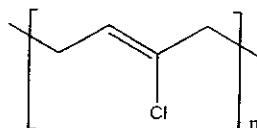
neoprene

Neoprene can be synthesised from 1,3-butadiene by the following route shown in Fig. **3.2**.
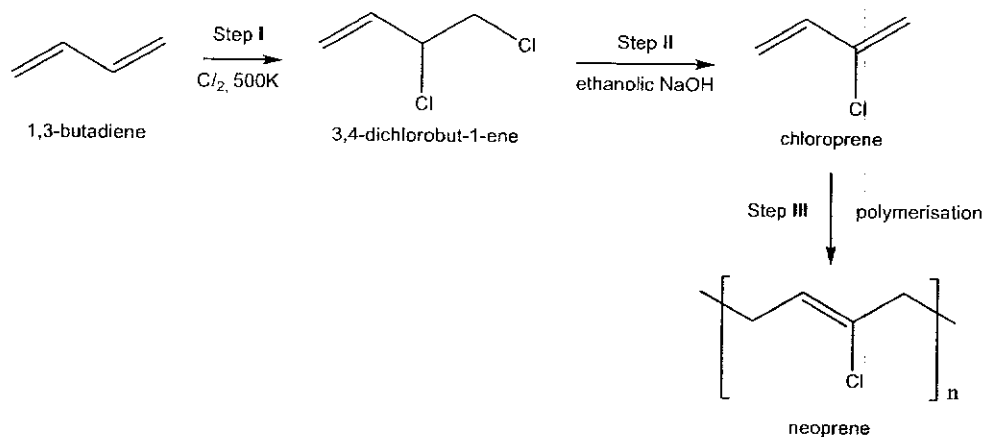
Fig. 3.2

(i) Draw the structure of a possible side product formed in Step I. **[1]**
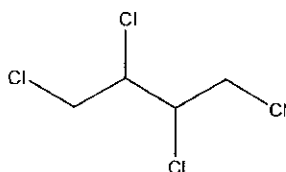
(ii) Suggest how to minimise formation of this side product in **(c)(i)**. **[1]**

Use **limited** chlorine / **excess** 1,3-butadiene

(iii) Name the type of reaction occurring in Step II. **[1]**

Elimination

(d) The polymerisation of chloroprene proceeds via a free radical mechanism. A common class of free radical polymerisation initiators are peroxide compounds, ROOR.

Explain what is meant by the term *free radical* and explain how the bond in ROOR breaks to form RO• free radicals. You may use a diagram in your answer. **[2]**

(i) Free radical is an atom or group of atoms/species having <u>an unpaired electron</u>.

The <u>homolytic fission</u> of the O–O bond within peroxide compounds forms RO• free radicals.

OR

$$RO\text{——}OR \longrightarrow 2RO\bullet$$
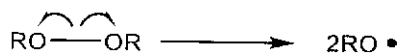
(ii) Suggest why only a trace amount of ROOR is required in the polymerisation of chloroprene.

[1]

Since the only function of the radical initiator, ROOR, is the <u>generation of the first RO•</u> involved in the chain reaction in the system, it is used in trace amounts.

OR

Radicals are (re)generated in the propagation step

OR

Mechanism is a chain reaction

(e) (i) Complete Fig. **3.3** to suggest the mechanism for the chain growth. Show the structure of the 2 unit intermediate and the movement of electrons in steps 1 and 2 by using curly arrows.

n unit intermediate + chloroprene → (n+1) unit intermediate

Fig. 3.3

[3]

chloroprene · 1 unit intermediate · 1 unit intermediate · chloroprene · 2 unit intermediate
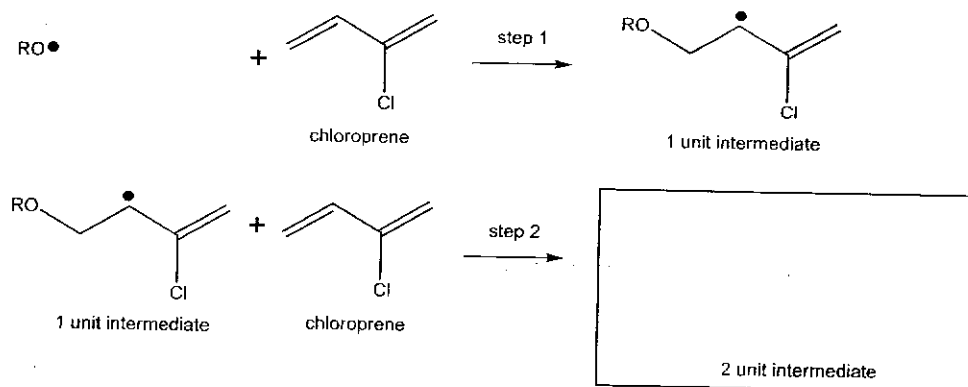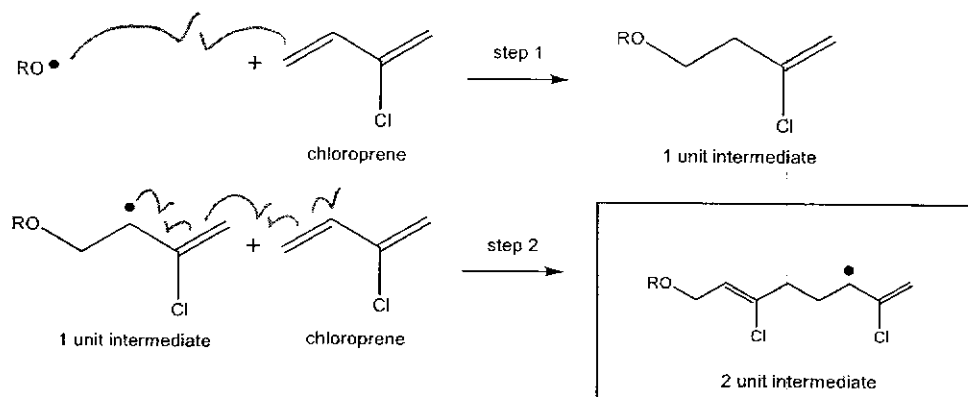
(ii) Explain the preferential production of the 1 unit intermediate over isomer **E** in step 1.
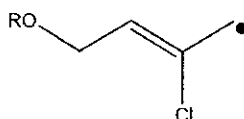
Isomer **E**

[1]

E is a primary radical, which is **less stable** than the actual secondary radical formed due to the presence of **fewer electron donating alkyl groups**.

(f) (i) Besides diving suits, neoprene can be used to make alkali resistant rubber gloves. Suggest a reason why neoprene is not susceptible to reaction with alkali such as aqueous NaOH.

[1]

- Electron rich double / C=C bond repels incoming OH⁻ nucleophile.
  OR

- Lone pair of electrons in p orbital of Cl overlap with C=C pi bond, resulting in partial double bond character

(ii) Under suitable conditions, NaOH can be used to distinguish between 3,4-dichlorobut-1-ene and chloroprene.

Describe the simple chemical test involving NaOH to distinguish between the two compounds. Write relevant balanced equations for the reactions that occurred.

[2]

Heat with aq NaOH, cool, and acidify with HNO₃, followed by aq AgNO₃

$2OH^- + CH_2=CH-CHCl-CH_2Cl \rightarrow CH_2=CH-CH(OH)-CH_2OH + 2Cl^-$

$Cl^- + Ag^+ \rightarrow AgCl$
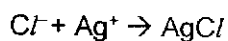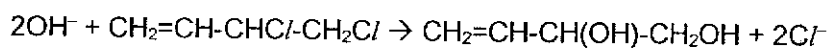
4 (a) Gallium is an element in Group 13.

A sample of gallium contains two isotopes, ^{69}Ga and ^{71}Ga. The relative atomic mass of the gallium in this sample is 69.8.

(i) Explain what is meant by the term *relative atomic mass*. **[1]**

The relative atomic mass (A_r) of an element is defined as the **ratio of the**

average mass of **one atom** of the element to $\dfrac{1}{12}$ **the mass of a ^{12}C atom**.

$$Or \quad A_r = \frac{\text{Average mass of 1 atom of the element}}{\frac{1}{12} \times \text{mass of 1 atom of } ^{12}C}$$

(ii) Calculate the percentage abundance of each of these isotopes. Show your working. **[2]**

Let % abundance of ^{69}Ga = x

(x/100 × 69) + ((1- x)/100 × 71) = 69.8

% abundance of ^{69}Ga , x = 60.0

% abundance of ^{71}Ga = 40.0

(iii) Complete the table which describes a gaseous atom of gallium. **[2]**

Isotope	Number of neutrons	Type of orbital contains electron in **highest** energy level	Total number of electrons in this **highest** occupied orbital
^{69}Ga	38	(4)p	1

(b) Gallium and its compounds show similar properties to aluminium and its compounds. Gallium reacts with excess chlorine to form gallium trichloride.

In their gaseous form, equimolar amounts of PH_3 and $GaCl_3$ combine to form a solid product PH_3GaCl_3 at 120 °C in a closed reaction vessel.

$$PH_3(g) + GaCl_3(g) \rightleftharpoons PH_3GaCl_3(s) \text{ ------------ Equilibrium 1}$$
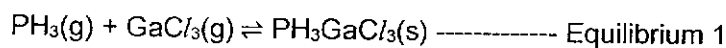
The equilibrium constant was determined to be 550 mol^{-2} dm^6.

(i) The reaction between PH_3 and $GaCl_3$ is similar to that between NH_3 and $AlCl_3$. **[2]**

Suggest the role of GaCl₃ in this reaction. Explain your answer.

GaCl₃ functions as a <u>Lewis acid</u> as it has energetically accessible <u>empty orbitals</u> <u>on Ga to accept lone pair of electrons from P</u> in PH₃.

(ii) Write the expression for the equilibrium constant, K_c, for equilibrium 1. Hence, **[2]** show that the concentration of PH₃ in the closed vessel was 0.0426 mol dm⁻³ after some solid PH₃GaCl₃ was formed at equilibrium.

Let x be the equilibrium concentration of the reacting gases, PH₃ and GaCl₃.

$$K_c = \frac{1}{[PH_3][GaCl_3]} = \frac{1}{x^2} = 550$$

$$x = 0.04264 = \underline{0.0426 \text{ mol dm}^{-3}}$$

(iii) Suggest what happens to the concentration of PH₃ when some of the solid **[1]** PH₃GaCl₃ is removed.

If some solid PH₃GaCl₃ is removed, the position of equilibrium remains unchanged and hence the <u>concentration of PH₃ (and GaCl₃) remains</u> <u>unchanged</u>.

(iv) Predict the effect on the equilibrium constant, K_c, when the reaction vessel is **[2]** heated. Explain your answer.

In the formation of PH₃GaCl₃, a dative bond exists within the molecule of PH₃GaCl₃.

Thus the <u>forward reaction is exothermic</u> due to the <u>formation of bond</u>.

An increase in temperature would increase the <u>rate constant of backward</u> <u>reaction to a greater extent</u> than that of the forward reaction / <u>rate of backward</u> <u>reaction increase more than rate of forward reaction</u>.

Since $K_c = \frac{k_f}{k_b}$, K_c will <u>decrease</u>.

(v) The value of K_c does not change when a catalyst is added. Explain why this is **[2]** the case.

A catalyst provides an <u>alternate reaction pathway</u> with a <u>lower activation energy</u> <u>for both the reaction</u> hence the rate increase. The <u>forward and backward</u> <u>reaction rate constants/</u> rate increases by the <u>same extent</u>.

$K_c = \dfrac{k_f}{k_b}$ does not change.

(c) Gallium is a silver-grey solid. Aluminium and gallium share many similar chemical properties.

Write the equation for the reaction between Ga_2O_3 and dilute hydrochloric acid.　　**[1]**

$Ga_2O_3 + 6HCl \rightarrow$ □ $2GaCl_3 + 3H_2O$
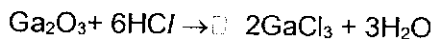
(d) Gallium objects have a thin insoluble oxide layer on their surfaces. This oxide layer can be removed by adding aqueous sodium hydroxide to the gallium object.

An initial reaction occurs during which no observations are made. After a short time, bubbles of hydrogen gas are produced. When these bubbles appear, the object is removed from the aqueous sodium hydroxide and rinsed.

(i) Explain why Ga_2O_3 is insoluble in water.　　**[1]**

Energy released in the <u>ion-dipole attractions</u> is <u>not sufficient</u> to overcome the <u>strong ionic bonds in Ga_2O_3</u> and <u>hydrogen bonds between water molecules</u>.

(ii) Write an equation, with state symbols, which describes the initial reaction occurring when NaOH(aq) is first added to the object, before the bubbles are seen.　　**[2]**

$Ga_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow$ □ $2NaGa(OH)_4$ (aq)

Or

$Ga_2O_3(s) + 2NaOH(aq) + H_2O(l) \rightarrow$ □ $2NaGaO_2$ (aq)
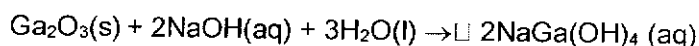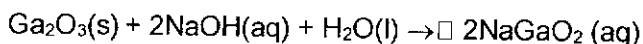
(iii) Explain, with the aid of a relevant equation, the reaction that resulted in the formation of H_2 gas.　　**[2]**

$Ga + 3H_2O \rightarrow Ga(OH)_3 + 3/2H_2$
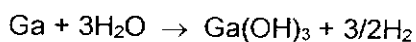
Once the Ga_2O_3 layer is removed by the NaOH(aq), Ga can react with water to form hydrogen gas.

[Total: 20 marks]

5 One important class of chemicals in everyday life are the azides, compounds which contain the azide anion N_3^-.

(a) Given the structure of the azide ion, deduce the hybridisation of the nitrogen atom labelled N_y, and state the number of σ and π bonds present in the ion.

$$^-N_x\!=\!\!=\!\overset{+}{N_y}\!=\!\!=\!N_z^-$$
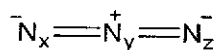
Azide ion [2]

Hybridisation: sp

Number of σ bonds: 2

Number of π bonds: 2

(b) The azide ion can be obtained from gaseous hydrazoic acid, HN_3, which has the following structure.

$$H\!-\!\!-\!N\!=\!\!=\!\overset{+}{N}\!=\!\!=\!N^-$$
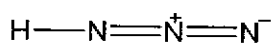
Hydrazoic acid

(i) The enthalpy change of formation of gaseous hydrazoic acid is +264 kJ mol^{-1}. Using the relevant bond energy values from Table **5.1**, calculate the average bond energy of the N=N double bond in hydrazoic acid.

You can assume that the bond energy in hydrazoic acid is not affected by the charges on the N atoms.

Bond	Bond energy / kJ mol^{-1}
H-H	436
N≡N	944
N-H	390

Table 5.1 [3]

$$\tfrac{1}{2}H_2(g) + 3/2\ N_2(g) \xrightarrow{\ \Delta H_f = +264\ } HN_3(g)$$

½ x 436 + 3/2 x 944 ↓ ↗ –(1 N-H bond + 2 N=N bonds)

H(g) + 3N(g)

OR
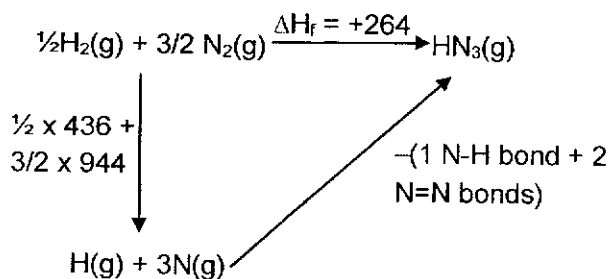
ΔH_f = energy of bonds broken – energy of bonds formed

+264 = (½ x 436 + 3/2 x 944) – (1 x 390 + 2 x N=N bond)

N=N bond energy = +490 kJ mol^{-1}

(ii) Suggest why the value calculated in **(b)(i)** is different from the value stated in the *Data Booklet*. **[1]**

The value from the Data Booklet is only an average value.

(c) Azides are also a functional group in organic chemistry with the structure $R-N_3$, where R is an alkyl group. These are known as alkyl azides.

In the Schmidt/Boyer reaction, alkyl azides react with carbonyl compounds under acidic conditions to form amides.
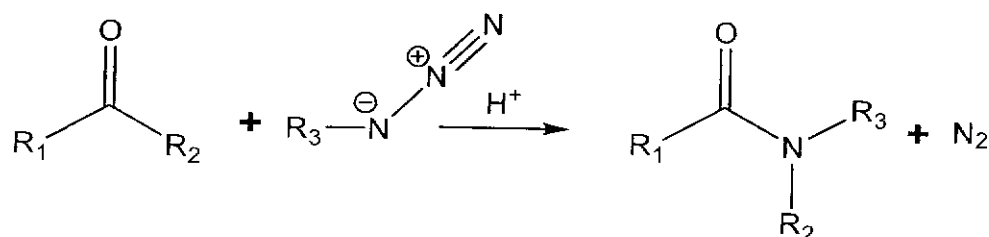
Where R_1/R_2 are H or alkyl groups.

For example, propanone reacts with methyl azide to form an amide.
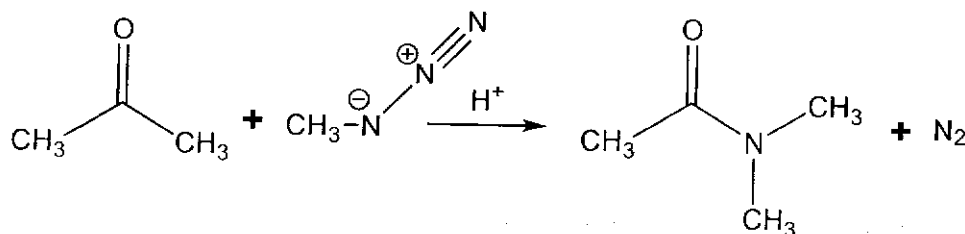
(i) When butanone reacts with methyl azide, two products are formed. Draw the structure of both organic products. **[2]**
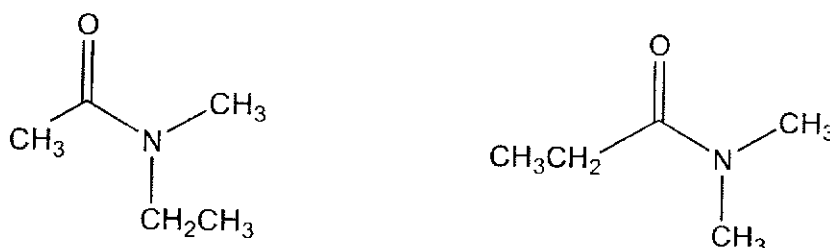
One mark for each product

(ii) The Schmidt/Boyer reaction is very useful in synthesising β-lactams, four-member cyclic amides, a structure found in many antibiotics.

[2]

Compound **R** is an example of a simple β-lactam. Compound **R** can be prepared by a sequence of reactions, starting from 3-chloro-2-methylpropanal as shown in Fig. 5.1.

Suggest the type of reaction for Reaction **1**, and suggest the structure of compound **Q**, which has an aldehyde and an azide group.
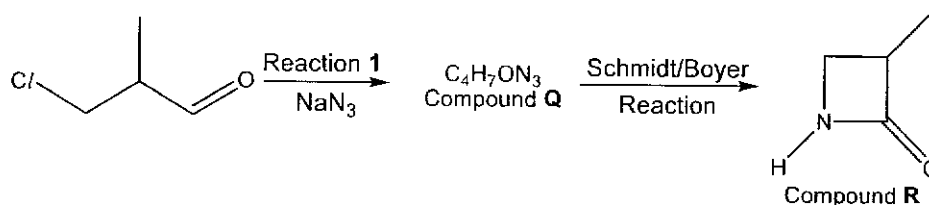
Fig 5.1

Reaction **1**: Nucleophilic substitution
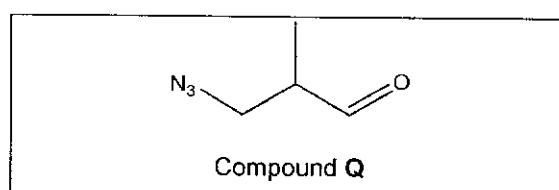
Compound **Q**

(iii)   Compound **R** is not basic. Explain.   [1]

The lone pair of electrons on the N atom are delocalised over the N-C-O group and hence not available for donation.

(iv)   Using VSEPR theory **only**, state the *expected* bond angle of the C-N-C bond in compound **R**.   [1]

3 bond pairs, 1 lone pair

Expected bond angle: 107°

(v)   The C-N-C bond in compound **R** has been experimentally found to be 90°. Using this information and your answer in **(c)(iv)**, suggest why compound **R** undergoes hydrolysis more readily than ethanamide.   [1]

There is **ring strain** present, hence the C-N bond is weak and easily broken.

[Total: 13 marks]

ST ANDREW'S JUNIOR COLLEGE

JC2 Preliminary Examinations

Higher 2

CANDIDATE NAME

CLASS

2	0	S		

CHEMISTRY

Paper 3 Free Response

Candidate answer on the Question Paper.
Additional Materials: Data Booklet

9729/03

15 September 2021

2 hours

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** the questions.

Section B
Answer one question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

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

For Examiner's Use		
Q1		24
Q2		17
Q3		19
Q4/5		20
Total		80

This document consists of **39** printed pages.

Section A

Answer **all** the questions in this section.

1 **(a)** Iodates are compounds that contain the IO_3^- anion.

(i) Draw the dot-and-cross diagram of IO_3^-. **[1]**

(ii) Use your knowledge of VSEPR theory to name the shape of and state the bond angle for IO_3^-. Explain your reasoning. **[3]**

(iii) Explain why BrO_3^- has a larger bond angle than IO_3^-. **[1]**

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(b) The decomposition of hydrogen peroxide, H_2O_2, can be catalysed by acidified IO_3^-.

$$2H_2O_2 \rightarrow 2\ H_2O + O_2$$
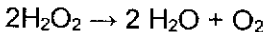
With the aid of relevant data from the *Data Booklet* and the information below, show that IO_3^- is a suitable catalyst for the decomposition of H_2O_2 under standard conditions.

$$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2 + 3H_2O \qquad\qquad E^\ominus = +1.19\ V$$
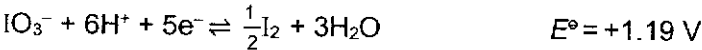
In your answer, give relevant equations for the reactions that occur. **[3]**

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(c) The kinetics of the catalytic decomposition of H_2O_2 by IO_3^- can be investigated.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

The concentration of H_2O_2 remaining can be determined by titrating with standard acidified $KMnO_4$.

Briefly outline how you would determine the rate of the catalysed decomposition of H_2O_2 using acidified $KMnO_4$.

[3]

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(d) (i) A student collects some data for the reaction of H_2O_2 with acidified IO_3^-, as shown in Table **1.2**.

Experiment	$[H_2O_2]/$ mol dm^{-3}	$[IO_3^-]/$ mol dm^{-3}	$[H^+]/$ mol dm^{-3}	Initial rate/ mol dm^{-3} s^{-1}
1	0.050	0.070	0.025	1.47×10^{-5}
2	0.100	0.070	0.050	2.94×10^{-5}
3	0.100	0.140	0.025	5.88×10^{-5}
4	0.150	0.140	0.025	8.82×10^{-5}

Table 1.2

Determine the order of reaction with respect to $[H_2O_2]$, $[IO_3^-]$ and $[H^+]$. Show your reasoning. **[3]**

(ii) Hence, write the rate equation for the reaction, and calculate a value for the rate constant using experiment **1**. Include units in your answer. **[2]**

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(e) (i) NH_4IO_3 is an unstable compound that readily decomposes when warmed as shown:

$$NH_4IO_3(s) \rightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + \frac{1}{2}I_2(s) + 2H_2O(l) \quad \Delta H_r^{\ominus}$$
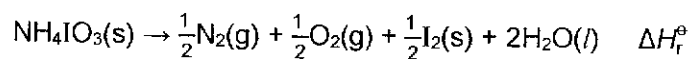
Using the information given below in Table **1.1**, calculate the standard enthalpy change $\Delta H_r^{\ominus}$ for the above reaction. **[1]**

Substance	Standard enthalpy change of formation / kJ mol⁻¹
NH_4IO_3 (s)	– 417.4
H_2O (l)	– 286

Table 1.1

(ii) Explain how the value and sign of $\Delta G_r^{\ominus}$ would compare to the value and sign of $\Delta H^{\ominus}$ for the decomposition of NH_4IO_3. **[2]**

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(f) (i) When 4.00 g a Group 2 metal iodate was heated strongly, 0.947 g of a metal oxide, a purple gas and a colourless gas which rekindles a glowing splint were produced.

Determine the identity of the Group 2 metal. [1]

(ii) Using your answer in **(f)(i)**, write a balanced equation, with state symbols, for the decomposition of the Group 2 iodate. [1]

(iii) To deduce which compound, calcium iodate or barium iodate, has a higher decomposition temperature, the following explanation was provided by a student:

'Calcium iodate has a higher decomposition temperature than barium iodate. The Ca^{2+} ion is a smaller ion than Ba^{2+}, hence the lattice energy of calcium iodate is more exothermic than that of barium iodate.'

Comment on why the student's answer was wrong and hence suggest a more appropriate answer. [3]

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2 Lithium is one of the most abundant elements on the Earth, and has gained widespread use in a variety of applications, from chemical synthesis to battery technology.

(a) Lithium aluminium hydride is often used in reactions to reduce organic compounds. However, it is not the only reducing agent available, and different reducing agents work on different functional groups.
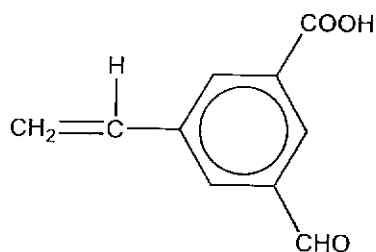
Compound **A**

Draw the structures of the organic products formed when Compound **A** reacts with the following reducing agents:

(i) LiAlH₄

[1]

(ii) NaBH₄

[1]

(iii) H₂ with Ni catalyst, heat

[1]

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(b) Fig **2.1** shows how the standard cell potential between the Li^+/Li half-cell and the Cl_2/Cl^- half-cell is measured.

$Cl_2(g)$ at 1 bar, 25°C

platinum electrode

$[Cl^-(aq)] = 1$ mol dm^{-3}

Li (s)

$[Li^+ (aq)] = 1$ mol dm^{-3}
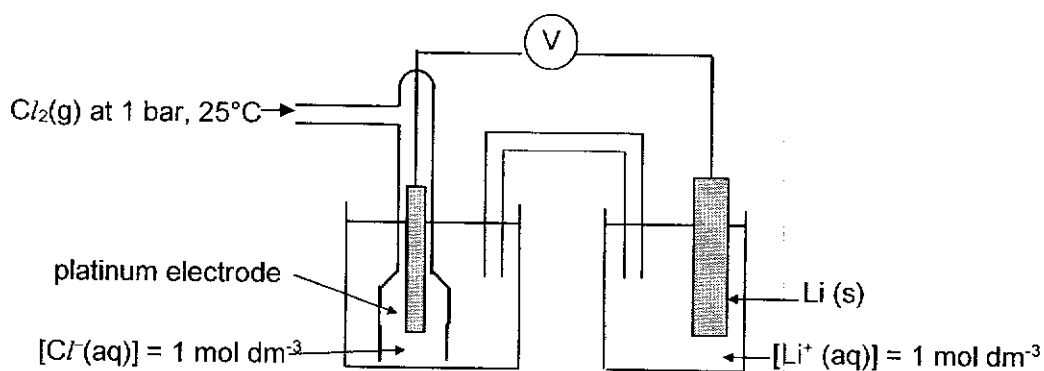
Fig 2.1

(i) Use of the *Data Booklet* is relevant to this question.

Describe the flow of electrons in the external circuit in the above electrochemical cell. Explain your reasoning. **[2]**

(ii) Predict the effect, if any, on the voltmeter reading when the pressure is increased at the Cl_2/Cl^- half-cell. Explain your answer. **[2]**

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(c) Lithium-ion batteries are lightweight and can hold a large amount of charge. The lithium-cobalt oxide battery was the first lithium-ion battery to be developed and sold by Sony in 1991. It consisted of a cobalt oxide electrode, and a graphite electrode with lithium intercalated within the graphite structure.

A simplified diagram of the lithium-cobalt oxide battery during the charging process is shown below. LiC_6 represents the lithium intercalated within the graphite structure.
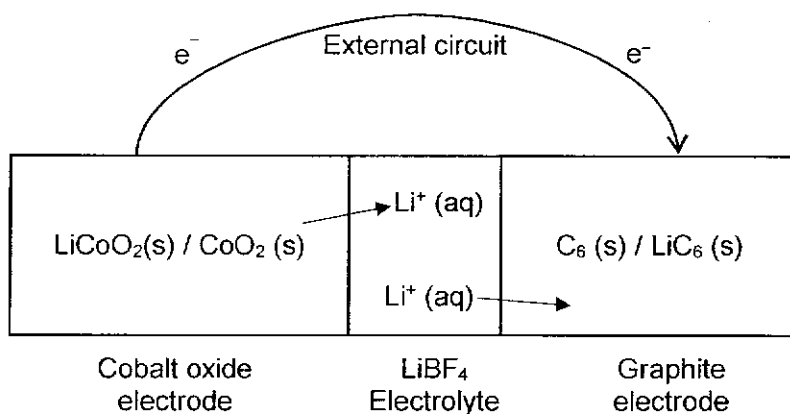
During charging, the following process occurs at the cobalt oxide electrode:

$$LiCoO_2 \longrightarrow CoO_2 + Li^+ + e^-$$
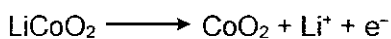
At the same time, at the graphite electrode, the following process occurs:

$$Li^+ + C_6 + e^- \longrightarrow LiC_6$$

12
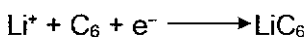
(i) Identify the electrode that is the anode during the *discharging* process.   [1]

(ii) Write half equations for the processes at the anode and cathode during *discharge*.   [1]

(iii) Given the following information, determine the E°_{cell} of the lithium cobalt oxide battery.

$CoO_2 + Li^+ + e^- \rightleftharpoons LiCoO_2$ $E^\circ = +1.00$ V

$Li^+ + C_6 + e^- \rightleftharpoons LiC_6$ $E^\circ = -3.00$ V   [1]
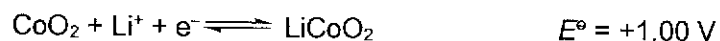
(iv) Calculate the standard Gibbs free energy change that occurs in the battery during discharge using your answer in **(c)(iii)**.   [1]

(v) The actual voltage of the lithium cobalt oxide battery is 3.60 V. Suggest why this value differs from your answer in **(c)(iii)**.   [1]

(vi) Explain the purpose of the electrolyte solution.   [1]

(vii) Suggest why modern lithium-ion batteries are superior to lead-acid batteries.   [1]

(viii) A batch of lithium-cobalt oxide batteries were defective due to the presence of potassium ions in the graphite electrode. Given that

$CoO_2 + K^+ + e^- \rightleftharpoons KCoO_2$ $E^\circ = +0.79V$

$K^+ + C_6 + e^- \rightleftharpoons KC_6$ $E^\circ = -2.88V$
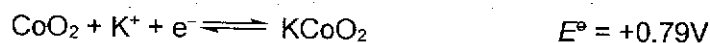
State and explain the effect, if any, of the presence of potassium ions on
(I) the charging process,
(II) the discharging process   [2]

(ix) Explain why the batteries in **(c)(viii)** are considered defective.   [1]

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[Total:17 marks]

3 (a) Organolithium reagents, RLi, are compounds which contains carbon-lithium bonds. They act as sources of negatively charged carbon, i.e. carbanions, and are useful reagents in organic synthesis involving carbon-carbon bond formation.

Organolithium reagents can be formed by reacting powdered lithium with halogenoalkanes in dry ether, as shown in the example below with bromomethane.

$$CH_3Br + 2Li \xrightarrow{\text{dry ether}} CH_3Li + LiBr$$
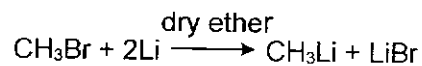
(i) State the oxidation state of carbon in CH_3Br and CH_3Li. [1]

(ii) Based on your answers in (a)(i), suggest why CH_3Li is formed by mixing Li and bromomethane in the ratio of 2:1. [1]

(iii) Suggest why the ether solvent used needs to be dry in this reaction. [1]

(b) A typical example of the use of an organolithium reagent is the two-step mechanism of CH_3Li with propanone, CH_3COCH_3, to form 2-methylpropan-2-ol.

$$CH_3Li + CH_3COCH_3 \xrightarrow{\text{step I}} \underset{\underset{CH_3}{|}}{\overset{\overset{O^- Li^+}{|}}{H_3C-\underset{}{C}-CH_3}} \xrightarrow[H_2O]{\text{step II}} \underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{H_3C-\underset{}{C}-CH_3}} + LiOH$$
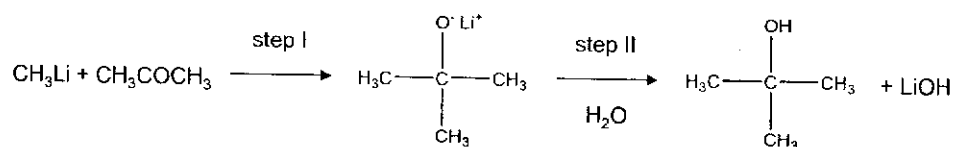
Assuming that CH_3Li produces the methyl carbanion, $:CH_3^-$, as the reacting species, name and describe the two-step mechanism for the reaction.

In your answer you should show all charges, dipoles and lone pairs and show the movement of electrons using curly arrows. **[3]**

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(c) **(i)** Suggest the **skeletal formula** of the final organic product formed when
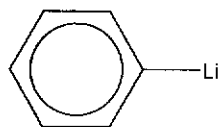
is reacted with butanone, $CH_3CH_2COCH_3$, in a similar two-step mechanism as in **(b)**. **[1]**

(ii) With reference to the mechanism identified in **(b)**, suggest whether the final product mixture in **(c)(i)** will rotate plane-polarised light. Explain why. **[2]**

18

(d) Compound **Y** can be synthesised by the following route involving an intramolecular organolithium reaction.

X gives a silver mirror when boiled with Tollens' reagent. **X** also gives a cream precipitate when heated with ethanolic silver nitrate.

State the reagents and conditions for step 1, and draw the structures of **W** and **X**.

$$\underset{(C_6H_{13}OBr)}{\textbf{W}} \xrightarrow{\text{Step 1}} \underset{(C_6H_{11}OBr)}{\textbf{X}} \xrightarrow[\text{2. }H_2O]{\text{1. Li in dry ether}} \underset{\textbf{Y}}{\text{(cyclohexanol with OH)}}$$
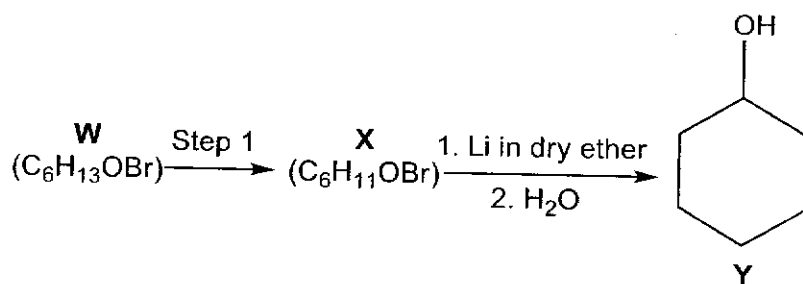
[3]

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(e) Fig. **3.1** shows a reaction synthesis.
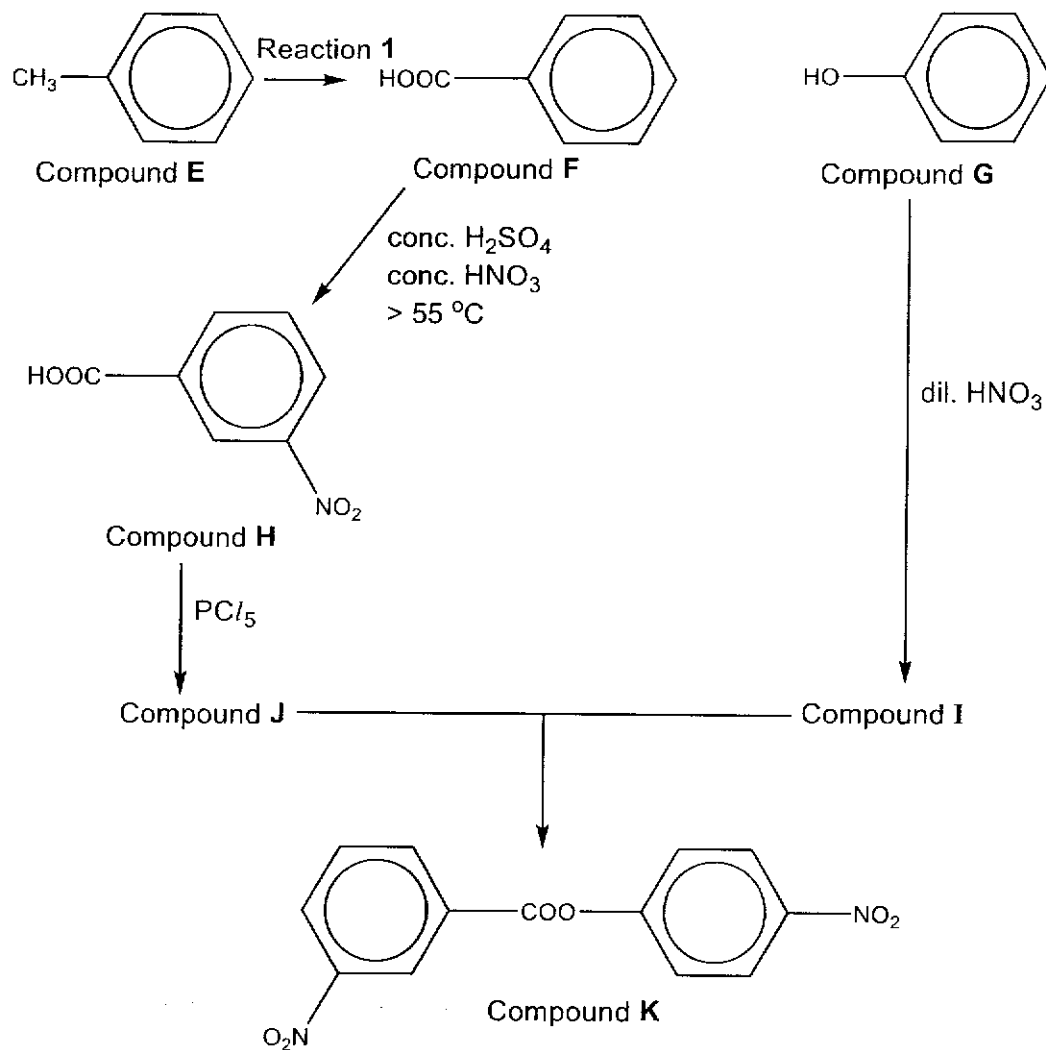
Fig 3.1

(i) Identify compound **J** and compound **I**. [2]

(ii) State the reagents and conditions required for Reaction **1**. [1]

(iii) Explain the differences in the conditions for the nitration of compound **F** and compound **G**. [2]

(iv) Suggest a simple chemical test to distinguish compound **F** and compound **G**. State any observations you would make with each compound. [2]

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[Total: 19 marks]

Section B

Answer **one** question from this section.

4 **(a)** **(i)** Use of the *Data Booklet* is relevant to this question. [2]
State how the reactivity of the halogens as oxidising agents varies down the group, and relate this variation to relevant $E^\ominus$ values.

(ii) Describe reactions that illustrate the relative oxidising abilities of chlorine and iodine. Include all relevant observations. [2]

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(b) **(i)** Calcium fluoride is sparingly soluble in water. It has a solubility of 0.00180 g in 100 cm^3 of water at 0 °C.

Write an expression for the solubility product, $K_{sp,}$ for calcium fluoride.

Calculate the K_{sp} for calcium fluoride, stating its units **[2]**

(ii) Use the data in Table **4.1** to calculate a value for the enthalpy change of solution of calcium fluoride. **[2]**

Process	$\Delta H^\ominus$/kJ mol^{-1}
$Ca^{2+}(g) \longrightarrow Ca^{2+}(aq)$	−1579
$F^-(g) \longrightarrow F^-(aq)$	−524
$Ca^{2+}(g) + 2F^-(g) \longrightarrow CaF_2(s)$	−2616

Table 4.1

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(c) Krypton reacts with liquid fluorine in the presence of ultraviolet light to make gaseous krypton difluoride, KrF_2.

$$Kr(g) + F_2(l) \rightarrow KrF_2(g) \text{ .... } \textbf{Reaction (1)}$$
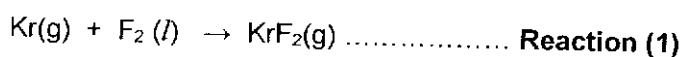
(i) Define the term *bond energy*.   **[1]**

(ii) Use the data in Table **4.2**, together with relevant data from the *Data Booklet*, construct an energy level diagram to calculate the value for the enthalpy change of the above reaction. Show your working.   **[3]**

	value/kJ mol^{-1}
Enthalpy change of vaporisation of fluorine	+ 3.27
Bond energy of Kr—F	+ 46.0

Table 4.2

(iii) The activation energy, E_a, for Reaction (1) is +394 kJ mol^{-1}.

Use all the information above to draw the reaction profile diagram for the formation of $KrF_2(g)$. Label E_a and ΔH_r on the diagram. Assume the reaction proceeds in one step.   **[1]**

24

(d) Carvone is the main active ingredient of the flavouring agent oil of spearmint.
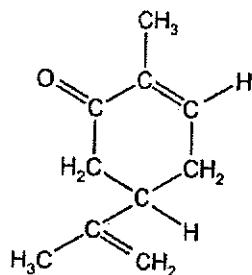
Carvone

Draw the structure of the major product when Carvone reacted with excess of HBr. State how many chiral centre(s) are present in the organic compound. **[2]**

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(e) The compound responsible for the hot taste of chilli peppers is capsaicin, which creates a burning effect on the tongue due to its weak acidic nature.

Its molecular structure can be deduced by the following reaction scheme:

capsaicin
$(C_{18}H_{27}NO_3)$ — **I** boil with H^+ → [aromatic ring with HO, OCH_3 substituents and $CH_2NH_3^+$] **+** **P** $(C_{10}H_{18}O_2)$

II heat with acidified $KMnO_4$

Q $(C_6H_{10}O_4)$ **+** **R** $(C_4H_8O_2)$

III $NC(CH_2)_4CN$

IV $(CH_3)_2CHCH_2OH$
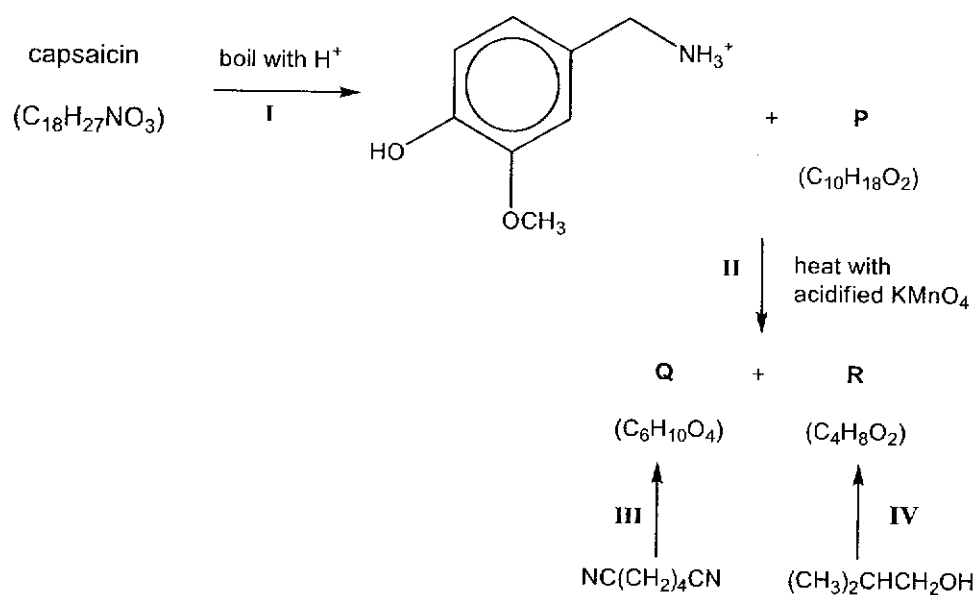
(i) Suggest the functional group present in compound **P** that has reacted with hot acidified $KMnO_4$. **[1]**

(ii) Suggest the reagent and conditions for reaction **IV**. **[1]**

(iii) Name the *type of reaction* in reaction **III**. **[1]**

(iv) Suggest the structures of compound **P** and capsaicin. **[2]**

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[Total: 20 marks]

5 (a) This part of the question is about the elements in Period 3.

The oxides MgO, Al_2O_3 and SiO_2 are all used as refractory materials due to their high melting points.

The last two are major constituents of gemstones, such as rubies, sapphires and amethysts.

(i) If a sample of one of the oxides was provided as a white powder, describe the reactions you could carry out on the powder to determine which of the three oxides it was. Write equation(s) to illustrate the reaction. **[3]**

(ii) Sketch a graph showing the variation of pH across the chlorides of Period 3 elements Na to P when they are added to water. Use relevant equations for $NaCl$, $AlCl_3$, and PCl_5, to show how these chlorides differ in their reactions with water. **[3]**

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(b) The hormone insulin is responsible for regulating the blood glucose level in our body. Partial hydrolysis of insulin gives the following tripeptide:

$$CH_2CH_2CO_2H$$
$$|$$
$$(CH_3)_2CHCH(NH_2)CONHCHCONHCH(CH_3)CO_2H$$
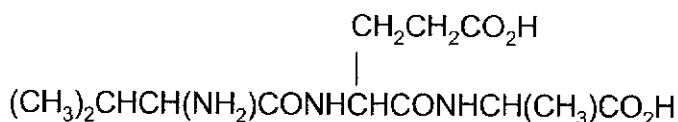
(i) Give the name and displayed formula of the linkage between amino acid residues in insulin. [1]

(ii) What reagents and conditions could you use to hydrolyse this tripeptide into its constituent amino acids? [1]

(iii) Draw the structural formula of the constituent amino acids that are obtained by further hydrolysis of the tripeptide. [2]

(iv) Amino acids exist as *zwitterions* in aqueous solution.
Draw the structural formula of the *zwitterion* formed from one of these amino acids, and write equations to show how it can act as a buffer. [2]

(v) The graph shows the results of an investigation of the initial rate of hydrolysis of the tripeptide by the enzyme amylase. In the experiments, the initial concentration of the tripeptide was varied but that of amylase was kept constant.
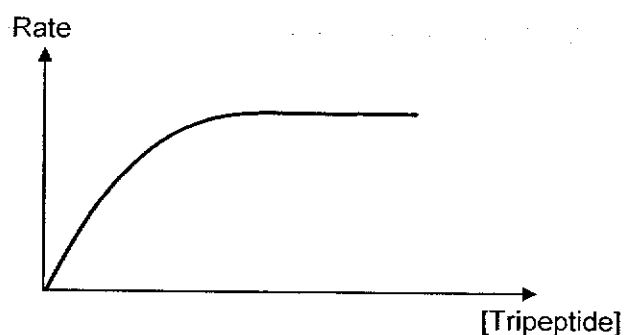
Explain the difference in the rate of hydrolysis at high and low concentrations of the tripeptide. [2]

(c) The following scheme of reactions illustrates the reactions involving an amino acid to form compound **F**:

$C_6H_5CH_2Cl + H_2N\text{-}CH(CH_3)\text{-}CO_2H$

step I $\downarrow$

$C_6H_5CH_2NH\text{-}CH(CH_3)\text{-}CO_2H$

step II $\downarrow$

$C_6H_5CH_2NH\text{-}CH(CH_3)\text{-}COCl$

step III $\downarrow$ $H_2NCH_2CO_2H$

$C_6H_5CH_2NH\text{-}CH(CH_3)\text{-}CO\text{-}NHCH_2CO_2H$

step IV $\downarrow$

$C_6H_5CH_2NH\text{-}CH(CH_3)\text{-}CH_2\text{-}NHCH_2CH_2OH$

F
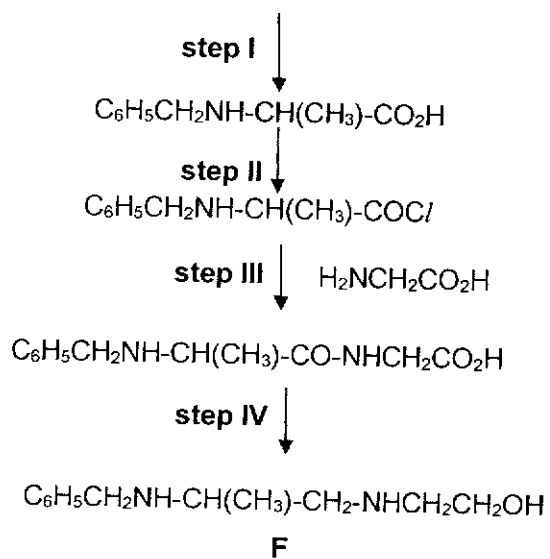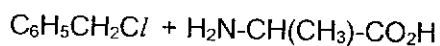
(i) What *types of reaction* is step I and step IV? [1]

(ii) Suggest suitable reagents for step II and IV. [2]

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(d) *Lidocaine* and *Procaine* are two common local anaesthetics used in dental surgeries and minor operations. Table **5.1** shows their pK_b values. You may assume they are both monobasic.

Compound	pK_b
Lidocaine	6.1
Procaine	5.1

Table 5.1

(i) A sample of *Procaine* was found to have higher electrical conductivity than a sample of *Lidocaine* of equal concentration.

Explain this observation with reference to the pK_b values. **[1]**

(ii) Hydrochloric acid is added to 1 dm³ of a 0.025 mol dm⁻³ *of Lidocaine* solution to produce a buffer solution. Determine the volume of 0.500 mol dm⁻³ HC*l* required to form a buffer solution of pH 7.5. **[2]**

[Total 20 marks]

Additional Answer Space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

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