H

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

CLASS

TUTOR'S NAME

CHEMISTRY **9729/03**

Paper 3 Free Response **14 September 2021**

2 hours

Candidates 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 an 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 questions.

Section B
Answer **one** question.

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

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	
1	**/22**
2	**/18**
3	**/20**
4	**/20**
5	**/20**
Total	**/80**

This document consists of **31** printed pages..

[Turn Over

Section A

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

1 Phosgene, $COCl_2$, is a colourless gas that has the odour of freshly cut hay. It is a major industrial chemical used to make plastics and pesticides. It is highly toxic and was used extensively during World War I as a choking agent.

(a) (i) Draw a dot-and-cross diagram of the phosgene molecule. [1]

(ii) The actual value of the Cl-C-Cl bond angle is 117 °. Using the principles of the VSEPR theory,

- deduce the expected Cl-C-Cl bond angle.
- compare the two values and suggest a reason for the discrepancy. [2]

(b) As phosgene is highly toxic and its odour may not be noticeable at low concentration, reactions involving phosgene must be carried out in a fume hood equipped with a method of monitoring phosgene concentration.

A simple method is to tape phosgene indicator papers, which changes colour upon exposure to gaseous phosgene, to the fume hood sill. The detection limit of one such indicator paper is 1.87 ppm (by volume). One part per million (ppm) denotes one part per 10^6 parts.

Calculate the concentration of phosgene, in mg dm^{-3}, that can be detected in the air by the phosgene indicator paper at room temperature and pressure. [2]

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(c) Phosgene can be converted into urea, $CO(NH_2)_2$, which can be used to remove oxides of nitrogen from the flue gases of power stations where hydrocarbon fuels are burnt.

(i) After conversion, urea only acts as a base when reacted with strong acids. Suggest an explanation. [1]

(ii) Explain why it is important to remove oxides of nitrogen from the flue gases. [1]

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(d) Phosgene was first prepared in 1811 by the photochemical reaction of carbon monoxide and chlorine in the presence of a catalyst at 150 °C.

$$CO(g) + Cl_2(g) \longrightarrow COCl_2(g) \qquad \Delta H_{reaction}$$

(i) Calculate a theoretical value for $\Delta H_{reaction}$ using *bond energies* from the *Data Booklet*. [2]

(ii) The actual value of $\Delta H_{reaction}$ is −107.6 kJ mol^{-1}. The two values are different as bond energies used in calculation of the theoretical value in **(d)(i)** are average values.

Identify which bond accounts for why the actual value is more exothermic. Explain your reasoning. [1]

(iii) By considering the entropy change during the preparation of phosgene, suggest how the Gibbs free energy change of the reaction varies with temperature. Hence, justify **fully** the conditions used for the reaction. [3]

(iv) The mechanism for the formation of phosgene is thought to involve three steps:

$$Cl_2 \overset{\text{Fast}}{\rightleftharpoons} 2\,Cl$$

$$Cl + CO \overset{\text{Fast}}{\rightleftharpoons} COCl$$

$$COCl + Cl_2 \overset{\text{Slow}}{\rightleftharpoons} COCl_2 + Cl$$

Suggest the rate equation for the formation of phosgene that would result from the given mechanism. [1]

(v) Define, with the aid of an equation, the term *standard enthalpy change of formation* of **liquid** phosgene. [2]

(vi) Use the following data, together with actual value of $\Delta H_{reaction}$ given in **(d)(ii)**, to calculate the standard enthalpy change of formation of **liquid** phosgene.

	value / kJ mol^{-1}
Standard enthalpy change of formation of CO(g)	−110.5
Standard enthalpy change of vaporisation of $COCl_2$(l)	+33.3

[2]

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(e) Describe the behaviour of the following oxides with the following bases and write equations for the reactions that occur. Explain **fully** whether the behaviour of the oxides is what you would expect from the position of the element in the Periodic Table.

- Al_2O_3 and NaOH
- P_4O_{10} and $Ba(OH)_2$

[4]

[Total: 22]

2 (a) (i) Use relevant E^{θ} values from the *Data Booklet* to describe the relative reactivity of the halogens as oxidising agents. [2]

(ii) Describe a reaction that illustrates the relative oxidising abilities of two halogens of your choice. [1]

(b) The volume of 0.40 mol of hydrogen chloride gas was measured at a temperature of 25 °C when various pressures were applied. The following results were obtained.

Table 2.1

pressure, *p* / atm	V / dm^3	pressure x volume, *p*V / atm dm^3
5	1.924	9.62
10	0.926	
15	0.592	

(i) Calculate the volume of 0.40 mol of an ideal gas at a temperature of 25 °C and at a pressure of 12 atm. [1]

(ii) Complete the third column in Table 2.1.

- Use your values of *p*V to estimate the value of *p*V when *p* = 12 atm.
- Use your estimated value of *p*V to calculate the value of V when *p* = 12 atm. [2]

(iii) Suggest an explanation for the difference in the values of *p*V you have obtained in **(b)(i)** and **(b)(ii)** in terms of the properties of HC*l* molecules. [1]

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(c) Hydrogen halides usually react with alkenes via an electrophilic addition mechanism. However, in the presence of organic peroxides, R-O-O-R, hydrogen bromide reacts with alkenes via a different mechanism, free radical addition.

The reaction is initiated by R – O ● free radicals produced by the breaking of an oxygen – oxygen bond in the peroxide. These free radicals then extract a hydrogen atom from a hydrogen bromide molecule to produce bromine radicals. The two initiation steps are shown below.

Initiation steps:

$$R-O-O-R \longrightarrow 2R-O\bullet$$

$$R-O\bullet + HBr \longrightarrow R-O-H + Br\bullet$$

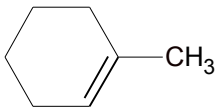
The bromine radical formed in the initiation step goes on to react with propene, forming $\bullet CH(CH_3)CH_2Br$ radicals first before forming 1-bromopropane as one of the final products.

(i) Outline the subsequent steps of the free radical addition mechanism, using curly arrows to indicate the movement of electrons. [3]

(ii) The reaction starts when the reactants are exposed to bright light. Suggest why the reaction continues with increasing rate after the brief exposure to the bright light has stopped. [2]

(iii) Unlike HBr, HC*l* does not react with alkenes via free radical addition under the same conditions. Suggest a reason why. [1]

(iv) Give the structural formula of all the organic products formed when 1-methylcyclohexene undergoes free radical addition with HBr in the presence of peroxide radicals.



1-methylcyclohexene

[2]

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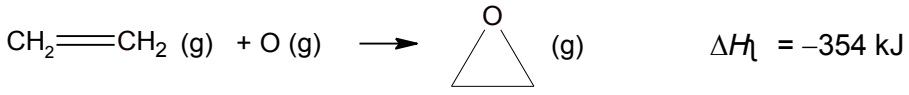
[Turn Over

(d) In another addition reaction, ethene reacts with oxygen atoms to form epoxyethane.



epoxyethane

Draw an energy level diagram to determine the enthalpy change of formation of epoxyethane, given that the standard enthalpy change of formation of ethene is +52 kJ mol^{-1}.

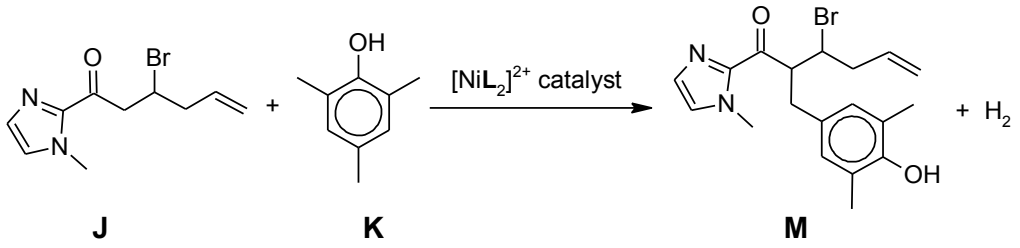
Your energy level diagram should include relevant data from the *Data Booklet*.

[3]

[Total: 18]

[Turn Over

3 In recent years, research in the field of organic electrosynthesis has received considerable attention. Organic electrosynthesis involves the synthesis of organic compounds in an electrolytic cell via anodic oxidation and cathodic reduction. An example of such organic electrosynthesis reaction is shown below.



J **K** **M**

Fig. 3.1 shows three metals **F**, **G** and **H** connected in pairs in two electrochemical cells under standard conditions.

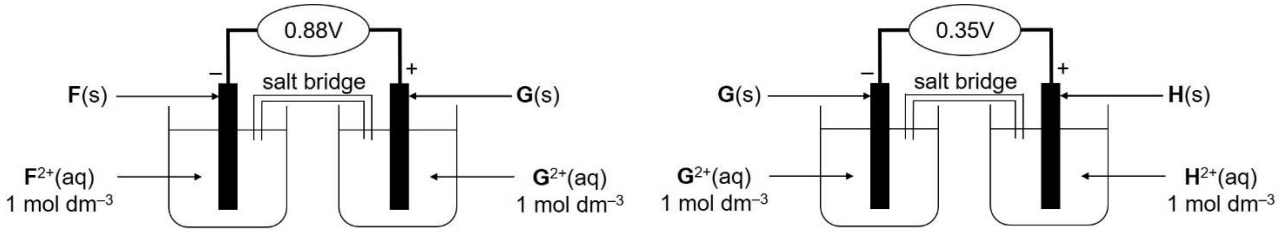


Fig. 3.1

Metals **F** and **H** were subsequently connected in an electrochemical cell. It is used to generate electrical voltage for an electrolytic cell used for organic electrosynthesis as shown in Fig. 3.2.

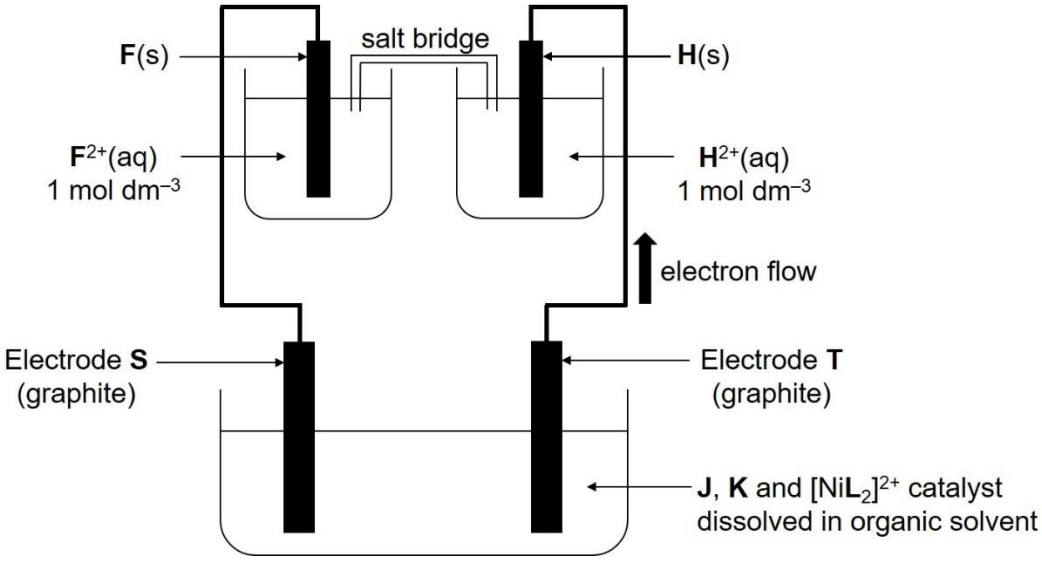


Fig. 3.2

(a) **(i)** With reference to Fig. 3.1, arrange $\mathcal{E}(\mathbf{F}^{2+}/\mathbf{F})$, $\mathcal{E}(\mathbf{G}^{2+}/\mathbf{G})$ and $\mathcal{E}(\mathbf{H}^{2+}/\mathbf{H})$ from the least positive to the most positive. [1]

(ii) Calculate the standard cell potential between metals **F** and **H** in the electrochemical cell used in Fig. 3.2. Write the overall equation, including state symbols. [2]

(iii) Calculate the standard Gibbs free energy change, ΔG , per mole of metal **H**. [1]

(b) Fig. 3.3 shows a series of steps for the organic electrosynthesis occurring at electrode **T** in Fig. 3.2.

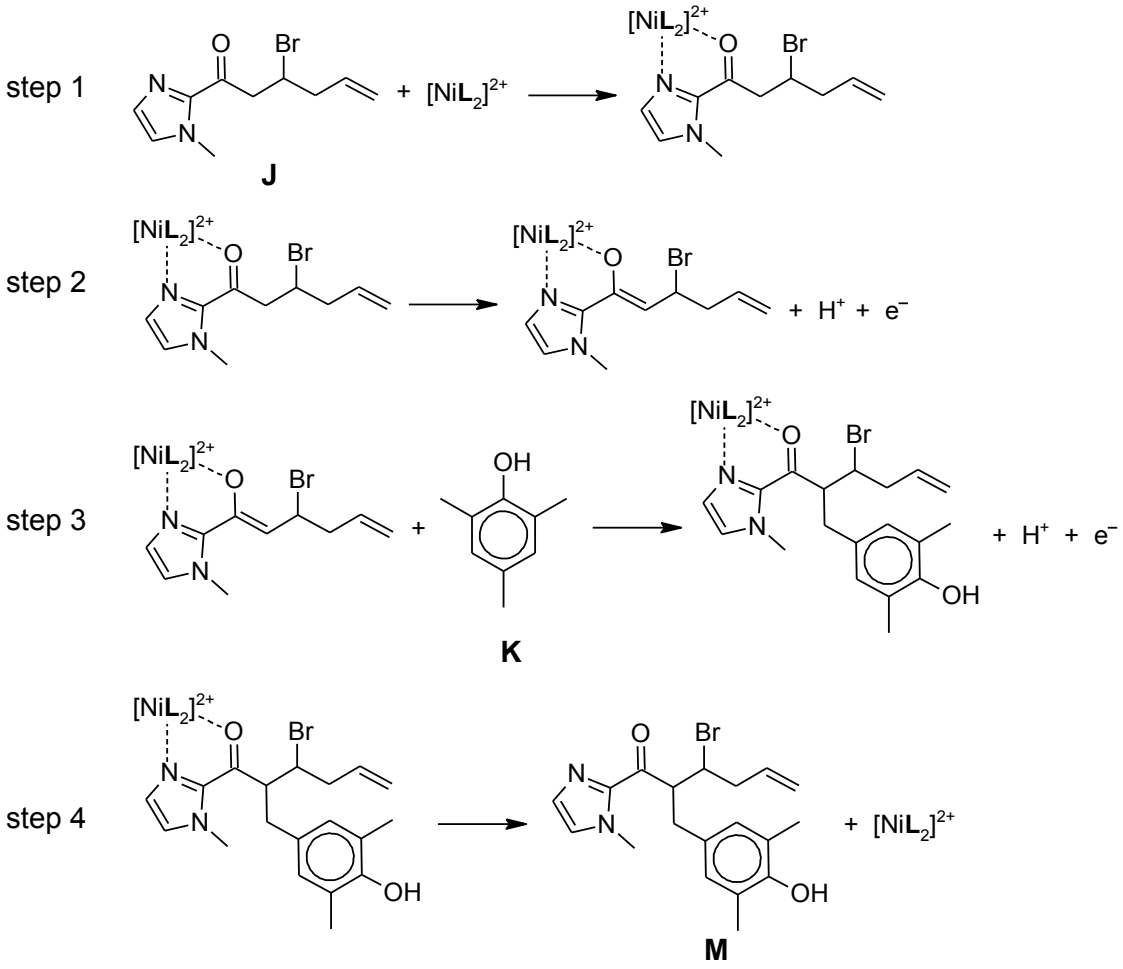


Fig. 3.3

(i) Using Fig. 3.3, suggest the half equation for the reaction occurring at electrode **T**. [1]

Ohm's law states that the current passing through a conductor between two points is directly proportional to the cell electrode potential across the two points. Introducing a proportionality constant, the mathematical equation that describes this relationship is as follows:

$$V = I \times R$$

where V is the cell electrode potential measured in volts (V)
I is the current measured in amperes (A)
R is the resistance measured in ohms (Ω)

(ii) Assuming the circuit obeys Ohm's law and the total resistance is 3.62 Ω, use your answer in **(a)(ii)** to calculate the current that passes through the electrolytic cell used for the organic electrosynthesis. [1]

(iii) The reaction occurring at electrode **S** is as follow: $2H^+ + 2e^- \rightarrow H_2$.
Determine the volume of gas evolved at electrode **S** when the electrolytic cell is run for 2.5 hours under standard temperature and pressure. [2]

[Turn Over

(c) Copper minerals often contain copper sulfide mixed with the sulfides of silver and zinc. After roasting in air to produce the oxides and reduction to the crude metal with carbon, the solid impure copper is purified by electrolysis.

(i) Suggest two **main** changes that must be done to the setup shown in Fig. 3.2 for the purification of copper by electrolysis. [2]

(ii) With reference to the *Data Booklet*, describe the electrode reactions that take place during the electrolysis and explain in detail how each of the two impurity metals is removed. [3]

(d) Compound **M** can be converted to compound **Q**, via intermediates **N** and **P**, as shown in Fig. 3.4.

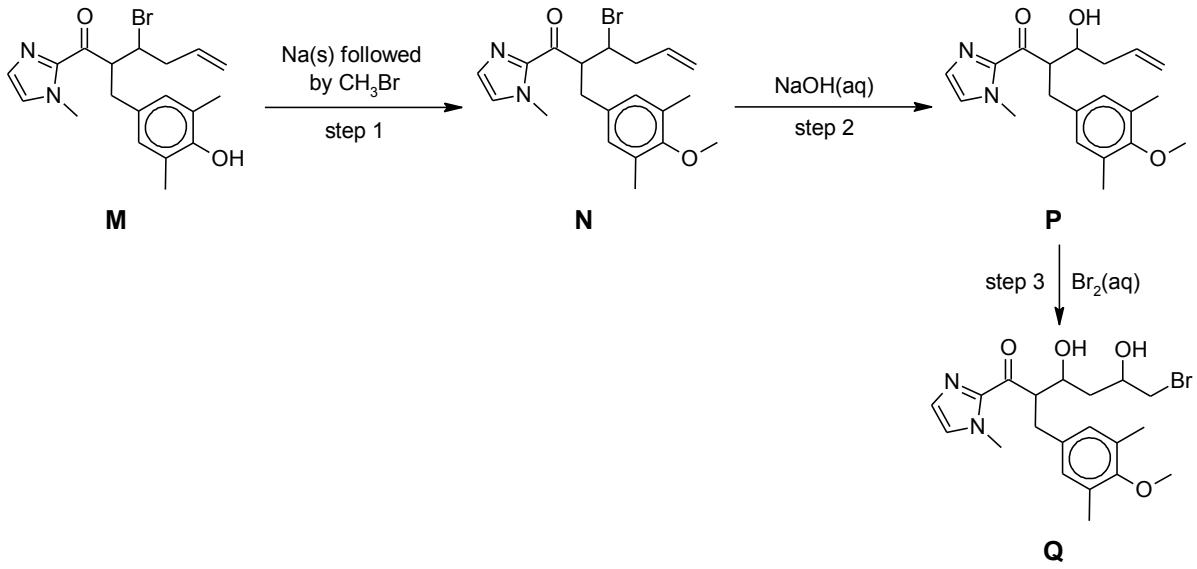


Fig. 3.4

The reaction in step 2 was investigated with other nucleophiles and the results were tabulated in Table 3.1.

Table 3.1

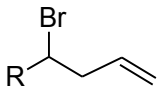
nucleophile	relative rate
NaOH	1.00
C_2H_5ONa	0.99
C_2H_5SNa	0.99
C_6H_5ONa	1.01

(i) Define the term *nucleophile*. [1]

(ii) Arrange the nucleophiles in order of increasing strength. [1]

(iii) Deduce the rate equation for the reaction in step 2. [1]

(iv) Hence, describe the mechanism of the reaction in step 2.

You may use  to represent compound **N**. In your answer, you should show all charges, lone pairs and show the movement of electrons by curly arrows. [2]

Compound **P** undergoes electrophilic addition with aqueous bromine to give compound **Q**. The first step of electrophilic addition involves the alkene being attacked by Br_2 to form a stable carbocation. However, no such reaction involving H_2O is possible.

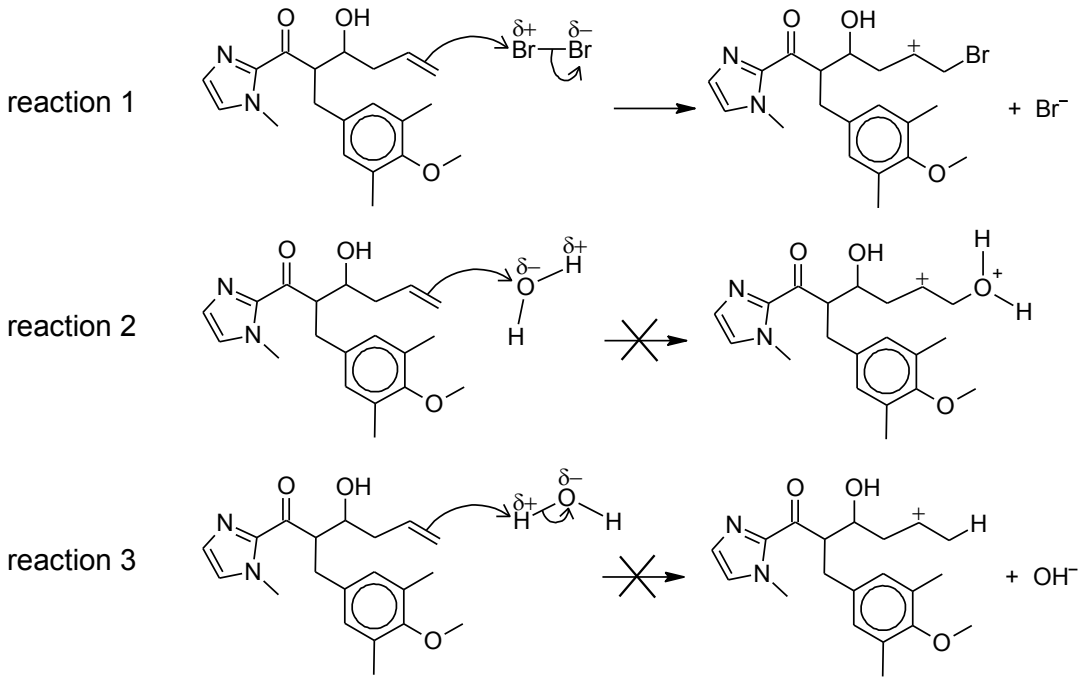


Fig. 3.5

(v) Suggest a reason to explain why reaction 2 cannot occur. [1]

(vi) With reference to the *Data Booklet*, suggest a reason to explain why reaction 1 occurs but not reaction 3. [1]

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Section B

Answer **one** question from this section.

4 Carbon is one of the most abundant elements on Earth. While it is found mainly in organic substances, carbon does exist in inorganic compounds such as carbon dioxide, carbonates and hydrogencarbonates.

(a) In order to determine the pH titration curve, a student titrated 25.0 cm^3 of 0.100 mol dm^{-3} HCO_3^-(aq) against 0.100 mol dm^{-3} of HC*l*(aq).

The K_b for HCO_3^- is 2.34 x 10^{-8} mol dm^{-3} at 298 K.

(i) Calculate the pH of the solution before the addition of HC*l*(aq). [2]

(ii) Calculate the pH of the solution at the equivalence point. [2]

(iii) Calculate the pH of the solution after 37.5 cm^3 of HC*l*(aq) was added. [2]

(iv) Using your answers from **(a)(i)** to **(a)(iii)**, sketch the pH titration curve. Label the various key points on the curve. [2]

[Turn Over

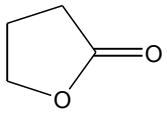
(b) A neutral compound **P** has molecular formula, $C_{15}H_{20}O_3NCl$. When **P** is refluxed with aqueous sodium hydroxide, three compounds **Q**, **R** and **S** are obtained.

Upon analysis, **Q** is found to be a straight–chain molecule having a relative molecular mass of 59.0, and its composition by mass is as follows:

61.0% C, 15.3% H, 23.7% N

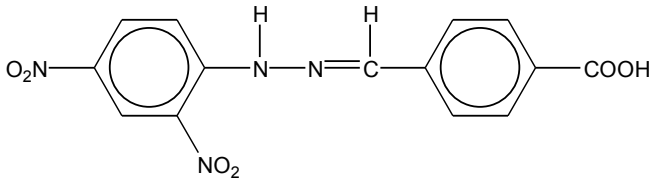
When **Q** is treated with excess iodomethane, **T** is formed. **T** has a relative formula mass of 229 and gives a yellow precipitate immediately when treated with aqueous silver nitrate.

R has the molecular formula $C_4H_7O_3Na$. Upon acidification, **R** yields **U**. **U** is also obtained when **P** is refluxed with dilute sulfuric acid. Heating **U** with a small amount of concentrated sulfuric acid produces a compound known as gamma–butyrolactone, which has the following structure:



gamma–butyrolactone

S has the molecular formula $C_8H_7O_3Na$. Upon addition of acidified potassium dichromate(VI) and heating with immediate distillation, **S** yields **V**. Treating **V** with 2,4–dinitrophenylhydrazine gives an orange precipitate which has the following structure:



(i) Determine the empirical and molecular formula of **Q**. Show your working clearly. [2]

(ii) Suggest the structures of **P** to **V**. [7]

Compound **U** can be used as a precursor of 4–aminobutanoic acid, which is also known as GABA (Gamma–AminoButyric Acid). GABA is the chief inhibitory neurotransmitter in the central nervous system and in the human retina. It also regulates muscle tone and other functions.

(iii) Both GABA and **U** have similar relative molecular masses. However, GABA is found to have a significantly higher melting point than **U**. Explain. [3]

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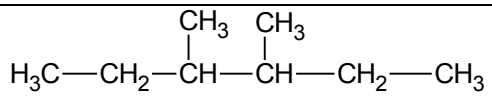
[Total: 20]

5 **(a)** The term "octane rating" is often used in the petroleum industry for rating the ability of octane's various branched isomers in reducing engine knock in vehicles.

Compounds **A**, **B**, **C** and **D** are isomers of the hydrocarbon octane, C_8H_{18}.
Table 5.1 below shows the boiling points and data relating to the optical activity of these compounds.

Table 5.1

structure	boiling points / ^oC	number of chiral centres	optical activity
isomer **A**	119	1	Yes
 isomer **B**	118	2	No
isomer **C**	110	1	Yes
isomer **D**	107	0	No

(i) Suggest why isomer **B** has no optical activity even though it has 2 chiral centres. [1]

(ii) Draw the structural formula of each of the isomers **A**, **C** and **D**. [3]

(iii) Explain in terms of structure and bonding, why isomers **A** to **D** have different boiling points. [2]

(iv) Controlled chlorination of isomer **B** in the presence of *UV* light produces four different isomers of formula $C_8H_{17}Cl$. Draw the skeletal formula of each of the four isomers and give the mole ratio in which they are formed. [2]

(v) Monochlorination of isomer **B** in **(a)(iv)** produces many by-products, one of which has the formula $C_{16}H_{34}$. Assuming that the carbon atoms in isomer **B** do not rearrange themselves during the reaction, draw the structural formula of the isomer of $C_{16}H_{34}$ that has the lowest boiling point. [1]

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(b) The following statements involve the chemistry of Group 1 elements.

(i) "Lithium is only slowly attacked by water at 25 ^{o}C, whereas, with water, sodium reacts vigorously, potassium inflames, and rubidium and caesium reacts explosively". Explain the difference in reactivity of the Group 1 metals with water. [2]

(ii) "Lithium and sodium metals are obtained by electrolysis of their molten salts. However this method is not suitable for obtaining potassium, rubidium and caesium". Explain this observation in terms of the structure and bonding of the different metals. [2]

(iii) "Lithium is the only Group 1 metal which produces the oxide, Li_2O, when heated in oxygen. Sodium, potassium, and the other Group 1 metals produce peroxides such as Na_2O_2 and superoxides such as KO_2 when heated in oxygen."
Explain the difference in products formed. [2]

(c) **W** is a compound of a Group 2 element **M**. When **W** was treated with dilute hydrochloric acid, a colourless gas **X** was evolved. On bubbling **X** through a small amount of limewater, a precipitate **Y** was formed, but passage of further gas resulted in a clear solution **Z**.

On strong heating, 1.9735 g of **W** decomposed, giving 1.5334 g of its oxide, which is a white solid. The white solid was dissolved in water and made up to 250 cm^3 in a standard flask. 25.0 cm^3 aliquots were titrated with acid and required 20.30 cm^3 of 0.0985 mol dm^{-3} hydrochloric acid.

(i) Identify compounds **X, Y** and **Z**. [2]

(ii) Calculate the relative molecular mass of **W**. [2]

(iii) Consider the identity of **W** and calculate the relative atomic mass of the Group 2 element **M** in **W**. Hence identify **M**. [1]

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Additional answer space

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