ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY H2

9729/03

Paper 3 Free Response

2 September 2019
2 hours

Candidates answer on separate paper.

Additional Materials: Cover Page
Answer Paper
Insert

READ THESE INSTRUCTIONS FIRST

Write your index number and name, form class and tutorial 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.

Section A
Answer **all** questions.

Section B
Answer **one** question.

Start each question on a new page of writing paper.
Fasten the insert in front of all writing paper at the end of the examination.

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.

This document consists of **14** printed pages.

Section A

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

1 (a) *Use of the insert is necessary for this question.*
Fasten the insert in front of all writing paper at the end of the examination.

An iodoalkane, RI, is hydrolysed by aqueous sodium hydroxide. The results obtained from two experiments are plotted on the insert. In each experiment, the overall [NaOH(aq)] remained virtually constant at the value given beside each graph.

(i) Use the graphs on the insert to determine the following. Show all workings clearly.

I Use the half-life method to deduce the order of reaction with respect to the iodoalkane.

II Use the initial rates method to deduce the order of reaction with respect to sodium hydroxide.

III Construct a rate equation for the reaction and use it to calculate a value for the rate constant. Include its units. [7]

(ii) Hence draw a fully labelled energy profile diagram of the reaction. [3]

(b) Silver(I) iodide and iodine are two solids which have low solubility in water. However when both are mixed together with water and left to stand, they dissolve completely to give a coloured solution of silver(I) triiodide.

(i) State the expected colour of the silver(I) triiodide solution. [1]

(ii) Write three relevant equilibria equations and use them to explain how the two solids can completely dissolve when mixed with water. [3]

(c) Another triiodide compound, nitrogen triiodide, NI_3 is a simple covalent molecule that is very sensitive to shock and will decompose rapidly. A touch of a feather or even alpha particles from radioactive decay can trigger an explosion.

$$2NI_3(s) \longrightarrow N_2(g) + 3I_2(g) \qquad \Delta H = -290 \text{ kJ mol}^{-1}$$

76.5 kJ mol^{-1} of energy is needed to convert solid NI_3 to gaseous NI_3.

Use the above information and relevant information from the *Data Booklet* to calculate the N–I bond energy. [2]

(d) Alpha particles, $^{4}_{2}He^{2+}$ are produced from the radioactive decay of certain isotopes. An example of one is from the decay of Americium-241.

$$^{241}_{95}Am \rightarrow {}^{4}_{2}He^{2+} + \mathbf{M}$$

(i) Use the *Data Booklet* to identify species **M** that is formed. [1]

(ii) Calculate the angle of deflection for **M** in a uniform electric field if the angle of deflection for $^{4}_{2}He^{2+}$ is +7.11°. [1]

Americium is often used in smoke detectors as the compound AmO_2 and is made from the thermal decomposition of americium(III) ethanedioate, $Am_2(C_2O_4)_3$.

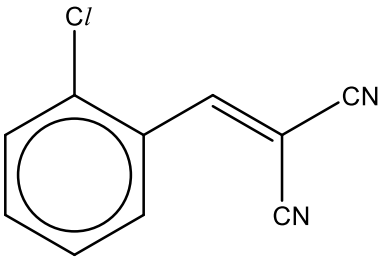
$$Am_2(C_2O_4)_3 \longrightarrow 2AmO_2 + 4CO + 2CO_2$$

(iii) Explain why the thermal decomposition is a redox reaction in terms of oxidation state changes. [2]

[Total: 20]

2 (a) On 12 June 2019, Hong Kong police fired tear gas into the crowds as many took to the streets to protest against a proposed extradition Bill.

The active compound in tear gas is 2-chlorobenzalmalononitrile.

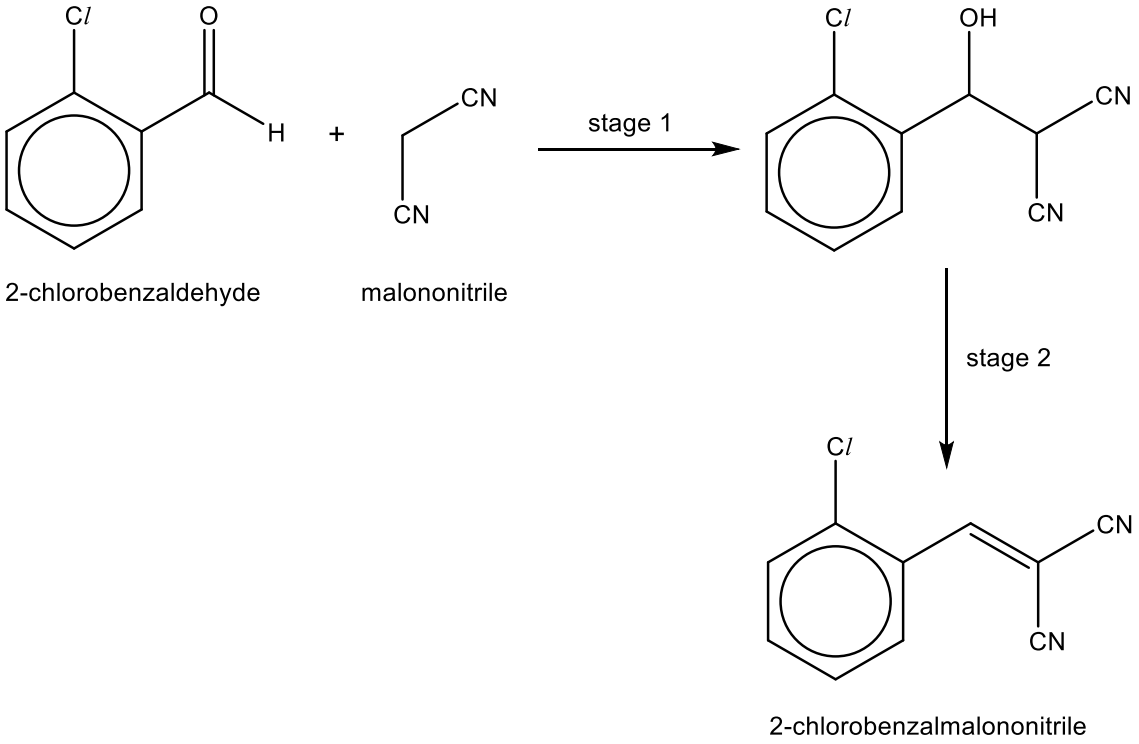


2-chlorobenzalmalononitrile

2-chlorobenzalmalononitrile is a solid at room temperature and is dispersed as an aerosol dissolved in a suitable organic solvent, typically dichloromethane, CH_2Cl_2. Its effects are felt when the solvent evaporates in air and the dry powder touches the eyes, nose and mouth.

(i) Suggest, with reasoning, two physical properties that make dichloromethane a suitable solvent. [2]

2-chlorobenzalmalononitrile can be synthesised via the 2-stage Knoevenagel condensation.



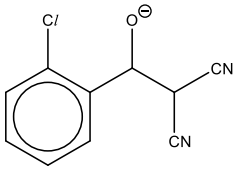
2-chlorobenzaldehyde malononitrile 2-chlorobenzalmalononitrile

(ii) State the type of the reaction in stage 2. [1]

(iii) Instead of purchasing malononitrile as a starting reagent, it can be made from dichloromethane.

Suggest the reagent and conditions needed to convert dichloromethane to malononitrile. [1]

The following 3-step mechanism illustrates stage 1.

- Malononitrile is deprotonated by a weak base, R_2NH to form its conjugate base, $(NC)_2CH^-$.
- The conjugate base of malononitrile undergoes nucleophilic addition with 2-chlorobenzaldehyde to give 

as an intermediate.
- The conjugate acid of R_2NH is deprotonated by the intermediate.

(iv) Describe the 3-step mechanism illustrated above.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [3]

(v) Suggest another role of the weak base, R_2NH. [1]

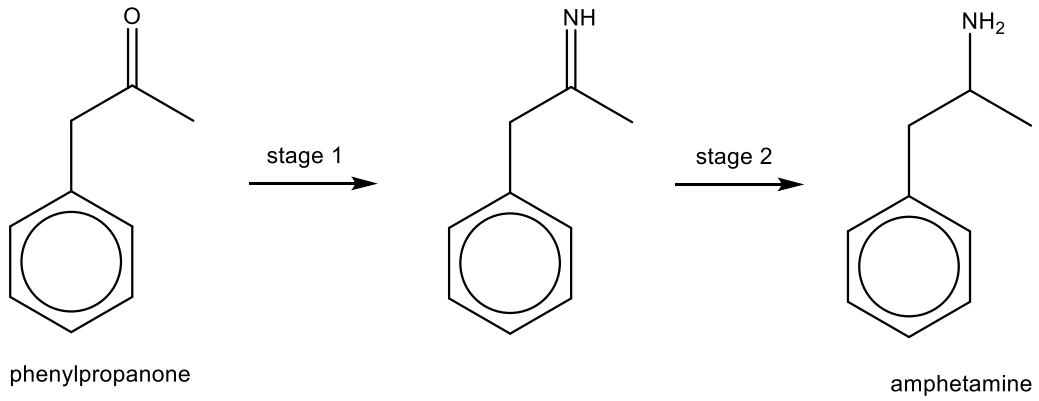
(vi) Compare, and explain, the relative acidities of dichloromethane and malononitrile. [2]

(vii) Draw the **only two** organic products formed when 2-chlorobenzalmalononitrile is heated with acidified potassium manganate(VII). [2]

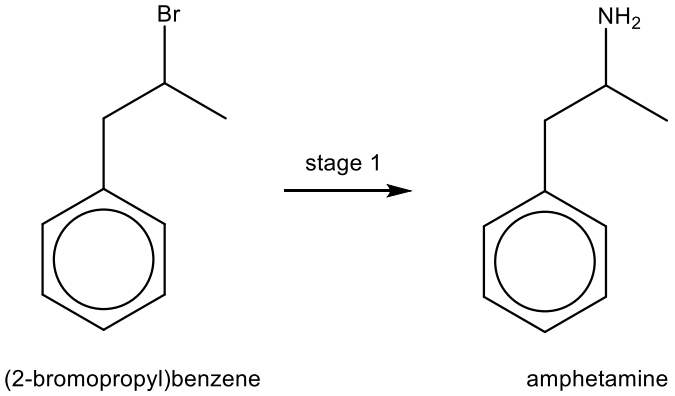
(b) During World War II, amphetamine pills were issued to the German army as they promoted alertness and self-confidence while reducing pain, hunger and the need for sleep.

Study the two methods of synthesis and answer the questions below.

Method 1



Method 2



(i) State the reagent used in stage 1 for both methods of synthesis. [1]

(ii) One would think that Method 2 would give better yield of amphetamine during synthesis since it only involves one stage as compared to two stages in Method 1, but this is not true.

Suggest why the yield of amphetamine via Method 2 would be poor. [1]

(iii) Only half of the product formed via Method 1 was biologically active in the body.

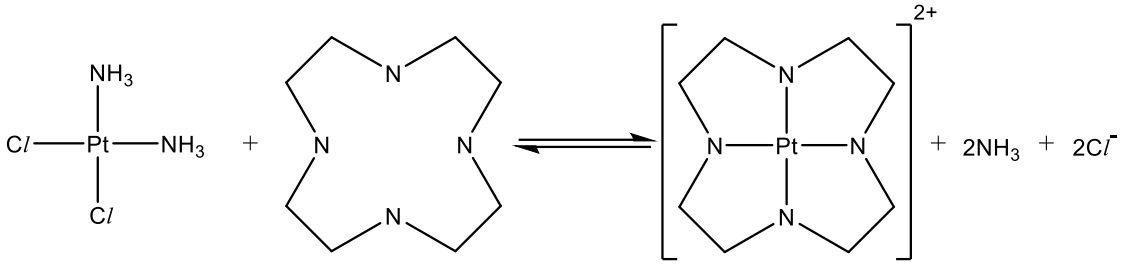
Account for this observation. [2]

(iv) Stage 2 of Method 1 employs the use of platinum metal as a catalyst.

State the type of catalysis involved and briefly outline the stages involved in the reaction. [3]

(v) Explain why transition metals are useful as catalysts. [1]

(c) Cisplatin is an anti-cancer drug containing a platinum centre and appears as a light yellow powder. When cisplatin is dissolved in water and allowed to react with the cyclen *ligand*, the position of equilibrium lies strongly to the right hand side.



cisplatin cyclen

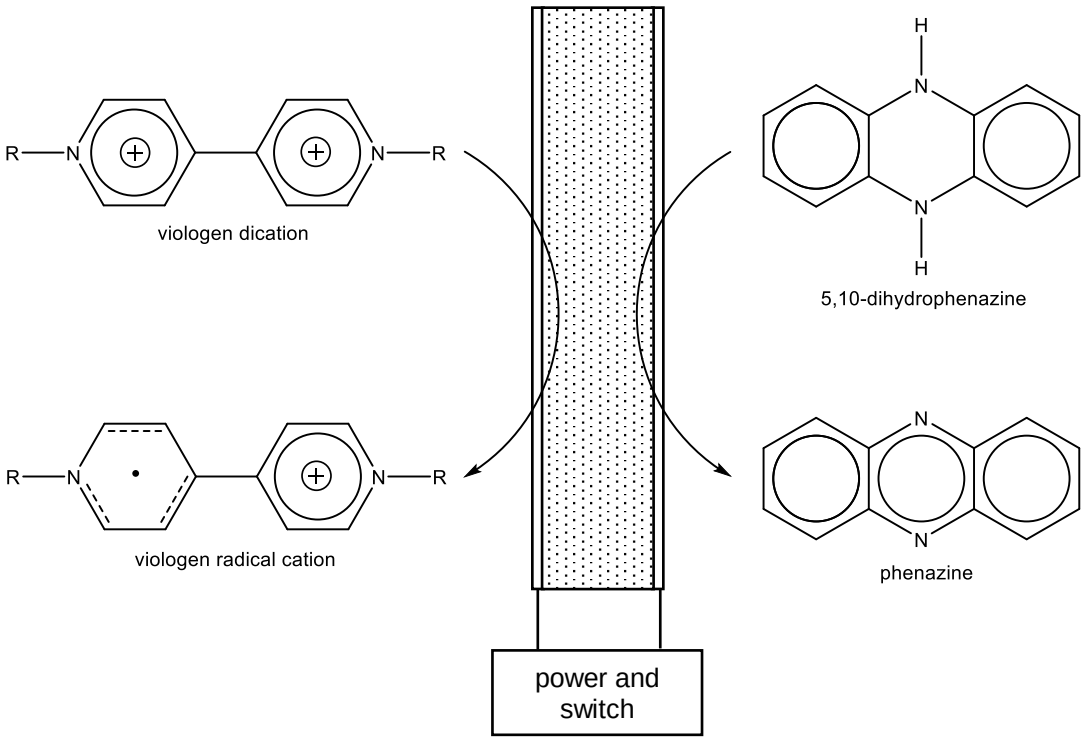
(i) Define the term *ligand*. [1]

(ii) Suggest signs for the enthalpy change of reaction and entropy change of reaction for the forward reaction, and comment on the spontaneity of the reaction across different temperatures. [2]

(iii) Explain why transition metal compounds are coloured. [2]

[Total: 25]

3 (a) Boeing 787-9 Dreamliners are equipped with electronically dimmable windows. When a constant current is applied, electrochemical reactions happen within a panel and the conversion of colourless viologen dication to viologen radical cation forms an intense dark purple that shields out sunlight. A simplified diagram together with the chemical changes is shown.



The viologen dication and phenazine are aromatic species. Hückel's rule states that planar cyclic species with 4n+2 pi electrons, where n = 0, 1, 2 ..., are considered aromatic.

(i) State the hybridisation of the nitrogen atoms in the viologen dication. [1]

(ii) State the number of pi electrons in phenazine. [1]

(iii) State the electrode at which the conversion of 5,10-dihydrophenazine to phenazine occurs. [1]

(iv) Write the half-equation for the reaction of 5,10-dihydrophenazine to phenazine in alkaline medium. You may write the names of both compounds respectively. [1]

(v) 0.0300 g of 5,10-dihydrophenazine is finely coated on to one side of the panel.

Calculate the time needed to react all of the coated 5,10-dihydrophenazine to completely darken a window panel, given that a constant current of 0.150 A is supplied. [4]

(b) It is mandatory for all aircrafts to provide an inflatable life vest for every passenger. One particular model of life vests uses a rapid inflation system of compressed CO_2 in a canister.

A student read that the canisters typically pack 11.0 g of CO_2 and commented that the amount of CO_2 present will inflate a life vest fully to 6.00 dm^3 in capacity.

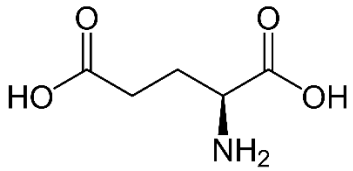
(i) Show how the student obtained 6.00 dm^3 as the capacity of the life vest and state the assumption made in the calculation. [2]

(ii) State two assumptions of the ideal gas law which allowed the student to make the calculations. [2]

(c) Passengers on planes often find that they are more drawn to *umami*-rich flavours as the sweet and salty tastes are dulled due to changes in altitude.

Monosodium glutamate (MSG) is one compound responsible for providing *umami* flavouring and it is the monosodium salt of glutamic acid.

The pK_a values associated with glutamic acid are 2.19, 4.25 and 9.67.



glutamic acid

(i) Draw the structure of glutamic acid at pH 1 and assign the three pK_a values. [2]

(ii) Draw the structure of monosodium glutamate. [1]

[Total: 15]

Section B

Answer **one** question from this section.

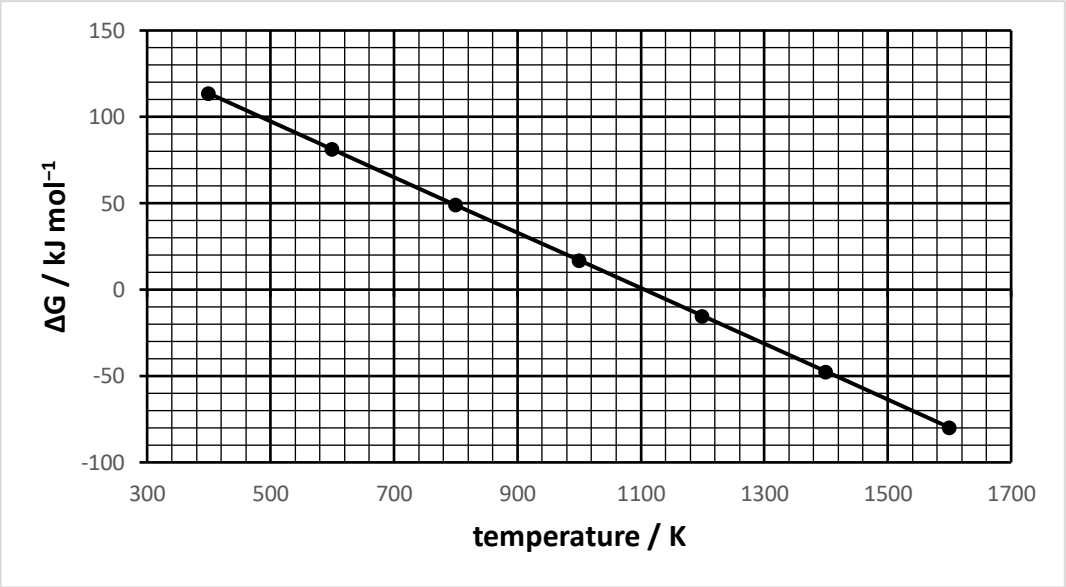
4 (a) The thermal decomposition reactions for calcium ethanoate and calcium methanoate are given as follows:

$Ca(HCOO)_2 \rightarrow CaCO_3 + HCHO$

$Ca(CH_3COO)_2 \rightarrow CaCO_3 + CH_3COCH_3$

Predict the organic product, other than propanone and methanal, when a mixture of calcium methanoate and calcium ethanoate undergoes thermal decomposition. [1]

(b) The following Ellingham diagram shows the variation of Gibbs free energy change with temperature for the thermal decomposition of calcium carbonate.



(i) State the range of temperatures where solid calcium carbonate would decompose upon heating. [1]

(ii) Calculate the entropy change of the reaction. [1]

(iii) Hence, calculate the enthalpy change of the reaction. [1]

(c) Dolomite consists of $CaCO_3$ and $MgCO_3$ with the formula $CaMg(CO_3)_2$. It can be added to soil or marine aquarium as a pH buffer.

(i) Write a balanced equation for the action of heat on dolomite. [1]

(ii) Each carbonate is heated separately.

Predict and explain the difference in the thermal decomposition temperatures of the two carbonates. [3]

(iii) Explain why Li_2CO_3 decomposes in a similar way compared to these two carbonates. [1]

(d) **(i)** Predict and explain the difference in melting points of calcium oxide and magnesium oxide. [2]

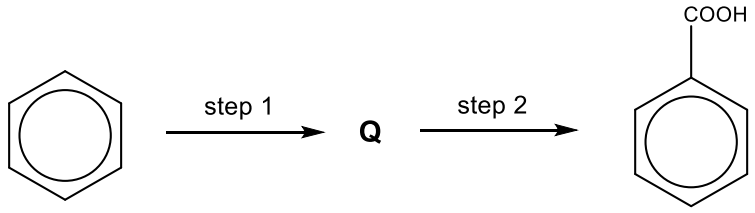
(ii) In power plant or trash incineration plant, large quantities of sulfur dioxide gas are produced. Calcium oxide can be used to remove sulfur dioxide from these exhaust gases in a process called flue-gas desulfurisation.

$$CaO + SO_2 \rightarrow CaSO_3$$

State the type of reaction for the above reaction. [1]

(e) Benzoic acid is an important precursor for the industrial synthesis of many other organic substances. Its salts are also used as food preservatives.

(i) Benzoic acid can be made from benzene by a two-step synthesis.



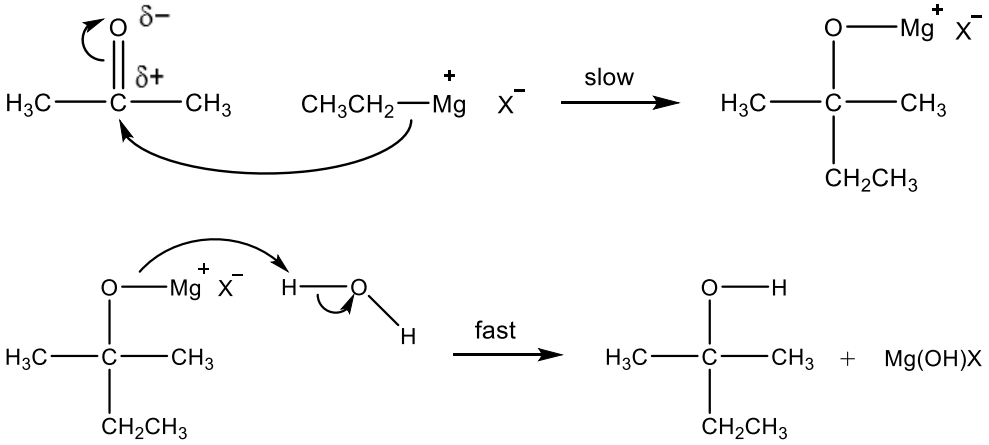
For steps 1 and 2, state the
- reagents and conditions, and
- type of reaction. [4]

(ii) Group 2 elements are known to form organometallic compounds. One example is the Grignard reagent with general formula RMgX. It is produced by reacting an alkyl halide or aryl halide with magnesium.

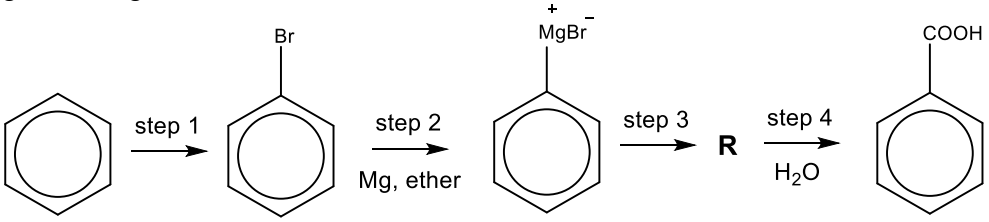
$RX + Mg \rightarrow R–Mg^{+} X^{-}$ where X can be C*l* or Br.

The carbon-magnesium covalent bond is polarised as such; $\overset{\delta-}{C}-\overset{\delta+}{Mg}$.

Grignard reaction is important in making a new C–C bond. The mechanism for the reaction of ethylmagnesium bromide with propanone is shown as follows.



Benzoic acid can also be made from benzene by a four-step synthesis, using the Grignard reagent.



For step 3, state the reagent and intermediate **R**.

For steps 3 and 4, state the type of reaction. [4]

[Total: 20]

5 (a) (i) A compound **X** consists only of carbon, hydrogen and oxygen. During the complete combustion of 4 g of the compound, 8 g of carbon dioxide and 3.273 g of water were produced.

Determine the empirical formula of the compound **X**. [2]

(ii) Another 4 g sample of compound **X** was vaporised at 160 ºC and 101 kPa, and found to occupy a volume of 1620 cm^3.

Determine the relative molecular mass of this compound. [1]

(iii) Hence determine the molecular formula of compound **X**. Show your working clearly. [1]

(b) Butanoic acid is used in the preparation of various esters. These esters have pleasant aromas or tastes. As a consequence, they are used as food and perfume additives.

(i) Biological methods have been developed to produce methane from waste organic matter using bacteria.

Based on the changes in oxidation numbers of carbon, construct a balanced equation for the disproportionation of **aqueous** butanoic acid to produce methane and carbon dioxide only. [1]

(ii) Given the following data,

- Enthalpy change of combustion of butanoic acid is −2184 kJ mol^{-1}.
- Enthalpy change of combustion of methane is −890 kJ mol^{-1}.

Calculate the enthalpy change for the reaction in **(b)(i)** for **liquid** butanoic acid instead of aqueous butanoic acid. [1]

(iii) Given that

$CH_3CH_2CH_2COOH(l) \rightarrow CH_3CH_2CH_2COOH(aq)$ $\Delta H^{\ominus}_{soln} = -16.7$ kJ mol^{-1}

Use you answer in **(b)(ii)** to calculate the enthalpy change of reaction in **(b)(i)**. [2]

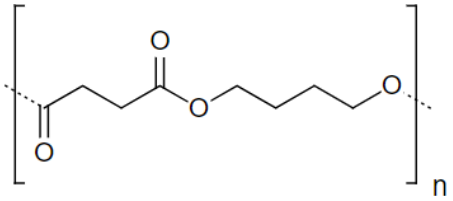
(iv) Butanoic acid boils at 117.7 ºC. During boiling, the liquid phase is at equilibrium with the gas phase.

Calculate the entropy change of vaporisation of butanoic acid, given that the enthalpy change of vaporisation of butanoic acid is +52.0 kJ mol^{-1}. [1]

(v) Trouton's Rule states that the entropy change of vaporisation of many liquids, such as benzene and propanone, is about +88 J mol^{-1} K^{-1}.

Compare and explain the calculated result in **(b)(iv)** in relation to Trouton's Rule. [1]

(c) Polybutylene succinate (PBS) is a polyester used in packaging. It is receiving renewed interest due to increased demand for biodegradable polymers.



Polybutylene succinate

Hydrolysis of PBS produces two monomers **E** and **F**.

E can be reduced to **F**.

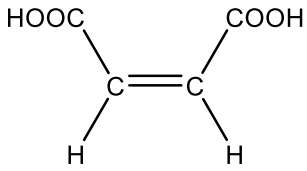
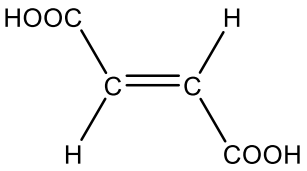
When an organic compound **D**, $C_{10}H_{18}O_2$ is heated with acidified potassium manganate (VII), two products, **E**, $C_4H_6O_4$ and **G**, $C_6H_{12}O$ are formed.

G produces a yellow precipitate on warming with iodine in aqueous sodium hydroxide, and rotates the plane of polarised light.

Upon gentle heating, **E** produces a neutral compound **H**, $C_4H_4O_3$, which does not react with sodium metal or give a precipitate with 2,4-dinitrophenylhydrazine.

Suggest structures for **D** to **H**, and explain the observations described above. [7]

(d) Maleic acid and fumaric acid are two isomers with the same molecular and structural formulae, but with very different physical properties.

	 maleic acid	 fumaric acid
melting point / ºC	130	287
pK_{a_1}	1.9	3.0
pK_{a_2}	6.5	4.5

(i) Give two reasons to explain why maleic acid has a lower melting point than fumaric acid. [2]

(ii) Explain why maleic acid has a lower pK_{a_1} value than fumaric acid. [1]

[Total: 20]

End of Paper