Name:		Centre/Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY 9729/03

Paper 3 Free Response Questions

21 September 2022

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class at the top of this page.
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.

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

For Examiner's Use	
Section A	
1	/20
2	/20
3	/20
Section B	
4 / 5	/20
Total	/80

This document consists of **32** printed pages.

Section A

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

1 (a) Alkynes is a class of organic compounds with the general formula, C_nH_{2n-2}.

(i) Describe what is meant by sp hybridisation with reference to one carbon atom in ethyne, C_2H_2. Draw the hybrid orbitals of the carbon atom. [2]

(ii) Use relevant radius values from the *Data Booklet* to calculate the bond length of a single carbon-hydrogen bond. Show your working clearly. [1]

(iii) Table 1.1 shows the carbon-hydrogen bond length in ethene and ethyne.

Table 1.1

molecule	carbon-hydrogen bond length/ nm
ethene	0.109
ethyne	0.106

With reference to Table 1.1, state which carbon-hydrogen bond is stronger. Use the concept of hybridisation to explain the difference in bond length of the carbon-hydrogen bond between these two molecules. [2]

(iv) Write a balanced equation for the complete combustion of propyne, C_3H_4. [1]

(v) A sample of propyne was burned in excess oxygen. When the remaining gases were passed through aqueous sodium hydroxide, the gas volume was reduced by 0.450 dm^3. Calculate the mass of propyne in the sample.

Assume all gas volumes were measured at r.t.p. [2]

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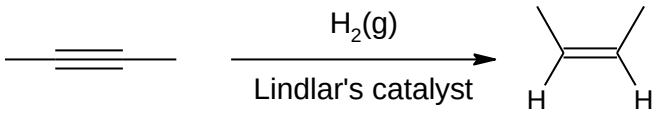
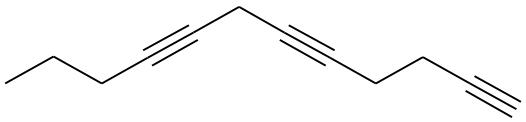
(b) The use of hydrogen gas with Lindlar's catalyst is a selective method which reduces alkynes to form the *cis*-isomer of alkenes.

As an example, but-2-yne, C_4H_6, can be reduced to give *cis*-but-2-ene only.



Suggest the structure of the alkene formed when compound **A** is reduced with the use of Lindlar's catalyst.



A

[1]

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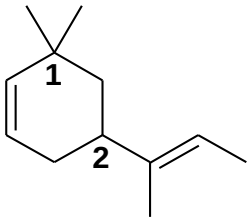
(c) Compound **B** has the following structure.



B

(i) State the isomeric relationship between **B** and your answer in **(b)**. [1]

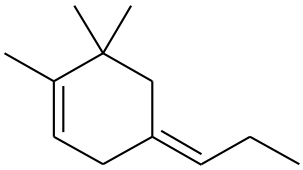
(ii) A student made the following deductions about compound **B**:

"*Since carbon atoms labelled **1** and **2** are chiral and there are two carbon-carbon double bonds, compound **B** has 16 possible stereoisomers."*

Explain where the student has gone wrong in his deductions. [3]

(iii) Draw all the organic products that are formed when compound **B** is heated with acidified potassium manganate(VII). [1]

(d) Compound **C** is an isomer of compound **B**.



C

Draw the structure of the major product formed when compound **C** is reacted with excess HBr(g). Explain your answer. [2]

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(e) Lithium aluminium hydride, LiAlH$_4$, is a reducing agent commonly used in organic chemistry.

(i) Assuming LiAlH$_4$ as a source of hydride (H^-) ions, suggest why the reduction of alkynes using LiAlH$_4$ is likely **not** a suitable method. [1]

(ii) LiAlH$_4$ can be synthesised from aluminium chloride, which exists as a dimer, Al_2Cl_6, at room temperature.

Draw a dot-and-cross diagram to illustrate the bonding present in Al_2Cl_6. [1]

(iii) When heated, LiAlH$_4$ decomposes to LiAl(s) as one of its products. LiAl(s) has a melting point of 718 °C. It can conduct electricity when in solid and molten states.

Suggest the structure of LiAl(s) and describe the bonding present. [2]

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2 (a) 1,2–diols are common precursors used in many pharmaceuticals, agrochemicals, and natural products.

Fig. 2.1 shows a *pinacol coupling reaction* which involves the *homo–coupling** of a carbonyl compound to produce a symmetrically substituted 1,2–diol.

**Two identical molecules react to form a different one*.

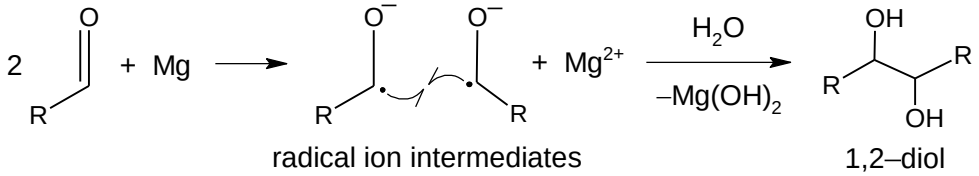


Fig. 2.1

The first step is single electron transfer involving the carbonyl group, which generates radical ion intermediates that couple via carbon–carbon bond formation to give a 1,2–diol.

(i) State the role of magnesium in the first step of Fig. 2.1 and give a reason for its suitability in this reaction. [2]

(ii) It is possible to synthesise a desired unsymmetrical diol using methods similar to the *pinacol coupling reaction* but a mixture of diols will be obtained.

Explain why a mixture of diols is formed. Suggest why this is unfavourable other than a low yield of the desired diol. [2]

The *pinacol coupling* can be followed up by a *pinacol rearrangement* to convert the 1,2–diol to a carbonyl compound.

Pinacolone is a carbonyl compound that can be produced via the *pinacol rearrangement*.

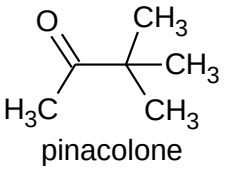


Fig. 2.2 shows the first step of the *pinacol rearrangement* to form pinacolone using pinacol as the starting reactant.

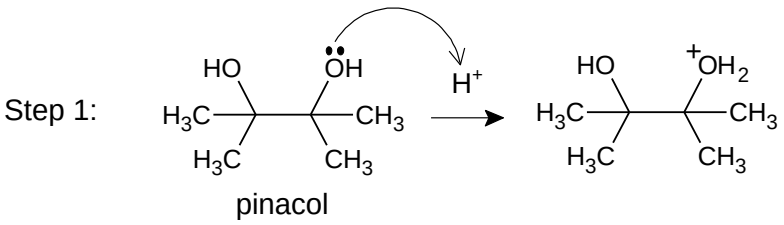


Fig. 2.2

(iii) Below describes the remaining three steps of the *pinacol rearrangement* to form pinacolone.

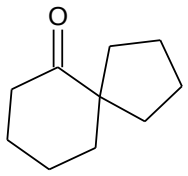
- Step 2 involves the removal of water from the intermediate in Step 1 in Fig. 2.2 to form a carbocation.
- Step 3 involves the shifting of an adjacent methyl group to the positively charged carbon to form another carbocation.
- Step 4 involves the deprotonation of the −OH group in the carbocation in Step 3 to form pinacolone.

Using the information provided, draw Steps 2 to 4 of the mechanism for the formation of pinacolone via *pinacol rearrangement*.

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

(iv) Suggest a simple chemical test that you could carry out to confirm the formation of pinacolone from pinacol. State the observations you would make and write a balanced equation for the reaction. [2]

(v) Compound **X** is a product formed from *pinacol rearrangment*.



compound **X**

Draw the structure of the 1,2-diol responsible for producing **X**. [1]

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(b) A research team in Kanazawa University was successful in selectively synthesising one species of 1,2-diol from an aldehyde and a ketone as the starting materials. The key to the success was a newly developed copper catalyst that could distinguish between the two different carbonyl compounds.

Fig. 2.3 shows the structure of the copper catalyst with N-heterocyclic carbene (NHC) as one of the ligands.

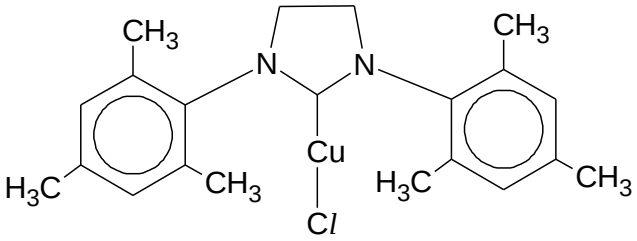
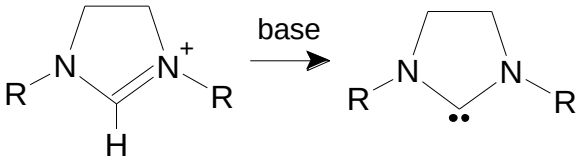


Fig. 2.3

Bases can be used to prepare the NHC ligand, as shown in Fig. 2.4.



R = bulky substituent NHC

Fig. 2.4

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

(ii) State the oxidation number of Cu in Fig. 2.3. [1]

(iii) Coordination number is defined as the number of dative bonds formed between ligands and the central metal atom or ion.

State the coordination number of Cu in Fig. 2.3. [1]

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(c) **(i)** Hexaaquairon(III) ions, $[Fe(H_2O)_6]^{3+}$, are pale violet.

Draw the structure of hexaaquairon(III) ion, showing the arrangement of the ligands in the structure. [1]

(ii) Explain why hexaaquairon(III) ions are coloured. [3]

(iii) When a few drops of KSCN(aq) are added to 5 cm^3 of Fe^{3+}(aq), followed by a few drops of KF(aq), the solution changes colour from violet to deep-red to colourless.

Identify the type of reaction occurring and explain the sequence of colour changes observed. [3]

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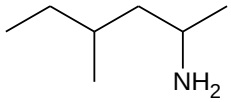
3 **(a)** Compound **Y** is a banned performance–enhancing stimulant. Usain Bolt lost one of his three gold medals from the 2008 Olympics because one of his relay team members tested positive for this drug.



Y

Compound **Y** may be prepared by the three–step synthesis shown in Fig. 3.1. Other products of each step are not shown.

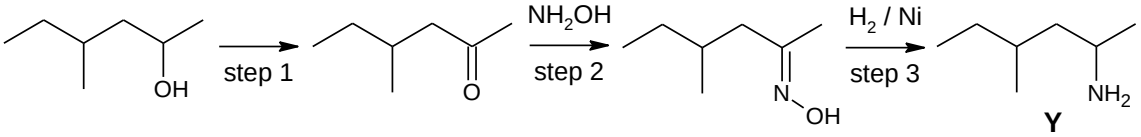


Fig. 3.1

(i) Name the starting organic material in step 1 of Fig. 3.1. [1]

(ii) Deduce the identity of the other product formed in step 2 of Fig. 3.1. [1]

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(b) A student suggested that compound **Y** could be prepared directly from the starting material in step 1 by reacting it with phosphorus pentachloride, PCl_5, followed by ammonia, NH_3.

(i) State the property of ammonia that makes this a possible synthesis route for compound **Y**. [1]

(ii) A second student suggested that the first student's proposal might work better if the reaction with ammonia was carried out in the presence of acid.

Explain if the second student's suggestion is correct. [1]

(iii) Thionyl chloride, $SOCl_2$, can be used as a replacement for PCl_5 in the reaction mentioned in **(b)**. $SOCl_2$ is difficult to handle safely and is similar to PCl_5 in terms of reactivity and cost.

Suggest an advantage of using $SOCl_2$ instead of PCl_5. [1]

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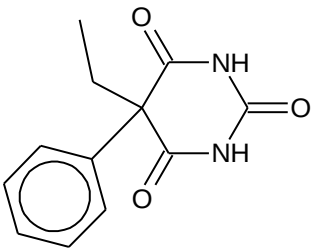
(c) Phenobarbital is a drug used in the treatment of seizures.



phenobarbital

(i) Comment on the basicity of phenobarbital. [1]

(ii) Predict the products of the alkaline hydrolysis of phenobarbital. [2]

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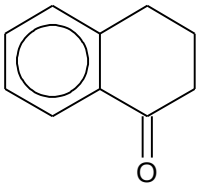
(d) 1–tetralone is used in the synthesis of propranolol, a drug used in the treatment of high blood pressure.



1–tetralone

Benzene can be used to make 1–tetralone.

(i) Suggest the structure of an organic reagent that could form 1–tetralone from benzene in a single step. [1]

(ii) Explain why benzene does not undergo addition reactions. [1]

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(e) Organic drug synthesis processes often involve alkali metals.

Alkali metals react with water as shown in the equation, where **M** represents the alkali metal.

$$\mathbf{M}(s) + H_2O(l) \rightarrow \mathbf{M}OH(aq) + \frac{1}{2}H_2(g) \qquad \Delta H_r^{\ominus}$$

For each of the alkali metals, Table 3.1 shows:

- the standard enthalpy change of atomisation, $\Delta H_{at}^{\ominus}$,
- the standard enthalpy change of hydration, $\Delta H_{hyd}^{\ominus}$,
- the first ionisation energy, 1st IE,
- the standard enthalpy change of reaction between alkali metal and water, $\Delta H_r^{\ominus}$.

Table 3.1

alkali metal	$\Delta H_{at}^{\ominus}$ (**M**) / kJ mol^{-1}	$\Delta H_{hyd}^{\ominus}$ ($\mathbf{M}^+$) / kJ mol^{-1}	1st IE (**M**) / kJ mol^{-1}	$\Delta H_r^{\ominus}$ (**M**) / kJ mol^{-1}
Li	+160	–519	+519	–222
Na	+109	–406	+495	–184
K	+90	–322	+418	–196
Rb	+86	–301	+402	–195
Cs	+79	–276	+376	–203

(i) Define the term *standard enthalpy change of hydration*. [1]

(ii) Explain the trend in the standard enthalpy change of hydration, $\Delta H_{hyd}^{\ominus}$, down the group. [2]

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(f) **(i)** Use relevant data from Table 3.1 to calculate the enthalpy change for the following reaction.

$$Na(s) \rightarrow Na^+(aq) + e^-$$ [1]

(ii) Using relevant data from Table 3.1 and your answer in **(f)(i)**, draw an energy cycle to determine the enthalpy change of **reaction 1**.

reaction 1 $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$

Show your working clearly. [2]

(iii) There is particular interest in lithium as an energy source due to its low density.

Use relevant data form Table 3.1 to calculate the energy change per gram of lithium for the reaction between lithium and water. [1]

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(g) Lithium carbonate undergoes thermal decomposition in a similar way to Group 2 carbonates, though a much higher temperature is required.

Explain why the reaction occurs at high temperatures. Refer to the signs of ΔH, ΔS and ΔG in your answer. [2]

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(h) Group 2 metals undergo reaction with water in a similar way to alkali metals.

However, magnesium and barium have different reactivities when added separately to water.

Use relevant $E^{\ominus}$ values from the *Data Booklet* to explain the difference in the reactivity of magnesium and barium with water. [1]

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[Total: 20]

Please Turn Over for Section B

Section B

Answer **one** question from this section.

4 (a) Alcohol is widely used in the preparation of aldehydes and ketones. The electrolysis of alcohols to carbonyl compounds is reported. A simplified diagram of the cell set-up is shown in Fig. 4.1.

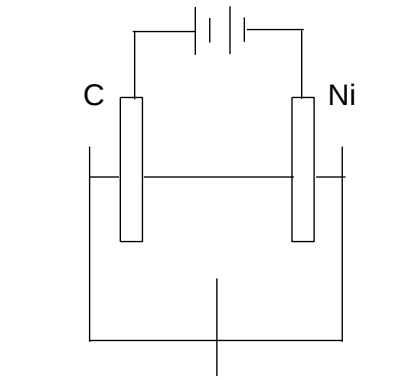
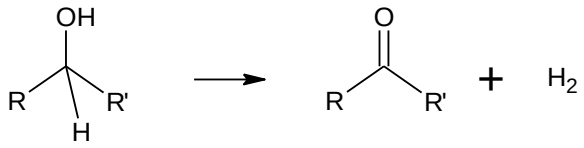


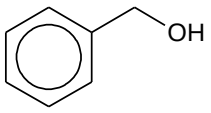
Fig. 4.1

The overall equation for the electrolysis of alcohol is shown.



where R = alkyl or aryl
R' = H, alkyl or aryl

(i) Write a balanced equation that shows the complete combustion of benzyl alcohol.



benzyl alcohol

[1]

(ii) Draw the structure of the product formed when benzyl alcohol is electrolysed. [1]

(iii) State and explain at which electrode does the conversion of the reactant alcohol take place. You should state the element that the electrode is made of. [2]

(iv) Suggest the role of Bu_4NBF_4 in the set-up in Fig. 4.1. [1]

(v) A constant current of 800 mA is delivered at room temperature over 10 minutes. By considering the change in the oxidation state of the reactive carbon, calculate the number of moles of carbonyl compound formed from the electrolysis given that the yield of this conversion is 90%. [3]

(vi) Anodising aluminium is another useful application of electrochemical method. Describe how anodising of aluminium is achieved. [2]

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(b) Iodine-based reagents are commonly used in organic synthesis owing to their unique chemical properties which are linked to their physical properties such as ionic radius and ionisation energy.

(i) State what is meant by the *first ionisation energy of iodine*. [1]

(ii) State and explain the variation of atomic radius down Group 17. [2]

(iii) Hydrofluoric acid and sodium fluoride can be used to form an acidic buffer. Explain how an acidic buffer controls the pH of a solution. [1]

(iv) Predict and explain if hydroiodic acid and sodium iodide can be used to form an acidic buffer. [1]

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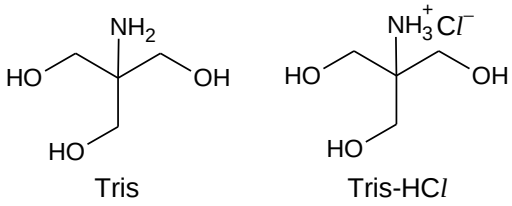
(c) Tris buffer is a biochemical buffer used in COVID–19 vaccines. The structure of Tris and Tris–HC*l* is shown below. The K_b of Tris is 1.05×10^{-6} mol dm^{-3}.



Tris Tris-HC*l*

A Tris buffer is formed by mixing 200 cm^3 of 1.50 mol dm^{-3} Tris with 200 cm^3 of 1.66 mol dm^{-3} Tris–HC*l*.

(i) Calculate the pH of the Tris buffer. [2]

(ii) 25.0 cm^3 of 0.500 mol dm^{-3} HNO_3 is added to 75.0 cm^3 of the Tris buffer prepared.

Calculate the pH of this solution. [3]

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5 (a) Fig. 5.1 shows a hydrogen–halogen fuel cell where H_2 gas is supplied to the anode while Br_2, dissolved in an aqueous solution of HBr, is provided to the cathode.

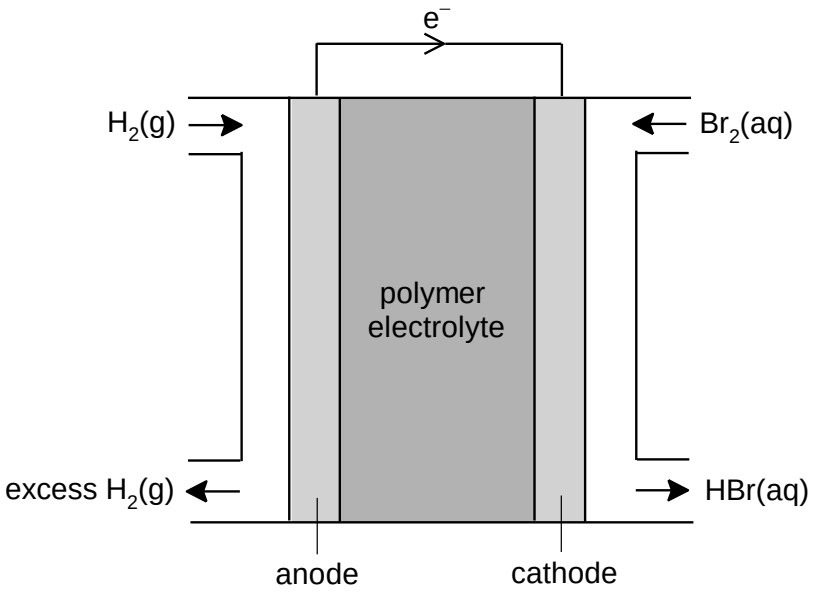

Fig. 5.1

(i) The polymer electrolyte allows the transfer of a simple ion from the anode to the cathode. Use Fig. 5.1 to suggest the identity of the ion and hence construct balanced equations for the reactions occurring at the electrodes. [2]

(ii) Use your answer in **(a)(i)** to write the overall equation when current flows and hence use the *Data Booklet* to calculate the standard cell potential, $E^{\ominus}_{cell}$, for this cell. [2]

(iii) Use your answer to **(a)(ii)** to calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for this electrochemical reaction. [1]

(iv) A similar hydrogen–halogen fuel cell is set up where Cl_2, dissolved in an aqueous solution of HCl, is supplied to the cathode.

How would you expect the standard Gibbs free energy change, $\Delta G^{\ominus}$, for this electrochemical reaction to compare with your answer in **(a)(iii)**?

Explain your answer in terms of the difference in relative reactivity of the halogens. [2]

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(b) The values of two solubility products are given.

K_{sp} ($PbBr_2$) = 1.9×10^{-5} mol^3 dm^{-9}
K_{sp} (AgBr) = 5.4×10^{-13} mol^2 dm^{-6}

(i) Solid $PbBr_2$ is shaken with water. The remaining solid is filtered off, leaving a saturated solution X. Calculate [Br^-(aq)] in X. [1]

(ii) Drops of dilute aqueous $AgNO_3$ are added to X until AgBr just precipitates. Calculate [Ag^+(aq)] in the resulting solution when AgBr just precipitates. [1]

(iii) HBr is a strong acid when dissolved in water.

Descibe what you will observe if equal volumes of 0.100 mol dm^{-3} solution of HBr and saturated solution of $PbBr_2$ were mixed. Explain your answer using appropriate calculations. [2]

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(c) Ethene reacts with hydrogen bromide exothermically to produce bromoethane.

$$CH_2{=}CH_2 + HBr \rightarrow CH_3CH_2Br$$

The reaction mechanism has two steps as shown.

step 1 $CH_2{=}CH_2 + HBr \rightarrow CH_3CH_2^+ + Br^-$

step 2 $CH_3CH_2^+ + Br^- \rightarrow CH_3CH_2Br$

(i) State the slow step and hence write the rate equation for the reaction. [1]

(ii) Use your answer in **(c)(i)** and the collision theory to explain the effect on the rate of reaction, if any, of

- decreasing the concentration of hydrogen bromide,
- increasing the temperature of the reaction. [2]

(iii) Use the mechanism to explain the role of $CH_3CH_2^+$. [1]

(iv) Draw the labelled energy profile diagram for the reaction. [2]

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(d) The strength of an acid is measured by its K_a value.

How would you expect the K_a values to compare for the following pairs of acids?

- HF and HC*l*
- CH_3COOH and CF_3COOH
- $[Al(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{2+}$

Explain your answer, quoting relevant data from the *Data Booklet* where appropriate.
[3]

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[Total: 20]

Additional answer space

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