Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination 2017
Year 6

H2 CHEMISTRY 9729/02

Paper 2 (Structured) **11 Sep 2017**

2 hours

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

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

2 Write in dark blue or black pen.

3 You may use an HB pencil for any diagrams or graphs.

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

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

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

You are advised to show all workings in calculations.

You are reminded of the need for good English and clear presentation in your answers.

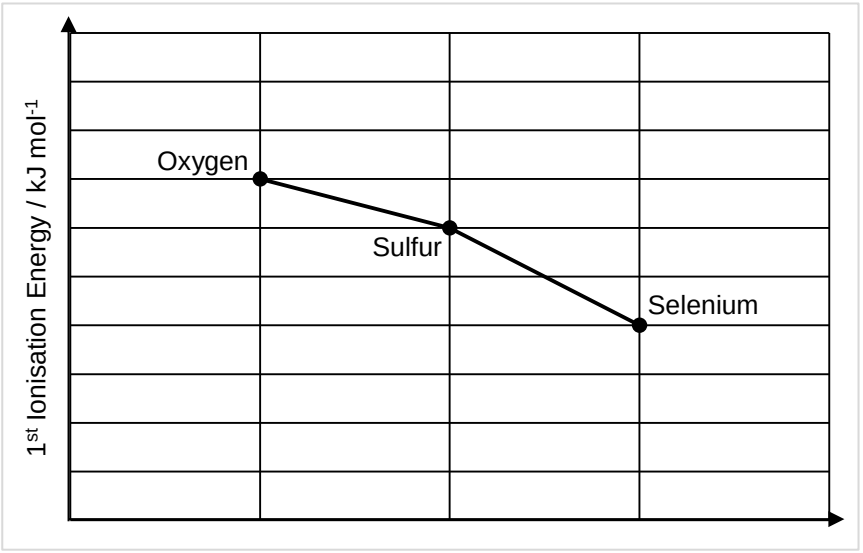
For Examiner's Use	
Question No.	Section A Marks
1	/13
2	/13
3	/20
4	/14
5	/15
Total	/75

[Turn over

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

1 The chalcogens, or the oxygen family, are the elements in group 16 of the Periodic Table. These elements are common in both organic and inorganic compounds.

(a) The graph below shows the trend in the first ionisation energies of oxygen, sulfur and selenium.



(i) Explain the trend in the first ionisation energies of oxygen, sulfur and selenium.

.....

.....

.....

.....

[2]

(ii) On the same grid above, sketch the trend in the first ionisation energies of nitrogen, phosphorus and arsenic.

[1]

(b) A common chalcogen-containing reagent used in both organic and inorganic synthesis is hydrogen peroxide, H_2O_2. Hydrogen peroxide readily decomposes at room temperature. However, this process is slow.

Iodide ions, I^-, catalyse this decomposition, as shown below:

$$\text{Step I: } H_2O_2 + I^- \rightarrow H_2O + IO^- \text{ (slow)}$$
$$\text{Step II: } H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$$

The overall equation for the decomposition of hydrogen peroxide is shown below:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The enthalpy and entropy changes for the reaction above are shown in the table below:

Enthalpy change / kJ mol^{-1}	–98
Entropy change / J K^{-1} mol^{-1}	+71

(i) Using the data above, complete the diagram below to show the energy profile diagram for the decomposition of hydrogen peroxide in the presence of iodide ions.

[2]

(ii) An unknown amount of hydrogen peroxide was allowed to decompose in a 5 dm^3 closed vessel at 120 ºC. When all the hydrogen peroxide was decomposed, a pressure of 177 kPa was measured in the vessel.

Determine the amount of hydrogen peroxide that decomposed in the vessel.

(Assume that H_2O and O_2 are ideal gases under the above reaction conditions)

[2]

(c) Chalcogens are also very commonly found in organic compounds. Table 1 below shows some common oxygen or sulfur containing organic functional groups.

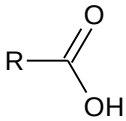
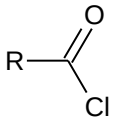
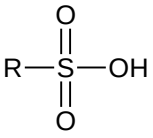
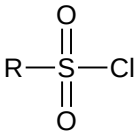
Oxygen-containing functional groups	Alcohols R–OH	Carboxylic acids 	Acyl chlorides 
Sulfur-containing functional groups	Thiols R–SH	Sulfonic acids 	Sulfonyl chlorides 

Table 1

(i) Explain why carboxylic acids are generally more acidic than alcohols.

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.....

[1]

(ii) Hence, suggest a reason why carboxylic acids are generally less acidic than their corresponding sulfonic acids.

.....

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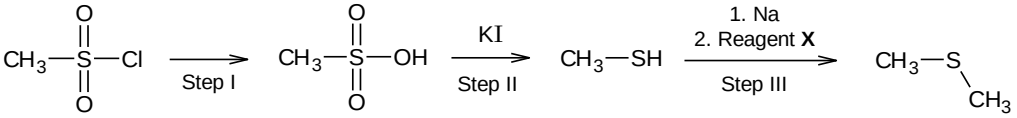
.....

.....

[1]

(iii) A reaction scheme for the synthesis of dimethyl sulfide (CH_3SCH_3) from methylsulfonyl chloride (CH_3SO_2Cl) is shown below:



Given that sulfur-containing functional groups undergo similar reactions as their corresponding oxygen-containing functional groups (Table 1), suggest:

I. The reagent(s) and condition(s) required for Step I.

.....

[1]

II. The role of KI in Step II.

.....

[1]

III. The identity of Reagent **X** in Step III.

.....

[1]

IV. The structure of the product(s) formed when methylsulfonic acid (CH_3SO_3H) is reacted with ethylamine ($CH_3CH_2NH_2$) at room temperature.

[1]

[Total: 13]

2 The electrolysis of dilute sulfuric acid was carried out using two different currents at room temperature and pressure.

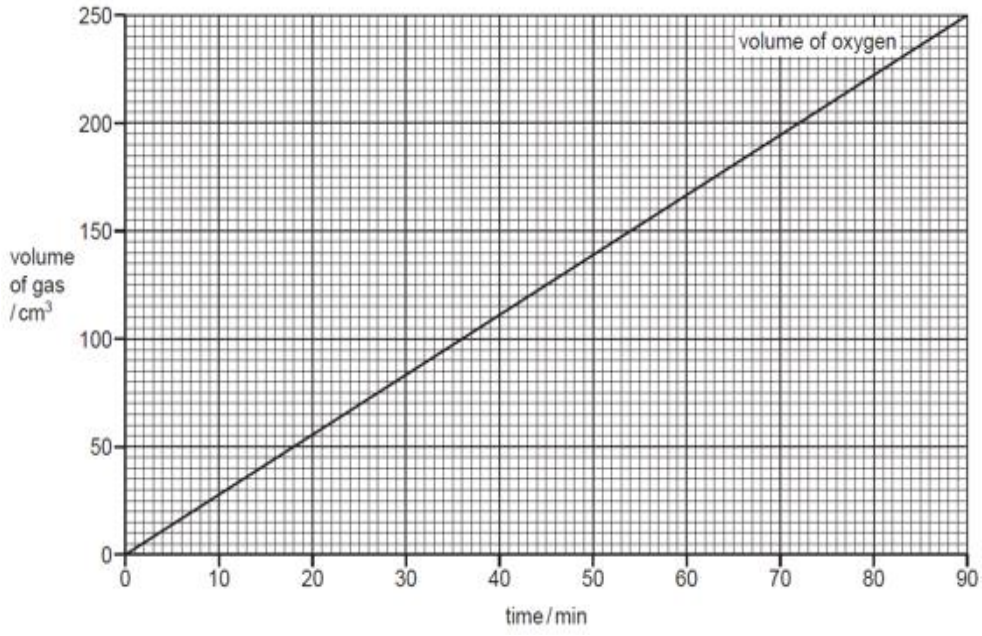
	Current / A	Duration / min
Experiment 1	0.75	90
Experiment 2	0.45	90

Oxygen gas is collected at one of the electrodes.

(a) (i) Calculate the final volume of oxygen produced in experiment 2.

[2]

(ii) The volume of oxygen collected for experiment 1 is shown below.



On the graph above, draw a line to show each of the following:

I. the volume of H_2 gas that would be given off in experiment 1 (Label this line **1**)

II. the volume of oxygen that would be produced in experiment 2 (Label this line **2**)

[2]

(b) In another experiment, electrolysis of aqueous potassium butanedioate, $(OOCCH_2CH_2COO)K_2$, was carried out. It was found that two gases, **Y** and **Z**, were liberated at the anode in a 2:1 ratio by volume.

Gas **Y** formed is absorbed by soda lime while gas **Z** is able to decolourise bromine water.

(i) Suggest the identities of gases **Y** and **Z**.

Gas **Y** is **……..** Gas **Z** is **……**

[1]

(ii) Construct the half-equation for the reaction that occurs at the anode and the cathode respectively.

Anode **……**

Cathode **……**

[2]

(iii) Predict the main organic product that would be obtained at the anode when a solution of potassium pentanedioate is electrolysed.

……

[1]

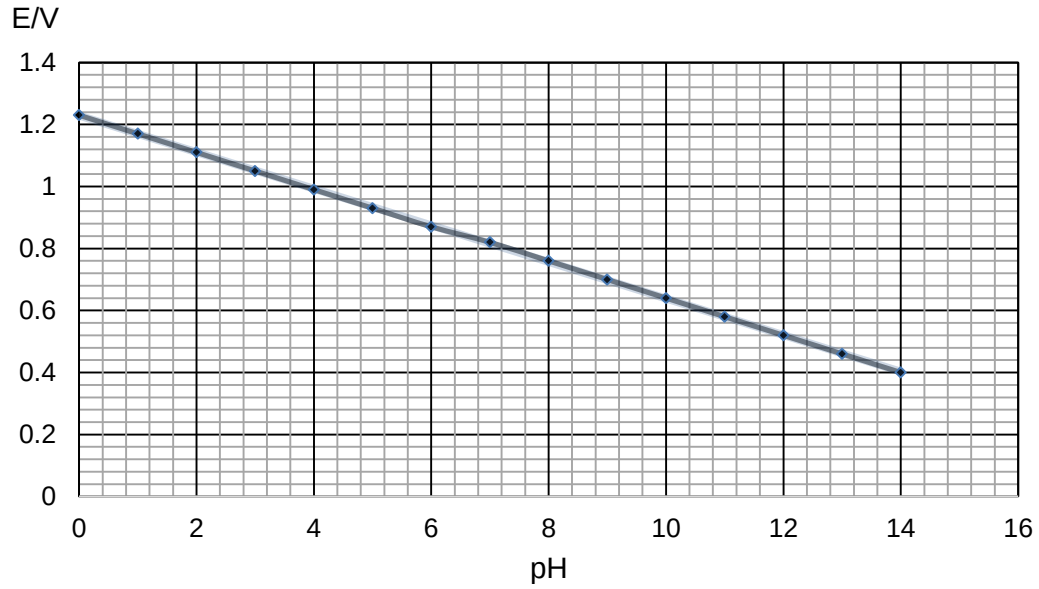
(c) Nicotinamide adenine dinucleotide (NAD^+) is involved in redox chemistry throughout the respiratory system. Aerobic respiration is the process of producing cellular energy involving oxygen.

The electrode potential for the reduction of NAD^+ in a *biological* system, E(pH 7), at 1 mol dm^{-3}, 25 °C and pH 7, is as shown.

Its oxidised and reduced forms are represented as NAD^+ and NADH respectively.

$$NAD^+ + H^+ + 2e^- \rightleftharpoons NADH \qquad E(\text{pH } 7) = -0.320 \text{ V}$$

The reduction electrode potential of oxygen at different pH is given below.



(i) With reference to the *Data Booklet* and the graph given above, calculate the value of E_{cell} for aerobic respiration. Write a balanced equation for this reaction.

[3]

(ii) State how the E_{cell} will differ if the aerobic reaction is performed at a pH of 7.4.

.....

[1]

(iii) Using your answer in **(c)(i),** calculate ΔG(pH 7) for the aerobic respiration process.

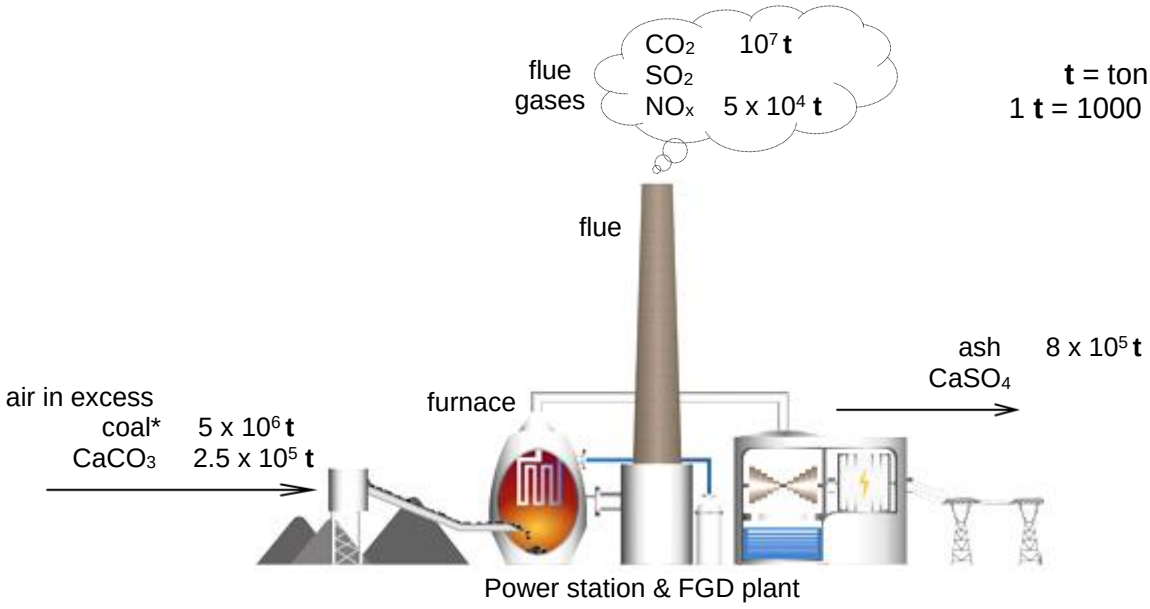
[1]

[Total: 13]

3 A coal-fired power station is fitted with a Flue Gas Desulfurisation (FGD) plant, which removes some of the sulfur dioxide from flue (waste) gases.

In the FGD plant, the flue gases are treated with powdered limestone, $CaCO_3$, where sulfur dioxide is absorbed and reacted to produce calcium sulfite, $CaSO_3$, which is oxidised by air to form solid calcium sulfate, $CaSO_4$.

The diagram below shows the amounts of substances used, and produced, by such a coal-fired power station with an FGD plant in **one** year.



**coal is chiefly hydrocarbons*

(a) (i) State the process that produces the energy in the power station.

.....

[1]

(ii) Identify a gas, not listed in the diagram, which will be a chief component of the flue gases.

.....

[1]

(iii) Explain why oxides of nitrogen (NO_x) are present in the flue gases.

.....

.....

[1]

(b) Write a balanced equation in each case to show how

- sulfur dioxide is removed from flue gases;

.....

- calcium sulfate is formed.

.....

[2]

(c) Using your answer in **(b)**, determine the maximum mass of sulfur dioxide which could be removed in the FGD plant.
[1**t** = 1 tonne = 1000 kg]

[1]

(d) Given that your answer in **(c)** was only 90% of the sulfur dioxide removed from the flue gases, calculate the mass of sulfur dioxide which is released into the atmosphere in **five** years by this power station when the same mass of coal is burnt each year.

[1]

(e) Another method for removing sulfur dioxide from the flue gases is to absorb it in a slurry of magnesium oxide, to produce magnesium sulfite, $MgSO_3$.

(i) Explain why magnesium oxide can also be used to remove sulfur dioxide.

.....

.....

[1]

(ii) Magnesium sulfite decomposes readily to give magnesium oxide and sulfur dioxide. Magnesium oxide could be recycled, while sulfur dioxide could be used to make sulfuric acid.

Explain whether it would be easier to obtain magnesium oxide or calcium oxide from its respective sulfite.

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.....

[3]

(f) When 1 mol of magnesium oxide, calcium oxide and other Group 2 metal oxides were separately dissolved in 1 dm^3 of deionised water, the pH of the resulting solutions were obtained.

Some data regarding these Group 2 metal oxides, **M**O, and their resulting solutions are provided in the table below.

ion	ionic radius/ nm	$\Delta H_{hydration}$ / kJ mol^{-1}	pH of **M**O in water	Electronegativity difference (ΔEN) in **M**O
O^{2-}	0.140			
Be^{2+}	0.031	–2370	7.0	1.87
Mg^{2+}	0.065	–2024	9.0	2.13
Ca^{2+}	0.099	–1680	9.5	2.44
Sr^{2+}	0.113	?	11	2.49
Ba^{2+}	0.135	–1314	12	2.55

(i) Suggest why there is no value for $\Delta H_{hydration}$ of the oxide ion, O^{2-}.

.....

[1]

(ii) Using the data given, estimate $\Delta H_{hydration}$ of Sr^{2+}.

enthalpy change of hydration of Sr^{2+} = ...

[1]

(iii) State and explain the trend in $\Delta H_{hydration}$ in the table, in terms of the interaction between cations and water.

.....

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.....

[2]

(iv) With reference to the relevant data given in **(f)**, suggest explanations for the increasing pH of the resulting solution from BeO to BaO in terms of:

I. Lattice energy and enthalpy change of solution of **M**O

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.....

.....

.....

[3]

II. ΔEN and the nature of the bonding in **M**O

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.....

.....

[2]

[Total: 20]

4 Vitamin C is an essential nutrient also known as ascorbic acid. A deficiency of vitamin C leads to a disease known as scurvy.

Ascorbic acid is known to have a M_r of 176.0 and contains 40.9% of carbon and 54.5% of oxygen by mass.

(a) Determine the molecular formula of ascorbic acid.

[2]

(b) Ascorbic acid is a monobasic acid, H**A**, and has a pK_a of 4.10. The amount of ascorbic acid contained in dietary supplement tablets can be verified by titration. A tablet containing 500 mg of ascorbic acid was dissolved in 25.0 cm^3 of deionised water.

(i) Calculate the volume of 0.100 mol dm^{-3} sodium hydroxide required for complete neutralisation.

[1]

(ii) Calculate the initial pH of the ascorbic acid solution.

[2]

(iii) Suggest a suitable indicator for the titration. Describe the expected colour change at the endpoint.

.....

.....

[1]

(iv) With the aid of a suitable equation, explain your choice of indicator in **(iii)**.

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[2]

(c) When a vitamin C tablet is swallowed, it dissolves in the stomach. The pH of the stomach is 2.

(i) Determine the percentage of ascorbic acid that is ionised in the stomach.

[2]

The pH of blood is maintained at 7.35 by a H_2CO_3/HCO_3^- buffer.

(ii) Using appropriate equations, explain how the buffer minimises changes in pH.

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[2]

(d) Organic acids like ascorbic acid react with amines in aqueous medium.

(i) State the type of bond formed during the reaction.

.....

[1]

(ii) Account for the increasing basicity of primary, secondary and tertiary amines in gas phase.

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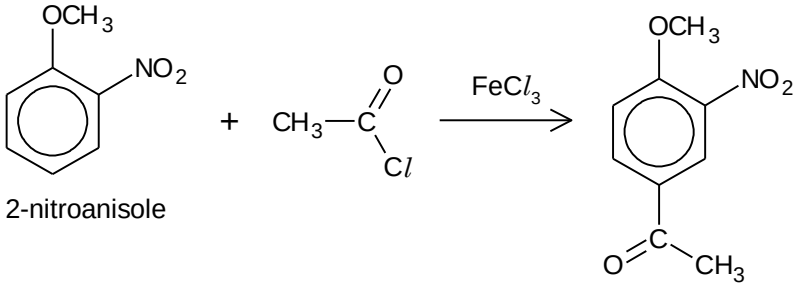
[1]

[Total: 14]

5 **(a)** In Friedel-Crafts acylation, $FeCl_3$ is employed to attach an acyl group to an aromatic ring via electrophilic substitution.

For example, compound **A** can be prepared by the reaction of 2-nitroanisole with ethanoyl chloride in the presence of $FeCl_3$.



2-nitroanisole

compound **A**

(i) Draw the displayed formula of the electrophile and write an equation to show how it is generated.

equation: .....

[2]

(ii) Using your answer in **(i)**, draw the mechanism of the acylation of 2-nitroanisole by ethanoyl chloride. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.

[2]

Empirical evidence shows that the electrophile generated in **(i)** is not exceptionally reactive. As such, the Friedel-Crafts acylation of nitrobenzene by ethanoyl chloride does not take place under any conditions.

(iii) Explain why nitrobenzene does not undergo acylation but the presence of the $–OCH_3$ group in 2-nitroanisole permits acylation.

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[2]

(b) Another iron compound, $Na_2[Fe(CO)_4]$, is used in the reaction between alkyl halides and carbon monoxide to synthesise ketones. This iron-based reagent is made as follows.

$$Fe(CO)_5 \xrightarrow{Na/Hg} \xrightarrow{-CO} 2Na^+ + [Fe(CO)_4]^{2-}$$

(i) Draw the structure of $Fe(CO)_5$ to show its shape clearly.

[1]

(ii) The oxidation state of Fe in $Fe(CO)_5$ is 0 and the CO ligands are neutral. Suggest the oxidation state of Fe in the $[Fe(CO)_4]^{2-}$ anion.

oxidation state of Fe in $[Fe(CO)_4]^{2-}$: .....

[1]

(iii) Besides the oxidation states exhibited in the above reaction, iron also exists in other oxidation states like +2 and +3.

State a property of iron that allows its compounds to behave in this manner and give a reason why this property arises in iron.

Property of iron: .....

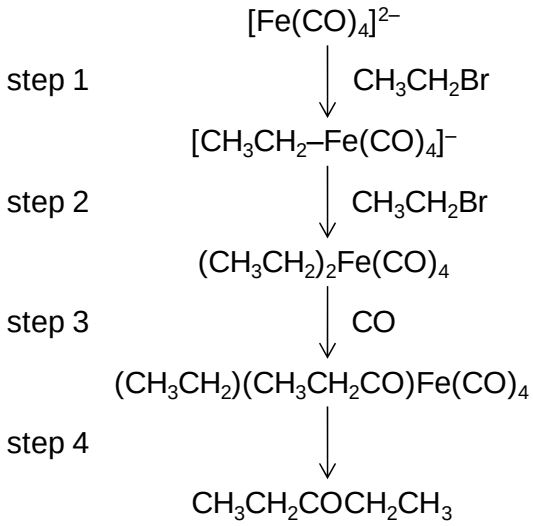
Reason: .....

.....

.....

[2]

The reaction between $[Fe(CO)_4]^{2-}$ and bromoethane takes place under an applied pressure of carbon monoxide via the following steps.



(iv) Explain what is meant by the term *coordination number* in the context of a metal complex.

State the coordination number of iron in $[Fe(CO)_4]^{2-}$ and $(CH_3CH_2)(CH_3CH_2CO)Fe(CO)_4$.

.....

.....

Coordination number of iron in $[Fe(CO)_4]^{2-}$: .....

Coordination number of iron in $(CH_3CH_2)(CH_3CH_2CO)Fe(CO)_4$: .....

[2]

(v) Studies show that steps 1 and 2 proceed via nucleophilic substitution.

If bromoethane were replaced by bromobenzene, the above reaction with $Na_2[Fe(CO)_4]$ would not work. With reference to the bonding and structure of bromobenzene, give **two** reasons why both S_N1 and S_N2 cannot occur.

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[3]

[Total: 15]

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