RIVER VALLEY HIGH SCHOOL
JC 2 PRELIMINARY EXAMINATION

CANDIDATE NAME	

CLASS	2	3	J		

CENTRE NUMBER	S					INDEX NUMBER				

H2 CHEMISTRY 9729/03

Paper 3 Free Response

17 September 2024

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, class and name on **all** the work that 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.
DO **NOT** WRITE IN ANY BARCODES.

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. **Circle** the question number of the question you attempted.

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								
Question Number	**1**	**2**	**3**	**4**	**5**	**units**	**s.f.**	**Total**
Marks	19	21	20	20	20			80

This document consists of **30** printed pages and **1** blank pages.

1 **(a)** 15.4 g of hydrogen iodide was allowed to partially dissociates into hydrogen and iodine in a 2.00 dm^3 vessel. At equilibrium, 10.2 g of hydrogen iodide was left.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g) \qquad \Delta H = +52 \text{ kJ mol}^{-1}$$

(i) Explain what is meant by *dynamic equilibrium*. [1]

(ii) Write an expression for the equilibrium constant, K_c, for the dissociation of HI. [1]

(iii) Hence, calculate the value of K_c of this reaction. [2]

(iv) With reference to position of equilibrium, state and explain the effect of an increase in temperature on the value of K_c. [2]

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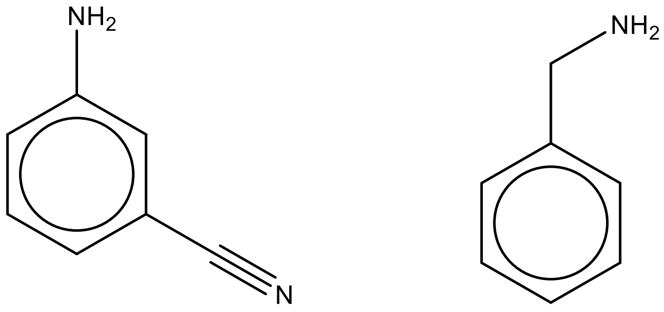
(b) Describe and explain the relative basicities of benzylamine, phenylamine and 3-aminobenzonitrile.



3-aminobenzonitrile   benzylamine

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(c) 3-bromophenylamine reacts with chlorine and iron to form three isomeric products, with the formula C_6H_6NBrCl.

(i) Suggest the structure of the isomer produced in the highest amount. Explain your answer. [1]

(ii) Name and describe the mechanism to produce the major product. [3]

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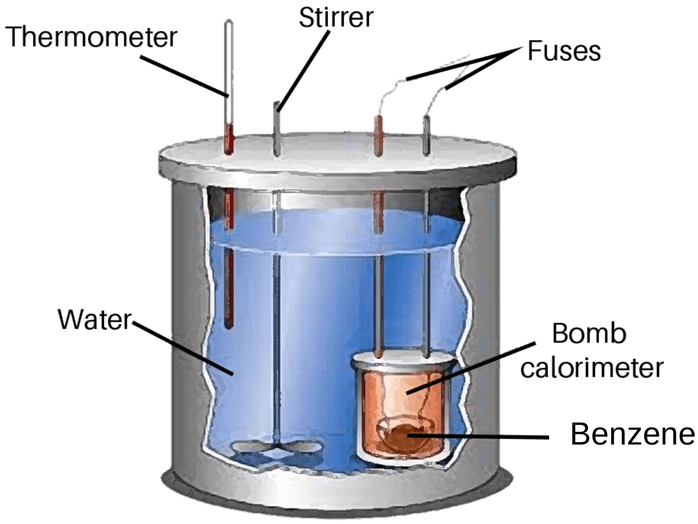
(d) The set-up below shows a bomb calorimeter which is used to determine the enthalpy of combustion, ΔH_c, of benzene.



In an experiment, 3.00 g of benzene was burned in a bomb calorimeter containing 0.600 kg of water. It was found that the temperature of the water changed from 25.0 °C to 40.0 °C. A layer of black solid was also observed in the bomb calorimeter.

(i) Calculate the apparent ΔH_c of benzene from these figures. Ignore the heat capacity of the bomb calorimeter, and use the figure of 4.18 J g^{-1} K^{-1} for the specific heat capacity of water. [2]

(ii) The bomb calorimeter is typically made of copper. Suggest a reason for doing so. [1]

(iii) The theoretical ΔH_c of benzene is reported to be –3268 kJ mol^{-1}. With reference to the observation, comment on the apparent value obtained and suggest a reason for the difference. [2]

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RVHS Chemistry

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2 (a) This question is about the oxides of Period 3 elements.

(i) Describe the action of water on the oxides of sodium and phosphorus. Write equations for any reactions that occur, and suggest the pH of each solution formed. [2]

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

A sample of white powder, containing only one of the oxides above, was provided. Describe simple chemical tests you would carry out on the sample to determine which oxide was present. [2]

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(b) Magnesium silicofluoride, $MgSiF_6$, is a white crystalline solid that is commonly used as a polishing agent for ceramic floors and a preservative of wood.

(i) Define the term *lattice energy of magnesium silicofluoride*. [1]

(ii) Using relevant data from the *Data Booklet* and the following experimental data, construct an appropriate energy cycle to calculate the lattice energy of magnesium silicofluoride.

standard enthalpy change of formation of $MgSiF_6(s)$	-2580 kJ mol^{-1}
standard enthalpy change of atomisation of Mg	$+148$ kJ mol^{-1}
standard enthalpy change of atomisation of Si	$+456$ kJ mol^{-1}
bond dissociation energy of Si#F	$+565$ kJ mol^{-1}
$SiF_4(g) + F_2(g) + 2e^- \rightarrow SiF_6^{2-}(g)$	-639 kJ mol^{-1}

[4]

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RVHS Chemistry

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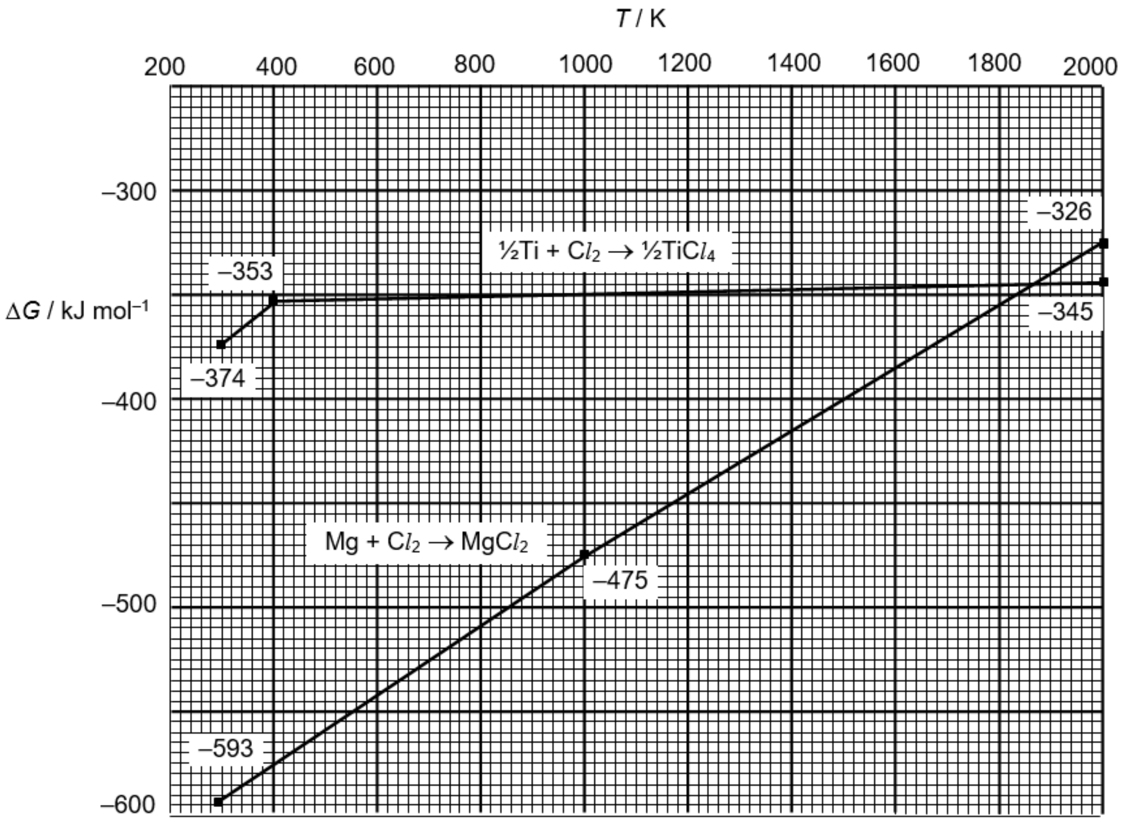
Titanium is a strong, low-density metal resistant to chemical attack. Although it is expensive to produce, it is highly in demand in the aerospace and medical industries.

(c) At present, titanium is commonly produced by reducing titanium tetrachloride with magnesium. Titanium tetrachloride is a colourless liquid that boils at 400 K.

To optimise this reduction process, it is necessary to know how ΔG of the reaction changes with temperature. Graphs of ΔG against T are known as Ellingham diagrams. The Ellingham diagram below shows how ΔG changes for the following reactions.

reaction 1: $\frac{1}{2}Ti + Cl_2 \rightarrow \frac{1}{2}TiCl_4$

reaction 2: $Mg + Cl_2 \rightarrow MgCl_2$



(i) Explain why the graph for reaction 1 becomes more positive between 300 K and 400 K but becomes almost independent of temperature from 400 K to 2000 K. [2]

Industrially, the reduction of titanium tetrachloride by magnesium is carried out at 1100 K in an atmosphere of argon.

(ii) Suggest a reason for the reduction to be carried out in an atmosphere of argon. [1]

(iii) Write a balanced equation for the reaction at this temperature. [1]

(iv) Calculate ΔG for the reaction in **(iii)** at 1100 K. [2]

(v) State the temperature above which the reduction of $TiCl_4$ with Mg becomes **not** feasible. [1]

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RVHS Chemistry

(d) Similar to aluminium anodising, titanium anodising is an electrolytic process to increase the thickness of the titanium dioxide layer on the surface of titanium.

Through anodising, titanium aeroplane parts become more protected from the effects of ageing, wear and corrosion. Likewise, anodised titanium parts are non-toxic and suitable for biomedical applications, such as orthopedic implants.

(i) Draw a labelled diagram of an electrolysis setup during the anodising of titanium. [2]

(ii) Write half-equations, including state symbols, for the reactions taking place at the anode and cathode. [1]

(iii) Copper(II) sulfate was used as the electrolyte instead. State and explain any observations in the electrolytic cell after a few hours. [2]

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3 (a) (i) A 1000 cm^3 bulb weighs 51.083 g when it is empty and 52.248 g when filled with a diatomic gas at a pressure of 101.3 kPa and 20 °C.

Calculate the molar mass of the gas and suggest two possible identities for the gas. [2]

(ii) State and explain which of the gases in **(a)(i)** behaves more ideally. [1]

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(b) **(i)** An alloy contains iron and copper. A sample of the alloy was analysed and four different types of atom were identified – **A**, **B**, **C**, **D**. Table 3.1 shows the information about the four types of atom found in the sample.

Table 3.1

atom	relative mass	relative abundance
A	53.9396	5.85
B	55.9349	91.75
C	62.9296	69.15
D	64.9278	30.85

Calculate the relative atomic mass of iron in this sample. Leave your answer to four significant figures. [2]

(ii) State the electronic configuration of a Cu^{2+} ion. [1]

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(c) A solution containing 1 mol dm^{-3} each of $Fe^{2+}(aq)$ and $Cu^{2+}(aq)$ can be separated by selective precipitation. The procedure involves passing $HCl(g)$ into the solution until a certain pH is reached and then saturating the solution with H_2S. The solubility products of FeS and CuS are given below:

$$K_{sp}(FeS) = 4.9 \times 10^{-21}\ mol^2\ dm^{-6};$$

$$K_{sp}(CuS) = 7.9 \times 10^{-30}\ mol^2\ dm^{-6}$$

In a saturated solution of hydrogen sulfide, the ionic product of hydrogen sulfide can be represented by:

$$[H^+]^2[S^{2-}] = 1.0 \times 10^{-30}\ mol^3\ dm^{-9}$$

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

(ii) Calculate the pH range that must be obtained from $HCl(g)$ for an effective separation. [3]

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(d) A pink complex salt **E** is subjected to elemental analysis and is found to have the following composition by mass: Co, 22.0%; N, 26.0%; H, 6.3%; O, 6.0% and C*l*, 39.7%.

0.845 g of **E** is dissolved in water and the solution is titrated with aqueous silver nitrate. The precipitate formed is filtered, washed and dried. The mass of the precipitate is found to be 1.354 g.

(i) Determine the empirical formula of **E**. [1]

(ii) Calculate the amount of free chloride ions per mole of **E** and suggest the structural formula of the complex ion in **E**. [2]

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(e) The dianion of **F**, $C_4H_7NO_4$, acts as a tridentate ligand to bind to the central metal ion in **E**. **F** is a straight chain molecule that does not rotate plane-polarised light. When 1 mole of **F** is separately reacted with 1 mole of aqueous Na_2CO_3 and 2 moles of ethanolic CH_3Br, the following observations are obtained:

reagent	observations
aqueous Na_2CO_3	24 dm^3 of gas evolved
ethanolic CH_3Br	quaternary ammonium bromide salt formed

F also reacts with limited ethanolic $CH_2(OH)CH(OH)Cl$ to form **G**, $C_6H_{11}NO_6$. When heated with a small amount of concentrated H_2SO_4, **G** forms bicyclic **H**, $C_6H_7NO_4$.

Deduce the structures of **F**, **G** and **H** and explain your reasoning. [6]

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(f) Draw the structure of the complex ion formed between the dianion of **F** and the central metal ion in **E**. [1]

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Section B

Answer **one** question from this section.

4 Bromine can form several compounds under suitable conditions:

Table 4.1

Bromine containing species	Oxidation number of Br
Br^-	–1
BrO^-	+1
BrF_4^-	+3
BrO_3^-	+5
BrO_4^-	+7

(a) Draw the dot-and-cross diagram for BrF_4^-. Hence, deduce its shape and suggest a value for its bond angle. [3]

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(b) When 9.909 g of Br_2(l) was added to an excess of NaOH solution, a reaction took place, forming two different bromine containing ions, **X** and **Y** (whose identities can be found in Table 4.1). This mixture was then made up to 250 cm^3 using deionised water, and labelled as solution **Q**.

The following steps were carried out on solution **Q**.

1. When 25.0 cm^3 of solution **Q** was mixed with an excess of acid followed by $AgNO_3$(aq), a cream precipitate was formed.
2. This precipitate was insoluble in NH_3(aq), and its mass was found to be 1.942 g.
3. To another 25.0 cm^3 portion of solution **Q**, excess KI solution was added. The I_2 liberated required 24.80 cm^3 of 0.500 mol dm^{-3} $Na_2S_2O_3$ for complete reaction as shown.

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

(i) Given that **X** is responsible for the formation of the cream precipitate, state the identity of **X**. [1]

(ii) Deduce the amount of **X** in 25.0 cm^3 of solution **Q**.

Hence, show that there are 0.00206 mol of **Y** in 25.0 cm^3 of solution **Q**. [3]

(iii) In step 3, **Y** reacts with KI to form **X**.

Deduce the oxidation state of Br in **Y**. [2]

(iv) Using your answers in **(ii)** and **(iii)**, construct the balanced equation for reaction between Br_2 and NaOH. [1]

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(c) Br^- reacts with BrO_3^- in the presence of an acidic medium in the following manner:

$$BrO_3^- + Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

The following data is obtained from kinetic experiments:

Expt	$[BrO_3^-]$/ mol dm^{-3}	$[Br^-]$/ mol dm^{-3}	$[H^+]$/ mol dm^{-3}	Overall rate/ mol dm^{-3} s^{-1}
1	0.120	0.100	0.150	1.00×10^{-5}
2	0.240	0.100	0.150	2.00×10^{-5}
3	0.180	0.200	0.150	3.00×10^{-5}
4	0.300	0.300	**a**	3.00×10^{-4}

(i) Deduce the order of reaction with respect to $[BrO_3^-]$ and $[Br^-]$. [2]

(ii) Given that the reaction is 2nd order with respect to $[H^+]$, deduce the value of **a**. [2]

(iii) A solution containing Br_2(aq) is coloured. It is possible to use this property to determine the $[Br_2]$ using the following method:

- A few cm^3 of Br_2(aq) solution is placed inside a machine, known as a *spectrometer*.
- This machine measures the amount of light that is absorbed when visible light is shone through the coloured Br_2(aq) solution.
- The amount of light absorbed is expressed as *absorbance value*.
- A 0.200 mol dm$^{#3}$ Br_2 solution would have twice the absorbance value as 0.100 mol dm$^{#3}$ Br_2 solution.

Utilising the above method, briefly describe a series of experiments to deduce the order of reaction with respect to $[H^+]$ in the reaction described in **(c)**.

Provide a sketch of a graph that can be used to confirm the reaction is 2nd order with respect to $[H^+]$.

There is no need to provide detailed quantitative information in your answer. [4]

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(d) HBr(g) is another bromine compound where oxidation state of Br is –1.

When HBr(g) is heated, a red-brown gas is observed. Heating of HC*l*(g) however does not produce any gas.

Explain this observation with reference to relevant data from the *Data Booklet*. No calculation is required. [2]

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5 Ionic salts have strong interactions between the cation and anions leading to a tightly packed ionic lattice structure. Many ionic salts, like $CaCl_2$ (m.p. 772 °C) and $BaCl_2$ (m.p. 962 °C) therefore exists as solids at room temperature and only melt at high temperatures.

(a) **(i)** Define the term *enthalpy change of reaction*. [1]

(ii) Use the *Data Booklet* to calculate the enthalpy change, ΔH_r, for each of the following ionisation reactions.

- $Ca(g) \rightarrow Ca^{2+}(g) + 2e^{-}$
- $Ba(g) \rightarrow Ba^{2+}(g) + 2e^{-}$ [2]

(iii) Briefly account for the difference in two ΔH_r values obtained in **(a)(ii)**. [1]

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(b) The standard electrode potentials quoted in the *Data Booklet* for calcium and barium are:

$$E^{\ominus}(Ca^{2+}/Ca) = -2.87\ V$$

$$E^{\ominus}(Ba^{2+}/Ba) = -2.90\ V$$

These $E^{\ominus}$ values are closely similar but the ΔH_r values calculated in **(a)** are not. Suggest a reason. [1]

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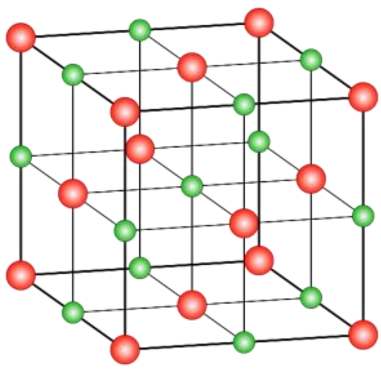
(c) Sodium chloride is a typical salt that has the following ionic lattice structure where the Na^{+} and $Cl^{\#}$ ions can pack closely together.



Ionic liquids, on the other hand, are salts that exist in the liquid state. Some examples of cations and anions that can form ionic liquids are shown in Table 5.1 below. The different cation-anion combination will give rise to ionic liquids with different melting points and properties.

Table 5.1

cation	anion
$(CH_3CH_2)_2(CH_3)_2N^{+}$ diethyldimethylammonium ion	$PF_6^{\#}$ hexafluorophosphate ion
$(CH_3CH_2)_2(CH_3)_2P^{+}$ diethyldimethylphosphonium ion	$BF_4^{\#}$ tetrafluoroborate ion

(i) With reference to Table 5.1, suggest a reason why the different cation-anion combinations exist as liquids. [1]

(ii) Predict and explain which pair of cation and anion in Table 5.1 will give the lowest melting point. [2]

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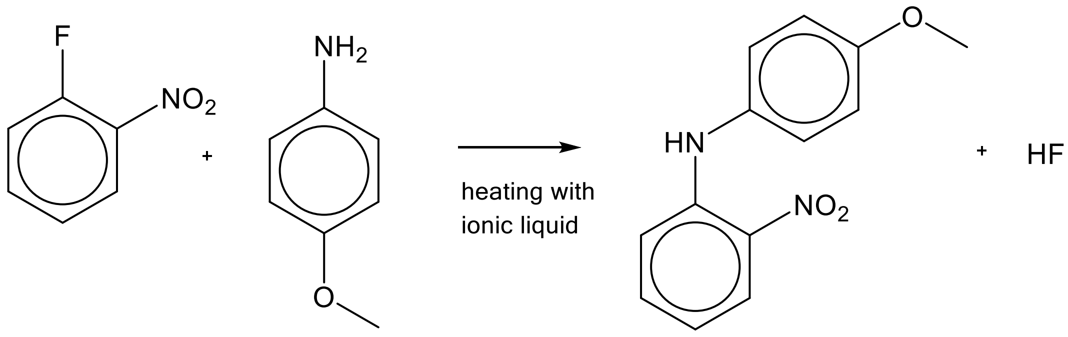
RVHS Chemistry

(iii) Outline the principles of the Valence Shell Electron Pair Repulsion (VSEPR) theory. [3]

(iv) Draw the dot-and-cross diagram showing the bonding in $BF_4^{\#}$. State and explain the shape of the ion. [2]

(d) Due to their low melting points, ionic liquids have the potential to replace conventional organic solvents. Their high stability, non-volatility and customisable polarity makes them suitable solvents for organic chemistry reactions that minimise environmental impact.

An example of a nucleophilic substitution done in ionic liquid is shown below.



D **E** **F**

(i) Outline a simple chemical test that could be carried out to distinguish between compound **D** and **E**. [2]

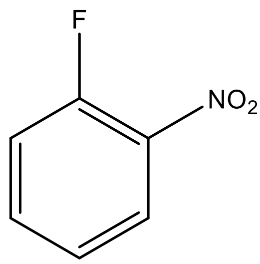
(ii) Apart from the solvent used, suggest two reasons why this nucleophilic substitution is usually not expected to occur. [2]

(iii) The mechanism for this nucleophilic substitution is thought to involve three steps.

- Nucleophile **E** attacks the benzene ring and a π bond breaks heterolytically. The intermediate generated has a negative charge on a carbon atom and a positive charge on another atom.
- To restore aromaticity, heterolytic cleavage of C#F bond occurs.
- Product **F** is formed after deprotonation.

Describe the mechanism for the reaction. Show all relevant charges, lone pairs and movement of electron pairs by using curly arrows.

You may find it useful to represent **D** as



in your mechanism. [3]

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Additional answer space

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