Section A

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

1 An experiment was conducted to determine the amount of ascorbic acid (vitamin C, $C_6H_8O_6$) in one supplement tablet.

A supplement tablet was dissolved in water and made up to 250 cm^3. 25.0 cm^3 of the solution was pipetted into a conical flask containing 5.0 cm^3 of 0.400 mol dm^{-3} KI and 5.0 cm^3 of 1 mol dm^{-3} HC*l*. A few drops of starch indicator were then added. This resulting solution was titrated against 4.00×10^{-3} mol dm^{-3} KIO_3. 23.90 cm^3 of KIO_3 was required for complete reaction.

When IO_3^- ions are added to an acidic solution containing I^- ions, a redox reaction occurs.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \text{ -------- } \mathbf{(1)}$$

The I_2 formed by this reaction then reacts with ascorbic acid to form dehydroascorbic acid ($C_6H_6O_6$).

$$C_6H_8O_6 + I_2 \rightarrow 2I^- + C_6H_6O_6 + 2H^+ \text{ -------- } \mathbf{(2)}$$

Due to reaction **(2)**, the I_2 formed in **(1)** will immediately react away as long as there is any ascorbic acid present. Once all the ascorbic acid has been reacted, the excess I_2 is free to react with the starch indicator, forming the blue-black starch-iodine complex, indicating the end-point of the reaction.

(a) Suggest a reason why the concentration of KI used was much higher than that of KIO_3.

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[1]

(b) Explain in terms of the change in oxidation number which species have been reduced in **(1)**. Write a half equation for this reduction.

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[2]

(c) **(i)** Calculate the amount, in moles, of ascorbic acid present in the original 250 cm^3 solution.

[3]

(ii) Hence, calculate the mass of ascorbic acid in one tablet.

[2]

(d) Ascorbic acid is susceptible to oxidation by atmospheric oxygen over time. A student used a sample of ascorbic acid that was prepared several hours prior to titration.

State, with reasoning, what effect this will have on the volume of KIO_3 required for complete reaction and hence the calculated mass of ascorbic acid.

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[2]

[Total: 10]

2 **(a)** The compound whose bonding most resembles pure ionic bonding is a Group 1 fluoride, **M**F.

(i) When the Group 1 cation is passed through an electric field, it is deflected through an angle of +5.0°.

Given that the same electric field deflected $^{92}Sr^{3+}$ through an angle of +22°, calculate the relative atomic mass (A_r) of **M**. Hence suggest a possible identity of the **M**.

[2]

(ii) Explain why the second ionisation energy of **M** is more endothermic than its first ionisation energy.

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(iii) Suggest a reason why the bonding in **M**F resembles pure ionic the most.

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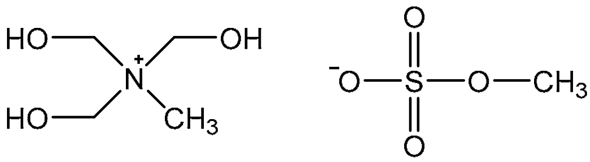
(iv) Draw a dot-cross diagram to show the bonding in **M**F. Show outer electrons only.

[1]

(b) Most ionic compounds are solids at room temperature and pressure. However, researchers have designed ionic compounds whose ionic bonding is so weak that they exist as liquids under these conditions.

An example of an ionic liquid is shown below.



Suggest two features of these ions that account for the compound having a low melting point.

1. ....

2. ....
[2]

(c) Hydrogen bonds are weaker than ionic or covalent bonds, but accounts for many important intermolecular attractions.

State an anomalous property of water that is the result of hydrogen bonding.

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[1]

(d) Draw and label the hydrogen bond between two water molecules. Indicate the bond angle around the hydrogen atom involved in the hydrogen bond. Include all relevant lone pairs and dipoles.

[2]

[Total: 10]

3 **(a)** Sodium and sulfur are elements in Period 3 in the Periodic Table.

Describe what you would observe when these two elements are separately burned in oxygen. Write equations for the reactions that occur.

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[4]

(b) The oxides, MgO, Al_2O_3 and P_4O_{10}, exist as white powdered solids with high melting points.

(i) Arrange the oxides in decreasing melting points and explain their relative melting points in terms of their structure and bonding.

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[4]

(ii) Describe two chemical reactions you could carry out on a sample of white powder to determine the identity of the oxide.

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[2]

[Total: 10]

4 **(a)** *Cracking* is a process used in the petroleum industry that converts large hydrocarbon molecules into smaller, more useful ones**.**

(i) In one particular reaction, a 16–carbon alkane undergoes cracking to form C_3H_6, C_4H_8 and C_6H_{14} as the **only** products.

Write a balanced equation to represent this reaction.

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[1]

(ii) The hydrocarbon, C_4H_8, formed from the above reaction is found to display *cis–trans isomerism*.

State the structural requirements for *cis–trans isomerism* to be displayed in an organic molecule.

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[2]

(iii) Hence, draw the displayed formulae of the cis–trans isomers of C_4H_8. Label each isomer clearly.

[2]

(b) Another important process in the petroleum industry is *reforming*, which increases the proportion of aromatic, cyclic and branched–chain hydrocarbons in petrol. This enables petrol to burn more smoothly in car engines.

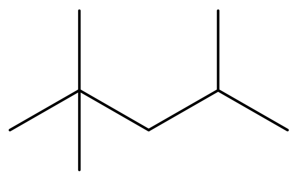
(i) One of the main products formed from the reforming process is methylbenzene, which undergoes two different reactions with bromine, depending on the conditions used.

For each reaction, state the conditions required and write a balanced equation, showing clearly the structure of **any one mono–brominated** organic product formed.

Conditions	**Equation**

[2]

(ii) Another product of the reforming process has the structure below:



State the name of the compound above.

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[1]

(c) Compound **C** has a symmetrical structure with the molecular formula $C_6H_{12}Br_2$. In the presence of alcoholic NaOH, **C** produces **D**, C_6H_{10}.

When **D** is oxidised by hot acidified $KMnO_4$, three compounds, CO_2, CH_3CO_2H and CH_3COCO_2H, are formed in equimolar amounts.

Deduce the structures of **C** and **D**.

C	**D**

[2]

[Total: 10]

Section B

Answer **two** questions from this section on separate answer papers.

5 **(a)** Nitrogen is an element that is essential to life on earth. In spite of nitrogen's abundance in the atmosphere, the quantity of nitrogen containing compounds that were available for human use was limited. The Haber process for the manufacture of ammonia and the Ostwald process for the conversion of ammonia to nitric acid were developed in the early 20th century.

Ammonia is manufactured from nitrogen and hydrogen by the Haber process as shown in the equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H_{rxn} = -45.9 \text{ kJ mol}^{-1}$$

(i) Write an expression for the equilibrium constant, K_c, for the Haber process. [1]

(ii) Calculate the value of K_c given the following equilibrium concentrations at 1000 K. State the units of K_c.

gas	**Concentration / mol dm^{-3}**
nitrogen	1.36
hydrogen	1.84
ammonia	0.142

[2]

(iii) Explain why the activation energy of the process is high. [1]

(iv) Hence describe and explain the conditions required for the favourable production of ammonia in the Haber process. [3]

(b) A large proportion of the ammonia manufactured is then used to manufacture nitric acid which is another industrially important compound. In Ostwald process, nitric acid is produced industrially from ammonia, air and water using the following sequence of reactions:

Step 1 $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$ $\Delta \boldsymbol{H}_{rxn}$ **(step 1)**

Step 2 $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\Delta \boldsymbol{H}_{rxn}$ **(step 2)**

Step 3 $4NO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 4HNO_3(aq)$ $\Delta \boldsymbol{H}_{rxn}$ **(step 3)**

Overall reaction $NH_3(g) + 2O_2(g) \rightarrow HNO_3(aq) + 2H_2O(l)$

(i) Using relevant bond energy data from the *Data Booklet* and the following value, calculate the enthalpy change, $\Delta \boldsymbol{H}_{rxn}$ **(step 1)**, for the reaction between ammonia and oxygen gas.

Bond energy for NO(g) = 607 kJ mol^{-1}

[2]

(ii) Using the following enthalpy changes, calculate the enthalpy changes, $\Delta \boldsymbol{H}_{rxn}$ **(step 2)** and $\Delta \boldsymbol{H}_{rxn}$ **(step 3)**.

$\Delta H_f (NO_2)$ = +33.2 kJ mol^{-1}
$\Delta H_f (NO)$ = +90.3 kJ mol^{-1}
$\Delta H_f (HNO_3)$ = –207.4 kJ mol^{-1}
$\Delta H_c (H_2)$ = –285.8 kJ mol^{-1}

[3]

(iii) Hence, or otherwise, calculate the enthalpy change for the **overall reaction**.

[2]

(c) A monobasic acid **HA,** extracted from a fruit has a pH of 3.5.

(i) Calculate the concentration, in mol dm^{-3}, of hydrogen ions in the acid **HA**.

[1]

(ii) 25.0 cm^3 of a sample of the acid **HA** was titrated with 0.25 mol dm^{-3} aqueous NaOH. 21.25 cm^3 of the aqueous NaOH was required to reach equivalence point.

Calculate the concentration, in mol dm^{-3}, of the acid **HA**.

[2]

(iii) Based on your answers to **(c)(i)** and **(c)(ii)** above, what can you deduce about the strength of the acid **HA**? Give a reason for your deduction.

[1]

(iv) Hence predict the volume of carbon dioxide evolved when 25.0 cm^3 of 0.40 mol dm^{-3} of HC*l* and **HA** reacts with excess Na_2CO_3 under standard conditions.

[2]

[Total: 20]

6 **(a)** Potassium reacts with ammonia to give a compound of KNH_2 as shown in the given equation:

$$2K + 2NH_3 \rightarrow 2KNH_2 + H_2$$

The rate of the reaction was investigated by using a freshly cut piece of potassium which was weighed and added to a large excess of ammonia. The experiment was conducted at room temperature and pressure.

The total volume of gas evolved at every minute was recorded and shown below.

Time/ min	0	1	2	3	4	5	6	7	8
Total volume of gas/ cm^3	0	23.0	36.5	46.0	51.0	55	58.0	60	60

(i) Plot the experimental results on graph paper. [2]

(ii) Hence deduce the order of reaction with respect to potassium. [1]

(iii) Write a rate equation for the reaction and calculate the rate constant, stating its units. [2]

(iv) In this experiment, the kinetics appear to be zero order with respect to ammonia. Suggest a reason for this. [1]

(v) Calculate the mass of potassium used in the experiment. [2]

(b) Ammonia is an important starting material in the manufacture of fertilisers as well as explosives and plastics. The Haber process is used to form ammonia as shown in the equation below.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(i) Draw a Maxwell Boltzmann distribution curve for the reactants at temperature $\mathbf{T_1}$. Label this curve **X**. Mark the position of the activation energy with a line. Label this as $\boldsymbol{E_a}$. [2]

(ii) On the axes that you have drawn, draw a **second** distribution curve that represents the reaction at a higher temperature $\mathbf{T_2}$. Label this curve **Y**.

Use curves **X** and **Y** to describe and explain the effects of an increase in temperature on the rate of a reaction. [3]

(iii) Name a catalyst that can be used for the Haber Process. [1]

(c) **(i)** Draw a dot-and-cross diagram to show the bonding in an ammonia molecule. [1]

(ii) By using the Valence Shell Electron Pair Repulsion theory, state the shape and bond angle in the ammonia molecule and explain in details how it arises. [2]

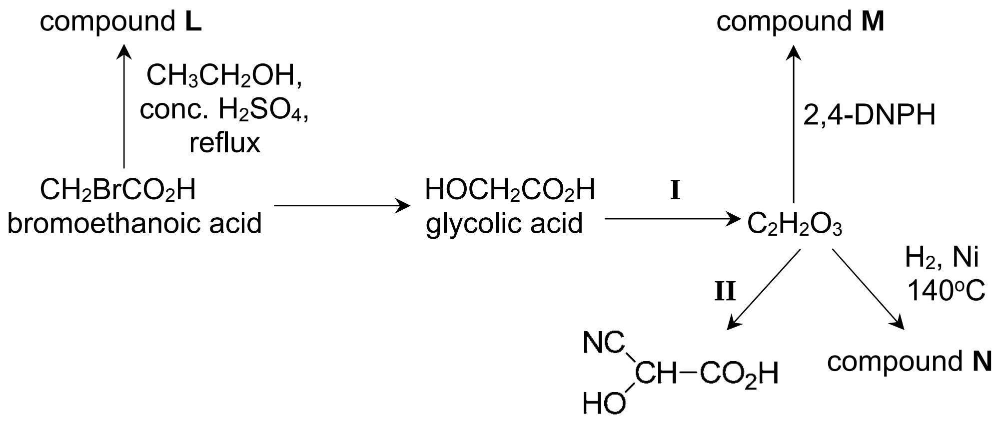
(iii) When ammonia is mixed with aluminium chloride in a 1:1 ratio, a new single compound is formed.

Suggest the type of bond that is formed between ammonia and aluminium chloride, explaining your answer clearly. Draw a ***displayed*** structure of the product formed, indicating the bond angle with respect to nitrogen and aluminium. [3]

[Total: 20]

7 **(a)** Glycolic acid, $HOCH_2CO_2H$, is a colourless, odourless and hygroscopic crystalline solid which is used in various skin-care products.

The reaction scheme below shows some reactions involving glycolic acid.



(i) State the reagents and conditions for reactions **I** and **II**.

[2]

(ii) Draw the structural formulae for compounds **L**, **M** and **N**.

[3]

(iii) The K_a of bromoethanoic acid is 1.38 x 10^{-3} mol dm^{-3}.

Predict, with reasons, whether the K_a of chloroethanoic acid would be greater or less than that of bromoethanoic acid.

[3]

(b) Bromoethane is used as a solvent, an anaesthetic in medicine and a refrigerant. It is also a useful intermediate for making other organic compounds, such as carboxylic acid.

(i) Bromoethane reacts with aqueous NaOH under heating condition.

How would you expect the rate of this reaction to compare to that of the reaction of iodoethane with aqueous NaOH? Explain your answer.

[3]

(ii) Bromoethane can be used to prepare propanal under laboratory conditions, using propanoic acid as an intermediate.

Suggest a synthesis involving not more than 4 steps for this conversion. Include reagents and conditions for each step, as well as the structures of the intermediate compounds formed.

[5]

(c) Propose appropriate test-tube reactions which would enable you to distinguish between the following compounds. Include expected observations for each compound in your answer.

I. bromoethane and iodoethane

[2]

II. $CH_3CH_2CO_2CH_3$ and $CH_3CH_2CO_2CH_2CH_3$

[2]

[Total : 20]