Section B

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

5 (a) Hydrogen sulfide is a colourless gas with a characteristic 'rotten egg' smell. It occurs naturally in crude petroleum and reacts with methane according to the following equilibrium.

$$CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g) \qquad \Delta H = +232 \text{ kJ mol}^{-1}$$

(i) State and explain the effect on the number of moles of methane when the volume of the vessel is reduced at a constant temperature.

(ii) Write an expression for the equilibrium constant, K_c, stating its units.

(iii) In an experiment, 1.00 mol of CH_4, 2.00 mol of H_2S, 1.00 mol of CS_2 and 2.00 mol of H_2 are mixed in a 250 cm^3 vessel at 960 °C. The concentration of methane is found to be 5.56 mol dm^{-3} when the system reaches equilibrium. Calculate the value of K_c at 960 °C.

(iv) The equilibrium constant varies with temperature according to the van't Hoff equation:

$$ln\frac{K_2}{K_1} = -\frac{\Delta H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

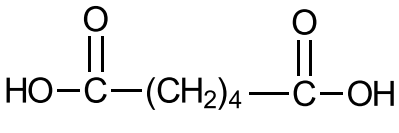
where K_1 is the equilibrium constant at temperature T_1
K_2 is the equilibrium constant at temperature T_2
$\Delta H^{\ominus}$ is the enthalpy change in J mol^{-1}
R is the ideal gas constant and
T is temperature in Kelvin.

Using your answer in **(iii)**, calculate the value of equilibrium constant at 480 °C.

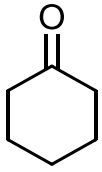
(v) Hydrogen sulfide can be removed by passing it through nitric acid. 0.15 mol of H_2S was found to react with 0.10 mol of HNO_3 to give sulfur and an oxide of nitrogen. Determine the oxidation state of nitrogen in the oxide. Hence, write a balanced equation for the reaction of H_2S and HNO_3.

[10]

(b) Adipic acid is one of the most important dicarboxylic acids and has a wide range of industrial applications. It is used as a monomer in the synthesis of nylon, and in the production of plasticizer and coatings.



adipic acid



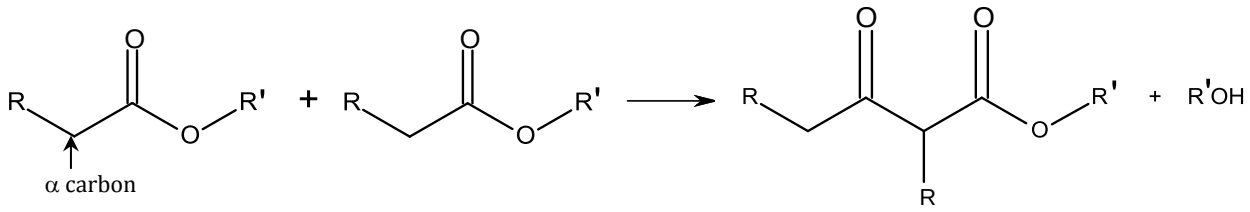
cyclohexanone

(i) Predict and explain the difference in boiling points of adipic acid and cyclohexanone.

(ii) Show a three-step synthetic route to obtain adipic acid from cyclohexanone. Suggest reagents and conditions you would use and show the structures of any intermediates formed.

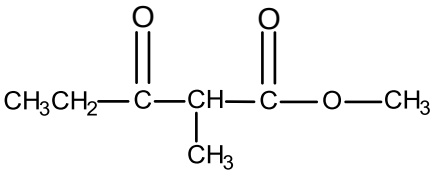
(iii) Suggest a simple chemical test to distinguish between adipic acid and cyclohexanone. State the observations and write a balanced equation for any reaction that occurs.

In the 1880s, German chemist Rainer Ludwig Claisen discovered that esters were able to react in the presence of a strong base to give a keto ester.



(iv) Name the type of reaction that has taken place between the ester molecules.

(v) Two molecules of an ester undergo the above reaction to give methanol and the following organic product.



Suggest the structure of the ester.

[10]
[Total: 20]

6 Aluminium chloride, $AlCl_3$, exhibits properties which differ from chlorides of other Period 3 elements. It sublimes at a relatively low temperature of 180ºC at atmospheric pressure due to the original lattice structure of $AlCl_3$ being converted into Al_2Cl_6 molecules. In the presence of excess water, aluminium chloride forms an acidic solution of pH 3 to 4.

(a) Describe and explain the reactions of aluminium chloride with excess water, writing equations where appropriate.

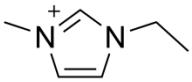
[2]

(b) Aluminium chloride reacts with sodium chloride to form sodium chloroaluminate, $NaAlCl_4$. Sodium chloroaluminate is one of the simplest compounds containing chloroaluminate anion and has a melting point of 185 ºC.

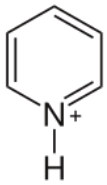
(i) Explain why sodium chloroaluminate would be formed from the above reaction, stating the type of bond that is formed during this reaction.

(ii) Draw the dot-and-cross diagram of chloroaluminate anion. Using the valence shell electron pair repulsion theory, state its shape and bond angle.

(iii) A class of compounds called room temperature ionic liquids (RTILs) can be formed from chloroaluminate anion and organic cations such as 1-ethyl-3-methylimidazolium and pyridinium ions.



1-ethyl-3-methylimidazolium



pyridinium ion

Explain the differences in physical states between RTILs and sodium chloroaluminate in terms of bonding.

[6]

(c) To determine the rate equation of the following chlorate-chloride reaction, an experiment was conducted using 0.000480 mol dm^{-3} of ClO_3^-, 0.1 mol dm^{-3} of Cl^- and 0.4 mol dm^{-3} of H^+.

$$2ClO_3^- + 2Cl^- + 4H^+ \rightarrow Cl_2 + 2ClO_2\bullet + 2H_2O$$

At regular 5-minutes intervals, small samples of the reaction mixture were withdrawn, quenched and placed into the UV-vis spectrometer to record its absorbance value. The absorbance value corresponds to the concentration of the product $ClO_2\bullet$.

(i) The results of the above experiment were shown below.

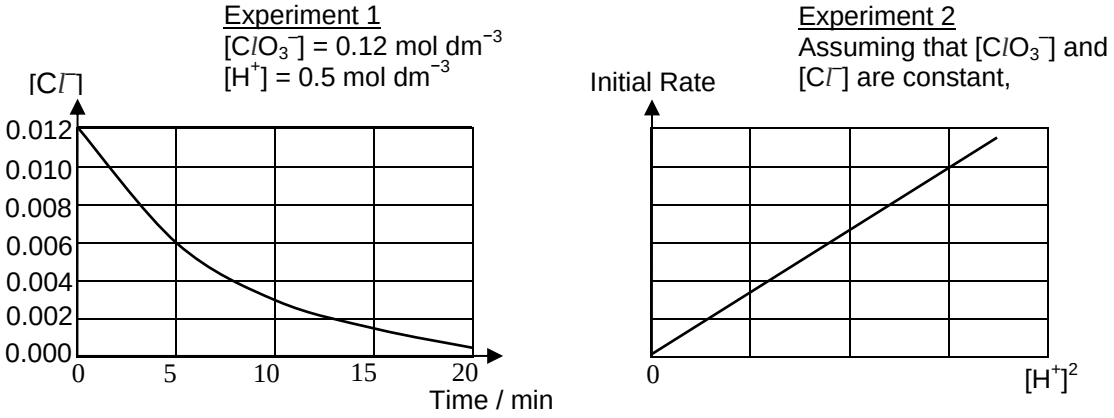
Time/min	0	5	10	15	20	*25*	∞
Absorbance/A	0.000	0.211	0.348	0.436	0.494	0.531	0.600

Plot the graph of absorbance/A against time/min.

(ii) Using your graph plotted in **(c)(i)**, determine the half-life of the experiment and hence the order of reaction with respect to $[ClO_3^-]$.

A research student carried out a series of experiments to further investigate the order of reaction with respect to [Cl^-] and [H^+] in the chlorate-chloride reaction.

The following graphs were plotted:



(iii) Using the above data, deduce the order of the reaction with respect to [Cl^-] and [H^+].

(iv) Hence, write a rate equation for the chlorate-chloride reaction.

[9]

(d) With the aid of a sketch of the Boltzman distribution, explain how an increase in temperature affects the rate of a chemical reaction.

[3]
[Total: 20]

7 During the cracking process, large hydrocarbon molecules are broken into smaller and more useful hydrocarbons such as alkanes and alkenes. When a saturated hydrocarbon **Z**, C_xH_y, undergoes cracking, hydrocarbons **A** and **B** are produced as shown by the equation below:

$$C_xH_y \longrightarrow \underset{\textbf{A}}{C_4H_{10}} + \underset{\textbf{B}}{C_5H_{10}}$$

Hydrocarbon **A** reacted with chlorine gas in the presence of u.v. light to form two monochlorinated products, **C** and **D**, in the ratio of 9 : 1 respectively.

Hydrocarbon **B** on strong heating with acidified potassium manganate(VII) produced **E**, C_3H_6O, and **F**, $C_2H_4O_2$. **E** gave a bright orange precipitate with 2,4-dinitrophenylhydrazine and a yellow precipitate with aqueous alkaline iodine. Effervescence was observed when aqueous sodium carbonate was added to **F**.

(a) Write the molecular formula of **Z**.

[1]

(b) State the type of reaction for the formation of the monochlorinated products.

[1]

(c) Give the structures of **C** and **D.** Hence, deduce the structure of **A**.

[3]

(d) Suggest the structural formula of **B, E** and **F**, explaining your reasoning.

[7]

(e) **(i)** Define the term *standard enthalpy change of formation of **A**, $C_4H_{10}(g)$.*

(ii) Write an equation for the standard enthalpy change of formation of **A**, $C_4H_{10}(g)$.

(iii) Calculate the standard enthalpy change of formation of **A**, $C_4H_{10}(g)$, given the following data:

Compound	**$\Delta H_c^{\ominus}$/kJ mol^{-1}**
C(s)	-393
$H_2(g)$	-286
$C_4H_{10}(g)$	-2870

(iv) When 0.070 g of C_4H_{10} was burned, the energy evolved was used to heat 100 cm^3 of water. Given that this process is only 80% efficient, use the data provided from **(e)(iii)** to calculate the change in temperature of water.
[Specific heat capacity of water = 4.18 J g^{-1} K^{-1}]

[8]
[Total: 20]