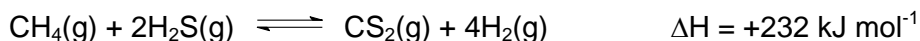


Section B

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.



- (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.

- When the volume of vessel is reduced, the pressure of the system increases. By Le Chatelier's Principle, the system counteracts the change by reducing the total pressure by favouring the backward reaction which generates less number of moles of gases.
- Hence, the number of moles of methane increases (answer must come with explanation to gain the credit).

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

- $K_c = \frac{[\text{CS}_2][\text{H}_2]^4}{[\text{CH}_4][\text{H}_2\text{S}]^2}$
- $\text{mol}^2\text{dm}^{-6}$

- (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 .

- working

	$\text{CH}_4(\text{g})$	+	$2\text{H}_2\text{S}(\text{g})$	\rightleftharpoons	$\text{CS}_2(\text{g})$	+	$4\text{H}_2(\text{g})$
Initial conc/mol dm^{-3}	4		8		4		8
Change/ mol dm^{-3}	+1.56		+3.12		-1.56		-6.24
Equilibrium/ mol dm^{-3}	5.56		11.12		2.44		1.76

- $K_c = 2.44 \times 1.76^4 / (5.56 \times 11.12^2) = 0.0341 \text{ mol}^2\text{dm}^{-6}$

- (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
 ΔH^\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.

- Working

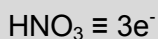
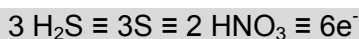
$$\ln \frac{K_c}{0.0341} = -\frac{232 \times 10^3}{8.31} \left(\frac{1}{753} - \frac{1}{1233} \right)$$

- $K_c = 1.84 \times 10^{-8} \text{ mol}^2\text{dm}^{-6}$

allow ECF from (iii)

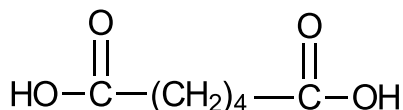
- (v) Hydrogen sulfide can be removed by passing it through nitric acid. 0.15 mol of H_2S was found to react with 0.10 mol of HNO_3 to give sulfur and an oxide of nitrogen. Determine the oxidation state of nitrogen in the oxide. Hence, write a balanced equation for the reaction of H_2S and HNO_3 .

[10]

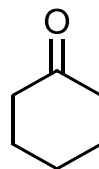


- Oxidation state of nitrogen decreases from +5 in HNO_3 to +2 in the product
- $3\text{H}_2\text{S} + 2\text{HNO}_3 \rightarrow 3\text{S} + 2\text{NO} + 4\text{H}_2\text{O}$

- (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

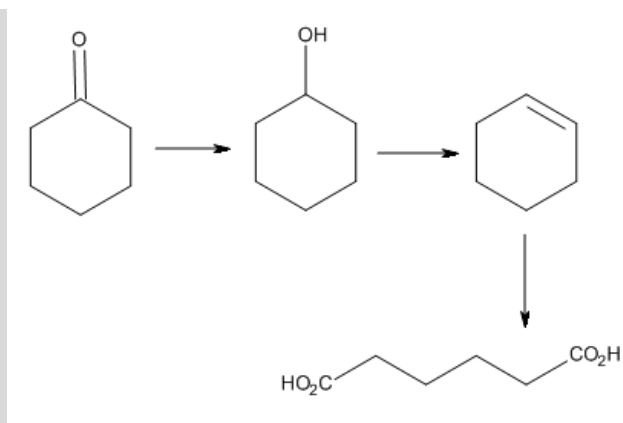


cyclohexanone

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

- Adipic acid has a higher boiling point than cyclohexanone.
- Boiling adipic acid involves breaking of hydrogen bonds between its molecules, which are stronger and require more energy to overcome compared to the van der Waal's forces of attraction between cyclohexanone molecules.

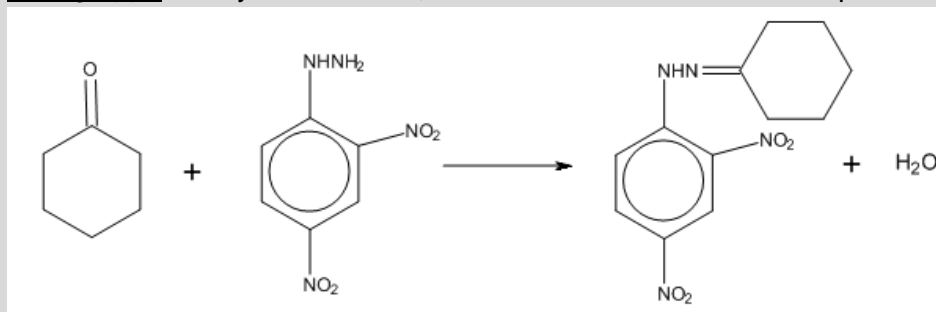
- (ii) Show a three-step synthetic route to obtain adipic acid from cyclohexanone. Suggest reagents and conditions you would use and show the structures of any intermediates formed.



- LiAlH_4 in dry ether, room temperature and pressure
Accept other reducing agents e.g. H_2/Ni , high temp or NaBH_4 , alcohol, rtp
- excess concentrated H_2SO_4 , 180°C
- acidic KMnO_4 , reflux
[reagent & condition + intermediate = 1 mark]

- (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.

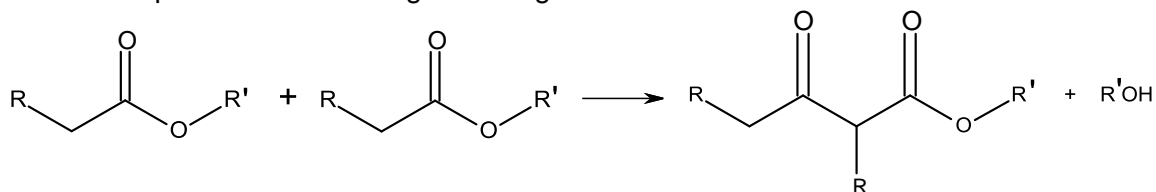
- 2,4-dinitrophenylhydrazine, rtp
- Orange ppt with cyclohexanone, no observable reaction with adipic acid



OR

- Na_2CO_3 (s), rtp
- Effervescence of CO_2 with adipic acid, no observable change with cyclohexanone
- $\text{HO}_2\text{C}-(\text{CH}_2)_4-\text{CO}_2\text{H} + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}^+ \text{O}_2\text{C}-(\text{CH}_2)_4-\text{CO}_2^- \text{Na}^+ + \text{CO}_2 + \text{H}_2\text{O}$

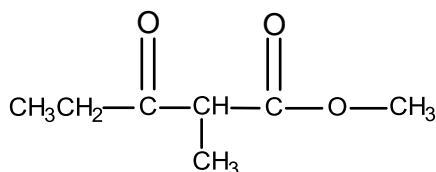
In the 1880s, German chemist Rainer Ludwig Claisen discovered that esters were able to react in the presence of a strong base to give a keto ester.



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

- condensation/ nucleophilic (acyl) substitution/ nucleophilic addition followed by elimination

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



Suggest the structure of the ester.

- $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3$

[10]

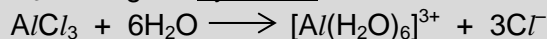
[Total: 20]

6 Aluminium chloride, AlCl_3 , exhibits properties which differ from chlorides of other Period 3 elements. It sublimes at a relatively low temperature of 180°C 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]

- AlCl_3 undergoes hydration in water and dissolves to give an aqueous solution.



- Hydrolysis also occurs due to the high charge density of Al^{3+} ions. It polarizes the water molecule and weakens the O-H bond of water making it easier for H^+ ion to leave the water molecule. An acidic solution of pH = 3 – 4 is obtained.



[Accept both full and equilibrium arrows for hydrolysis reaction]

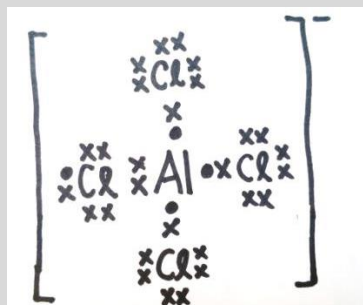
- (b) Aluminium chloride reacts with sodium chloride to form sodium chloroaluminate, NaAlCl_4 . Sodium chloroaluminate is one of the simplest compounds containing chloroaluminate anion and has a melting point of 185°C .

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

- Aluminium in AlCl_3 is electron deficient (or has vacant orbitals) as it only has 6 electrons around it and Cl^- anion has lone pairs of electrons and thus,
- dative bond is formed in the chloroaluminate anion.

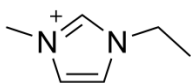
- (ii) Draw the dot-and-cross diagram of chloroaluminate anion. Using the valence shell electron pair repulsion theory, state its shape and bond angle.

•1m – dot-and-cross

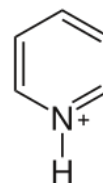


•Shape: Tetrahedral
Bond angle: 109.5°

- (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



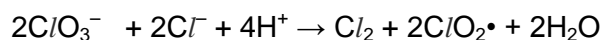
pyridinium ion

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

[6]

RTIL have a lower melting point and exists as a liquid and sodium chloroaluminate exists as a solid because the organic cation in RTIL is larger and thus, weaker ionic bonds exist between the oppositely-charged ions in RTIL as lattice energy $\propto \frac{q_+q_-}{r_+ + r_-}$.

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

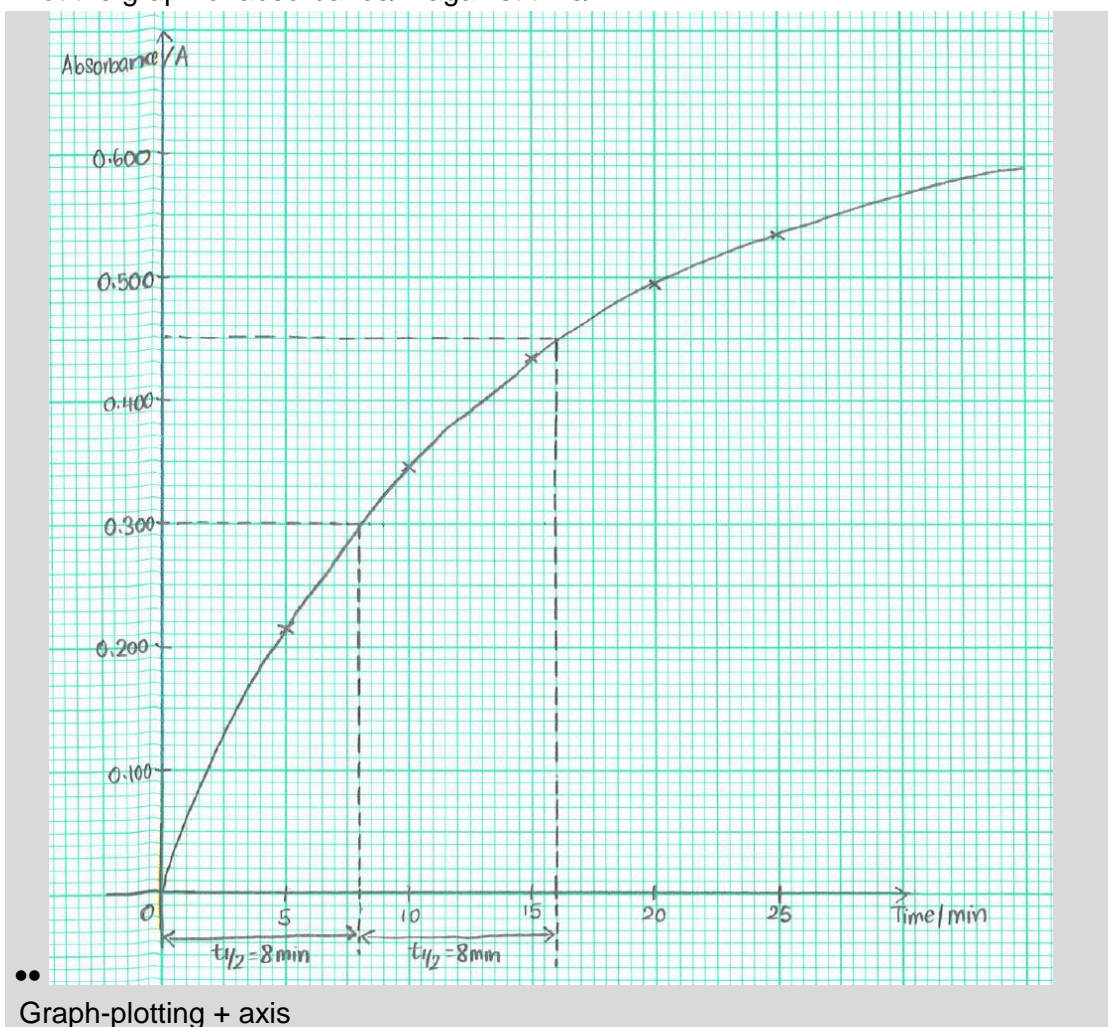


At regular 5-minutes intervals, small samples of the reaction mixture were withdrawn, quenched and placed into the UV-vis spectrometer to record its absorbance value. The absorbance value corresponds to the concentration of the product $\text{ClO}_2\cdot$.

- (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.



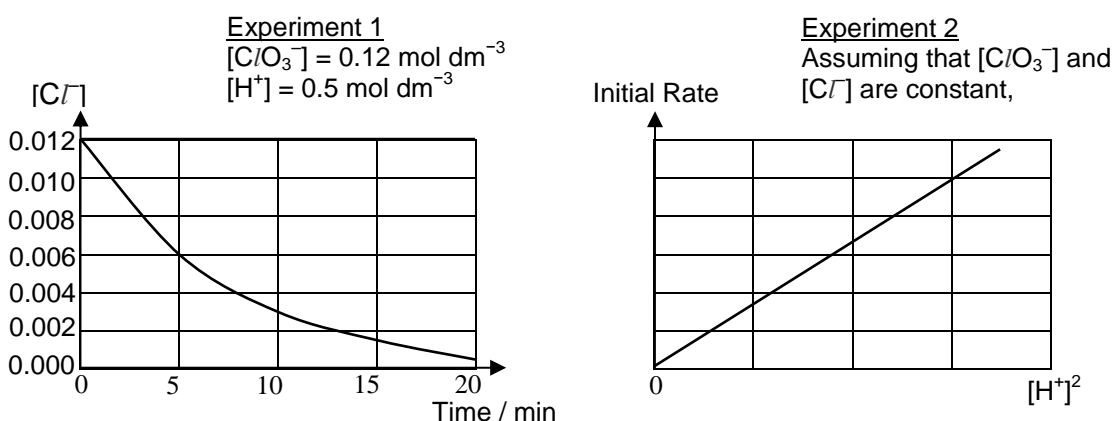
- (ii) Using your graph plotted in (c)(i), determine the half-life of the experiment and hence the order of reaction with respect to $[\text{ClO}_3^-]$.

*refer to graph plotted in (i)

- 1m – dotted lines to read off half-life ($t_{1/2}$) on the graph. Show at least 2 $t_{1/2}$.
- Since half-life ($t_{1/2}$) is constant at 8 min, the reaction is 1st order with respect to $[\text{ClO}_3^-]$.

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

The following graphs were plotted:



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

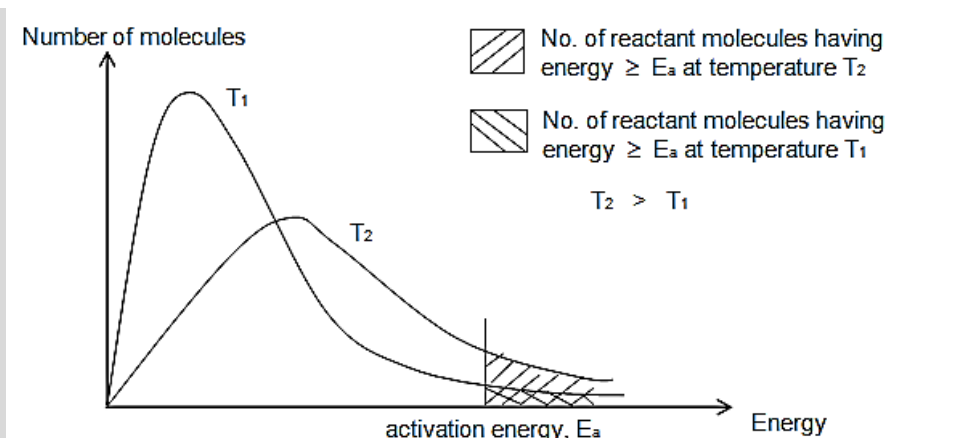
- From experiment 1, the graph of $[\text{Cl}^-]$ shows a constant half-life of 5 min.
 $\text{Rate} \propto [\text{Cl}^-]^1$
- 1st order with respect to $[\text{Cl}^-]$
- From experiment 2, the graph of initial rate vs. $[\text{H}^+]^2$ is a straight line, hence rate of reaction is directly proportional to $[\text{H}^+]^2$. $\text{Rate} \propto [\text{H}^+]^2$
- 2nd order with respect to $[\text{H}^+]$.

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

[9]

• $\text{Rate} = k[\text{ClO}_3^-][\text{Cl}^-][\text{H}^+]^2$

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



- Shape of Boltzmann distribution
- Legend and shaded area to show that number of reactants molecules having energy $> E_a$ at higher temperature is larger.

Explanation

- The increase in the average kinetic energy of the reacting molecules leads to an increase in the collision frequency.

The fraction of molecules having energy greater than the activation energy, E_a , is significantly increased when the temperature is increased.

Hence the frequency of **effective** collisions increases and the rate increases.

[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:



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]

- C_9H_{20}

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

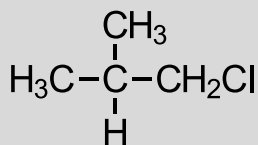
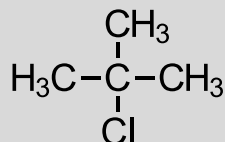
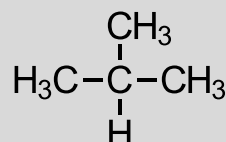
[1]

- Free radical substitution

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

[3]

...

**C****D****A**

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

[7]

- **E** is a ketone as it gives a positive test with 2,4-DNPH.

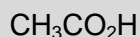
- **E** has $\text{CH}_3\text{C}=\text{O}$ as it gives positive triiodomethane test.

- Structure of **E**:



- **F** is a carboxylic acid as it liberates CO_2 with Na_2CO_3 .

- Structure of **F**:



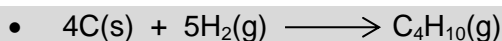
- **B** is an alkene as it undergoes strong oxidation with KMnO_4 (total bond cleavage).

- Structure of **B**:
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{C}-\text{C}=\text{C}-\text{H} \\ | \\ \text{CH}_3 \end{array}$$

(e) (i) Define the term *standard enthalpy change of formation* of **A**, $\text{C}_4\text{H}_{10}(\text{g})$.

- Standard enthalpy change of formation of **A** is the enthalpy change when 1 mole of $\text{C}_4\text{H}_{10}(\text{g})$ is formed from its constituent elements in their standard states, that is $\text{C}(\text{s})$ and $\text{H}_2(\text{g})$ under standard conditions of 298 K and 1 atm.

(ii) Write an equation for the standard enthalpy change of formation of **A**, $\text{C}_4\text{H}_{10}(\text{g})$.



(iii) Calculate the standard enthalpy change of formation of **A**, $\text{C}_4\text{H}_{10}(\text{g})$, given the following data:

Compound	$\Delta H_c^\circ / \text{kJ mol}^{-1}$
$\text{C}(\text{s})$	-393
$\text{H}_2(\text{g})$	-286
$\text{C}_4\text{H}_{10}(\text{g})$	-2870

$$\begin{aligned} \bullet \Delta H_f^\ominus &= [(4x-393) + (5x-286)] - (-2870) \text{ kJ mol}^{-1} \\ \bullet &= -132 \text{ kJ mol}^{-1} \end{aligned}$$

- (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 = $4.18 \text{ J g}^{-1} \text{ K}^{-1}$]

[8]

$$\text{Amount } \text{C}_4\text{H}_{10} \text{ burned} = 0.070/58.0 = 1.21 \times 10^{-3} \text{ mol}$$

- Heat evolved when 0.070 g C_4H_{10} undergoes combustion
 $= 1.21 \times 10^{-3} \times 2870 \text{ kJ}$
 $= 3.47 \text{ kJ}$
- Heat transferred to water = $80/100 \times 3.47 \text{ kJ} = 2.78 \text{ kJ}$
- Heat evolved = $mc\Delta T$
 $2780 = 100 \times 4.18 \times \Delta T$
- $\Delta T = 6.65 \text{ K}$

[Total: 20]