

Q1. The table below gives some values of standard enthalpy changes. Use these values to answer the questions.

Name of enthalpy change	ΔH° /kJ mol ⁻¹
Enthalpy of atomisation of chlorine	+121
Electron affinity of chlorine	-364
Enthalpy of atomisation of silver	+289
First ionisation enthalpy of silver	+732
Enthalpy of formation of silver chloride	-127

(a) Calculate the bond enthalpy of a Cl-Cl bond.

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(1)

(b) Explain why the bond enthalpy of a Cl-Cl bond is greater than that of a Br-Br bond.

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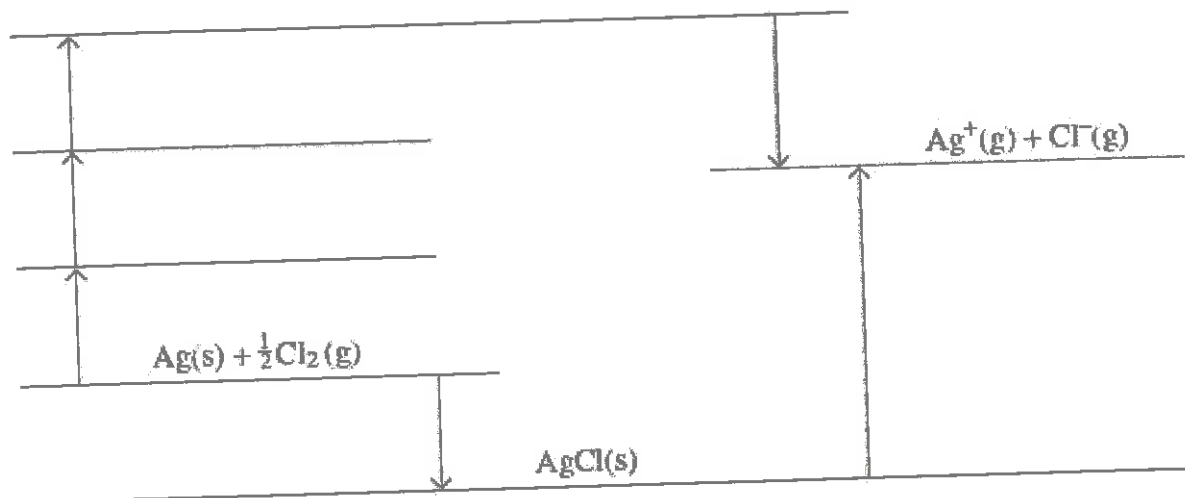
(2)

(c) Suggest why the electron affinity of chlorine is an exothermic change.

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(1)

- (d) The diagram below is an incomplete Born–Haber cycle for the formation of silver chloride. The diagram is not to scale.



- (i) Complete the diagram by writing the appropriate chemical symbols, with state symbols, on each of the three blank lines. (3)

- (ii) Calculate a value for the enthalpy of lattice dissociation for silver chloride.

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(2)

- (e) The enthalpy of lattice dissociation for silver chloride can also be calculated theoretically assuming a perfect ionic model.

- (i) Explain the meaning of the term *perfect ionic model*.

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(1)

- (ii) State whether you would expect the value of the theoretical enthalpy of lattice dissociation for silver chloride to be greater than, equal to or less than that for silver bromide. Explain your answer.

Theoretical lattice enthalpy for silver chloride

Explanation

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(3)

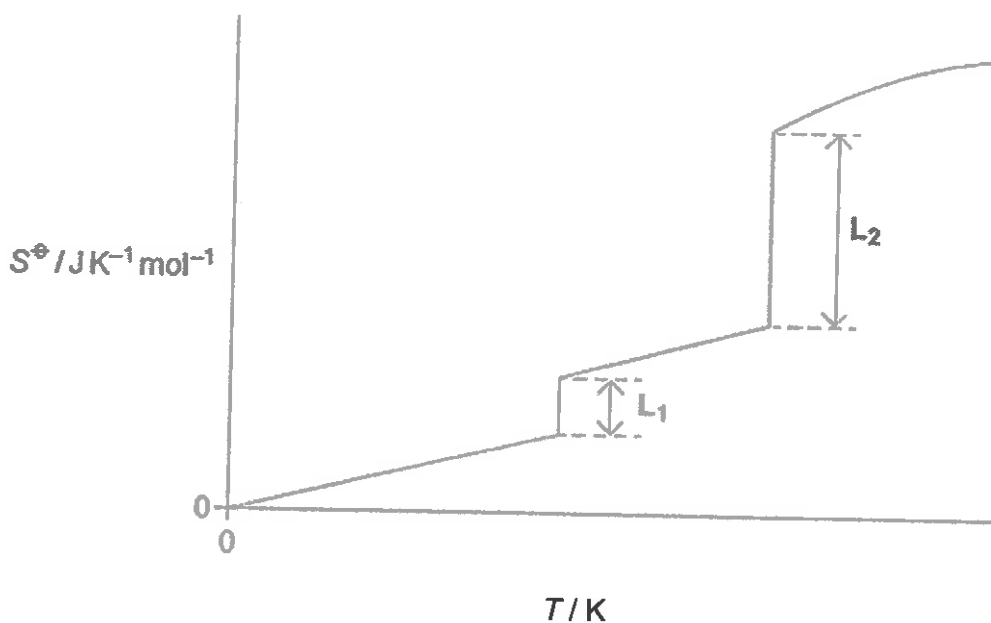
- (iii) Suggest why your answer to part (d) (ii) is greater than the theoretical value for the enthalpy of lattice dissociation for silver chloride.

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(2)
(Total 15 marks)

Q2.(a) Figure 1 shows how the entropy of a molecular substance X varies with temperature.

Figure 1



- (i) Explain, in terms of molecules, why the entropy is zero when the temperature is zero Kelvin.

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(Extra space)
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(2)

- (ii) Explain, in terms of molecules, why the first part of the graph in **Figure 1** is a line that slopes up from the origin.

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(2)

- (iii) On **Figure 1**, mark on the appropriate axis the boiling point (T_b) of substance **X**.

(1)

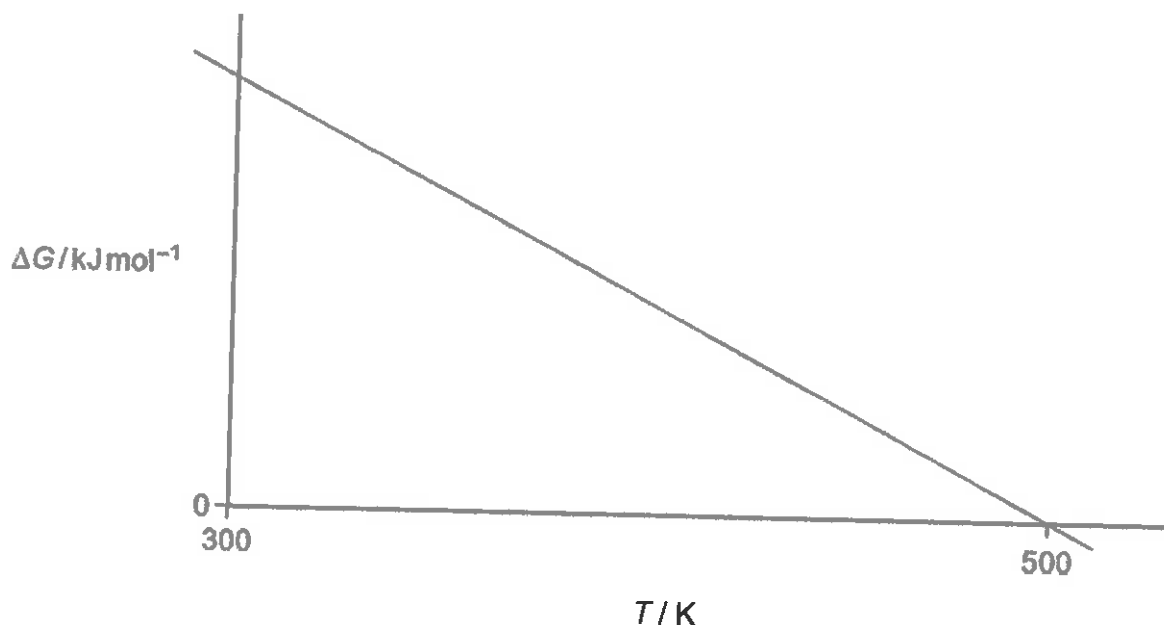
- (iv) In terms of the behaviour of molecules, explain why L_2 is longer than L_1 in **Figure 1**.

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(Extra space)
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(2)

- (b) **Figure 2** shows how the free-energy change for a particular gas-phase reaction varies with temperature.

Figure 2



- (i) Explain, with the aid of a thermodynamic equation, why this line obeys the mathematical equation for a straight line, $y = mx + c$.

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(2)

- (ii) Explain why the magnitude of ΔG decreases as T increases in this reaction.

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(1)

- (iii) State what you can deduce about the feasibility of this reaction at temperatures lower than 500 K.

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(1)

- (c) The following reaction becomes feasible at temperatures above 5440 K.



The entropies of the species involved are shown in the following table.

	$\text{H}_2\text{O}(\text{g})$	$\text{H}_2(\text{g})$	$\text{O}_2(\text{g})$
$S / \text{J K}^{-1} \text{mol}^{-1}$	189	131	205

- (i) Calculate the entropy change ΔS for this reaction.

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(1)

- (ii) Calculate a value, with units, for the enthalpy change for this reaction at 5440 K.

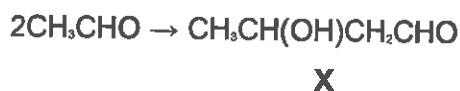
(If you have been unable to answer part (c)(i), you may assume that the value of the entropy change is $+98 \text{ J K}^{-1} \text{ mol}^{-1}$. This is **not** the correct value.)

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(3)

(Total 15 marks)

Q3. A reaction mechanism is a series of steps by which an overall reaction may proceed. The reactions occurring in these steps may be deduced from a study of reaction rates. Experimental evidence about initial rates leads to a rate equation. A mechanism is then proposed which agrees with this rate equation. Ethanal dimerises in dilute alkaline solution to form compound **X** as shown in the following equation.



A chemist studied the kinetics of the reaction at 298 K and then proposed the following rate equation.

$$\text{Rate} = k [\text{CH}_3\text{CHO}][\text{OH}^-]$$

(a) Give the IUPAC name of compound **X**.

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(1)

(b) The initial rate of the reaction at 298K was found to be $2.2 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ when the initial concentration of ethanal was 0.10 mol dm^{-3} and the initial concentration of sodium hydroxide was $0.020 \text{ mol dm}^{-3}$. Calculate a value for the rate constant at this temperature and give its units.

Calculation

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Units

(3)

(c) The sample of **X** produced consists of a racemic mixture (racemate). Explain how this racemic mixture is formed.

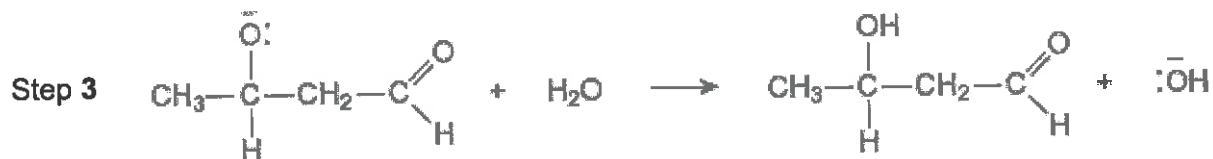
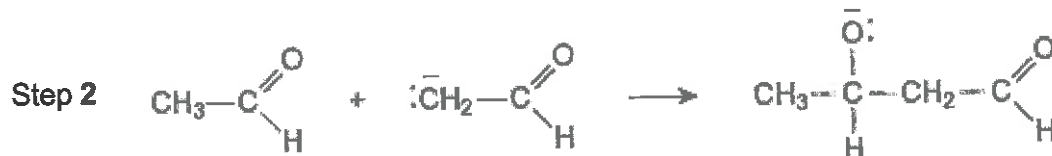
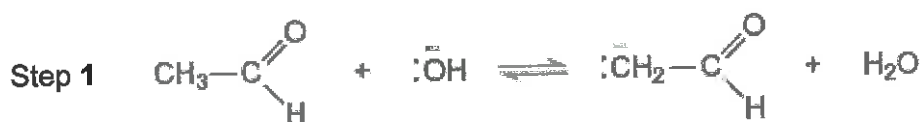
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(2)

- (d) A three-step mechanism has been proposed for this reaction according to the following equations.



- (i) Using the rate equation, predict which of the three steps is the rate-determining step. Explain your answer.

Rate-determining step

Explanation

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(2)

- (ii) Deduce the role of ethanal in Step 1.

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(1)

- (iii) Use your knowledge of reaction mechanisms to deduce the type of reaction occurring in Step 2.

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(1)

- (iv) In the space below draw out the mechanism of Step 2 showing the relevant curly arrows.

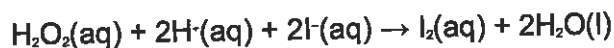
(2)

- (e) In a similar three-step mechanism, one molecule of X reacts further with one molecule of ethanal. The product is a trimer containing six carbon atoms.

Deduce the structure of this trimer.

(1)
(Total 13 marks)

Q4.Hydrogen peroxide is a powerful oxidising agent. Acidified hydrogen peroxide reacts with iodide ions to form iodine according to the following equation.



The **initial rate** of this reaction is investigated by measuring the time taken to produce sufficient iodine to give a blue colour with starch solution.

A series of experiments was carried out, in which the concentration of iodide ions was varied, while keeping the concentrations of all of the other reagents the same. In each experiment the time taken (t) for the reaction mixture to turn blue was recorded.

The initial rate of the reaction can be represented as $\frac{1}{t}$, and the initial concentration of iodide ions can be represented by the volume of potassium iodide solution used.

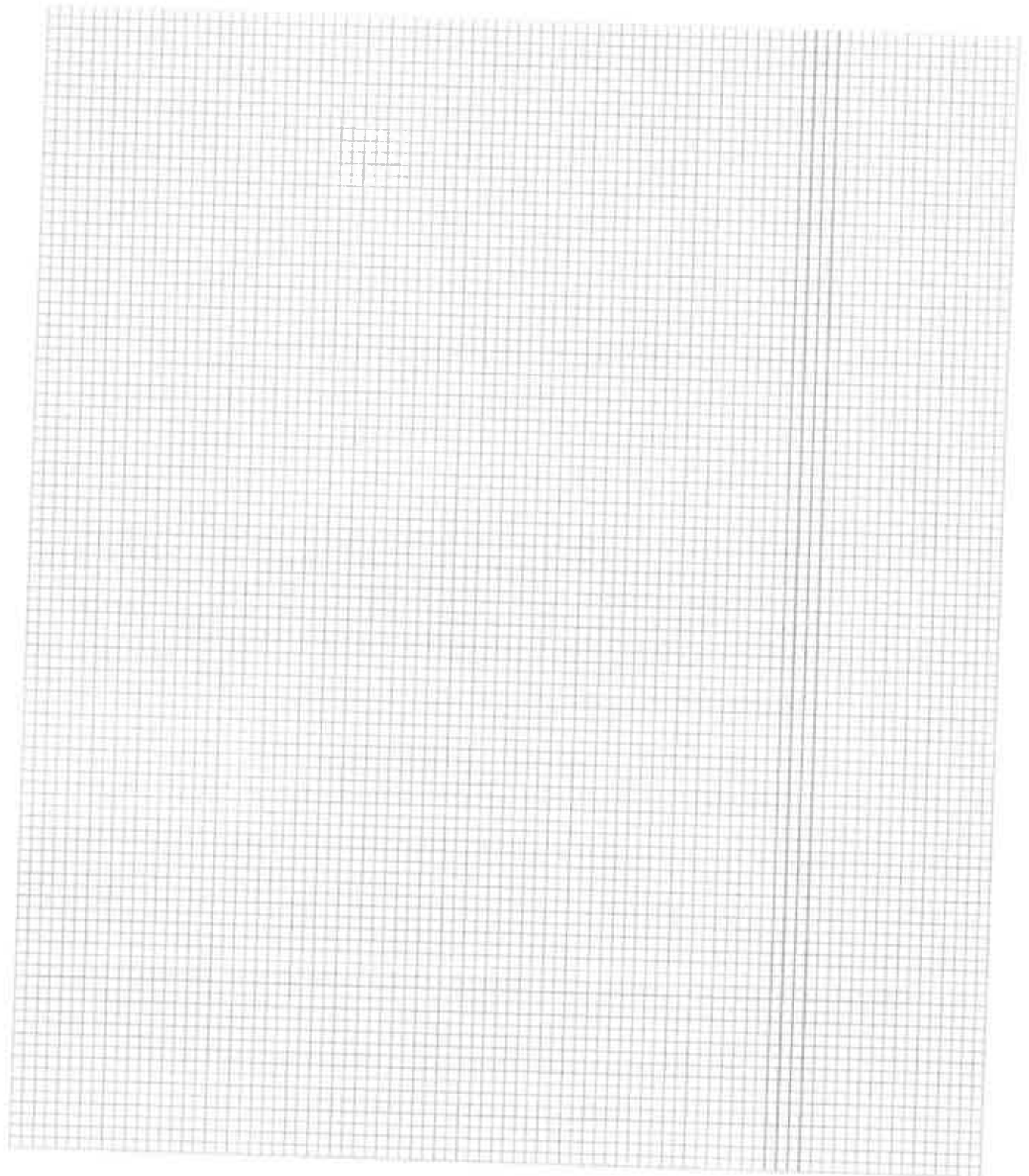
A graph of $\log_{10} \left(\frac{1}{t} \right)$ on the y -axis against $\log_{10} (\text{volume of KI(aq)})$ is a straight line. The gradient of this straight line is equal to the order of the reaction with respect to iodide ions.

The results obtained are given in the table below. The time taken for each mixture to turn blue was recorded on a stopclock graduated in seconds.

Expt.	Volume of KI(aq) / cm ³	$\log_{10} (\text{volume of KI(aq)})$	Time / s	$\log_{10} \left(\frac{1}{t} \right)$
1	5	0.70	71	-1.85
2	8	0.90	46	-1.66
3	10	1.00	37	-1.57
4	15	1.18	25	-1.40
5	20	1.30	19	-1.28
6	25	1.40	14	-1.15

(a) Use the results given in the table to plot a graph of $\log_{10} \left(\frac{1}{t} \right)$ on the y -axis against $\log_{10} (\text{volume of KI(aq)})$.

Draw a straight line of best fit on the graph, ignoring any anomalous points.



(5)

- (b) Determine the gradient of the line you have drawn. Give your answer to two decimal places. Show your working.

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(3)

- (c) Deduce the order of reaction with respect to iodide ions.

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(1)

- (d) A student carried out the experiment using a flask on the laboratory bench. The student recorded the time taken for the reaction mixture to turn blue. State **one** way this method could be improved, other than by repeating the experiment or by improving the precision of time or volume measurements. Explain why the accuracy of the experiment would be improved.

Improvement

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Explanation

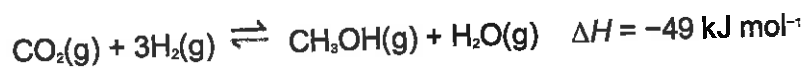
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(2)

(Total 11 marks)

Q5. Many chemical processes release waste products into the atmosphere. Scientists are developing new solid catalysts to convert more efficiently these emissions into useful products, such as fuels. One example is a catalyst to convert these emissions into methanol. The catalyst is thought to work by breaking a H-H bond.

An equation for this formation of methanol is given below.



Some mean bond enthalpies are shown in the following table.

Bond	C=O	C-H	C-O	O-H
Mean bond enthalpy / kJ mol ⁻¹	743	412	360	463

- (a) Use the enthalpy change for the reaction and data from the table to calculate a value for the H–H bond enthalpy.

H–H bond enthalpy = kJ mol⁻¹

(3)

- (b) A data book value for the H–H bond enthalpy is 436 kJ mol⁻¹.

Suggest **one** reason why this value is different from your answer to part (a).

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(1)

- (c) Suggest **one** environmental advantage of manufacturing methanol fuel by this reaction.

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(1)

- (d) Use Le Chatelier's principle to justify why the reaction is carried out at a high pressure rather than at atmospheric pressure.

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(3)

- (e) Suggest why the catalyst used in this process may become less efficient if the carbon dioxide and hydrogen contain impurities.

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(1)

- (f) In a laboratory experiment to investigate the reaction shown in the equation below, 1.0 mol of carbon dioxide and 3.0 mol of hydrogen were sealed into a container. After the mixture had reached equilibrium, at a pressure of 500 kPa, the yield of methanol was 0.86 mol.

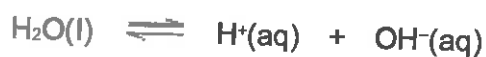


Calculate a value for K_p .
Give your answer to the appropriate number of significant figures.
Give units with your answer.

$K_p =$ Units =

(7)
(Total 16 marks)

Q6. Water dissociates slightly according to the equation:



The ionic product of water, K_w , is given by the expression

$$K_w = [\text{H}^+][\text{OH}^-]$$

K_w varies with temperature as shown in the table.

Temperature / °C	$K_w / \text{mol}^2 \text{dm}^{-6}$
25	1.00×10^{-14}
50	5.48×10^{-14}

(a) Explain why the expression for K_w does **not** include the concentration of water.

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(2)

(b) Explain why the value of K_w increases as the temperature increases.

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(2)

(c) Calculate the pH of pure water at 50 °C.
Give your answer to 2 decimal places.

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(3)

- (d) Calculate the pH of 0.12 mol dm⁻³ aqueous NaOH at 50 °C.
Give your answer to 2 decimal places.

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(3)
(Total 10 marks)

Q7. The acid dissociation constant, K_a , for ethanoic acid is given by the expression

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

The value of K_a for ethanoic acid is 1.74×10^{-5} mol dm⁻³ at 25 °C.

- (a) A buffer solution is prepared using ethanoic acid and sodium ethanoate. In the buffer solution, the concentration of ethanoic acid is 0.186 mol dm⁻³ and the concentration of sodium ethanoate is 0.105 mol dm⁻³.

Calculate the pH of this buffer solution.
Give your answer to 2 decimal places.

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(3)

- (b) In a different buffer solution, the concentration of ethanoic acid is $0.251 \text{ mol dm}^{-3}$ and the concentration of sodium ethanoate is $0.140 \text{ mol dm}^{-3}$.

A sample of hydrochloric acid containing 0.015 mol of HCl is added to 1000 cm^3 of this buffer solution.

Calculate the pH of the buffer solution after the hydrochloric acid has been added. You should ignore any change in total volume.

Give your answer to 2 decimal places.

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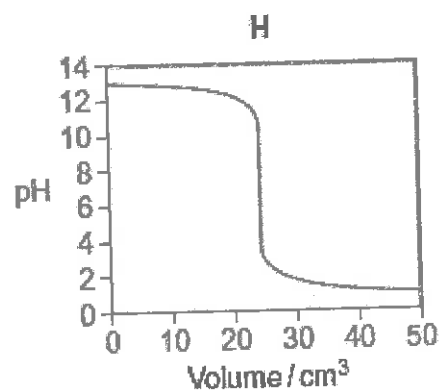
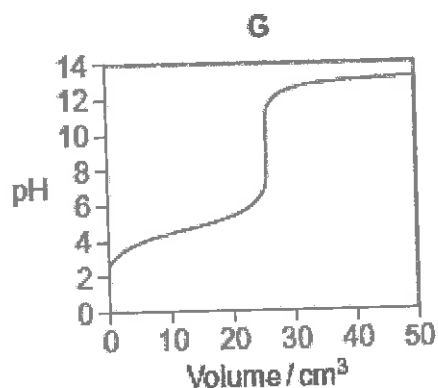
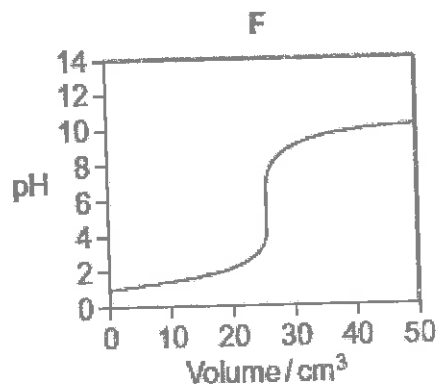
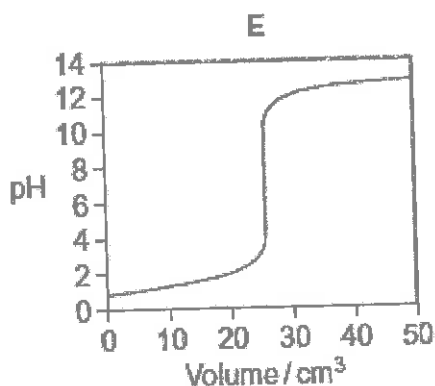
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(5)
(Total 8 marks)

Q8. Titration curves, labelled **E**, **F**, **G** and **H**, for combinations of different aqueous solutions of acids and bases are shown below.

All solutions have concentrations of 0.1 mol dm^{-3} .



(a) In this part of the question, write the appropriate letter in each box.

From the curves **E**, **F**, **G** and **H**, choose the curve produced by the addition of

(i) sodium hydroxide to 25 cm^3 of ethanoic acid

(1)

(ii) ammonia to 25 cm^3 hydrobromic acid

(1)

(iii) hydrochloric acid to 25 cm^3 of potassium hydroxide

(1)

(b) The table shows information about some acid-base indicators.

Indicator	pH range	Lower pH colour	Higher pH colour
pentamethoxy red	1.2–3.2	violet	colourless
naphthyl red	3.7–5.0	red	yellow
4–nitrophenol	5.6–7.0	colourless	yellow
cresol purple	7.6–9.2	yellow	purple

(i) Which indicator in the table could be used for the titration that produces curve E but **not** for the titration that produces curve F?

Tick (✓) **one** box.

pentamethoxy red

naphthyl red

4–nitrophenol

cresol purple

(1)

(ii) Give the colour change at the end point of the titration that produces curve H when naphthyl red is used as the indicator.

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(1)

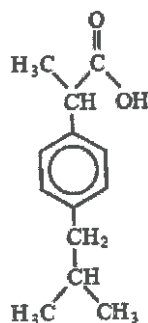
(iii) A beaker contains 25 cm³ of a buffer solution at pH = 6.0
Two drops of each of the four indicators in the table are added to this solution.

State the colour of the mixture of indicators in this buffer solution.
You should assume that the indicators do **not** react with each other.

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(1)
(Total 6 marks)

Q9. Ibuprofen is a drug used as an alternative to aspirin for the relief of pain, fever and inflammation. The structure of ibuprofen is shown below.



Which one of the following statements is **not** correct?

- A It has optical isomers.
- B It liberates carbon dioxide with sodium carbonate solution.
- D It undergoes esterification with ethanol.
- D It undergoes oxidation with acidified potassium dichromate(VI).

(Total 1 mark)

Q10. How many structural isomers, which are esters, have the molecular formula $C_4H_8O_2$?

- A 2
- B 3
- C 4
- D 5

(Total 1 mark)

Q11. The structural formula of ethyl 2-methylpropanoate is

- A
- B
- C
- D

(Total 1 mark)

Q12. An excess of methanol was mixed with 12 g of ethanoic acid and an acid catalyst. At equilibrium the mixture contained 8 g of methyl ethanoate. The percentage yield of ester present was

- A 11
- B 20
- C 54
- D 67

(Total 1 mark)

Q13. Which compound is formed by the reaction of ethane-1,2-diol with an acid?

- A
$$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$$
- B
$$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$$
- C
$$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$$
- D
$$\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2\text{OH}$$

(Total 1 mark)

Q14. Butan-1-ol was converted into butyl propanoate by reaction with an excess of propanoic acid. In the reaction, 6.0 g of the alcohol gave 7.4 g of the ester. The percentage yield of ester was

- A 57
- B 70
- C 75
- D 81

(Total 1 mark)


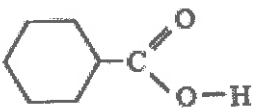
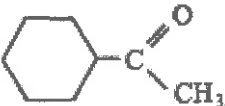
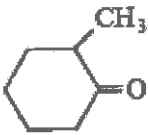
Q15. Propanoic acid reacts with methanol in the presence of a small amount of concentrated sulphuric acid. The empirical formula of the ester formed is

- A CH_2O
- B $\text{C}_2\text{H}_6\text{O}_2$
- C $\text{C}_2\text{H}_4\text{O}_2$
- D $\text{C}_2\text{H}_4\text{O}$

(Total 1 mark)

Q16. The compound lithium tetrahydridoaluminate(III), LiAlH_4 , is a useful reducing agent. It behaves in a similar fashion to NaBH_4 . Carbonyl compounds and carboxylic acids are reduced to alcohols. However, LiAlH_4 also reduces water in a violent reaction so that it must be used in an organic solvent.

Which one of the following can be reduced by LiAlH_4 to a primary alcohol?

- A 
- B 
- C 
- D 

(Total 1 mark)

Q17. Propanone can be reduced to form an alcohol. A functional group isomer of the alcohol formed is

- A $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- B $\text{CH}_3\text{CH}_2\text{CHO}$
- C $\text{CH}_3\text{OCH}_2\text{CH}_3$
- D CH_3COCH_3

(Total 1 mark)

Q18. Which alcohol could **not** be produced by the reduction of an aldehyde or a ketone?

- A 2-methylbutan-1-ol
- B 2-methylbutan-2-ol
- C 3-methylbutan-1-ol
- D 3-methylbutan-2-ol

(Total 1 mark)

Q19. Which compound forms optically active compounds on reduction?

- A $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_3$
- B $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$
- C CH_3COCH_3
- D $\text{CH}_3\text{CH}_2\text{COCH}_3$

(Total 1 mark)

Q20.

Summarised directions for recording responses to multiple completion questions			
A (i), (ii) and (iii) only	B (i) and (iii) only	C (ii) and (iv) only	D (iv) alone

Isomers of the ester $\text{HCOOCH}_2\text{CH}_2\text{CH}_3$, include

- (i) ethyl ethanoate
(ii) methyl propanoate
(iii) butanoic acid
(iv) butyl methanoate

(Total 1 mark)

Q21.

Summarised directions for recording responses to multiple completion questions			
A (i), (ii) and (iii) only	B (i) and (iii) only	C (ii) and (iv) only	D (iv) alone

Products from the acid hydrolysis of the ester $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$ include

- (i) $\text{CH}_3\text{CH}_2\text{COOH}$
(ii) CH_3COOH
(iii) $\text{CH}_3\text{CH}_2\text{OH}$
(v) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

(Total 1 mark)

