

SECTION A

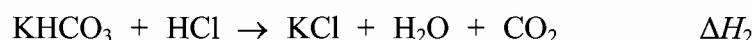
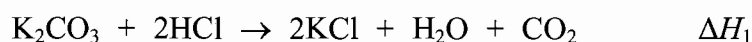
Answer ALL parts of this question in the spaces provided.

1. The enthalpy change for some reactions cannot be determined directly.

One such reaction is the thermal decomposition of potassium hydrogencarbonate, which in a closed system at 200 °C is an equilibrium reaction.



However, by determining the enthalpy change for the neutralisation of the two potassium salts with hydrochloric acid, ΔH for the reaction above can be found. The equations for the neutralisation reactions are:



ΔH_1 and ΔH_2 for the neutralisation reactions were determined as follows:

- 30 cm³ of 2 mol dm⁻³ hydrochloric acid (an excess) was placed in a polystyrene cup, and its temperature measured to the nearest 0.1 °C.
- A weighed quantity of the potassium salt (either the carbonate or the hydrogencarbonate) was added to the acid with rapid stirring, and the temperature measured again when the reaction was complete.

For the neutralisation using potassium carbonate, the results were as follows:

Amount of potassium carbonate used = 0.0187 mol

Initial temperature = 23.7 °C

Final temperature = 30.1 °C

- (a) State Hess's Law.

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(1)



- (b) Use the data for the neutralisation of potassium carbonate to calculate the value of ΔH_1 to **two** significant figures. Remember to include a sign and units in your answer.

[Assume that the heat capacity of the solution is $4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$, and that it has a mass of 30 g.]

(3)

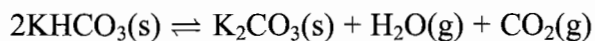
- (c) (i) Show how the two equations for the neutralisation reactions and their ΔH values can be combined to find a value of ΔH for the thermal decomposition of potassium hydrogencarbonate.

Calculate this enthalpy change using your value for ΔH_1 from part (b), given that $\Delta H_2 = + 29.3 \text{ kJ mol}^{-1}$.

(3)



- (ii) Explain why you would need to include the enthalpy of vaporisation of H₂O(l), in order to obtain an accurate value of the enthalpy of decomposition of potassium hydrogencarbonate.



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(1)

- (d) State and explain the effect of a decrease in temperature on the value of the equilibrium constant for the decomposition reaction and **hence** on the composition of the equilibrium mixture.

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(2)

Q1

(Total 10 marks)

TOTAL FOR SECTION A: 10 MARKS



SECTION B

Answer any TWO questions from this section in the spaces provided.

If you answer Question 2 put a cross in this box ☒.

2. (a) (i) Propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$, can be made from ethene via a Grignard reagent.

Draw the reaction scheme. For each step give the reagents and include the formula of the Grignard reagent.

(5)

- (ii) What **type** of reagent is a Grignard reagent? Justify your answer by reference to the reaction used in part (i).

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(2)



(b) Esters can be made either from carboxylic acids or from acid chlorides.

(i) Give in each case the equation for the reaction between:

ethanol and propanoyl chloride

(1)

ethanol and propanoic acid.

(1)

(ii) Explain which method gives the better yield of ester.

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(1)

(c) A mixture of aqueous propanoic acid and sodium propanoate forms a buffer solution.

(i) What is a buffer solution?

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(2)



- (ii) Calculate the mass of sodium propanoate that needs to be added to 125 cm³ of a 0.10 mol dm⁻³ solution of propanoic acid at 25 °C, to give a buffer solution of pH 5.06.

[The value of K_a for propanoic acid at 25 °C is 1.30×10^{-5} mol dm⁻³; molar mass of sodium propanoate is 96 g mol⁻¹]

(4)

- (iii) Calculate the concentration of hydroxide ions in the buffer solution in part (ii).

[The value of K_w at 25 °C is 1.0×10^{-14} mol² dm⁻⁶]

(2)

QUESTION 2 CONTINUES ON THE NEXT PAGE



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(iv) Why is a solution of propanoic acid alone **not** a buffer?

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(2)

Q2

(Total 20 marks)



If you answer Question 3 put a cross in this box ☒.

3. (a) (i) Draw the shape of a water molecule. Justify your answer.

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(2)

(ii) Water has intermolecular hydrogen bonds, but hydrogen sulphide, H₂S, does not.

Explain how these arise in water and why they do **not** occur in hydrogen sulphide.

Give ONE resulting difference in physical properties of water and hydrogen sulphide.

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(3)



(b) Copper(II) sulphate pentahydrate crystals, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, contain hydrated copper(II) ions and are blue.

If heated strongly they turn white and steam is evolved.

If the white solid is cooled to room temperature and water is added the solid turns blue again and it gets very hot.

(i) Explain why the product is white.

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(3)

(ii) Explain, in terms of bonding, why the anhydrous solid gets hot when water is added to it.

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(2)

(c) Explain why the solubility in water of the hydroxides of Group 2 (Be to Ba) increases down the group.

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(3)



If you answer Question 4 put a cross in this box ☒.

4. (a) The conversion of butan-2-ol to 2-bromobutane can be performed as outlined below:

- Butan-2-ol is heated with a mixture of 50 % aqueous sulphuric acid and sodium bromide for 45 minutes.
- The crude 2-bromobutane is distilled off.
- The crude 2-bromobutane is shaken with pure water, which removes the sulphuric acid and some of the butan-2-ol that contaminates the product.
- The organic layer is separated and then shaken with concentrated hydrochloric acid to remove residual butan-2-ol.
- The organic layer is then shaken with dilute sodium carbonate solution.
- Anhydrous calcium chloride is added to the organic layer and allowed to stand for some hours.
- The organic layer is then redistilled in a dry apparatus.

(i) Explain, in terms of kinetic factors, why the mixture is heated for a significant amount of time.

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(1)

(ii) Why is sulphuric acid necessary in the reaction mixture?

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(2)

(iii) Suggest why butan-2-ol, which is only partially miscible with water, is much more soluble in concentrated hydrochloric acid.

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(2)



(iv) Why is the organic layer shaken with dilute sodium carbonate solution?

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(1)

(v) What is the purpose of the anhydrous calcium chloride?

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(1)

(vi) How would you heat the mixture safely? Explain your choice of method.

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(2)

QUESTION 4 CONTINUES ON THE NEXT PAGE

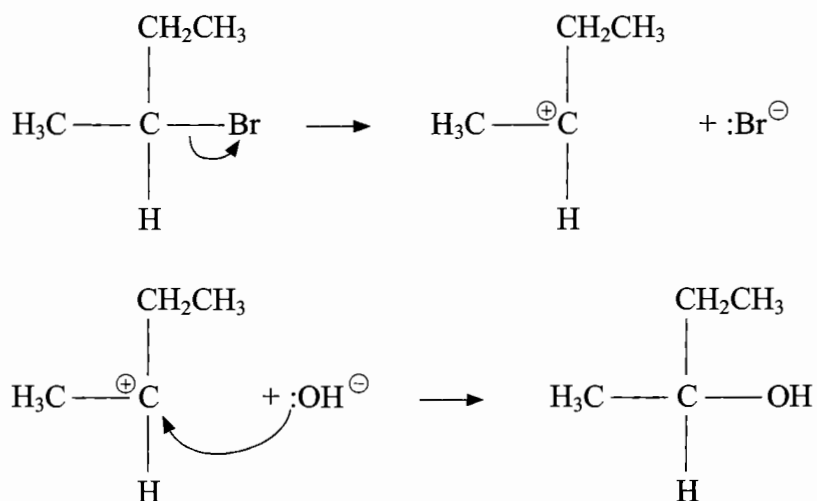


(b) Both 2-bromobutane and butan-2-ol are chiral molecules.

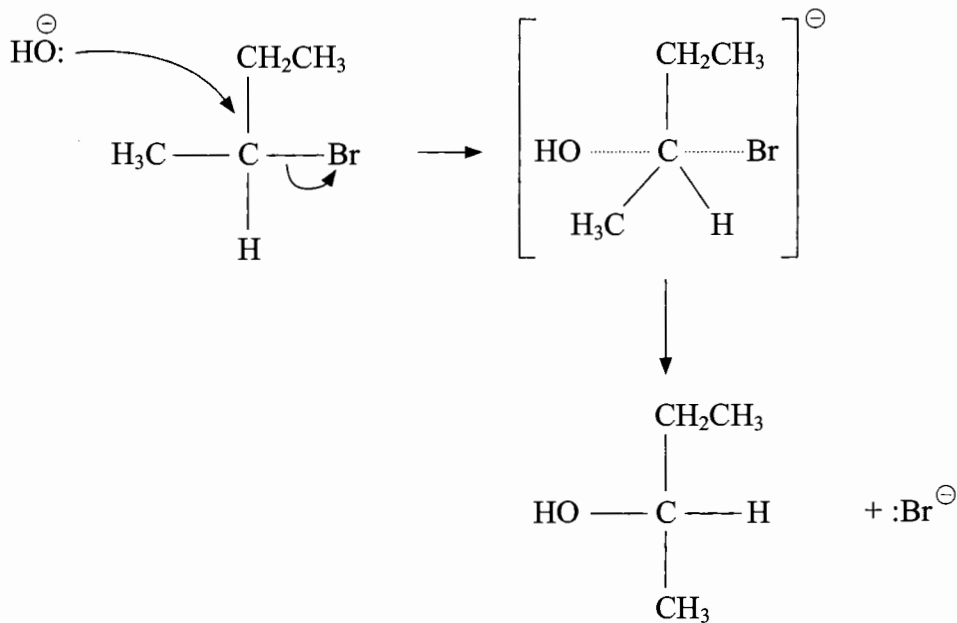
If one optical isomer of 2-bromobutane is used to make butan-2-ol by reaction with aqueous hydroxide ions, the product mixture is **not** optically active.

The mechanism for the reaction is either S_N1 or S_N2 ; these are given below

S_N1



S_N2



Explain which one of these mechanisms is consistent with the lack of optical activity in the product mixture.

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(3)

(c) The oxidation of butan-2-ol with hot potassium dichromate(VI) in acidic solution produces butanone, CH₃COCH₂CH₃.

(i) What would you see as the reaction proceeds?

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(1)

(ii) The dichromate(VI) ion is reduced under these conditions to chromium(III) ions.

The half-equation for the oxidation of butan-2-ol to butanone is



Write the ionic half-equation for the reduction of dichromate(VI) ions, and hence derive the overall equation for the oxidation of butan-2-ol.

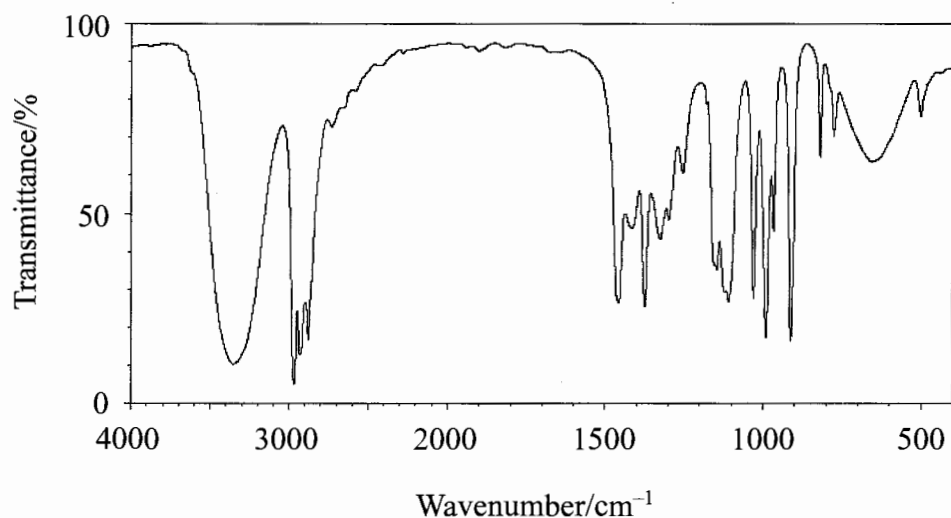
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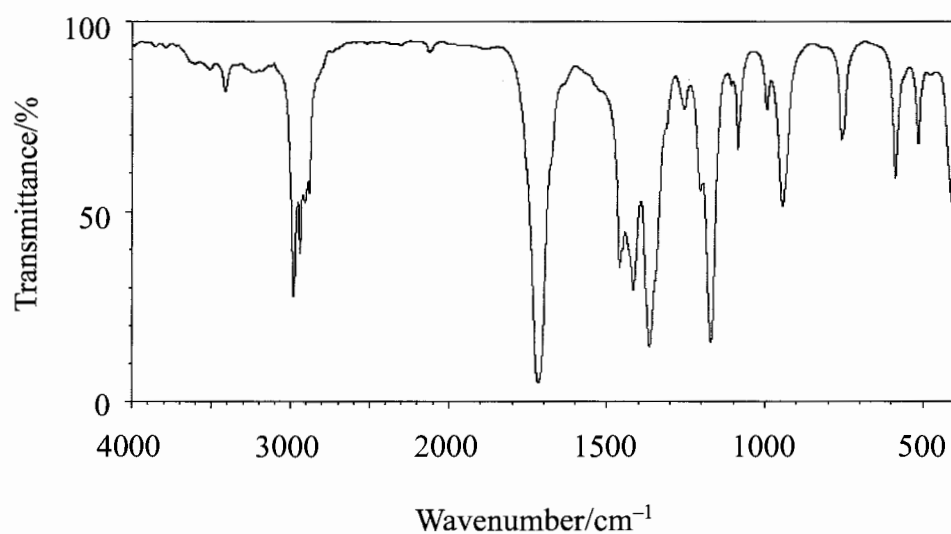


(iii) The IR spectra of butan-2-ol and of the organic product from its oxidation with dichromate(VI) ions are given below.

Spectrum of butan-2-ol



Spectrum of the organic product from the oxidation of butan-2-ol



Bond	Wavenumber/cm ⁻¹	Bond	Wavenumber/cm ⁻¹
C—H (alkanes)	2850–3000	C—O (alcohols, esters)	1000–1300
C—H (alkenes)	3000–3100	O—H (hydrogen-bonded alcohols)	3230–3550
C=O (aldehydes, ketones, carboxylic acids)	1680–1750	O—H (hydrogen-bonded carboxylic acids)	2500–3300



What evidence is there from the spectra that the reaction in part (ii) has occurred?

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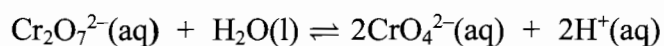
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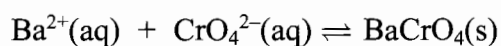
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(2)

(d) When potassium dichromate(VI) is dissolved in water, the following equilibrium is set up



(i) If a solution of barium ions is then added to **this solution**, solid barium chromate, BaCrO_4 , is precipitated; it is sparingly soluble in water, so the equilibrium given below also exists in the solution



Explain what happens to the pH when the barium ions are added.

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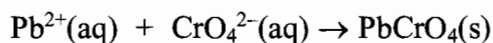
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(2)

QUESTION 4 CONTINUES ON THE NEXT PAGE



- (ii) If a solution of lead(II) ions is added instead of barium ions, solid PbCrO_4 is precipitated. This is almost completely insoluble in water so all chromate(VI) ions are removed from solution



State how the pH of this solution differs from your answer in part (i).

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(1)

Q4

(Total 20 marks)

TOTAL FOR SECTION B: 40 MARKS

TOTAL FOR PAPER: 50 MARKS

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