SECTION A

Answer ALL the questions in this section. You should aim to spend no more than 20 minutes on this section. For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind, put a line through the box ☒ and then mark your new answer with a cross ☒.

1 Methods for investigating reaction rates include

A colorimetry

B collecting and measuring the volume of a gas

C quenching, followed by titration with acid

D quenching, followed by titration with iodine solution.

Which method would be most suitable to investigate the rate of the following reactions?

(a) $H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow 2H_2O(l) + I_2(aq)$

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) $C_4H_9Br(l) + OH^-(aq) \rightarrow C_4H_9OH(l) + Br^-(aq)$

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for Question 1 = 2 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.

2 For a given initial reactant pressure, the half-life for a first order gaseous reaction was found to be 30 minutes.

If the experiment were repeated at half the initial reactant pressure, the half-life would be

☒ **A** 15 minutes.

☒ **B** 30 minutes.

☒ **C** 45 minutes.

☒ **D** 60 minutes.

(Total for Question 2 = 1 mark)

3 To determine the activation energy (E_a) for a reaction, the variation of reaction rate with temperature is investigated.

The rate constant, k, for the reaction is related to the absolute temperature, T, by the expression

$$\ln k = -\frac{E_a}{R} \times \left(\frac{1}{T}\right) + \text{constant}$$

where R is the gas constant.

The activation energy for the reaction could be obtained by plotting a graph of

	vertical axis	**horizontal axis**
☒ **A**	k	T
☒ **B**	k	$\frac{1}{T}$
☒ **C**	$\ln k$	T
☒ **D**	$\ln k$	$\frac{1}{T}$

(Total for Question 3 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

4 Energy is evolved when one mole of gaseous calcium ions is hydrated.

$$Ca^{2+}(g) + aq \rightarrow Ca^{2+}(aq)$$

This reaction is more exothermic than the corresponding value for barium ions, Ba^{2+}, because the

☒ **A** ionization energy of calcium is greater than that of barium.

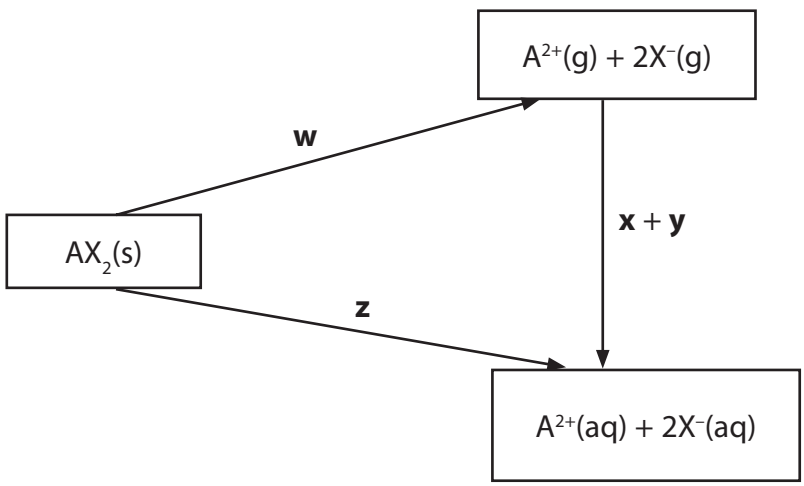
☒ **B** lattice energy of calcium oxide is more exothermic than that of barium oxide.

☒ **C** solubility of calcium hydroxide in water is less than that of barium hydroxide.

☒ **D** ionic radius of Ca^{2+} is less than that of Ba^{2+}.

(Total for Question 4 = 1 mark)

5 The following cycle represents the enthalpy changes **w**, **x**, **y** and **z**, occurring when an ionic solute, $AX_2(s)$, dissolves in water.



Which of the changes is the lattice energy of $AX_2(s)$?

☒ **A** ½ **w**

☒ **B** − **w**

☒ **C** **z**

☒ **D** **z** − **x** − **y**

(Total for Question 5 = 1 mark)

6 The equation for the synthesis of methanol is

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

At equilibrium, when the temperature is 340 K, the total pressure is 20 atm. The moles of each component present at equilibrium are shown in the table below.

Formula	Equilibrium moles / mol	Mole fraction
CO	0.15	0.23
H_2	0.32	
CH_3OH	0.18	0.28

(a) The mole fraction of hydrogen in the equilibrium mixture is

(1)

☒ **A** 0.23

☒ **B** 0.46

☒ **C** 0.49

☒ **D** 0.92

(b) The numerical value for the equilibrium partial pressure of the carbon monoxide, in atmospheres, is

(1)

☒ **A** 3.0

☒ **B** 4.6

☒ **C** 5.0

☒ **D** 9.2

(c) Units for the equilibrium constant, K_p, for this reaction are

(1)

☒ **A** no units

☒ **B** atm

☒ **C** atm^{-1}

☒ **D** atm^{-2}

(Total for Question 6 = 3 marks)

7 An aqueous solution of ammonium chloride, NH_4Cl, has a pH of less than 7 because

☒ **A** the ammonium ions donate protons to water molecules giving rise to oxonium ions, $H_3O^+(aq)$.

☒ **B** the chloride ions combine with hydrogen ions from water to form hydrochloric acid, HCl(aq).

☒ **C** an aqueous solution of ammonium chloride is unstable and evolves ammonia gas, $NH_3(g)$, leaving dilute hydrochloric acid.

☒ **D** the ammonium chloride reacts with carbon dioxide from the atmosphere giving ammonium carbonate, $(NH_4)_2CO_3(aq)$, and hydrochloric acid, HCl(aq).

(Total for Question 7 = 1 mark)

8 Which one of the following indicators is most suitable for titrating ethanoic acid with 0.1 mol dm^{-3} sodium hydroxide?

(Refer to page 19 of your data booklet.)

☒ **A** Thymol blue (acid)

☒ **B** Bromothymol blue

☒ **C** Thymol blue (base)

☒ **D** Alizarin yellow R

(Total for Question 8 = 1 mark)

9 What is the conjugate base of the acid, HCO_3^-?

☒ **A** H_2CO_3

☒ **B** CO_3^{2-}

☒ **C** OH^-

☒ **D** CO_2

(Total for Question 9 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

10 What is the approximate pH of a buffer solution containing 0.20 mol of a weak acid, HA, (pK_a = 4.8) and 0.20 mol of the sodium salt of the acid, NaA, in a total volume of 1 dm^3 of solution?

- ☒ **A** 7.0
- ☒ **B** 5.8
- ☒ **C** 4.8
- ☒ **D** 3.8

(Total for Question 10 = 1 mark)

Question 11: N/A

Question 12: N/A

Question 13: N/A

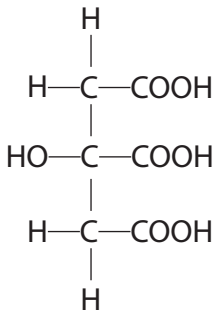
Question 14: N/A

SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

15 Citric acid is found in lemon juice.

The structure and formula of citric acid are shown below.



$C_6H_8O_7$

(a) In the presence of a small amount of moisture, citric acid reacts with sodium hydrogencarbonate as shown in the equation below.

$$C_6H_8O_7(s) + 3NaHCO_3(s) \rightarrow Na_3C_6H_5O_7(s) + 3CO_2(g) + 3H_2O(l)$$

Use the structural formula of citric acid to explain why one mole of citric acid neutralizes three moles of sodium hydrogencarbonate.

(1)

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(b) You will need to refer to the data booklet in the calculations which follow.

You should also use the values given below.

compound	$S^{\ominus}$ / J mol^{-1} K^{-1}
$Na_3C_6H_5O_7(s)$	200.5
$C_6H_8O_7(s)$	199.9

(i) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, for the following reaction at 298 K. Include a sign and units in your answer.

(2)

$$C_6H_8O_7(s) + 3NaHCO_3(s) \rightarrow Na_3C_6H_5O_7(s) + 3CO_2(g) + 3H_2O(l)$$

*(ii) Explain how the sign of your answer to (b)(i) could be predicted from the equation for the reaction between citric acid and sodium hydrogencarbonate.

(2)

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(iii) Given that $\Delta H^{\ominus}_{298}$ for the reaction shown in (b)(i) is +70 kJ mol^{-1}, calculate the standard entropy change of the surroundings, $\Delta S^{\ominus}_{surroundings}$, for this reaction at 298 K. Include a sign and units in your answer.

(2)

(iv) Calculate the total entropy change, $\Delta S^{\ominus}_{total}$, for this reaction at 298 K.

(1)

(v) What does the sign of $\Delta S^{\ominus}_{total}$ suggest about this reaction at 298 K?

(1)

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.....

(Total for Question 15 = 9 marks)

16 Methanoic acid, HCOOH, is present in ant stings.

A scientist analyzed 25.0 cm^3 of an aqueous solution of methanoic acid, solution **Z**, by titrating it with dilute sodium hydroxide, NaOH(aq).

- 20.0 cm^3 of sodium hydroxide was required to neutralize the methanoic acid
- The equation for the neutralization of methanoic acid is

$$HCOOH(aq) + NaOH(aq) \rightarrow HCOONa(aq) + H_2O(l)$$

(a) (i) Give the expression for K_w, the ionic product of water.

(1)

(ii) The concentration of the sodium hydroxide, NaOH(aq), used in the titration was 0.00750 mol dm^{-3}.

Calculate the pH of the sodium hydroxide solution.

[$K_w = 1.00 \times 10^{-14}$ $mol^2\,dm^{-6}$]

(2)

(b) Use the equation for the reaction and the data from the titration to show that the concentration of the methanoic acid in solution **Z** was 6.00×10^{-3} mol dm^{-3}.

(2)

(c) Methanoic acid is a weak acid.

(i) Explain the term **weak acid**.

(2)

Weak .....

.....

Acid .....

.....

(ii) The equation for the dissociation of methanoic acid in aqueous solution is shown below.

$$HCOOH(aq) \rightleftharpoons HCOO^-(aq) + H^+(aq)$$

Write the expression for the acid dissociation constant, K_a, for methanoic acid.

(1)

*(iii) At 298 K, the acid in ant stings has a concentration of 6.00×10^{-3} mol dm^{-3} and a pH of 3.01.

Calculate the value of K_a for methanoic acid at 298 K.

State clearly any assumptions that you have made.

(4)

Calculation:

Assumption(s):

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(Total for Question 16 = 12 marks)

17 Ethanoic acid and ethanol react together to form the ester ethyl ethanoate, $CH_3COOC_2H_5$, and water.

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$$

(a) (i) Give the expression for K_c.

(1)

(ii) An equilibrium was reached when the amounts of substances shown in the table below were used.

Complete the table to show the amounts of each substance present at equilibrium.

(2)

Component	$CH_3COOH(l)$	$CH_3CH_2OH(l)$	$CH_3COOCH_2CH_3(l)$	$H_2O(l)$
Initial amount / mol	0.40	0.30	0.00	0.15
Equilibrium amount / mol	0.20			

(iii) Explain why K_c for this reaction has no units.

(1)

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(iv) Calculate the numerical value of K_c.

(1)

(b) The esterification reaction above was carried out in the presence of hydrochloric acid as the catalyst.

State the effect on the equilibrium position and the rate of attainment of equilibrium if the concentration of the acid catalyst were to be increased.

(2)

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(c) (i) Identify which bonds are broken and which bonds are made in the esterification reaction.

(2)

Bonds broken:

Bonds made:

(ii) Explain why ΔH for this reaction is not **exactly** zero.
(A calculation is not required.)

(1)

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(d) (i) State the relationship between ΔS_{total} and the equilibrium constant, K, of a reaction.

(1)

*(ii) Use entropy considerations and your answer to (d)(i) to predict any effect of an increase in temperature on the value of the equilibrium constant of a reaction for which ΔH is zero. Assume that ΔS_{system} does not change with temperature.

(3)

(e) An alternative method for preparing ethyl ethanoate is to react ethanoyl chloride with ethanol.

(i) Give the equation for the reaction.

(1)

(ii) Draw the **skeletal** formula of ethyl ethanoate.

(1)

(iii) Ethanoyl chloride also reacts with concentrated ammonia. Draw the **displayed** formula of the organic product of this reaction.

(1)

(f) (i) Complete the equation below for the alkaline hydrolysis of ethyl ethanoate using sodium hydroxide. State symbols are **not** required.

(1)

$CH_3COOCH_2CH_3 + NaOH \rightarrow$

(ii) Explain why the reaction in (f)(i) gives a better yield of the alcohol compared with acid hydrolysis of the ethyl ethanoate.

(1)

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(Total for Question 17 = 19 marks)

18 Bromate(V) ions, BrO_3^-, oxidize bromide ions, Br^-, in the presence of dilute acid, H^+, as shown in the equation below.

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

Three experiments were carried out using different initial concentrations of the three reactants.

The initial rate of reaction was calculated for each experiment.

The results are shown in the table below.

Experiment number	$[BrO_3^-(aq)]$ / mol dm^{-3}	$[Br^-(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	0.050	0.25	0.30	1.68×10^{-5}
2	0.050	0.25	0.60	6.72×10^{-5}
3	0.15	0.50	0.30	1.01×10^{-4}

*(a) (i) This reaction is first order with respect to $BrO_3^-(aq)$. State, with reasons, including appropriate experiment numbers, the order of reaction with respect to

(5)

$H^+(aq)$

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$Br^-(aq)$

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(ii) Write the rate equation for the reaction.

(1)

(iii) Use the data from experiment 1 and your answer to (a)(ii) to calculate the value of the rate constant. Include units in your answer.

(3)

(b) What evidence suggests that this reaction proceeds by more than one step?

(1)

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(c) The initial rate of reaction was obtained from measurements of the concentration of bromine at regular time intervals. How is the **initial** rate of formation of bromine calculated from a concentration-time graph?

(2)

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(Total for Question 18 = 12 marks)

TOTAL FOR SECTION B = 52 MARKS

19 This question is about the equilibrium reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92 \text{ kJ mol}^{-1}$$

Which statement is **not** correct?

☒ **A** The units of K_p are atm^{-2}.

☒ **B** K_p increases as temperature is decreased.

☒ **C** K_p increases when the pressure increases.

☒ **D** K_p increases when the total entropy change, ΔS_{total}, increases.

(Total for Question 19 = 1 mark)

20 1,2-dichloroethane decomposes in the presence of a catalyst.

$$CH_2ClCH_2Cl(g) \rightleftharpoons CH_2{=}CHCl(g) + HCl(g) \qquad \Delta H = +51 \text{ kJ mol}^{-1}$$

Which of the following would result in an increase in the equilibrium yield of chloroethene?

☒ **A** Increasing the temperature.

☒ **B** Increasing the pressure.

☒ **C** Increasing the surface area of the catalyst.

☒ **D** Changing the catalyst to a more efficient one.

(Total for Question 20 = 1 mark)

Answer ALL the questions. Write your answers in the spaces provided.

21 A bromoalkane has the molecular formula C_4H_9Br. The ionic equation for the hydrolysis of this compound with aqueous sodium hydroxide is shown below.

$$C_4H_9Br + OH^- \rightarrow C_4H_9OH + Br^-$$

(a) The rate of hydrolysis was investigated by mixing a large excess of the bromoalkane with aqueous sodium hydroxide, and measuring the time taken for **all** the hydroxide ions to be used up. This was carried out with different initial concentrations of the bromoalkane and the hydroxide ions. The results are shown in the table below.

Experiment	$[C_4H_9Br]$ /mol dm^{-3}	$[OH^-]$ /mol dm^{-3}	Time for OH^- to be used up/s	Initial rate /mol dm^{-3} s^{-1}
1	0.017	0.0012	42	2.9×10^{-5}
2	0.034	0.0012	21	5.7×10^{-5}
3	0.034	0.0020	35	.....

(i) Complete the missing value of the initial rate in the table.

(1)

(ii) State the order of the reaction with respect to C_4H_9Br and to OH^-. Justify each answer by reference to the concentrations of both reactants.

(3)

Order with respect to C_4H_9Br .....

Reason .....

.....

Order with respect to OH^- .....

Reason .....

.....

(iii) Deduce the rate equation for the reaction.

(1)

Rate = ...

(iv) Use the results for the first experiment in the table to calculate the rate constant and give its units.

(2)

Units .....

(b) What evidence supports the theory that there is more than one step in the reaction mechanism?

(1)

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.....

(c) Write the mechanism for the hydrolysis of C_4H_9Br which is consistent with your rate equation. Show the structure of C_4H_9Br clearly in your mechanism.

(3)

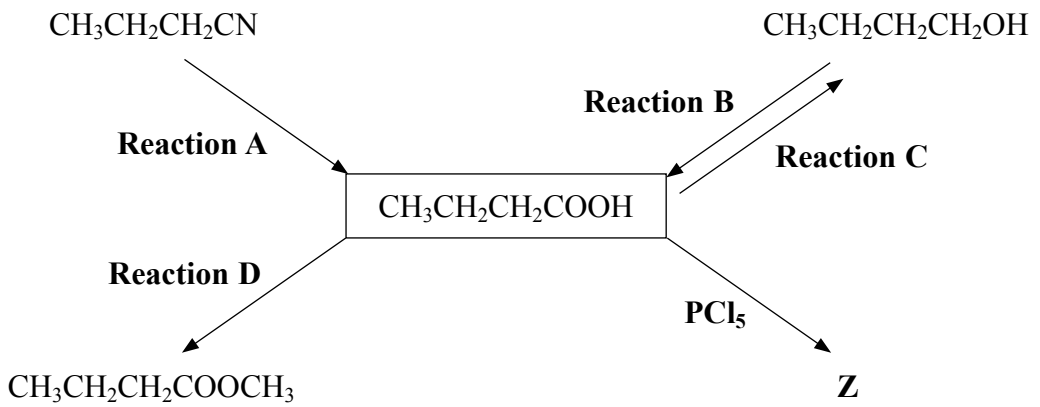
*(d) Explain why primary and tertiary bromoalkanes are hydrolysed by different mechanisms.

(2)

(Total for Question 21 = 13 marks)

22 This question is about butanoic acid, $CH_3CH_2CH_2COOH$.

(a) Some reactions involving butanoic acid are shown below.



(i) What type of reaction is **Reaction A**?

(1)

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(ii) Identify, by name or formula, the reagent which is used with sulfuric acid to carry out **Reaction B**.

(1)

.....

(iii) What reagent is used in **Reaction C**?

(1)

.....

(iv) Name the organic product of **Reaction D** and write a balanced equation for its formation.

(2)

Name .....

Equation

(v) Write the **displayed** formula for **Z**, the organic product of the reaction of butanoic acid with phosphorus(V) chloride, PCl_5.

(1)

(b) Butanoic acid and propane-1,2,3-triol are formed when fats in milk are hydrolysed. The presence of milk fat in low fat spreads is detected by hydrolysing the spread, and then analysing the products using gas chromatography (also called gas-liquid chromatography, GLC).

(i) Explain why nitrogen, rather than oxygen, is used as the carrier gas in GLC.

(1)

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(ii) What property determines whether butanoic acid or propane-1,2,3-triol would move faster through the chromatography column?

(1)

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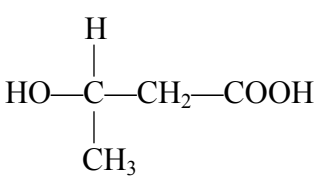
(c) The formula of 3-hydroxybutanoic acid is shown below.



(i) 3-hydroxybutanoic acid can form a polymer which is used to make "green" packaging as it is biodegradable.

Draw a section of this polymer, showing TWO monomer units. Clearly show any double bonds.

(2)

(ii) The polymer cannot be used in acidic conditions. What reaction would occur when the polymer is in prolonged contact with an acid?

(1)

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.....

(Total for Question 22 = 11 marks)

23 Ethanoic acid can be manufactured by the following reaction, which is carried out between 150 °C and 200 °C.

$$CH_3OH(g) + CO(g) \rightleftharpoons CH_3COOH(g)$$

(a) A mixture of 50.0 mol of methanol and 50.0 mol of carbon monoxide reaches equilibrium at a pressure of 32.0 atm. At 175 °C, the equilibrium partial pressure of ethanoic acid is 22.2 atm.

(i) Write the expression for the equilibrium constant in terms of pressure, K_p, for this reaction.

(1)

(ii) Calculate the partial pressures of methanol and carbon monoxide at equilibrium.

(2)

Methanol .....

Carbon monoxide .....

(iii) Calculate the value of K_p for this reaction at 175 °C. Include a unit in your answer and give your answer to **three** significant figures.

(2)

(b) Another sample of 50.0 mol of methanol and 50.0 mol of carbon monoxide was allowed to reach equilibrium at the same pressure of 32.0 atm, but at a lower temperature. 93.6 % of the methanol was converted at equilibrium.

(i) Complete the table below to show the number of moles of each species in the equilibrium mixture.

(2)

	CH_3OH	CO	CH_3COOH
Number of moles at start	50.0	50.0	0
Number of moles at equilibrium			

(ii) Calculate the partial pressure of ethanoic acid in the equilibrium mixture.

(1)

(iii) Is the reaction exothermic or endothermic? Explain your answer.

(1)

(c) How, if at all, does the addition of methanol to the equilibrium mixture affect the following? Justify your answers.

$$CH_3OH(g) + CO(g) \rightleftharpoons CH_3COOH(g)$$

(i) The equilibrium constant for the formation of ethanoic acid.

(1)

(ii) The equilibrium yield of ethanoic acid.

(1)

(d) In industry, catalysts are used even though they are often expensive.

State and explain ONE benefit to the **environment** resulting from the use of catalysts in industrial processes.

(2)

(Total for Question 23 = 13 marks)

24 Vinegar is used as a food preservative. It is an acidic solution containing ethanoic acid, CH_3COOH.

(a) A titration was carried out to measure the concentration of ethanoic acid in a sample of vinegar. 25.0 cm^3 of a vinegar solution was titrated with a solution of sodium hydroxide, concentration 0.250 mol dm^{-3}. The concentration of the ethanoic acid in the vinegar solution was found to be 0.125 mol dm^{-3}.

(i) Calculate the pH of 0.250 mol dm^{-3} sodium hydroxide at 298 K.

[$K_w = 1.00 \times 10^{-14}$ $mol^2\ dm^{-6}$ at 298 K.]

(2)

(ii) Write the expression for the acid dissociation constant, K_a, for ethanoic acid.

(1)

(iii) Calculate the pH of 0.125 mol dm^{-3} ethanoic acid at 298 K.

[K_a for ethanoic acid is 1.7×10^{-5} mol dm^{-3} at 298 K.]

(2)

(iv) When half the ethanoic acid is neutralized, the concentration of the remaining ethanoic acid equals the concentration of the sodium ethanoate which has formed. What is the pH of the mixture at this point? Justify your answer.

(2)

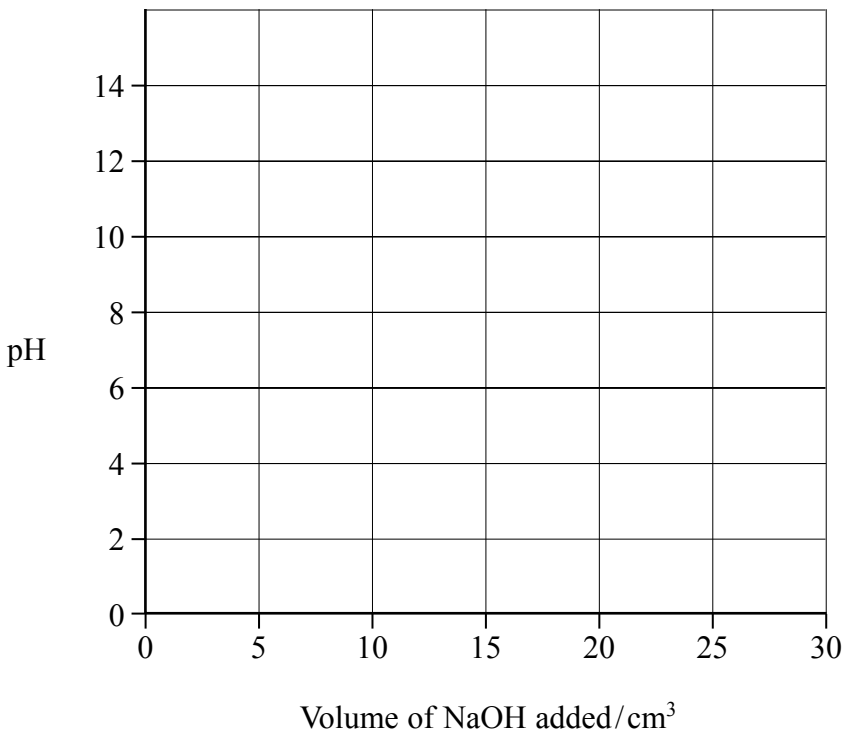
pH .....

Justification .....

.....

(v) On the axes below, sketch the titration curve for this reaction when 30 cm^3 of the sodium hydroxide is added to 25.0 cm^3 of the vinegar solution.

(3)



*(vi) The only indicators which were available for this titration were methyl yellow (in ethanol) and thymolphthalein. Explain which indicator is more suitable for this titration and why the other is unsuitable. You will need to refer to your data booklet.

(2)

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(b) In the food industry, ethanoic acid is described as an acidity regulator, additive number E260.

Ethanoic acid can neutralize alkalis. What substance could be mixed with ethanoic acid so that it regulates pH as a buffer in foodstuffs?

(1)

.....

(Total for Question 24 = 13 marks)

TOTAL

SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

25 (a) Crystals of hydrated cobalt(II) chloride, $CoCl_2.6H_2O$, lose water when they are heated, forming anhydrous cobalt(II) chloride, $CoCl_2$.

$$CoCl_2.6H_2O(s) \rightarrow CoCl_2(s) + 6H_2O(l)$$

(i) Calculate the entropy change of the system, $\Delta S^{\ominus}_{system}$, at 298 K. Include a sign and units in your answer. You will need to refer to your data booklet.

(2)

(ii) Explain whether the sign of your answer to (a)(i) is as expected from the equation for the reaction.

(1)

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.....

.....

(iii) The standard enthalpy change for the reaction, $\Delta H^{\ominus}$, is +88.1 kJ mol^{-1}. Calculate the entropy change in the surroundings, $\Delta S^{\ominus}_{surroundings}$, at 298 K for this reaction. Include a sign and units in your answer.

(2)

(iv) Calculate the total entropy change, $\Delta S^{\ominus}_{total}$, at 298 K for the reaction.

(1)

(v) Does your answer to (a)(iv) indicate whether hydrated cobalt(II) chloride can be stored at 298 K without decomposition? Explain your answer.

(1)

(b) A student attempted to measure the enthalpy change of solution of anhydrous cobalt(II) chloride by adding 2.00 g of cobalt(II) chloride to 50.0 cm^3 of water in a well-insulated container. A temperature rise of 1.5 °C was recorded.

The student used a balance which reads to 0.01g, a 50.0 cm^3 pipette, and a thermometer which can be read to 0.25 °C.

(i) Which measuring instrument should be changed to give a result which is closer to the accepted value? Justify your answer.

(2)

(ii) Suggest ONE **other** change the student could make to give a result which is closer to the accepted value. Justify your suggestion.

(2)

*(c) The lattice energies of magnesium chloride, $MgCl_2$, calcium chloride, $CaCl_2$, and strontium chloride, $SrCl_2$ are shown in the table below.

Chloride	Lattice energy/kJ mol^{-1}
$MgCl_2$	–2526
$CaCl_2$	–2258
$SrCl_2$	–2156

(i) Use data on ionic radii, from your data booklet, to explain the trend in these values. Estimate a value for the lattice energy of cobalt(II) chloride, giving ONE piece of data to justify your estimate.

(4)

(ii) Explain how lattice energy values, together with other data, can be used to predict the solubility of ionic compounds.

(3)

*(d) Cobalt forms another chloride, $CoCl_3$, but scientists predict that $MgCl_3$ cannot be made. Suggest a reason for this.

You should consider the enthalpy changes in the Born-Haber cycle, which provide evidence about why cobalt(III) chloride is known but magnesium(III) chloride is not.

(2)

(Total for Question 25 = 20 marks)