1 Which of the following mixtures would form the best buffer solution with pH 9 for use in a school laboratory?

- ☒ **A** Ethanoic acid and sodium ethanoate
- ☒ **B** Sodium chloride and sodium hydroxide
- ☒ **C** Hydrocyanic acid and sodium cyanide
- ☒ **D** Ammonium chloride and ammonia

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

2 Select the correct pH for each of the following solutions.

(a) 2 mol dm^{-3} nitric acid.

(1)

- ☒ **A** −2
- ☒ **B** −0.3
- ☒ **C** +0.3
- ☒ **D** +2

(b) 0.10 mol dm^{-3} barium hydroxide, $Ba(OH)_2$. $K_w = 1.0 \times 10^{-14}$ $mol^2\ dm^{-6}$.

(1)

- ☒ **A** 13.0
- ☒ **B** 13.3
- ☒ **C** 13.7
- ☒ **D** 14.3

(c) A mixture of 20 cm^3 of 1.0 mol dm^{-3} hydrochloric acid and 10 cm^3 of 1.0 mol dm^{-3} sodium hydroxide.

(1)

- ☒ **A** 0
- ☒ **B** 0.30
- ☒ **C** 0.48
- ☒ **D** 7

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3 Ammonia reacts with water in a reversible reaction. Which are the Brønsted-Lowry bases?

- ☒ **A** H_2O and OH^-
- ☒ **B** NH_3 and OH^-
- ☒ **C** NH_4^+ and H_2O
- ☒ **D** NH_4^+ and NH_3

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4 Methane hydrate is found on continental shelves deep in oceans. It forms methane in an endothermic equilibrium reaction, which may be represented as

$$CH_4.6H_2O(s) \rightleftharpoons CH_4(g) + 6H_2O(l)$$

(a) Which of the following changes would **increase** the equilibrium yield of methane?

(1)

☒ **A** Increasing the temperature and decreasing the pressure.

☒ **B** Decreasing both the temperature and the pressure.

☒ **C** Increasing both the temperature and the pressure.

☒ **D** Decreasing the temperature and increasing the pressure.

(b) Which of the following would **decrease** the value of the equilibrium constant, K_p, for the above equilibrium?

(1)

☒ **A** Decreasing the pressure

☒ **B** Increasing the pressure

☒ **C** Decreasing the temperature

☒ **D** Increasing the temperature

SECTION B

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

5 This question is about magnesium chloride, $MgCl_2$.

It can be formed by burning magnesium in chlorine.

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s) \qquad \Delta S^{\ominus}_{surroundings} = +2152\ J\ mol^{-1}\ K^{-1}$$

Remember to include a sign and units in your answers to the calculations in this question.

(a) (i) The standard molar entropy at 298 K for 1 mol chlorine molecules, Cl_2, is $+165\ J\ mol^{-1}\ K^{-1}$. Use this, and appropriate values from your Data Booklet, to calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, for this reaction.

(2)

*(ii) Explain fully why the sign for the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, is as you would expect.

(2)

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(b) Calculate the total entropy change, $\Delta S^{\ominus}_{total}$, in $J\ mol^{-1}\ K^{-1}$, for this reaction, giving your answer to three significant figures.

(2)

(c) Use the standard entropy change of the surroundings, $\Delta S^{\ominus}_{surroundings}$, to calculate the standard enthalpy change, $\Delta H^{\ominus}$, in kJ mol^{-1}, for the reaction at 298 K.

(2)

(d) 0.0300 mol of magnesium chloride, prepared by burning magnesium in chlorine, is added to 51.5 cm^3 of water.
50.0 cm^3 of 1.00 mol dm^{-3} solution is formed, and the temperature rise, ΔT, is 22.5°C.

(i) Calculate the energy transferred in joules for this process using:

Energy transferred in joules = volume of **solution** $\times$ 4.2 $\times$ ΔT

(1)

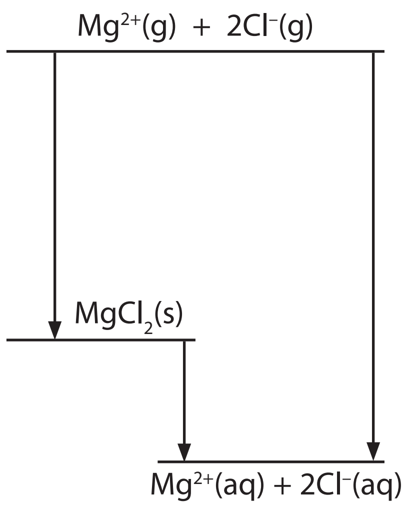
(ii) Calculate the enthalpy change of solution, $\Delta H_{solution}$, of magnesium chloride in kJ mol^{-1}.

(2)

*(iii) The enthalpy change of hydration of Mg^{2+}(g) is –1920 kJ mol^{-1}.

Use this, your value from (d)(ii), and the experimental lattice energy from your Data Booklet, to calculate the enthalpy change of hydration of Cl^{-}(g).

(3)



Answer .... kJ mol^{-1}

(iv) Draw a diagram to represent a hydrated chloride ion.

(1)

(v) Suggest why the addition of anhydrous magnesium chloride to water results in an increase in temperature and a decrease in volume.

(2)

Temperature increases ....

....

....

Volume decreases ....

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(Total for Question = 17 marks) 6

Write your answers in the spaces provided.

6 This question is about an experiment to determine the equilibrium constant, K_c, for the reaction between ethanoic acid and ethanol to form ethyl ethanoate and water.

Two sealed test tubes were prepared.

The first test tube contained 0.0400 mol ethanoic acid, 0.0400 mol of ethanol and 0.20 cm^3 of concentrated hydrochloric acid.

The second test tube contained 0.0400 mol ethyl ethanoate, 0.0400 mol of water and 0.20 cm^3 of concentrated hydrochloric acid.

After standing at 25°C for two weeks, to ensure equilibrium is reached, the contents of each test tube were separately titrated with 0.200 mol dm^{-3} sodium hydroxide solution.

0.20 cm^3 of concentrated hydrochloric acid was also titrated with the same sodium hydroxide solution.

(a) (i) Using data from the Data Booklet, calculate the volume, in cm^3, of 0.0400 mol of ethanoic acid.

(2)

(ii) What would be the best piece of apparatus to measure out the volumes of the liquids for the sealed test tubes?

(1)

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(iii) Suggest a reason why the test tubes were sealed.

(1)

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....

(iv) Suggest a suitable indicator for the titration of the equilibrium mixture in either test tube, with the expected colour change. Justify your suggestion.

(3)

Indicator ....

Colour change from .... to ....

Justification ....

.... 7

(b) In this experiment, the following titres were obtained.

Titration	Volume of 0.200 mol dm^{-3} sodium hydroxide solution/cm^3
Contents of first test tube	77.10
Contents of second test tube	77.05
0.20 cm^3 concentrated hydrochloric acid	11.70

(i) Write the equation for the reaction between ethanoic acid and ethanol to form ethyl ethanoate and water, using structural formulae. State symbols are not required.

(1)

(ii) Calculate the number of moles of ethanoic acid present at equilibrium in the first test tube.

(2)

(iii) Deduce the number of moles of ethanol present at equilibrium in the first test tube.

(1)

(iv) Calculate the number of moles of ethyl ethanoate formed at equilibrium in the first test tube.

(1)

(v) Write an expression for the equilibrium constant, K_c, for the reaction. Assuming the number of moles of water and ethyl ethanoate present at equilibrium are the same, calculate the equilibrium constant, K_c.

(2)

(vi) Explain why the equilibrium constant for this reaction has no units.

(1)

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(vii) Why, in fact, is the number of moles of water present in the equilibrium mixture greater than the number of moles of ethyl ethanoate?

(1)

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(c) (i) What is the type of reaction that took place in each test tube?

(2)

First test tube ....

Second test tube ....

*(ii) Comment on the value of the titre for the equilibrium mixture in the second test tube compared to the first test tube.

What characteristic feature of equilibrium reactions is demonstrated by the values of these titres?

(2)

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(iii) State the role of the concentrated hydrochloric acid in the equilibrium reaction.

(1)

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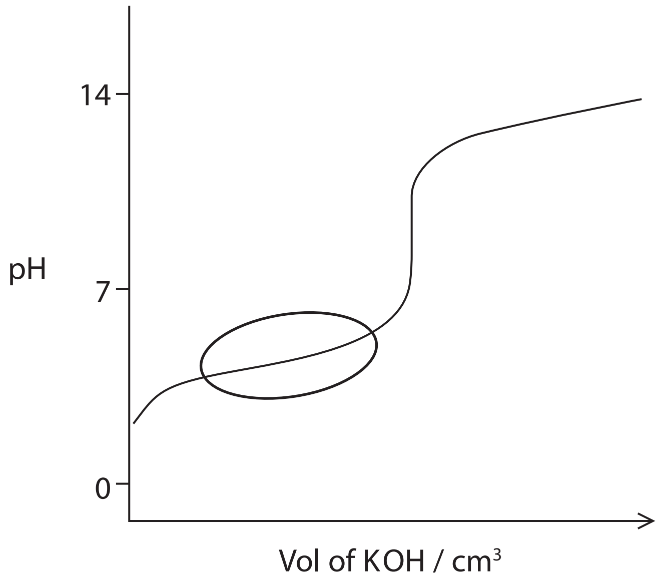
(Total for Question = 21 Marks)

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

7 A student carried out a titration by adding 0.032 mol dm^{-3} potassium hydroxide solution to 25.0 cm^3 of 0.024 mol dm^{-3} propanoic acid. A sketch graph of pH against volume of potassium hydroxide solution added is shown below.



(a) *(i) Describe and explain the behaviour of the solution formed in the region circled on the sketch graph.

(3)

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*(ii) Explain why the pH at the equivalence point of this titration is greater than 7.

(3)

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(iii) By considering the amount of excess alkali remaining, calculate the pH of the solution formed when 40 cm^3 of 0.032 mol dm^{-3} potassium hydroxide solution has been added to 25.0 cm^3 of 0.024 mol dm^{-3} propanoic acid.

$$K_w = 1.0 \times 10^{-14}\ mol^2\ dm^{-6} \text{ at } 298\ K$$

(5)

(b) The student made the following statement:

'The pH of pure water is always 7.0'

Is the student correct? Use the following information to justify your answer.

- $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$
- $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} at 298 K
- ΔH is positive for the forward reaction in the equilibrium.

(3)

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(Total for Question = 14 marks)

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

8 Adipic acid, $HOOC(CH_2)_4COOH$, is a dicarboxylic acid used in the production of polymers. It can be made by the reaction of buta-1,3-diene with carbon monoxide and water.

$$CH_2CHCHCH_2(g) + 2CO(g) + 2H_2O(l) \rightarrow HOOC(CH_2)_4COOH(s)$$

(a) (i) Use the Data Booklet to complete the table below.

(2)

	$CH_2CHCHCH_2(g)$	$CO(g)$	$H_2O(l)$	$HOOC(CH_2)_4COOH(s)$
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	+109.9			–994.3
$S^{\ominus}$ / J mol^{-1} K^{-1}	278.7			250.0

(ii) Use data from the table to calculate the standard enthalpy change, in kJ mol^{-1}, when adipic acid is formed from buta-1,3-diene, carbon monoxide and water.

(2)

(iii) Use data from the table to calculate the standard entropy change of the system, in J mol^{-1} K^{-1}, when adipic acid is formed from buta-1,3-diene, carbon monoxide and water.

(2)

(iv) Use your answers to (a)(ii) and (a)(iii) to calculate $\Delta S_{surroundings}$ and ΔS_{total} for the reaction at 298 K.

(3)

(v) It was suggested that **decreasing** the temperature of the reaction to less than 298 K would produce a greater yield of adipic acid.

Explain, in terms of the effect on ΔS_{system}, $\Delta S_{surroundings}$ and hence ΔS_{total}, whether this would be the case.

(3)

(b) Infrared spectroscopy can be used to follow the progress of reactions. During the reaction to produce adipic acid, suggest **one** peak which diminishes and **one** peak which appears.

Use information from the Data Booklet to identify two such possible peaks, giving their wave numbers and the bonds involved.

(2)

(c) Adipic acid is used as an additive in some fruit jellies. Suggest what effect the adipic acid will have on the flavour of the jelly.

(1)

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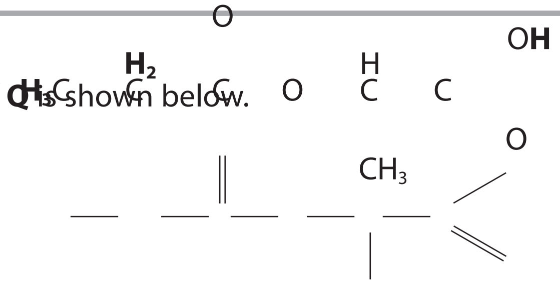
(d) An organic compound, **Q**, is found to contain 49.3% carbon and 6.8% hydrogen by mass.

(i) Use these data to confirm its empirical formula is $C_3H_5O_2$.

(3)

(ii) The structure of **Q** is shown below.



The table below summarises some information about parts of the nmr spectrum of compound **Q**.

Use the Data Booklet, and your knowledge of splitting patterns, to complete the table with respect to the features of compound **Q** shown in bold.

(4)

Feature of compound **Q**	Chemical shift / ppm	Splitting pattern
C**H**$_3$	0.1 – 1.9	
C**H**$_2$		
COO**H**		singlet

(Total for Question = 22 marks)