1 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)

.....

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

(1)

.....

.....

(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 .....

.....

(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)

.....

.....

(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)

.....

.....

(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)

.....

.....

.....

.....

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

(1)

.....

.....

(Total for Question = 21 Marks)

2 This question is about the equilibrium reaction below.

$$Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

The equilibrium is reached slowly.

*(a) Describe the changes you would see if aqueous solutions of iron(II) sulfate and silver nitrate were mixed and allowed to stand for a few hours.

(2)

.....

.....

.....

.....

(b) The concentration of silver ions in the equilibrium mixture can be found by titration with potassium thiocyanate. Silver thiocyanate precipitates.

$$Ag^{+}(aq) + CNS\ (aq) \rightleftharpoons AgCNS(s)$$

When all the silver ions have reacted, a deep red complex ion of iron(III) thiocyanate forms.

In an experiment, 25.0 cm^3 of 0.100 mol dm^{-3} silver nitrate solution was added to 25.0 cm^3 of 0.100 mol dm^{-3} of iron(II) sulfate solution, mixed thoroughly, and allowed to stand overnight in an air-tight container.

10.0 cm^3 samples of the reaction mixture were then titrated with 0.0200 mol dm^{-3} potassium thiocyanate solution. The average titre was 5.60 cm^3.

(i) The initial concentrations of silver ions and iron(II) ions **in the reaction mixture** are the same.

Calculate this initial concentration in mol dm^{-3}.

(1)

(ii) Calculate the number of moles of silver ions in the 10.0 cm^3 sample at equilibrium and hence calculate the equilibrium concentration of silver ions in the mixture.

(2)

(iii) Deduce the equilibrium concentration of iron(II) ions.

(1)

(iv) Hence calculate the equilibrium concentration of iron(III) ions.

(1)

(v) Write the expression for the equilibrium constant, K_c, for the reaction

$$Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

Calculate its value and give your answer, with appropriate units, to **three** significant figures.

(4)

(c) (i) The relationship between the total entropy change for a reaction and the equilibrium constant is

$$\Delta S^{\ominus}_{\text{total}} = R \ln K$$

Calculate the total entropy change for this reaction, giving a sign and appropriate units.

[$R = 8.31$ J mol^{-1} K^{-1}]

(2)

(ii) $Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$

$\Delta S^{\ominus}_{\text{system}}$ for this reaction is –208.3 J mol^{-1} K^{-1}

Use ideas about entropy to explain why this value is negative.

(2)

.....

.....

.....

.....

(iii) Calculate the entropy change of the surroundings, $\Delta S^{\ominus}_{\text{surroundings}}$.

(1)

(iv) Use your answer to (c)(iii) to calculate the standard enthalpy change, $\Delta H^{\ominus}$, for this reaction at 298 K.

Hence state and explain the effect of increasing temperature on the value of ΔS_{total}.

(3)

*(d) After the samples from the original mixture for the titration are taken, the remainder was filtered and then allowed to stand overnight, in an air-tight container at the same temperature. Another 10.0 cm^3 sample was taken and titrated. How, if at all, would you expect the titre to change?

Justify your answer. A calculation is not required.

(2)

(Total for Question = 21 marks)

3 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) 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 = 13 marks)