1 Sulfuric acid, H_2SO_4, is a well known acid containing sulfur. However, two other sulfur-containing acids are hydrogen sulfide, H_2S, and sulfurous acid, H_2SO_3.

(a) Hydrogen sulfide is a weak acid and dissociates in two stages as shown.

Stage 1 $H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$ $K_{a1} = 8.91 \times 10^{-8}$ mol dm^{-3}

Stage 2 $HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq)$ $K_{a2} = 1.20 \times 10^{-13}$ mol dm^{-3}

Write the K_a expressions for

(2)

Stage 1 $K_{a1} =$

Stage 2 $K_{a2} =$

(b) A solution of hydrogen sulfide has an initial concentration of 0.100 mol dm^{-3}.

$$K_{a1} = 8.91 \times 10^{-8} \text{ mol dm}^{-3}$$

(i) Use K_{a1} to calculate the equilibrium concentration, in mol dm^{-3}, of the hydrogensulfide ion, HS^-. Give your answer to **three** significant figures.

(2)

(ii) Use your answer to (b)(i) to calculate the pH of this solution.

(1)

*(iii) State the **three** assumptions you have made in your calculations in (b)(i) and (b)(ii).

(3)

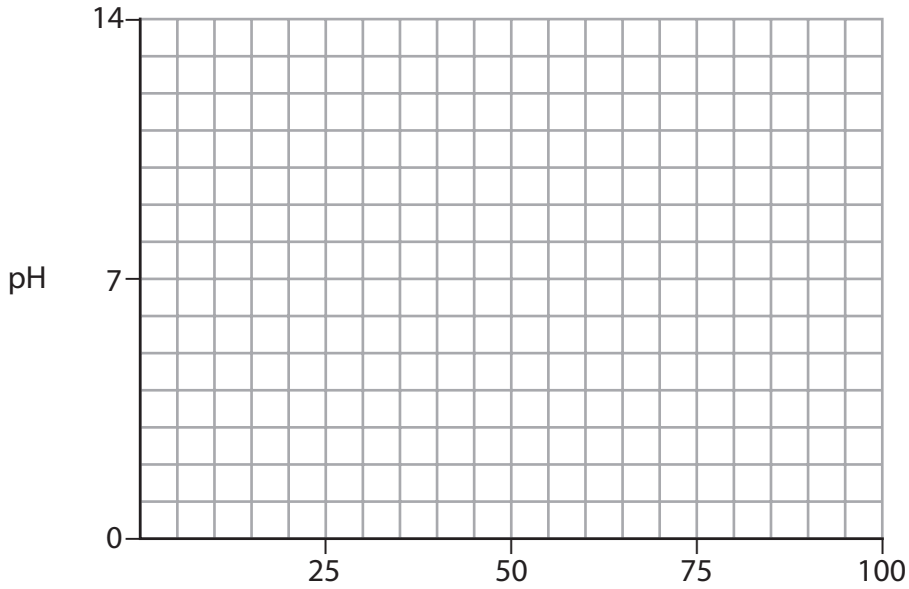
(c) Sulfurous acid, H_2SO_3, is also a diprotic acid. The values of K_{a1} and K_{a2} can be determined from the results of an acid-base titration. Diprotic acids require two OH^- ions per molecule for complete neutralization.

Sulfurous acid, H_2SO_3, is a stronger acid than H_2S and a 0.100 mol dm^{-3} solution has a pH of 1.5.

(i) On the grid below, sketch the likely shape of the titration curve for sulfurous acid, H_2SO_3, during the neutralization process.

Clearly label any equivalence points in the sketch.

(5)

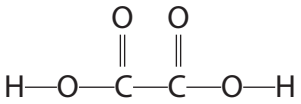


(ii) Describe how you would use this graph to confirm the value of pK_{a1}.

(1)

(Total for Question = 14 marks)

2 Ethanedioic acid, $H_2C_2O_4$, is a dicarboxylic acid which occurs in many plants, for example in rhubarb leaves, and is used as a rust remover and strong descaler. The structure of ethanedioic acid is shown below.



Ethanedioic acid is a much stronger acid than carboxylic acids such as ethanoic acid, having a pK_a of 1.38. The hydrogenethanedioate ion, $HC_2O_4^-$, is a weaker acid than ethanedioic acid, having a pK_a of 4.28, although slightly stronger than ethanoic acid.

(a) (i) Write an equation for the reaction of the hydrogenethanedioate ion with water to form an acidic solution. Include state symbols in your equation.

(2)

(ii) Write the expression for the acid dissociation constant, K_a, of the weak acid, $HC_2O_4^-$.

(1)

(iii) A solution containing hydrogenethanedioate ions behaves as a typical weak acid. Use your answer to (a)(ii) and the pK_a of the hydrogenethanedioate ion to calculate the pH of a 0.050 mol dm^{-3} solution of sodium hydrogenethanedioate, $NaHC_2O_4$.

(3)

(b) (i) State **two** approximations used in the calculation of pH in (a)(iii).

(2)

1. .....

.....

.....

2. .....

.....

.....

*(ii) Explain why the calculation of the pH of a solution of sodium hydrogenethanedioate gives a more accurate value than a similar calculation for ethanedioic acid.

(2)

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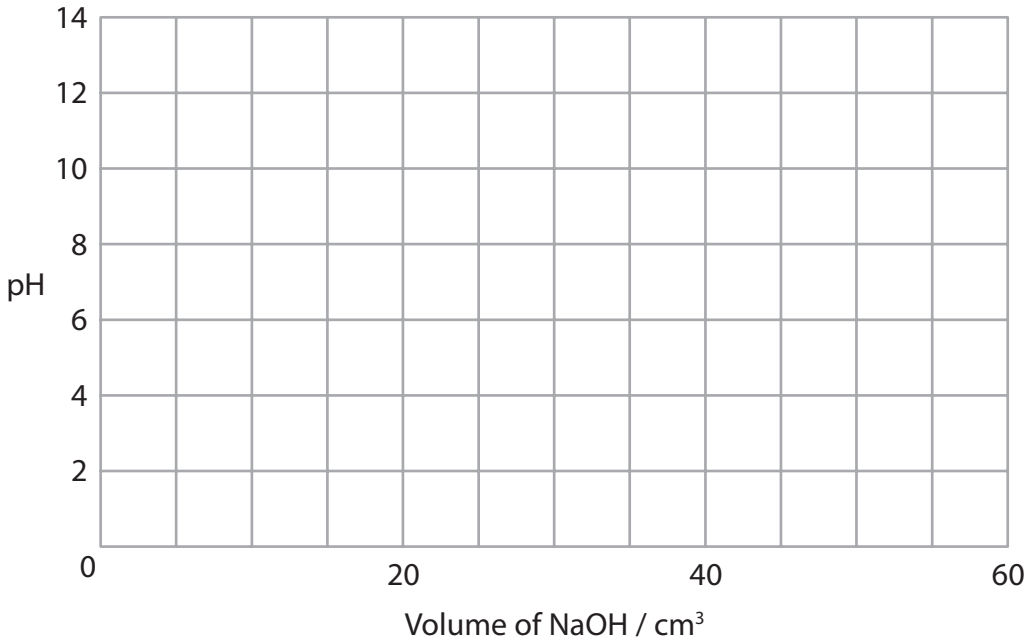
.....

.....

(c) 25 cm^3 of a 0.050 mol dm^{-3} solution of sodium hydrogenethanedioate was titrated with a sodium hydroxide solution of the same concentration.

(i) On the axis below, sketch the curve for this titration.

(3)



*(ii) When 25 cm^3 of a 0.050 mol dm^{-3} solution of **ethanedioic acid** is titrated with sodium hydroxide solution of the same concentration using phenolphthalein as the indicator, the end point is 50 cm^3.

When methyl yellow indicator is used, the colour changes at around 25 cm^3.

Using the information given at the start of the question and quoting data from page 19 of your data booklet, suggest why these volumes are different.

(2)

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(Total for Question = 15 marks)

3 In a pH titration, 30 cm^3 of sodium hydroxide solution was added, in 1 cm^3 portions, to 20 cm^3 of ethanoic acid solution, $CH_3COOH(aq)$. The concentration of both solutions was 0.50 mol dm^{-3}. After the addition of each 1 cm^3, the pH was recorded using a pH meter.

(a) (i) Write the K_a expression for ethanoic acid.

(1)

(ii) Using your answer to (i), calculate the pH of the 0.50 mol dm^{-3} ethanoic acid solution before the titration starts. Refer to page 18 of the data booklet.

(2)

(iii) Deduce the volume of sodium hydroxide solution required to reach the end point.

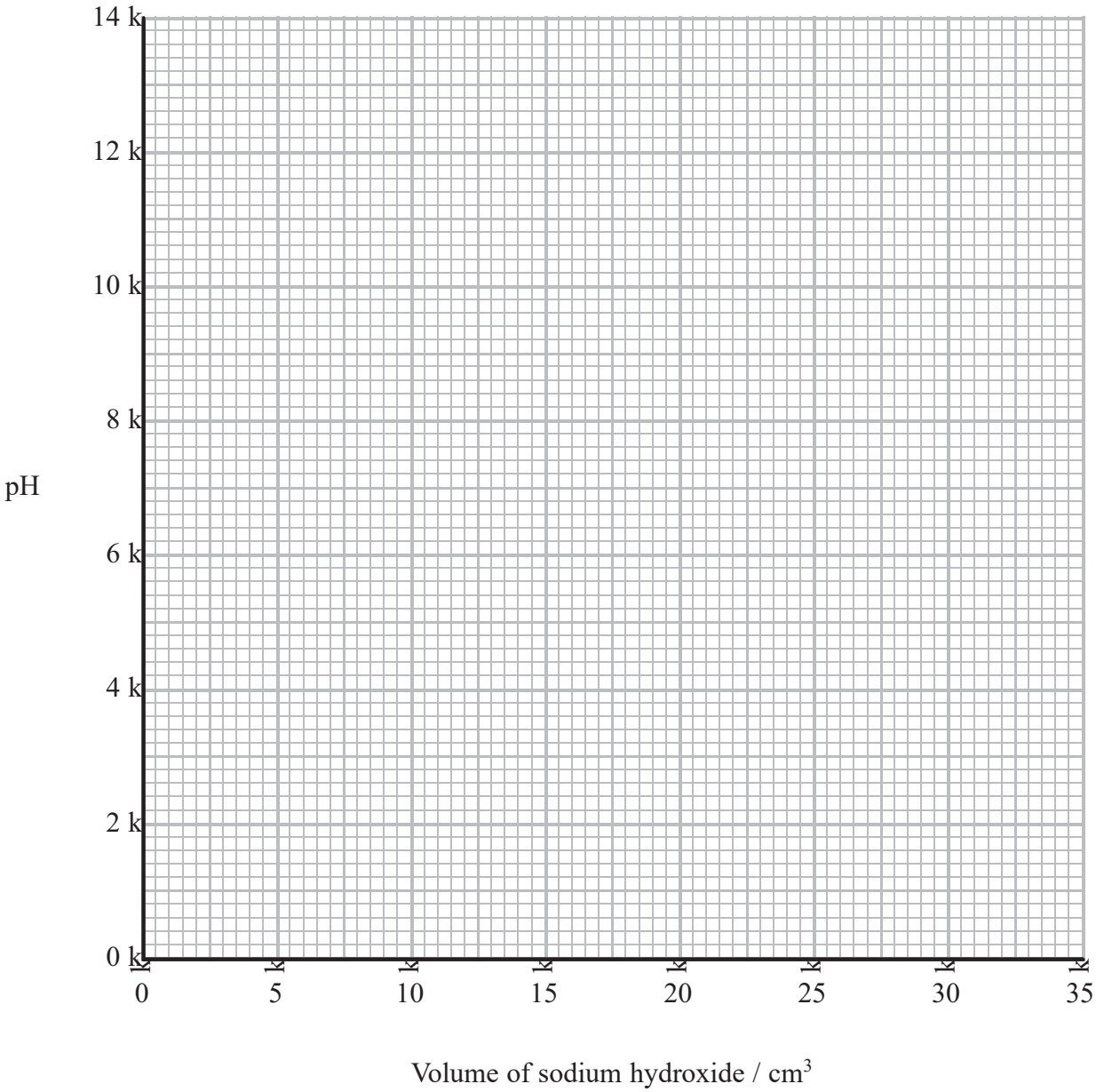
(1)

(iv) Calculate the pH of the solution after all of the sodium hydroxide is added.

(4)

titration.

(3)


14 k
12 k
10 k
8 k
pH
6 k
4 k
2 k
0 k
0
5
10
15
20
25
30
35
Volume of sodium hydroxide / cm3

(b) An acidic buffer solution can be made by mixing together a solution of ethanoic acid and solid sodium ethanoate.

(i) Calculate the mass of solid sodium ethanoate (molar mass = 82 g mol^{-1}) that would be added to 500 cm^3 of ethanoic acid, concentration 1.0 mol dm^{-3}, in order to make a ;<7fer solution of pH 4.70.

(4)

*(ii) Explain how this buffer solution resists a change in pH when a few drops of sodium hydroxide are added.

(3)

(Total for Question = 18 marks)

4 Methanoic acid, ethanoic acid and iodic(I) acid, HIO, are all weak acids.

(a) The values of the acid dissociation constant, K_a, for methanoic and ethanoic acid at 298 K are given below. Iodic(I) acid has a pK_a of 10.64. Complete the table by calculating the value of K_a for iodic(I) acid.

(1)

Acid	K_a / mol dm^{-3}
methanoic acid	1.6×10^{-4}
ethanoic acid	1.7×10^{-5}
iodic(I) acid	

(b) (i) Write the expression for K_a for methanoic acid, HCOOH.

(1)

(ii) Calculate the pH of a solution of methanoic acid with concentration 0.50 mol dm^{-3} at 298 K.

(3)

(iii) State **one** of the assumptions you have made when calculating the pH in (ii).

(1)

(c) The following equilibrium occurs in a mixture of pure methanoic and ethanoic acids.

$$HCOOH + CH_3COOH \rightleftharpoons HCOO^- + CH_3COOH_2^+$$

(i) Give the formulae of the two Brønsted-Lowry acids in this equilibrium.

(1)

(ii) Write an equation showing the products of the equilibrium which is set up when iodic(I) acid is mixed with ethanoic acid.

(1)

$HIO + CH_3COOH \rightleftharpoons$ ..... + ...

(d) A shampoo is buffered by the addition of a mixture of methanoic acid and sodium methanoate.

The pH of this shampoo is 4.9. Calculate the hydrogen ion concentration in the shampoo, and hence the ratio of methanoate ions to methanoic acid.

(2)

(Total for Question = 10 marks)