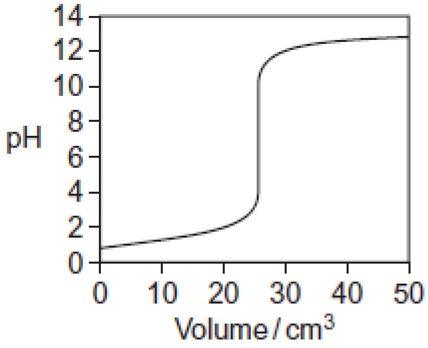
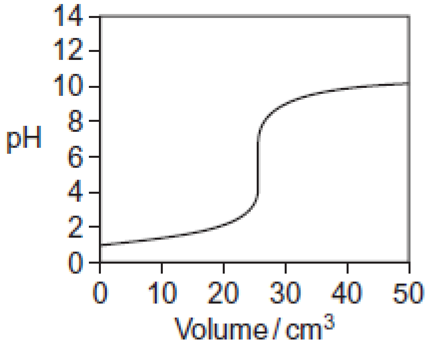
1 Titration curves, labelled **E**, **F**, **G** and **H**, for combinations of different aqueous solutions of acids and bases are shown below.

All solutions have concentrations of 0.1 mol dm^{-3}.

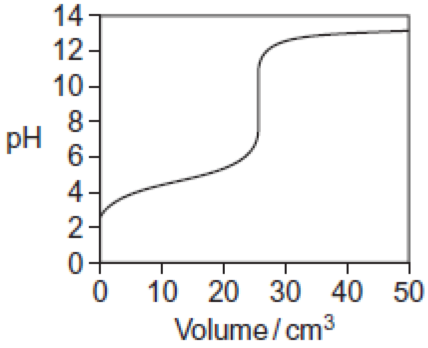
E



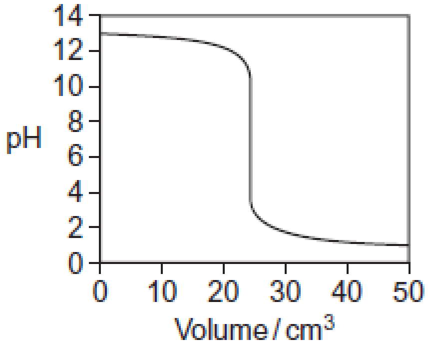
F



G



H



(a) In this part of the question, write the appropriate letter in each box.

From the curves **E**, **F**, **G** and **H**, choose the curve produced by the addition of

(i) sodium hydroxide to 25 cm^3 of ethanoic acid ☐

(1)

(ii) ammonia to 25 cm^3 hydrobromic acid ☐

(1)

(iii) hydrochloric acid to 25 cm^3 of potassium hydroxide ☐

(1)

(b) The table shows information about some acid-base indicators.

Indicator	**pH range**	**Lower pH colour**	**Higher pH colour**
pentamethoxy red	1.2−3.2	violet	colourless
naphthyl red	3.7−5.0	red	yellow
4−nitrophenol	5.6−7.0	colourless	yellow
cresol purple	7.6−9.2	yellow	purple

(i) Which indicator in the table could be used for the titration that produces curve **E** but **not** for the titration that produces curve **F**?

Tick (✓) **one** box.

pentamethoxy red ☐

naphthyl red ☐

4−nitrophenol ☐

cresol purple ☐

(1)

(ii) Give the colour change at the end point of the titration that produces curve **H** when naphthyl red is used as the indicator.

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(1)

(iii) A beaker contains 25 cm^3 of a buffer solution at pH = 6.0
Two drops of each of the four indicators in the table are added to this solution.

State the colour of the mixture of indicators in this buffer solution.
You should assume that the indicators do **not** react with each other.

....

(1)
(Total 6 marks)

2 Water dissociates slightly according to the equation:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The ionic product of water, K_w, is given by the expression

$$K_w = [H^+][OH^-]$$

K_w varies with temperature as shown in the table.

Temperature / °C	**K_w / mol^2 dm^{-6}**
25	1.00×10^{-14}
50	5.48×10^{-14}

(a) Explain why the expression for K_w does **not** include the concentration of water.

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(2)

(b) Explain why the value of K_w increases as the temperature increases.

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(2)

(c) Calculate the pH of pure water at 50 °C.
Give your answer to 2 decimal places.

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(3)

(d) Calculate the pH of 0.12 mol dm^{-3} aqueous NaOH at 50 °C.
Give your answer to 2 decimal places.

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(3)
(Total 10 marks)

3 The acid dissociation constant, K_a, for ethanoic acid is given by the expression

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

The value of K_a for ethanoic acid is 1.74×10^{-5} mol dm^{-3} at 25 °C.

(a) A buffer solution is prepared using ethanoic acid and sodium ethanoate. In the buffer solution, the concentration of ethanoic acid is 0.186 mol dm^{-3} and the concentration of sodium ethanoate is 0.105 mol dm^{-3}.

Calculate the pH of this buffer solution.
Give your answer to 2 decimal places.

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(3)

(b) In a different buffer solution, the concentration of ethanoic acid is 0.251 mol dm^{-3} and the concentration of sodium ethanoate is 0.140 mol dm^{-3}.

A sample of hydrochloric acid containing 0.015 mol of HCl is added to 1000 cm^3 of this buffer solution.

Calculate the pH of the buffer solution after the hydrochloric acid has been added.
You should ignore any change in total volume.
Give your answer to 2 decimal places.

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(5)
(Total 8 marks)

4 A solution of chlorine in water is acidic. Swimming pool managers maintain pool water at a constant pH by using a buffer. They do so by adding sodium hydrogencarbonate and sodium carbonate.

(a) Hydrogen carbonate ions (HCO_3^-) act as a weak acid in aqueous solution. Write an equation for this equilibrium.

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(1)

(b) Use the equation in part (a) to explain how a solution containing sodium hydrogencarbonate and sodium carbonate can act as a buffer when small amounts of acid or small amounts of alkali are added.

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(3)
(Total 4 marks)

5 In a titration experiment, a good technique is essential for an accurate result to be obtained.

(a) Suggest a reason for removing the funnel after it has been used for filling the burette.

....

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(1)

(b) Suggest **one** other source of error in using the burette to carry out a titration.

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(1)

(c) During the titration, the inside of the conical flask is rinsed with distilled water.

Suggest why rinsing improves the accuracy of the titre.

....

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(1)

(d) Explain why adding this extra water does **not** change the volume of EDTA solution that is required in the titration.

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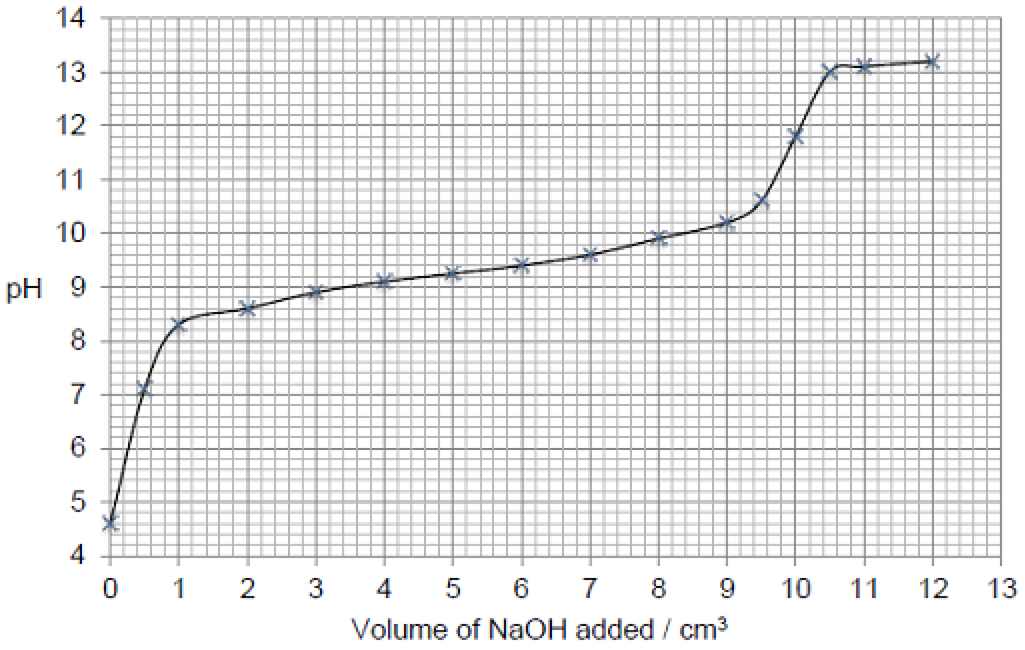
(1)
(Total 4 marks)

6 Ammonium chloride, when dissolved in water, can act as a weak acid as shown by the following equation.

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

The following figure shows a graph of data obtained by a student when a solution of sodium hydroxide was added to a solution of ammonium chloride. The pH of the reaction mixture was measured initially and after each addition of the sodium hydroxide solution.



(a) Suggest a suitable piece of apparatus that could be used to measure out the sodium hydroxide solution.
Explain why this apparatus is more suitable than a pipette for this purpose.

Apparatus ....

Explanation ....

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(2)

(b) Use information from the curve in the figure above to explain why the end point of this reaction would be difficult to judge accurately using an indicator.

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(2)

(c) The pH at the end point of this reaction is 11.8.

Use this pH value and the ionic product of water, $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}, to calculate the concentration of hydroxide ions at the end point of the reaction.

Concentration = ... mol dm^{-3}

(3)

(d) The expression for the acid dissociation constant for aqueous ammonium ions is

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

The initial concentration of the ammonium chloride solution was 2.00 mol dm^{-3}.

Use the pH of this solution, before any sodium hydroxide had been added, to calculate a value for K_a

K_a = ... mol dm^{-3}

(3)

(e) A solution contains equal concentrations of ammonia and ammonium ions.

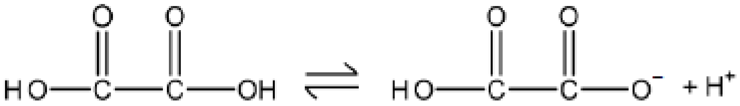
Use your value of K_a from part **(d)** to calculate the pH of this solution. Explain your working.

(If you were unable to calculate a value for K_a you may assume that it has the value 4.75×10^{-9} mol dm^{-3}. This is **not** the correct value.)

pH= ....

(2)
(Total 12 marks)

7 Ethanedioic acid is a weak acid.
Ethanedioic acid acts, initially, as a monoprotic acid.



(a) Use the concept of electronegativity to justify why the acid strengths of ethanedioic acid and ethanoic acid are different.

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(6)

(b) A buffer solution is made by adding 6.00×10^{-2} mol of sodium hydroxide to a solution containing 1.00×10^{-1} mol of ethanedioic acid ($H_2C_2O_4$).
Assume that the sodium hydroxide reacts as shown in the following equation and that in this buffer solution, the ethanedioic acid behaves as a monoprotic acid.

$$H_2C_2O_4(aq) + OH^-(aq) \longrightarrow HC_2O_4{-}(aq) + H_2O(l)$$

The dissociation constant K_a for ethanedioic acid is 5.89×10^{-2} mol dm^{-3}.

Calculate a value for the pH of the buffer solution.
Give your answer to the appropriate number of significant figures.

pH = ...

(5)

(c) In a titration, the end point was reached when 25.0 cm^3 of an acidified solution containing ethanedioic acid reacted with 20.20 cm^3 of 2.00 $\times 10^{-2}$ mol dm^{-3} potassium manganate(VII) solution.

Deduce an equation for the reaction that occurs and use it to calculate the original concentration of the ethanedioic acid solution.

Equation ....

Calculation

Original concentration = ... mol dm^{-3}

(4)
(Total 15 marks)

8 What is the pH of a 0.020 mol dm^{-3} solution of a diprotic acid which is completely dissociated?

A 1.00 ○

B 1.40 ○

C 1.70 ○

D 4.00 ○

(Total 1 mark)

9 The acid dissociation constant, K_a, of a weak acid HA has the value 2.56×10^{-4} mol dm^{-3}.

What is the pH of a 4.25×10^{-3}mol dm^{-3} solution of HA?

A 5.96 ○

B 3.59 ○

C 2.98 ○

D 2.37 ○

(Total 1 mark)

10 This question is about alkalis and carboxylic acids.

In this question, all data are quoted at 25 °C.

(a) Carboxylic acids are weak acids.

State the meaning of the term **weak** as applied to carboxylic acids.

....

....

(1)

(b) Write an equation for the reaction of propanoic acid with sodium carbonate.

....

(1)

(c) Calculate the pH of a 0.0120 mol dm^{-3} solution of calcium hydroxide.
The ionic product of water $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6}.
Give your answer to 2 decimal places.

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(Extra space)...

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(3)

(d) The value of the acid dissociation constant K_a for benzenecarboxylic acid (C_6H_5COOH) is 6.31×10^{-5} mol dm^{-3}.

(i) Write an expression for the acid dissociation constant K_a for benzenecarboxylic acid.

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(1)

(ii) Calculate the pH of a 0.0120 mol dm^{-3} solution of benzenecarboxylic acid.
Give your answer to 2 decimal places.

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(Extra space)..

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(3)

(iii) A buffer solution with a pH of 4.00 is made using benzenecarboxylic acid and sodium benzenecarboxylate.

Calculate the mass of sodium benzenecarboxylate (M_r = 144.0) that should be dissolved in 1.00 dm^3 of a 0.0120 mol dm^{-3} solution of benzenecarboxylic acid to produce a buffer solution with a pH of 4.00

The value of the acid dissociation constant K_a for benzenecarboxylic acid (C_6H_5COOH) is 6.31×10^{-5} mol dm^{-3}.

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(Extra space) ....

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(5)

(e) Two solutions, one with a pH of 4.00 and the other with a pH of 9.00, were left open to the air.

The pH of the pH 9.00 solution changed more than that of the other solution.

Suggest what substance might be present in the air to cause the pH to change.
Explain how and why the pH of the pH 9.00 solution changes.

Substance present in air ....

Explanation ....

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(3)
(Total 17 marks)

11 In an experiment to determine the acid dissociation constant (K_a) of a weak acid, 25.0 cm^3 of an approximately 0.1 mol dm^{-3} solution of this acid were titrated with a 0.10 mol dm^{-3} solution of sodium hydroxide.
The pH was measured at intervals and recorded. The table below shows the results.

Volume of NaOH / cm^3	0.0	1.0	2.0	3.0	4.0	5.0	10.0	15.0
pH	5.1	7.8	8.1	8.7	8.4	8.5	8.9	9.3

Volume of NaOH / cm^3	20.0	22.0	23.0	24.0	25.0	26.0	27.0	28.0
pH	9.7	10.0	10.2	11.0	11.3	11.4	11.5	11.6

(a) On the grid below, plot the values from the table above on a graph of pH (y-axis) against volume of NaOH.

You should start your y-axis at pH 4.0.

Draw a curve that represents the curve of best fit through these points. Ignore any anomalous points.

(4)

(b) Deduce the volume of the sodium hydroxide solution that would have been added at the half-neutralisation point of this experiment. This is the point where half the amount of the weak acid has been neutralised.

....

(1)

(c) When half of the weak acid has been neutralised, the pH of the mixture at this point is equal to the pK_a of the weak acid.

Use your answer to part (b) and your graph to determine the pK_a of the weak acid and, hence, its K_a value.

pK_a ....

K_a ....

(2)

(d) State the pH value for the anomalous point on your graph.
Suggest **one** reason for this anomaly. Assume that the reading on the pH meter is correct.

pH ....

Reason for anomaly ....

....

....

(1)

(e) Suggest how the experimental procedure could be slightly modified in order to give a more reliable value for the end-point.

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(1)
(Total 9 marks)

12 This question is about Brønsted-Lowry acids of different strengths.

(a) State the meaning of the term *Brønsted–Lowry acid*.

....

(1)

(b) (i) Write an expression for the acid dissociation constant K_a for ethanoic acid.

....

....

(1)

(ii) The value of K_a for ethanoic acid is 1.75×10^{-5} mol dm^{-3} at 25 °C.

Calculate the concentration of ethanoic acid in a solution of the acid that has a pH of 2.69

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(4)

(c) The value of K_a for chloroethanoic acid ($ClCH_2COOH$) is 1.38×10^{-3} mol dm^{-3} at 25 °C.

(i) Write an equation for the dissociation of chloroethanoic acid in aqueous solution.

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(1)

(ii) Suggest why chloroethanoic acid is a stronger acid than ethanoic acid.

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(2)

(d) **P** and **Q** are acids. **X** and **Y** are bases. The table shows the strength of each acid and base.

Acids		**Bases**	
strong	weak	strong	weak
P	**Q**	**X**	**Y**

The two acids were titrated separately with the two bases using methyl orange as indicator.
The titrations were then repeated using phenolphthalein as indicator.
The pH range for methyl orange is 3.1 − 4.4
The pH range for phenolphthalein is 8.3 − 10.0

For each of the following titrations, select the letter, **A, B, C,** or **D**, for the correct statement about the indicator(s) that would give a precise end-point.
Write your answer in the box provided.

A Both indicators give a precise end-point.

B Only methyl orange gives a precise end-point.

C Only phenolphthalein gives a precise end-point.

D Neither indicator gives a precise end-point.

(i) Acid **P** with base **X** ☐

(1)

(ii) Acid **Q** with base **X** ☐

(1)

(iii) Acid **Q** with base **Y** ☐

(1)

(e) Using a burette, 26.40 cm^3 of 0.550 mol dm^{-3} sulfuric acid were added to a conical flask containing 19.60 cm^3 of 0.720 mol dm^{-3} aqueous sodium hydroxide.
Assume that the sulfuric acid is fully dissociated.

Calculate the pH of the solution formed.

Give your answer to 2 decimal places.

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(Extra space) ....

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(6)
(Total 18 marks)

13 In order to obtain a pH curve, you are provided with a conical flask containing 25.0 cm^3 of a 0.100 mol dm^{-3} carboxylic acid solution and a burette filled with 0.100 mol dm^{-3} sodium hydroxide solution. You are also provided with a calibrated pH meter.

(a) State why calibrating a pH meter just before it is used improves the accuracy of the pH measurement.

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(1)

(b) Describe how you would obtain the pH curve for the titration.

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(5)
(Total 6 marks)

14 In this question, give all values of pH to 2 decimal places.

(a) The ionic product of water has the symbol K_w

(i) Write an expression for the ionic product of water.

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(1)

(ii) At 42°C, the value of K_w is 3.46×10^{-14} mol^2 dm^{-6}.

Calculate the pH of pure water at this temperature.

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(2)

(iii) At 75 °C, a 0.0470 mol dm^{-3} solution of sodium hydroxide has a pH of 11.36.

Calculate a value for K_w at this temperature.

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(2)

(b) Methanoic acid (HCOOH) dissociates slightly in aqueous solution.

(i) Write an equation for this dissociation.

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(1)

(ii) Write an expression for the acid dissociation constant K_a for methanoic acid.

....

....

(1)

(iii) The value of K_a for methanoic acid is 1.78×10^{-4} mol dm^{-3} at 25 °C.

Calculate the pH of a 0.0560 mol dm^{-3} solution of methanoic acid.

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(3)

(iv) The dissociation of methanoic acid in aqueous solution is endothermic.

Deduce whether the pH of a solution of methanoic acid will increase, decrease or stay the same if the solution is heated. Explain your answer.

Effect on pH ....

Explanation ....

....

....

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(Extra space) ....

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(3)

(c) The value of K_a for methanoic acid is 1.78×10^{-4} mol dm^{-3} at 25°C.
A buffer solution is prepared containing 2.35×10^{-2} mol of methanoic acid and 1.84×10^{-2} mol of sodium methanoate in 1.00 dm^3 of solution.

(i) Calculate the pH of this buffer solution at 25°C.

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(Extra space) ....

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(3)

(ii) A 5.00 cm^3 sample of 0.100 mol dm^{-3} hydrochloric acid is added to the buffer solution in part (c)(i).

Calculate the pH of the buffer solution after this addition.

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(Extra space) ....

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(4)
(Total 20 marks)

15 This question is about several Brønsted–Lowry acids and bases.

(a) Define the term *Brønsted–Lowry* acid.

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(1)

(b) Three equilibria are shown below. For each reaction, indicate whether the substance immediately **above** the box is acting as a Brønsted–Lowry acid (**A**) or a Brønsted–Lowry base (**B**) by writing **A** or **B** in each of the six boxes.

(i) $$CH_3COOH + \underset{\boxed{}}{H_2O} \rightleftharpoons \underset{\boxed{}}{CH_3COO^-} + H_3O^+$$

(1)

(ii) $CH_3NH_2 + \underset{\square}{H_2O} \rightleftharpoons \underset{\square}{CH_3NH_3^+} + OH^-$

(1)

(iii) $\underset{\square}{HNO_3} + H_2SO_4 \rightleftharpoons \underset{\square}{H_2NO_3^+} + HSO_4^-$

(1)

(c) A 25.0 cm^3 sample of 0.0850 mol dm^{-3} hydrochloric acid was placed in a beaker. Distilled water was added until the pH of the solution was 1.25.

Calculate the total volume of the solution formed. State the units.

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(Extra space) ....

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(3)

(d) At 298 K, the value of the acid dissociation constant (K_a) for the weak acid HX in aqueous solution is 3.01×10^{-5} mol dm^{-3}.

(i) Calculate the value of pK_a for HX at this temperature.
Give your answer to 2 decimal places.

....

....

(1)

(ii) Write an expression for the acid dissociation constant (K_a) for the weak acid HX.

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(1)

(iii) Calculate the pH of a 0.174 mol dm^{-3} solution of HX at this temperature.
Give your answer to 2 decimal places.

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(Extra space) ....

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(3)

(e) An acidic buffer solution is formed when 10.0 cm^3 of 0.125 mol dm^{-3} aqueous sodium hydroxide are added to 15.0 cm^3 of 0.174 mol dm^{-3} aqueous HX.
The value of K_a for the weak acid HX is 3.01×10^{-5} mol dm^{-3}.

Calculate the pH of this buffer solution at 298 K.
Give your answer to 2 decimal places.

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(Extra space) ....

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(6)
(Total 18 marks)

16 When 1.00 mol dm^{-3} solutions of salicylic acid and sodium hydroxide are mixed a buffer solution can be formed. Salicylic acid is a monoprotic acid that can be represented by the formula HA.

(a) Select a mixture from the table below that would produce a buffer solution. Give a reason for your choice.

Mixture	**Volume of 1.00 mol dm^{-3} salicylic acid solution / cm^3**	**Volume of 1.00 mol dm^{-3} sodium hydroxide solution / cm^3**
X	25	75
Y	50	50
Z	75	25

Mixture ....

Reason ....

....

....

(2)

(b) Another mixture, formed by adding 50 cm^3 of 1.00 mol dm^{-3} salicylic acid solution to 25 cm^3 of 1.00 mol dm^{-3} sodium hydroxide solution, can be used to determine the pK_a of salicylic acid. State **one** measurement that must be made for this mixture and explain how this measurement can be used to determine the pK_a of salicylic acid.

Measurement ....

Explanation ....

....

....

(3)
(Total 5 marks)

17 A student was given a task to determine the percentage purity of a sample of salicylic acid. The method used by the student to prepare a solution of salicylic acid is described below.

- 0.500 g of an impure sample of salicylic acid was placed in a weighing bottle.
- The contents were tipped into a beaker and 100 cm^3 of distilled water were added.
- Salicylic acid does not dissolve well in cold water so the beaker and its contents were heated gently until all the solid had dissolved.
- The solution was poured into a 250 cm^3 graduated flask and made up to the mark with distilled water.

(a) Give **two** additional instructions that would improve this method for making up the salicylic acid solution.

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(2)

(b) The pH of this solution was measured and a value of 2.50 was obtained.
Calculate the concentration of salicylic acid in this solution.
Assume that salicylic acid is the only acid in this solution. The K_a for salicylic acid is 1.07×10^{-3} mol dm^{-3}. You may represent salicylic acid as HA.
Show your working.

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(3)

(c) Use your answer to part (b) to calculate the mass of salicylic acid (M_r = 138.0) present in the original sample.
(If you were unable to complete the calculation in part (b), assume that the concentration of salicylic acid is 8.50×10^{-3} mol dm^{-3}. This is **not** the correct answer.)

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(2)

(d) Use your answer to part (c) to calculate the percentage purity of the salicylic acid used to make the solution.
(If you were unable to complete the calculation in part (c), assume that the mass of salicylic acid is 0.347 g. This is **not** the correct answer.)

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(1)
(Total 8 marks)

18 Ammonia and ethylamine are examples of weak Brønsted–Lowry bases.

(a) State the meaning of the term *Brønsted–Lowry base*.

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(1)

(b) (i) Write an equation for the reaction of ethylamine ($CH_3CH_2NH_2$) with water to form a weakly alkaline solution.

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(1)

(ii) In terms of this reaction, state why the solution formed is **weakly** alkaline.

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(1)

(c) State which is the stronger base, ammonia or ethylamine. Explain your answer.

Stronger base ....

Explanation ....

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(Extra space) ....

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(3)

(d) Give the formula of an organic compound that forms an alkaline buffer solution when added to a solution of ethylamine.

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(1)

(e) Explain qualitatively how the buffer solution in part (d) maintains an almost constant pH when a small amount of hydrochloric acid is added to it.

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(Extra space) ....

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(2)
(Total 9 marks)

19 This question involves calculations about two strong acids and one weak acid.
All measurements were carried out at 25 °C.

(a) A 25.0 cm^3 sample of 0.0850 mol dm^{-3} hydrochloric acid was placed in a beaker and 100 cm^3 of distilled water were added.
Calculate the pH of the new solution formed.
Give your answer to 2 decimal places.

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(Extra space) ....

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(2)

(b) HX is a weak monobasic acid.

(i) Write an expression for the acid dissociation constant, K_a, for HX.

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(1)

(ii) The pH of a 0.0850 mol dm^{-3} solution of HX is 2.79
Calculate a value for the acid dissociation constant, K_a, of this acid.
Give your answer to 3 significant figures.

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(Extra space) ....

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(3)

(c) A 25.0 cm^3 sample of 0.620 mol dm^{-3} nitric acid was placed in a beaker and 38.2 cm^3 of 0.550 mol dm^{-3} aqueous sodium hydroxide were added.
Calculate the pH of the solution formed.
Give your answer to 2 decimal places.

The ionic product of water $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} at 25 °C.

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(Extra space) ....

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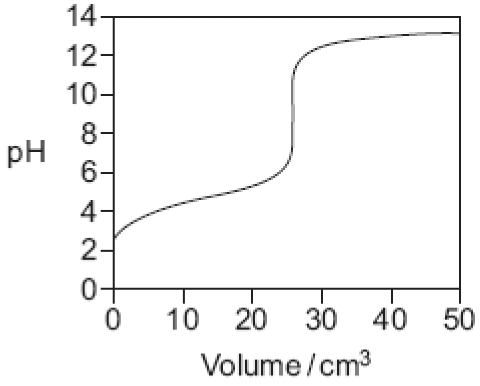
(6)
(Total 12 marks)

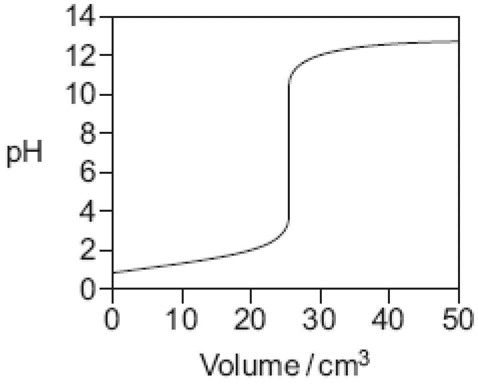
20 Titration curves labelled **A**, **B**, **C** and **D** for combinations of different aqueous solutions of acids and bases are shown below.

All solutions have a concentration of 0.1 mol dm^{-3}.

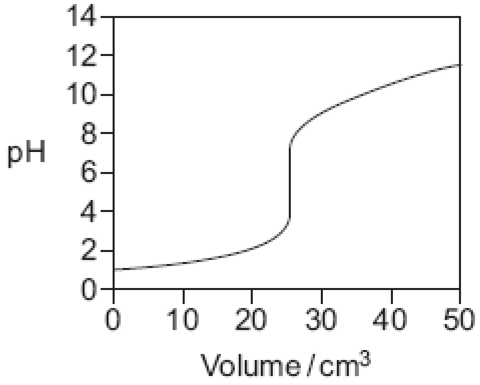
A



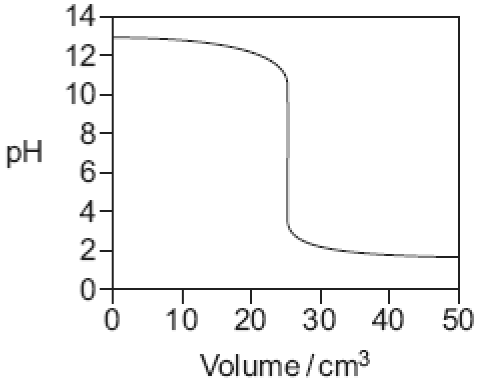
B



C



D



(a) In this part of the question write the appropriate letter in each box.

From the curves **A**, **B**, **C** and **D**, choose the curve produced by the addition of

ammonia to 25 cm^3 of hydrochloric acid ☐

sodium hydroxide to 25 cm^3 of ethanoic acid ☐

nitric acid to 25 cm^3 of potassium hydroxide ☐

(3)

(b) A table of acid.base indicators is shown below.
The pH ranges over which the indicators change colour and their colours in acid and alkali are also shown.

Indicator	**pH range**	**Colour in acid**	**Colour in alkali**
Trapaeolin	1.3 – 3.0	red	yellow
Bromocresol green	3.8 – 5.4	yellow	blue
Cresol purple	7.6 – 9.2	yellow	purple
Alizarin yellow	10.1 – 12.0	yellow	orange

(i) Select from the table an indicator that could be used in the titration that produces curve **B** but **not** in the titration that produces curve **A**.

....

(1)

(ii) Give the colour change at the end point of the titration that produces curve **D** when cresol purple is used as the indicator.

....

(1)
(Total 5 marks)

21 This question is about the pH of some solutions containing potassium hydroxide and ethanoic acid.

Give all values of pH to 2 decimal places.

(a) (i) Write an expression for pH.

....

(1)

(ii) Write an expression for the ionic product of water, K_w

....

(1)

(iii) At 10 °C, a 0.154 mol dm^{-3} solution of potassium hydroxide has a pH of 13.72. Calculate the value of K_w at 10 °C.

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(Extra space) ....

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(2)

(b) At 25 °C, the acid dissociation constant K_a for ethanoic acid has the value 1.75 × 10^{-5} mol dm^{-3}.

(i) Write an expression for K_a for ethanoic acid.

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(1)

(ii) Calculate the pH of a 0.154 mol dm^{-3} solution of ethanoic acid at 25 °C.

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(Extra space) ....

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(3)

(c) At 25 °C, the acid dissociation constant K_a for ethanoic acid has the value 1.75×10^{-5} mol dm^{-3}.

(i) Calculate the pH of the solution formed when 10.0 cm^3 of 0.154 mol dm^{-3} potassium hydroxide are added to 20.0 cm^3 of 0.154 mol dm^{-3} ethanoic acid at 25 °C.

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(Extra space) ....

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(4)

(ii) Calculate the pH of the solution formed when 40.0 cm^3 of 0.154 mol dm^{-3} potassium hydroxide are added to 20.0 cm^3 of 0.154 mol dm^{-3} ethanoic acid at 25 °C.

At 25 °C, K_w has the value 1.00×10^{-14} mol^2 dm^{-6}.

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(Extra space) ....

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(4)
(Total 16 marks)

22 When iron(II) sulfate is used for killing weeds in lawns, it is often mixed with the fertiliser ammonium sulfate. Ammonium sulfate also makes the soil acidic.

(a) Write an equation to show how the ammonium ion behaves as a Brønsted–Lowry acid in water.

....

(1)

(b) Compounds such as ammonium sulfate react on warming with sodium hydroxide solution as shown in the equation below.

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O$$

Use this information to describe a simple test, other than smell, to show that ammonia is evolved. State what you would observe.

Test ....

....

Observation ....

(2)
(Total 3 marks)

23 Iron(II) sulfate is used to kill weeds in garden lawns. It is a by-product of the manufacture of steel. When a lawn is treated with iron(II) sulfate, the iron(II) ions are oxidised to form iron(III) ions.

Iron(III) ions are acidic in aqueous solution as shown by the following equation.

$$[Fe(H_2O)_6]^{3+}(aq) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$$

In an experiment, a calibrated pH meter was used to measure the pH of an iron(III) salt in solution. At 20 °C the pH of a 0.100 mol dm^{-3} solution of iron(III) sulfate was found to be 1.62.

(a) Explain briefly why a pH meter should be calibrated before use.

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(1)

(b) Write an expression for the equilibrium constant, K_a, for the dissociation of iron(III) ions in aqueous solution.

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....

(1)

(c) Use your answer from part (b) to calculate the value of K_a for this reaction at 20 °C.
Give your answer to the appropriate precision. Show your working.

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(4)

(d) Name the substance that is most likely to oxidise the iron(II) ions when iron(II) sulfate is used as a weed killer.

....

(1)

(e) Suggest a value for the pH of a 0.100 mol dm^{-3} solution of iron(II) sulfate.

....

(1)
(Total 8 marks)

24 This question is about the pH of several solutions.

Give all values of pH to 2 decimal places.

(a) (i) Write an expression for pH.

....

(1)

(ii) Calculate the pH of 0.154 mol dm^{-3} hydrochloric acid.

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....

(1)

(iii) Calculate the pH of the solution formed when 10.0 cm^3 of 0.154 mol dm^{-3} hydrochloric acid are added to 990 cm^3 of water.

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(2)

(b) The acid dissociation constant, K_a, for the weak acid HX has the value 4.83×10^{-5} mol dm^{-3} at 25 °C.
A solution of HX has a pH of 2.48

Calculate the concentration of HX in the solution.

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(4)

(c) Explain why the pH of an acidic buffer solution remains almost constant despite the addition of a small amount of sodium hydroxide.

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(2)

(d) The acid dissociation constant, K_a, for the weak acid HY has the value 1.35×10^{-5} mol dm^{-3} at 25 °C.

A buffer solution was prepared by dissolving 0.0236 mol of the salt NaY in 50.0 cm^3 of a 0.428 mol dm^{-3} solution of the weak acid HY

(i) Calculate the pH of this buffer solution.

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(4)

(ii) A 5.00×10^{-4} mol sample of sodium hydroxide was added to this buffer solution.

Calculate the pH of the buffer solution after the sodium hydroxide was added.

(4)
(Total 18 marks)

25 In this question, give all values of pH to two decimal places.

Calculating the pH of aqueous solutions can involve the use of equilibrium constants such as K_w and K_a

K_w is the ionic product of water. The value of K_w is 5.48×10^{-14} mol^2 dm^{-6} at 50 °C.

(a) (i) Write an expression for pH.

(1)

(ii) Write an expression for K_w

(1)

(b) (i) Calculate the pH of pure water at 50 °C.

(2)

(ii) Suggest why this pure water is **not** acidic.

....

....

(1)

(iii) Calculate the pH of 0.140 mol dm^{-3} aqueous sodium hydroxide at 50 °C.

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(3)

(c) Calculate the pH of the solution formed when 25.0 cm^3 of 0.150 mol dm^{-3} aqueous sulfuric acid are added to 30.0 cm^3 of 0.200 mol dm^{-3} aqueous potassium hydroxide at 25 °C.
Assume that the sulfuric acid is fully dissociated.

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(6)
(Total 14 marks)

26 Ethanoic acid is manufactured in industry from methanol and carbon monoxide in a multi-step process involving hydrogen iodide. Ethanoic acid is obtained from the reaction mixture by fractional distillation. Methanoic acid is a useful by-product of this process.

The K_a value of an organic acid can be determined by using the pH curve obtained when the acid is titrated against sodium hydroxide. The pH of the solution formed when exactly half of the acid has been neutralised is equal to the pK_a value of the acid. The K_a value of the acid can be used to confirm its identity.

A chemist used a pH curve to determine the pK_a value of acid **Y**, formed during the manufacture of ethanoic acid. The chemist transferred 25.0 cm^3 of a solution of acid **Y** into a beaker using a pipette, and measured the pH of the acid solution using a pH meter which could be read to one decimal place. A solution of sodium hydroxide of concentration 0.100 mol dm^{-3} was added from a burette in small portions. The pH of the mixture was recorded after each addition of the sodium hydroxide solution. The chemist's results are given in the table below.

Volume of sodium hydroxide solution added / cm^3	pH
0.0	3.0
2.0	3.4
4.0	3.5
8.0	3.7
12.0	4.3
16.0	4.1
20.0	4.3
22.0	4.7

Volume of sodium hydroxide solution added / cm^3	pH
23.5	5.1
24.0	5.5
24.5	11.8
25.0	12.1
26.0	12.3
27.0	12.4
28.0	12.5
30.0	12.5

(a) Use the results given in the table above to plot a graph of pH (*y*-axis) against volume of sodium hydroxide solution added. Use the points to draw the pH curve, ignoring any anomalous results.

(6)

(b) Use your graph from part (a) to determine the

(i) volume of sodium hydroxide solution at the end-point of the titration

.... cm^3

(ii) volume of sodium hydroxide solution needed to neutralise half the acid

.... cm^3

(iii) pH of the half-neutralised mixture. Give your answer to one decimal place.

....

(3)

(c) Use the pH of the half-neutralised mixture from part (b) (iii) to calculate the value of the acid dissociation constant, K_a, of the acid **Y**. Show your working.

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(2)

(d) The table below shows the K_a values for some organic acids.

Acid	K_a / mol dm^{-3}
Methanoic acid	1.6×10^{-4}
Ethanoic acid	1.7×10^{-5}
Iodoethanoic acid	6.8×10^{-4}
Propanoic acid	1.3×10^{-5}

Use your answer from part (c) to identify acid **Y** from this table.

....

(1)

(e) For the pipette and the burette, the maximum total errors are shown below. These errors take into account multiple measurements.

pipette	± 0.05 cm^3
burette	± 0.15 cm^3

Estimate the percentage error in using each of these pieces of apparatus. You should use your answer to part (b) (i) to estimate the percentage error in using the burette.

....

....

....

(1)

(f) Calculate the difference between the K_a value from part (c) and the K_a value of the acid you identified as the acid **Y** in the table in part (d).

Express this difference as a percentage of the value given in the table in part (d). (If you could not complete the calculation in part (c), you should assume that the K_a value determined from the graph is 1.9×10^{-4} mol dm^{-3}. This is not the correct value.)

....

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(1)

(g) Other than by using a different pH meter, state **one** way in which the accuracy of the pH readings could be improved.

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(1)

(h) State why there was little change in the pH value of the mixture when between 8 cm^3 and 20 cm^3 of alkali were added.

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(1)
(Total 16 marks)

27 Describe briefly how you would ensure that a reading from a pH meter is accurate.

....

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....

(Total 2 marks)

28 In this question, give all values of pH to 2 decimal places.

(a) (i) Write an expression for the term pH.

....

(1)

(ii) Calculate the concentration, in mol dm^{-3}, of an aqueous solution of sulfuric acid that has a pH of 0.25

....

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....

(2)

(b) A student carried out a titration by adding an aqueous solution of sodium hydroxide from a burette to an aqueous solution of ethanoic acid. The end-point was reached when 22.60 cm^3 of the sodium hydroxide solution had been added to 25.00 cm^3 of 0.410 mol dm^{-3} ethanoic acid.

(i) Write an equation for the reaction between sodium hydroxide and ethanoic acid.

....

(1)

(ii) Calculate the concentration, in mol dm^{-3}, of the sodium hydroxide solution used.

....

....

....

....

(2)

(iii) A list of indicators is shown below.

Indicator	**pH range**
thymol blue	1.2–2.8
bromophenol blue	3.0–4.6
litmus	5.0–8.0
cresol purple	7.6–9.2

Select from the list the most suitable indicator for the end-point of this titration.

....

(1)

(iv) Suggest why the concentration of sodium hydroxide in a solution slowly decreases when left open to air.

....

....

(1)

(c) At 298 K, the value of the acid dissociation constant, K_a, for ethanoic acid in aqueous solution is 1.74×10^{-5} mol dm^{-3}

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

....

....

(1)

(ii) Calculate the pH of 0.410 mol dm^{-3} ethanoic acid at this temperature.

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....

(3)

(iii) Calculate the pH of the buffer solution formed when 10.00 cm^3 of 0.100 mol dm^{-3} potassium hydroxide are added to 25.00 cm^3 of 0.410 mol dm^{-3} ethanoic acid.

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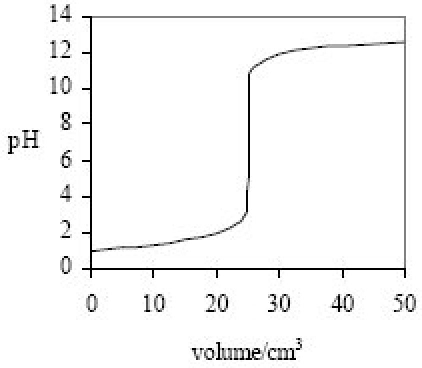
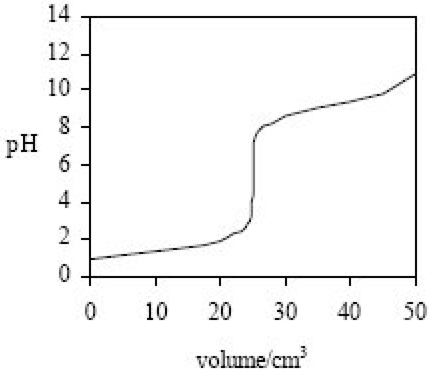
(6)
(Total 18 marks)

29 Indicators and pH curves can be used to determine the end point in a titration.

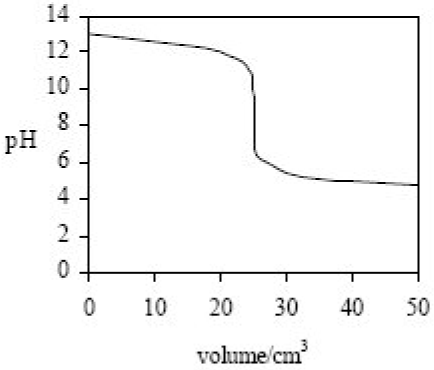
(a) The pH curves labelled **J, K, L** and **M** for combinations of different acids and bases are shown below. All solutions have a concentration of 0.1 mol dm^{-3}.



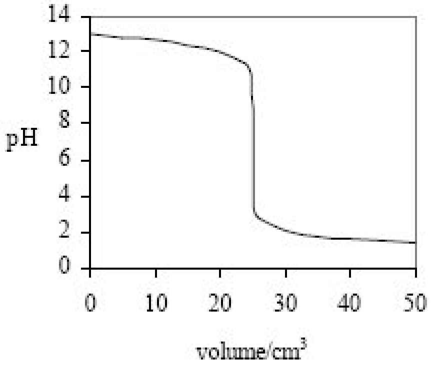
J



K



L



M

(i) Select from **J**, **K**, **L** and **M** the curve produced by the addition of

ammonia to 25 cm^3 of hydrochloric acid ....

ethanoic acid to 25 cm^3 of sodium hydroxide ....

sodium hydroxide to 25 cm^3 of hydrochloric acid ....

(ii) A table of acid–base indicators and the pH ranges over which they change colour is shown below.

Indicator	**pH range**
Thymol blue	1.2 – 2.8
Bromophenol blue	3.0 – 4.6
Methyl red	4.2 – 6.3
Cresolphthalein	8.2 – 9.8
Thymolphthalein	9.3 – 10.5

Select from the list above an indicator which could be used in the titration which produces curve **J** but not in the titration which produces curve **K**.

....

(4)

(b) The acid dissociation constant, K_a, for the weak acid, ethanoic acid, has a value of 1.74×10^{-5} mol dm^{-3} at 25 °C.

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

(i) Write an expression for the term pH.

....

(ii) Calculate the pH of a 0.15 mol dm^{-3} solution of ethanoic acid. Give your answer to 2 decimal places.

....

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....

....

(4)
(Total 8 marks)

30 Buffer solutions are important in biological systems and in industry to maintain almost constant pH values.

(a) In the human body, one important buffer system in blood involves the hydrogencarbonate ion, HCO_3^- , and carbonic acid, H_2CO_3, which is formed when carbon dioxide dissolves in water.

(i) Use the following equation to explain how this buffer maintains a constant pH of 7.41 even if a small amount of acid enters the bloodstream.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

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(ii) In a sample of blood with a pH of 7.41, the concentration of HCO_3^- (aq) ions is 2.50×10^{-2} mol dm^{-3} and the concentration of H_2CO_3(aq) is 1.25×10^{-3} mol dm^{-3}. Calculate a value for the acid dissociation constant, K_a, for carbonic acid at this temperature.

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(5)

(b) In industry, the pH of a solution used to dye cloth must be controlled or else the colour varies.

A solution of dye in a beaker is buffered by the presence of ethanoic acid and sodium ethanoate. In the solution, the concentration of ethanoic acid is 0.15 mol dm^{-3} and the concentration of sodium ethanoate is 0.10 mol dm^{-3}. The value of K_a for ethanoic acid is 1.74×10^{-5} mol dm^{-3} at 298 K.

(i) A 10.0 cm^3 portion of 1.00 mol dm^{-3} hydrochloric acid is added to 1000 cm^3 of this buffered solution.

Calculate the number of moles of hydrochloric acid added.

....

(ii) Calculate the number of moles of ethanoic acid and the number of moles of sodium ethanoate in the solution after addition of the hydrochloric acid.

Mol of ethanoic acid after addition ....

....

Mol of sodium ethanoate after addition ....

....

(iii) Hence calculate the pH of this new solution. Give your answer to 2 decimal places.

....

....

....

(6)
(Total 11 marks)

31

Summarised directions for recording responses to multiple completion questions			
A (i), (ii) and (iii) correct only	**B** (i) and (iii) correct only	**C** (ii) and (iv) correct only	**D** (iv) alone correct

Brønsted-Lowry acid-base reactions include

(i) $OH^- + CH_3Cl \rightarrow CH_3OH + Cl^-$

(ii) $NH_3 + HCl \rightarrow NH_4^+ + Cl^-$

(iii) $KF + PF_5 \rightarrow K^+ + PF_6^-$

(iv) $H_2O + H_2O \rightarrow H_3O^+ + OH^-$

(Total 1 mark)

32 (a) A sample of hydrochloric acid has a pH of 2.34
Write an expression for pH and calculate the concentration of this acid.

pH ....

Concentration ....

....

(2)

(b) A 0.150 mol dm^{-3} solution of a weak acid, HX, also has a pH of 2.34

(i) Write an expression for the acid dissociation constant, K_a, for the acid HX.

....

....

(ii) Calculate the value of K_a for this acid and state its units.

Calculation ....

....

....

Units ....

(iii) Calculate the value of pK_a for the acid HX. Give your answer to two decimal places.

....

(5)

(c) A 30.0 cm^3 sample of a 0.480 mol dm^{-3} solution of potassium hydroxide was partially neutralised by the addition of 18.0 cm^3 of a 0.350 mol dm^{-3} solution of sulphuric acid.

(i) Calculate the initial number of moles of potassium hydroxide.

....

....

(ii) Calculate the number of moles of sulphuric acid added.

....

....

(iii) Calculate the number of moles of potassium hydroxide remaining in excess in the solution formed.

....

....

(iv) Calculate the concentration of hydroxide ions in the solution formed.

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(v) Hence calculate the pH of the solution formed. Give your answer to two decimal places.

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(6)
(Total 13 marks)

33 The hydrolysis of methyl propanoate was studied in acidic conditions at 25°C and the rate equation was found to be

$$\text{rate} = k[CH_3CH_2COOCH_3][H^+]$$

(a) Use the data below to calculate the value of the rate constant, *k*, at this temperature. Deduce its units.

Initial rate of reaction / mol dm^{-3} s^{-1}	Initial concentration of methyl propanoate / mol dm^{-3}	Initial concentration of hydrochloric acid / mol dm^{-3}
1.15×10^{-4}	0.150	0.555

Rate constant ....

....

....

Units ....

....

(3)

(b) The reaction in part (a) was repeated at the same temperature, but water was added so that the volume of the reaction mixture was doubled. Calculate the initial rate of reaction under these conditions.

....

....

(1)

(c) A third experiment was carried out at a different temperature. Some data from this experiment are shown in the table below.

Initial rate of reaction / mol dm^{-3} s^{-1}	Value of rate constant at this different temperature	Initial methyl propanoate / mol dm^{-3}
4.56×10^{-5}	8.94×10^{-4}	0.123

Calculate the initial pH of the reaction mixture. Give your answer to two decimal places.

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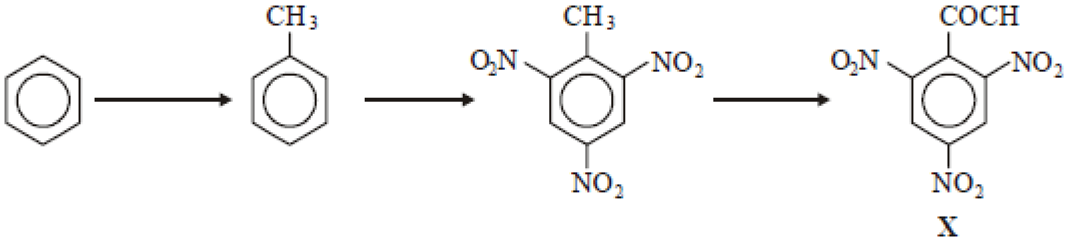
(3)
(Total 7 marks)

34 This question is based on the reactions and compounds shown in the scheme below.



A 0.100 mol dm^{-3} solution of **X** is found to have a pH of 2.50. The value of K_a in mol dm^{-3} is

A 3.16×10^{-2}

B 3.16×10^{-3}

C 1.00×10^{-4}

D 1.00×10^{-5}

(Total 1 mark)

35 In this question, give all pH values to 2 decimal places.

(a) (i) Write expressions for the ionic product of water, K_w, and for pH.

K_W = …...

pH = ...

(ii) At 318 K, the value of K_w is 4.02×10^{-14} mol^2 dm^{-6} and hence the pH of pure water is 6.70
State why pure water is not acidic at 318 K.

....

....

(iii) Calculate the number of moles of sodium hydroxide in 2.00 cm^3 of 0.500 mol dm^{-3} aqueous sodium hydroxide.

....

....

(iv) Use the value of K_w given above and your answer to part (a)(iii) to calculate the pH of the solution formed when 2.00 cm^3 of 0.500 mol dm^{-3} aqueous sodium hydroxide are added to 998 cm^3 of pure water at 318 K.

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(6)

(b) At 298 K, the acid dissociation constant, K_a, for propanoic acid, CH_3CH_2COOH, has the value 1.35×10^{-5}mol dm^{-3}.

(i) Write an expression for K_a for propanoic acid.

....

....

(ii) Calculate the pH of 0.125 mol dm^{-3} aqueous propanoic acid at 298 K.

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(4)

(c) Sodium hydroxide reacts with propanoic acid as shown in the following equation.

$$NaOH + CH_3CH_2COOH \rightarrow CH_3CH_2COONa + H_2O$$

A buffer solution is formed when sodium hydroxide is added to an excess of aqueous propanoic acid.

(i) Calculate the number of moles of propanoic acid in 50.0 cm^3 of 0.125 mol dm^{-3} aqueous propanoic acid.

....

....

(ii) Use your answers to part (a)(iii) and part (c)(i) to calculate the number of moles of propanoic acid in the buffer solution formed when 2.00 cm^3 of 0.500 mol dm^{-3} aqueous sodium hydroxide are added to 50.0 cm^3 of 0.125 mol dm^{-3} aqueous propanoic acid.

....

....

....

(iii) Hence calculate the pH of this buffer solution at 298 K.

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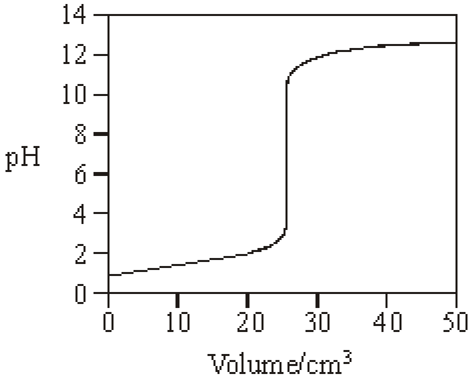
....

....

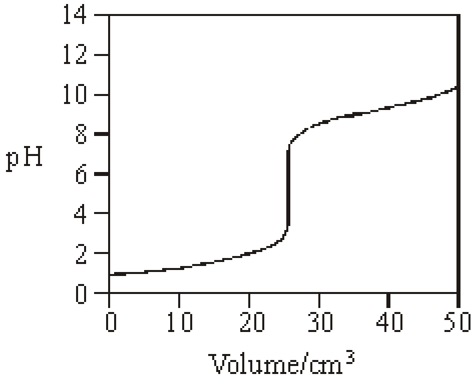
(6)
(Total 16 marks)

36

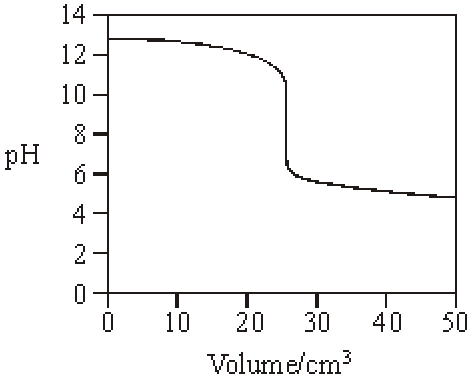
(a) Titration curves labelled **A**, **B**, **C** and **D** for combinations of different acids and bases are shown below. All solutions have a concentration of 0.1 mol dm^{-3}.



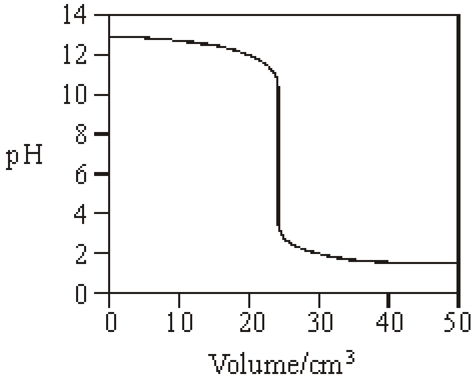
A



B



C



D

(i) Select from **A**, **B**, **C** and **D** the curve produced by the addition of

ammonia to 25 cm^3 of hydrochloric acid ....

ethanoic acid to 25 cm^3 of sodium hydroxide ....

sodium hydroxide to 25 cm^3 of hydrochloric acid ....

(ii) A table of acid–base indicators and the pH ranges over which they change colour is shown below.

Indicator	**pH range**
Thymol blue	1.2 – 2.8
Bromophenol blue	3.0 – 4.6
Methyl red	4.2 – 6.3
Cresolphthalein	8.2 – 9.8
Thymolphthalein	9.3 – 10.5

Select from the table an indicator which could be used in the titration which produces curve **A** but not in the titration which produces curve **B**.

....

(4)

(b) (i) Write an expression for the term *pH*.

....

(ii) A solution of potassium hydroxide has a pH of 11.90 at 25°C. Calculate the concentration of potassium hydroxide in the solution.

....

....

....

....

(4)

(c) The acid dissociation constant, K_a, for propanoic acid has the value of 1.35×10^{-5}mol dm^{-3} at 25 °C.

$$K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$$

In each of the calculations below, give your answer to 2 decimal places.

(i) Calculate the pH of a 0.117 mol dm^{-3} aqueous solution of propanoic acid.

....

....

....

....

(ii) Calculate the pH of a mixture formed by adding 25 cm^3 of a 0.117 mol dm^{-3} aqueous solution of sodium propanoate to 25 cm^3 of a 0.117 mol dm^{-3} aqueous solution of propanoic acid.

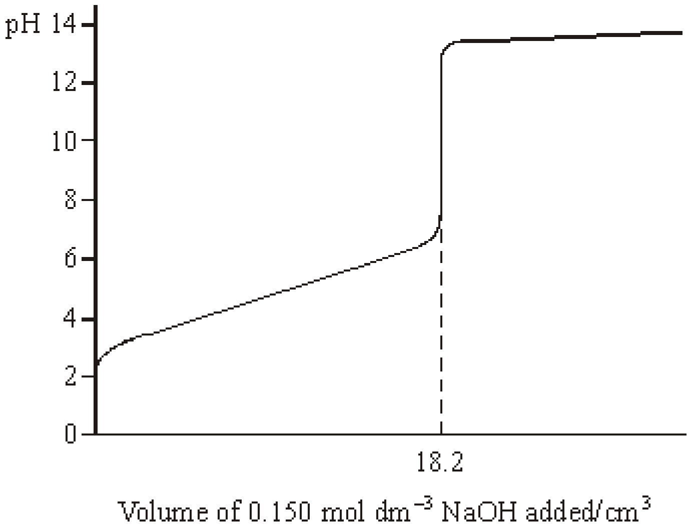
....

....

....

(5)
(Total 13 marks)

37 The pH curve shown below was obtained when a 0.150 mol dm^{-3} solution of sodium hydroxide was added to 25.0 cm^3 of an aqueous solution of a weak monoprotic acid, HA.



(a) Use the information given to calculate the concentration of the acid.

....

....

....

(2)

(b) (i) Write an expression for the acid dissociation constant, K_a, for HA.

....

(ii) Write an expression for pK_a

....

(iii) Using your answers to parts (b)(i) and (b)(ii), show that when sufficient sodium hydroxide has been added to neutralise half of the acid,

pH of the solution = pK_a for the acid HA

....

....

....

(4)

(c) Explain why dilution with a small volume of water does not affect the pH of a buffer solution.

....

....

(2)

(d) (i) Calculate the change in pH when 0.250 mol dm^{-3} hydrochloric acid is diluted with water to produce 0.150 mol dm^{-3} hydrochloric acid.

....

....

....

(ii) Calculate the volume of water which must be added to 30.0 cm^{3} of 0.250 mol dm^{-3} hydrochloric acid in order to reduce its concentration to 0.150 mol dm^{-3}.

....

....

....

(4)
(Total 12 marks)

38 Use the information about the following solutions to answer the question below.

Solution F: This is a mixture of 1 mol of propanoic acid, 1 mol of methanol and 2 mol of water.

Solution G: This was originally the same mixture as solution **F** but it has been left to reach equilibrium.

Compared to the pH of solution **F**, the pH of solution **G** will be

A considerably lower.

B slightly lower.

C slightly higher.

D exactly the same.

(Total 1 mark)

39 This question concerns the weak acid, ethanoic acid, for which the acid dissociation constant, K_a, has a value of 1.74×10^{-5} mol dm^{-3} at 25 °C.

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

In each of the calculations below, give your answer to 2 decimal places.

(a) Write an expression for the term *pH*. Calculate the pH of a 0.150 mol dm^{-3} solution of ethanoic acid.

(4)

(b) A buffer solution is prepared by mixing a solution of ethanoic acid with a solution of sodium ethanoate.

(i) Explain what is meant by the term *buffer solution*.

(ii) Write an equation for the reaction which occurs when a small amount of hydrochloric acid is added to this buffer solution.

(3)

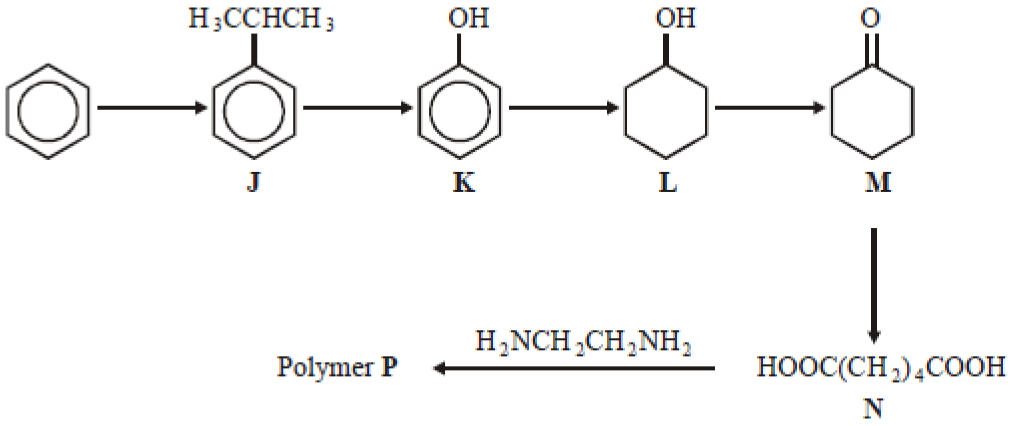
(c) In a buffer solution, the concentration of ethanoic acid is 0.150 mol dm^{-3} and the concentration of sodium ethanoate is 0.100 mol dm^{-3}.

(i) Calculate the pH of this buffer solution.

(ii) A 10.0 cm^3 portion of 1.00 mol dm^{-3} hydrochloric acid is added to 1000 cm^3 of this buffer solution.
Calculate the number of moles of ethanoic acid and the number of moles of sodium ethanoate in the solution after addition of the hydrochloric acid. Hence, find the pH of this new solution.

(8)
(Total 15 marks)

40 This question is about the following reaction scheme which shows the preparation of polymer **P**.



K is a weak acid with a pK_a of 9.95. The pH of a 0.10 mol dm^{-3} solution of **K** is

A 4.48

B 4.98

C 5.48

D 5.98

(Total 1 mark)

41 The value of the acid dissociation constant, K_a, for the weak acid HA, at 298 K, is 1.45×10^{-4} mol dm^{-3}.

(a) Write an expression for the term K_a for the weak acid HA.

....

....

(1)

(b) Calculate the pH of a 0.250 mol dm^{-3} solution of HA at 298 K.

....

....

....

....

....

(4)

(c) A mixture of the acid HA and the sodium salt of this acid, NaA, can be used to prepare a buffer solution.

(i) State and explain the effect on the pH of this buffer solution when a small amount of hydrochloric acid is added.

....

....

....

(ii) The concentration of HA in a buffer solution is 0.250 mol dm^{-3}. Calculate the concentration of A^- in this buffer solution when the pH is 3.59

....

....

....

....

....

....

(6)

(Total 11 marks)

42 In which one of the following reactions is the role of the reagent stated correctly?

	Reaction	**Role of reagent**
A	$TiO_2 + 2C + 2Cl_2 \rightarrow TiCl_4 + 2CO$	TiO_2 is an oxidising agent
B	$HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^-$	HNO_3 is a Brønsted-Lowry acid
C	$CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$	$AlCl_3$ is a Lewis base
D	$2CO + 2NO \rightarrow 2CO_2 + N_2$	CO is a reducing agent

(Total 1 mark)

43 For this question **one or more** of the options given may be correct. Select your answer by means of the following code

A if **1**, **2** and **3** only are correct

B if **1** and **3** only are correct

C if **2** and **4** only are correct

C if **4** alone is correct

Directions summarised			
A	**B**	**C**	**D**
1, **2** and **3** only correct	**1** and **3** only correct	**2** and **4** only correct	**4** only correct

Solutions with a pH of 1.0 include

1 0.1 mol dm^{-3} hydrochloric acid

2 0.1 mol dm^{-3} ethanoic acid

3 0.05 mol dm^{-3} sulphuric acid

4 0.2 mol dm^{-3} nitric acid

(Total 1 mark)

44 (a) By reference to the forces between molecules, explain why ammonia is very soluble in water.

....

....

(2)

(b) Aqueous solutions of ammonia have a pH greater than 7.

(i) Write an equation for the reaction of ammonia with water.

....

(ii) Explain why the pH of a solution containing 1.0 mol dm^{-3} of ammonia is less than 14 at 298 K.

....

....

(3)

(c) An ammonium ion in aqueous solution can behave as a Brønsted–Lowry acid. State what is meant by the term *Brønsted–Lowry acid*.

....

(1)

(d) State what is meant by the term *buffer solution*. Identify a reagent which could be added to a solution of ammonia in order to form a buffer solution.

Buffer solution ....

....

Reagent ....

(3)

(e) An acidic buffer solution is obtained when sodium ethanoate is dissolved in aqueous ethanoic acid.

(i) Calculate the pH of the buffer solution formed at 298 K when 0.125 mol of sodium ethanoate is dissolved in 250 cm^3 of a 1.00 mol dm^{-3} solution of ethanoic acid. The acid dissociation constant, K_a, for ethanoic acid is 1.70×10^{-5} mol dm^{-3} at 298 K.

....

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....

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....

....

(ii) Write an ionic equation for the reaction which occurs when a small volume of dilute hydrochloric acid is added to this buffer solution.

....

(5)
(Total 14 marks)

45 Use the information below to answer this question.

A saturated solution of magnesium hydroxide, $Mg(OH)_2$, contains 0.1166 g of $Mg(OH)_2$ in 10.00 dm^3 of solution. In this solution the magnesium hydroxide is fully dissociated into ions.

Which one of the following is the pH of a solution of magnesium hydroxide containing 4.0×10^{-5} mol dm^{-3} of hydroxide ions at 298 K?
($K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} at 298 K)

A 9.6

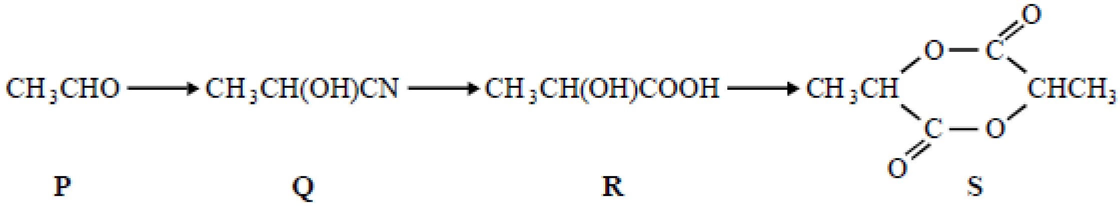
B 9.5

C 8.6

D 8.3

(Total 1 mark)

46 This question refers to the reaction sequence below.



HCN is a weak acid with a pK_a value of 9.40. If a 0.010 mol dm^{-3} solution of HCN was used in the first step, the concentration of cyanide ions, in mol dm^{-3}, would be

A 2.0×10^{-6}

B 6.4×10^{-5}

C 2.0×10^{-5}

D 3.1×10^{-1}

(Total 1 mark)

47 (a) At 50°C, the ionic product of water, K_w, has the value 5.48×10^{-14} mol^2 dm^{-6}.

(i) Define the term K_w

....

(ii) Define the term *pH*

....

(iii) Calculate the pH of pure water at 50 °C. Explain why pure water at 50 °C is still neutral even though its pH is not 7.

Calculation ....

....

....

Explanation ....

....

(5)

(b) At 25°C, K_w has the value 1.00×10^{-14} mol^2 dm^{-6}. Calculate the pH at 25 °C of

(i) a 0.150 mol dm^{-3} solution of sodium hydroxide,

....

....

....

(ii) the solution formed when 35.0 cm^3 of this solution of sodium hydroxide is mixed with 40.0 cm^3 of a 0.120 mol dm^{-3} solution of hydrochloric acid.

....

....

....

....

....

....

....

(8)

(c) In a 0.150 mol dm^{-3} solution of a weak acid HX at 25 °C, 1.80% of the acid molecules are dissociated into ions.

(i) Write an expression for K_a for the acid HX.

....

....

(ii) Calculate the value of K_a for the acid HX at this temperature and state its units.

....

....

....

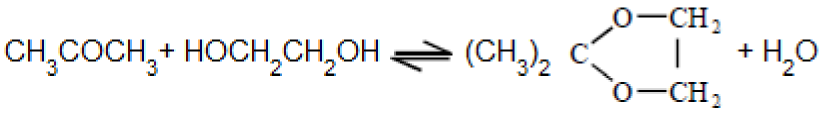
....

....

....

(5)
(Total 18 marks)

48 This question is about the reaction between propanone and an excess of ethane-1,2-diol, the equation for which is given below.



Y

In a typical procedure, a mixture of 1.00 g of propanone, 5.00 g of ethane-1,2-diol and 0.100 g of benzenesulphonic acid, $C_6H_5SO_3H$, is heated under reflux in an inert solvent. Benzenesulphonic acid is a strong acid.

If 0.100 g of the strong monoprotic acid, benzenesulphonic acid, was dissolved in 100 cm^3 of water, the pH of the solution would be

A 0.20

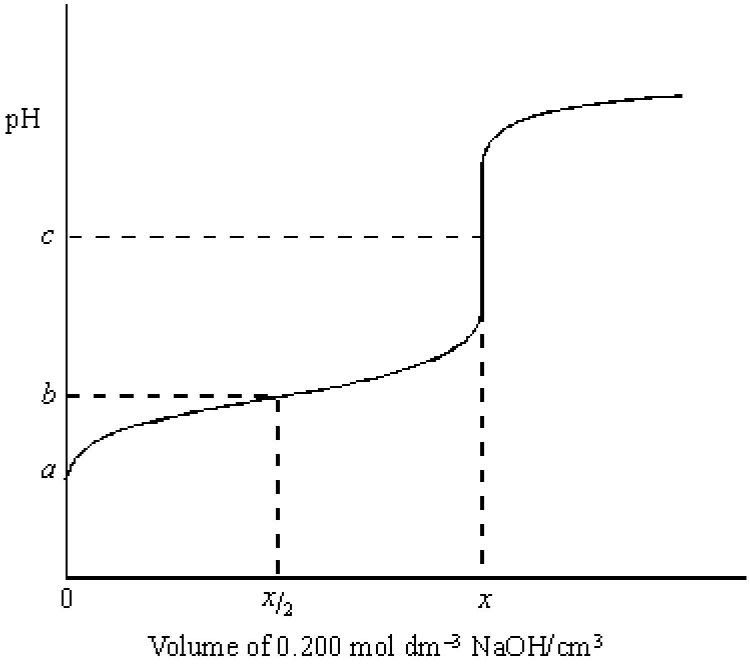
B 1.20

C 2.20

D 3.20

(Total 1 mark)

49 The sketch below shows the change in pH when a 0.200 mol dm^{-3} solution of sodium hydroxide is added from a burette to 25.0 cm^{3} of a 0.150 mol dm^{-3} solution of the weak acid HA at 25 °C.



(a) The volume of sodium hydroxide solution added at the equivalence point is x cm^{3}. Calculate the value of x.

....

....

....

(2)

(b) (i) Define the term pH.

....

(ii) The pH at the equivalence point is c. Suggest a value for c.

....

(iii) Identify a suitable indicator for detecting the equivalence point of the titration.

....

(3)

(c) The value of K_c for the weak acid HA at 25 °C is 2.75 × 10^{-5} mol dm^{-3}.

(i) Explain the term *weak* as applied to the acid HA.

....

(ii) Write an expression for K_a for the acid HA.

....

(iii) Calculate the pH of the 0.150 mol dm^{-3} solution of acid HA before any sodium hydroxide is added, i.e. the pH at point *a*.

....

....

....

....

....

(5)

(d) Calculate the pH of the solution formed when $x/2$ cm^3 of the 0.200 mol dm^{-3} solution of sodium hydroxide are added to 25.0 cm^3 of the 0.150 mol dm^{-3} solution of HA, i.e. the pH at point *b*.

....

....

....

(3)
(Total 13 marks)

50 An aqueous solution contains 4.0 g of sodium hydroxide in 250 cm^3 of solution.
(K_w = 1.00 × 10^{-14} mol^2 dm^{-6})

The pH of the solution is

A 13.0

B 13.3

C 13.6

D 13.9

(Total 1 mark)

51 Iodine and propanone react in acid solution according to the equation

$$I_2 + CH_3COCH_3 \rightarrow CH_3COCH_2I + HI$$

The rate equation for the reaction is found to be

$$\text{rate} = k\,[CH_3COCH_3][H^+]$$

(a) Deduce the order of reaction with respect to iodine and the overall order of reaction.

Order with respect to iodine ....

Overall order ....

(2)

(b) At the start of the experiment, the rate of reaction was found to be 2.00×10^{-5} mol dm^{-3} s^{-1} when the concentrations of the reactants were as shown below.

Reactant	Concentration / mol dm^{-3}
CH_3COCH_3	1.50
I_2	2.00×10^{-2}
H^+	3.00×10^{-2}

Use these data to calculate a value for the rate constant and deduce its units.

Rate constant ....

....

....

Units ....

(3)

(c) How can you tell that H^+ acts as a catalyst in this reaction?

....

....

....

(2)

(d) Calculate the initial rate of reaction if the experiment were to be repeated at the same temperature and with the same concentrations of iodine and propanone as in part (b) but at a pH of 1.25

....

....

....

....

....

....

(3)
(Total 10 marks)

52 A 0.210 mol dm^{-3} solution of potassium hydroxide was added from a burette to 25.0 cm^{3} of a 0.160 mol dm^{-3} solution of ethanoic acid in a conical flask.
Given that the value of the acid dissociation constant, K_a, for ethanoic acid is 1.74×10^{-5} mol dm^{-3}, calculate the pH at 25 °C of the solution in the conical flask at the following three points:

before any potassium hydroxide had been added;

after 8.0 cm^{3} of potassium hydroxide solution had been added;

after 40.0 cm^{3} of potassium hydroxide solution had been added.

(Total 16 marks)

53 The value of the acid dissociation constant, K_a, for ethanoic acid is 1.74×10^{-5} mol dm^{-3} at 298 K.

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

....

(ii) Calculate the pH at 298 K of a 0.220 mol dm^{-3} solution of ethanoic acid.

....

....

....

....

....

....

(5)

(b) A sample of the 0.220 mol dm^{-3} solution of ethanoic acid was titrated against sodium hydroxide solution.

(i) Calculate the volume of a 0.150 mol dm^{-3} solution of sodium hydroxide required to neutralise 25.0 cm^3 of the ethanoic acid solution.

....

....

....

....

(ii) From the list below, select the best indicator for this titration and explain your choice.

Name of indicator	**pH range**
bromophenol blue	3.0 – 4.6
methyl red	4.2 – 6.3
bromothymol blue	6.0 – 7.6
thymol blue	8.0 – 9.6

Indicator ....

Explanation ....

....

....

(5)

(c) A buffer solution is formed when 2.00 g of sodium hydroxide are added to 1.00 dm^3 of a 0.220 mol dm^{-3} solution of ethanoic acid.

Calculate the pH at 298 K of this buffer solution.

....

....

....

....

....

....

....

(6)
(Total 16 marks)

54 The equation and rate law for the reaction of substance P with substance Q are given below.

$$2P + Q \rightarrow R + S$$

$$rate = k[P]^2[H^+]$$

Under which one of the following conditions, all at the same temperature, would the rate of reaction be slowest?

	[P] / mol dm^{-3}	pH
A	0.1	0
B	1	2
C	3	3
D	10	4

(Total 1 mark)

55 Addition of which one of the following to 10 cm^3 of 1.0 M NaOH would result in the pH being halved?

A 10 cm^3 of water

B 100 cm^3 of water

C 5 cm^3 of 1.0 M HCl

D 10 cm^3 of 1.0 M HCl

(Total 1 mark)

56 A solution of sodium ethanoate has a pH of 8.91 at 25 °C. The hydrogen ion and hydroxide ion concentrations in this solution are

A $[H^+] = 1.00 \times 10^{-9}$ mol dm^{-3} $[OH^-] = 1.00 \times 10^{-5}$ mol dm^{-3}

B $[H^+] = 1.00 \times 10^{-9}$ mol dm^{-3} $[OH^-] = 8.13 \times 10^{-6}$ mol dm^{-3}

C $[H^+] = 1.23 \times 10^{-9}$ mol dm^{-3} $[OH^-] = 1.00 \times 10^{-5}$ mol dm^{-3}

D $[H^+] = 1.23 \times 10^{-9}$ mol dm^{-3} $[OH^-] = 8.13 \times 10^{-6}$ mol dm^{-3}

(Total 1 mark)

57 A weak acid HA dissociates in aqueous solution as shown below

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq) \qquad \Delta H = +20 \text{ kJ mol}^{-1}$$

Which one of the following changes will result in a decrease in the pH of an aqueous solution of the acid?

A addition of a little aqueous sodium hydroxide solution

B raising the temperature of the solution

C dissolving a little of the sodium salt, NaA, in the solution

D adding a platinum catalyst to the solution

(Total 1 mark)

58 The pH of 0.001 M NaOH at 25°C is

A 13

B 11

C 9

D 3

(Total 1 mark)

59 Which one of the following could be true in an aqueous solution of sodium hydroxide?

A $[H^+] = (OH^-]$

B $pH = -\log_{10} [OH^-]$

C pH = 1.2

D pH = 12.8

(Total 1 mark)

60 Which one of the following is the change in units of pH which occurs when 10.0 cm^3 of a 1.0 M solution of a strong monoprotic acid are made up to 1.0 dm^3 with water?

A 1

B 2

C 3

D 5

(Total 1 mark)

Mark schemes

1 (a) (i) G

1

(ii) F

1

(iii) H

1

(b) (i) cresol purple

1

(ii) yellow to red

both colours needed and must be in this order

1

(iii) yellow or pale yellow

Not allow any other colour with yellow

1

[6]

2 (a) $[H_2O]$ is <u>very</u> high (compared with $[H^+]$ and $[OH^-]$)

OR

<u>Very few</u> H^+ and OH^- ions

OR

<u>Only / very</u> slightly dissociates

OR

Equilibrium lies <u>far</u> to the left

Not partially dissociates

M1

1

$[H_2O]$ is (effectively) constant
OR is incorporated into the constant K

Allow changes by only a very small amount

M2

1

(b) (Dissociation OR breaking bonds) is endothermic

1

∴ Equilibrium moves to RHS (at higher T) <u>to absorb heat or to lower T or oppose increase in T</u>

Allow to oppose change only if increase T mentioned

1

(c) $[H^+]$ $= \sqrt{K_w}$ (or $= \sqrt{5.48 \times 10^{-14}}$)

Correct pH answer scores 3

1

If wrong method no marks

Using alternative K_w (1.00×10^{-14}) gives pH = 7.<u>00</u> which scores 1

$= 2.34 \times 10^{-7}$

1

pH = 6.63

Final answer must have 2dp

1

(d) $[H^+]$ $= K_w / [OH^-]$ or ($= 5.48 \times 10^{-14} / 0.12$)

Correct pH answer scores 3

1

If wrong method no marks

If use alternative K_w (1.00×10^{-14}) again, do not penalise repeat error so pH = 13.08 scores 3

$= 4.566 \times 10^{-13}$

1

pH = 12.34

*If use alternative K_w (1.00×10^{-14}) **not** as a repeat error, pH = 13.08 scores 1*

If AE in K_w value made in part (c) is repeated here, do not penalise again.

Final answer must have 2dp, but if dp penalised in (c) allow more than 2dp here but not fewer.

1

[10]

3

(a) $[H^+] = \frac{K_a \times [CH_3COOH]}{CH_3COO^-}$ or $= 1.74 \times 10^{-5} \times \frac{0.186}{0.105}$

Allow ( )

M1

1

$= \quad 3.08 \times 10^{-5}$

If [HX] / [X⁻] or $\frac{0.186}{0.105}$ upside down, or any addition or subtraction lose M1 & M2.

M2

1

pH = 4.51 (correct answer scores 3)

Can score M3 for correct pH conseq to their $[H^+]$, so pH = 5.01 scores one

Must be to 2 dp

M3

1

Alternative using Henderson−Hasselbach Equation

$pH = pKa - \log[HX] / X^-] = -\log(1.74 \times 10^{-5}) - \log(\frac{0.186}{0.105})$

Allow ( )

M1

pKa = 4.76 − 0.248

If [HX] / [X⁻] or $\frac{0.186}{0.105}$ upside down, can only score 1

M2

pH = = 4.51

so pH = 5.01

Must be to 2 dp

M3

(b) mol HX after addition (= 0.251 + 0.015) = 0.266

For HX, if no addition or error in addition (other than AE) (or subsequent extra add or sub) MAX 3

M1

1

mol X^- after subtraction (= 0.140 − 0.015) = 0.125

For X^- if no subtraction or error in subtraction (other than AE) (or subsequent extra add or sub) MAX 3

M2

1

$[H^+]$ = ($\frac{K_a \times [CH_3COOH]}{CH_3COO^-}$) = $\frac{1.74 \times 10^{-5} \times 0.266}{0.125}$

If errors above in both addition AND subtraction can only score M3 for insertion of their numbers in rearranged expression. One exception, if addition and subtraction reversed then pH =4.58 scores 2

M3

1

$[H^+] = 3.703 \times 10^{-}5$ (mol dm^{-3})

If $[HX] / [X^-]$ upside down, lose M3 & M4 (or next two marks) but can score M5 for correct pH conseq to their $[H^+]$, so if M1 & M2 correct, pH = 5.09 scores 3.

M4

1

pH = 4.43

Correct use of HX and X^- values from (d) gives
pH= 4.41 and scores 4

If wrong method, e.g. √ or no use of rearranged K_a expression, may score M1 & M2 but no more.

Allow more but not fewer than 2dp here.

M5

1

Alternative using Henderson−Hasselbach Equation

mol acid after addition = 0.251 + 0.015 = 0.266

For HX, if no addition or error in addition (other than AE) (or subsequent extra add or sub) MAX 3

M1

mol salt after addition = 0.140 − 0.015 = 0.125

For X^- if no subtraction or error in subtraction (other than AE) (or subsequent extra add or sub) MAX 3

M2

pH = (pKa − log[HX] / [X^-]) = −log(1.74 × 10^{-5}) − log(0.266 / 0.125)

If errors above in both addition AND subtraction can only score M3 for insertion of their numbers − except if addition and subtraction reversed then pH = 4.58 scores 2

M3

pH = 4.76 − 0.328

M4

pH = = 4.43

If [HX] / [X^-] upside down, lose M3 & M4 (or next two marks) but can score M5 for correct pH conseq to their working, so if M1 & M2 correct, pH = 5.09 scores 3.

Allow more but not fewer than 2dp here.

M5

[8]

4 (a) $HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$

or

$H_2O + HCO_3^- \rightleftharpoons CO_3^{2-} + H_3O^+$

Must have equilibrium sign but mark on to (b)

Ignore state symbols

1

(b) Acid: Increase in concentration of H^+ ions, equilibrium moves to the left.

Allow H^+ ions react with carbonate ions (to form HCO_3^-)

1

Alkali: OH^- reacts with H^+ ions, equilibrium moves to the right (to replace the H^+ ions)

1

Concentration of H^+ remains (almost) constant

1

[4]

5 (a) As a droplet from the funnel could enter the burette / affect volume / readings / titre

1

(b) Air bubble in jet or wtte

Do not allow misreading burette or overshooting end point.

1

(c) Ensures **all** reagents are able to react / mix / come into contact

Accept no reagent is left unreacted on sides of flask

Do not allow any reference to 'removal' of the solution unless it is clear that it is added to the flask.

1

(d) The added water does not affect the mols / amount of reagents / reactants / solution Z

Do not allow mols of solution or mols in the flask.

Allow water does not react with the reagents / water is not one of the reactants

Do not allow 'water is not involved'

1

[4]

6 (a) Burette

1

Because it can deliver variable volumes

1

(b) The change in pH is gradual / not rapid at the end point

1

An indicator would change colour over a range of volumes of sodium hydroxide

Allow indicator would not change colour rapidly / with a few drops of NaOH

1

(c) $[H^+] = 10^{-pH} = 1.58 \times 10^{-12}$

1

$K_w = [H^+][OH^-]$ therefore $[OH^-] = K_w / [H^+]$

1

Therefore, $[OH^-] = 1 \times 10^{-14} / 1.58 \times 10^{-12} = 6.33 \times 10^{-3}$ (mol dm^{-3})

Allow 6.31–6.33 × 10^{-3} (mol dm^{-3})

1

(d) At this point, $[NH_3] = [H^+]$

Therefore $K_a = \dfrac{[H^+]^2}{[NH_4^+]}$

1

$[H^+] = 10^{-4.6} = 2.51 \times 10^{-5}$

1

$K_a = (2.51 \times 10^{-5})^2 / 2 = 3.15 \times 10^{-10}$ (mol dm^{-3})

Allow 3.15 – 3.16 × 10^{-10} (mol dm^{-3})

1

(e) When $[NH_3] = [NH_4^+]$, $K_a = [H^+]$ therefore $- \log K_a = - \log [H^+]$

Answer using alternative value

1

Therefore $pH = -\log_{10}(3.15 \times 10^{-10}) = 9.50$

M2 $pH = - \log_{10}(4.75 \times 10^{-9}) = 8.32$

Allow consequential marking based on answer from part (d)

1

[12]

7 (a) This question is marked using levels of response. Refer to the Mark Scheme Instructions for Examiners for guidance on how to mark this question.

All stages are covered and the explanation of each stage is generally correct and virtually complete.

Answer is communicated coherently and shows a logical progression from stage 1 and stage 2 to stage 3. Steps in stage 3 must be complete, ordered and include a comparison.

Level 3
5 – 6 marks

All stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies OR two stages are covered and the explanations are generally correct and virtually complete.

Answer is mainly coherent and shows a progression from stage 1 and stage 2 to stage 3.

Level 2
3 – 4 marks

Two stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies, OR only one stage is covered but the explanation is generally correct and virtually complete.

Answer includes some isolated statements, but these are not presented in a logical order or show confused reasoning.

Level 1
1 – 2 marks

Insufficient correct Chemistry to warrant a mark.

Level 0
0 marks

Indicative Chemistry content

Stage 1: difference in structure of the two acids
- The acids are of the form RCOOH
- but in ethanoic acid R = CH_3
- whilst in ethanedioic acid R = COOH

Stage 2: the inductive effect
- The unionised COOH group contains two very electronegative oxygen atoms
- therefore has a negative inductive (electron withdrawing)effect
- The CH_3 group has a positive inductive (electron pushing) effect

Stage 3: how the polarity of OH affects acid strength
- The O–H bond in the ethanedioic acid is more polarised / H becomes more δ^+
- More dissociation into H^+ ions
- Ethanedioic acid is stronger than ethanoic acid

6

(b) Moles of NaOH = Moles of $HOOCCOO^-$ formed = 6.00×10^{-2}

Extended response

1

Moles of HOOCCOOH remaining = $1.00 \times 10^{-1} - 6.00 \times 10^{-2}$

$= 4.00 \times 10^{-2}$

1

$K_a = [H^+][A^-] / [HA]$

$[H^+] = K_a \times [HA] / [A^-]$

1

$[H^+] = 5.89 \times 10^{-2} \times (4.00 \times 10^{-2} / V) / (6.00 \times 10^{-2} / V) = 3.927 \times 10^{-2}$

1

pH = $-\log_{10}(3.927 \times 10^{-2}) = 1.406 = 1.41$

Answer must be given to this precision

1

(c) $5H_2C_2O_4 + 6H^+ + 2MnO_4^- \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

OR $5C_2O_4^{2-} + 16H^+ + 2MnO_4^- \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

1

Moles of $KMnO_4 = 20.2 \times 2.00 \times 10^{-2} / 1000 = 4.04 \times 10^{-4}$

1

Moles of $H_2C_2O_4 = 5 / 2 \times 4.04 \times 10^{-4} = 1.01 \times 10^{-3}$

1

Concentration = moles / volume (in dm^3)

$= 1.01 \times 10^{-3} \times 1000 / 25 = 4.04 \times 10^{-2}$ (mol dm^{-3})

If 1:1 ratio or incorrect ratio used, M2 and M4 can be scored

1

[15]

8 B

[1]

9 C

[1]

10 (a) (only) slightly or partially dissociated / ionised

Ignore 'not fully dissociated'.

Allow low tendency to dissociate or to lose / donate a proton.

Allow shown equilibrium well to the left.

Otherwise ignore equations.

1

(b) $2CH_3CH_2COOH + Na_2CO_3 \longrightarrow 2CH_3CH_2COONa + H_2O + CO_2$

OR

$2CH_3CH_2COOH + CO_3^{2-} \longrightarrow 2CH_3CH_2COO^- + H_2O + CO_2$

OR

$CH_3CH_2COOH + Na_2CO_3 \longrightarrow CH_3CH_2COONa + NaHCO_3$

OR

$CH_3CH_2COOH + CO_3^{2-} \longrightarrow CH_3CH_2COO^- + HCO_3^-$

Must be propanoic acid, allow C_2H_5COOH.

Not molecular formulae.

Allow multiples.

Ignore reversible sign.

Not H_2CO_3.

1

(c) $[OH^-] = 2 \times 0.0120 = 0.0240$ M1

Correct answer for pH with or without working scores 3.

1

$[H^+] = \frac{1 \times 10^{-14}}{0.0240} = 4.166 \times 10^{-13}$ ***OR*** pOH = 1.62 M2

If × 2 missed or used wrongly can only score M3 for correct calculation of pH from their $[H^+]$.

1

pH = $12.\underline{38}$ M3

Lose M3 if not 2 decimal places: 12.4 scores 2.

12.08 scores 1 (missing × 2) ; 12.1 scores 0.

11.78 scores 1 (dividing by 2) 11.8 scores 0.

1

(d) (i) $K_a = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]}$

Ignore ( ) here but brackets must be present.

Must be correct acid and salt.

If wrong, mark part (ii) independently.

1

(ii) M1 $K_a = \frac{[H^+]^2}{[C_6H_5COOH]}$ **OR** with numbers

Correct answer for pH with or without working scores 3.

Allow HX, HA and ignore ( ) here.

May score M1 in part (i).

1

M2 $[H^+] = \sqrt{}(6.31 \times 10^{-5} \times 0.0120)$ or $\sqrt{}(K_a \times [C_6H_5COOH])$
$(= \sqrt{}(7.572 \times 10^{-7} = 8.70 \times 10^{\times 4})$

pH = 6.12 may score 2 if correct working shown and they show the square root but fail to take it.

But if no working shown or wrong $K_a = \frac{[H^+]}{[C_6H_5COOH]}$

used which also leads to 6.12, then zero scored.

1

M3 pH = 3.<u>06</u>

Must be 2 decimal places ie 3.1 loses M3.

1

(iii) M1 $[H^+] = 10^{-4.00} = 1.00 \times 10^{-4}$

Correct answer for mass with or without working scores 5.

Allow 1×10^{-4}.

1

M2 $[X^-] = \frac{Ka \ x \ [HX]}{[H^+]}$

Ignore ( ) here.

If [HX] / [X⁻] upside down, can score M1 plus M4 for 5.26×10^{-7}.

1

M3 $= \frac{6.31 \times 10^{-5} \ x \ 0.0120}{1.00 \times 10^{-4}}$

And M5 for 7.57×10^{-5} *g.*

1

M4 $= 7.572 \times 10^{-3}$

1

M5 Mass (C_6H_5COONa) = $7.572 \times 10^{-3} \times 144$ =1.09 g
or 1.1 g

Wrong method, eg using $[H^+]^2$ *may only score M1 and M5 for correct multiplication of their M4 by 144*

(provided not of obviously wrong substance).

1

(e) M1 CO_2

Allow NO_x and SO_2.

1

M2 <u>pH</u> <u>(It)</u> <u>falls / decreases</u>

If M1 wrong, no further marks.

1

M3 mark M2 & M3 independently

acidic (gas)

OR reacts with alkali(ne solution) / OH^-

OR $CO_2 + 2OH^- \longrightarrow CO_3^{2-} + H_2O$

OR $CO_2 + OH^- \longrightarrow HCO_3^-$

Not forms H_2CO_3 H_2SO_3 H_2SO_4 etc OR H^+ ions.

1

[17]

11 (a) Correct orientation of graph (pH on *y*-axis)

1

Scale – plotted points cover at least half the grid and *y*-axis should start at pH 4

1

All points plotted correctly

+ / – one small square.

1

<u>Curve</u> of best fit drawn correctly

Allow some leniency here with a complex graph – it is important that the section between pH 8.5 and 9.7 is close to linear.

Lose this mark if the line is pulled towards the anomaly at 3.0 cm^3.

Lose this mark if first point at pH 5.1 is treated as an anomaly.

Do not accept doubled lines but allow some slight discontinuity where the curve changes direction.

1

(b) 11.6-11.9 (cm^3) only

Do not mark consequentially to student's graph.

1

(c) pK_a = value of pH related to part (b) **M1**

Mark consequentially on student's graph – ideally 9.0-9.1

Do not penalise precision of answer.

1

$K_a = 10^{-pK_a}$ **M2**

Ideally 1.0×10^{-9} to 7.9×10^{-10}

*Ignore precision of answer but lose **M2** for 1 significant figure here.*

1

(d) pH 8.7

Ineffective stirring / swirling of the mixture

Both points needed for this mark.

Do not allow pH 5.1

Do not allow 'overshooting (at 3 cm ^{3} addition)'.

1

(e) Take more pH readings around the end-point / add smaller volumes of NaOH near the end-point

Do not allow 'use a more accurate / reliable pH meter / probe'.

Do not allow the use of a thermostatted mixture.

1

[9]

12 (a) Proton donor or H^+ donor

1

(b) (i) $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$ or $\frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$

If K_a wrong, can only score M1 below.

Must be ethanoic acid not HA

Must have square brackets (penalise here only) but mark on in (b)(ii).

1

(ii) M1 $[H^+] = 10^{-2.69}$ ***OR*** 2.042×10^{-3} (mol dm^{-3})

1

M2 $CH_3COOH] = \frac{[H^+]^2}{K_a}$

Ignore ( )
Mark for correctly rearranged expression incl $[H^+]^2$

1

M3

$$= \frac{(2.042 \times 10^{-3})^2}{1.75 \times 10^{-5}}$$

If M2 wrong no further marks.

1

M4 = 0.238 (mol dm^{-3}) Allow 0.229 − 0.24

1

(c) (i) $ClCH_2COOH \rightleftharpoons ClCH_2COO^- + H^+$

OR $ClCH_2COOH + H_2O \rightleftharpoons ClCH_2COO^- + H_3O^+$

Allow $\longrightarrow$

Allow $ClCH_2CO_2H$ *and* $ClCH_2CO_2^-$

1

(ii) M1 Cl is (more electronegative so) withdraws electrons

OR negative inductive effect of Cl

Ignore electronegativity.

Ignore chloroethanoic acid has a lower K_a *value.*

Allow Cl reduces +ve inductive effect of methyl group.

1

M2 Weakens O–H bond

OR O–H bond is more polar

OR reduces negative charge on COO^-

OR stabilizes COO^- (more)

M1 & M2 are independent marks.

Ignore H^+ *lost more easily.*

1

(d) (i) **A**

1

(ii) **C**

1

(iii) **D**

1

(e) M1 Mol NaOH = mol OH^- = $(19.6 \times 10^{-3}) \times 0.720 = 1.41(1) \times 10^{-2}$

Mark for answer.

1

M2 Mol H_2SO_4 = $(26.4 \times 10^{-3}) \times 0.550 = 1.45(2) \times 10^{-2}$

Mark for answer.

1

M3 Mol H^+ added = **2 ×** $(1.452 \times 10^{-2}) = 2.90(4) \times 10^{-2}$

OR

XS mol H_2SO_4 = $7.46(4) \times 10^{-3}$

If factor × 2 missed completely (pH = 2.05)

or used wrongly later,

can score max 4 for M1, M2, M5 & M6

1

M4 XS mol H^+ = 0.0149(3)

1

M5 For dividing by volume

$[H^+] = 0.0149(3) \times (1000 / 46.0) = 0.324 - 0.325$ mol dm^{-3}

If no use or wrong use of volume lose M5 and M6

ie can score 4 for pH = 1.83 (no use of vol)

Treat missing 1000 as AE (−1) & score 5 for pH = 3.49

1

M6 pH = 0.49

2dp *(penalise more or less).*

If × 2 missed & vol not used, pH = 3.39 scores M1 & M2 only.

1

[18]

13 (a) Over time / after storage meter does not give accurate readings

Do not allow 'to get an accurate reading' or 'reading drifts' on its own.

Allow 'temperature variations affect readings'.

1

(b) Any **five** from:

Ignore references to the use of the pipette, the filling of the burette and the calibration of the pH meter.

- Measure pH (of the acid)
- Add alkali in known small portions

  Allow 1 – 2cm^3.
- Stir mixture
- Measure pH (after each addition)
- Repeat until alkali in excess

  Allow 27 – 50cm^3.
- Add in smaller increments near endpoint

  Allow 0.1 – 0.5cm^3.

To score full marks, the sequence must follow a logical order.

5 max

[6]

14 (a) (i) $[H^+][OH^-]$ ***OR*** $[H_3O^+][OH^-]$

Ignore (aq)

Must have [ ] not ( )

1

(ii) $\sqrt{3.46 \times 10^{-14}}$ $(= 1.86 \times 10^{-7})$

If no square root, CE=0

1

pH = 6.73

Must be 2dp

1

(iii) $[H^+] = 10^{-11.36}$ ($= 4.365 \times 10^{-12}$ OR 4.37×10^{-12})

Mark for working

1

$Kw = [4.365 \times 10^{-12}$ ***OR*** $4.37 \times 10^{-12} \times 0.047] = 2.05 \times 10^{-13}$

Allow $2.05 \times 10^{-13} - 2.1 \times 10^{-13}$

Mark for answer

Ignore units

1

(b) (i) $HCOOH \rightleftharpoons HCOO^- + H^+$

Must have $\rightleftharpoons$ but ignore brackets.

OR $HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$

Allow HCO_2^- or $CHOO^-$ ie minus must be on oxygen, so penalise $COOH^-$

1

(ii) $$K_a = \frac{[H^+][HCOO^-]}{HCOOH} \quad \textbf{OR} \quad \frac{[H_3O^+][HCOO^-]}{HCOOH}$$

Must have all brackets but allow ( )

Must be HCOOH etc.

Allow ecf in formulae from (b)(i)

1

(iii) M1

$$K_a = \frac{[H^+]^2}{[HCOOH]} \quad \left([H^+]^2 = 1.78 \times 10^{-4} \times 0.056 = 9.97 \times 10^{-6}\right)$$

Allow HA or HX etc.

Allow $[H^+] = \sqrt{(Ka \times [HA])}$ for M1

1

M2 $[H^+] = 3.16 \times 10^{-3}$

Mark for answer

1

M3 pH = 2.50 allow more than 2 dp but not fewer

***Allow correct pH from their wrong** $[H^+]$ **here only** If square root shown but not taken, pH = 5.00 can score max 2 for M1 and M3*

1

(iv) M1 Decrease **Mark M1 independently**

1

M2 Eqm <u>shifts / moves</u> to RHS **OR** more H^+ **OR** K_a increases
OR more dissociation

1

M3 To reduce temperature or oppose increase / change in temperature

Only award M3 following correct M2

1

(c) (i) M1 $[H^+] = \dfrac{Ka \times [HX]}{[X^-]}$ **OR** $pH = pK_a - \log \dfrac{[HX]}{[X^-]}$

If $[HX]/[X^-]$ upside down, no marks

1

M2 $\dfrac{1.78 \times 10^{-4} \times 2.35 \times 10^{-2}}{1.84 \times 10^{-2}}$ **OR** $pH = 3.75 - \log \dfrac{2.35 \times 10^{-2}}{1.84 \times 10^{-2}}$

$(= 2.27 \times 10^{-4})$

1

M3 pH = 3.64 allow more than 2 dp but not fewer

pH calc NOT allowed from their wrong $[H^+]$ here

1

(ii) M1 Mol H^+ added = 5.00×10^{-4}

Mark on from AE in moles of HCl (eg 5×10^{-3} gives pH = 3.42 scores 3)

1

M2 Mol HCOOH = 2.40×10^{-2} **and** Mol $HCOO^-$ = 1.79×10^{-2}

If either wrong no further marks except AE (−1) OR if ECF in mol acid and / or mol salt from (c)(i), can score all 4

1

M3 $[H^+] \left(= \dfrac{Ka \times [XH]}{[X^-]}\right) = \dfrac{1.78 \times 10^{-4} \times 2.40 \times 10^{-2}}{1.79 \times 10^{-2}} \; (= 2.39 \times 10^{-4})$

If $[HX]/[X^-]$ upside down here after correct expression in (c)(i), no further marks

OR $pH = 3.75 - \log \dfrac{2.40 \times 10^{-2}}{1.79 \times 10^{-2}}$

If $[HX]/[X^-]$ upside down here and is repeat error from (c)(i), max 3 (pH = 3.88 after 3.86 in (c)(i))

1

M4 pH = 3.62 allow more than 2 dp but not fewer

pH calc NOT allowed from their wrong [H$^+$] here

1

[20]

15 (a) Proton donor or H$^+$ donor

Allow donator

1

(b) (i) B B

Both need to be correct to score the mark

1

(ii) A A

Both need to be correct to score the mark

1

(iii) B A

Both need to be correct to score the mark

1

(c) **M1** [H$^+$] = $10^{-1.25}$ OR 0.05623

1

M2 mol HCl = $(25 \times 10^{-3}) \times 0.0850$ (= 2.125×10^{-3})

Mark for Working

1

M3 vol $\left(= \dfrac{2.125 \times 10^{-3}}{0.05623}\right)$ = 0.0378 dm^3 or 37.8 cm^3

allow 0.0375 – 0.038 dm^3 or 37.5 – 38 cm^3

Units and answer tied

Lose M3 if total given as (25 + 37.8) = 62.8 cm^3

Ignore "vol added = 12.8 cm ^{3} " after correct answer

1

(d) (i) 4.52

Must be 2dp

1

(ii) $K_a = \dfrac{[H^+][H^-]}{[HX]}$ ignore = $\dfrac{[H^+]^2}{[HX]}$ but this may score M1 in (d)(iii)

Must have all brackets but allow ( ) Allow HA etc

***NO** mark for 10^{-pKa}*

1

(iii) **M1** $K_a = \frac{[H^+]^2}{[HX]}$ or with numbers

Allow $[H^+] = \sqrt{(Ka \times [HA])}$ *for M1*

1

M2 $[H^+] = (\sqrt{(3.01 \times 10^{-5} \times 0.174)} = \sqrt{(5.24 \times 10^{-6})}\ )$

$= 2.29 \times 10^{-3}$ - 2.3×10^{-3}

Mark for <u>answer</u>

1

M3 pH = 2.64 (allow more than 2dp but not fewer)

Allow 1 for correct pH from their wrong $[H^+]$

If square root forgotten, pH = 5.28 scores 2 for M1 and M3

1

(e) **M1** mol OH^- = $(10.0 \times 10^{-3}) \times 0.125 = 1.25 \times 10^{-3}$

Mark for answer

1

M2 orig mol HX = $(15.0 \times 10^{-3}) \times 0.174 = 2.61 \times 10^{\times 3}$

Mark for answer

1

M3 mol HX in buffer = orig mol HX – mol OH^-

Mark for answer

$= 2.61 \times 10^{-3} - 1.25 \times 10^{-3} = 1.36 \times 10^{-3}$

Allow conseq on their (M2 – M1)

$([HX] = 1.36 \times 10^{-3}/25 \times 10^{-3} = 0.0544)$

If no subtraction, max 3 for M1, M2 & M4 (pH = 4.20)

If $[H^+] = [X^-]$ *&* $\sqrt{}$*used, max 3 for M1, M2 & M3 (pH = 2.89)*

1

M4 mol X^- in buffer = mol OH^- = 1.25×10^{-3}

$([X^-] = 1.25 \times 10^{-3}/25 \times 10^{-3} = 0.05)$

May be scored in M5 expression

1

M5 $[H^+]$ $\left(= \frac{Ka \times [HX]}{[X^-]}\right)$

If use $K_a = \frac{[H^+]^2}{[HX]}$ *no further marks*

$$= \frac{3.01 \times 10^{-5} \times 1.36 \times 10^{-3}}{1.25 \times 10^{-3}} \text{ OR } \frac{3.01 \times 10^{-5} \times 0.0544}{0.05}$$

(= 3.27×10^{-5})

If either value of HX or X^- used wrongly or expression upside down, no further marks

1

M6 pH = 4.48 or 4.49 (allow more than 2dp but not fewer)

*Do **not** allow M6 for correct calculation of pH using their $[H^+]$ - this only applies in (d)(iii) - apart from earlier AE*

1

[18]

16 (a) **Z**

Mark independently.

1

The idea that the solution contains both HA and A^-

1

(b) pH

1

$[HA] = [A^-]$

Accept solution half neutralised.

1

pH = pK_a

Accept $[H^+] = K_a$

1

[5]

17 (a) Any **two** from:

Weigh by difference or rinse weighing bottle and add to beaker

Rinse beaker and add washings to graduated flask

Invert flask several times to ensure uniform solution

Use a funnel to transfer to the flask and rinse the funnel

Use a stirrer to prepare the solution and rinse the stirrer

If more than two answers apply the list rule.

Max 2

(b) $K_a = [H^+]^2 / [HA]$

Allow any correct expression relating K_a, $[H^+]$ and $[HA]$

1

$[HA] = (10^{-2.50})^2 / 1.07 \times 10^{-3}$

M2 also scores M1

1

$= 9.35 \times 10^{-3}$ (mol dm^{-3})

Do not allow 9.4 (answer is 9.346).

Correct answer only scores 1 mark.

Do not penalise precision but must be to at least two significant figures.

1

(c) (b) × 138.0 / 4

1

= 0.322

Using 8.50×10^{-3} gives 0.293

Correct answer scores M1 and M2.

Do not penalise precision but must be to at least two significant figures.

1

(d) (c) × 100 / 0.500 = 64.5%

Using 0.293 from (c) gives 58.7%

Using 0.347 gives 69.4%

Do not penalise precision.

1

[8]

18 (a) Proton acceptor

1

(b) (i) $CH_3CH_2NH_2 + H_2O \longrightarrow CH_3CH_2NH_3^+ + OH^-$

allow eq with or without $\rightleftharpoons$

allow $C_2H_5NH_2$ *and* $C_2H_5NH_3^+$ *(plus can be on N or H or 3)*

allow RHS as $C_2H_5NH_3OH$

1

(ii) Mark independently of (b)(i)

Allow

Ethylamine is only partly/slightly dissociated

OR

Ethylamine is only partly/slightly ionized

reaction/equilibrium lies to left or low $[OH^-]$ ***OR*** little OH^- formed

OR little ethylamine has reacted

Ignore “not fully dissociated” or “not fully ionized”

Ignore reference to ionisation or dissociation of water

1

(c) **M1** Ethylamine

If wrong no marks in (c)

1

M2 alkyl group is electron releasing/donating

OR alkyl group has (positive) inductive effect

1

M3 increases electron density <u>on N(H₂)</u>

OR increased availability of <u>lp</u>

OR increases ability of <u>lp</u> (to accept H(+))

Mark M3 is independent of M2

1

(d) $CH_3CH_2NH_3Cl$

Or any amine hydrochloride

allow name (ethylammonium chloride or ethylamine hydrochloride) or other halide for Cl

or a strong ***organic*** *acid*

NOT NH_4Cl

1

(e) Mark independently of (d)

Extra H^+ reacts with ethylamine or OH^-

Or makes reference to Equilibrium (in (b)(i)) with amine on LHS

1

OR $CH_3CH_2NH_2 + H^+ \longrightarrow CH_3CH_2NH_3^+$

OR $H^+ + OH^- \longrightarrow H_2O$

Equilibrium shifts to RHS

OR ratio $[CH_3CH_2NH_3^+]/[CH_3CH_2NH_2]$ remains almost constant

1

[9]

19 (a) **M1** $[H^+] = 0.0170$

1

M2 pH = 1.77

2 dp

Allow M2 for correct pH calculation from their wrong $[H^+]$ for this pH calculation only

1

(b) (i) $K_a = \dfrac{[H^+][X^-]}{[HX]^2}$ Ignore $K_a = \dfrac{[H^+]^2}{[HX]}$

Penalize missing [ ] here ***and not elsewhere***

Allow HA instead of HX

1

(ii) **M1** $[H^+] = 10^{-2.79}$ OR $1.6218\ldots \times 10^{-3}$

If $[H^+]$ wrong, can only score M2

1

M2 $K_a = \dfrac{[H^+]^2}{[HX]}$ OR $\dfrac{[1.62 \times 10^{-3}]^2}{[0.0850]}$

Allow HA instead of HX

1

M3 $K_a = 3.09 \times 10^{-5}$ 3sfs min

(allow 3.10×10^{-5} if 1.6218 rounded to 1.622)
Ignore units

If [HX] used as $(0.0850 - 1.62 \times 10^{-3})$

this gives $K_a = 3.15 \times 10^{-5}$

$(0.0016)^2/0.085 = 3.01 \times 10^{-5}$ scores 2 for AE

1

(c) **M1** mol OH^- (= $(38.2 \times 10^{-3}) \times 0.550$)

= $2.10(1) \times 10^{-2}$ or 0.0210(1)

Mark for answer

1

M2 Mol H^+ (= $(25.0 \times 10^{-3}) \times 0.620$)

= 1.55×10^{-2} or 0.0155

Mark for answer

1

M3 excess mol OH^- = $5.5(1) \times 10^{-3}$

Allow conseq for M1 – M2

If wrong method *e.g. no subtraction or use of* √

can only score max of M1, M2, M3 and M4.

1

M4 $[OH^-] = 5.51 \times 10^{-3} \times \frac{10^3}{63.2}$ [= 0.08718 (0.0872)]

OR $[OH^-] = 5.5 \times 10^{-3} \times \frac{10^3}{63.2}$ = 0.0870(2)

(M1 – M2) / vol in dm^3 *mark for dividing by volume*

(take use of 63.2 without 10^{-3} *as AE so 9.94 scores 5)*

If no use or wrong use of vol lose M4 & M6

Can score M5 for showing (10^{-14}*/ their XS alkali)*

1

M5 $[H^+] = \frac{10^{-14}}{0.08718} = 1.147 \times 10^{-13}$

OR $\frac{10^{-14}}{0.0870} = 1.149 \times 10^{-13}$

OR pOH = 1.06

If no use or wrong use of K_w *or pOH no further marks*

1

M6 pH = 12.9(4) allow 3sf

If vol missed score max 4 for 11.7(4)

If acid– alkali reversed max 4 for pH = 1.06

Any excess acid – max 4

1

[12]

20 (a) C

1

A

1

D

1

(b) (i) Bromocresol green

Allow wrong spellings

1

(ii) Purple to yellow

Must have both colours:

Purple start – yellow finish

1

[5]

21 (a) (i) - log[H^+]

penalise missing [ ] here ***and not elsewhere***

1

(ii) [H^+][$OH^–$]

Allow ( ) brackets, but must have charges

1

(iii) Mark independently from a(ii)

[H^+] = $10^{-13.72}$ = 1.905 × $10^{–14}$

If wrong no further mark

1

K_w = 1.905 × $10^{–14}$ × 0.154 = = (2.93 – 2.94) × $10^{–15}$

1

(b) (i) $Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

Must have charges and all brackets, allow ( )

Acid/salt shown must be CH_3COOH not HA

and correct formulae needed

1

(ii) **In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp**
For values above 10, allow 3sfs - do not insist on 2 dp

$$K_a = \frac{[H^+]^2}{[CH_3COOH]}$$

Allow HA

1

$([H^+]^2 = 1.75 \times 10^{-5} \times 0.154 = 2.695 \times 10^{-6} = 2.70 \times 10^{-6})$

If √ shown but not done gets pH = 5.57 (scores 2)

$[H^+] = 1.64 \times 10^{-3}$

Allow mark for pH conseq to their [H+] ***here only***

1

pH = 2.78 or 2.79

1

(c) (i) **In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp**

For values above 10, allow 3sfs - do not insist on 2 dp

M1 Initially

mol OH^- = $(10 \times 10^{-3}) \times 0.154$ **and**

mol HA = $(20 \times 10^{-3}) \times 0.154$

or mol OH^- = 1.54×10^{-3} **and** mol HA = 3.08×10^{-3}

1

M2 $[H^+] = K_a \frac{[CH_3COOH]}{[CH_3COOH^-]}$

or with numbers

Allow Henderson Hasselbach

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

M3 mol ethanoic acid left = (mol ethanoate ions) = 1.54×10^{-3}

$K_a = [H^+]$ **or** $pH = pK_a$ scores **M1**, **M2** and **M3**

1 If either mol acid in mixture or mol salt wrong

- max 2 for M1 and M2

Any mention of $[H^+]^2$ *- max 2 for M1 and M3*

1

M4 pH (= - log 1.75×10^{-5}) = 4.76 or 4.757

Not 4.75

1

If no subtraction (so mol ethanoic acid in buffer = original mol)
pH = 4.46 scores 2 for **M1** and **M2**

If $[H+]^2$ used, pH = 3.02 scores 2 for **M1** and **M3**

(ii) **In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp**
For values above 10, allow 3sfs - do not insist on 2 dp

M1 XS mol KOH (= $(20 \times 10^{-3}) \times 0.154$) = 3.08×10^{-3}

If no subtraction: max 1 for correct use of volume

No subtraction and no use of volume scores zero

If wrong subtraction or wrong moles

*Can only score **M2** and **M3** for process*

1

M2 $[OH^-] = 3.08 \times 10^{-3} \times \frac{10^3}{60} = 0.0513(3)$

*Mark for dividing their answer to **M1** by correct volume (method mark)*

*If no volume or wrong volume or multiplied by volume, max 2 for **M1** and **M3** process*

1

M3 $[H^+] = \frac{10^{-14}}{0.05133}$ (= 1.948×10^{-13} to 1.95×10^{-13})

or pOH = 1.29

*Mark for K_w divided by their answer to **M2***

If pOH route, give one mark for 14 – pOH

1

M4 pH = 12.7(1)

Allow 3sf but not 12.70

1

If no subtraction and no use of volume (pH = 11.79 scores zero)

If no subtraction, max 1 for correct use of volume, ($60cm^3$)
(pH = 13.01 scores 1)
If volume not used, pH = 11.49 (gets 2)
If multiplied by vol, pH = 10.27 (gets 2)

[16]

22 (a) $NH_4^+ \rightarrow NH_3 + H^+$

Accept multiples.

Accept $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$

Ignore state symbols, even if incorrect.

1

(b) Test indicator / conc HCl

Do not accept 'smell'.

Do not accept precipitation reactions of aqueous ammonia.

1

Observation colour for an alkali / white fumes

If wrong test then lose second mark.

1

[3]

23 (a) Idea that <u>over time / after storage</u> meter does not give accurate readings

Do not accept 'to get an accurate reading' without further qualification.

Allow 'temperature variations affect reading'.

1

(b) $$\frac{[[Fe(H_2O)_5OH]^{2+}(aq)]\,[H^+(aq)]}{[[Fe(H_2O)_6]^{3+}(aq)]}$$

Allow without (aq) symbols.

Need at least one set of square brackets around complex ions

1

(c) pH = –log [H^+]

1

[H^+] = 0.0240

Do not penalise precision of [H^+]

Correct answer scores M1 and M2.

1

K_a = $(0.0240)^2$ / 0.1 = 5.75 × 10^{-3} or 5.76 × 10^{-3}

Correct answer without working loses M1 and M2.

Allow 7.58 × 10^{-3}

1

Answer, even if incorrect, given to 3 sig figs

1

(d) Oxygen (in the air) / O_2

Ignore ‘air’ or ‘the atmosphere’ or ‘chemicals in soil’.

List principle.

1

(e) 4.0 – 6.9

Do not penalise precision.

[7]

24 (a) (i) – log[H^+] or log 1/[H^+]

penalise missing square brackets here only

1

(ii) 0.81

2dp required, no other answer allowed

1

(iii) **M1** mol H^+ = 1.54 × 10^{-3}

if wrong no further mark

if 1.5 × 10^{-3} allow M1 but not M2 for 2.82

1

M2 pH = 2.81

allow more than 2dp but not fewer

1

(b) **M1** $[H^+] = 3.31 \times 10^{-3}$

1

M2 $K_a = \frac{[H^+][X^-]}{[HX]}$ or $\frac{[H^+]^2}{[HX]}$ or using numbers

do not penalise ( ) or one or more missing [ ]

1

M3 $[HX] = \frac{[H^+]^2}{K_a} = \frac{(3.31 \times 10^{-3})^2}{4.83 \times 10^{-5}}$

allow conseq on their $[H^+]^2/(4.83 \times 10^{-5})$ (AE)
if upside down, no further marks after M2

1

M4 $[HX] = 0.227$

allow 0.225 – 0.23

1

(c) **M1** extra/added OH^- removed by reaction with H^+ or the acid

1

M2 correct discussion of equn shift i.e. $HX \rightleftharpoons H^+ + X^-$ moves to right

1

OR

ratio $\frac{[HX]}{[X^-]}$ remains almost constant

(d) (i) **M1** mol HY = $(50 \times 10^{-3}) \times 0.428 = 0.0214$

OR $[Y] = .0236 \times \frac{1000}{50} = 0.472$

mark for answer

1

M2 $[H^+] = 1.35 \times 10^{-5} \times \frac{0.0214}{0.0236}$

OR $1.35 \times 10^{-5} = [H^+] \times \frac{0.0236}{0.0214}$

OR $[H^+] = 1.35 \times 10^{-5} \times \frac{0.428}{0.472}$

OR $1.35 \times 10^{-5} = [H^+] \times \frac{0.472}{0.428}$

must be numbers not just rearrangement of Ka expression

If either HY value or Y^- value wrong, (apart from AE -1) lose M2 and M3

1

M3 $[H^+] = 1.22 \times 10^{-5}$

mark for answer

1

M4 pH = 4.91

allow more than 2dp but not fewer

allow M4 for correct pH calculation using their $[H^+]$ (this applies in (d)(i) only)

1

If Henderson Hasselbalch equation used:

M1 mol HY = $(50 \times 10^{-3}) \times 0.428 = 0.0214$

OR $[Y] = .0236 \times \frac{1000}{50} = 0.472$

mark for answer

1

M2 p*K*a = 4.87

1

M3 $\log\left(\frac{0.0214}{0.0236}\right) = -0.043$

$\log\left(\frac{0.428}{0.472}\right) = -0.043$

If either HY value or Y⁻ value wrong, (apart from AE-1) lose M3 and M4

1

M4 pH = 4.87 – (– 0.043) = 4.91

allow more than 2dp but not fewer

1

(ii) Can score full marks for correct consequential use of their HY and Y^- values from d(i)

M1 Mol HY after adding NaOH = $0.0214 - 5.0 \times 10^{-4} = 0.0209$

AE in subtraction loses just M1
If wrong initial mol HY (i.e. not conseq to part d(i)) or no subtraction or subtraction of wrong amount, lose M1 and M3

1

M2 Mol Y^- after adding NaOH = $0.0236 + 5.0 \times 10^{-4} = 0.0241$

AE in addition loses just M2

If wrong mol Y^- (i.e. not conseq to part d(i)) or no addition or addition of wrong amount lose M2 and next mark gained

1

M3 $[H^+] = 1.35 \times 10^{-5} \times \frac{0.0209}{0.0241}$ $(= 1.17 \times 10^{-5})$

if convert to concentrations

$[H^+] = 1.35 \times 10^{-5} \times \frac{0.418}{0.482}$ $(= 1.17 \times 10^{-5})$

1

if HY/Y^- upside down, no further marks

M4 pH = 4.93

allow more than 2dp but not fewer

NOT allow M4 for correct pH calculation using their $[H^+]$ (this allowance applies in (d)(i) only)

1

If Henderson Hasselbalch equation used:

Can score full marks for correct consequential use of their HY and Y^{-} values from d(i)

M1 Mol HY after adding NaOH = 0.0214 – 5.0 ×10^{-4} = 0.0209

AE in subtraction loses just M1
If wrong initial mol HY (i.e. not conseq to part d(i)) or no subtraction or subtraction of wrong amount lose M1 and M3

1

M2 Mol Y^{-} after adding NaOH = 0.0236 + 5.0 × 10^{-4} = 0.0241

AE in addition loses just M2

If wrong mol Y^{-} (i.e. not conseq to part d(i)) or no addition or addition of wrong amount lose M2 and next mark gained

1

M3 $\log\left(\frac{0.0209}{0.0241}\right) = -0.062$

if HY/Y^{--} upside down, no further marks

1

M4 pH = 4.87 – (– 0.062) = 4.93

allow more than 2dp but not fewer

1

[18]

25 (a) (i) –log[H^{+}]

Penalise missing [ ] here ***and not elsewhere***

1

(ii) [H^{+}][OH^{-}]

1

(b) (i) [H^{+}] = 2.34 × 10^{-7}

1

pH = 6.63

Penalise fewer than 3 sig figs but allow more than 2 dp

1

(ii) [H^{+}] = [OH^{-}]

1

(iii) **M1** $[H^+] = K_w/[OH^-]$

if upside down or CE, allow M3 only for correct use of their $[H^+]$

1

M2 $(= 5.48 \times 10^{-14}/0.140) = 3.91 \times 10^{-13}$

1

M3 pH = 12.4(1)

not 12.40 (AE from 12.407)

1

Penalise fewer than 3 sig figs but allow more than 3 sfs
For values above 10, allow 3sfs - do not insist on 2 dp.
For values below 1, allow 2dp – do not insist on 3 sig figs

Not allow pH = 14 – pOH but can award M3 only for pH = 13.1(46)
Can award all three marks if $pK_w = 13.26$ *is used*

(c) **M1** mol NaOH = mol OH^- = $(30 \times 10^{-3}) \times 0.20 = 6.0 \times 10^{-3}$

mark for answer

1

M2 mol H_2SO_4 = $(25 \times 10^{-3}) \times 0.15 = 3.75 \times 10^{-3}$

mark for answer

1

M3 mol H^+ = $(25 \times 10^{-3}) \times 0.15 \times 2 = 7.5 \times 10^{-3}$
OR XS mol H_2SO_4 = 0.75×10^{-3}

if factor of 2 missed or used wrongly, CE - lose M3 and next mark gained. In this case they must then use K_w *to score any more.*
see examples below

1

M4 XS mol H^+ = 1.5×10^{-3}

1

M5 $[H^+] = (1.5 \times 10^{-3}) \times (1000/55) = 0.0273$

if no use or wrong use of volume, lose M5 and M6 except if 1000 missed
AE –1 (pH = 4.56)

1

M6 pH = 1.56

Penalise fewer than 3 sig figs but allow more than 3 sfs
For values above 10, allow 3sfs - do not insist on 2 dp.
For values below 1, allow 2dp – do not insist on 3 sig figs

1

[14]

26 (a) pH on the *y*-axis, volume of alkali on the *x*-axis

If axes unlabelled use data to decide that pH is on y-axis.

1

Uses sensible scales

Lose this mark if plotted paths do not cover ***half*** *of the paper.*

Lose this mark if the graph plot goes off the squared paper.

1

Labels the axes

Allow mark for axes labelled 'pH' and 'volume'.

1

Plots all of the points correctly

1

Line through the points is smooth and has the correct profile

Ignore 0–5 cm^3 section of the graph.

Lose this mark if graph is kinked or not a single line.

1

Line ignores the point at 12 cm^3

Lose this mark if point clearly not treated as an anomaly.

1

(b) (i) 24.4 cm^3 ± 0.2

If no answer in (i) allow answer written on the graph.

Allow this answer ***only****.*

Do not penalise precision.

1

(ii) 12.2 cm^3 ± 0.1

If no answer in (ii), allow answer written on the graph.

Allow answer to (i) divided by 2.

Do not penalise precision.

1

(iii) 3.9 ± 0.2

If no answer in (iii), allow answer written on the graph.

Consequential marking from (ii)

Lose this mark if answer not given to 1 dp.

1

(c) $pK_a = -\log K_a$ or $K_a = 10^x$, where $x = -$ (answer to b(iii))

1

1.26×10^{-4}

3.7 to 4.1 gives $K_a = 7.9 \times 10^{-5}$ *to* 2.0×10^{-4}

Consequential marking from b(i).

Correct answer without working scores 1 mark only.

Do not penalise precision.

1

(d) Methanoic acid

Consequential marking from (c).

$pK_a = 3.7$ gives methanoic acid.

$pK_a = 4.1$ gives ethanoic acid.

No lucky guesses – candidates must apply answer from (c).

Do not allow answers based on data given in (f).

1

(e) Error in using pipette is 0.2% **and**
Error in using burette is 0.15 × 100 / (answer to b(i))

Using 24.4 for burette gives 0.6%

Do not penalise precision.

Allow if errors are given without working.

Lose mark if the burette error is not calculated on b(i).

*If the error being calculated is **not** stated, allow **if** the calculations are in the same order as in the question (pipette, burette).*

1

(f) Difference is $1.6 \times 10^{-4} - 1.26 \times 10^{-4} = 0.34 \times 10^{-4}$

Allow consequential answer from (c).

Do not penalise precision.

0.34 × 100 / 1.6 is a 21% error

Correct final answer without working scores 1 mark.

Using 1.9×10^{-4} gives 0.3×10^{-4} and 18.8%.

1

(g) Calibrate meter **or** thermostat the mixture **or** maintain constant temperature

Do not allow 'repeat experiment'.

1

(h) Mixture is a buffer

1

[16]

27 (Calibrate) meter with solution(s) of known pH/buffer(s)

Do not accept 'repeat reading'

1

Adjust meter/plot calibration curve

1

[2]

28 (a) (i) $-\log[H^+]$

or $\log 1/[H^+]$
penalise ( )

1

(ii) $[H^+] = 0.56$

mark for the answer; allow 2dp or more

1

$[H_2SO_4] = ½ × 0.56 = 0.28$

1

(b) (i) $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

OR

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

Allow CH_3CO_2H etc

1

(ii) mol acid = $(25.0 × 10^{-3}) × 0.41 = 1.025 × 10^{-2}$ or $1.03 × 10^{-2}$

1

$[NaOH] = 1.025 × 10^{-2}/22.6 × 10^{-3} = 0.45(4)$

mark for answer
if not 0.454 look back for error

1

OR

$[NaOH] = 1.03 × 10^{-2}/22.6 × 10^{-3} = 0.456$ or 0.46

(iii) cresol purple

1

(iv) NaOH reacts with <u>carbon dioxide</u> (in the air)

1

(c) (i) $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

allow molecular formulae or minor slip in formulae

penalise ( )
allow H_3O^+
not allow HA etc

1

(ii) $K_a = \frac{[H^+]^2}{[CH_3COOH]}$ or with numbers

1

allow HA etc here
This can be scored in part (c)(i) but doesn't score there.

$[H^+] = (\sqrt{(1.74 \times 10^{-5} \times 0.410)} = \sqrt{(7.13 \times 10^{-6})}) = 2.67 \times 10^{-3}$

1

mark for 2.67×10^{-3} or 2.7×10^{-3} either gives 2.57

pH = 2.57 can give three ticks here for (c)(ii)
penalise decimal places < 2 >

1

pH mark conseq on their $[H^+]$

so 5.15 gets 2 marks where square root not taken

(iii) **M1** mol $OH^- = (10.0 \times 10^{-3}) \times 0.10 = 1.0 \times 10^{-3}$

If no subtraction or other wrong chemistry the max score is 3 for M1, M2 and M4

1

M2 orig mol HA = $(25.0 \times 10^{-3}) \times 0.41 = 0.01025$

1

or 1.025×10^{-2} or 1.03×10^{-2}

M3 mol <u>HA</u> in buffer = orig mol HA – mol OH^-

1

= 0.00925 or 0.0093

If A^- is wrong, max 3 for M1, M2 and M3 or use of

pH = pKa – log $[HA]/[A^-]$

M4 mol A^- in buffer = mol $OH^- = 1.0 \times 10^{-3}$

Mark is for insertion of correct numbers in correct expression for $[H^+]$

1

M5 $[H^+] = \left(\frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} = \right)$

1

$$\frac{(1.74 \times 10^{-5})(0.00925)}{0.0010} \text{ or } \frac{(1.74 \times 10^{-5})(0.00930)}{0.0010}$$

(= 1.61×10^{-4} or 1.62×10^{-4})

M6 pH = 3.79 can give six ticks for 3.79

if $[HA]/[A^-]$ upside down lose M5 & M6

If wrong method e.g. $[H^+]^2/[HA]$ max 3 for M1, M2 and M3

Some may calculate concentrations

$[HA] = 0.264$ and $[A^-] = 0.0286$ and rounding this to 0.029 gives pH = 3.80 (which is OK)

NB Unlike (c)(ii), this pH mark is NOT awarded conseq to their $[H^+]$ unless following AE

BEWARE: using 0.01025 wrongly instead of 0.00925 gives pH = 3.75
(this gets 3 for M1, M2 & M4)

1

[18]

29 (a) (i) **B** 1

C

1

A

1

(ii) cresolphthalein or thymolphthalein

1

(b) pH = $-\log[H^+]$

1

$K_a = \frac{[H^+]^2}{[CH_3COOH]}$ or $[H^+] = [A^-]$

1

$[H^+] = \sqrt{1.74 \times 10^{-5} \times 0.15}$ (or 1.62×10^{-3})

1

pH = 2.79 (penalise 1 dp or more than 2dp once in the qu)

1

[8]

30 (a) (i) addition of small amounts of acid send eqm to left or extra H^+ removed by reaction with HCO_3^-

1

ratio $[H_2CO_3]/[HCO_3^-]$ remains constant hence $[H^+]$ and pH remain const

1

(ii) pH = 7.41 ∴ $[H^+] = 3.89 \times 10^{-8}$ mol dm^{-3}

1

$$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

1

$$= \frac{(3.89 \times 10^{-8})(2.5 \times 10^{-2})}{1.25 \times 10^{-2}} = 7.78 \times 10^{-8} \text{ mol dm}^{-3}$$

allow error carried forward mark. Do not penalise twice.

1

(b) (i) moles H^+ added = $10 \times 10^{-3} \times 1.0 = 0.01$

1

(ii) moles ethanoic acid after addition = 0.15 + 0.01 = 0.16

1

moles ethanoate ions after addition = 0.10 – 0.01 = 0.09

1

(iii) $$[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$$

1

$$= 1.74 \times 10^{-5} \times \frac{0.16/V}{0.09/V}$$

1

pH = 4.51

1

[11]

31 C

[1]

32 (a) –log $[H^+]$

ecf if [ ] wrong and already penalised

1

4.57×10^{-3}

allow 4.6×10^{-3}

ignore units

1

(b) (i) $K_a = \frac{[H^+][X^-]}{[HX]}$ allow HA etc

not $\frac{[H^+]^2}{[HX]}$ *but mark on*

If expression wrong allow conseq units in (ii)
but no other marks in (ii)

1

(ii) $\frac{[H^+]^2}{[HX]} = \frac{(4.57 \times 10^{-3})^2}{[0.150]}$

If use 4.6×10^{-3}

1

$K_a = 1.4(1) \times 10^{-4}$ *and pKa = 3.85*

$= 1.39 \times 10^{-4}$

allow $1.39 - 1.41 \times 10^{-4}$ *mol* dm^{-3}

1

(iii) $pK_a = 3.86$

Penalise dp of final answer < or > 2 in pH once in paper

1

(c) (i) $\frac{30}{1000} \times 0.480 = 0.0144$ or $1.4(4) \times 10^{-2}$

Mark is for answer (M1)

1

(ii) $\frac{18}{1000} \times 0.350 = 0.0063$ or 6.3×10^{-3}

Mark is for answer (M2)

1

(iii) $0.0144 - 2(0.0063) = 1.80 \times 10^{-3}$

M3 is for (i) – 2(ii)

If x 2 missed, CE i.e. lose M3 and the next mark gained

1

(iv) $1.80 \times 10^{-3} \times \frac{1000}{48} = 0.0375\ (0.038)$

M4 is for answer

If vol is not 48×10^{-3} (unless AE) lose M4 and next mark gained
If multiply by 48 - this is AE - i.e. lose only M4
If multiply by 48×10^{-3} this is AE - i.e. lose only M4

1

(v) $10^{-14} / 0.0375$ ($10^{-14} / 0.038$)

M5 for $K_w/[OH^-]$

1

($= 2.66 \times 10^{-13}$) ($= 2.63 \times 10^{-13}$)

or pOH

or pOH = 1.426 (or pOH = 1.420)

If no attempt to use K_w or pOH lose both M5 and M6

1

pH = 12.57 (12.58) M6

Allow M6 conseq on AE in M5 if method OK

1

[13]

33 (a) $k = \text{rate}/[CH_3CH_2COOCH_3][H^+]$

1

or

$$= \frac{1\cdot 15 \times 10^{-4}}{(0.150)(0.555)}$$

$= 1.38 \times 10^{-3}$ to 1.4×10^{-3}

1

$mol^{-1}\ dm^3\ s^{-1}$

1

(b) ans = rate constant × (½ × 0.150) × (½ × 0.555)

ignore units

= rate constant × 0.0208

2.88×10^{-5} (1.38×10^{-3} gives 2.87×10^{-5})

Allow $2.87 – 2.91 \times 10^{-5}$ (1.4×10^{-3} gives 2.91×10^{-5})

1

(c) $[H^+]$ = rate/ k$[CH_3COOCH_2CH_3]$

1

$$= \frac{4.56 \times 10^{-5}}{(8 \cdot 94 \times 10^{-4})(0 \cdot 123)}$$

= 0.415 (0.4146)

1

pH = 0.38 mark independently

$[H^+]$ = 0.41 gives pH = 0.39

1

[7]

34 C

[1]

35 (a) (i) $[H^+][OH^-]$

1

– log $[H^+]$

1

(ii) $[H^+] = [OH^-]$

1

(iii) $(2.0 \times 10^{-3}) \times 0.5 = 1.0 \times 10^{-3}$

1

(iv) $[H^+] = \dfrac{4.02 \times 10^{-14}}{1.0 \times 10^{-3}}$ $(= 4.02 \times 10^{-11})$

1

pH = 10.40

1

(b) (i) $K_a = \dfrac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$

1

$= \dfrac{[H^+]^2}{[CH_3CH_2COOH]}$

1

$[H^+] = \sqrt{(1.35 \times 10^{-5}) \times 0.125}$ $(= 1.30 \times 10^{-3})$

1

pH = 2.89

1

(c) (i) $(50.0 \times 10^{-3}) \times 0.125 = 6.25 \times 10^{-3}$

1

(ii) $(6.25 \times 10^{-3}) - (1.0 \times 10–3) = 5.25 \times 10^{-3}$

1

(iii) mol salt formed = 1.0×10^{-3}

1

$$[H^+] = K_a \times \frac{[CH_3CH_2COOH]}{[CH_3CH_2COO–)}$$

1

$$= (1.35 \times 10^{-5}) \times \frac{(5.25 \times 10^{-3})/V}{(1.0 \times 10^{-3})/V} \; (= 7.088 \times 10^{-5})$$

1

pH = 4.15

1

[16]

36 (a) (i) B;

1

C;

1

A;

1

(ii) cresolphthalein

OR

thymolphthalein;

1

(b) (i) $-\log[H^+]$;

1

(ii) $[H^+] = 1.259 \times 10^{-12}$ (or 1.26 or 1.3)

OR

OH = 14 – pH;

1

$$[OH^-] = \frac{10^{-14}}{1.258 \times 10^{-12}}$$

OR

= 2.10;

1

$= 7.9(4) \times 10^{-3}$;

(if $[H^+]$ is wrong allow 1 for $[OH] = K_W/[H^+]$ or as numbers)

1

(c) (i) $K_a = [H^+]^2/[CH_3CH_2COOH]$

OR

$[H+]^2/[HA]$

OR

$[H^+] = [A^-]$ etc;

1

$[H^+] = \surd l.35 \times l0^{-5} \times 0.117$ or expression without numbers;

1

$= 1.257 \times l0^{-3}$

pH = 2.9$\underline{0}$;

1

(iii) $K_a = [H^+]$

OR

$pK_a = pH$;

1

pH = 4.8<u>7</u>;

(penalise 1dp once)

1

[13]

37 (a) Concentration of acid: $m_1v_1 = m_2v_2$ hence $25 \times m_1 = 18.2 \times 0.150$

OR

moles NaOH = 2.73×10^{-3};

1

$m_1 = 18.2 \times 0.150/25 = 0.109$;

1

(b) (i) $K_a=[H^+][A^-]/[HA]$ *not* $K_a = [H^+]^2 / [HA]$;

1

(ii) $pK_a = -\log K_a$;

1

(iii) $[A^-] = [HA]$;

1

hence $K_a = [H^+] [A^-] / [HA] = [H^+]$

and $-\log K_a = -\log[H^+]$;

1

(c) ratio $[A^-]$: [HA] remains constant;

1

hence as $[H^+] = K_a [HA] / [A^-]$; $[H^+]$ remains constant;

1

(d) (i) pH of 0.250 mol dm^{-3} HCl = 0.60
and pH of 0.150 mol dm^{-3} HCl = 0.82;

1

pH change = 0.22;

1

(ii) moles HCl = $30 \times 0.250 \times 10^{-3} = v \times 0.150 \times 10^{-3} = 7.50 \times 10^{-3}$

OR

$v = 30 \times 0.250 \times 10^{-3} / 0.150 \times 10^{-3} = 50$;

1

water added = 50 – 30 = 20 cm^3;

1

[12]

38 C

[1]

39 (a) pH = –log[H^+]

1

$$K_a = \frac{[H^+]^2}{[CH_3COOH]} \quad \text{or } [H^+]=[A^-]$$

1

$[H^+] = \sqrt{1.74 \times 10^{-5} \times 0.15}$ (or 1.62×10^{-3})

1

pH = 2.79 (penalise 1 dp or more than 2dp once in the qu)

1

(b) (i) Solution which resists change in pH /maintains pH

1

despite the addition of (small amounts of) <u>acid/base</u> (or dilution)

1

(ii) $CH_3COO + H^+ \rightarrow CH_3COOH$

must show an equation full or ionic in which ethanoate ions are converted to ethanoic acid

1

(c) (i) $[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$ if rearrangement incorrect, no further marks

1

$= 1.74 \times 10^{-5} \times \frac{0.15}{0.10}$

1

$(= 2.61 \times 10^{-5})$

pH = 4.58

1

(ii) MI moles H^+ added = $10 \times 10^{-3} \times 1.0 = 0.01$

1

M2 moles ethanoic acid after addition = 0.15 + 0.01 = 0.16

1

M3 moles ethanoate ions after addition = 0.10 -0.01 = 0.09

1

M4 $$[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]} = 1.74 \times 10^{-5} \times \frac{0.16/V}{0.09/V}$$

1

(= 3.09×10^{-5})

M5 pH = 4.51

The essential part of this calculation is addition/subtraction of 0.01 moles to gain marks M2 and M3. If both of these are missing, only mark M1 is available. Thereafter treat each mark independently, except if the expression in M4 is wrong, in which case both M4 and M5 are lost.

1

[15]

alternative scheme for part (c)(i)

$$pH\ pK_a - \log\frac{[CH_3COOH]}{[CH_3COO^-]}$$

1

$pK_a = 4.76$

1

$$pH = (4.76 - \log\frac{0.15}{0.10}) = 4.58$$

1

alternative for penultimate mark of part (c)(ii)

$$pH = 4.76 - \log\frac{0.16}{0.09}$$

1

C
40

[1]

41 (a) $K_a = \frac{[H^+][A^-]}{[HA]}$

(All three sets of square brackets needed, penalise missing brackets or missing charge once in the question)

(Don't penalise extra $[H^+]^2/[HA]$)

1

(b) $K_a = \frac{[H^+]^2}{[HA]}$ or $[H^+] = [A^-]$

$[H^+] = \sqrt{(1.45 \times 10^{-4}) \times 0.25}$

$= 6.02 \times 10^{-3}$pH = 2.22

(must be to 2dp)

(allow 4th mark consequential on their $[H^+]$)

1

(c) (i) pH (almost) unchanged

(Must be correct to score explanation)

1

H^+ removed by A^- forming HA
or acid reacts with salt
or more HA formed

1

(ii) $[H^+] = 10^{-3.59} = 2.57 \times 10^{-4}$ or 2.6×10^{-4}

1

$[A^-] = \frac{K_a[HA]}{[H^+]}$

1

$= \frac{(1.45 \times 10^{-4}] \times 0.25}{2.57 \times 10^{-4}}$

1

= 0.141 (mol dm^{-3})

(Allow 0.139 to 0.141 and allow 0.14)

(If not used 3.59, to find $[H^+]$ can only score M2 for working)

(If 3.59 used but $[H^+]$ is wrong, can score M2 for correct method and conseq M4)

If wrong method and wrong expression, can only score M1)

1

(ii) *Alternative scheme for first three marks of part (c)(ii)*

$$pH = pK_a - \log\frac{[HA]}{[A^-]}$$

1

$pK_a = 3.84$

1

$$3.59 = 3.84 - \log\frac{0.250}{[A^-]}$$

1

[11]

42 D

[1]

43 B

[1]

44 (a) Hydrogen bonding **(1)**
between H_2O and NH_3 **(1)**

2

(b) (i) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ **(1)**

(ii) Ammonia is weak base **(1)**

NOT partially ionised

Equilibrium to left or incomplete reaction **(1)**

3

(c) A proton donor **(1)**

1

(d) *Buffer solution*: A solution which resists change in pH **(1)**
when small amounts of acid or base added or on dilution **(1)**

Reagent: NH_4Cl **(1)**

Allow a correct strong acid

3

(e) (i) $K_a = [H^+] [A^-] / [HA]$ **(1)**

$= [H^+] [0.125 \times 4]$ **(1)** $/ 1.00$

$[H^+] = 1.70 \times 10^{-5} / 0.125 \times 4 = 3.40 \times 10^{-5}$ **(1)**

$pH = -\log_{10} [H^+] = 4.47$ **(1)**

Allow pH conseq to [H⁺] if 2 place decimals given

(ii) $H^+ + CH_3COO^- \rightarrow CH_3COOH$ **(1)**

5

[14]

45 A

[1]

46 A

[1]

47 Penalise pH given to 1 dp <u>first</u> time it would have scored only

(a) (i) $K_w = [H^+] [OH^-]$ **(1)**

(ii) $pH = -\log [H^+]$ **(1)**

or in words or below unless contradiction

(iii) *Calculation*: $[H^+] = \sqrt{5.48 \times 10^{-14}}$ **(1)**

$= 2.34 \times 10^{-7}$

$\therefore$ pH = 6.63 or 6.64 **(1)**

Explanation: pure water $\therefore$ $[H^+] = [OH^-]$ **(1)**

5

(b) (i) $[OH^-] = 0.150$ $\therefore$ $[H^+] = 10^{-14}/0.15 = 6.66 \times 10^{-14}$

or pOH = 0.82

$\therefore$ pH = 13.18 **(1)**

or pH= 13.17

(ii) moles OH^- = $(35 \times 10^{-3}) \times 0.150 = 5.25 \times 10^{-3}$ **(1)**[a]

moles H^+ = $(40 \times 10^{-3}) \times 0.120 = 4.8(0) \times 10^{-3}$ **(1)**[b]

$\therefore$ excess moles of OH^- = 4.5×10^{-4} **(1)**[c]

$\therefore$ $[OH^-] = (4.5(0) \times 10^{-4}) \times 1000/\underline{75}$[d] **(1)**[e]
$= 6.0(0) \times 10^{-3}$

$[H^+] = \dfrac{10^{-14}}{6.00 \times 10^{-3}} = 1.66 \times 10^{-12}$ or pOH = 2.22

$\therefore$ pH = 11.78 **(1)**[f]
or 11.77

8

(c) (i) $K_a = \dfrac{[H^+][X^-]}{[HX]}$ **(1)**

(ii) $[H^+] = 1.80 \times 10^{-2} \times 0.150 = 2.70 \times 10^{-3}$ (1)

$K_a = \dfrac{[H^+]^2}{[HX]}(1) = \dfrac{(2.70 \times 10^{-3})^2}{0.150} = 4.86 \times 10^{-5}$ **(1)** mol dm^{-3} **(1)**

or $\dfrac{(2.70 \times 10^{-3})^2}{0.1473} = 4.95 \times 10^{-5}$

5

Notes

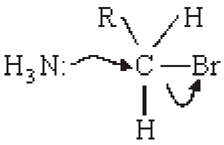
(a) If K_w includes H_2O allow 6.63 if seen otherwise no marks likely

(b) (ii) If no vol, max 4 for a, b, c, f answer = 10.65
If wrong volume max 5 for a, b, c, e, f
If no substraction max 3 for a, b, d
If missing 1000 max 5 for a, b, c, d, f answer = 8.78
If uses excess as acid, max 4 for a, b, d, f answer = 2.22
If uses excess as acid and no volume, max 2 for a,
b answer = 3.35

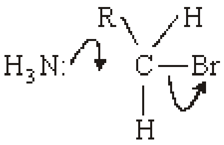
(c) If wrong K_a in (i) max 2 in part (ii) for $[H^+]$ **(1)** and conseq units **(1)**
but mark on fully from minor errors
eg no [ ] or charges missing

Organic points

(1) Curly arrows: must show movement of a pair of electrons, i.e. from bond to atom or from lp to atom / space
e.g.

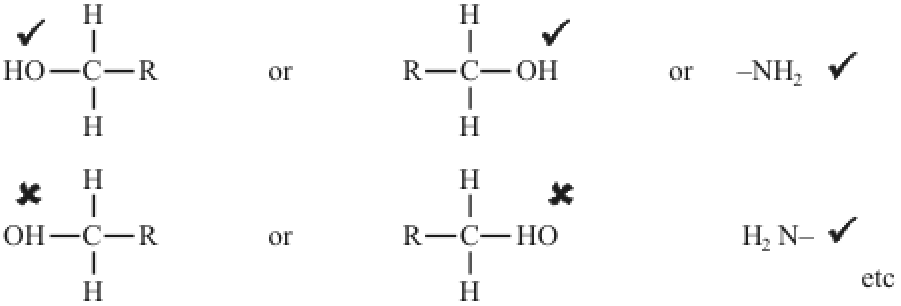


OR



(2) Structures

penalise sticks (i.e. $-\overset{|}{\underset{|}{C}}-$) once per paper



$HO-CH_2-R$ ✓ or $R-CH_2-OH$ ✓ or $-NH_2$ ✓

$OH-CH_2-R$ ✗ or $R-CH_2-HO$ ✗ H_2N- ✓

etc

Penalise once per paper

allow CH_3- or $-CH_3$ or $\underset{|}{CH_3}$ or CH_3
or H_3C-

[18]

48 C

[1]

49 (a) moles HA = $\frac{25}{10^3}$ × 0.150 = 3.75×10^{-3} **(1)**

$\therefore$ vol NaOH = $\frac{3.75 \times 10^{-3}}{0.20}$ = 1.875×10^{-2} dm^3 **(1)**

or 18.75 cm^3

(b) (i) $\mathrm{pH} = -\log_{10}[\mathrm{H}^+]$ **(1)**

(ii) Value above 7 but below 11 **(1)**

(iii) phenol red / thymol blue / phenolphthalein / thymolphthalein

i.e. indicator with $7 < \mathrm{p}K_{in} < 11$

3

(c) (i) Only slightly dissociated/ionised **(1)**

NOT “not fully dissociated / ionised”

(ii) $K_a = \dfrac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]}$ **(1)**

NOT $\dfrac{[\mathrm{H}^+]^2}{[\mathrm{HA}]}$

(iii) For weak acid alone:

$\mathrm{Ka} = \dfrac{[H^+]^2}{[HA]}$ **(1)**

$\therefore\ [\mathrm{H}^+] = \sqrt{(2.75 \times 10^{-5}) \times 0.15}$

$= 2.03 \times 10^{-3}$ (1)

$\therefore$ pH = 2.69 (1)

pH should be given to 2 decimal places
penalise answer to 1 d.p. once in question

5

(d) moles OH^- added = 1.875×10^{-3} = moles A^- = moles HA left **(1)**

or $[\mathrm{A}^-] = [\mathrm{HA}]$

$\therefore$ $\mathrm{Ka} = [\mathrm{H}^+]$ **or** $\mathrm{pH} = \mathrm{p}K_a$ **(1)**

$\therefore$ pH = 4.56 (1)

3

[13]

50 C

[1]

51 (a) *Order with respect to iodine*: 0 **(1)**
Overall order: 2 **(1)**

2

(b) *Rate constant*: k = $\frac{2 \times 10^{-5}}{(1.5) \times (3 \times 10^{-2})}$ = 4.4(4) × 10^{-4} **(1)**

Units: $mol^{-1}\ dm^{3}\ s^{-1}$ **(1)**

3

(c) Appears in rate equation **(1)**

OR implied by mention of concentration or order

does not appear in (stoichiometric / overall) equation (1)

2

(d) pH = $-\log_{10}[H^+]$ **(1)**

= 1.25

$[H^+]$ = 0.056(2) **(1)**

∴ rate = (4.44 × 10^{-4}) × (1.50) × (0.0562)

= 3.75 × 10^{-5} **(1)** (mol $dm^3\ s^{-1}$)

(3.7 — 3.8)

Can score all 3 conseq on k from part (b)

3

[10]

52 (a) before any KOH added: $K_a = \frac{[H^+][A^-]}{[HA]}$ **or** $\frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ **(1)**

∴ $K_a = \frac{[H^+]^2}{[CH_3COOH]}$ **(1)**

∴ $[H^+] = \sqrt{1.74 \times 10^{-5} \times 0.160}$ = 1.67 × 10^{-3} **(1)**

∴ pH = 2.78 **(1)**

4

(b) at 8 cm^3 KOH:

Moles KOH added = $(8 \times 10^{-3}) \times 0.210 = 1.68 \times 10^{-3}$ **(1)**

∴ moles of CH_3COO^- formed = 1.68×10^{-3} **(1)**

Original moles of $CH_3COOH = (25 \times 10^{-3}) \times 0.160 = 4.0 \times 10^{-3}$ **(1)**

∴ moles of CH_3COOH left = $(4.0 \times 10^{-3}) - (1.68 \times 10^{-3})$

$= 2.32 \times 10^{-3}$ **(1)**

$[H^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]}$ **(1)**

$= 1.74 \times 10^{-5} \times \frac{2.32 \times 10^{-3} / V}{1.68 \times 10^{-3} / V} = 2.40 \times 10^{-5}$ **(1)**

∴ <u>pH = 4.62</u> **(1)**

It forget subtraction : max 5

If K_a expression not used max 5

if moles of CH_3COOH wrong but substitution used max 5

7

(c) at 40 cm^3 of KOH:

Total moles of KOH = $(40 \times 10^{-3}) \times 0.21 = 8.4 \times 10^{-3}$ **(1)**

∴ excess moles of KOH = (8.4×10^{-3}) - (4.0×10^{-3})

$= 4.4 \times 10^{-3}$ **(1)**

in total volume = 40 + 25 = 65 cm^3 **(1)**

∴ $[OH^-] = 4.4 \times 10^{-3} \times \frac{1000}{65} = 0.0677$ **(1)**

∴ $[H^+] = \frac{10^{-14}}{0.0677}$

OR pOH =1.17

$= 1.477 \times 10^{-13}$ **(1)**

∴ pH = 12.8<u>3</u> **(1)**

If volume missed : max 4

If moles of acid wrong but method includes subtraction : max 5

If no subtraction : max 4

6

[Max 16]

53

or H_3O^+

(a) (i) $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ **(1)**

(ii) (1) $K_a = \frac{[H^+]^2}{[CH_3COOH]}$ **(1)**

(2) $[H^+] = \sqrt{1.74 \times 10^{-5} \times 0.220} = 1.96 \times 10^{-3}$ **(1)**

(3) pH = $-\log_{10}[H^+]$ **(1)**

can score independently

(4) pH = 2.<u>71</u> **(1)**

2 d.p. essential

If forget √ can score (1) and (3) for pH = 5.42

5

(b) (i) moles acid = $\frac{25}{1000} \times 0220$ **(1)** = 5.50×10^{-3}

$= \frac{x}{10^3} \times 0.150$

$\therefore\ x = 25 \times \frac{0.220}{0.150}$ **or** $5.50 \times 10^{-3} \times \frac{1000}{0.150}$

= 36.7 (or 37) cm^3 (or 36.6) **(1)**

NOT 36 NOR 37.0 units must match

(ii) *Indicator*: thymol blue **(1)**

Explanation: weak acid – strong base **(1)**
equivalent at pH > 7 **(1)**
or high pH

5

(c) (1) mol NaOH added = $\frac{2.0}{40.0}$ = 0.050 **(1)**

If wrong M_r: CE ∴ lose marks (1) and (2) then mark on consequentially → max 4

(2) mol CH_3COOH left = 0.220 – 0.050 = 0.170 **(1)**

(3) mol CH_3COO^- formed = 0.050 **(1)**

(4) $[H^+] = Ka \frac{[acid]}{[salt]}$ OR $pH = pKa + \log\frac{[A^-]}{[HA]}$ etc **(1)**

If expression wrong no marks for 4 / 5 / 6

can score (1) to (4) in (5)

(5) $[H^+] = 1.74 \times 10^{-5} \times \frac{(0.170)}{(0.05)}$ OR $pH = 4.76 + \log\left(\frac{0.05}{0.17}\right)$ **(1)**

(6) pH = 4.23 **(1)**

Correct answer gets ***(1)(1)(1)(1)(1)(1)***
Mark (5) is for use of correct values of (acid moles) and (salt moles)
if one wrong allow pH conseq
if both wrong, no further marks
e.g. if candidate forgets substitution in (2)
he loses (2) and (5) but can score (1) (3) (4) (6) = max 4

for pH = 4.12 if $\frac{[acid]}{[salt]}$ *upside down; answer 5.29 scores 3 for (1) (2) (3)*

6

[16]

54 C **[1]**

55 D **[1]**

56 D **[1]**

57 B **[1]**

58 B **[1]**

59 D **[1]**

60 B **[1]**